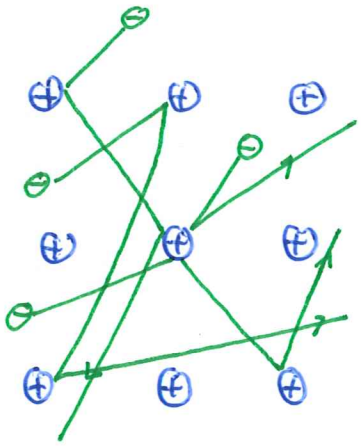
The Drude model

- uses concepts from kinetic gas theory to describe electrons that move around in a solid and scatter with fixed ions
- one of the first microscopic models for solid (1900 -... discovery of electron only 1897)



- motion between collisions

$$\dot{\vec{p}} = \vec{F}_L = -e\left(\vec{E} + \frac{1}{c}\frac{\vec{p}}{m} \times \vec{B}\right)$$

(Lorentz force)

- collision propability in $[t, t+dt]$: $\frac{dt}{\tau}$

τ: relaxation time

- after collisions: electrons have equilibrium (Maxwell Boltzmann) distribution

$$\rightsquigarrow \boxed{\frac{d\vec{p}}{dt} = -F_L - \frac{\vec{p}}{\tau}}$$

equation of motion for average momentum

⇒ can be used to compute various transport properties, e.g. conductivity:

$\vec{j} = -en\,\vec{p}/m$ — j: current density, n: density of electrons

$\vec{E}(t) = \vec{E}(\omega)e^{-i\omega t} \rightsquigarrow j(\omega) = E(\omega)\sigma(\omega)$

with $\boxed{\sigma(\omega) = \frac{\sigma_0}{1-i\omega\tau} \qquad \sigma_0 = \frac{ne^2\tau}{m}}$ ← DC conductivity

this turns out to be very useful as a phenomenological description, but there are "severe" problems with microscopic formulations:

1. Scattering rate $1/\tau$ cannot be related to scattering with ions: σ_{dc} decreases $\downarrow 0$ in a perfect crystal (no defects) at $T \downarrow 0$.
(also: temperature-dependence of τ not captured)
$\rightsquigarrow$ electrons can move almost free in a perfect periodic crystal $\rightsquigarrow$ Bloch theorem, quasi-momentum conservation

② Kinetic gas theory makes some "very wrong" predictions, e.g. specific heat

$C_V = \frac{3}{2} n k_B$ (really $C_V \propto T$)

⇝ electrons in a crystal have to be described quantum mechanically (Fermi statistics instead of Maxwell Boltzmann statistics)

- rough argument when quantum statistics should be used:

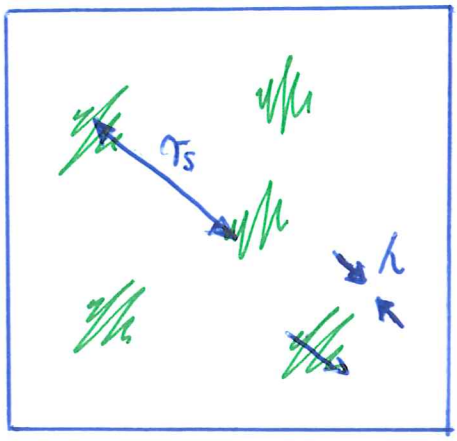
$r_s \simeq n^{-\frac{1}{3}}$! $\lesssim$ $\frac{2\pi\hbar}{\sqrt{3m k_B T}}$

typical inter-particle distance

average de Broglie wavelength $\lambda = \frac{2\pi\hbar}{\langle p \rangle}$

for particle in ideal gas at temperature T: $\left\langle \frac{m}{2} v^2 \right\rangle = \left\langle \frac{p^2}{2m} \right\rangle = \frac{3}{2} k_B T$

classical



quantum

check: above estimate $r_s \lesssim \langle \lambda \rangle$ up to constant equivalent to $E_F \gtrsim T$, where E_F is the Fermi energy of free electrons with density n: $E_F = (3\pi^2 n)^{2/3} \frac{\hbar^2}{2m}$

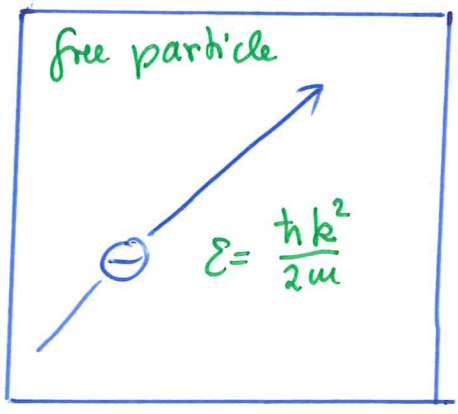
typical value for metals:

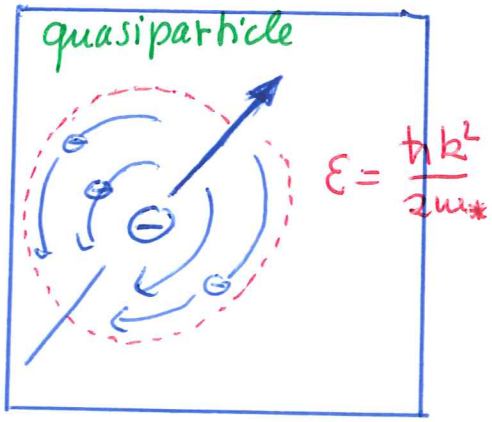
$$E_F \sim 1\text{-}20\ \text{eV} \gg k_B T \simeq 0.01\text{eV}$$

Note $k_B T = 1\text{eV} \hat{=} 11604$ Kelvin

(3) In real materials, the ratio $\frac{e}{m}$ of the Drude model can take a whole range of values (as if there are many kinds of electrons, even with positive charge!)

On the other hand, the success of the Drude model indicates that the picture of "something" scattering with "something else" is not so wrong. But in the solid, "particles" are excitations of the ground state with given energy momentum relation, and those particles have often very different properties from original particles (~> quasiparticles)

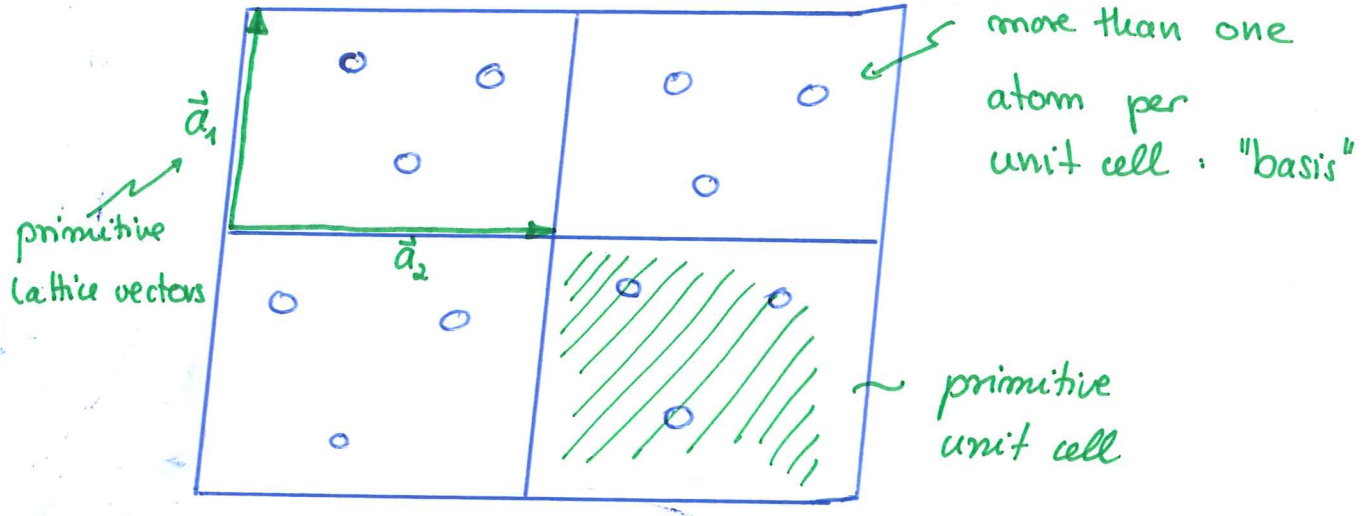




~> many different ground states: Fermi liquid, superconductor, magnetic order, with different excitations

Electrons in a periodic potential - band theory

- periodic structures - crystal symmetries



$$\{ \vec{R} : \vec{R} = \sum_{i=1}^{3} n_i \vec{a}_i \quad n_i = 0, \pm 1, \pm 2, \dots \}$$

is called the Bravais lattice (= lattice with simplest possible, i.e. spherically symmetric, basis)

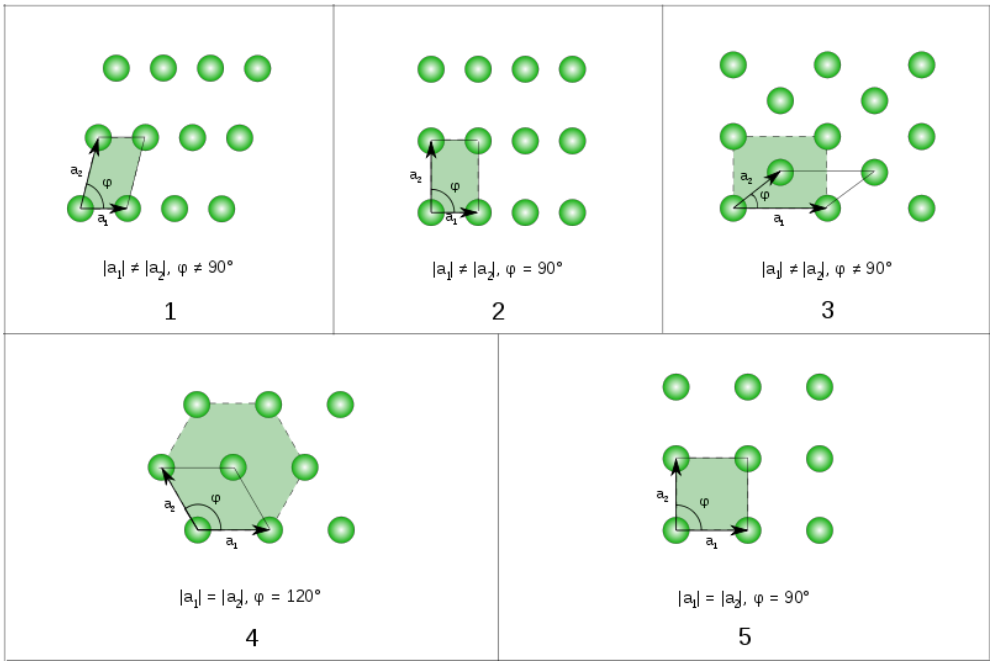
- classification of lattice by symmetry (not in this lecture, see texts on crystallography):

Point group: symmetry operations which leave one point fixed

Space group: full symmetry group

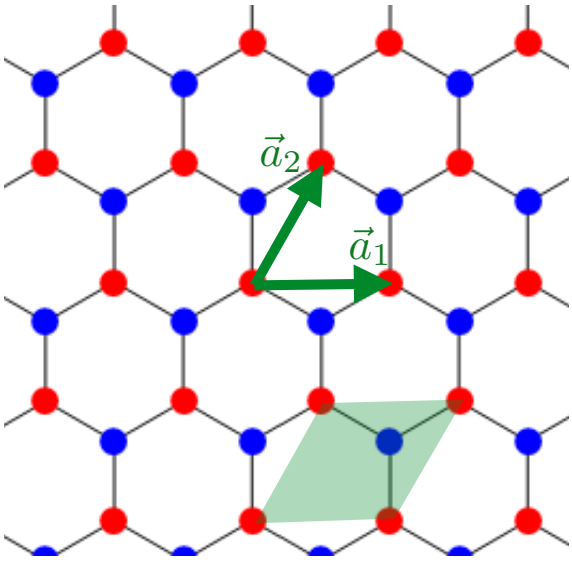
$\vec{r} \to \underline{\underline{D}}\vec{r} + \vec{a}$: $\underline{\underline{D}}$: point groups, $\vec{a}$: translation

Example - Bravais lattices in d=2



https://commons.wikimedia.org/wiki/File:2d-bravais.svg

Example - Honeycomb lattice: not a Bravais lattice



Basis: 2 atoms per unit cell

- in dimension $d=3$: Bravais lattice can have 7 point groups (crystal systems) and 14 space groups (Bravais ~ 1850)
- in dimension $d=2$: space groups $\hat{=}$ wallpaper groups (see e.g. wikipedia)

- Importance of symmetry for description of solids:
  - quantum numbers (quasimomentum) $\rightsquigarrow$ see below
  - Symmetry determines response coefficients of a solid. In general, physical observables must be invariant under crystal symmetries

    Example: conductivity, cubic symmetry

    general linear response relation:

    $$j_\alpha = \sum_{\alpha'} \sigma_{\alpha\alpha'} E_{\alpha'} \qquad \alpha, \alpha' = x, y, z$$

    Invariance $D \sigma D^{-1} \overset{!}{=} \sigma$ for all point group operations

Rotation 180° around $\hat{z}$-Axis:

$$D = \begin{pmatrix} -1 & & \\ & -1 & \\ & & +1 \end{pmatrix}$$

$$D \begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{pmatrix} D^{-1} = \begin{pmatrix} +\sigma_{11} & +\sigma_{12} & -\sigma_{13} \\ +\sigma_{21} & +\sigma_{22} & -\sigma_{23} \\ -\sigma_{31} & -\sigma_{32} & +\sigma_{33} \end{pmatrix} \overset{!}{=} \underline{\underline{\sigma}}$$

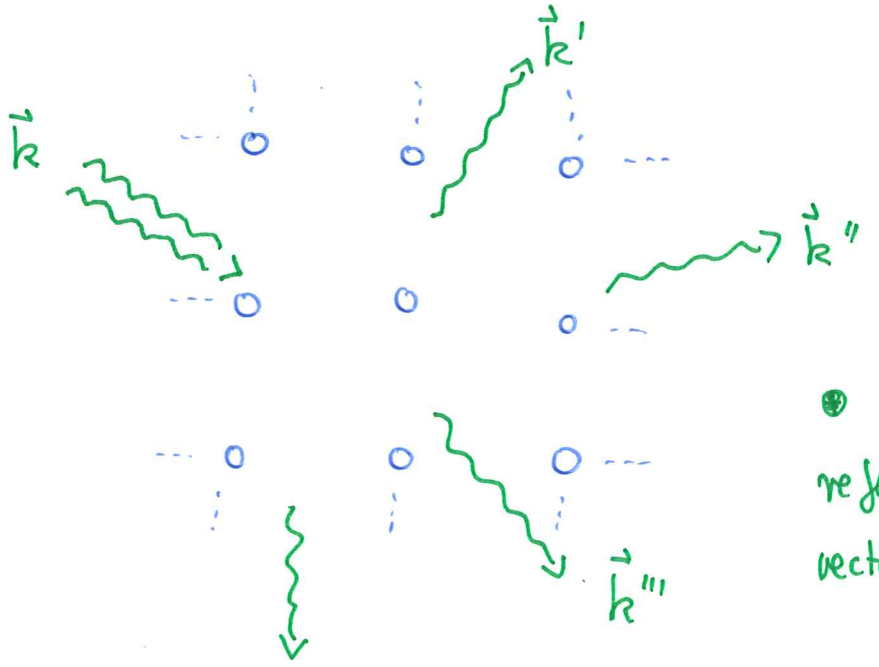
$$\Rightarrow \sigma_{13} = \sigma_{23} = \sigma_{31} = \sigma_{32} = 0$$

Similar: rotations around $\hat{x}, \hat{y} \Rightarrow \underline{\underline{\sigma}}$ diagonal

rotation 120° around body diagonal

$\Rightarrow$ permutations of $x, y, z \Rightarrow \underline{\underline{\sigma}} = \underline{\underline{1}} \cdot \sigma$

Scattering waves off periodic structures



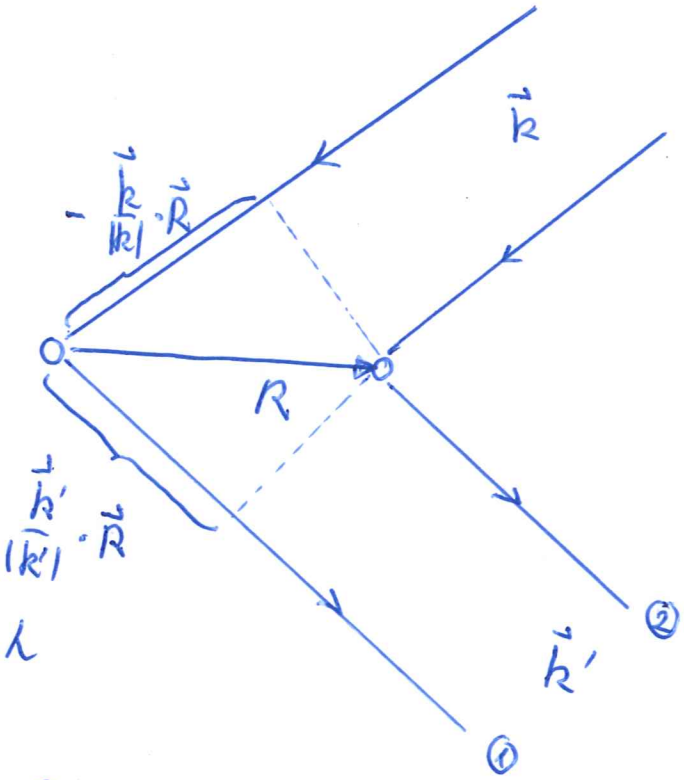
- discrete Bragg reflexes with wave vector $\vec{k}', \vec{k}'', \ldots$

- condition for constructive interference of scattered wave in direction $\vec{k}'$:

$$(\vec{k} - \vec{k}') \cdot \vec{R} = 2\pi n \quad | n \in \mathbb{Z})$$

for all $\vec{R}$ in Lattice (von Laue)

proof:



path difference of ① and ②:

$$\left(\frac{\vec{k}}{|k|} - \frac{\vec{k}'}{|k'|}\right) \cdot \vec{R} \stackrel{!}{=} n \cdot \lambda$$

with $|k| = |k'| = 2\pi / \lambda$ (elastic scattering)

one gets the von Laue condition.

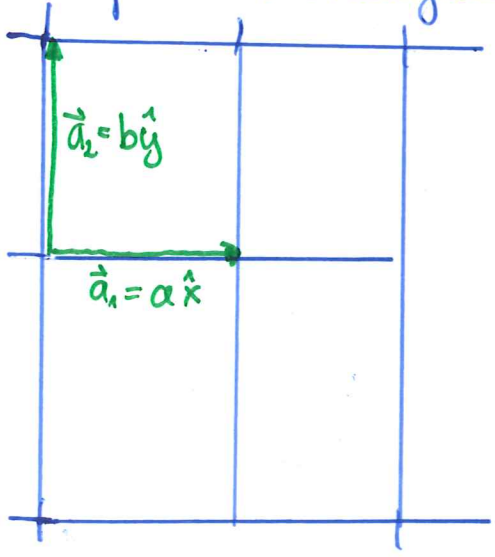
the reciprocal lattice

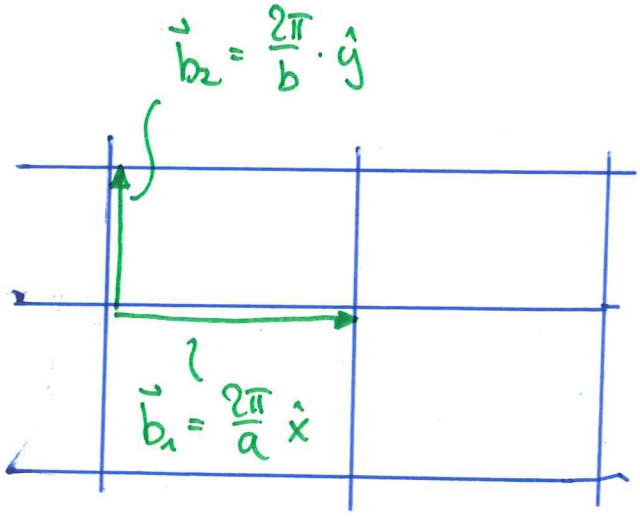
For a lattice $\mathcal{G} = \{\vec{R}\}$, the reciprocal lattice is given by all vectors $\vec{G}$ which satisfy $\vec{G}\cdot\vec{R} = 2n\pi$, $(n \in \mathbb{Z})$ for all $\vec{R} \in \mathcal{G}$,
(i.e. $e^{i\vec{G}\vec{R}} = 1 \quad \forall\ \vec{R} \in \mathcal{G}$)

For a Bravais lattice with primitive vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$, the reciprocal lattice is given by a Bravais lattice with primitive vectors b_i that satisfy $\vec{b}_i \cdot \vec{a}_j = 2\pi\,\delta_{ij}$.

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{|a_1 \cdot (\vec{a}_2 \times \vec{a}_3)|} \qquad 1,2,3 \text{ cyclic}$$

Example: rectangular lattice:





- reformulation of von Laue condition:
  constructive interference if $\vec{k} - \vec{k}'$ is a vector of reciprocal lattice

- technical remark: reziprocal lattice also defines Fourier components of a function while is periodic on the lattice:

  if $f(\vec{r} + \vec{R}) = f(\vec{r}) \quad \forall \vec{R} \in G$

  $\Rightarrow$

$$f(\vec{r}) = \sum_G f_{\vec{G}} e^{i \vec{G} \vec{r}}$$

$$f_{\vec{G}} = \frac{1}{\text{Vol}} \int_{\text{unit cell}} d^3r \, e^{-i \vec{G} \vec{r}} f(\vec{r})$$

Momentum conservation on the lattice

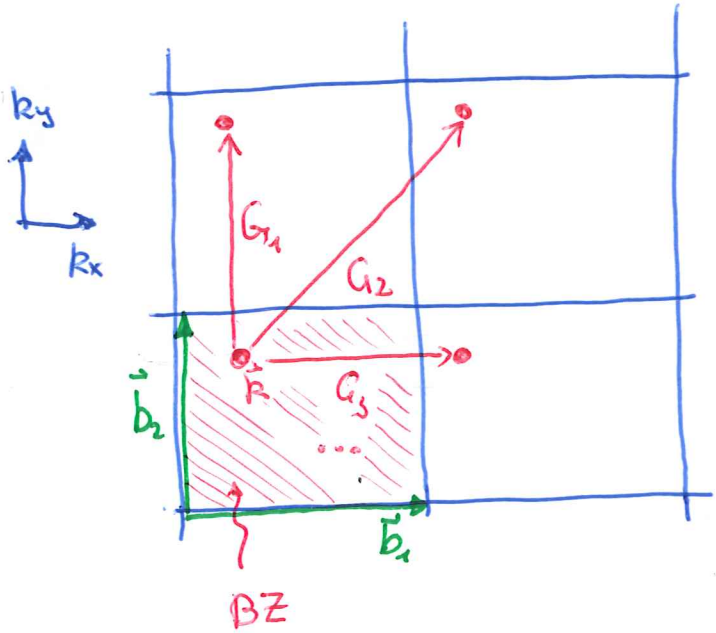
The analysis of the scattering of plane waves shows that on a periodic structure momentum $\vec{k}$ is scattered only into $\vec{k}'$ with $\vec{k}' - \vec{k} = \vec{G} \in \mathcal{G}^*$

$\Rightarrow$ momentum conservation up to reziprocal lattice vector

State $|\Psi\rangle$ has "good quasimomentum $\vec{k}$"

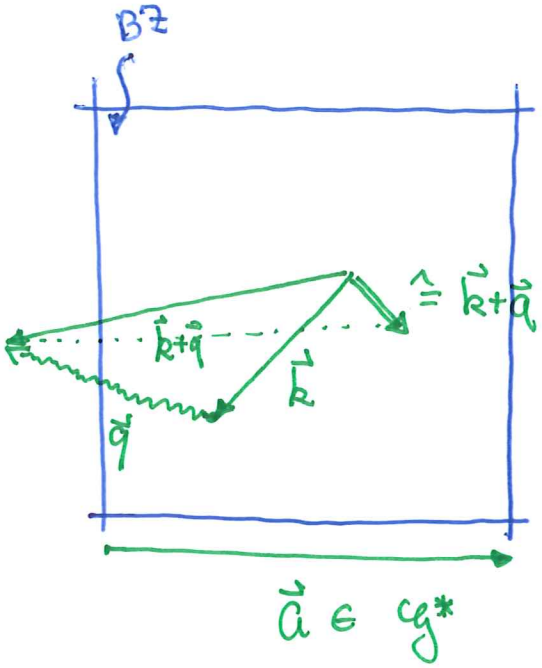
$\Leftrightarrow$ $|\Psi\rangle$ superposition of states with momentum $\vec{k}+\vec{G}, \vec{G} \in \mathcal{G}^*$

On a periodic lattice, quasimomentum is conserved.



without loss of generality, $\vec{k}$ can be taken from 1. Brillouin zone (Wigner Seitz unit cell of the reziprocal lattice.

Illustration: Umklapp scattering.



Scattering of electron with quasimomentum $\vec{k}$ with something else (phonon, another e^-, ...) with quasimomentum $\vec{q}$

Momentum conservation: algebraic formulation

In a periodic crystal, $\hat{H}$ commutes with all translation operators:

$$\boxed{[H, T_R] = 0 \qquad \forall \vec{R} \in \mathcal{G}}$$

(translation operator $(T_R \psi)(\vec{r}) = \psi(r - R)$)

$\Rightarrow$ Choose eigenfunctions of H to be simultaneous eigenfunctions of all T_R:

$$T_R |\psi\rangle = c(\vec{R}) |\psi\rangle \qquad \forall \vec{R}$$

$\vec{R} = \sum_i n_i \vec{a}_i \quad \Rightarrow \quad T_{\vec{R}} = (T_{\vec{a}_1})^{n_1} (T_{a_2})^{n_2} (T_{a_3})^{n_3}$

(because translation operators commute!)

$\Rightarrow T_R |\psi\rangle = c(a_1)^{n_1} c(a_2)^{n_2} c(a_3)^{n_3} |\psi\rangle \quad \forall n_i \in \mathbb{Z}$

because $\| |\psi\rangle \| = \| T_R |\psi\rangle \| \Rightarrow |c(R)| = 1$

$\Rightarrow$ implicitly define $\vec{k}$ such that $c(a_i) = e^{i \vec{k} \vec{a}_i}$ $i=1,2,3$

$\Rightarrow c(R) = \exp\left(i \sum_j \vec{a}_j n_j \right) = e^{i \vec{k} \vec{R}}$

$\vec{k}$ (quasimomentum): Quantum number which characterizes how wave function behaves under translation:

$|\psi\rangle$ has quasimomentum $\vec{k} \Leftrightarrow T_R |\psi\rangle = e^{i \vec{k} \vec{R}} |\psi\rangle \quad \forall R \in \mathcal{G}$

- Note: apparently $\vec{k}$ and $\vec{k} + \vec{G}$ with $\vec{G} \in \mathcal{G}^*$ are the same quasimomentum
- compare: L^2, L_z: Quantum numbers which characterize transformation under rotations ... etc.

(2) Electrons in the periodic crystal

In this chapter, we solve the Schrödinger equation for electrons in the solid. Approximations:

- nuclear positions are kept fixed in space (Born-Oppenheimer approximation), valid for $m_e \ll m_{Nuclei}$ (see later)
- electron-electron interaction is neglected ⊛

$\rightsquigarrow$ goal: determine eigenvalue spectrum of $H = \frac{\vec{p}^2}{2m} + V(\vec{r})$ $\quad V(\vec{r}) = V(\vec{r}+\vec{R})$ $\forall \vec{R} \in$ Bravais lattice $\mathcal{G}$

Note: Why does ⊛ make sense at all ?

- "deep reason": electrons in solid can behave like weakly interacting e^- with "renormalized" properties (different mass etc.) ($\rightarrow$ screening, Fermi liquid theory, see below)

- "practical reason": If electron-electron interaction is included in the simplest approximation (mean-field, Hartree), $V(\vec{r})$ simply includes the time averaged interaction with all other electrons. $V(\vec{r})$ is then an effective potential which is determined self-consistently. Similar, a (more sophisticated) effective single particle problem has to be solved in the more accurate density functional theory. The techniques to do so are the same as presented in this chapter.

Bloch theorem

H commutes with all translations $T_{\vec{R}}$, $\vec{R} \in \mathbb{G}$

$\Rightarrow$ eigenstates of H have good quasimomentum

$$T_R |\Psi\rangle(r) = \Psi(\vec{r}+\vec{R}) \tag{2.1}$$

$$\| \quad e^{i\vec{k}\vec{R}} \Psi(\vec{r})$$

$\vec{k}$ = quasi-momentum

$\Rightarrow$ the function $e^{-i\vec{k}\vec{r}}\,\psi(\vec{r}) \equiv u_{\vec{k}}(\vec{r})$

is periodic, $u_k(\vec{r}+\vec{R}) = u_k(\vec{r})$

$\Rightarrow$ **(Bloch) Eigenfunctions of H can be written as $\psi_k(\vec{r}) = e^{i\vec{k}\vec{r}}\, u_k(\vec{r})$, where $\vec{k}$ can be restricted to the first Brillouin zone, and $u_k(\vec{r}+\vec{R}) = u_k(\vec{r})$ $\forall \vec{R}$.** (2.2)

Note: An analogous theorem is used for the description of systems which are periodic in time (Floquet, 1883). If

$$i\,\partial_t \psi(t) = H(t)\,\psi(t) \quad \text{with} \quad H(t+T) = H(t)$$

then the solutions are of the form

$$\psi(t) = e^{-i\epsilon t}\, u(t)$$

$u(t)$: periodic

ϵ: can be restricted to $[0, \frac{2\pi}{T}]$ "quasi-energy"

using Bloch theorem, the Schrödinger equation can be rewritten as an equation for u_k:

$$\hat{p} \hat{=} -i\hbar\vec{\nabla} \quad \rightsquigarrow \quad \hat{p}\, e^{i\vec{k}\vec{r}} f(\vec{r}) = e^{i\vec{k}\vec{r}} (\hat{p} + \hbar\vec{k}) f(\vec{r})$$

$$\Rightarrow \quad \left[\frac{(\hat{p} + \hbar\vec{k})^2}{2m} + V(\vec{r}) \right] u_k(\vec{r}) = \varepsilon_k u_k(\vec{r}) \,, \tag{2.3}$$

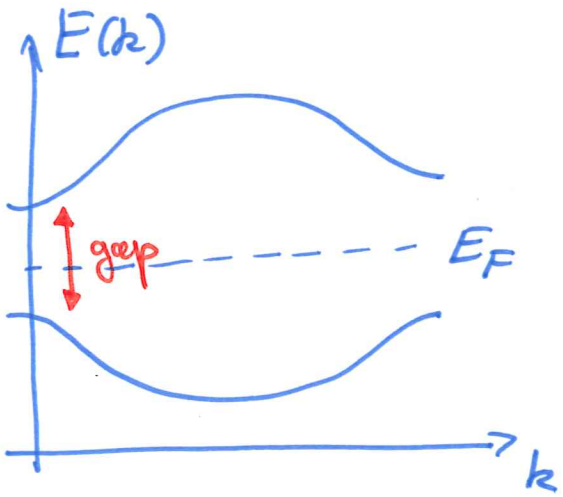
to be solved on one unit cell (e.g. Wigner Seitz) with periodic boundary conditions.

This defines an eigenvalue problem on a finite volume $\rightarrow$ discrete energy spectrum for each $\vec{k}$, each level only finitely degenerate

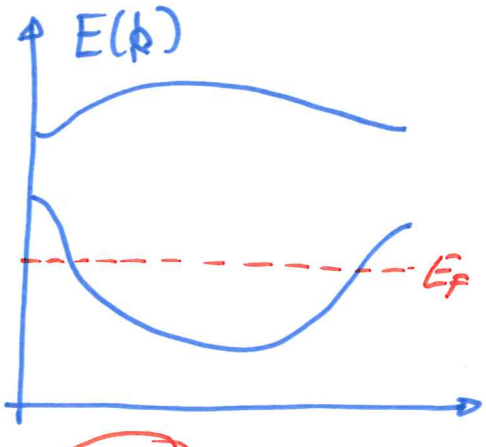
$\Rightarrow$ Energy bands $E_n(\vec{k})$ $n = 1, 2, 3, \ldots$

- continuous as a function of $\vec{k}$ (if not degenerate, i.e. at band crossings)
- periodic over the Brillouin zone $E_n(\vec{k} + \vec{G}) = E_n(\vec{k})$ $\vec{G} \in \mathcal{G}^*$

- The level spectrum is crucial for most properties of the solid: In an independent electron approximation, all ~~el-el~~ levels up to the Fermi-energy E_F are occupied. If E_F falls in a forbidden energy region (gap), electrons can only be excited with a minimum energy, and the system behaves as an insulator. In a metal, $\vec{k}$ with $E_n(\vec{k}) = E_F$ form the Fermi surface. It can be a multiply connected surface that lies in several bands. Its topology is important for many properties of the solid (transport, instabilities to certain kinds of order ...)



insulator, semiconductor



metal

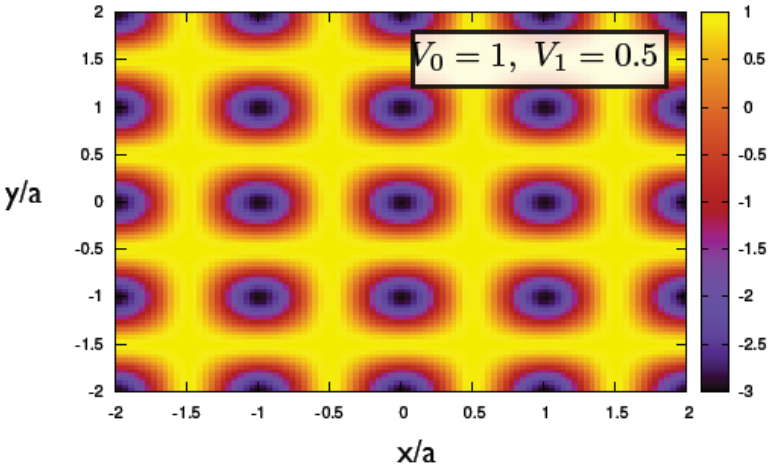
Band structure for the square lattice in 2 dimensions

lattice: $\mathcal{G} = \left\{ a \begin{pmatrix} n_x \\ n_y \end{pmatrix}, \quad n_x, n_y \in \mathbb{Z} \right\}$

unit $a \equiv 1$

reziprokal lattice: $\mathcal{G}^* = \left\{ \frac{2\pi}{a} \begin{pmatrix} n_x \\ n_y \end{pmatrix}, \quad n_x, n_y \in \mathbb{Z} \right\}$

periodic potential: $V(x,y) = -V_0 \left[\cos\left(\frac{2\pi x}{a}\right) + \cos\left(\frac{2\pi y}{a}\right) \right] - V_1 \cos\left(\frac{2\pi(x+y)}{a}\right)$



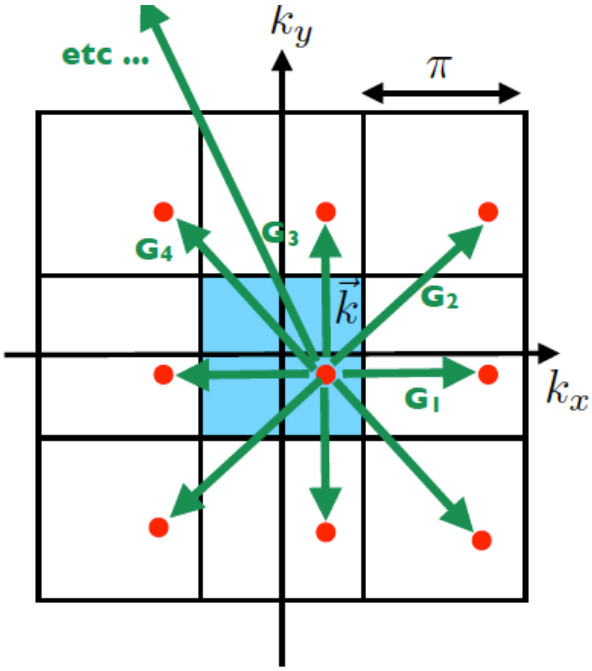
e.g., good approximation for optical lattice for cold atoms, see, e.g., I. Bloch, J. Dalibard, and W. Zwerger, Rev. Mod. Phys. **80**, 885 (2008)

Schrödinger equation in reziprocal space:

Ansatz: $u_{\vec{k}}(\vec{r}) = \sum_{\vec{G} \in \mathcal{G}^*} u_{\vec{k},\vec{G}} \ e^{i\vec{G}\vec{r}}$

$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{G} \in \mathcal{G}^*} u_{\vec{k},\vec{G}} e^{i(\vec{G}+\vec{k})\vec{r}}$

Bloch wave at $\vec{k}$: superposition of plane waves with momentum $\vec{k} + \vec{G}, \vec{G} \in \mathcal{G}$



Matrix equation:

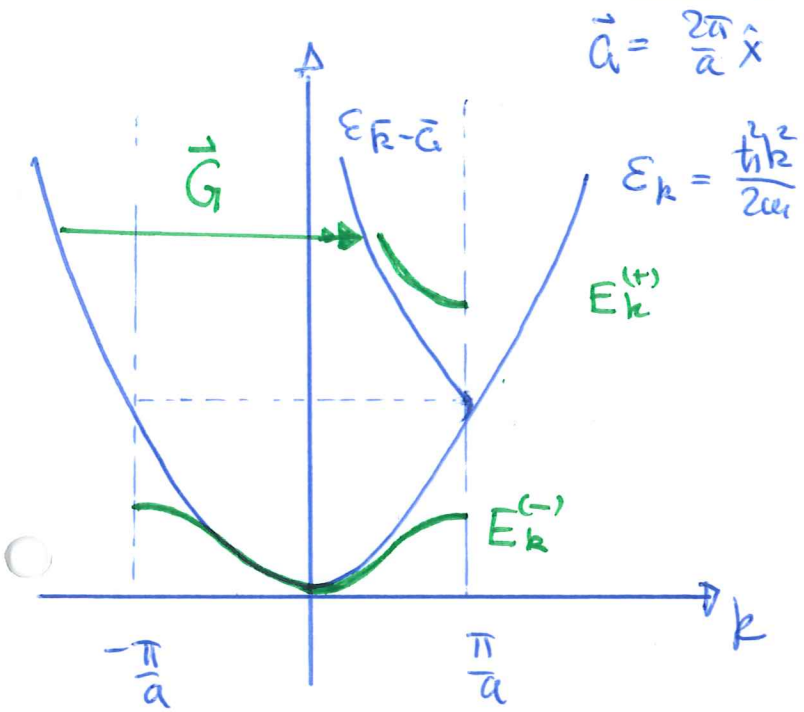
$$\frac{\hbar^2(\vec{k}-\vec{G})^2}{2m} u_{\vec{k},\vec{G}} + \sum_{\vec{G}'} V_{\vec{G}'-\vec{G}} u_{\vec{k},-\vec{G}'} = E_{\vec{k}}\, u_{\vec{k},\vec{G}}$$

energy unit in the following: $\frac{\hbar^2}{2ma^2}$

Here $V_{(\pi,0)} = V_{(-\pi,0)} = V_{(0,\pi)} = V_{(0,-\pi)} = -V_0/2$

$V_{(\pi,\pi)} = V_{(-\pi,\pi)} = V_{(\pi,-\pi)} = V_{(-\pi,-\pi)} = -V_1/2$

- one-dimensional case



weak potential: perturbative analysis close to degenerate point: $k \cong G/2$

$\rightsquigarrow$ take into account two plane waves:

$$u_k(\vec{r}) = \sum_{\vec{G}} c_G^{(k)} e^{i\vec{G}\vec{r}}$$

only $c_0, c_G \neq 0$ $\Rightarrow$

Schrödinger equation becomes 2×2 eigenvalue problem

$$\begin{pmatrix} \varepsilon_k & V_G \\ V_G^* & \varepsilon_{k-G} \end{pmatrix} \begin{pmatrix} c_0 \\ c_G \end{pmatrix} = E_k \begin{pmatrix} c_0 \\ c_G \end{pmatrix}$$

$$E_k^{\pm} = \frac{1}{2}\left((\varepsilon_k + \varepsilon_{k-G}) \pm \sqrt{(\varepsilon_k - \varepsilon_{k-G})^2 + 4|V_G|^2} \right)$$

with $V(x) = 2V_0 \cos(Gx)$ $\qquad G = \frac{2\pi}{a}$

at $k \simeq G/2$ $\qquad (\epsilon_k = \epsilon_{k-G} \equiv \epsilon_0)$

$$\begin{pmatrix} \epsilon_0 & V_0 \\ V_0 & \epsilon_0 \end{pmatrix} \begin{pmatrix} C_0 \\ C_G \end{pmatrix} = E \begin{pmatrix} C_0 \\ C_G \end{pmatrix}$$

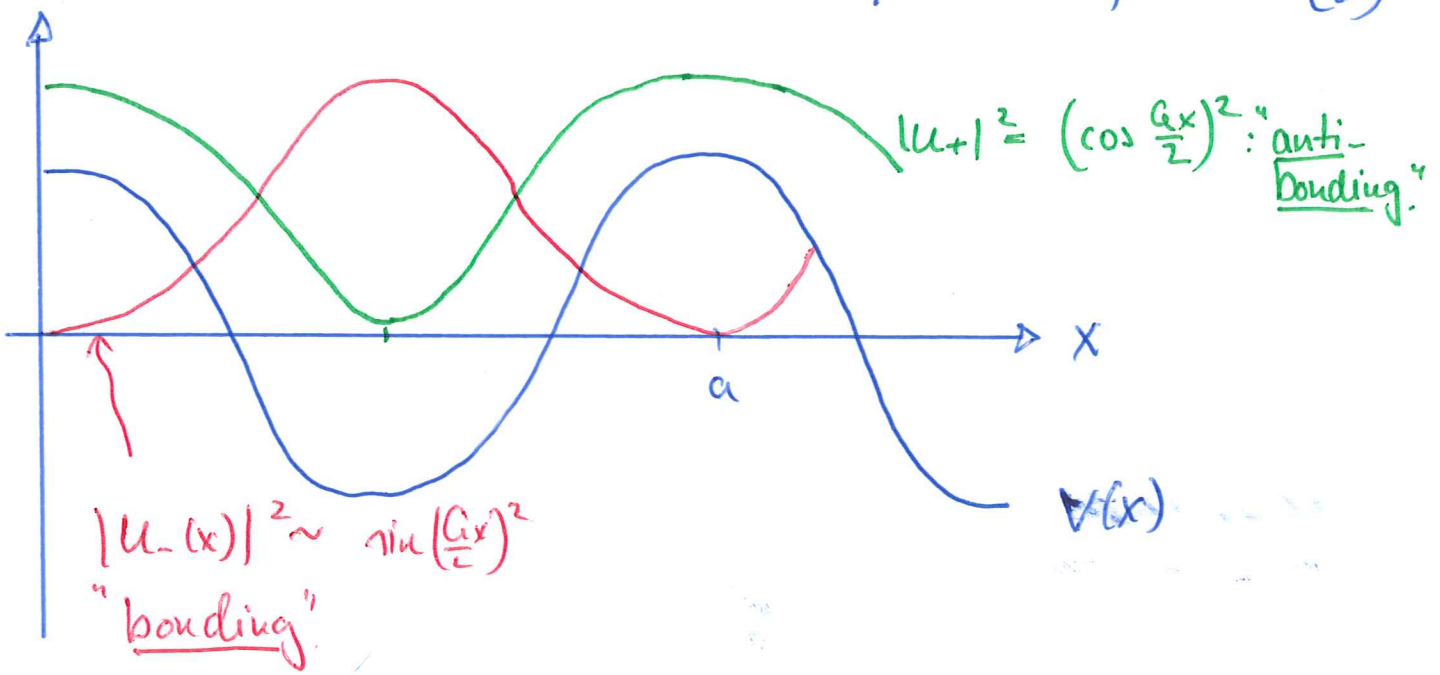
solutions:

- $\begin{pmatrix} C_0 \\ C_G \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \end{pmatrix} / \sqrt{2} \quad \Rightarrow E^{(+)} = \epsilon_0 + V_0$

$$|u(x)|^2 \sim |1 + e^{iGx}|^2 \sim \cos\left(\frac{Gx}{2}\right)^2$$

- $\begin{pmatrix} C_0 \\ C_1 \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \end{pmatrix} / \sqrt{2} \quad \Rightarrow E^{(-)} = \epsilon_0 - V_0$

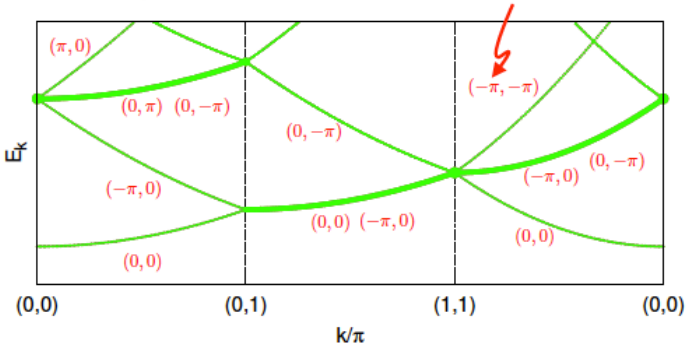
$$|u(x)|^2 \sim |1 - e^{iGx}|^2 \sim \sin\left(\frac{Gx}{2}\right)^2$$

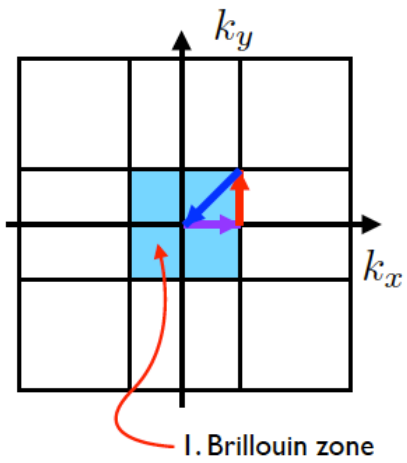


V(r)=0: Backfolding of plane waves:

Band-structure along path through 1st BZ:

$V_0 = 1,\ V_1 = 0$





Pointsize: degeneracy (1,2,4)
Label: Plane wave label G (line ↔ plane wave at k+G)

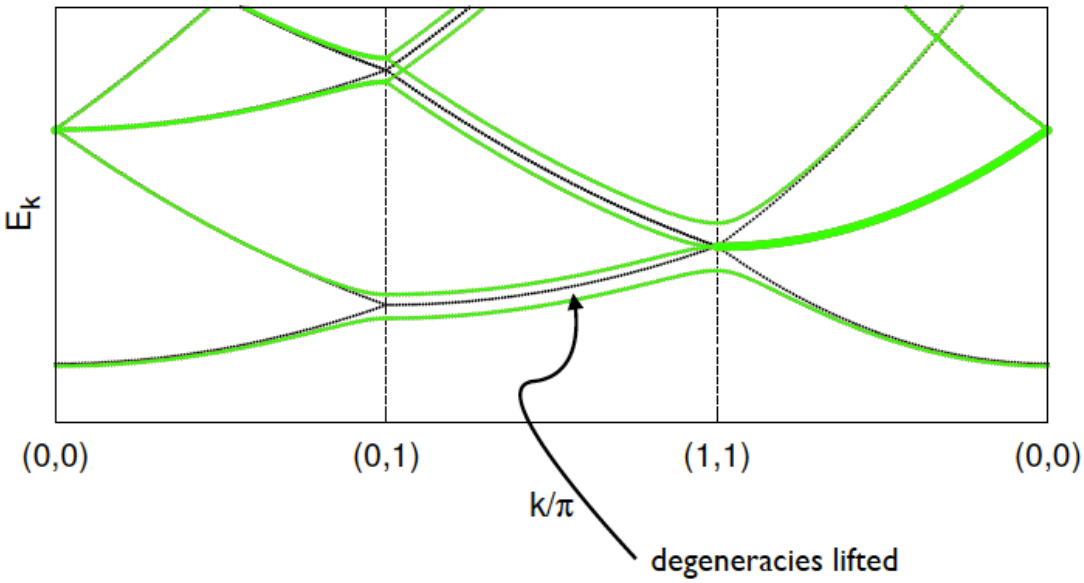
Now: Numerical solution with finitely many plane waves: (please try !)

$$\vec{G} \in \left\{ \frac{2\pi}{a} \begin{pmatrix} n_x \\ n_y \end{pmatrix},\quad n_x, n_y = -N \ldots N \right\}$$

choose N large enough to converge solution
Below: N=3,4

$V_0 = 4,\ V_1 = 0$

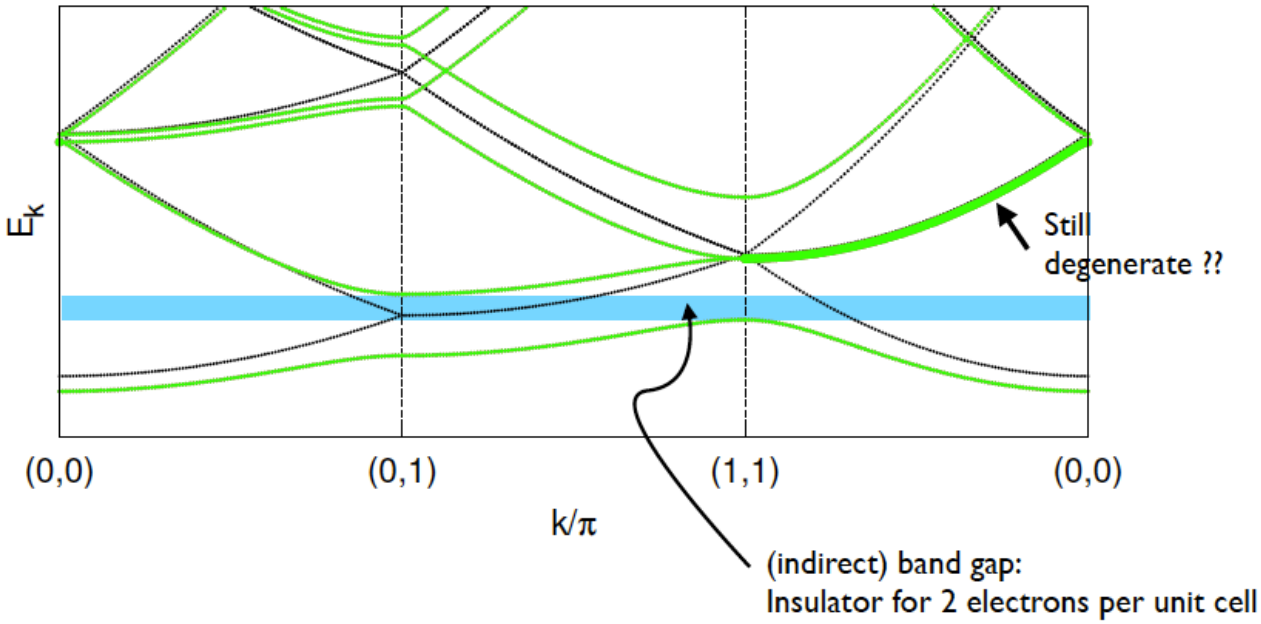
Black: free dispersion



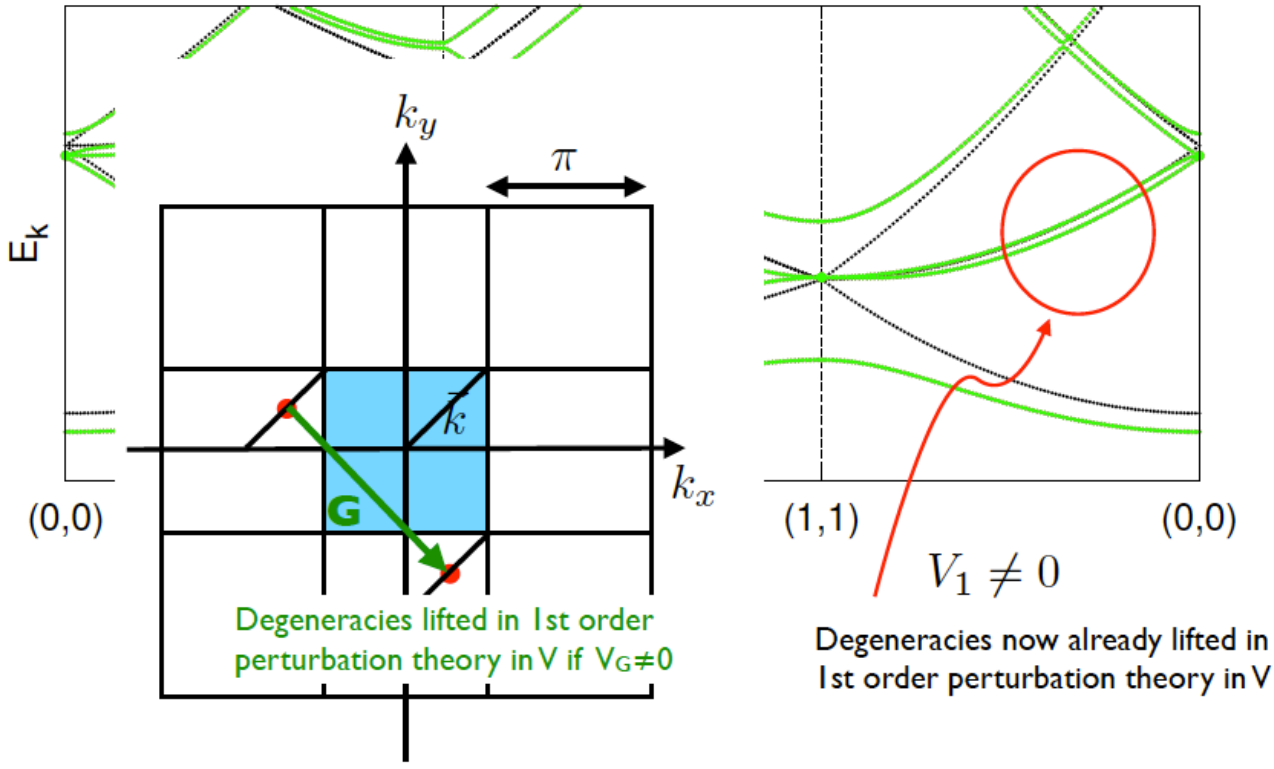
Weak potential: System still metallic

Fermi-surface for two electrons per unit cell:
hole pockets in 1st band, electron pockets in 2nd band

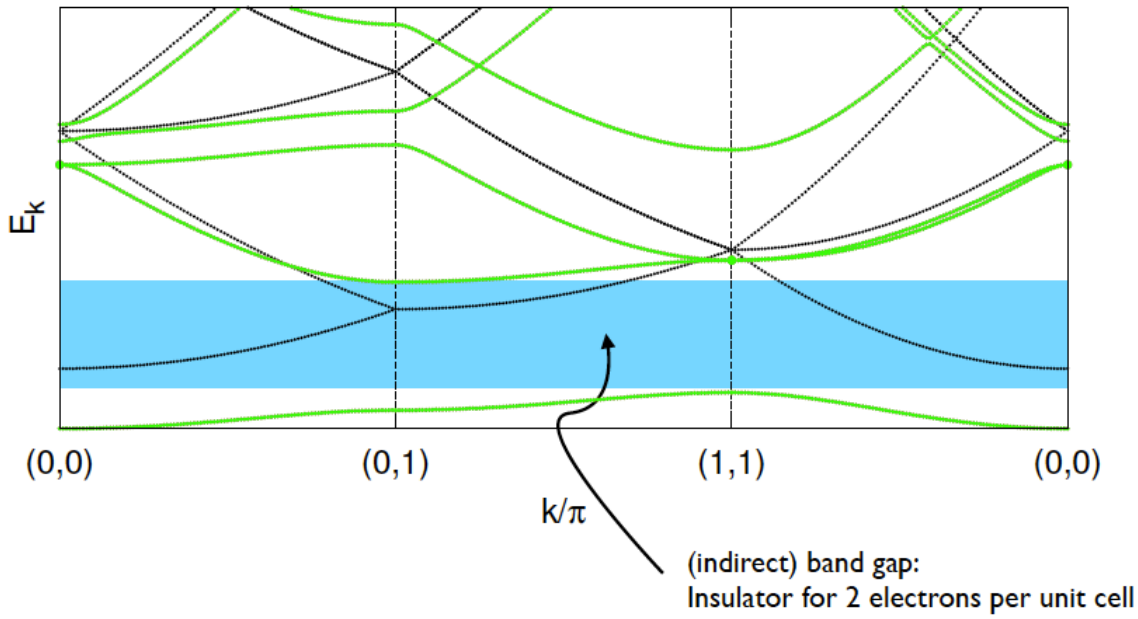
$V_0 = 10,\ V_1 = 0$



$V_0 = 10,\ V_1 = 2$



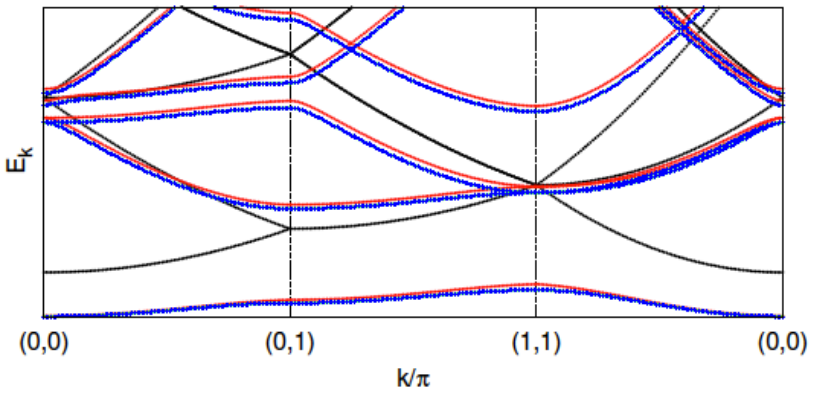
$V_0 = 20, V_1 = 2$



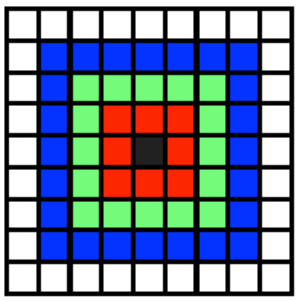
Strong-potential: Lowest band becomes flat
tight-binding limit (see below)

Convergence of the result with N (number of plane waves)

$V_0 = 20, V_1 = 2$



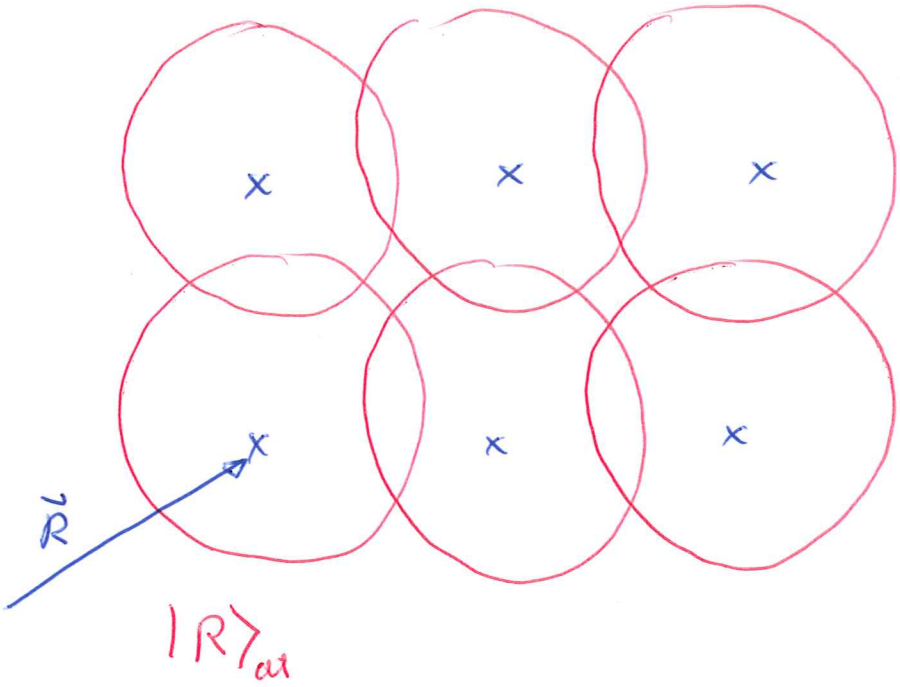
black: plane waves
red: N=1
green: N=2
blue: N=3



Relatively fast convergence because potential
is smooth and not too strong

tight-binding description

starting point for the description of solids: well localized "atomic" orbitals:



$\langle r|\vec{R}\rangle_{at} = \varphi_{at}(r-R)$ φ_{at}: atomic orbitals

- assume that description can be restricted on only limited set of orbitals (because others are far off in energy) Here: for simplicity of notation: only one orbital ($\hat{=}$ H-crystal.)

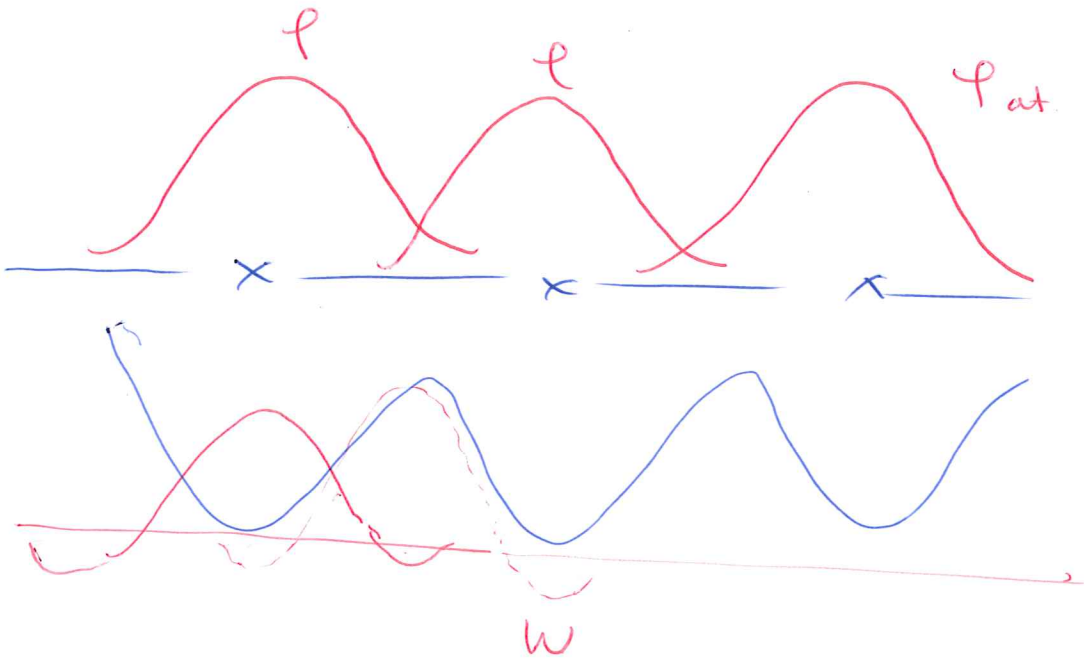
≈> to find band-structure, diagonalize Hamiltonian $H = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r})$ in subset $\{|R\rangle_{at}\}$

"Problem": atomic orbitals at different sites not orthogonal: ${}_{at}\langle R|R'\rangle_{at} \neq \delta_{RR'}$

≈> somehow construct (by linear combinations) $|R\rangle = \sum_{R'} U_{RR'}|R'\rangle_{at}$ with suitable choice of $\underline{\underline{U}}$) another basis which is mutually orthogonal: $\langle R|R'\rangle = \delta_{RR'}$

Such a real-space basis is called a Wannier basis

When atomic orbitals are well localized. (so that $\langle R|R'\rangle \sim e^{-|\vec{R}-\vec{R}'|/s}$ falls off exponentially, also WF will be localized



H ouG NL:

$$t_{RR'} = \begin{cases} \varepsilon \\ t \end{cases}$$

$$H = \sum_{RR'}$$

solut. $$|\psi_k\rangle = \frac{1}{\sqrt{L}} \sum_R |R\rangle e^{ikR}$$

$$\langle k|H|k\rangle = \frac{1}{L} \sum_{RR'} \underbrace{\langle R|H|R'\rangle}\, e^{ik(R-R')}$$

$$= \sum_R \langle R|H|0\rangle\, e^{ikR} \equiv \underline{\varepsilon_k}$$

- Representation of Hamiltonian:

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

$$H = \sum_{RR'} |R\rangle \underbrace{\langle R|\, H \,|R'\rangle}_{h_{\bar{R}-\bar{R}'}} \langle R'|$$

Matrix element for tunneling between wannier orbitals.

- If wannier orbitals are well localized $h_{\bar{R}-\bar{R}'}$ falls off exponentially. Simplest approximation:

$$h_{\bar{R}-\bar{R}'} = \begin{cases} \varepsilon & \bar{R} = \bar{R}' \\ -J & \bar{R}, \bar{R} \text{ nearest neighbors} \\ 0 & \text{otherwise zero} \end{cases}$$

- Band structure:

Bloch state $|k\rangle = \frac{1}{\sqrt{L}} \sum_R |R\rangle\, e^{i\vec{k}\vec{R}}$

<u>check</u> $\psi_k(r) = e^{ikr} \underbrace{\left\{ \frac{1}{L} \sum_k w(r-R)\, e^{ik(R-r)} \right\}}_{\text{periodic}}$

$\hat{H}$ is diagonalized by the Bloch functions (Band index omitted, one band only)

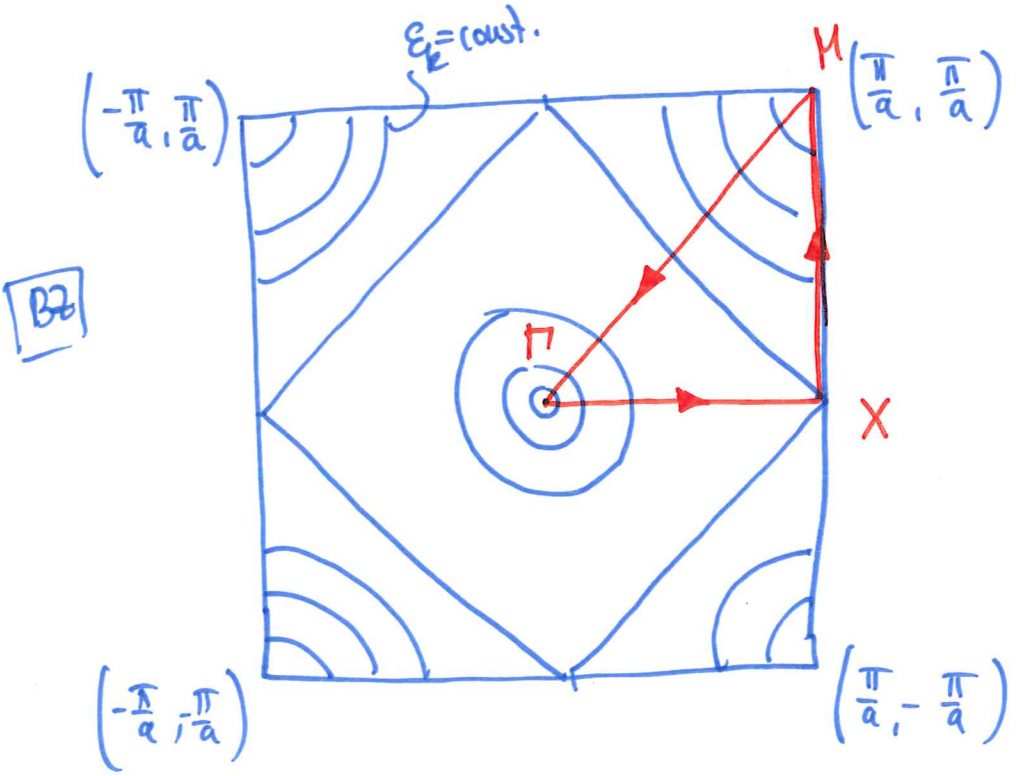
$$|\psi_k\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{+i\vec{k}\vec{R}} |\vec{R}\rangle$$

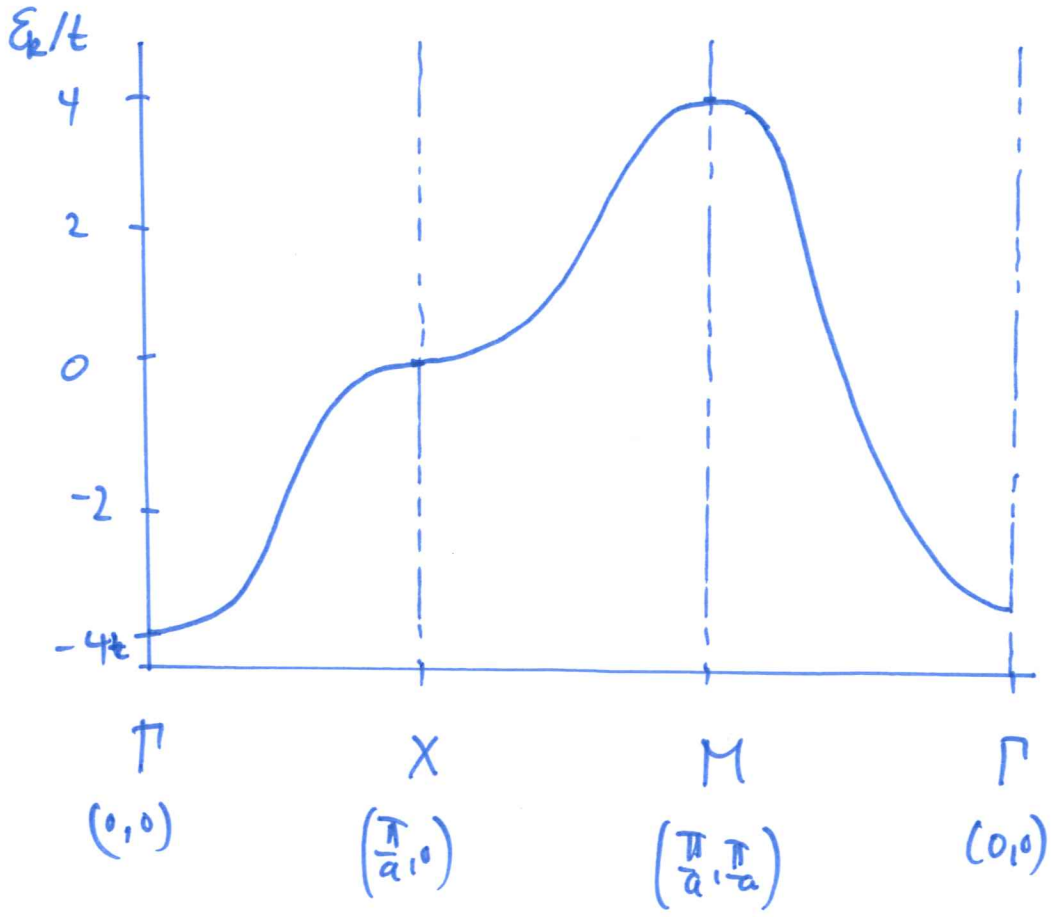
$$\hat{H}|\psi_k\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\vec{R}} \{ \varepsilon_0 |\vec{R}\rangle - t\,|\vec{R}+\vec{a}_1\rangle - t\,|\vec{R}-\vec{a}_1\rangle - t\,|\vec{R}+\vec{a}_2\rangle - t\,|\vec{R}-\vec{a}_2\rangle \}$$

(shift of summation index $\vec{R}+\vec{a}_1 \to \vec{R}$)

$$= \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\vec{R}} |\vec{R}\rangle \{ \varepsilon_0 - t e^{-i\vec{k}\vec{a}_1} - t e^{i\vec{k}\vec{a}_1} - t e^{-i\vec{k}\vec{a}_2} - t e^{i\vec{k}\vec{a}_2} \}$$

$$\boxed{\hat{H}|\psi_k\rangle = \underbrace{[\varepsilon_0 - 2t\cos(k_x a) - 2t\cos(k_y a)]}_{\varepsilon_k} |\psi_k\rangle}$$




ε_k/t
4
2
0
-2
$-4t$
Γ
X
M
Γ
(0,0)
$(\frac{\pi}{a},0)$
$(\frac{\pi}{a},\frac{\pi}{a})$
(0,0)

• Dynamics of Bloch electrons

Semiclassical equations of motion:

electron with momentum ***k*** and ***r,*** in external fields ***E(r)***, ***B(r)***

wave packet $\Delta r, \Delta k$:

$\Delta k \ll$ size of 1st BZ $\quad \Leftrightarrow \quad \Delta r \gg$ lattice spacing

still variation of *E(r)* and *B(r)* on scales larger than Δr

equations of motion:

$$\dot{\vec{r}} = \vec{v}_n(\vec{r},\vec{k}) = \frac{1}{\hbar}\frac{\partial E_n(\vec{k})}{\partial \vec{k}}$$

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

band index *n* conserved

$\vec{k} \equiv \vec{k} + \vec{G}$ equivalent, i.e., k in 1.BZ

(no further derivation here)

Example: acceleration in external field E:

$$\frac{d}{dt}v_\alpha = \frac{d}{dt}\frac{1}{\hbar}\frac{\partial E_n(\vec{k})}{\partial k_\alpha} = \sum_\beta \frac{1}{\hbar}\frac{\partial^2 E_n(\vec{k})}{\partial k_\beta \partial k_\alpha}\dot{k}_\beta \qquad \alpha,\beta = x,y,z$$

$\dot{k}_\beta \rightarrow -eE_\beta$

c.f. acceleration of free electrons:

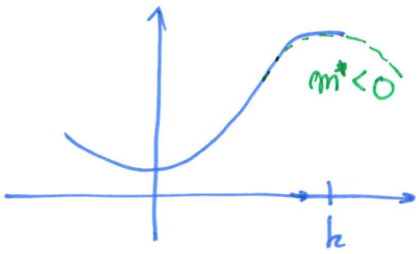
$$\dot{\vec{v}} = -\frac{e}{m}\vec{E}(\vec{r})$$

mass tensor: $\quad \left(\frac{1}{m}\right)_{\alpha\beta} = \frac{1}{\hbar^2}\frac{\partial^2 E_n(\vec{k})}{\partial k_\beta \partial k_\alpha}$

e.g. diagonal tensor (symmetry) $\quad \underline{m} = \begin{pmatrix} m_* & 0 & 0 \\ 0 & m_* & 0 \\ 0 & 0 & m_* \end{pmatrix} \Leftrightarrow \quad \dot{\vec{v}} = -\frac{e}{m_*}\dot{\vec{E}}$

band electrons behave like particles with a different effective mass

good metals: m same order of magnitude*



Bloch-oscillations

consider one-dimensional band $\epsilon(k) = -2t_0 \cos(ka)$

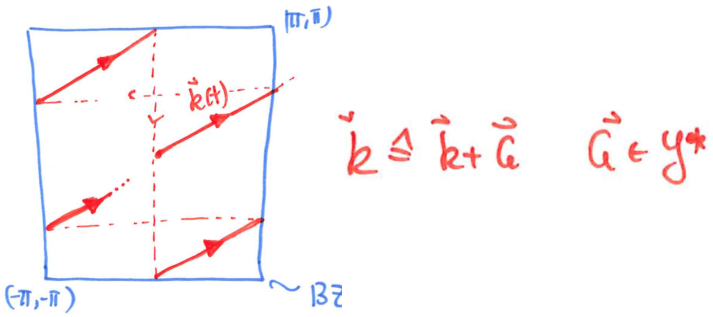
$$\hbar\dot{k} = -eE \qquad v(t) = \frac{1}{\hbar}\frac{\partial\epsilon(k)}{\partial k} = \frac{2t_0 a}{\hbar}\sin(k(t)a)$$

$$k(t) = -\frac{eEt}{\hbar} \qquad = \frac{2t_0 a}{\hbar}\sin\left(\frac{Eae}{\hbar}t\right)$$

periodic motion with Bloch frequency $\Omega = \dfrac{Eae}{\hbar}$

$$x(t) = const. - \frac{2t_0}{Ee}\cos\left(\frac{Eae}{\hbar}t\right)$$

Motion in more than one dimension



$\vec{k} \equiv \vec{k} + \vec{G} \qquad \vec{G} \in y^*$

large field: $\dfrac{1kV}{cm} \quad a = 1\mathring{A} \qquad \Omega = \dfrac{Eea}{\hbar} = \dfrac{10^{-5}eV}{\hbar}$

$$\Rightarrow \quad \frac{2\pi}{\Omega} \gg \text{time between incoherent scattering events}$$

$$\Delta x = \frac{2t_0}{eEa}a = \frac{1eV}{10^{-5}eV}a = 10^5 a$$

$$\frac{\hbar}{eV} = 0.66fs$$

Bloch oscillations usually destroyed by scattering

AC field: $E(t) = E_0 \cos(\Omega t)$ *(switch on at t=0)*

$$\Rightarrow \; k(t) = k(0) - \frac{E_0 e}{\hbar \Omega} \sin(\Omega t)$$

$\Rightarrow$ *current:*

$$\langle j(t) \rangle = \sum_{|k(0)|<k_F} v(k(t))$$

$$= \int_{-k_F}^{k_F} \frac{dk}{2\pi} \, 2t_0 a \sin\left(ka - \frac{E_0 e a}{\hbar \Omega} \sin(\Omega t) \right)$$

$$= -\sin\left(\frac{E_0 e a}{\hbar \Omega} \sin(\Omega t) \right) \int_{-k_F}^{k_F} \frac{dk}{2\pi} \, 2t_0 a \cos(ka)$$

all odd harmonics present!

nature photonics

LETTERS

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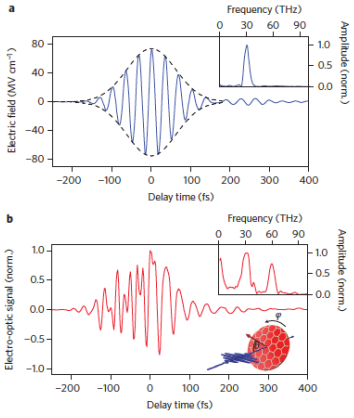
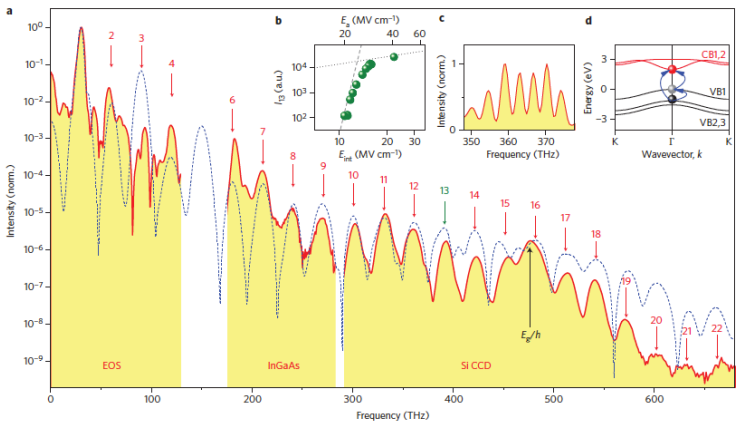
Sub-cycle control of terahertz high-harmonic generation by dynamical Bloch oscillations

GaSe

O. Schubert[1], M. Hohenleutner[1], F. Langer[1], B. Urbanek[1], C. Lange[1], U. Huttner[2], D. Golde[2], T. Meier[3], M. Kira[2], S. W. Koch[2] and R. Huber[1]*





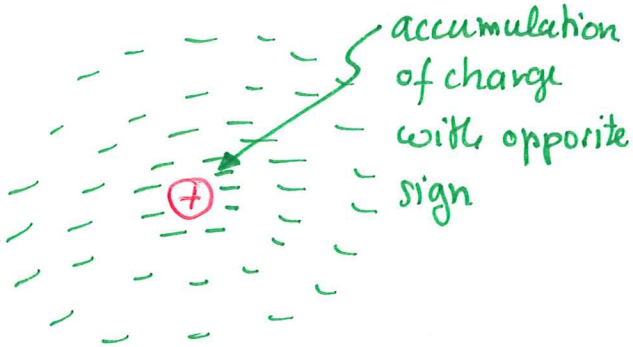
also even harmonics (band effects)

Screening - dielectric response of solids

In solids (in particular in metals) the long-range Coulomb interaction is strongly modified (and becomes short range) because the ~~charge~~ collective response of all mobile charges induces a counter charge on a very fast timescale.

$\phi(r) = q/r$

"bare charge"



Motivation:

- relation to dielectric response $\rightsquigarrow$ optical conductivity
- understand effective interactions between (quasi) particles in the solid (e.g. attractive interactions which lead to superconductivity)
- response functions $\rightsquigarrow$ excitation spectrum, collective excitations

• Macroscopic description

Maxwell: (cgs)

$$\bar{\nabla}\cdot\bar{E} = 4\pi\rho$$

$$\bar{\nabla}\times\bar{B} = \frac{4\pi}{c}\vec{j} + \frac{1}{c}\frac{\partial\bar{E}}{\partial t}$$

$$\bar{\nabla}\times\bar{E} = -\frac{1}{c}\frac{\partial\bar{B}}{\partial t}$$

$$\bar{\nabla}\cdot\bar{B} = 0$$

ρ, $\vec{j}$: microscopic charges : "external + induced"

↳ macroscopic Maxwell-eq equations:

$$\vec{\nabla}\cdot\vec{D} = 4\pi\rho_{ext}$$

$$\bar{\nabla}\times\bar{H} = \frac{4\pi}{c}\vec{j}_{ext} + \frac{1}{c}\frac{\partial\vec{D}}{\partial t}$$

ρ_{ext}, j_{ext} : external charges

+ linear response $\bar{D} = \varepsilon\bar{E}$, $\bar{B} = \mu\bar{H}$

Note: linear-response relations in general non-local in space and time

$$D_\alpha(\vec{r},t) = \int_{-\infty}^{t} dt' \; \tilde{\varepsilon}_{\alpha\beta}(t-t', \vec{r}-\vec{r}') \, E_\beta(\vec{r}',t')$$

($\tilde{\varepsilon}$: tensor)

causal relation! retarded response

≈> Fourier transformation: $D(\vec{r},t) = \int d^3q \int d\omega \; e^{i\vec{q}\vec{r}-i\omega t} D_{q,\omega}$

$$\boxed{D(q,\omega) = \varepsilon(q,\omega)\, E(q,\omega)}$$

• Interpretation of dielectric function ε

consider some "bare" potential due to "external" charge density:

$$-\bar{\nabla}^2 \phi_{ext} = 4\pi \rho_{ext}$$

$$\bar{\nabla}\cdot\bar{D} = \bar{\nabla}(\varepsilon E) = \varepsilon \nabla E = -\varepsilon \bar{\nabla}^2 \phi$$

(transl. invariance)

$$\Rightarrow \boxed{\phi_{q,\omega} = \frac{\phi_{ext}(q,\omega)}{\varepsilon(q,\omega)}}$$

⇒ phenomenologically: ε describes screening, i.e. reduction of free-space potential ϕ_{ext} due to induced charge.

• Relation to conductivity

$$\nabla \times B = \frac{4\pi}{c} j_{ext} + \frac{1}{c}\frac{\partial D}{\partial t}$$ ⇝ for non mag. material with $j_{ext}=0$

$$\nabla \times B = -\frac{i\omega}{c} D \qquad (\text{Fourier } \partial_t \to -i\omega)$$

$$= -\frac{i\omega\varepsilon}{c} E \qquad (*)$$

microscopic equation (j = induced current)

$$\nabla \times \tilde{B} = \frac{4\pi}{c} \underbrace{j}_{\sigma E} - \frac{i\omega}{c} E \quad \leftarrow \text{definition of conductivity}$$

$$= -\frac{i\omega}{c}\left(1 + i\,\frac{4\pi\sigma(\omega)}{\omega}\right) E$$

compare with ⊛ :

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

$1 + i\frac{\sigma}{\omega}$ in SI units

optical response : measurement at $q \to 0$
($\lambda \gg$ atomic spacing)

- Relation to charge response function

define $\delta n = \chi\, \delta V_{ext}$

response of density δn to external potential

energy ($\rho = -e\,\delta n$ $V = -e\phi$)

Poisson: $\underbrace{\phi}_{\frac{\phi_{ext}}{\varepsilon}} = \frac{4\pi}{q^2}\underbrace{(\rho_{ext} + \rho_{induced})}_{\phi_{ext}}$

$$\frac{1}{\varepsilon(q,\omega)} = 1 + \frac{4\pi e^2}{q^2}\,\chi(q,\omega)$$

useful for calculation of ε, χ, but usually difficult to calculate $\chi = \frac{\delta n}{\delta V_{ext}}$ for interacting many particle system.

Often (and exclusively in this lecture!) we use a mean-field approximation (also random phase approximation RPA):

$$\delta n = \chi\,\delta V_{ext} \approx \chi_{free}\,(\delta V_{ext} + \delta V_{ind})$$

response of interacting electrons to external potential $\approx$ response χ_{free} of non-interacting electrons to full potential (external + induced)

with $\delta V_{ind} = -e\,\phi_{ind} \overset{\text{Poisson}}{=} \frac{4\pi e^2}{q^2}\,\delta n$

$$\Rightarrow \quad \delta n = \chi_{free}\left(\delta V_{ext} + \frac{4\pi e^2}{q^2}\,\delta n\right)$$

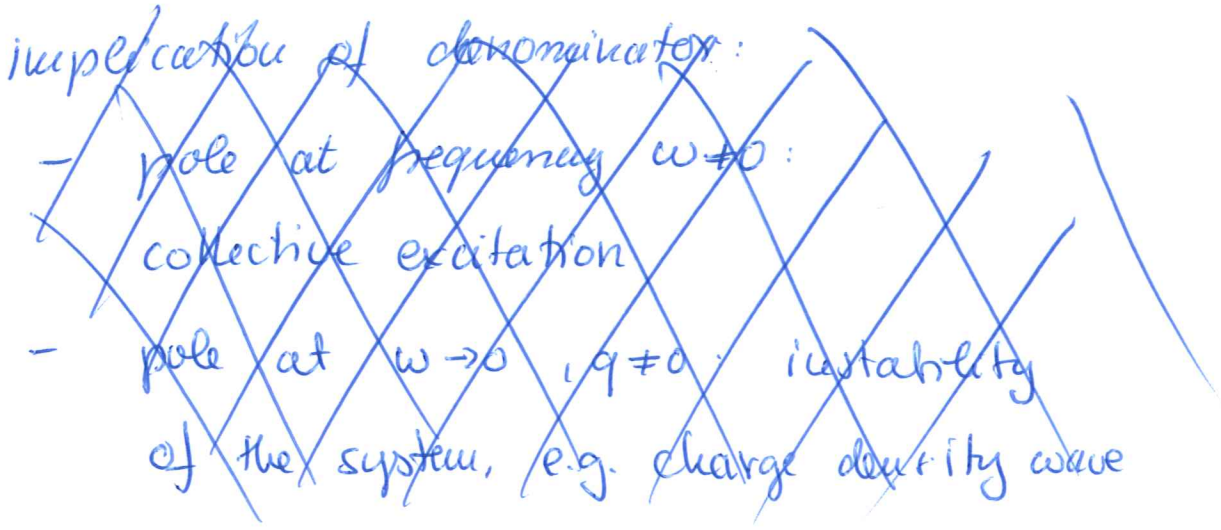
$$\Rightarrow \quad \delta n = \chi\,\delta V_{ext} \quad \text{with}$$

$$\boxed{\chi(q,\omega) = \frac{\chi_{free}(q,\omega)}{1 - \frac{4\pi e^2}{q^2}\chi_{free}(q,\omega)}}$$

RPA mean-field susceptibility

Implications of denominator (see below)

- pole at $\omega > 0$: collective excitation
- pole at $\omega \to 0$: instability, charge density wave (at $q \neq 0$) etc...



Static screening: Thomas Fermi model

Simplest model for χ_{free}:

Density $n(\vec{r}_0)$ at given point $\vec{r}_0 \cong$
Density of homogeneous electron gas in potential
$V \equiv V(\vec{r}_0)$ ("local density approximation")

homogeneous electron gas: ($n_F(x) = \frac{1}{e^{x/k_BT}+1}$ Fermi function)

$$n(V) = \int \frac{d^3k}{(2\pi)^3} n_F\left(\frac{\hbar^2 k^2}{2m} + V - \mu\right)$$

≈ 0

$$\boxed{\chi_{free} \cong -\frac{\partial n}{\partial \mu}} \quad \text{Thomas Fermi}$$

- dielectric function:

$$\varepsilon = \frac{1}{1 + \frac{4\pi e^2}{q^2}\chi} \overset{\swarrow}{=} \chi = \frac{\chi_{free}}{1 - \frac{4\pi e^2}{q^2}\chi_{free}}$$

$$= 1 - \frac{4\pi e^2}{q^2}\chi_{free} \underset{\text{Thomas Fermi}}{\overset{\uparrow}{=}} 1 + \frac{4\pi e^2 \frac{\partial n}{\partial \mu}}{q^2}$$

define Thomas-Fermi wave vector

$$k_{TF}^2 = 4\pi e^2 \frac{\partial n}{\partial \mu} \quad \Rightarrow \quad \boxed{\varepsilon = 1 + \frac{k_{TF}^2}{q^2}}$$

- at temperature $T=0$:

$$n(\mu) = \int_{|k|<k_F} d^3k/(2\pi)^3 \qquad \text{with } \hbar^2 k_F^2/2m = \mu$$

$$\Rightarrow \ldots \quad k_{TF}^2 = \frac{4me^2}{\pi\hbar^2} k_F \sim \frac{1}{k_{TF}} = O(\text{few Å})$$

for typical densities in metals.

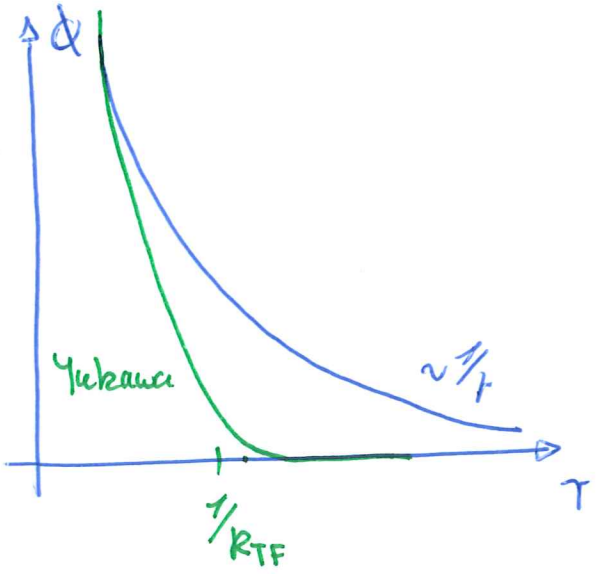
- Screened potential of an extra point charge (impurity atom / defect in crystal, ...)

$$\phi(\vec{q}) = \underbrace{\frac{4\pi Q}{q^2}}_{\phi_{ext}} \cdot \frac{1}{\varepsilon(\vec{q})} \underset{\text{Thomas F.}}{\overset{\uparrow}{=}} \frac{4\pi Q}{k_{TF}^2 + q^2}$$

Fourier transformation : $\rightsquigarrow$

$$\phi(\vec{r}) = \frac{Q}{r} e^{-r \cdot k_{TF}}$$

Yukawa potential,
screening length $1/k_{TF}$.



- more accurate $\chi_{free}(\vec{q})$: exact response of homogeneous electron gas : Lindhard theory.

$$\chi_{free}(\vec{q}, \omega=0) \overset{d=3}{=} -\frac{2m}{\hbar^2} \frac{k_F}{2\pi^2} \left\{ 1 - \frac{s}{4}\left(1 - \frac{4}{s^2}\right) \ln\left|\frac{s+2}{s-2}\right| \right\}$$

$$\chi_{free}(q, \omega=0) \overset{d=2}{=} -\frac{2m}{\hbar^2} \frac{1}{2\pi} \left\{ 1 - \left(1 - \frac{4}{s^2}\right) \Theta(s-2) \right\}$$

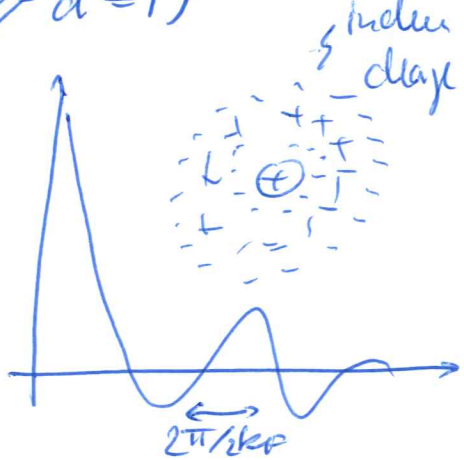
$$\chi_{free}(q, \omega=0) \overset{d=1}{=} -\frac{2m}{\hbar^2} \frac{1}{2\pi q} \left\{ \ln\left|\frac{s+2}{s-2}\right| \right\} \qquad s = q/k_F$$

more and more singular at $|q| = 2k_F$ for lower dimension ($\rightsquigarrow$ instability for $d=1$)

$\rightsquigarrow$ Interference effects
(Friedel oscillations)

In $d=3$: $\phi(r) = C \frac{\cos(2k_F r)}{r^3}$

$T=0$



Dynamic (frequency-dependent) screening

• Some general properties of response functions

Linear response $H = H_0 + \hat{A} f(t)$

($\hat{A}$: field; f: field)

(e.g. $\hat{A} = e\hat{n}$ density, $f \equiv \phi_{ext}$)

$$\langle A(t) \rangle = \int_{-\infty}^{t} dt' \, \chi(t-t') f(t')$$

1) Fourier transform.

$\chi(t)$ causal (i.e. $\chi(t) = 0$ for $t < 0$)

$\Rightarrow$ FT defined for frequencies z with $\mathrm{Im}\, z > 0$

$$\chi(\omega) \equiv \chi(\omega + i\delta) = \int_0^{\infty} dt \, \chi(t) \, e^{i(\omega + i\delta)t} \qquad \delta \downarrow 0$$

Meaning: $\chi(\omega + i\delta)$ $\delta \downarrow 0$ $\hat{=}$ response to perturbation

$f(t) = f_\omega e^{-i\omega t} e^{\delta t}$ $\hat{=}$ adiabatic switch on of field

2) analytic properties ($\chi(z)$ analytic for $\mathrm{Im}\, z > 0$, $\chi(z) \to 0$ for $|z| \to \infty$) imply relation between real and imaginary part: $\chi = \chi' + i\chi''$

$$\chi'(\omega + i0^+) = \frac{1}{\pi} \int d\omega' \, \frac{\chi''(\omega' + i0^+)}{\omega' - \omega}$$

$$\chi''(\omega + i0^+) = -\frac{1}{\pi} \int d\omega' \, \frac{\chi'(\omega' + i0^+)}{\omega' - \omega}$$

Kramers Kronig relation

example: check for $\chi = \frac{1}{\omega + i0^+} \Rightarrow \begin{cases} \chi'' = -\pi \delta(\omega) \\ \chi' = \underset{\omega \neq 0}{\frac{1}{\omega}} \end{cases}$

3) $\mathrm{Im}\, \chi \iff$ energy absorbtion

consider $f(t) = e^{\delta t} \left(f_\omega e^{-i\omega t} + f_\omega^* e^{i\omega t} \right)$

$$E(t) = \langle H_0 + \hat{A} f(t) \rangle$$

$$\frac{dE}{dt} \overset{\circledast}{=} \left\langle \frac{dH}{dt} \right\rangle = \frac{df}{dt} \underbrace{\langle A(t) \rangle}_{\chi \cdot f}$$

... itself χ, f ... average over one period:

$$\frac{d\bar{E}}{dt} \equiv \frac{1}{T} \int_0^T dt \, \frac{dE}{dt} = -2\omega \, \chi_\omega'' \, |f_\omega|^2$$

Note: proof of ⊛ : analogous to Hellmann Feynman theorem:

$$\frac{d}{dt}\langle\psi(t)|H(t)|\psi(t)\rangle = \underbrace{\frac{d\langle\psi|}{dt}}_{i\hbar\langle\psi|H}|H|\psi\rangle + \langle\psi|H|\underbrace{\frac{d|\psi\rangle}{dt}}_{-\frac{i}{\hbar}H|\psi\rangle} + \langle\psi|\frac{dH}{dt}|\psi\rangle$$

$= 0$

4) Absorbtion ⟺ excitation spectrum

Fermi - golden rule : e.g. system at $T=0$ $\omega > 0$:

$$\frac{dE}{dt} = \sum_{|n\rangle} \overbrace{W_{0\to n}}^{\text{transition rate}} (E_f - E_0)$$

$|n\rangle$ final states : all possible many particle eigenstates

$$\frac{2\pi}{\hbar}|\langle n|\hat{A}|0\rangle|^2 \delta(\omega + E_0 - E_n) \qquad (\hbar = 1)$$

compare with absorbtion, ~~also positive fx~~

... also for $\omega < 0$ ...

$$\chi''(\omega+i0) = -\pi \sum_n |\langle n|\hat{A}|0\rangle|^2 [\delta(\omega + E_0 - E_n) - \delta(\omega + E_n - E_0)]$$

$T>0$:

$$\boxed{\chi''_\omega = -\pi \sum_{nm} \frac{e^{-\beta E_n} - e^{-\beta E_m}}{Z} |\langle n|A|m\rangle|^2 \delta(\omega + E_n - E_m)}$$

Note: this result is equivalent to the

Kubo formula:

$$\chi(t-\bar{t}) = -i\,\theta(t-\bar{t})\,\mathrm{Tr}\left(e^{-\beta H}\,[A(t), A(\bar{t})]\right)/Z$$

which is derived from standard time-dependent perturbation theory.

5) Fluctuations $\longleftrightarrow$ response / dissipation

auto correlation function:

$$\langle (A(t) - \langle A\rangle)\,(A(t') - \langle A\rangle\rangle = \langle A(t)\,A(t')\rangle - \langle A\rangle^2$$

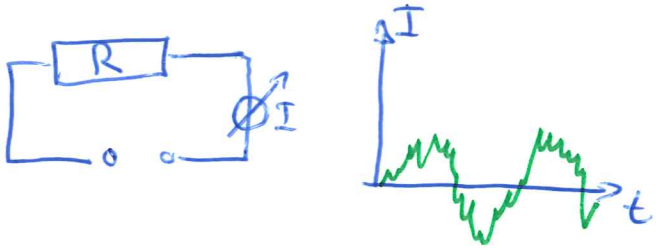
$$C(t) = \langle A(t)\,A(0) + A(0)\,A(t)\rangle$$

$$C(\omega) = -2\,\chi''(\omega)\,\coth\left(\frac{\beta\omega}{2}\right)$$

Fluctuation-dissipation theorem

(check, e.g., expand $C(\omega)$ in eigenstates and compare with results above)

Example: resistor noise



Noise power density:

$$|I(\omega)|^2 + |I(-\omega)|^2 = \frac{1}{T}\int_0^T dt\,dt'\, e^{-i\omega(t-t')} \times$$

$$\times \langle I(t)\,I(t') + I(t')\,I(t)\rangle = C(\omega)$$

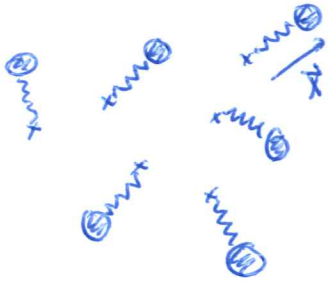
$$C(\omega) = 2\sigma(\omega)\,\omega\,\coth\frac{\beta\omega}{2} \underset{\omega \ll T}{=} \frac{4k_BT}{R}$$

<u>Universal ratio Between fluctuations and response</u>
(→ "thermometer")

<u>Back to density response $\chi = \delta n/\delta V_{ext}$</u>

<u>Example 1 : oscillator model</u>

density n_0 of oscillators



$$m\ddot{\vec{x}} = -m\omega_0^2 x + \underbrace{f_{ex}}_{-\nabla V_{ext}}$$

$$\ddot{\vec{x}}\,(\omega_0^2-\omega^2) = -\frac{1}{m}\vec{\nabla} V_{ext}$$

<u>density:</u> $\delta n / n_0 = -\vec{\nabla}\cdot\vec{x} =$

↑

in Fourier space: $\frac{\delta n}{n_0} = \mp i\vec{q}\cdot\vec{x}$

$$\vec{x} = -\frac{1}{m(\omega_0^2-\omega^2)}\, i\vec{q}\, V_{ext}$$

$$\delta n = q^2 \underbrace{\frac{n_0/m}{\omega^2 - \omega_0^2}}_{\chi_{free}} V_{ext}$$

"free": no coulomb interaction between the oscillators. at least ok for low density

$$\chi_{free} = \frac{q^2 n_0}{m} \left(\frac{1}{\omega - \omega_0} - \frac{1}{\omega + \omega_0} \right) \frac{1}{2\omega_0}$$

(really: $\chi_{free}(\omega + i0^+) = \frac{q^2 n_0}{m} \left(\frac{1}{\omega + i0^+ - \omega_0} - \frac{1}{\omega + i0^+ + \omega_0} \right)$

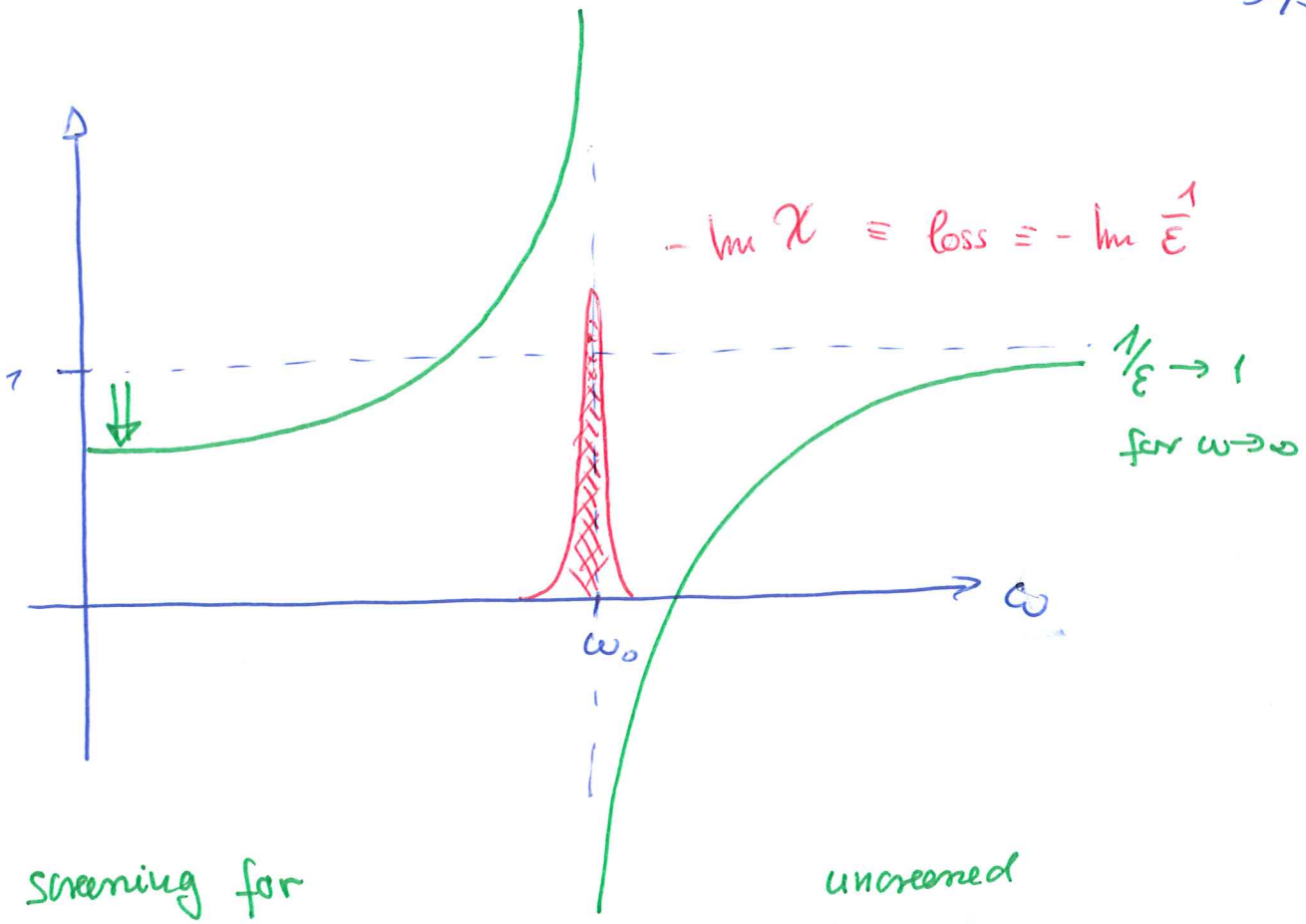
$$\mathrm{Im}\, \chi_{free}(\omega + i0^+) = -\pi \frac{q^2 n_0}{2m\omega_0} \left[\delta(\omega - \omega_0) - \delta(\omega + \omega_0) \right]$$

⇒ excitation spectrum: excitation of oscillator "quantum" $\hbar\omega_0$

$$\frac{1}{\varepsilon(q,\omega)} = 1 + \frac{4\pi e^2}{q^2} \underbrace{\chi}_{\chi = \chi_{free}} = 1 + \frac{4\pi e^2 n_0/m}{\omega^2 - \omega_0^2}$$

$4\pi e^2 n_0/m$ has unit $\Rightarrow \left[\frac{1}{\text{time}^2}\right]$

$4\pi e^2 n_0/m \equiv \omega_p^2$ ω_p: plasma frequency

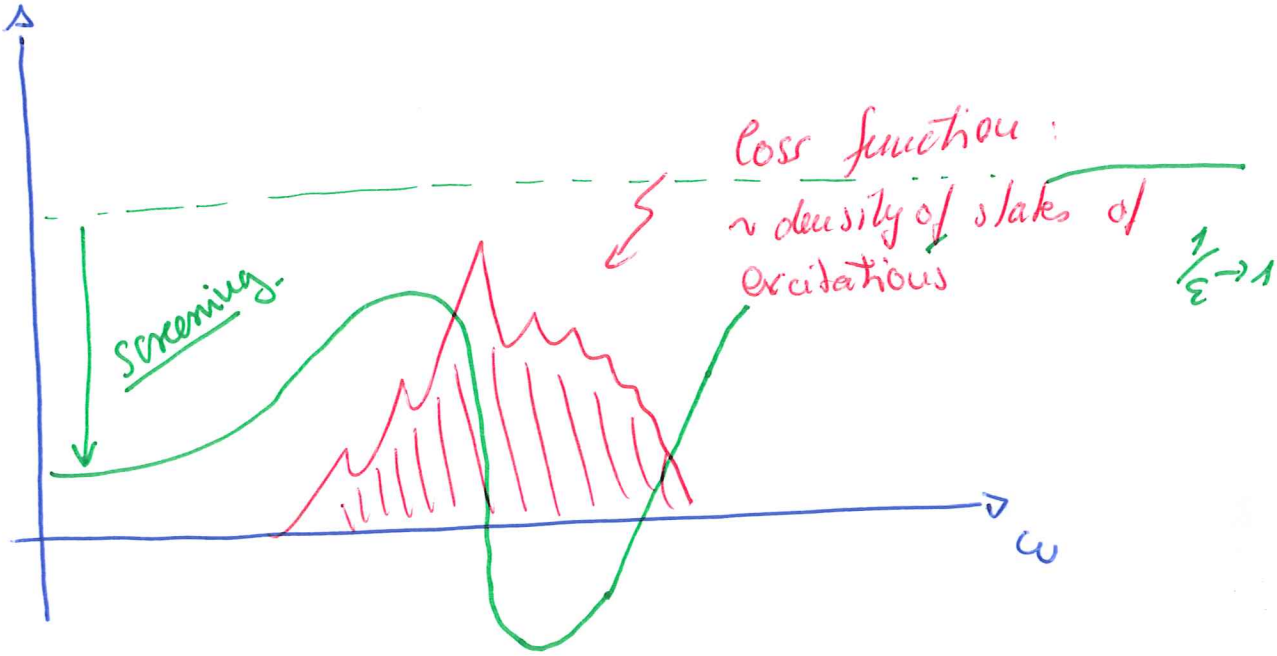


screening for
$\omega \ll \omega_0$

uncreened
for $\omega \gg \omega_0$

dielectric loss for $\omega = \omega_0$

Real material:



"unbound" particles $\omega_0 = 0$

(e.g. electrons in metal)

$$\chi_{free} = q^2 \frac{n_0/m}{\omega^2} \quad \Rightarrow \text{Absorbtion only at } \omega = 0?$$

with interactions between particles:

$$\chi = \frac{\chi_{free}}{1 - \frac{4\pi e^2}{q^2}\chi_{free}} = \frac{q^2 n_0/m}{\omega^2\left(1 - \frac{4\pi e^2 n_0/m}{\omega^2}\right)}$$

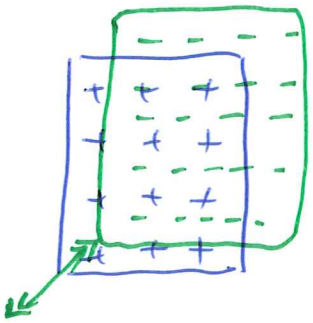
$$= \frac{q^2 n_0/m}{\omega^2 - \omega_p^2}$$

$\omega_p^2 = 4\pi e^2 n_0/m$

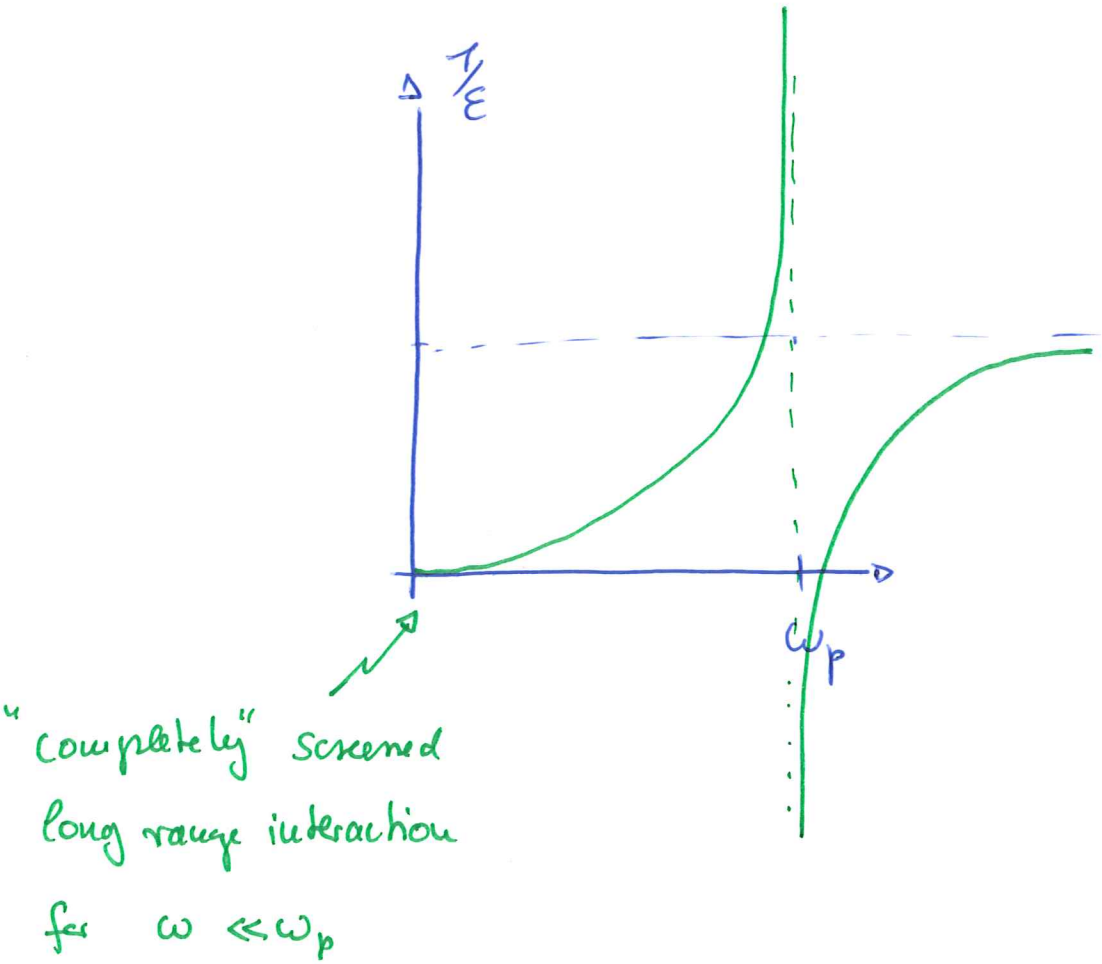
$$\chi''(\omega) = -\pi \frac{q^2 n_0/m}{2\omega_p}\left[\delta(\omega - \omega_p) - \delta(\omega + \omega_p)\right]$$

$\Rightarrow$ new "collective excitation" in the system, present only due to interaction

- corresponds to long-lived oscillation of mobile negative charges in front of positively charged background:



- check. $\frac{1}{\varepsilon} = \frac{\omega^2}{\omega^2 - \omega_p^2}$



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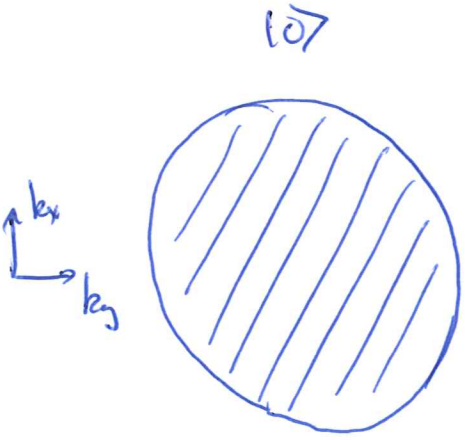
• Excitation spectrum of electrons $\varepsilon_k = \frac{\hbar^2 k^2}{2m}$

Fermi golden rule:

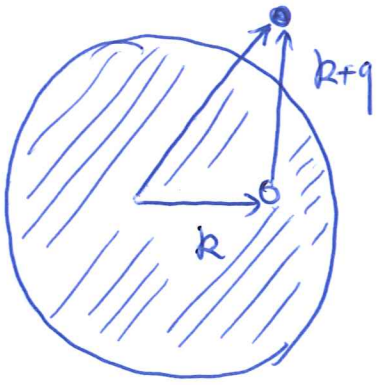
$$\chi''_{free}(\omega, q) \overset{\omega>0}{\sim} -\pi \sum_f \underbrace{|\langle f | \hat{n}_q | 0 \rangle|^2}_{\text{transition matrix element}} \delta(\omega + E_0 - E_f)$$

ground state → excited state due to density modulation (momentum transfer $\vec{q}$)



Fermi see

excitation with momentum transfer q



particle-hole excitation

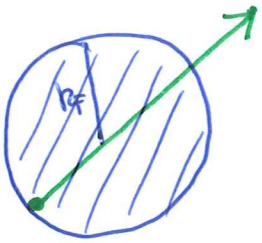
$k+q$ must be empty $|k+q| > k_F$

k must be occupied $|k| < |k_F|$

Skeppsted

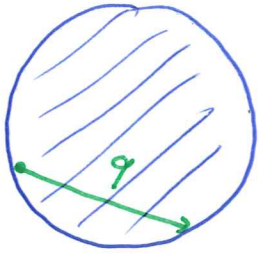
"excitation map" for vehicle q, ω are excitations possible:

- minimum energy transfer for given $|\vec{q}|$:



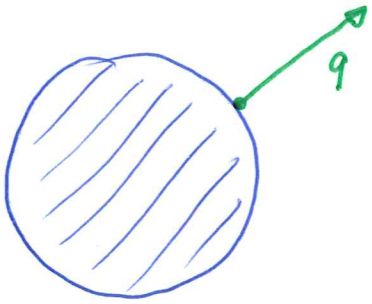
$|q| > 2k_F \Rightarrow$

$$\omega_{min} = \frac{\hbar^2}{2m}(q - k_F)^2$$

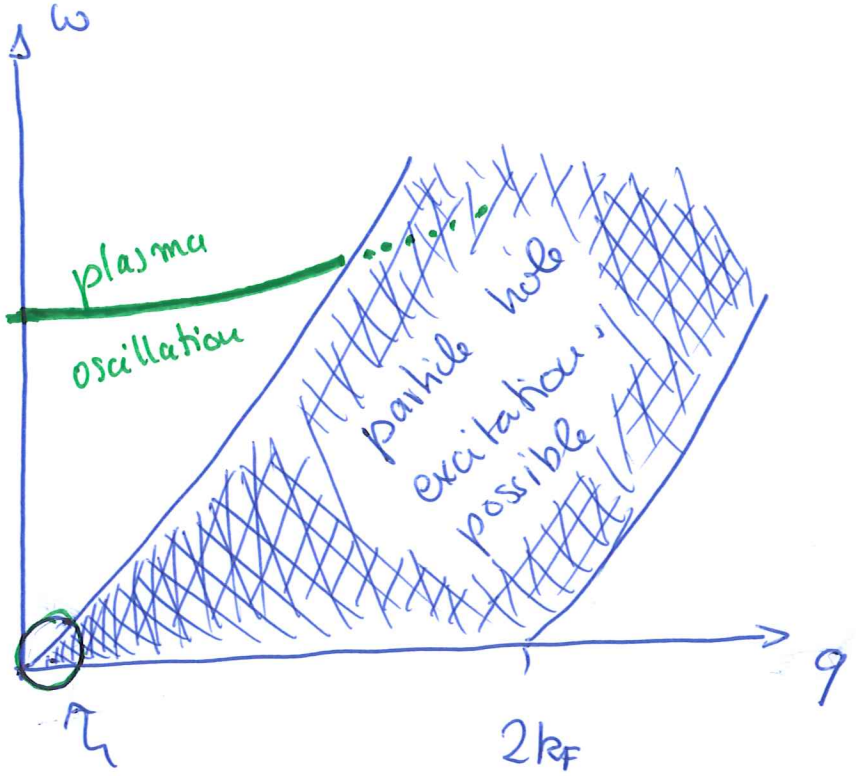


$|q| < 2k_F \Rightarrow \omega_{min} = 0$

- maximum energy transfer for given $|q|$:



$$\omega_{max} = \frac{\hbar^2}{2m}(q + k_F)^2$$



Sum rule for
excitations $\int_0^\infty d\omega\ \omega\ \mathrm{Im}\,\chi(\omega) = -\pi \frac{n_0 / m\, q^2}{2}$

for $q \to 0$ like for classical particles

$\Rightarrow$ same collective excitation $\Leftrightarrow$

pole in $\chi = \dfrac{\chi_{free}}{1 - \frac{4\pi e^2}{q^2}\chi_{free}}$

for density of good metals $\Rightarrow$ $\omega_p \sim$ several eV

$\Rightarrow$ short range interaction ok for
low energy processes.

Note: Form of collective excitation crucially depends on interaction.

What changes if interaction between particles is short range?

e.g. $\phi(r) = e^{-r/\lambda}\frac{1}{r} \quad \leftrightarrow \quad \phi(q) = \frac{4\pi}{q^2 + 1/\lambda^2} \equiv 4\pi$

back to mean field formula page 40:

$$\delta n = \chi\, \delta V_{ext} \simeq \chi_{free}\,(\delta V_{ext} + \delta V_{ind})$$

now: $V_{induced} = \frac{4\pi e^2}{q^2 + 1/\lambda^2}\,\delta n$

↑ poisson with extra screening

$$\chi = \frac{\chi_{free}}{1 - \frac{4\pi e^2 \lambda^2}{(q\lambda)^2 + 1}\chi_{free}} \xrightarrow{q \to 0} \frac{\chi_{free}}{1 - \frac{4\pi e^2 \lambda^2 q^2 n_0/m}{\omega^2}}$$

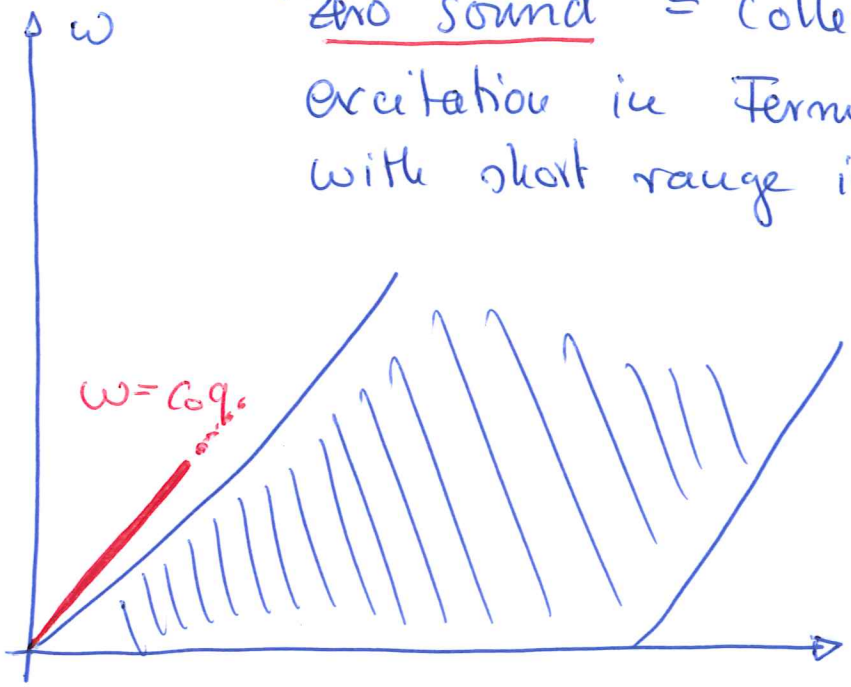
$$= \frac{q^2 n_0/m}{\omega^2 - 4\pi e^2 \lambda^2 n_0/m \cdot q^2}$$

⇒ now there is a pole at

$$\omega = c_0 |q|$$

$$c_0 = \sqrt{4\pi e^2 n_0 / m} \, l^2 = \underline{\underline{\omega_p \, l}}$$

⇒ sound-like dispersion



"zero sound" ≙ collective excitation in Fermi system with short range interaction

Phonons

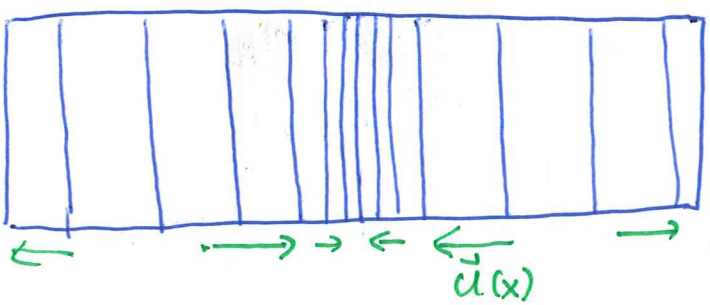
Phonons: ≙ elementary excitations of the lattice distortion. From the atomistic point of view, phonons correspond to $3N-3$ normal modes of the crystal of N atoms. On the macroscopic scale, phonons become manifest in the propagation of (transverse or longitudinal) sound waves, so in this chapter we start from this macroscopic picture:

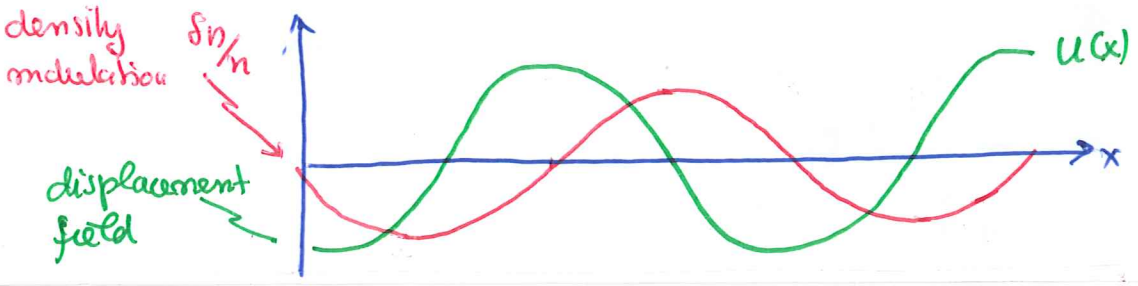
"Quantum description of sound in solids"

Sound waves:

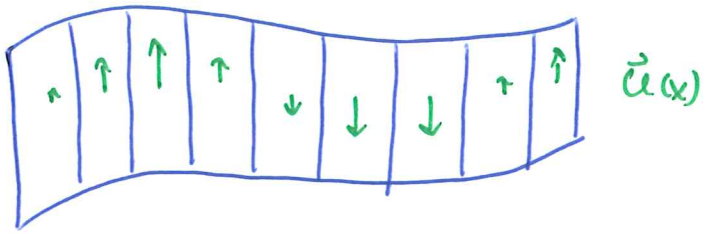
Longitudinal

"compression wave"





Shear wave:



- dynamics of sound waves in the solid:

- for simplicity, we consider only longitudinal waves in isotropic medium. transverse waves analogous (see below)

- elastic energy: $E_{el} = \frac{\lambda}{2} \int d^3r \left(\frac{\delta n}{n}\right)^2$

(λ: compressibility; $\frac{\delta n}{n}$: relative compression)

- $\frac{\delta n}{n} = -\vec{\nabla} \cdot \vec{u}(\vec{r})$ (e.g. from Gauss theorem, or see picture above)

- kinetic energy: $E_{kin} = \frac{\rho_0}{2} \int d^3r \, \dot{u}(r)^2$

(ρ_0: density)

$\Rightarrow$ equation of motion: from $L[u, \dot{u}] = E_{kin} - E_{pot}$

$$\boxed{\rho_0 \frac{\partial^2 u}{\partial t^2} = \lambda \, \vec{\nabla}(\vec{\nabla} \cdot \vec{u})}$$

$\Rightarrow$ plane wave solution

$$u(\vec{r},t) = u_k e^{i\vec{k}\vec{r}}$$

in equation of motion:

$$\rho_0 \ddot{\vec{u}}_k = -\lambda \vec{k}\cdot(\vec{k}\cdot\vec{u}_k)$$

non trivial solutions for

$\vec{k} \parallel \vec{u}_k$ (longitudinal), otherwise $\vec{k}\cdot\vec{u}_k = 0$

$$\boxed{\ddot{u}_k = -c^2k^2 u_k \qquad c = \sqrt{\frac{\lambda}{\rho_0}}}$$

- set of independent harmonic oscillator modes with frequency $\omega_k = c|k|$ (linear dispersion $\rightarrow$ sound)

- each mode corresponds to plane wave

$$u(r,t) = u_k^{(0)} e^{i(\vec{k}\vec{r} - \omega_k t)}$$

• quantization of normal modes

$$m\ddot{x} = -m\omega_0^2 x$$

quantum ⇝ harmonic oscillator

energy spectrum

$$E_n|n\rangle = H|n\rangle$$

$$E_n = \hbar\omega_0\left(n+\tfrac{1}{2}\right)$$

$$n = 0, 1, 2, \ldots$$

$$\hat{=}\quad H = \hbar\omega_0\left(a^+a + \tfrac{1}{2}\right)$$

↑ ⤵

create / annihilate oscillator quantum

$$x = \sqrt{\frac{\hbar}{2m\omega_0}}\,(a^+ + a)$$

• Normal modes in solid : ⇝

$$H = \sum_k \hbar\omega_k\left(b_k^+ b_k + \tfrac{1}{2}\right)$$

$$\vec{u}(\vec{r}) = \sqrt{\frac{1}{Vol}}\sum_k \hat{\varepsilon}_k \sqrt{\frac{\hbar}{2\rho\omega_k}}\left(b_k e^{i\vec{k}\vec{r}} + b_k^+ e^{-i\vec{k}\vec{r}}\right)$$

↑ polarization vector $\sim \hat{k}$

(for information, more formal derivation next page)

<u>Shear waves</u>: analogous, with polarization vector $\hat{\varepsilon}_k \perp \hat{k}$

total

$$H = \sum_{ks} \hbar\omega_{ks}\left(b_{ks}^+ b_{ks} + \tfrac{1}{2}\right) \quad s: \text{mode}$$

$\Rightarrow$ better representation in normal coordinates and momenta of these oscillators:

$$\boxed{H = \frac{1}{2}\sum_k \left(P_k^2 + \omega_k^2 Q_k^2\right)}$$

$$Q_k = \sqrt{\rho_0}\,(q_k + q_k^*)$$

$$P_k = \sqrt{\rho_0}\, i\omega_k\,(q_k - i q_k^*)$$

$$u(r) = \frac{1}{\sqrt{Vol}}\sum_k \left(q_k(t)\, e^{ikr} + q_k(t)^*\, e^{-ikr}\right)\vec{\epsilon}_k$$

($\vec{\epsilon}_k$: polarisation, $\vec{\epsilon}_k = \hat{k}$)

($\leftrightarrow$ check that Hamilton-equations give correct equations of motion)

- Quantum theory of sound-waves:

$$P_k \to \hat{P}_k \qquad Q_k \to \hat{Q}_k \qquad [Q_k, P_k] = i\hbar \qquad H = \sum_k \left(\hat{P}_k^2 + \hat{Q}_k^2\omega_k^2\right)/2$$

or:

$$b_k = \frac{1}{\sqrt{2\hbar\omega_k}}\left(\omega_k \hat{Q}_k + i\hat{P}_k\right)$$

$$b_k^+ = \frac{1}{\sqrt{2\hbar\omega_k}}\left(\omega_k \hat{Q}_k - i\hat{P}_k\right)$$

$$\boxed{[b_k, b_{k'}^+] = \delta_{kk'}\,, \quad H = \sum_k \hbar\omega_k\left(b_k^+ b_k + \tfrac{1}{2}\right)}$$

⇒ independent, bosonic, quasiparticles with linear dispersion $\omega_k = c|k|$:

"longitudinal acoustical phonons"

- Do we need a quantum description?
  - Many processes in which one can "see" single ~~quasi~~ phonons, like neutron scattering (see below)
  - Most prominent manifestation: specific heat

total energy of classical oscillators:

$$U = k_B T \times N_{modes} \quad \leftarrow 2?$$

(equipartition theorem)

$$C_V = \frac{\partial U}{\partial T} = k_B N_{modes}$$

T-independent: valid only for very large T.

total energy of quantum phonons:

$$U = \sum_k U_k, \quad U_k = \frac{\sum_{n=0}^{\infty} e^{-\beta E_n} E_n}{\sum_{n=0}^{\infty} e^{-\beta E_n}} \quad \leftarrow E_n = n\hbar\omega_k + \frac{1}{2}$$

$$\Rightarrow U = \sum_k \frac{\hbar\omega_k}{-1 + e^{+\beta\hbar\omega_k}} \quad \leftarrow \text{Bose distribution } \frac{1}{e^{\beta x} - 1}$$

- simple estimate:

$$\sum_k \to \sum_{|k|<k_D} \quad \text{with} \quad \sum_{|k|<k_D} = N_{\text{modes}} = N_{\text{atoms}} \equiv N$$

(longitudinal only)

$$\sum_k \to \left(\frac{L}{2\pi}\right)^3 \int d^3k \quad \Rightarrow \quad N = \frac{L^3}{(2\pi)^3}\,\frac{4\pi}{3}\,k_D^3$$

$$\boxed{k_D = \left(\frac{N}{L^3}\,6\pi^2\right)^{1/3}}$$

"upper cutoff"
Debye wave vector

$$U = \left(\frac{L}{2\pi}\right)^3 \underbrace{\int_{k<k_D} d^3k}_{4\pi \int_0^{k_D} dk\, k^2} \frac{\hbar c k}{e^{\beta \hbar c k} - 1}$$

$x = \beta \hbar c k$

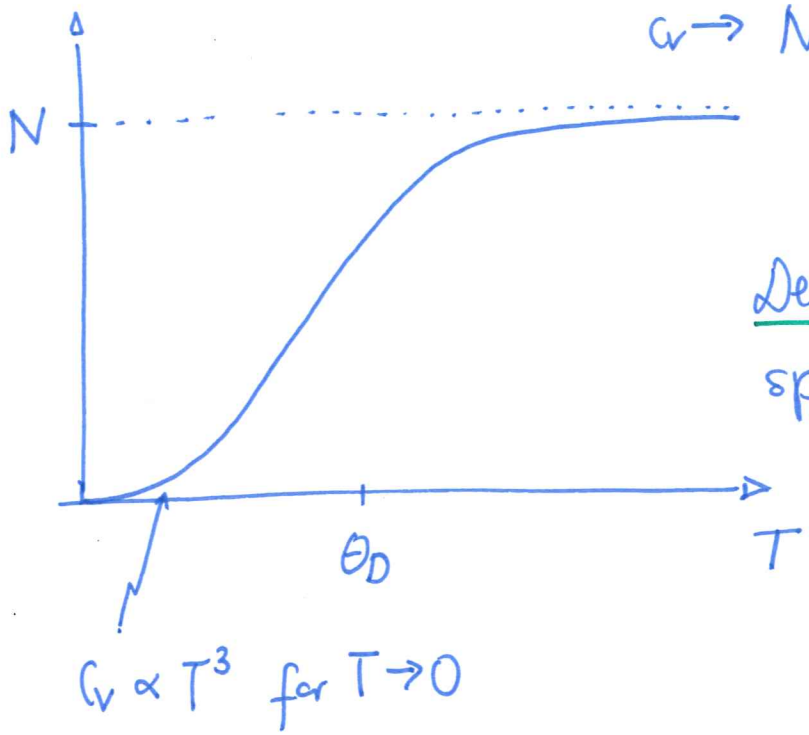
$$= \frac{L^3}{2\pi^2}\,\frac{T^4}{(\hbar c)^3} \int_0^{\beta \hbar c k_D} \frac{dx\, x^3}{e^x - 1}$$

$$= 3N\,\frac{T^4}{(\hbar c k_D)^3} \underbrace{\int_0^{\beta \hbar c k_D} \frac{dx\, x^3}{e^x - 1}}_{\to \text{const for } \beta \to \infty,} \xrightarrow{T \to \infty} NT \;\checkmark$$

i.e. such that $U \propto T^4$

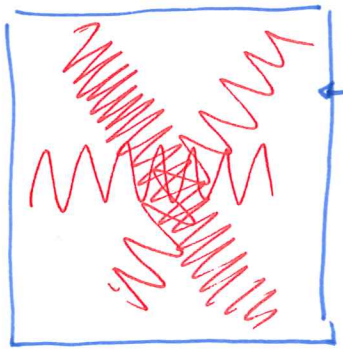
$$\boxed{C_V = \frac{\partial U}{\partial T} = \dots = 3\,\frac{N}{L^3}\left(\frac{T}{\theta_D}\right)^3 \int_0^{T/\theta_D} dx\, \frac{x^4 e^x}{e^x - 1} \qquad \theta_D = \hbar c k_D}$$

Note! only one branch (longitudinal)



Debye form of specific heat

- Remark: analogy to black-body relation:



- independent oscillator modes
  $\omega_k = kc$ c: Light velocity
- 2 (transverse) modes per k

here: no apparent upper cutoff for number of modes ⇒ classical C_V, $U = \infty$, because all modes occupied.

→ Planck: use quantum mechanics (!)

⇒ $U \propto T^4$ (Stefan-Boltzmann law) etc. ...

- how large is the average displacement

$$\overline{\Delta u} = \frac{1}{\text{Vol}} \int d^3r \langle u(r)^2 \rangle \quad ?$$

... for the experts: use expression for $\vec{u}(r)$ in terms of b_k on page 62, and $b_k^+ b_{k'} \simeq \delta_{kk'}$ ...

easier: • modes for different k are orthogonal

$\Rightarrow$ sum contribution to Δu from all modes k

• contribution from one mode:

$$\frac{1}{\text{Vol}} \int d^3r \; u_k(r)^2 = \frac{1}{\text{Vol}} \int d^3r \underbrace{\frac{1}{k^2} (\nabla u_k)^2}$$

because $\nabla u_k \sim k u_k$

$$= \frac{1}{\text{Vol}} \frac{2}{k^2 \lambda} \underbrace{E_{\text{pot}}}_{\frac{\lambda}{2} \int d^3r (\nabla u)^2} = \textcircled{\#}$$

λ: compressibility, see above!

for harmonic oscillator, $\langle E_{pot} \rangle = \langle E_{kin} \rangle =$

$$= \frac{1}{2} \langle E \rangle = \frac{1}{2} \frac{\hbar \omega_k}{e^{\beta \hbar \omega_k} - 1}$$

↑ see above

$$\Rightarrow \text{(\#)} = \frac{hc}{\lambda} \frac{1}{k} \frac{1}{e^{\beta \hbar c k} - 1}$$

$$\overline{\Delta u} = \frac{1}{Vol} \sum_k$$

$$\sim \int \frac{d^d k}{(2\pi)^d} \frac{1}{k} \frac{1}{e^{\beta \hbar c k} - 1}$$

d: spacial dimension

most interesting for low-dimensional system.

$$d=2 \quad \overline{\Delta u} \sim \underbrace{\int d^2 k \frac{1}{|k|}}_{2\pi \int_0^{\infty k_D} k \, dk} \frac{1}{e^{\beta \hbar c k} - 1}$$

$$\sim \int_0^{k_D} \frac{dk}{e^{\beta \hbar c k} - 1} \longrightarrow \infty$$

Because integrand $\sim \frac{1}{k}$ for $k \to 0$.

in $d=2$ dimensions:

sound waves destroy (melt) the solid at arbitrary low temperature (just not at $T=0$) $\Rightarrow$ special case of general statement no breaking of continuous symmetry in $d \leq 2$ dimensions.

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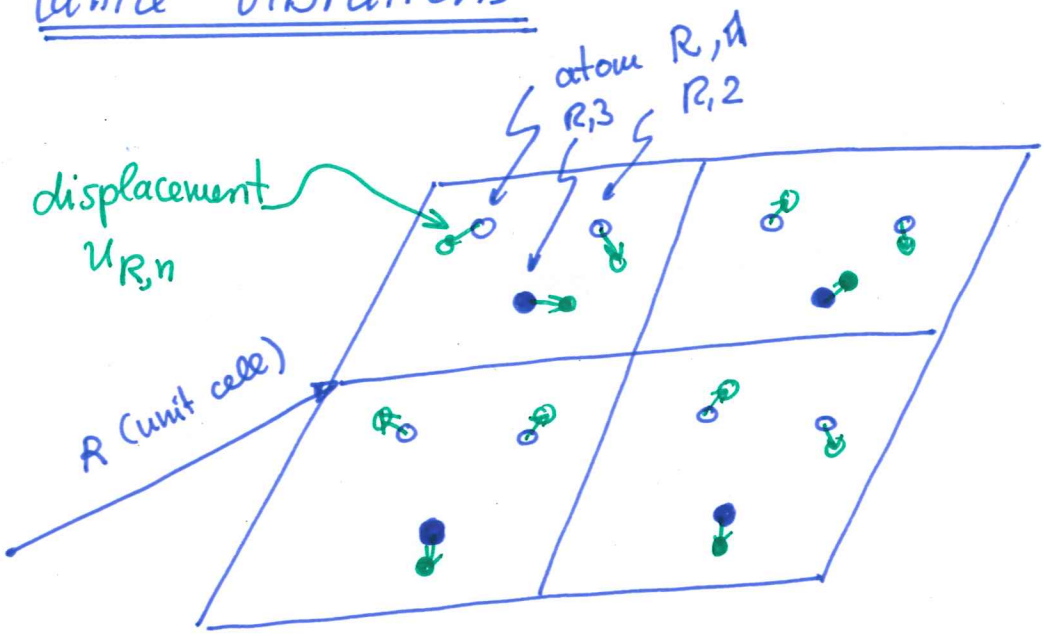
Microscopic description: quantized lattice vibrations



- Potential energy:

$E_{pot}(\{r_{R,n}\})$ depends on all atomic positions

E_{pot} = ionic electrostatic energy + electronic contribution (binding energy)

Born-Oppenheimer approximation:
electrons follow atoms instantaneously

$E_{binding} = \langle \Psi_0(\{r_{R,n}\}) | H^{electron} + H^{electron-ion}(\{r_{R,n}\}) | \Psi_0(..) \rangle$

= electronic ground state energy for fixed ion configurations r_{Rn}

Skipped

- **harmonic approximation**

$$E_{pot} = E_{pot}\left(\{\tau^{(0)}_{R,n}\}\right) + \frac{1}{2}\sum_{\substack{RR' \\ nn' \\ \alpha,\alpha'=x,y,z}} u^{\alpha}_{R,n} \left.\frac{\partial^2 E}{\partial \tau^{\alpha}_{R,n}\,\partial \tau^{\alpha'}_{R',n'}}\right|_{\tau=\tau^{(0)}} u^{\alpha'}_{R',n'} + \dots$$

equilibrium

translationally invariant:

$$\frac{\partial^2 E}{\partial \tau^{\alpha}_{R,n}\,\partial \tau^{\alpha'}_{R',n'}} \equiv D_{n\alpha,n'\alpha'}(\vec{R}-\vec{R}')$$

$$E_{kin} = \frac{1}{2}\sum_{R,n,\alpha} (\dot{u}^{\alpha}_{R,n})^2 M_n$$

Eq. of motion:

$$M_n \ddot{u}^{\alpha}_{Rn} = \sum_{R'n'\alpha'} D_{n\alpha,n'\alpha'}(R-R')\, u^{\alpha'}_{R'n'}$$

Now: FT on lattice $\Rightarrow$ $k \in$ 1. Brillouin zone.

$$u_{R,n\alpha} = \frac{1}{\Omega}\int_{1.BZ} d^3k\; e^{-ikR}\, u_{k n\alpha}, \quad u_k = \sum_R u_R e^{-ikR}$$

$$\Rightarrow M_n \ddot{u}_{k n\alpha} = \sum_{n'\alpha'} D(k)_{n\alpha,n'\alpha'}\, u_{k n'\alpha'}$$

$$\underline{\underline{D}}(k) = \sum_R e^{-i\vec{k}\vec{R}}\, \underline{\underline{D}}(R)$$

skipped

- coupled equations ⇒ diagonalize D :

$$\tilde{D}_{m\alpha|m'\alpha'} = \frac{D_{m\alpha|m'\alpha'}}{\sqrt{M_m M_{m'}}} \qquad \left(\tilde{u}_{m\alpha} = \sqrt{M_m}\, u\right)$$

$$\tilde{\underline{\underline{D}}}_{m\alpha,m'\alpha'} = \underline{\underline{P}}_{m\alpha|s}\ \omega_{ks}^2\ \underline{\underline{P}}_{s|m\alpha}$$

$\Rightarrow$ $3N_b$ independent harmonic oscillator modes for each $k \in 1.\,BZ$.

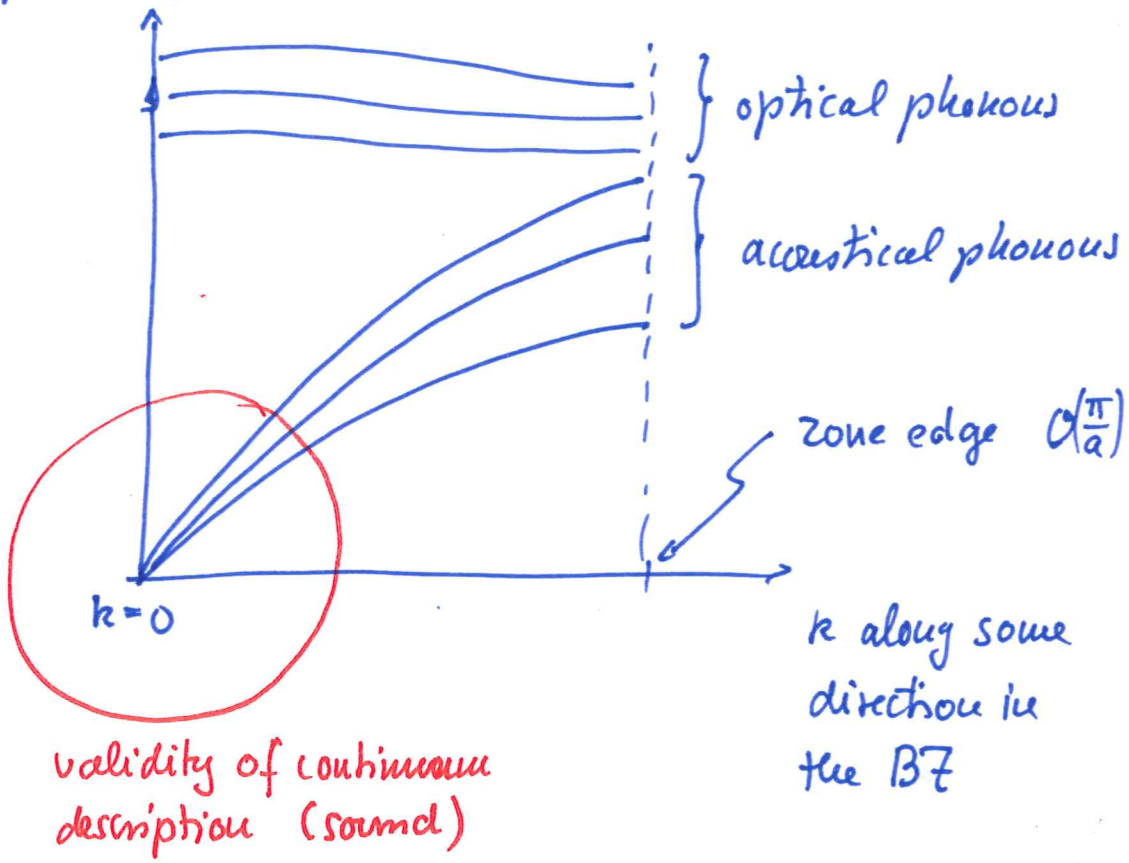
- Also for this case, it is convenient to choose normal coordinates:

$$\boxed{H = \frac{1}{2}\sum_{ks}\left(Q_{ks}^2\,\omega_{ks}^2 + P_{ks}^2\right)}$$

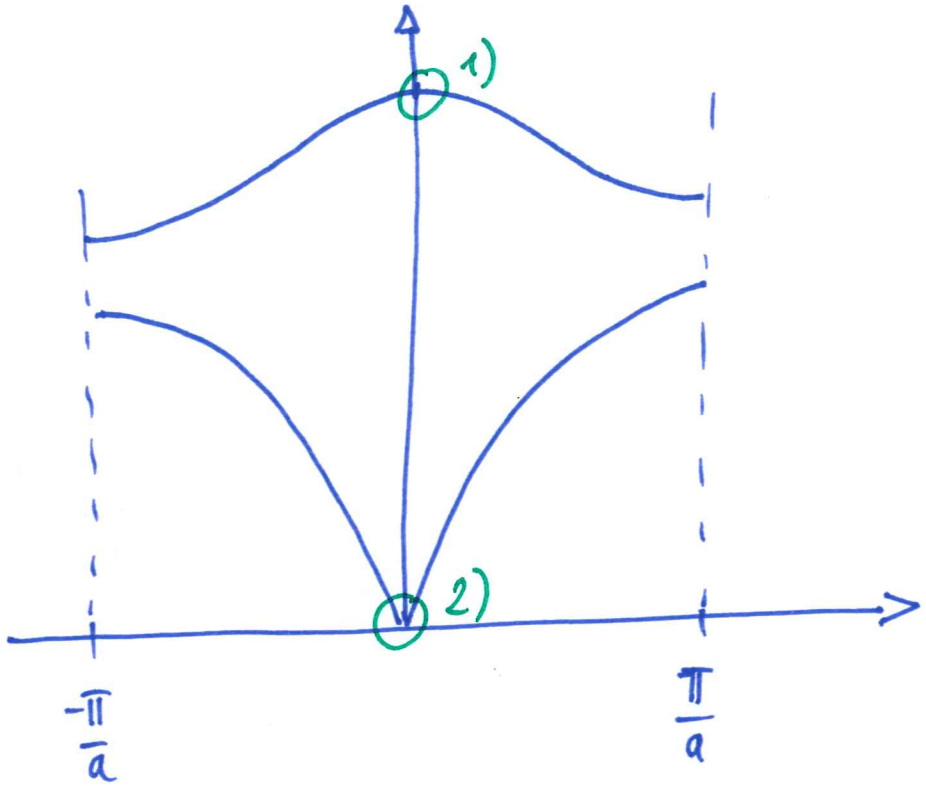
$$u_{m\alpha}(R) = \sum_{ks} \ldots$$

- in the crystal we have $3N_b$ modes, where N_b is the number of atoms per unit cell.

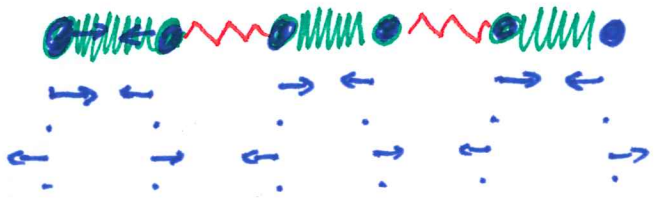
For $k \to 0$, three modes must reduce to the three acoustical phonon modes (sound waves). The others are called optical phonons.



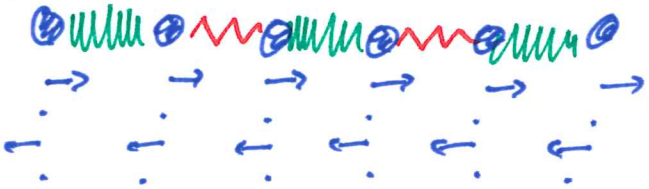
Example: (might be useful for exercise)



1)



2)



optical phonon
≈ molecular vibrations of ●—●, in phase

Sound!

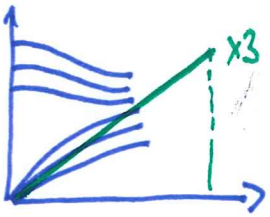
- **specific heat:**

$$E_{tot} = \sum_{ks} \frac{\hbar\omega_{sk}}{-1 + e^{\beta\hbar\omega_{ks}}}$$

depends on details of the phonon band structure

"interpolation formula":

all branches ⇒ 3 acoustical branches with



- $\hbar\omega = ck$,

c = average c, so that low-T limit is fit correctly

$$\left(\frac{1}{c^3} = \int \frac{d\Omega}{2\pi} \left(\frac{1}{c_k} \right)^3 \right)$$

state counting:

states up to k_D

$$= \left(\frac{L}{2\pi}\right)^3 \int_{k \le k_D} d^3k = \frac{1}{6\pi^2} k_D^3 \stackrel{!}{=} N_{atoms}$$

- maximum $k = k_D$, such that

modes = # atoms × 3

resulting equation is then the same as for sound waves.

Useful scales: k_D Debye vector

$\omega_D = c k_D$ Debye frequency

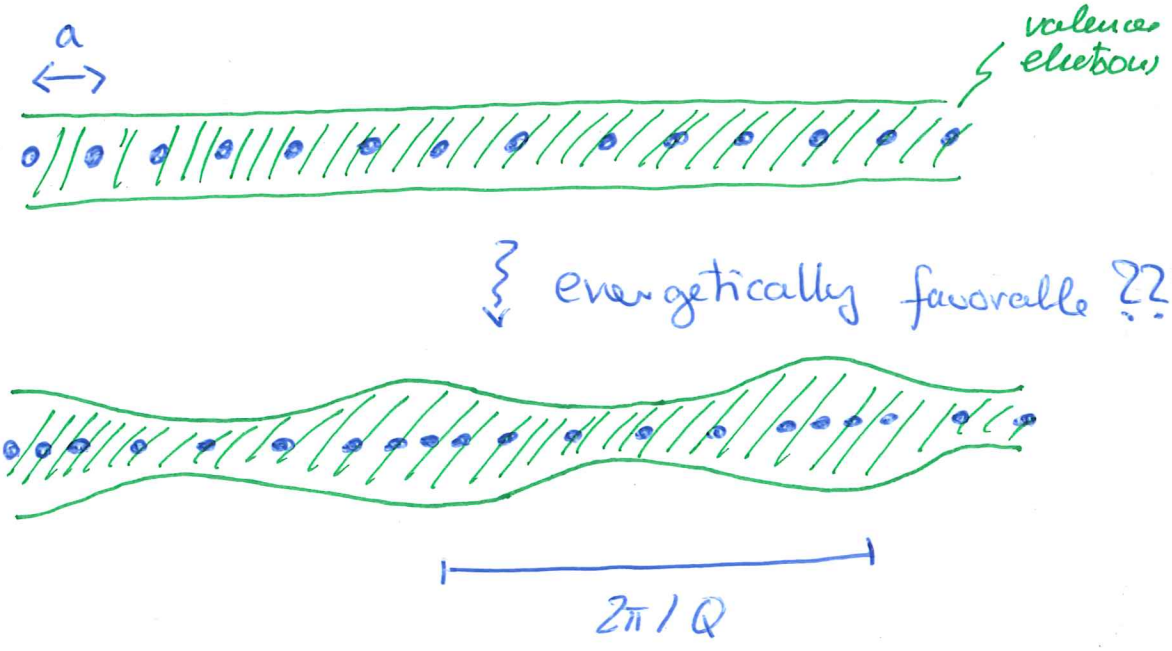
$$\Theta_D = \frac{\hbar\omega_D}{k_B}$$ Debye temperature

then:

$$C_V = 9 n k_B \left(T/\Theta_D\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x dx}{(e^x - 1)^2}$$

Peierls transition

Usually, a lattice distortion increases the energy. For some situations, the electron-phonon interaction can renormalize the phonon frequency to be "negative", i.e., the system becomes unstable towards spontaneous formation of a charge density wave:



We discuss this phenomenon in the continuum limit, For large electron fillings, the unstable wave vector Q is close to π/a, but the argument is quite similar in this case.

- potential energy:

$$E_{pot} = \underbrace{E_{electron}}_{①} + \underbrace{\text{elastic energy}}_{②}$$

② : assume distortion $u(x) = |u_0| \cos(Qx + \varphi)$

$$\equiv \frac{1}{2}\left(u_0 e^{iQx} + \text{h.c.}\right)$$

$$u_0 = |u_0| e^{i\varphi}$$

$$\text{elastic energy} = \frac{\lambda}{2}\int dx \left(\frac{du}{dx}\right)^2 = |u_0|^2 L \frac{\lambda Q^2}{4}$$

Note: the discussion is for a one-dimensional system, because instability is most prominent for $d=1$ (see below)

① for electronic energy, use Born-Oppenheimer approximation: (e^- react instantaneously to positions of ions, $E_{electron} \cong$ ground state energy of electrons in static potential $V(x)$ due to ions.

- $V(x)$ is also of periodic form:

charge density of ions: $\frac{\delta n}{n_0} = \frac{du}{dx}$

n_0: equilibrium density

+ Poisson equation

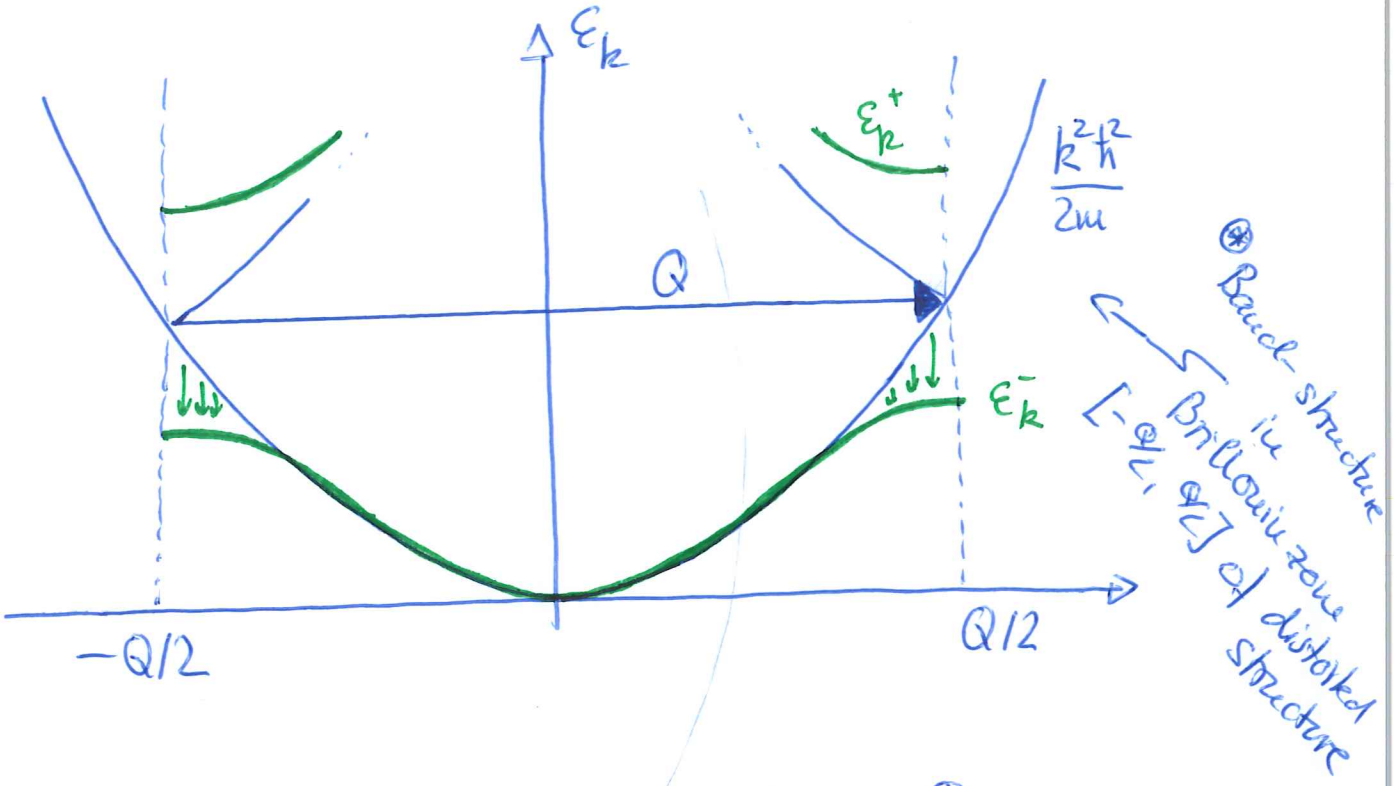
$$\phi_q = \underbrace{\frac{4\pi}{q^2 \varepsilon_q}}_{v_q} \rho_q = v_q n_0 u_q$$

$$\Rightarrow V(x) = u_Q e^{iQx} + h.c.$$

$$= \Delta_Q e^{iQx} + h.c.$$

$$\Delta_Q = \alpha u_Q \qquad \alpha = i v_Q n_0 Q$$

⇒ the periodic potential opens a gap at $k = Q/2$ (compare discussion of band-structure of almost free electrons)



⇒ if filling is such that $k_F < \frac{Q}{2}$ ⇒ electronic energy is lowered

<u>maximum gain for $Q = 2k_F$</u>

we thus investigate instability at this wave vector ⇝ can energy gain overcome energy cost $\propto L \frac{\Delta Q^2}{4}$?

for small u_0, calculate shift perturbatively, taking into account two states $k, k-Q$ which become degenerate for $k = k_F$

(for $k<0$, take $k, k+Q$)

Schrödinger equation $\Rightarrow$ diagonalize matrix

$$\begin{pmatrix} \epsilon_k & \Delta_Q \\ \Delta_Q^* & \epsilon_{k-Q} \end{pmatrix} \qquad \epsilon_k = \frac{\hbar^2 k^2}{2m}$$

$$\Delta = u_0 \underbrace{n_0 V_Q Q}_{\alpha} \equiv \alpha u_0$$

$$\boxed{\epsilon_k^{\pm} = \frac{1}{2}\left[(\epsilon_{k-Q} - \epsilon_k) \pm \sqrt{(\epsilon_{k-Q} - \epsilon_k)^2 + 4|\Delta_Q|^2} \right]}$$

$$E(u_0) = \underbrace{2 \sum_{|k|<k_F} \epsilon_k^-}_{\text{energy of occupied states}} + \underbrace{\frac{L \chi Q^2}{4} (u_0)^2}_{\text{energy cost}}$$

energy decrease

$\Rightarrow$ find minimum $\frac{dE}{du_0} = 0$

with $\sum_{|k|<k_F} \equiv \frac{L}{2\pi} \int_{-k_F}^{k_F} dk$

and $$\frac{d\varepsilon_k^-}{d|u_0|} = \frac{2|\alpha|^2 |u_0|}{\sqrt{(\varepsilon_{k-Q} - \varepsilon_k)^2 + 4|\Delta_Q|^2}}$$

the integral can be evaluated, which is a bit lengthy, but quite straight forward ...

$$\frac{1}{L}\frac{dE_0}{d|u_0|} = -|u_0| \frac{8\alpha^2 \omega}{\hbar^2 Q \pi} \operatorname{arsinh}\left(\frac{\hbar^2 Q^2}{\omega |\Delta_Q|}\right) + \frac{2Q^2}{2} |u_0|^2$$

limit $|u_0| \to 0$ ($\operatorname{arsinh}(x) \simeq \ln(2x)$ for $x \to \infty$)

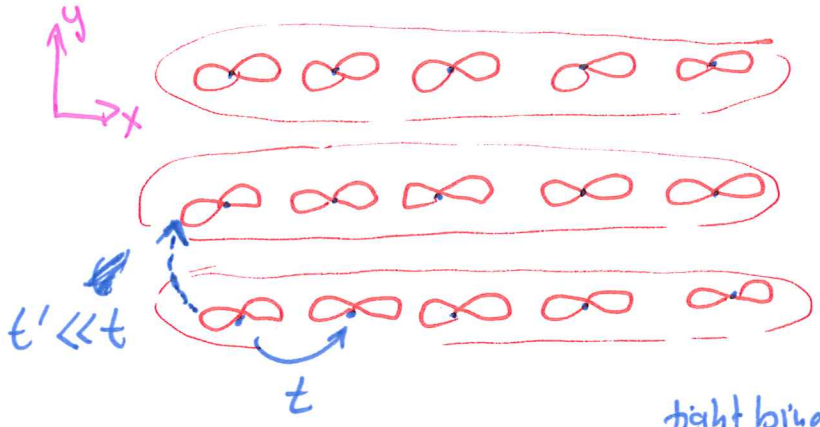
$$|\Delta_0| = |\alpha u_0| = 4 E_F e^{-\frac{1}{N(\varepsilon_F)\cdot g}} \qquad g = \frac{4|\alpha|^2}{2Q^2}$$

$N(\varepsilon_F)$: Density of states at the Fermi surface

⇒ for arbitrary small interaction α, a gap is opened at the Fermi surface

⇒ instability occurs for "half-filled" system.

- Real materials are not one-dimensional ?

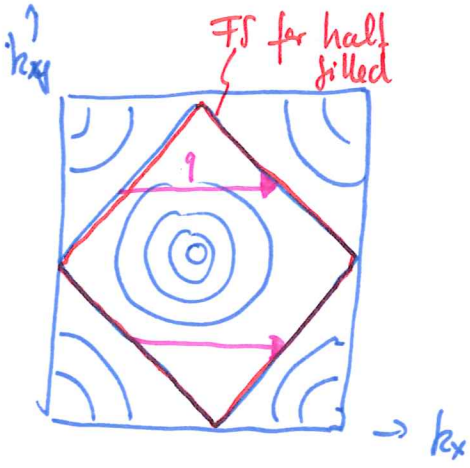


Stack of weakly coupled 1d chains

tight binding

$$\varepsilon_k = \varepsilon(k_x, k_y) = -2t \cos k_x a - 2t' \cos k_y a$$

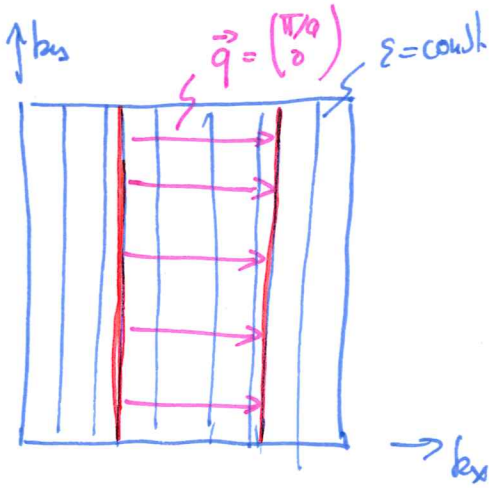
almost one-d. for $t' \ll t$



$t = t'$

(2-dimensional)

⇒ $q = \begin{pmatrix} \pi/a \\ 0 \end{pmatrix}$ can only connect single points on FS.



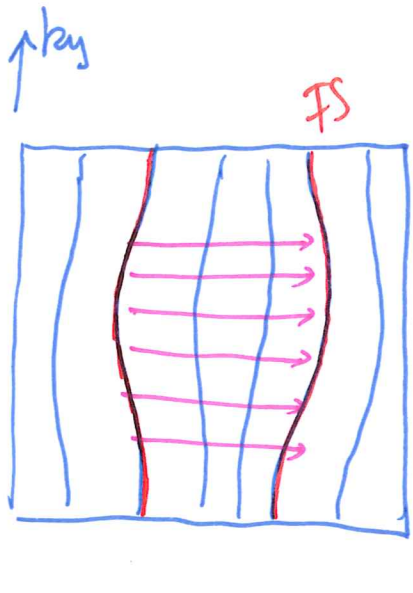
$t' = 0$

- gap opened at whole Fermi surface

⇒ instability

Fermi surface is nested by nesting vector q

But: Nesting at (pi,pi), i.e. cheque-board ordering (!) This is special for nearest neighbour hopping, otherwise there is no perfect nesting.



FS almost nested
⇒ instability can occur when t' is small enough.
(⇝ see slides)

realistic : $t \gg t' \neq 0$

Final remark: The same "Fermi surface nesting instability" underlies other phenomena, e.g. spin-density wave formation.

transition at finite temperature. E ⇒ free energy

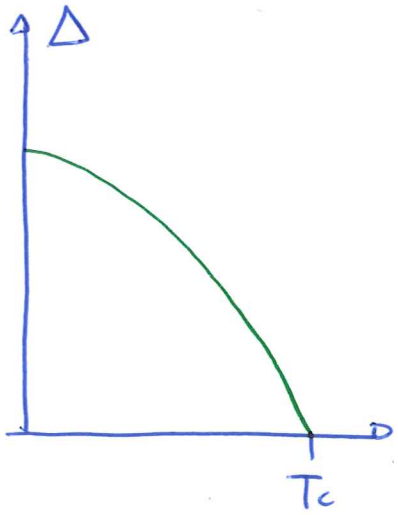
$$F[u_0] = \alpha |u_0|^2 + F_{\text{electron}}[u_0]$$

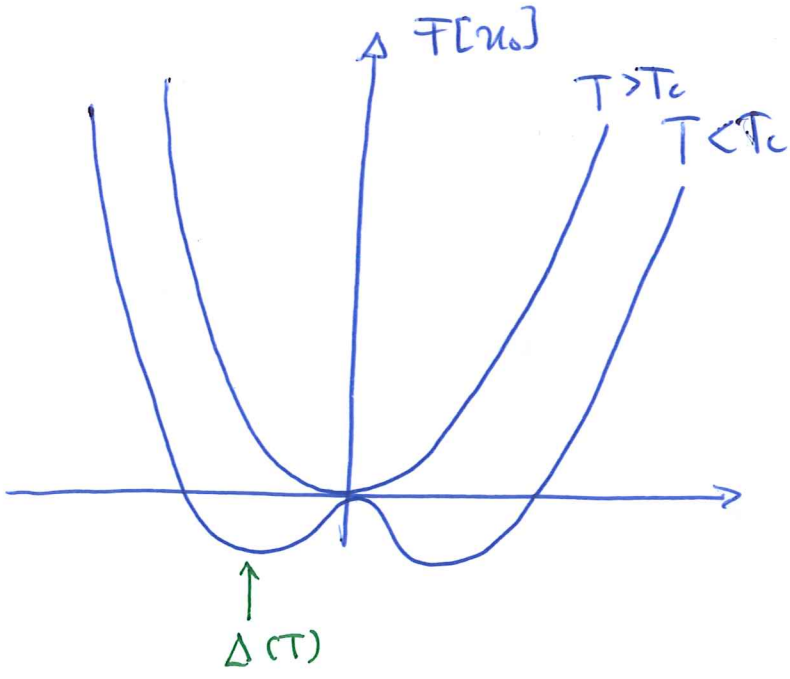
$$F_{\text{electron}} = E - TS$$

$$E = \frac{1}{2\pi} \int_{-Q/2}^{Q/2} dk \sum_{s=\pm} \frac{\epsilon_k^s}{e^{\beta \epsilon_k^s} + 1}$$

$k_B T \gg \Delta_{T=0}$ (gap at $T=0$) ⇒

energy gain due to opening a gap becomes small compared to energy cost for deformation.





≙ minimum $u_0(T)$

Ginzburg-Landau theory

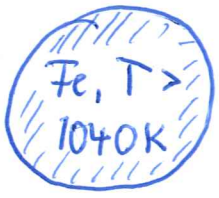
- phenomenological theory for phase transitions with spontaneous symmetry breaking
- formulated for SC : 1950,
  relation to BCS theory clarified by Gorkov ~1960

The order parameter

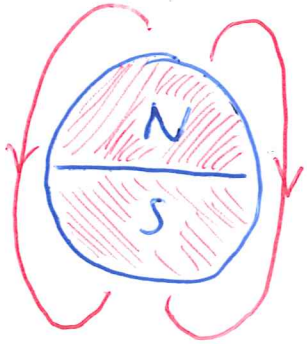
The order parameter $\mathcal{O}$ is a macroscopic quantity which is nonzero below the transition temperature ($T<T_c$) and zero for $T>T_c$.

Examples:

- Ferromagnet : $\mathcal{O} \hat{=} M$ (magnetization density)
  ($\hat{=}$ vector in $\mathbb{R}^3$)



(paramagnet)

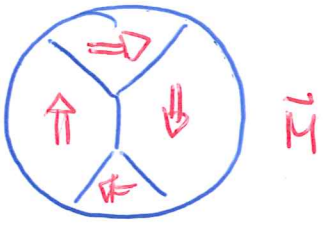


$T < 1040K$

• Peierls transition

$O \triangleq$ Fourier component of density A_Q

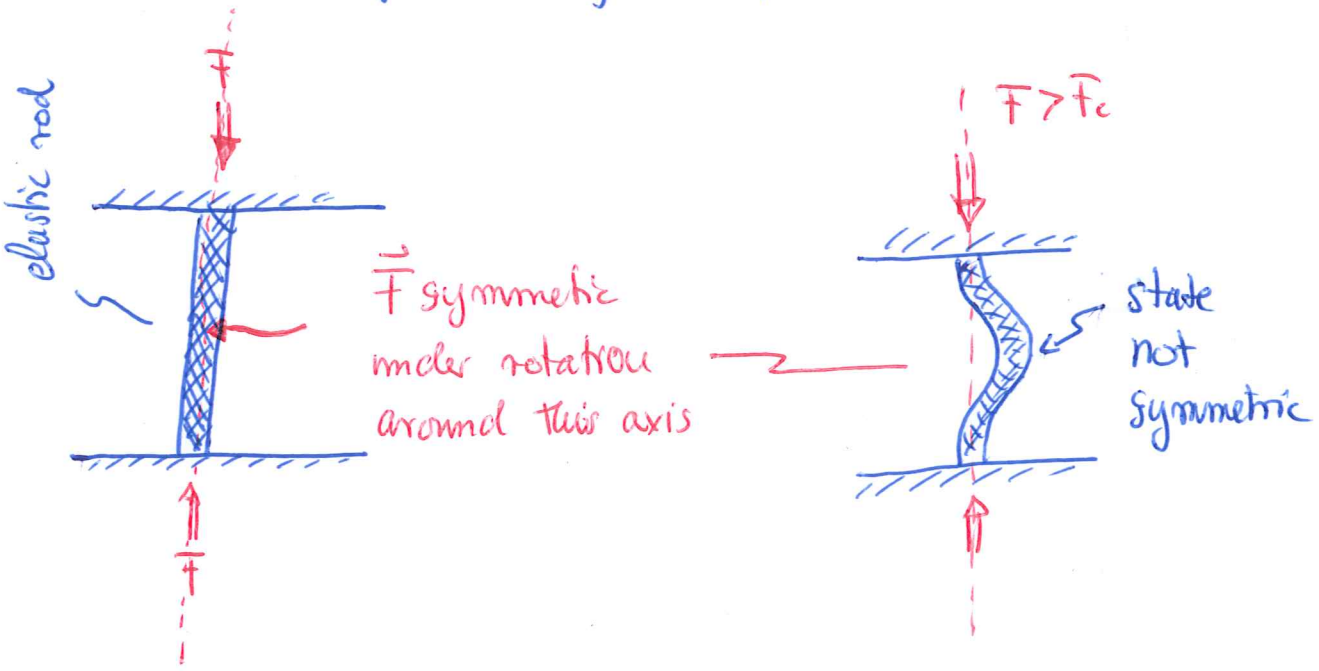
Note 1) The order parameter can in general be a function of position. Example: magnetic domains



Note 2) Non zero order parameter is related to spontaneous symmetry breaking, i.e. the symmetry of the state is lower than the symmetry of the underlying (microscopic) description.

- Example Ferromagnet:
  - microscopic Spin model : invariant under all rotations
  - state below T_c : only invariant under rotations around magnetization axis

- "Classical example" : (of course, not a thermal transition!)



- general phenomenological description of second order phase transitions in terms of order parameter: Landau ~ 1930
- Ginzburg & Landau (1950) : observed effects in SC (Meissner effect) described if one associates the SC phase with an order parameter which is a complex number $\psi(\vec{r})$ ⇝ macroscopic, classical field

- In the Landau theory, the order parameter $\mathcal{O}$ is determined by minimization of a free energy function $F[\mathcal{O}(x), T]$

$F[\mathcal{O}]$ is unknown in general, but many general features of the phase transition follow from very few assumptions on the functional form of F:

1) $\mathcal{O} = 0$ must be minimum of F in the high symmetry phase ($T > T_c$)
2) $F[\mathcal{O}]$ must be invariant under all symmetry operations of high-symmetry phase
3) For $T \to T_c$, $\mathcal{O}$ vanishes continuously (2nd order transition) and we can expand $F[\mathcal{O}]$ in powers of $\mathcal{O}$.

"Recipe": get most general form of F and see what theory predicts.

Example:

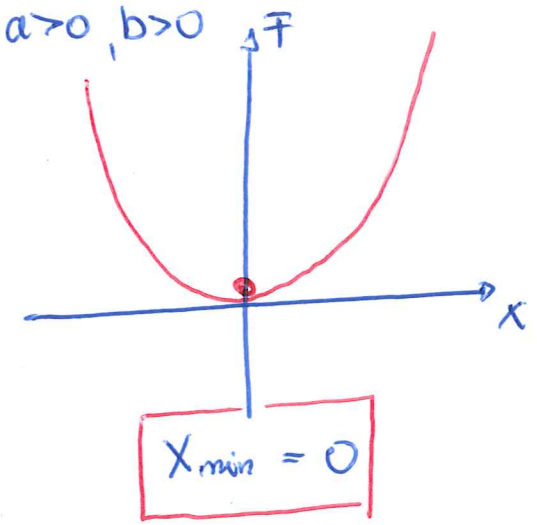
charge density wave formation in homogeneous system

- scalar order parameter X
- inversion symmetry $X \to -X$

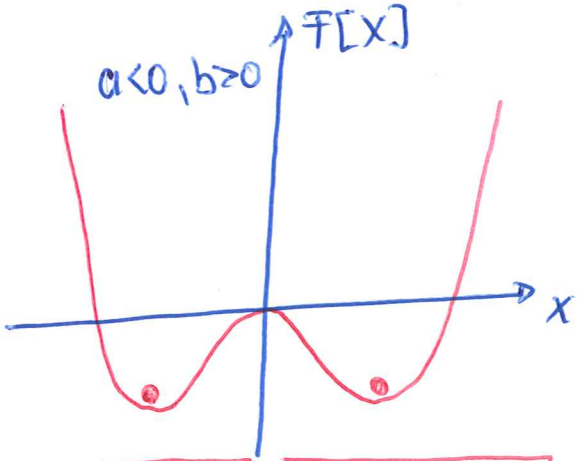
$$F(X,T) = F_n(T) + a(T) X^2 + \frac{b(T)}{2} X^4 + \dots$$

$F_n(T)$: normal phase

$a(T) X^2 + \frac{b(T)}{2} X^4 + \dots$: expansion around $X=0$, no odd terms because of inversion symmetry



$X_{min} = 0$

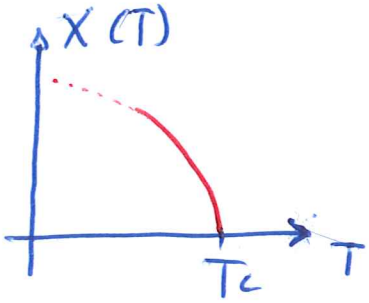


$X_{min} = \pm \sqrt{-a/b}$

$\rightsquigarrow$ phase transition $\triangleq$ $a = 0$ $\Rightarrow$ $a(T_c) = 0$

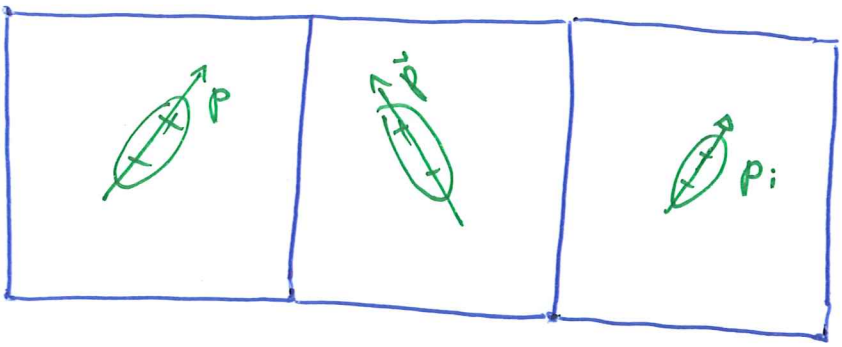
$\rightsquigarrow$ expand $a(T) \simeq \underbrace{\dot{a}}_{>0} (T - T_c)$

$\rightsquigarrow$ $X(T) \underset{T \lesssim T_c}{=} \sqrt{\frac{\dot{a}}{b(T_c)}} \sqrt{T_c - T}$



- More advanced example:

Vector order parameter (e.g. Polarization) in cubic environment.



e.g. polar molecules in cubic crystal

order parameter $\hat{=}$ macroscopic polarization $\vec{P}$

(microscopically $\vec{P} = \frac{1}{N}\sum_i \vec{p}_i \hat{=}$ average over all $\vec{p}_i$

$F[\vec{P}]$: must be invariant under all point group operations of cubic symmetry

most general form of Taylor expansion $F[P]$:

$$F[\vec{P}] = \alpha \vec{P}^2 + \beta \vec{P}^4 + \gamma (P_x^4 + P_y^4 + P_z^4) + \dots$$

this term would not be possible in isotropic medium; not invariant under all rotations.

$\rightsquigarrow$ additional phenomenological parameter γ ($\hat{=}$ crystalline anisotropy)

$\rightsquigarrow$ depending on β or γ, the transition can occur only in two possible ways:

1) $\vec{P}$ along crystal axis

2) $\vec{P}$ along body diagonal

(see free-energy plots on next page)

this is a rather nontrivial prediction from the GL theory, which is based only on symmetry considerations

Remark: Here we have an example in which a discrete symmetry is broken. As a consequence, there is no "continuous degeneracy" of the minimum in $F[\vec{P}]$, and no zero energy excitations (no "Goldstone modes")

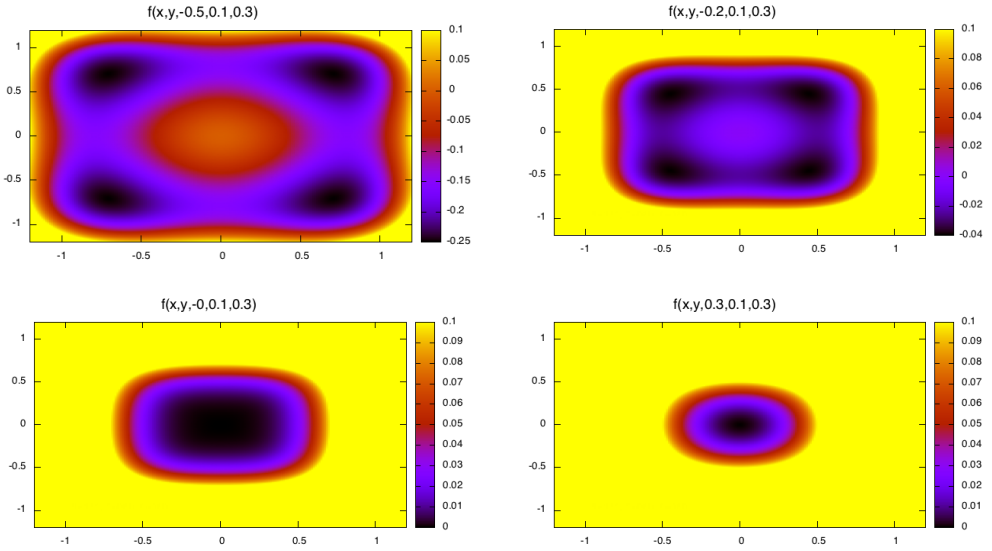
GL Free energy : vector order parameter in cubic environment

$$F = a|M|^2 + b|M|^4 + c(M_x^4 + M_y^4 + M_z^4)$$

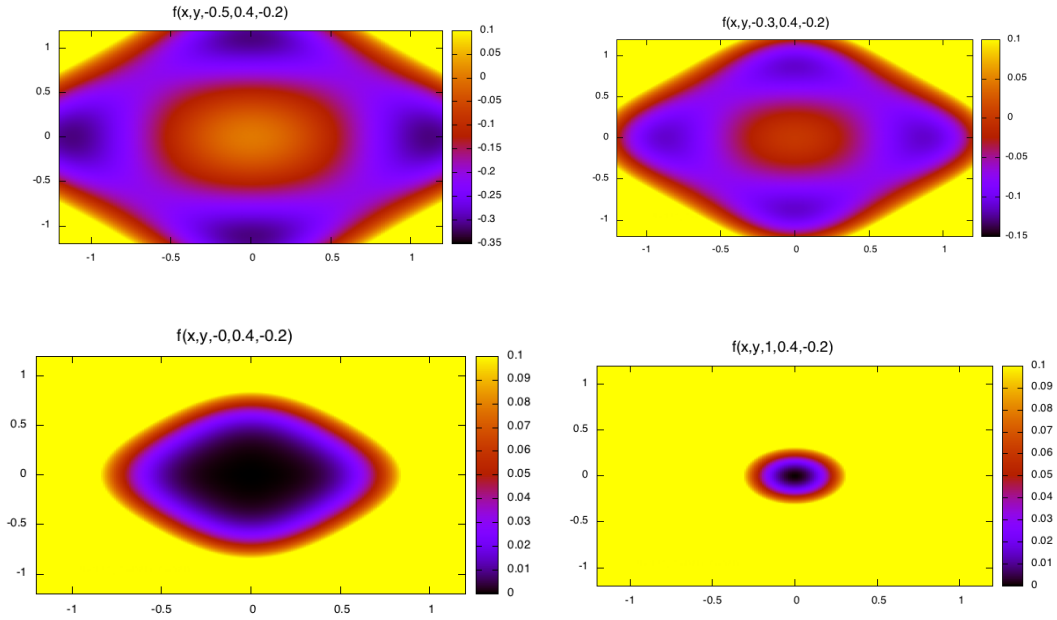
just two possible orientations with respect to the lattice, depending on values of b and c

M ll body diagonal

$f(M_x, M_y, a, b, c)$



M ll x or y axis



Note: No breaking of continuous symmetry : no Goldstone modes

- **Coherence length**

spacially dependent order parameter $\mathcal{O}(\vec{r})$

(e.g. domains)

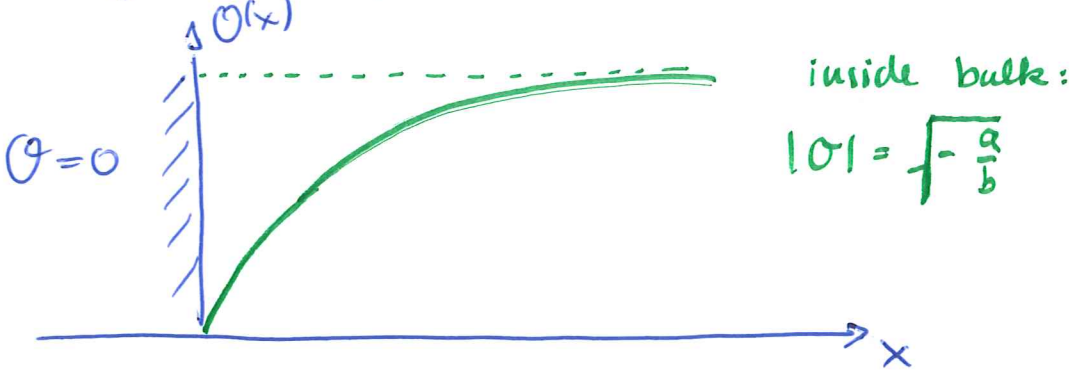
$\Rightarrow$ Free energy (for scalar, for simplicity)

$$F[\mathcal{O}] = \int d^3r \left\{ a|\mathcal{O}|^2 + \frac{b}{2}|\mathcal{O}|^4 + \underbrace{\xi_0^2 |\vec{\nabla}\mathcal{O}|^2}_{\text{most simple, symmetry allowed non-local term}} \right\} \circledast$$

$\hat{=}$ free energy cost for deformation

consequence: order parameter cannot vary abruptly, but only on a certain healing or correlation length

e.g.: surface



inside bulk: $|\mathcal{O}| = \sqrt{-\frac{a}{b}}$

minimization of $\circledast$ ($\hat{=} F[\mathcal{O}+\delta\mathcal{O}]$ ... term linear in $\delta\mathcal{O}$ vanishes)

$\hat{=}$ differential equation $\rightsquigarrow$ $\xi_0^2 \vec{\nabla}^2 \mathcal{O} = a\mathcal{O} + b|\mathcal{O}|^2\mathcal{O}$

asymptotic behavior:

$$\varphi(x) = \underbrace{\varphi_\infty}_{\sqrt{-\frac{a}{b}}} + \text{const.}\; e^{-x/\xi}$$

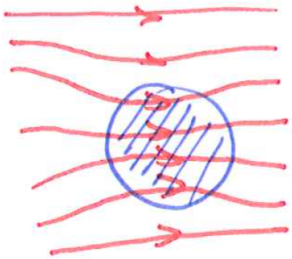
$$\xi(T) = \frac{\xi_0}{\sqrt{-2a(T)}} \;\overset{\uparrow}{\underset{a = \dot{a}(T - T_c)}{\sim}}\; \frac{1}{\sqrt{T_c - T}}$$

order parameter changes only on some healing length, <u>correlation length</u>, which <u>diverges at the transition</u>.

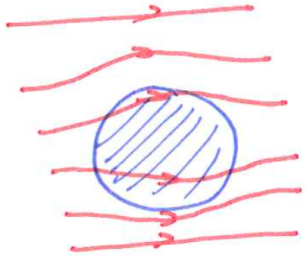
<u>Note</u>: GL theory makes many qualitatively correct predictions close to the phase transition. Main drawback: missing treatment of fluctuations. As a consequence, it predicts long range order also for low dimensions, where fluctuations diverge (see discussion of phonons), and the precise scaling of correlations functions (critical exponents like $\frac{1}{(T_c - T)^{1/2}}$ etc.) are not correct.

- **Magnetism: definitions, phenomenology**

Interaction of matter with magnetic fields:



Paramagnets: induced magnetisation parallel to external field, fields increased inside material



Diamagnets: induced magnetisation antiparallel to external field, fields decreased inside material

Macroscopic description:

$$\vec{\nabla}\vec{B} = 0$$

$$\vec{\nabla} \times \vec{H} = \frac{4\pi}{c}\vec{j}_{ext}$$

$$B = H + 4\pi M$$

magnetization, due to induced currents

$M(H)$: material relation

$\frac{\partial M}{\partial H} > 0$: paramagnet

$\frac{\partial M}{\partial H} < 0$: diamagnet.

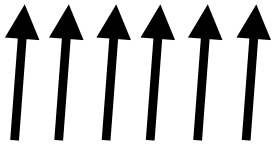
- ***diamagnetic materials expel magnetic fields >> Levitation***

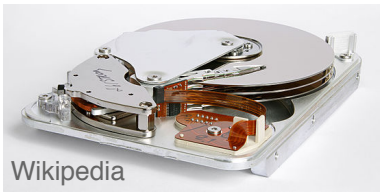
https://en.wikipedia.org/wiki/Superconductivity#/File:Meissner_effect_p1390048.jpg

Magnetic order:

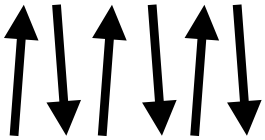
***Ferromagnets**: permanent magnetization "spontaneous alignment of microscopic magnetic moments"*

magnetic compass (11th century, China)?

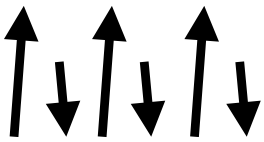




***Antiferromagnets**:"spontaneous anti-parallel alignment of neighbouring microscopic magnetic moments"*



***Ferrimagnets**:"spontaneous anti-parallel alignment of neighbouring microscopic magnetic moments"*



- spontaneous magnetic order occurs at rather high temperatures (e.g. Fe becomes ferromagnetic for $T < T_c \simeq 1033\,K$, Co $T_c \simeq 1400\,K$ Ni $\simeq 630\,K$ ...). Yet all magnetic response of matter is in principle a purely quantum mechanical effect. In a classical physics description, the free energy of a material is simply independent of any external field $\vec{B}$ (Bohr & van Leeuwen 1911)

In short: classical partition function

$$Z \sim \int d^{3N}r\, d^{3N}p\, e^{-\beta \mathcal{H}(p,r)}$$

$$\mathcal{H}(p,r) = \sum_{i=1}^{N} \frac{(\vec{p}_i - \frac{e}{c}\vec{A}(\vec{r}_i))^2}{2m} + V(r_1,\dots,r_N) \qquad B = \vec{\nabla}\times\vec{A}$$

shift of variables $p \to \vec{p} - \frac{e}{c}\vec{A}(\vec{r}_i) = \tilde{p}$

$$d^{3N}p = d^{3N}\tilde{p}$$

$\Rightarrow Z$ does not depend on $\vec{B}$.

magnetic moment of isolated atoms

classical picture

current I

Energy in external field:

$$E = -\vec{\mu}\cdot\vec{B} \qquad \vec{\mu} = \frac{1}{2}\int d^3r\ \vec{r}\times\vec{j}$$

$\vec{\mu}$: magnetic moment

$\Leftrightarrow$ thermodynamic description:

magnetization $M = -\frac{\partial F}{\partial B}$ F: free energy

- quantum mechanical description:

atom (or any object) in state n:

$$\mu_n = -\frac{\partial E_n}{\partial B}$$

single electron: Zeeman energy $H = -\mu_B\, g\, \vec{S}/\hbar\cdot\vec{B}$

(g: 2 by Dirac theory; $\vec{S}/\hbar$: spin)

$$\boxed{\vec{\mu} = 2\mu_B\,\vec{S}/\hbar \qquad \mu_B = \frac{e\hbar}{2mc} \simeq 10^{-4}\,\frac{eV}{T}}$$

value of μ_B already shows that magnetic energies are often small compared to other typical energies in the solid at typical laboratory fields.

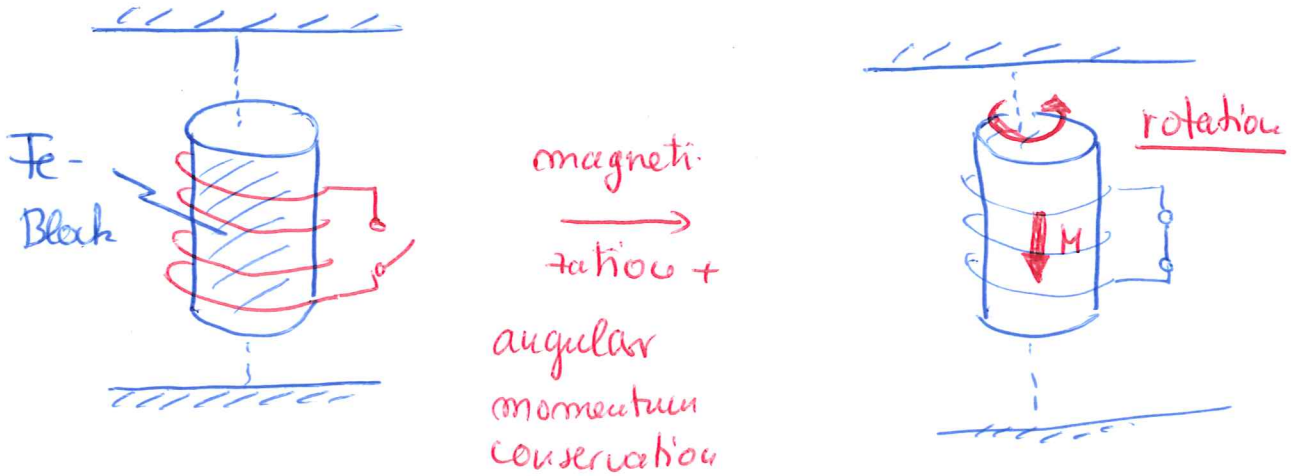
Note: in all cases, magnetic moment is linked to angular momentum $\vec{J}$

$$\vec{\mu} = \gamma \vec{J}$$

γ : gyromagnetic ratio

→ Einstein de Haas effect:

conversion of spin angular momentum (magnetization) to lattice angular momentum



moment of isolated atoms:

$$\mu = -\frac{\partial E_0}{\partial B}$$ 0: ground state

$$\Delta E_0 = -\vec{B}\cdot\vec{\mu} + \underbrace{\mathcal{O}(B^2)}_{\text{induced moments, ie particular diamagnetic response}}$$

nonzero if ground state has nonzero angular momentum.

$$\vec{\mu} = \mu_B\underbrace{(\vec{L} + \underbrace{g}_{2}\vec{S})}_{\text{contribution from orbital / spin angular momentum}} \underbrace{=}_{\text{restricted to GS manifold}} \gamma\vec{J}$$

$\gamma\vec{J}$: nontrivial to get, see e.g. Ashcroft Mermin

- what determines $\vec{L}, \vec{S}, \vec{J}$ in ground state?

e.g. ℓ electrons in 3d orbitals of magnetic ion $\Rightarrow$ many possible states $\binom{e}{10} = \frac{10!\,(10-e)!}{e!}$

Lifting of degeneracy:

- Coulomb interaction + Pauli principle
  ($\hat{=}$ intra-atomic exchange interaction)
- spin-orbit coupling

Hund's rules

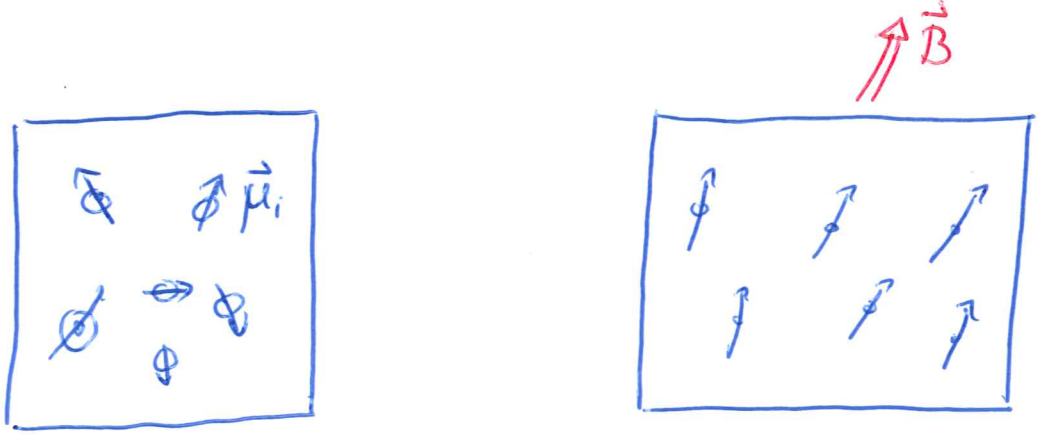
- for weak SO coupling we have

  1) maximum $\vec{S}$
  2) max $\vec{L}$ for given $\vec{S}$

  $\hat{=}$ { ferromagnetic intra atomic exchange, see below

- **paramagnetic response of isolated atoms**

- ions align in external field:



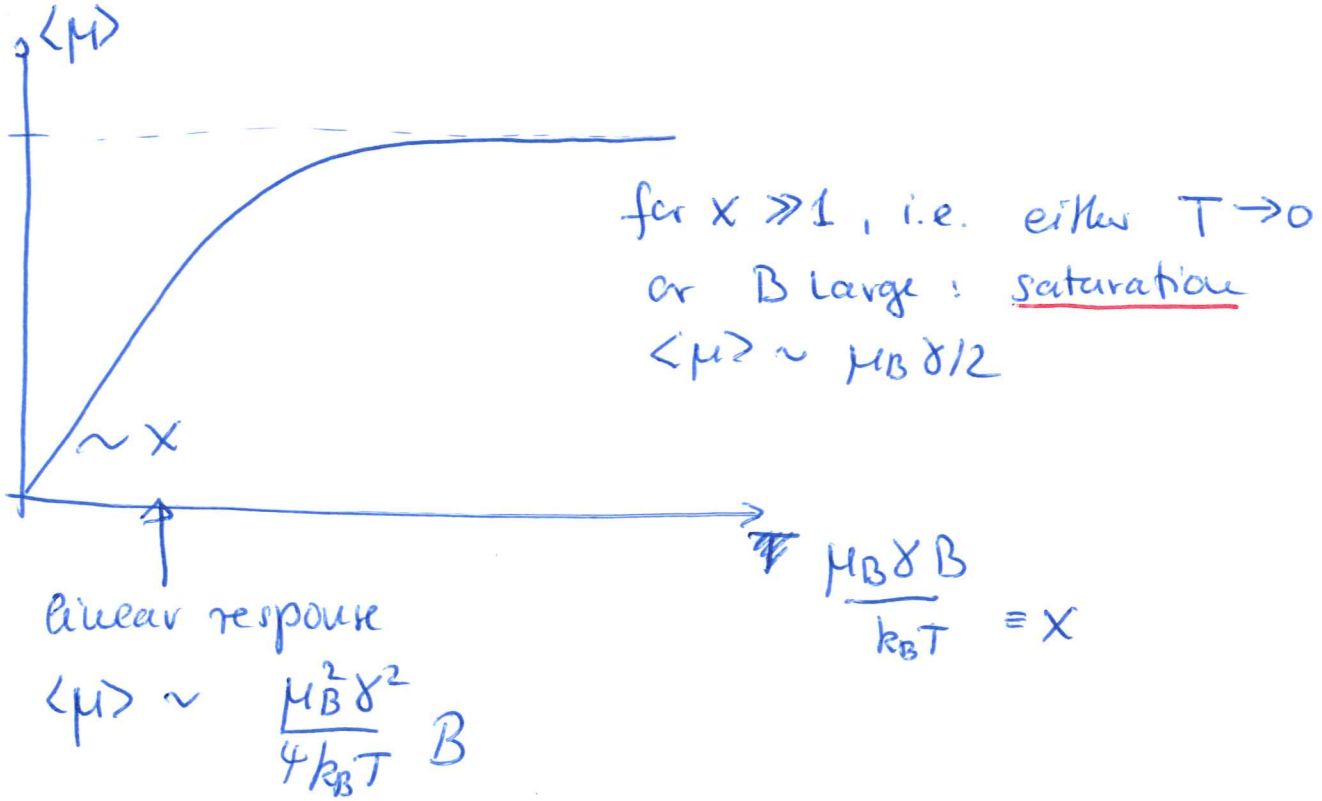
for simplicity. consider $J = \frac{1}{2}$ $\vec{\mu} = \gamma \vec{J}$:

average magnetization :

$$M = n \langle \vec{\mu} \rangle \qquad n: \text{density}$$

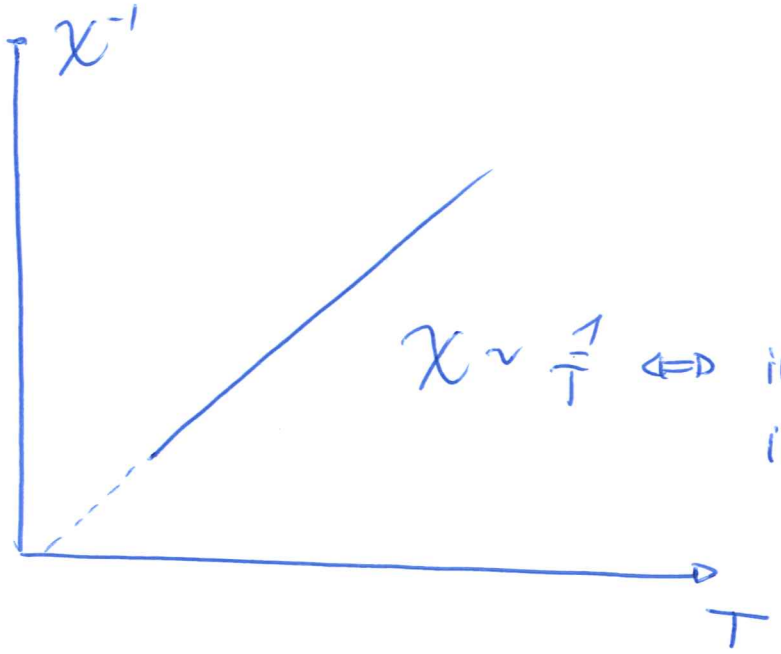
$$\langle \vec{\mu} \rangle = \frac{\sum_{m=-J}^{J} \mu_B \gamma m \, e^{\beta \mu_B \gamma m B}}{\sum_{m=-J}^{J} e^{\beta \mu_B \gamma m B}}$$

$$= \mu_B \gamma / 2 \tanh\left(\frac{\beta \mu_B \gamma m B}{2} \right)$$



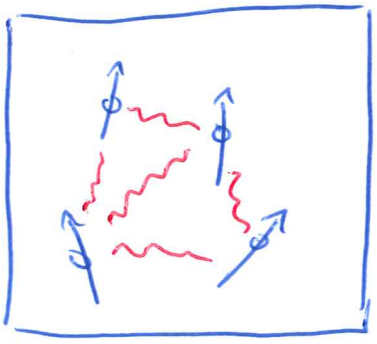
$\Rightarrow$ susceptibility of isolated magnetic moments

$$\chi = \frac{\partial M}{\partial B} = \frac{\mu_B^2 g^2}{4} \frac{1}{k_B T}$$ Curie law



$\chi \sim \frac{1}{T}$ $\Leftrightarrow$ indication of isolated moments

Behavior of interacting moments ?



interaction

$$H = -\sum_{ij} \vec{S}_i \cdot \vec{S}_j \, J_{ij}$$

exchange interaction*, $|J| > 0$ favors parallel alignment of spins

* physical origin: see below

- mean field description of response:

$$\chi = \frac{\partial M}{\partial B} \qquad M = \sum_j \langle S_j \rangle \quad \text{average moment}$$

$$\delta M \tilde{=} \chi_{free} \left(B + B_{induced} \right)$$

δM: mean field; χ_{free}: response of free moments $\sim 1/T$

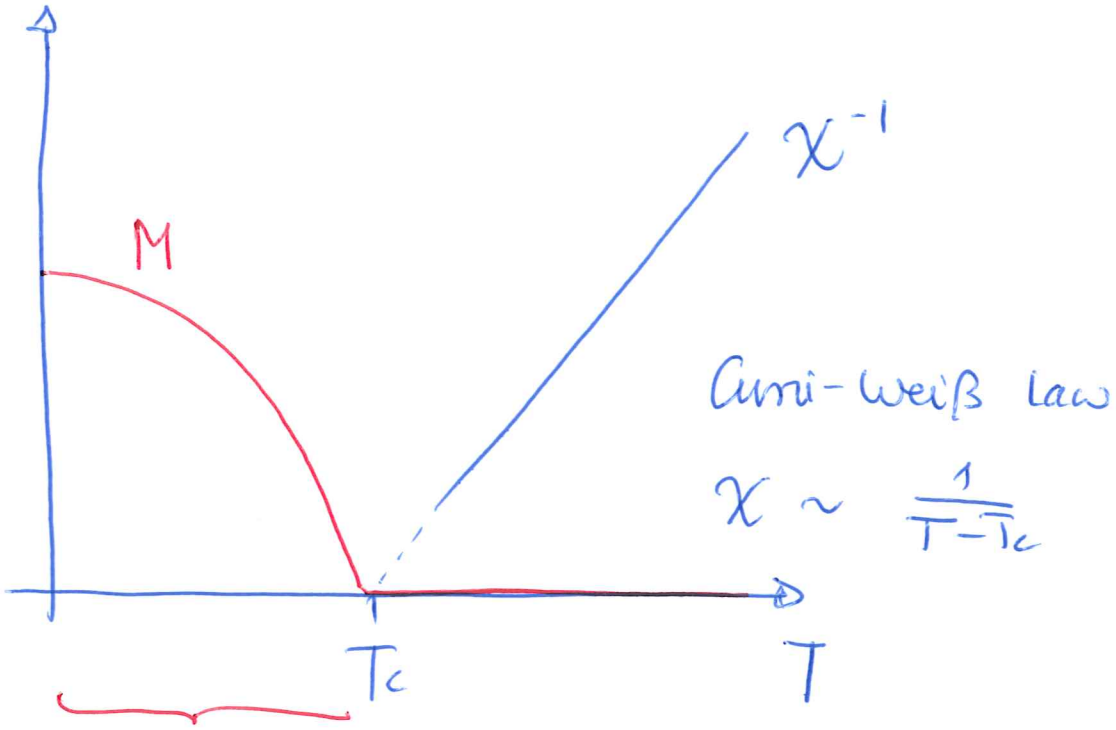
$$B_{induced} \text{ (at ion \#i)} = \sum_j J_{ij} \langle S_j \rangle = J_0 \underbrace{\sum_j \langle S_j \rangle}_{\delta M}$$

$$\chi = \frac{\chi_{free}}{1 - J_0 \chi_{free}} \sim \frac{1}{T - T_c}$$

$\chi_{free} \sim \frac{1}{T}$

where $T_c \sim J_0$

instability of the system for $T \lesssim T_c$:
ordering of moments for infinitesimally small field! Ferromagnetic transition



Curi-Weiß law

$\chi \sim \frac{1}{T - T_c}$

ferromagnetic
state, long-range order,

Exchange interaction

general principle :

Pauli principle $\Rightarrow$ n-electron wave function symmetric under exchange of both spin (σ) and position ($\vec{r}$) :

Symmetric under exchange of σ_i $\Rightarrow$ anti-symmetric under exchange of $\vec{r}_i$

anti-symmetric under exchange of σ_i $\Rightarrow$ symmetric under exchange of $\vec{r}_i$

$\Updownarrow$

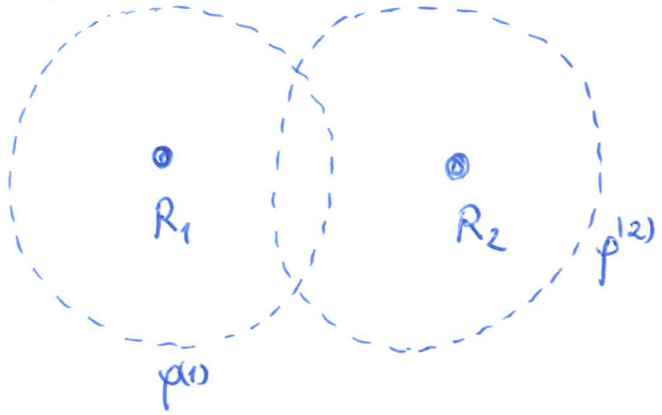
Effective interaction between spins (exchange interaction) $\Leftarrow$ Coulomb energy depends on this form of the wave function

! Exchange interaction is "not a fundamental force"

$\rightsquigarrow$ can take various forms (ferromagnetic, anti-ferro long range / short range) depending on the electronic state of the solid.

Direct exchange

example: two-electron system



$$H = \underbrace{\frac{p_1^2}{2m} + \frac{p_2^2}{2m} + V(r_1) + V(r_2)}_{H_0} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

Basis:
- Wannier orbitals $\varphi^{(1)}, \varphi^{(2)}$ (localized at nuclear positions R_1, R_2)
- tightly bound electrons, $\varphi_i^{(i)} \simeq$ atomic orbitals, take into account only one orbital per site (others are at "high energy").
- neglect hopping $T = \int d^3r\, \varphi^{(1)*}(\vec{r}) \left[\frac{p^2}{2m} + V(\vec{r})\right] \varphi^{(2)}(\vec{r})$

(⇝ leads to different type of exchange, see below)

goal: find ground state

$$\Phi(\vec{r}_1\sigma_1; \vec{r}_2\sigma_2) = \underbrace{\psi(\vec{r}_1, \vec{r}_2)}_{\text{orbital part}} \underbrace{\chi(\sigma_1, \sigma_2)}_{\text{spin part}}$$

excluding ionized states (both electrons in $\varphi^{(1)}$ or $\varphi^{(2)}$)

possible combinations

- $\chi(\sigma_1,\sigma_2) \equiv \chi^s(\sigma_1\sigma_2) = \frac{1}{\sqrt{2}}\left(\delta_{\sigma_1\uparrow}\delta_{\sigma_2\downarrow} - \delta_{\sigma_1\downarrow}\delta_{\sigma_1\uparrow}\right)$

  $\hat{=}$ singlet $S_{tot}=0$ (i.e. $(\vec{S}_1+\vec{S}_2)^2 = 0$)

antisymmetric under $1 \leftrightarrow 2$ $\Rightarrow$

orbital part $\equiv \varphi^{+}(r_1,r_2) \propto \left(\varphi^{(1)}(r_1)\varphi^{(2)}(r_2) + \varphi^{(1)}(r_2)\varphi^{(2)}(r_1)\right)$

- $\chi(\sigma_1\sigma_2) \equiv \begin{cases} \chi^{(t_s,+1)}(\sigma_1\sigma_2) = \delta_{\sigma_1\uparrow}\delta_{\sigma_2\uparrow} \\ \chi^{(t,0)}(\sigma_1\sigma_2) = \frac{1}{\sqrt{2}}\left(\delta_{\sigma_1\uparrow}\delta_{\sigma_2\downarrow} + \delta_{\sigma_1\downarrow}\delta_{\sigma_2\uparrow}\right) \\ \chi^{(t,-1)}(\sigma_1\sigma_2) = \delta_{\sigma_1\downarrow}\delta_{\sigma_2\downarrow} \end{cases}$

$\hat{=}$ triplet $S_{tot}=1$, $(\vec{S}_1+\vec{S}_2)^2 = S_{tot}(S_{tot}+1) = 2$

symmetric under $1 \leftrightarrow 2$ $\Rightarrow$

orbital part $\equiv \varphi^{-}(r_1,r_2) \propto \left(\varphi^{(1)}(r_1)\varphi^{(2)}(r_2) \pm \varphi^{(1)}(r_2)\varphi^{(2)}(r_1)\right)$

Energy expectation value: ($\pm \hat{=}$ singlet / triplet)

$$E^{(\pm)} = \langle \Phi^{\pm} | H | \Phi^{\pm} \rangle$$

(note: $|\Phi\rangle$ normalized, because $\varphi^{(i)}$ are Wannier-functions)

$$= \int d^3r_1 d^3r_2 \; \varphi^{\pm}(r_1, r_2) \, H(r_1, r_2) \, \varphi^{\pm}(r_1, r_2)$$

H: does not depend on spin!

$$\equiv E_1 + E_2 + C_1 \pm C_2$$

(neglect hopping!)

$$E_{1,2} = \int d^3r \; \varphi^{(1,2)}(\vec{r})^* \left(\frac{p^2}{2m} + V(\vec{r}) \right) \varphi^{(1,2)}(\vec{r})$$

$$C_1 = \int d^3r_1 d^3r_2 \; \frac{e^2 \, |\varphi^{(1)}(r_1)|^2 \, |\varphi^{(2)}(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|}$$

↙ { classical Coulomb energy

$$C_2 = \int d^3r_1 d^3r_2 \; \frac{e^2}{|r_1 - r_2|} \; \varphi^{(1)}(r_1)^* \, \varphi^{(2)}(r_2)^* \, \varphi^{(2)}(r_1) \, \varphi^{(1)}(r_2)$$

⇒ up to the constant energy shift $E_1 + E_2 + C_1$ the spectrum $E^{(\pm)}$ can be obtained by the equivalent spin Hamiltonian:

$$\boxed{H_{eff} = -J \, \vec{S}_1 \cdot \vec{S}_2 \qquad J = \frac{2C_2}{\hbar^2}}$$

proof:

H_{eff} acts only on spin

$$\langle \Phi^{\pm} | H_{eff} | \Phi^{\pm} \rangle = \langle \chi^{S/t} | H_{eff} | \chi^{S/t} \rangle$$

$$= -J \langle \chi^{S/t} | \underbrace{\left[\underbrace{(\vec{S}_1 + \vec{S}_2)^2}_{\hbar^2 S_{tot}(S_{tot}+1)} - \vec{S}_1^2 - \underbrace{\vec{S}_2^2}_{\hbar^2 \frac{3}{4}, \text{ for spin-}\frac{1}{2}, S = \frac{1}{2}(\frac{1}{2}+1)} \right]}_{\vec{S}_1 \cdot \vec{S}_2} \frac{1}{2} | \chi^{S/t} \rangle$$

$$= \begin{cases} \hbar^2 J \frac{3}{4} & \text{singlet} \\ -\hbar^2 J \frac{1}{4} & \text{triplet} \end{cases}$$

$$\underbrace{E^+ - E^-}_{2C_2} \stackrel{!}{=} E^{(s)} - E^{(t)} = \hbar^2 J \quad \checkmark$$

Notes:

- "direct exchange": directly related to Coulomb matrix element
- depends on overlap of $\varphi^{(1)}$ and $\varphi^{(2)}$ $\Rightarrow$ decays exponentially with distance
- Let $\varphi^{(1)}$, $\varphi^{(2)}$ be atomic orbitals of same atom $\rightsquigarrow$ calculation can be seen as model calculation for intra-atomic exchange
  $\hat{=}$ 1.st Hunds rule (maximal S favored)

- in solids: more often other exchange mechanisms relevant (see below)
- argument for localized electrons $\rightsquigarrow$ applies to insulators.

Superexchange (kinetic exchange)

many magnetic oxides (MnO, NiO, ...) have well defined magnetic moments ("localized electrons") but their distance is too large for direct exchange. $\rightsquigarrow$ exchange mechanism involving hopping of electrons between ions, or between oxigen and ions. $\rightsquigarrow$ exchange due to lowering of kinetic energy.

- Simplest model for "kinetic energy driven exchange": two orbitals (does not yet contain the O-ion, just single band)

$$H = -t \underbrace{\sum_{\sigma} \left(c_{1\sigma}^{+} c_{2\sigma} + \text{h.c.} \right)}_{\text{hopping}} + \underbrace{U \sum_{i=2,1} n_{i\uparrow} n_{i\downarrow}}_{\substack{\text{intra-orbital} \\ \text{Coulomb energy}}}$$

occupation number basis: (sign!)

$$|n_{1\uparrow}\, n_{1\downarrow}\, n_{2\uparrow}\, n_{2\downarrow}\rangle \equiv \left(c_{1\uparrow}^{+}\right)^{n_{1\uparrow}} \left(c_{1\downarrow}^{+}\right)^{n_{1\downarrow}} \left(c_{2\uparrow}^{+}\right)^{n_{2\uparrow}} \left(c_{2\downarrow}^{+}\right)^{n_{2\downarrow}} |0\rangle$$

⇒ <u>6 states for two electrons</u>:

$$\left.\begin{aligned} |1\,0\;1\,0\rangle &\equiv |\uparrow,\uparrow\rangle \\ |0\,1\;0\,1\rangle &\equiv |\downarrow,\downarrow\rangle \\ |1\,0\;0\,1\rangle &\equiv |\uparrow,\downarrow\rangle \\ |0\,1\;1\,0\rangle &\equiv |\downarrow,\uparrow\rangle \end{aligned}\right\} \text{low energy states}$$

$$\left.\begin{aligned} |1\,1\;0\,0\rangle &\equiv |\uparrow\downarrow, 0\rangle \\ |0\,0\;1\,1\rangle &\equiv |0, \uparrow\downarrow\rangle \end{aligned}\right\} \begin{array}{l}\text{high-energy states} \\ (E \approx U)\end{array}$$

ε: on-site energy

$$H = \left(\begin{array}{cc|cccc} 2\varepsilon & 0 & 0 & 0 & 0 & 0 \\ 0 & 2\varepsilon & 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 2\varepsilon & 0 & -t & -t \\ 0 & 0 & 0 & 2\varepsilon & t & t \\ 0 & 0 & -t & t & 2\varepsilon+U & 0 \\ 0 & 0 & -t & t & 0 & 2\varepsilon+U \end{array}\right)$$

analytic diagonalization posible, noting that

- $(|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle)\frac{1}{\sqrt{2}} \equiv (0,0,1,1,0,0)^+/\sqrt{2}$

  $|\uparrow,\uparrow\rangle$, $|\downarrow\downarrow\rangle$ are eigenstates with energy $E_t = 2\varepsilon$

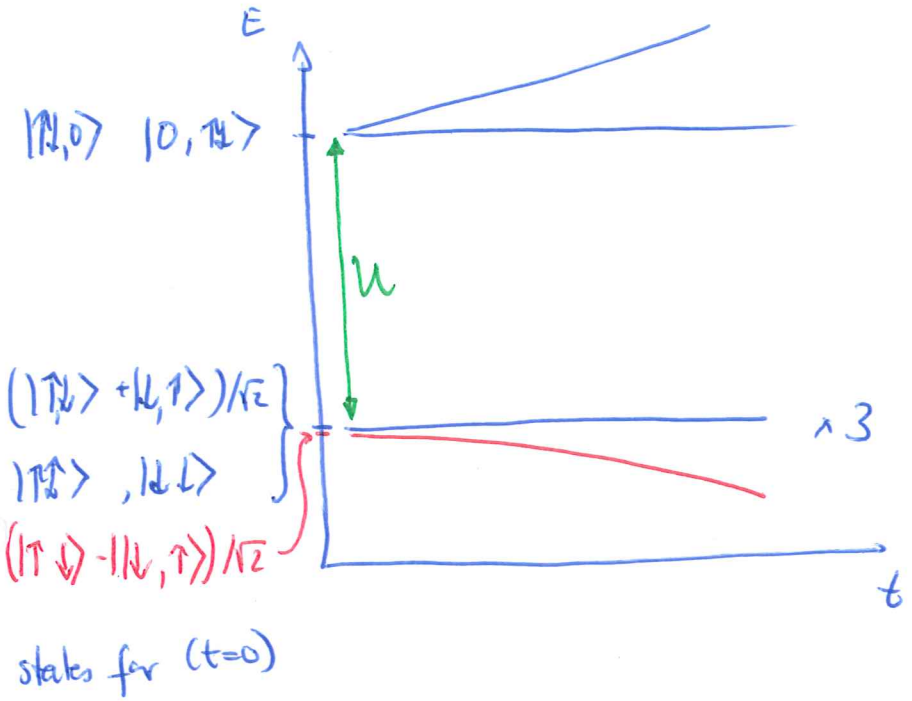
  } triplet!

- $(|\uparrow\downarrow,0\rangle - |0,\uparrow\downarrow\rangle)/\sqrt{2}$ eigenstate energy $2\varepsilon+U$

  $\rightsquigarrow$ remaining 2×2 matrix:

  Ground state $E_s = 2\varepsilon + \frac{U}{2} - \sqrt{\left(\frac{U}{2}\right)^2 + 4t^2}$ } singlet

result important for $t \ll U$:



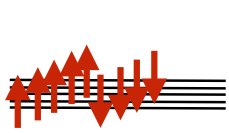
$H_{eff} = J \vec{S}_1 \cdot \vec{S}_2$

$J = \frac{4t^2}{U}$

$= E_t - E_s$ like above

- Singlet lowered due to virtual hopping processes (kinetic energy). Virtual hopping excluded for triplet due to Pauli principle.

Spin-orbital exchange (Kugel-Khomski model KCuF3)



Cu 3d orbitals
9 electrons

eg orbitals

t2g orbitals

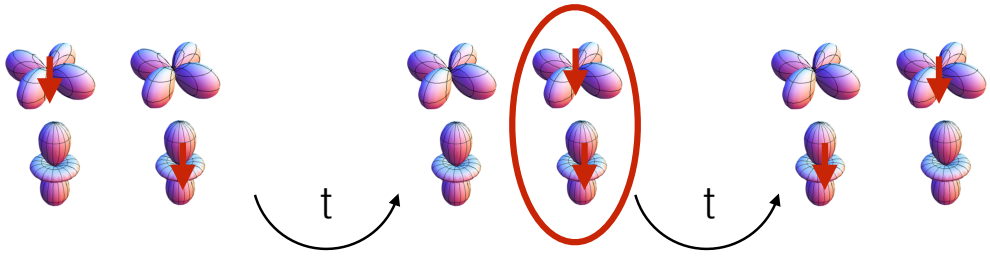
Low-energy manifold in either of the two e.g. orbitals:

Orbital pseudospin:	$\tau_z = \frac{1}{2}$	$\tau_z = -\frac{1}{2}$	$\tau_z = \frac{1}{2}$	$\tau_z = -\frac{1}{2}$
Spin:	$s_z = \frac{1}{2}$	$s_z = \frac{1}{2}$	$s_z = -\frac{1}{2}$	$s_z = -\frac{1}{2}$

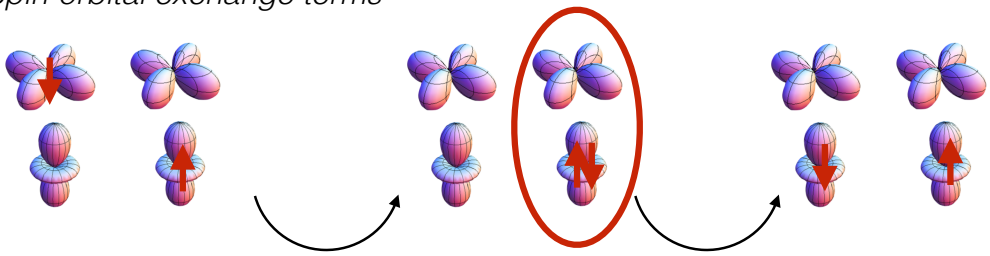
Interaction: intra-orbital Coulomb, inter-orbital Coulomb, Hunds-Coupling

Orbital-orbital exchange, and mixed orbital-spin exchange

Orbital-orbital exchange



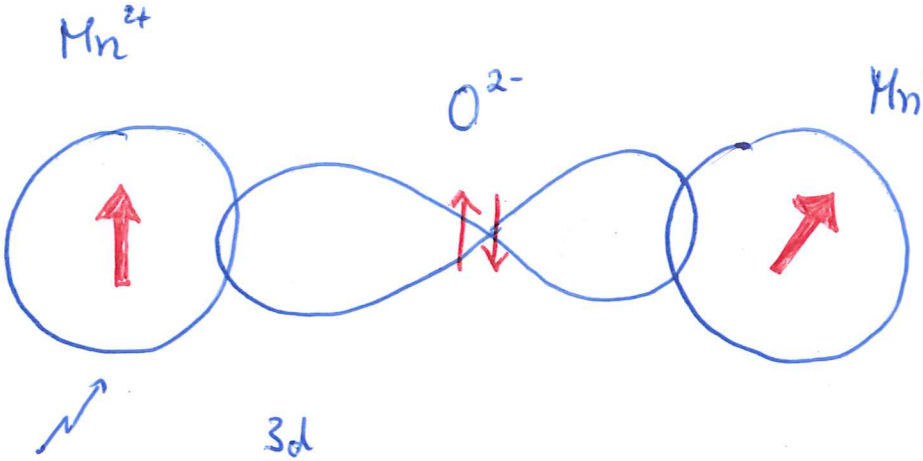
Spin-orbital exchange terms



Superexchange via oxygen ion

MnO, NiO ... no direct overlap between magnetic ions

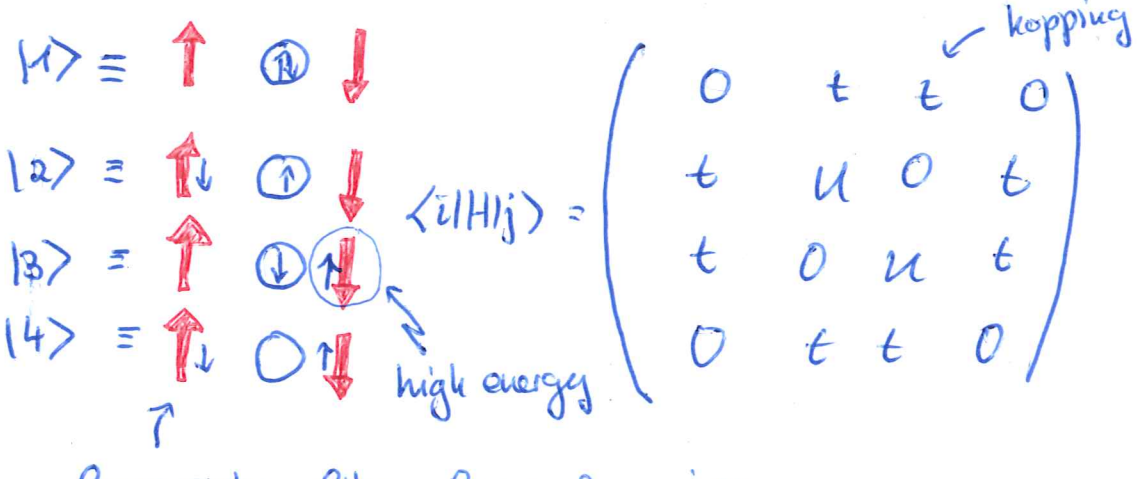
Simple cluster model:



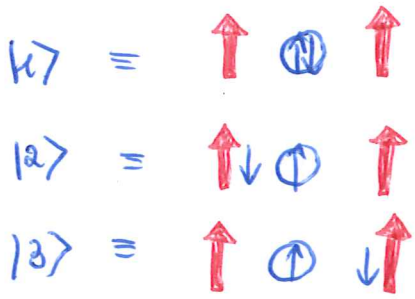
half-filled shell $(\uparrow\uparrow\uparrow\uparrow\uparrow)$ $S = 5/2$ due to Hunds rule

$\rightsquigarrow$ an electron which hops from O^{2-} to Mn^{2+} must be anti-parallel to spin on Mn^{2+}

- possible states for antiparallel alignment of Mn spins:



- for parallel alignment:

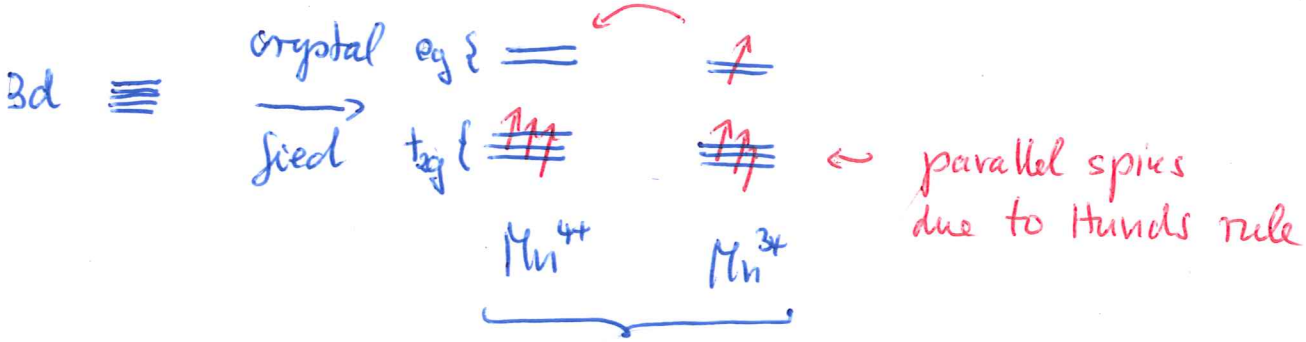


$$\langle i|H|j\rangle \approx \begin{pmatrix} 0 & t & t \\ t & U & 0 \\ t & 0 & U \end{pmatrix}$$

~ again "singlet" (anti-parallel Mn^{2+} spins)
lower in energy, because O^{2-} electrons more delocalized, i.e. lower kinetic energy
(difference in 4th order perturbation theory)

Double exchange

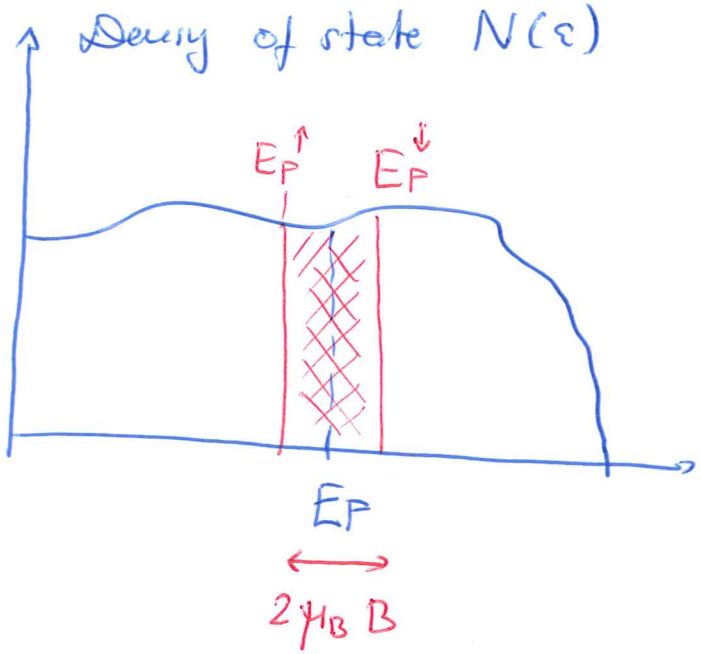
eg. mixed valence Mn^{3+} / Mn^{4+}



if Mn-spins are parallel ⇒ extra eg electron can move freely (without violating Hunds rule) ⇒ lower kinetic energy ⇒ ferromagnetic exchange

Itinerant ferromagnetism (e.g. Fe) : only brief summary ...

response of band electrons (paramagnetism)



$B \Rightarrow$ shift of chemical potential of $\downarrow, \uparrow$ electrons due to Zeeman energy $\Rightarrow$

$$\chi = \frac{\partial M}{\partial B} \sim N(\varepsilon_F)$$

Local coulomb interaction (density-density

$$U\, n_\uparrow(\vec{r})\, n_\downarrow(\vec{r}) = \frac{U}{4}\left[n(r)^2 - S_z^2 \right]$$

Because of Pauli principle only electrons with opposite spin interact locally

$\frac{n_\uparrow - n_\downarrow}{2} \hat{=}$ local magnetization

≈> local interaction leads to induced magnetic field $\sim U\langle M\rangle$ in mean field description.

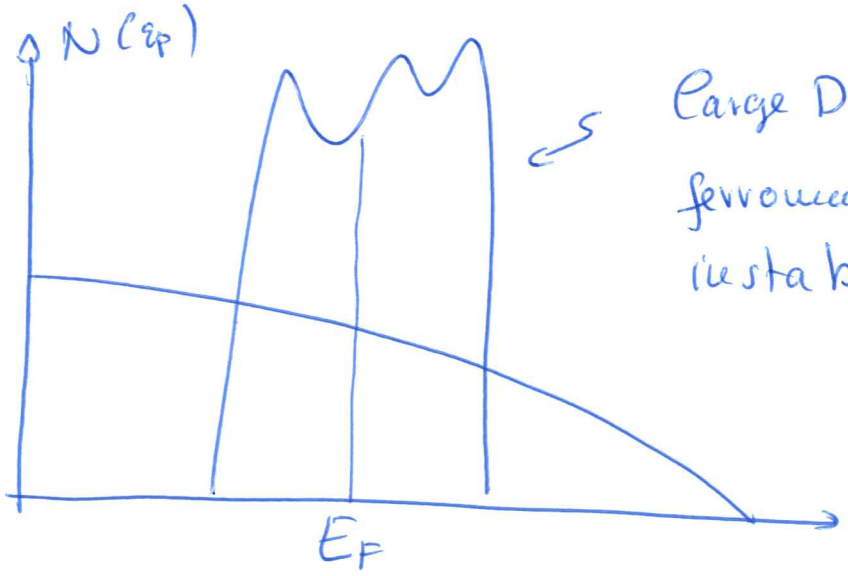
$$\chi = \frac{\chi_{free}}{1 - U \underbrace{N(\varepsilon_F)}_{\leq}}$$

instability $\hat{=}$ magnetic ordering for

$U N(\varepsilon_F) = 1$ Stoner criterion

↑

enhanced for large Coulomb interaction or large density of states (can have singularities, flat bands, ...)



large DOS $\hat{=}$ ferromagnetic instability