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)

\[ \vec{p} = \vec{F}_L = -e \left( \vec{E} + \frac{\vec{v}_e \times \vec{B}}{c} \right) \]

(Lorentz force)

- motion between collisions

\[ \frac{d\vec{p}}{dt} = -\vec{F}_L - \vec{p} \]

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

\[ \Gamma : \text{relaxation time} \]
can be used to compute various transport properties, e.g. conductivity:

\[ \mathbf{j} = -en \mathbf{F} \mathbf{n} \]

\( \mathbf{j} \): current density  
\( n \): density of electrons

\[ \mathbf{E}(\omega) = \mathbf{E}(\omega) e^{-i \omega t} \quad \Rightarrow \quad \mathbf{j}(\omega) = \mathbf{E}(\omega) \mathcal{S}(\omega) \]

with \( \mathcal{S}(\omega) = \frac{\mathcal{S}_0}{1 - i \omega \tau} \)

\( \mathcal{S}_0 = \frac{ne^2\tau}{m} \)

DC conductivity

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

1. Scattering rate \( \mathcal{S} \) cannot be related to scattering with ions: As decreases \( \mathcal{S}_0 \) in a perfect crystal (no defects) at \( T \neq 0 \)

(also: temperature-dependence of \( \mathcal{S} \) not captured)

\[ \mathcal{S} \approx \text{electrons can move almost free in a perfect periodic crystal} \]  

\[ \text{ quasi-momentum conservation } \]
Kinetic gas theory makes some "wrong" predictions, e.g. specific heat 
\[ C_v = \frac{3}{2} n k_B \] (really \( C_v \propto T \))

\[ \Rightarrow \] 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:

\[ n_s \approx n^{-\frac{1}{2}} \]

\[ \text{typical inter-} \]

\[ \text{particle distance} \]

\[ \frac{2\pi \hbar}{\sqrt{3} \pi n k_B T} \]

average de Broglie wavelength \( \lambda = \frac{2\pi h}{\sqrt{3} n} \)

for particle in ideal gas at temperature \( T \):

\[ \langle \frac{1}{2} n^2 \rangle = \langle \frac{1}{2} k_B T \rangle \]

\[ \langle \frac{p^2}{2m} \rangle = \frac{3}{2} k_B T \]
Check: above estimate $\gamma_s \lesssim \langle \gamma \rangle$ up to constant equivalent to $E_F \gtrsim T$, where $E_F$ is the Fermi energy of free electrons with density $n$: $E_F = \left( \frac{2\pi^2}{3} n \right)^{\frac{2}{3}} \frac{\hbar^2}{2m}$

Typical value for metals:

$E_F \sim 1 - 20 \text{ eV} \gg k_BT \sim 0.01 \text{ eV}$

Note $k_BT = 1 \text{ eV} \approx 11604 \text{ Kelvin}$
In real materials, the ratio $\frac{\nu}{\omega}$ 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 these particles have often very different properties from original particles (\textit{\(\implies\)} quasi-particles)

\[ E = \frac{\hbar k^2}{2m} \]

\[ E = \frac{\hbar k^2}{2m} \]

\textit{\(\approx\)} many different ground states: Fermi liquid, superconductor, magnetic order, with different excitations
Electrons in a periodic potential - band theory

1. **Periodic structures - crystal symmetries**

   - Primitive lattice vectors
   - More than one atom per unit cell: "basis"
   - Primitive unit cell

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

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

2. Classification of lattice by symmetry
(Note in this lecture, see texts on crystallography):

   - **Point group**: symmetry operations which leave one point fixed
   - **Space group**: full symmetry group

\[
\vec{r} \rightarrow \vec{D} \vec{r} + \vec{a} ; \quad \vec{D} : \text{point group} \quad \vec{a} : \text{translation} \]
Example - Bravais lattices in $d=2$

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Example - Honeycomb lattice: not a Bravais lattice

Basis: 2 atoms per unit cell
in dimension $d=3$: Bravais lattices can have 7 point groups (crystal systems) and 14 space groups (Bravais ~ 1850).

- in dimension $d=2$: space groups = \underline{wallpaper groups} (see e.g. wikipedia)

- Importance of symmetry for description of solids:
  - quantum mechanics (quasi-momentum) - 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:

$$j_a = \sum_{a'} \sigma_{a a'} E_{a'} \quad a, a' = x, y, z$$

Invariance $D \sigma D^{-1} = \sigma$ for all point group operations.
Rotations $180^\circ$ around $2$- Axis:

$$D = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad D^{-1} = \begin{pmatrix} +\sigma_{11} + \sigma_{22} - \sigma_{33} \\ +\sigma_{21} + \sigma_{32} - \sigma_{13} \\ -\sigma_{31} - \sigma_{32} + \sigma_{13} \end{pmatrix} = \mathbf{\sigma}$$

$$\Rightarrow \sigma_{12} = \sigma_{23} = \sigma_{31} = 0,$$ \quad $\sigma_{13} = \sigma_{32} = 0$

Similar rotations around $x, y, z = \mathbf{\sigma}$ diagonal rotation $120^\circ$ around body diagonal

$=$ permutations of $x, y, z = \mathbf{\sigma}^2 = 1 \cdot \mathbf{\sigma}$

Scattering waves off periodic structures

\[ \mathbf{k} \rightarrow \mathbf{k}', \mathbf{k}'' \]
Condition for constructive interference of scattered wave in direction \( \vec{h}' \):

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

for all \( \vec{R} \) in lattice (you trace)

Proof:

Path difference of \( \odot \) and \( \odot' \):

\[
\left( \frac{\vec{k}}{k} - \frac{\vec{k}'}{k'} \right) \cdot \vec{R} = 2\pi n \cdot \lambda
\]

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

one gets the von Laue condition.
the reciprocal lattice

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

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

\[
\tilde{b}_1 = 2\pi \frac{\tilde{a}_2 \times \tilde{a}_3}{|\tilde{a}_1 \cdot (\tilde{a}_2 \times \tilde{a}_3)|}
\]
1,2,3 cyclic

Example: rectangular lattice:

\( \tilde{b}_x = \frac{2\pi}{b_x} \tilde{a}_x \)
• reformulation of von Laue condition: constructive interference if \( \mathbf{k} - \mathbf{k}' \) is a vector of reciprocal lattice.

• Technical remark: reciprocal lattice also defines Fourier components of a function which is periodic on the lattice:

\[
\text{if } f(\mathbf{\vec{r}} + \mathbf{R}) = f(\mathbf{\vec{r}}) \quad \forall \mathbf{R} \in \mathbf{L}
\]

\[\Rightarrow \quad f(\mathbf{\vec{r}}) = \sum_{\mathbf{G}} f_{\mathbf{G}} e^{i \mathbf{G} \cdot \mathbf{\vec{r}}}
\]

\[f_{\mathbf{G}} = \frac{1}{\text{Vol}} \int d^3r \ e^{-i \mathbf{G} \cdot \mathbf{\vec{r}}} f(\mathbf{\vec{r}})
\]

\]
Momentum conservation on the lattice

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

$\Rightarrow$ momentum conservation up to reciprocal lattice vector

Stark $|\psi\rangle$ has "good quasimomentum $\mathbf{\tilde{k}}$"

$\Rightarrow |\psi\rangle$ superposition of states with momentum $\mathbf{k} + \mathbf{G}, \mathbf{G} \in \mathbf{G}^*$

On a periodic lattice, quasimomentum is conserved.

without loss of generality, $\mathbf{k}$ can be taken from 1st Brillouin zone (Wigner-Seitz unit cell of the reciprocal lattice).
Illustration: Umklapp scattering.

\[ \vec{a} \in g^* \]

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

---

**Momentum conservation: algebraic formulation**

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

\[ [H, T_R] = 0 \quad \forall \vec{R} \in g \]

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

\[ \Rightarrow \text{choose eigenfunctions of } H \text{ to be simultaneous eigenfunctions of all } T_R \]

\[ T_R \Psi \psi = C_R(\vec{R}) \Psi \psi \quad \forall \vec{R} \]
\[ \bar{R} = \sum_i n_i \hat{a}_i \quad \Rightarrow \quad T_{\bar{R}} = (T_{\hat{a}_1})^{n_1}(T_{\hat{a}_2})^{n_2}(T_{\hat{a}_3})^{n_3} \]

(Because translation operators commute !)

\[ \Rightarrow \quad T_{\bar{R}} |\Psi\rangle = C(a_1)^{n_1} C(a_2)^{n_2} C(a_3)^{n_3} |\Psi\rangle \quad \forall n_i \in \mathbb{Z} \]

Because \( |\Psi\rangle \| = \| T_{\bar{R}} |\Psi\rangle \| \quad \Rightarrow \quad |C(\bar{R})| = 1 \)

\[ \Rightarrow \quad \text{implicitly define } \bar{\kappa} \text{ such that } C(a_i) = e^{i \bar{\kappa} \hat{a}_i} \]

\[ \Rightarrow \quad C(\bar{R}) = \exp \left( i \sum_j \bar{\kappa}_j \hat{a}_j \right) = e^{i \bar{\kappa} \bar{R}} \]

\[ \bar{k} \quad (\text{quasimomentum}) \quad \text{Quantum number which characterizes how wave function behaves under translation:} \]

|\Psi\rangle \text{ has quasimomentum } \bar{k} \quad \Rightarrow \quad T_{\bar{R}} |\Psi\rangle = e^{i \bar{\kappa} \bar{R}} |\Psi\rangle \]

- Note: apparently \( \bar{k} \) and \( \bar{k} + \bar{\kappa} \) with \( \bar{\kappa} \in \mathbb{R}^* \) are the same quasimomentum

- compare: \( L^2, L_z \): Quantum numbers which characterize transformation under rotations ... etc.
2) Elecrons 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 $m_e \ll m_{\text{nuclei}}$ (see later).
- Electron-electron interaction is neglected.

$\Rightarrow$ goal: Determine eigenvalue spectrum

$$H = \frac{\hat{p}^2}{2m} + V(\vec{r}) \quad V(\vec{r}) = V(\vec{r} + \vec{R})$$

Note: Why does $\otimes$ 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, Herbec), $V(\vec{r})$ 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 $T_{\vec{R}}$, $\vec{R} \in \mathbb{R}$

$\Rightarrow$ eigenstates of $H$ have good quasimomentum

$$T_{\vec{R}} \Psi(x) = \Psi(x + \vec{R})$$

$$e^{i \vec{p} \cdot \vec{R}} \Psi(\vec{x})$$

(2.1)
The function \( e^{-i\vec{k}\cdot\vec{r}} \psi(\vec{r}) = \psi_k(\vec{r}) \) is periodic, \( \psi_k(\vec{r} + \vec{R}) = \psi_k(\vec{r}) \)

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

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

\[ i \frac{d}{dt} \psi(t) = H(t) \psi(t) \] with \( H(t+T) = H(t) \)

Then the solutions are of the form

\[ \psi(t) = e^{-i\epsilon t} \psi(t) \]

\( \epsilon \) periodic

can be restricted to \( [0, \frac{2\pi}{T}] \) "quasi-energy"
using Bloch theorem, the Schrödinger equation can be rewritten as an equation for \( \psi \):

\[
\hat{p} = -i\hbar \nabla \Rightarrow \hat{p} e^{i\hat{k} \cdot \vec{r}} = e^{i\hat{k} \cdot \vec{r}} (\hat{p} + i\hbar \vec{k}) f(\vec{r})
\]

\[
\left[ \frac{(\hat{p} + i\hbar \vec{k})^2}{2m} + V(\vec{r}) \right] U_k(\vec{r}) = E_k U_k(\vec{r})
\]

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

\[ \text{Energy bands } E_n(\vec{k}) \quad n=1,2,3,... \]

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

\( \mathcal{G} \)
The level spectrum is crucial for most properties of the solid. In an independent electron approximation, all 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, $k$ with $E_n(k) = E_F$ forms 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...)

![Graphs showing the energy levels for insulator, semiconductor, and metal.](image-url)
Band structure for the square lattice in 2 dimensions

lattice: \( g = \left\{ a \begin{pmatrix} n_x \\ n_y \end{pmatrix}, \quad n_x, n_y \in \mathbb{Z} \right\} \)

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

\( V_0 = 1, \quad V_1 = 0.5 \)

Schrödinger equation in reziprokal space:

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

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

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

Here \( V_{\pi, 0} = V_{-\pi, 0} = V_{0, \pi} = V_{0, -\pi} = -V_0 / 2 \)
\( V_{(\pi, \pi)} = V_{(-\pi, \pi)} = V_{(\pi, -\pi)} = V_{(-\pi, -\pi)} = -V_1 / 2 \)

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)
one-dimensional case

\[ \bar{a} = \frac{2\pi}{\lambda} \hat{x} \]

\[ \varepsilon_k = \left( \frac{\hbar^2}{2m} \right) \frac{k^2}{2} \]

\[ E_k^\pm \]

\[ E_k^c, E_k^s \]

\[ -\frac{\pi}{a} \leq k \leq \frac{\pi}{a} \]

Weak potential: perturbative analysis close to degenerate point: \( k \approx \frac{\theta}{2} \)

\( \Rightarrow \) take into account two plane waves:

\[ U_k(\xi) = \sum \frac{C_G}{a} e^{i\bar{a} \xi} \]

only \( c_0, C_G \neq 0 \)

Schrödinger equation becomes 2x2 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 \( V(x) = 2V_0 \cos(ax) \) and \( a = \frac{2\pi}{\alpha} \)

at \( k = \frac{\alpha}{2} \) \( (\varepsilon_k = \varepsilon_{k+\alpha} = \varepsilon_0) \)

\[
\begin{pmatrix}
\varepsilon_0 & V_0 \\
V_0 & \varepsilon_0
\end{pmatrix}
\begin{pmatrix}
C_0 \\
C_n
\end{pmatrix}
= E
\begin{pmatrix}
C_0 \\
C_n
\end{pmatrix}
\]

**Solutions:**

- \( \begin{pmatrix} C_0 \\ C_0 \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \end{pmatrix} / \sqrt{2} \Rightarrow E^{(+)} = \varepsilon_0 + V_0 \)
  \[ |U(x)|^2 \sim \frac{1}{1 + e^{iGx}} \]
  \[ \sim \cos \left( \frac{ax}{2} \right)^2 \]

- \( \begin{pmatrix} C_0 \\ C_n \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \end{pmatrix} / \sqrt{2} \Rightarrow E^{(-)} = \varepsilon_0 - V_0 \)
  \[ |U(x)|^2 \sim \frac{1}{1 - e^{iGx}} \]
  \[ \sim \sin \left( \frac{ax}{2} \right)^2 \]

\[ |U_+(x)|^2 = \left( \cos \frac{ax}{2} \right)^2 \text{ "anti-Bonding"} \]

\[ |U_-(x)|^2 \sim \sin \left( \frac{ax}{2} \right)^2 \text{ "bonding"} \]
\( V(r) = 0 \): Backfolding of plane waves:

Band-structure along path through 1st BZ:

\[ V_0 = 1, \quad V_1 = 0 \]

Point size: 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!)

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

choose \( N \) large enough to converge solution

Below: \( N = 3, 4 \)

\[ V_0 = 4, \quad V_1 = 0 \]

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
\[ V_0 = 10, \ V_1 = 0 \]

(indirect) band gap:
Insulator for 2 electrons per unit cell

\[ V_0 = 10, \ V_1 = 2 \]

Degeneracies lifted in 1st order perturbation theory in V if \( V_G \neq 0 \)

Degeneracies now already lifted in 1st order perturbation theory in V
\[ V_0 = 20, V_1 = 2 \]

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:

\[ \langle \mathbf{R} \rangle_{at} = \Psi_{at} (\mathbf{R} - \mathbf{R}) \quad \Psi_{at}: \text{atomic orbitals} \]

- assume that description can be restricted to only limited set of orbitals (because others are far off in energy) here: for simplicity of notation: only one orbital (\( \cong H - \text{crystal} \))
to find band structure, diagonalize Hamiltonian $H = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r})$ in subset \{ $|R\rangle_{at}$ \}

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

So somehow construct (by linear combinations) $|R\rangle = \sum_{R'} U_{RR'} |R\rangle_{at}$ with suitable choice of $U$ — 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 $\langle R | R' \rangle \sim e^{-|R-R'|/\sigma}$ falls off exponentially), also WF will be localized
\[ H \quad \text{any} \quad N\mathbb{N}: \]

\[ \hat{t} + \hat{r}_n = \sum \hat{c} \]

\[ H = \sum \frac{1}{2i} \]

Solve...

\[ |\psi_k\rangle = \frac{1}{\sqrt{L}} \sum_{k} |R\rangle e^{ikx} \]

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

\[ = \sum_{R} \langle R | H | 0 \rangle e^{ihR} \equiv \varepsilon_k \]
\( H = -\frac{\hbar^2}{2m} \hat{\nabla}^2 + V(r) \)

\[
H = \sum_{RR'} \langle R | H | R' \rangle \langle R' | \quad \hbar \bar{r} - \bar{r}'
\]

Matrix element for tunneling between Wannier orbitals.

If Wannier orbitals are well localized, \( \hbar \bar{r} - \bar{r}' \) falls off exponentially. Simplest approximation:

\[
\hbar \bar{r} - \bar{r}' = \begin{cases} 
\varepsilon & \bar{R} = \bar{R}' \\
-J & \bar{R}, \bar{R}' nearest \text{neighboring} \\
0 & \text{otherwise zero}
\end{cases}
\]

Band structure:

Bloch state \( |k> = \frac{1}{L} \sum_R \langle R | \ e^{i k \bar{r}} \)

\[
\text{c.f.: } \phi(k) = e^{i \hbar \omega} \left\{ \frac{1}{\sqrt{L}} \sum \bar{w}(v-r) e^{i \hbar (R-v)} \right\}
\]
$\hat{A}$ is diagonalized by the Bloch functions (Barel index omitted, one band only)

$|\psi_{Rk}\rangle = \frac{1}{N} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} |\mathbf{R}\rangle$

$\hat{A} |\psi_{Rk}\rangle = \frac{1}{N} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \left\{ e^{i\mathbf{k} \cdot \mathbf{a}} \langle R |^{k_{x} a} - t | \mathbf{R} + \mathbf{a}_{1} \rangle - t | \mathbf{R} + \mathbf{a}_{2} \rangle - t | \mathbf{R} - \mathbf{a}_{1} \rangle \right\}$

$= \frac{1}{N} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} |\mathbf{R}\rangle \left\{ e_{0} - te^{-i\mathbf{k} \cdot \mathbf{a}} - te^{i\mathbf{k} \cdot \mathbf{a}} - te^{-i\mathbf{k} \cdot \mathbf{a}} \right\}$

$H |\psi_{Rk}\rangle = \left[ e_{0} - 2t \cos(k_{x}a) - 2t \cos(k_{y}a) \right] |\psi_{Rk}\rangle$

$\varepsilon_{k}$

$(-\frac{\pi}{a}, \frac{\pi}{a})$

$\varepsilon_{k} = \text{const.}$

$(\frac{\pi}{a}, \frac{\pi}{a})$

$(\frac{\pi}{a}, -\frac{\pi}{a})$

$(-\frac{\pi}{a}, -\frac{\pi}{a})$
• Dynamics of Bloch electrons

Semiclassical equations of motion:

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

wave packet \( \Delta r, \Delta k \):

\[
\Delta k \ll \text{size of 1st BZ} \iff \Delta r \gg \text{lattice spacing}
\]

still variation of \( E(r) \) and \( B(r) \) on scales larger than \( \Delta r \)

\[
\text{equations of motion:}
\]

\[
\begin{align*}
\dot{\vec{r}} &= \vec{v}_n(\vec{r}, \vec{k}) = \frac{1}{\hbar} \frac{\partial E_n(\vec{k})}{\partial \vec{k}} \\
\hbar \dot{\vec{k}} &= -e\vec{E}(\vec{r}) - \frac{e}{c} \vec{v}_n(\vec{k}) \times \vec{B}(\vec{r})
\end{align*}
\]

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 \( E \):

\[
\frac{d}{dt} v_\alpha = \frac{d}{dt} \frac{1}{\hbar} \frac{\partial E_n(\vec{k})}{\partial k_\alpha} = \sum_\beta \frac{1}{\hbar} \frac{\partial^2 E_n(\vec{k})}{\partial k_\beta \partial k_\alpha} \dot{k}_\beta - e E_\beta
\]

\( \alpha, \beta = x, y, z \)

c.f. acceleration of free electrons:

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

mass tensor:

\[
\left( \frac{1}{m} \right)_{\alpha\beta} = \frac{1}{\hbar^2} \frac{\partial^2 E_n(\vec{k})}{\partial k_\beta \partial k_\alpha}
\]

\[
e.g. \text{diagonal tensor (symmetry)} \quad m = \begin{pmatrix}
m_* & 0 & 0 \\
0 & m_* & 0 \\
0 & 0 & m
\end{pmatrix} \iff \quad \dot{\vec{v}} = -\frac{e}{m_*} \vec{E}
\]

band electrons behave like particles
\textit{with a different effective mass}

good metals: \( m^* \) same order of magnitude
**Bloch-oscillations**

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

\[
\begin{align*}
\hbar \dot{k} &= -eE \\
k(t) &= -\frac{eE' t}{\hbar} \\
v(t) &= \frac{1}{\hbar} \frac{\partial \epsilon(k)}{\partial k} = \frac{2t_0 a}{\hbar} \sin(k(t)a)
\end{align*}
\]

periodic motion with Bloch frequency  \( \Omega = \frac{Eea}{\hbar} \)

\[
x(t) = \text{const.} - \frac{2t_0}{Ee} \cos \left( \frac{Eea}{\hbar} t \right)
\]

**Motion in more than one dimension**

large field:  \( \frac{1kV}{cm} \)  \( a = 1\AA \)  \( \Omega = \frac{Eea}{\hbar} = \frac{10^{-5}eV}{\hbar} \)

\[ \Rightarrow \frac{2\pi}{\Omega} \gg \text{time between incoherent scattering events} \]

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

**Bloch oscillations usually destroyed by scattering**
AC field: \[ E(t) = E_0 \cos(\Omega t) \quad \text{(switch on at } t=0) \]

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

\[ \Rightarrow \text{current:} \]

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

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

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

\textit{all odd harmonics present!}

\textit{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 collective response of all mobile charges induces a counter charge on a very fast timescale.

\[ \Phi(r) = \frac{q}{r} \]

"bare charge"

Motivation:

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

Maxwell: (cgs)
\[ \nabla \cdot \mathbf{E} = 4\pi \rho \]
\[ \nabla \times \mathbf{B} = \frac{4\pi}{c} J + \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} \]
\[ \nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} \]
\[ \nabla \cdot \mathbf{B} = 0 \]

\[ \Rightarrow \text{ macroscopic Maxwell - \(\Phi\) equation:} \]
\[ \nabla \cdot \mathbf{D} = 4\pi \rho_{\text{ext}} \]
\[ \nabla \times \mathbf{H} = \frac{4\pi}{c} J_{\text{ext}} + \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} \]

+ Linear response \( \mathbf{D} = \varepsilon \mathbf{E}, \mathbf{B} = \mu \mathbf{H} \)

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

\[ \mathbf{D}(\mathbf{r},t) = \int_{-\infty}^{t} dt' \mathcal{E}_{\beta}(t-t') \mathbf{E}_{\beta}(\mathbf{r}',t') \]

\[ \text{causal relation! retarded response} \]

\[ \xrightarrow{\text{Fourier transformation}}: \quad \mathbf{D}(\mathbf{r},t) = \int_{-\infty}^{\infty} dq \mathbf{D}(q,t) e^{iq \cdot \mathbf{r}} e^{-i\omega t} \]

\[ \mathbf{D}(q,t) = \varepsilon(q \cdot w) \mathbf{E}(q,\omega) \]
Interpretation of dielectric function $\varepsilon$

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

\[-\nabla^2 \phi_{\text{ext}} = 4\pi \rho_{\text{ext}}\]

\[\nabla \cdot \vec{D} = \nabla (\varepsilon E) = \varepsilon \nabla E = -\varepsilon \nabla^2 \phi\]

\[\varepsilon \text{ trans. invariance}\]

\[\phi_{q,\omega} = \frac{\phi_{\text{ext}}(q,\omega)}{\varepsilon(q,\omega)}\]

Phenomenologically, $\varepsilon$ describes screening, i.e. reduction of free-space potential due to induced charge.

Relation to conductivity:

\[\nabla \times B = \frac{4\pi}{c} J_{\text{ext}} + \frac{1}{c} \frac{\partial D}{\partial t} \sim \text{ for mom way: material with } j_{\omega} = 0\]

\[\nabla \times B = -\frac{i\omega}{c} D \quad (\text{for } \omega \rightarrow -i\omega)\]

\[= -\frac{i\omega \varepsilon}{c} \nabla E\]
microscopic equation \( j = \text{induced current} \)

\[
\mathbf{\nabla} \times \mathbf{B} = \epsilon \frac{4\pi}{c} \mathbf{j} - \frac{i\omega}{c} \mathbf{E}
\]

\[
\mathbf{\nabla} \times \mathbf{E} = \text{definition of conductivity}
\]

\[
= \frac{-i\omega}{c} \left( 1 + i \frac{4\pi\sigma}{\omega} \right) \mathbf{E}
\]

\[\text{compared with } \Theta:\]

\[
\mathbf{\varepsilon}(\omega) = 1 + i \frac{4\pi\sigma}{\omega} \quad \text{[\text{in SI units]}
\]

optical response: measurement at \( q \rightarrow 0 \)

\( (\lambda \gg \text{atomic spacing}) \)

Relation to charge response function

define \( \delta n = \mathbf{\nabla} \delta \mathbf{\nabla} \mathbf{\varepsilon}(\omega) \)

response of density \( \delta n \) to external potential energy \( \rho = -\epsilon \delta n \quad \text{\( V = -\epsilon \mathbf{\nabla} \phi \)} \)

Poisson: \( \phi = \frac{4\pi}{q_2} \left( \text{Pert} + \text{Purcular} \right) \)

\[
\frac{\rho_{\text{Pert}}}{E} - \frac{\rho_{\text{Purcular}}}{E}
\]
\[ \frac{1}{\varepsilon(q, \omega)} = 1 + \frac{4\pi e^2}{q^2} \chi(q, \omega) \]

useful for calculation of \( \varepsilon, \chi \), but usually difficult to calculate \( \chi = \frac{S_n}{S_{\text{ext}}} \) for interacting many particle system.

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

\[ S_n = \chi S_{\text{ext}} \approx \chi_{\text{free}} (S_{\text{ext}} + S_{\text{ind}}) \]

\text{response of interacting electrons to external potential} \approx \text{response } \chi_{\text{free}} \text{ of non-interacting electrons to full potential (external+induced)}
with \( \delta V_{\text{ind}} = -e \phi_{\text{ind}} = \frac{4\pi e^2}{q^2} \delta n \)

\[ = 0 \quad \delta n = X_{\text{free}} (\delta V_{\text{ext}} + \frac{4\pi e^2}{q^2} \delta n) \]

\[ = 0 \quad \delta n = X S V_{\text{ext}} \quad \text{with} \]

\[ X(q, \omega) = \frac{X_{\text{free}}(q, \omega)}{1 - \frac{4\pi e^2}{q^2} X_{\text{free}}(q, \omega)} \quad \text{RPA mean-field susceptibility} \]

Implications of denominator (see below)

- pole at \( \omega > 0 \): collective excitation
- pole at \( \omega < 0 \): instability, charge density wave (at \( q \neq 0 \)) etc...
implied carbon of denominator:
- pole at frequency \( w \rightarrow 0 \):
  collective excitation
- pole at \( w \rightarrow \infty, q \neq 0 \): instability of the system, e.g. charge density wave

Static screening: Thomas Fermi model

Simplest model for \( \chi_{\text{free}} \):

Density \( n ( r_0 ) \) at given point \( r_0 \) \( \approx \) density of homogeneous electron gas in potential \( V = V ( r_0 ) \) ("local density approximation")

Homogeneous electron gas: \( n_F ( x ) = \frac{1}{e^{x / k_B T} + 1} \) (Fermi function)

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

\[\chi_{\text{free}} \approx - \frac{\partial n}{\partial \mu} \text{ Thomas Fermi}\]
• dielectric function:

\[ E = \frac{1}{1 + \frac{4\pi e^2}{q^2} \chi} \]

\[ \chi = \frac{\chi_{\text{free}}}{1 - \frac{4\pi e^2}{q^2} \chi_{\text{free}}} \]

\[ = 1 - \frac{4\pi e^2}{q^2} \chi_{\text{free}} \]

\[ \uparrow \]

Thomas-Fermi

definite Thomas-Fermi wave vector

\[ k_{TF}^2 = \frac{4\pi e^2}{\hbar^2} \frac{\partial n}{\partial \mu} \sim \frac{1}{k_{TF}^2} = O(\text{few } \AA) \]

for typical densities in metals.

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

\[ \phi(C_q) = \frac{4\pi Q}{q^2} \left( \frac{1}{\phi_{\text{ext}}} \right) \sim \frac{4\pi Q}{k_{TF}^2 + q^2} \]
Fourier transformation:

\[ \Phi(\vec{r}) = \frac{\Theta}{r} e^{-\vec{r} \cdot \vec{k}_F} \]

Yukawa potential,
Screening length \( \frac{1}{k_F} \).

More accurate \( K_{\text{free}}(q) \) exact.
Response of homogeneous electron gas: Liquid hard theory.

\[
K_{\text{free}}(q, \omega = 0) = \frac{d}{3} \frac{2\mu}{\hbar^2} \frac{k_F}{2\pi^2} \left\{ 1 - \frac{S}{4} \left( 1 - \frac{4}{S} \right) \ln \left| \frac{S + 2}{S - 2} \right| \right\}
\]

\[
K_{\mu\nu}(q, \omega = 0) = \frac{d}{2} \frac{2\mu}{\hbar^2} \frac{1}{2\pi} \left\{ 1 - \left( 1 - \frac{4}{S} \right) \Theta(S - 2) \right\}
\]

\[
K_{\mu\nu}(q, \omega = 0) = \frac{d}{1} \frac{2\mu}{\hbar^2} \frac{1}{2\pi^2} \left\{ \ln \left| \frac{S + 2}{S - 2} \right| \right\} S = \frac{9}{k_F}
\]

More and more single-las at \( |q| = 2k_F \) for low dimension. \( \omega \) instability for \( q \cdot d = 1 \).

Interference effect
(Friedel oscillation)

\[ \Phi(r) = c \frac{\cos(2k_F r)}{r^3} \]
Dynamic (frequency-dependent) screening

- Some general properties of response functions

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

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

\[
\langle A(t) \rangle = \int_{-\infty}^{\infty} dt' K(t-t') f(t')
\]

1. Fourier transform

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

\( \omega \) FT defined for frequencies \( \omega \) with \( \text{Im} \, \omega > 0 \)

\( X(\omega) = X(\omega + i \delta) = \int_{0}^{\infty} dt K(t) e^{i (\omega + i \delta) t} \delta > 0 \)

**Meaning:** \( X(\omega + i \delta) \delta > 0 \) \( \Rightarrow \) response to perturbation

\( f(t) = \int_{0}^{\infty} e^{-i \omega t} e^{St} \Rightarrow \text{adiabatic switch on field} \)
2) Analytic properties \( X(z) \) analytic for \( m \geq 0 \), 
\( X(z) \to 0 \) for \( |z| \to \infty \) imply relation between real and imaginary part: 
\[ X = X' + iX'' \]

\[
\begin{align*}
X'(\omega + i0^+) &= \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{X''(\omega' + i0^+)}{\omega' - \omega} d\omega', \\
X''(\omega + i0^+) &= -i \int_{-\infty}^{\infty} \frac{X'(\omega' + i0^+)}{\omega' - \omega} d\omega'.
\end{align*}
\]

Example: check for 
\[ X = \frac{1}{\omega + i0^+} \Rightarrow \begin{cases} X'' = -\pi \delta(\omega) \\
X' = \frac{1}{\omega} \end{cases} \]

3) \( \text{Im} X \) \( \leftrightarrow \) energy absorption

Consider 
\[ f(t) = e^{st} (f_0 e^{-i\omega t} + f^* e^{i\omega t}) \]

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

\[ \frac{dE}{dt} = \langle \frac{dH}{dt} \rangle = \frac{df}{dt} \langle A(t) \rangle \\
\]

... insert \( X, f \) ... average over one period:

\[ \frac{dE}{dt} = \frac{1}{T} \int_{0}^{T} \frac{dE}{dt} dt = -2\omega X''|f_0|^2 \]
Note: proof of $\psi$: analogous to Bellman-Feynman theorem:

\[
\frac{d}{dt} \langle \psi(t) | H(t) | \psi(t) \rangle = \frac{d}{dt} \langle \psi | H | \psi \rangle + \langle \psi | H | \frac{d}{dt} \psi \rangle
\]

4) Absorption $\leftrightarrow$ excitation spectrum

Fermi's golden rule: e.g. system at $T=0$ $\omega > 0$:

\[
\frac{dE}{dt} = \sum_{\text{transition mode}} \frac{2\pi}{\hbar} |\langle \chi_{\omega} | A | \chi_{\omega} \rangle|^2 S(\omega + E_{\omega} - E_{n})
\]

\(k=1\) compared with absorption, also possible for $\omega < 0$ ...

\[
\chi''(\omega + i\delta) = -\pi \sum_{n} |\langle \chi_{\omega} | A | \chi_{\omega} \rangle|^2 \left[ S(\omega + E_{\omega} - E_{n}) - S(\omega + E_{n} - E_{\omega}) \right]
\]

$T>0$:

\[
\chi''_{\omega} = -\pi \sum_{n,m} e^{-\beta E_{n}} e^{-\beta E_{m}} \frac{1}{2} |\langle n | A | m \rangle|^2 S(\omega + E_{n} - E_{m})
\]
Note: this result is equivalent to the Rubo formula:

\[ \chi(t-t) = -i \Theta(t-t) \text{Tr}(e^{-\beta H} [A(t), A(t^-)])/\mathcal{Z} \]

which is derived from standard time-dependent perturbation theory.

5) Fluctuations \leftrightarrow response / dissipation

auto correlation function:

\[ \langle (A(t) - \langle A \rangle) (A(t^\prime) - \langle A \rangle) \rangle = \langle A(t) A(t^\prime) \rangle - \langle A \rangle^2 \]

\[ C(t) = \langle A(t) A(0) + A(0) A(t) \rangle \]

\[ C(\omega) = -2 \chi''(\omega) \coth(\frac{\beta \omega}{2}) \]

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

Example: resistor noise
Noise power density:

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

\[ \langle I(t) I(t') + I(t') I(t) \rangle = C(\omega) \]

\[ C(\omega) = 2 \sigma(\omega) \omega \coth \left( \frac{\beta \omega}{2} \right) = \frac{4 k_B T}{\omega < T} \]

Universal ratio between fluctuations and response

(\rightarrow "thermometer")

Back to density response \[ \chi = \frac{\delta n}{\delta V_{\text{ext}}} \]

Example 1: oscillator model

Density no of oscillators

\[ \dot{x} \quad \omega^2 x = - \omega c x^2 + f_{\text{ext}} \]

\[ \nabla \cdot \nabla V_{\text{ext}} \]

\[ \dot{x} (\omega^2 - \omega^2) = - \frac{1}{\omega} \nabla \cdot \nabla V_{\text{ext}} \]

Density:

\[ \frac{\delta n}{n_0} = - \nabla \cdot \dot{x} = \uparrow \]

In Fourier space:

\[ \frac{\delta n}{n_0} = \mp i q \cdot \dot{x} \]

\[ \dot{x} = - \frac{1}{\omega (\omega^2 - \omega^2)} i q V_{\text{ext}} \]
\[ s_n = q^2 \frac{n_0/m}{\omega^2 - \omega_0^2} \]

\[ \chi_{\text{free}} \quad \text{free: no coulomb interaction between the oscillators, at least ok for low density} \]

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

(really: \[ \chi_{\text{free}}(\omega + i\delta) = \frac{q^2 n_0}{\mu} \left( \frac{1}{\omega + i\delta - \omega_0} - \frac{1}{\omega + i\delta + \omega_0} \right) \]

\[ \text{Im} \chi_{\text{free}}(\omega + i\delta) = -\pi \frac{q^2 n_0}{2\mu \omega_0} \left[ S(\omega - \omega_0) - S(\omega + \omega_0) \right] \]

\[ \approx \text{excitation spectrum: excitation of oscillator} \]

\[ \text{quantum} \quad \hbar \omega \]

\[ \frac{1}{\varepsilon(q,\omega)} = 1 + \frac{4\pi e^2}{q^2} \chi = 1 + \frac{4\pi e^2 n_0/m}{\omega^2 - \omega_0^2} \]

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

\[ 4\pi e^2 n_0/e = \omega_p^2 \quad \omega_p: \text{plasma frequency} \]
\[ \text{screening for } w \ll \omega_0 \]

\[ \text{unscreened } \quad \text{for } w \gg \omega_0 \]

\[ \text{dielectric loss for } w = \omega_0. \]

Real material:

\[ \text{Loss function: } \]

\[ \text{density of states of oscillations} \]
unbound particles \( \omega_0 = 0 \)

(c.g. electrons in metal)

\[ X_{\text{free}} = q^2 \frac{n_0/m}{\omega^2} \Rightarrow \text{Absorption only at } \omega = 0? \]

with interactions between particles:

\[ X = \frac{X_{\text{free}}}{1 - \frac{4\pi e^2}{q^2} X_{\text{free}}} = \frac{q^2 n_0/m}{\omega^2 \left(1 - \frac{4\pi e^2 n_0/m}{\omega^2} \right)} \]

\[ \omega_p^2 = \frac{4\pi e^2 n_0/m}{\omega} \]

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

= 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.

\[
\frac{1}{\bar{E}} = \frac{\omega^2}{\omega^2 - \omega_p^2}
\]

"completely" screened long range interaction for \( \omega \ll \omega_p \)
Excitation spectrum of electrons: $E_k = \frac{\hbar^2 k^2}{2m}$

Fermi golden rule:

$$\chi_{kk'}(\omega, \mathbf{q}) \sim -\frac{\hbar}{\pi} \sum_{f} \left| \langle f | \hat{\eta}_q | 10 \rangle \right|^2 \delta(\omega + E_0 - E_f)$$

Transitions matrix element

ground state $\rightarrow$ excited state

due to density modulation

(momentum transfer $\mathbf{q}$)

$|\mathbf{k} + \mathbf{q}|$ must be

empty $|\mathbf{k} + \mathbf{q}| > |\mathbf{k}|$

$|\mathbf{k}|$ must be occupied

$|\mathbf{k}| < |\mathbf{k}|$
"Excitation map" for which \( q, \omega \) are excitations possible:

- Minimum energy transfer for given \( |q| \):

\[-|q| > 2k_F = 0\]

\[\omega_{\text{min}} = \frac{h^2}{2m} (q - k_F)^2\]

- Maximum energy transfer for given \( |q| \):

\[|q| < 2k_F = 0 \quad \omega = 0\]

\[\omega_{\text{max}} = \frac{h^2}{2m} (q + k_F)^2\]
Some rule for

Excitations: \( \int_0^\infty dw \omega \text{Im} X(w) = \pi \frac{n_0/m}{\omega^2} \)

for \( q \to 0 \) like for classical particles

\( \Rightarrow \) same collective excitation \( \Rightarrow \)

pole in \( X = \frac{X_{free}}{1 - \frac{4\pi \rho}{q^2} X_{free}} \)

for density of good metals \( \Rightarrow \) \( \omega p \sim \text{several eV} \)

\( \Rightarrow \) 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. \( \phi(r) = e^{-r/a} \) \( \rightarrow \) \( \phi(q) = \frac{4\pi}{q^2 + \frac{1}{a^2}} = \frac{4\pi}{q^2} \)

back to mean field formula page 40:

\[ S_n = \chi \, sV_{\text{ext}} \simeq \chi_{\text{free}} \left( sV_{\text{ext}} + sV_{\text{ind}} \right) \]

Now: \( V_{\text{induced}} = \frac{4\pi e^2}{q^2 + \frac{1}{a^2}} \, S_n \)

\[ \chi = \frac{\chi_{\text{free}}}{1 - \frac{4\pi e^2 \chi^2}{(q\lambda)^2 + 1}} \chi_{\text{free}} \]

\[ = \frac{q \cdot \text{no.m}}{c \omega^2 - 4\pi e^2 \text{no.m} \cdot q^2} \]
now there is a pole at

\[ \omega = c_0 |q| \]

\[ c_0 = \sqrt{\frac{4\pi e^2 n^* a}{m^*}} = \omega_{ph} \]

sound-like dispersion

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

\[ \omega = c_0 q \]
Phonons

Phonons: elementary excitations of the lattice distortion. From the atomic 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 media. Transverse waves analogues (see below)

- elastic energy: \( E_{ee} = \frac{\lambda}{2} \int \mathbf{d}^3r \left( \frac{S_n}{n} \right)^2 \)

- relative compression

\[ \frac{S_n}{n} = - \nabla \cdot \mathbf{u}(\mathbf{r}) \]

(eq. from Gauss theorem, or see picture above)

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

\[ \rho_0 \frac{\mathbf{u}}{\partial t^2} = \nabla \left( \nabla \cdot \mathbf{u} \right) \]

\( \text{equation of motion: } \)

\( \text{from } L(\mathbf{u}, \mathbf{u}) = E_{kin} - E_{pot} \)
plane wave solution

\[ u(\vec{x},t) = u_k e^{i \vec{k} \cdot \vec{x}} \]

in equation of motion:

\[ p_0 \ddot{u}_k = -k \vec{k} \cdot (\vec{k} \cdot \vec{u}_k) \]

non-trivial solutions for \( \vec{k} \parallel \vec{u}_k \) (longitudinal), otherwise \( \vec{k} \cdot \vec{u}_k = 0 \)

\[ \ddot{u}_k = -C^2 k^2 \dot{u}_k \quad c = \sqrt{\frac{k}{p_0}} \]

- set of independent harmonic oscillator modes with frequency \( \omega_k = ck \mid k \)
  (linear dispersion \( \rightarrow \) sound)

- each mode corresponds to plane wave

\[ u(\vec{x},t) = u_k^0 e^{i(\vec{k} \cdot \vec{x} - \omega_k t)} \]
**Quantization of Normal Modes**

\[ m \dddot{x} = -m \omega_0^2 x \]

\[ \Rightarrow \text{Harmonic Oscillator} \]

\[ E_n |\nu> = H |\nu> \]

\[ E_n = \hbar \omega_0 (n + \frac{1}{2}) \]

\[ n = 0, 1, 2, \ldots \]

\[ H = \frac{\hbar \omega_0}{2} (a^+ a + \frac{1}{2}) \]

Create/Annihilate Oscillator Quantums

\[ x = \sqrt{\frac{k}{2 \hbar \omega_0}} (a^+ a) \]

**Normal Modes in Solid**

\[ H = \sum_k \hbar \omega_k (b_k^+ b_k + \frac{1}{2}) \]

\[ \mathbf{\bar{U}(\mathbf{\hat{r}})} = \sqrt{\frac{1}{\text{Vol}}} \sum_k \sqrt{\frac{k}{2 \rho_0 \omega_k}} (b_k e^{i \mathbf{k} \mathbf{\hat{r}}} + b_k^+ e^{-i \mathbf{k} \mathbf{\hat{r}}}) \]

\[ (\text{for information, more formal derivation next page}) \]

**Shear Waves**: Analogous, with polarization vector \( \mathbf{\hat{e}}_k \perp \mathbf{k} \)

**Total**

\[ H = \sum_{k,s} \hbar \omega_{ks} (b_{ks}^+ b_{ks} + \frac{1}{2}) \]

S mode.
better representation in normal coordinates
and momenta of these oscillators:

\[ H = \frac{1}{2} \sum_k \left( p_k^2 + \omega_k^2 q_k^2 \right) \]

\[ q_k = \sqrt{\rho_0} \left( q_{k0} + q_{k0}^* \right) \]

\[ p_k = \sqrt{\rho_0} \, i \omega_k \left( q_{k0} - i q_{k0}^* \right) \]

\[ u(\tau) = \frac{1}{V \operatorname{Vol}} \sum_k \left( q_k(\tau) e^{i k r} + q_k(\tau)^* e^{-i k r} \right) \hat{e}_k \]

(check that Hamilton equations
give correct equations of motion)

- Quantum theory of sound-waves:

\[ p_k \rightarrow \hat{p}_k \]

\[ q_k \rightarrow \hat{q}_k \]

\[ [q_{k1}, p_{k2}] = i \hbar \]

\[ H = \sum_k \left( \hat{p}_k^2 + \hat{q}_k^2 \omega_k^2 \right) \]

or:

\[ b_k = \frac{1}{\sqrt{2 \hbar \omega_k}} \left( \omega_k \hat{q}_k + i \hat{p}_k \right) \]

\[ b_k^+ = \frac{1}{\sqrt{2 \hbar \omega_k}} \left( \omega_k \hat{q}_k - i \hat{p}_k \right) \]

\[ [b_{k1}, b_{k2}^+] = \delta_{kk'} \]

\[ H = \sum_k \hbar \omega_k (b_k^+ b_k + \frac{1}{2}) \]
\( \Rightarrow \) independent, bosonic, quasi-particles with linear dispersion \( \omega_k = c k \) : "longitudinal acoustical phonons"

- Do we need a quantum description?

- Many processes in which one can "see" single phonons, like neutron scattering (see below)

- Most prominent manifestation: **specific heat**

**Total energy of classical oscillators**:

\[ U = k_B T \times N_{\text{modes}} \] (equipartition theorem)

\[ C_v = \frac{\partial U}{\partial T} = k_B N_{\text{modes}} \]

\( T \)-independent: valid only for very large \( T \).

**Total energy of quantum phonons**:

\[ U = \sum_k U_k \]

\[ U_k = \frac{\sum_{n=0}^{\infty} e^{-\beta E_n} E_n}{\sum_{k=0}^{\infty} e^{-\beta E_n}} \]

\( \Rightarrow \)

\[ U = \sum_k \frac{n \hbar \omega_k}{k - 1 + e^{\beta \hbar \omega_k}} \]

Bose distribution

\[ \frac{1}{e^{\beta x} - 1} \]
simple estimate:

\[ \sum_{h \leq k} \rightarrow \sum_{|h| < k_D} \quad \text{with} \quad \sum_{|h| < k_D} = N_{\text{mode}} = N_{\text{atoms}} = N \]

\[ \sum_{k} \rightarrow \left( \frac{L}{2\pi} \right)^3 \int d^3k = 0 \quad N = \frac{L^3}{(2\pi)^3} \frac{4\pi}{3} k_D^3 \]

\[ k_D = \left( \frac{N}{L^3} \frac{6\pi^2}{\Gamma} \right)^{1/3} \]

"upper cutoff"

Debye wave vector

\[ U = \left( \frac{L}{2\pi} \right)^3 \int \frac{d^3k}{k < k_D} \frac{\hbar c k}{e^{\beta \hbar c k} - 1} \]

\[ x = \beta \hbar c k \]

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

\[ = 3N \frac{T^4}{(\hbar c k_D)^3} \int_0^{\beta \hbar c k_D} \frac{dx}{e^x - 1} \]

\[ \rightarrow \text{count for } \beta \rightarrow \infty, \]

\[ \text{rule that } U \propto T^4 \]

\[ c_V = \frac{\partial U}{\partial T} = \ldots = 3 \frac{N}{L^3} \left( \frac{T}{\Theta_D} \right)^3 \int dx \frac{x^4 e^x}{e^x - 1} \quad \Theta_D = \hbar c k_D \]

Note! Only one branch (longitudinal)
\[ C_v \propto T^3 \text{ for } T \to 0 \]

- **Remark:** analogy to black-body relation

- independent oscillator modes
  \[ \omega_k = k c \quad c: \text{Light velocity} \]
  - 2 (transverse) modes per \( k \)

Here: no apparent upper cutoff for number of modes \( \Rightarrow \) classical \( C_v, U = \infty \), because all modes occupied.

\[ \Rightarrow \text{Planck: use quantum mechanics} \]
\[ \Rightarrow U \propto T^4 \quad \text{(Stefan-Boltzmann law)} \] etc. ...
how large is the average displacement

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

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

easier: modes for different $k$ are orthogonal

$$= \text{sum contribution to } \overline{\Delta u} \text{ from all modes } k$$

contribution from one mode:

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

because $\nabla u_k \cdot \nabla u_k$

$$= \frac{1}{2 \ \text{Vol} k^2} \ \frac{1}{k^2} \ E_{\text{pot}} = \Theta$$

$$\frac{1}{2} \int d^3r \ (\nabla u)^2$$

$\lambda$: compressibility, na above!
for harmonic oscillator, $\langle E_{\text{pot}} \rangle = \langle E_{\text{kin}} \rangle = \frac{1}{2} \langle E \rangle = \frac{1}{2} \frac{\hbar \omega_k}{e^{\beta \hbar \omega_k} - 1}$

we above

$\# \, \downarrow$$\frac{\hbar c}{\lambda} \frac{1}{k} \frac{1}{e^{\beta \hbar c k} - 1}$

\[ \Delta u = \frac{1}{V \lambda} \sum_k \]

\[ \sim \int \frac{d^d k}{(2\pi)^d} \frac{1}{k} \frac{1}{e^{\beta \hbar c k} - 1} \quad \text{d: spatial dimension} \]

most interesting for low-dimensional systems

\[ d=2 \quad \Delta u \sim \int \frac{d^2 k}{|k|} \frac{1}{e^{\beta \hbar c k} - 1} \]

Because infrared

\[ \sim \int_0^{k_0} \frac{dk}{e^{\beta \hbar c k} - 1} \quad \text{for } k \to 0 \]

\[ \to \infty \]
in $d=2$ dimensions:

sound waves destroy (melt) the solid at arbitrary low temperature (just not at $T=0$) as a special case of general statement no breaking of continuous symmetry in $d \leq 2$ dimensions.
Microscopic description: quantized lattice vibrations

Potential energy:

\[ E_{\text{pot}} (\{ \mathbf{r}_{R,n} \}) \]

depends on all atomic positions

\[ E_{\text{pot}} = \text{ionic electrostatic energy + electronic contribution (binding energy)} \]

Born-Oppenheimer approximation:

electrons follow atoms instantaneously

\[ E_{\text{binding}} = \left\langle \psi_0 \left| \sum_{n} \mathbf{r}_{R,n} \right| H_{\text{electron}} + H_{\text{electrostatic}} \left\{ \mathbf{r}_{R,n} \right\} \psi_0 \right\rangle \]

= electronic ground state energy for fixed ion configurations \( \mathbf{r}_{R,n} \)
harmonic approximation

\[ E_{\text{pot}} = E_{\text{pot}} \left( \{ R_{\mu}^{(0)} \} \right) \]
\[ + \frac{1}{2} \sum_{R \neq R'} R_{\mu}^R R_{\mu}^{R'} \frac{\partial^2 E}{\partial R_{\mu}^R \partial R_{\mu}^{R'}} \bigg|_{R = R^{(0)}} U_{R_{\mu}}^R U_{R_{\mu}}^{R'} + \ldots \]

translatedly invariant:

\[ \frac{\partial^2 E}{\partial R_{\mu}^R \partial R_{\mu}^{R'}} = D_{\mu \mu'} \delta(R-R') \]

\[ E_{\text{kin}} = \frac{1}{2} \sum_{R \mu \mu'} (U_{R_{\mu}}^R)^2 M_{\mu} \]

Eq. of motion:

\[ M_m \ddot{U}_{R_{\mu}}^R = \sum_{R' \mu' \mu''} D_{\mu \mu'} (R-R') U_{R_{\mu'}}^{R' \mu''} \]

Now: FT on lattice \( \rightarrow \) \( k \) in 1. Brillouin zone.

\[ U_{R_{\mu \nu}} = \frac{1}{N} \int d^3 \hat{r} e^{-i \hat{r} \cdot \hat{k}} U_{R_{\mu \nu}} , \quad U_{k \mu \nu} = \sum_{R} U_{R_{\mu \nu}} e^{-i \hat{r} \cdot \hat{k}} \]

\[ \Rightarrow M_m \ddot{U}_{R_{\mu \nu}} = \sum_{\mu' \nu'} D(k)_{\mu \mu', \nu \nu'} U_{R_{\mu' \nu'}} \]

\[ D(k) = \sum_R e^{-i \frac{\hat{k}^2}{D(R)} \hat{k} \cdot \hat{R}} D(R) \]
• coupled equations ⇒ diagonalize $D$:

$$\tilde{D}_{\mu \mu'} = \frac{D_{\mu \mu'} \tilde{w}_{\mu \mu'}}{\sqrt{M_{\mu} M_{\mu'}}} \quad (\tilde{w}_{\mu} = \sqrt{M_{\mu} w})$$

$$\tilde{D} = \tilde{P}_{\mu \mu} \tilde{s}_{\mu} \omega_{\mu} \tilde{P}_{\mu \mu}$$

⇒ 3 $N_o$ independent harmonic oscillator modes for each $k \in 1. BZ$.

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

$$H = \frac{1}{2} \sum_{k s} \left( Q^2_{k s} \omega_{k s}^2 + P^2_{k s} \right)$$

$$U_{\mu \sigma}(R) = \sum_{k s} ...$$
in the crystal, we have $3N_b$ modes, where $N_b$ is the number of atoms per unit cell. For $k \to 0$, these three modes must reduce to the three acoustical phonon modes (sound waves). The others are called optical phonons.

validity of continuous description (sound)

$\mathbf{k} = 0$

zone edge $\mathbf{q}^{(1)} = \frac{\pi}{a}$

$k$ along some direction in the BZ
Example: (might be useful for exercise)

Spring $K'$  $K + K'$

1)...

optical phonon
≈ molecular vibrations of $\ldots \ldots$

in phase

Sound!
Specific heat:

\[ E_{\text{tot}} = \sum_{k} \frac{\hbar \omega_{2k}}{1 + e^\beta \omega_{2k}} \]

depends on details of the phonon band structure.

"Interpolation formula": all bands $\Rightarrow$ 3 acoustic bands with

- $\hbar \omega = c k$
- $c = \text{average } c$, so that low-$T$ limit is fit correctly

\[
\frac{1}{c^3} = \int \frac{d\mathbf{k}}{2\pi^3} \left( \frac{1}{c^2} \right)^3
\]

State counting:

- $\frac{1}{3} \left( \frac{1}{2\pi} \right)^3 \int d^3k = \frac{1}{6\pi^2} k_D^3 = N_{\text{atoms}}$

resulting equation is then the same as for sound wave.

Useful scales:

- $\mathbf{k}_D$: Debye vector
- $\omega_D = \frac{c \hbar k_D}{k_B}$: Debye frequency
- $\Theta_D = \frac{\hbar \omega_D}{k_B}$: Debye temperature

then:

\[ C_V = 9 n k_B \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} x^4 e^x dx \left( e^x - 1 \right)^2 \]
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 \( \frac{2\pi}{Q} \) is close to \( \frac{\pi}{a} \), but the argument is quite similar in this case.
potential energy:

\[ E_{\text{pot}} = E_{\text{electron}} + E_{\text{elastic energy}} \]

\(1\): assume distortion \( u(x) = |u_0| \cos(Qx + \varphi) \)

\(2\): \( u_0 = |u_0| e^{i\varphi} \)

\[ \text{elastic energy} = \frac{1}{2} \int \text{d}x \left( \frac{\text{d}u}{\text{d}x} \right)^2 = |u_0|^2 L \frac{Q^2}{4} \]

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: \( e^{-\text{react instantaneously to position of ions}}, \text{Electronic} \cong \text{ground state energy of electrons in static potential} \ V(x) \) 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

\[
\psi_q = \frac{qU^{III}}{q^2 E_q} \quad \rho_q = n_q n_0 u_q
\]

\[
\Rightarrow V(x) = u_q e^{iQx} + h.c.
\]

\[
= \Delta q e^{iQx} + h.c.
\]

\[
\Delta q = \Delta u \Delta n_0 \quad \Delta = i \frac{\nu}{\psi_0 n_0 Q}
\]
The periodic potential opens a gap at \( k = 0/12 \) (compare discussion of band structure of almost free electrons).

If filling is such that \( k_F < \frac{Q}{2} \), electronic energy is lowered. The maximum gain for \( Q = 2k_F \) becomes

We thus investigate instability at this wave vector, as energy gain can overcome energy cost \( \hbar^2 k^2 \ell^2 \frac{\Delta Q^2}{4} \).
for small $\omega_0$, calculate shift perturbatively, taking into account two states $k, k-Q$ which become degenerate for $k = k_F$ (for $k < 0$, take $k, k+\delta$)

Schrödinger equation $\rightarrow$ diagonalize matrix

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

$$
\Delta = \omega_0 n_0 V_{qQ} Q = \alpha \omega_0
$$

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

$$
E(\omega_0) = 2 \sum_{|k| < k_F} \epsilon_k^- + \frac{L \omega_0^2}{4} (\omega_0)^2
$$

Energy of occupied states

Energy decrease

$\rightarrow$ find minimum $\frac{dE}{d\omega_0} = 0$
with \( \sum_{l \nu < k_F} \frac{1}{2\pi} \int dk \) 

and \( \frac{\Delta \tilde{E}_0}{d|u_0|} = \frac{2|\lambda|^2 |u_0|}{\sqrt{(\tilde{E}_k - \tilde{E}_n)^2 + 4|\Delta_0|^2}} \) 

The integral can be evaluated, which is a bit lengthy, but quite straightforward...

\[
\frac{1}{L} \frac{dE_0}{d|u_0|} = -|u_0| \frac{g_2^2\pi}{Q^2} \text{arsinh}\left(\frac{h^2Q^2}{\pi e|\Delta_0|}\right) + \frac{2Q^2}{2} |u_0|^2
\]

Limit \( |u_0| \to 0 \) \( (\text{arsinh}(x) \approx \ln(2x) \text{ for } x \to \infty) \)

\[
|\Delta_0| = |\lambda u_0| = 4E_F e^{-\frac{1}{N(\tilde{E}_F)g}} \quad g = \frac{4|\lambda|^2}{2Q^2}
\]

\( N(\tilde{E}_F) \): Density of states at the Fermi surface

\( \Rightarrow \) for arbitrary small interaction \( \lambda \), a gap is opened at the Fermi surface
instability occurs for "half-filled" system.

- Real materials are not one-dimensional?

\[ \varepsilon_k = \varepsilon(k_{x_1}, k_{y_1}) = -2t \cos k_x a - 2t' \cos k_y b \]

almost one-d. for \( t' \ll t \)

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

- gap opened at whole Fermi surface

\[ \varepsilon = \text{const} \]

- Fermi surface is nested by nesting vector \( \mathbf{q} \)
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, $E \Rightarrow$ free energy

$F[U_0] = \alpha |U_0|^2 + F_{	ext{elec}}[U_0]$ 

$F_{	ext{elec}} = E - TS$

$E = \frac{1}{2\pi} \int_{-Q/2}^{Q/2} dk \sum_{\sigma = \pm} \frac{E_{k\sigma}^+}{\epsilon_{\beta E_{k\sigma}^+} + 1}$

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

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

\[ \Delta(T) \]

$F[U_0]$

$T > T_c$

$T < T_c$

$\Delta \text{ (minimum) } U_0(T)$
Ginzburg-Landau theory.

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

The order parameter

The order parameter $O$ is a macroscopic quantity which is non-zero below the transition temperature ($T<T_c$) and zero for $T>T_c$.

Examples:

- Ferromagnet: $O \propto M$ (magnetization density) ($\vec{M}$ vector in $\mathbb{R}^3$)

Fe, $T > 1040K$

Paramagnet

T < 1040K
Peierls transition

\[ T > T_c \]

\[ T < T_c \]

\[ \Delta = \text{Fourier component of density} \]

**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!)

  ![Diagram](image)

  - elastic red
  - $T > T_c$
  - $T_{symmetric}$
  - under rotation around this axis
  - state not symmetric

- general phenomenological description of second order phase transitions in terms of order parameter: Landau ~ 1930

- Ginzburg & Landau (1950): observed effects in SC (Heissner effect) described if one associates the SC phase with an order parameter which is a complex number $\Psi(\vec{r}) \sim$ macroscopic, classical field
In the Landau theory, the order parameter $O$ is determined by minimization of a free energy function $F[O(x), T]$

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

1. $O = 0$ must be minimum of $F$ in the high symmetry phase ($T > T_c$)

2. $F[O]$ must be invariant under all symmetry operations of high-symmetry phase

3. For $T > T_c$, $O$ vanishes continuously (2nd order transition) and we can expand $F[O]$ in powers of $O$.

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

charge density wave formation in homogeneous system

\[ T(X,T) = T_n(T) + a(T)X^2 + \frac{b(T)}{2}X^4 + \ldots \]

normal phase

- scalar order parameter \( X \)
- inversion symmetry \( X \rightarrow -X \)

expansion around \( X = 0 \), no odd terms because of inversion symmetry

\( X_{\min} = \pm \sqrt{-\frac{a}{b}} \)

\( a > 0, b > 0 \)

\( T \)

\( X_{\min} = 0 \)

\( X \rightarrow \) phase transition \( \Rightarrow a = 0 \Rightarrow a(T_c) = 0 \)

\( \Rightarrow \) expand \( a(T) \approx \frac{a}{X^2} (T-T_c) \)

\[ X(T) = \frac{\sqrt{\frac{a}{b}}} {T-T_c} \sqrt{\frac{T_c}{T_c-T}} \]
More advanced example:

Vector order parameter (e.g., polarization)
in cubic environment.

\[ \mathbf{P} = \sum \mathbf{P}_i \]

Order parameter = macroscopic polarization \( \mathbf{P} \)

[Microscopically, \( \mathbf{P} = \sum \mathbf{P}_i \) is average over all \( \mathbf{P}_i \).]

\( F[\mathbf{P}] \) must be invariant under all point group operations of cubic symmetry.

Most general form of Taylor expansion \( F[\mathbf{P}] \):

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

This term would not be possible in isotropic medium; not invariant under all rotations.
Additional phenomenological parameters $\xi$

( crysalline anisotropy )

Depending on $\beta$ or $\xi$, the transition can occur only in two possible ways:

1) $\beta$ along crystal axis

2) $\beta$ 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 $F(\beta)$, 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 \(c\)

\(M \parallel\) body diagonal

\[ f(M_x, M_y, a, b, c) \]

\(M \parallel\) \(x\) or \(y\) axis

\[ f(M_x, M_y, 0.4, 0.2) \]

Note: No breaking of continuous symmetry: no Goldstone modes
Spatially dependent order parameter $O(x)$  
(e.g. domains)

$\mathcal{F}[O] = \int d^3r \left\{ a |O|^2 + \frac{1}{2} |O|^4 + \frac{\eta_0^2}{2} |\nabla O|^2 \right\}$

- Most simple symmetry
- Allowed non-local term
- $\Rightarrow$ 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:

$|O| = \sqrt{\frac{a}{b}}$

minimization of $\mathcal{F}$ ($\equiv \mathcal{F}[O + \delta O]$) term linear in $\delta O$ vanish

$\Rightarrow$ differential equation

$\frac{\partial^2}{\partial x^2} O = a O + b \frac{|O|^2}{O}$
asymptotic behavior:

\[ G(x) = \frac{G_0}{\sqrt{1 - \frac{x^2}{\delta^2}}} e^{-\frac{x}{\sqrt{\delta^2 - x^2}}} \]

\[ g(T) = \frac{g_0}{\sqrt{1 - 2a(T)}} \sim \frac{1}{\sqrt{T_c - T}} \]

\[ a = a(T - T_c) \]

order parameter changes only on some healing of correlation length, which diverges at the transition.

Note: A\( L \) 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 correlation functions (critical exponents like \( (T_c - T)^\nu \) 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:**

\[ \nabla \cdot \mathbf{B} = 0 \]
\[ \nabla \times \mathbf{H} = \frac{4\pi}{c} \mathbf{J}_{\text{ext}} \]
\[ \mathbf{B} = \mathbf{H} + 4\pi \mathbf{M} \]

\( \frac{\partial \mathbf{H}}{\partial t} \): material relation,
\( \frac{\partial \mathbf{H}}{\partial H} > 0 \): paramagnet,
\( \frac{\partial \mathbf{H}}{\partial H} < 0 \): diamagnet.
• **diamagnetic materials expel magnetic fields >> Levitation**

**Magnetic order:**

**Ferromagnets:** permanent magnetization
“spontaneous alignment of microscopic magnetic moments”

**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. Ti becomes ferromagnetic for $T < T_c \approx 1033K$, Co $T_c \approx 1400K$, Ni $\approx 630K$ ...). 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

$$Z = \int d^3p d^3\pi e^{-\beta \mathcal{H}(p,\pi)}$$

$$= \sum_{\{\pi_i\}} \frac{\left(\vec{p}_i - \vec{e}_i \vec{A}(\vec{r}_i)\right)^2}{2m} + V(\vec{r}_1,...,\vec{r}_N)$$

shift of variables $p \rightarrow \vec{p} = \vec{e} \vec{A}(\vec{r}_i) = \vec{p}$

differentials $d^3p = d^3\vec{p}$

$\Rightarrow Z$ does not depend on $\vec{B}$. 
magnetic moment of isolated atoms

classical picture

\[ E = - \vec{\mu} \cdot \vec{B} \]
\[ \vec{\mu} = \frac{1}{2} \int \rho(\mathbf{r}) \mathbf{r} \times \mathbf{j} \]

\( \vec{\mu} \): 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 \( H = -\mu_B g \frac{\hbar}{2} \cdot \vec{B} \)

\[ \vec{\mu} = 2\mu_B \frac{3}{2} h \]
\[ \mu_B = \frac{e h}{2m_c} \approx 10^{-4} \text{ ev/T} \]
The value of $\mu_B$ 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 $\vec{J}$

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

$\gamma$: gyromagnetic ratio

→ Einstein de Haas effect:  
convenience of spin angular momentum 
(magnetization) to lattice angular momentum.
\[ \mu = - \frac{\partial E_0}{\partial B} \quad 0: \text{ground state} \]

\[ \Delta E_0 = - \vec{B} \cdot \vec{\mu} + O(B^2) \]

\[ \text{induced moments, i.e. particular diamagnetic response} \]

nonzero if ground state has nonzero angular momentum.

\[ \vec{\mu} = \mu_B \left( \vec{L} + \vec{S} \right) \]

contribution from orbital/spin angular momentum

\[ \vec{L} + \vec{S} \]

\[ \gamma J \]

\[ \text{resticked to as manifold} \]

\[ \text{nontrivial to get, see e.g. Ackrath, Hermin} \]

What determines \( \vec{L}, \vec{S}, \vec{J} \) in ground state?

\[ \text{e.g. 4 electrons in 3d orbitals of magnetic ion} \rightarrow \text{many possible states} \]

\[ \frac{e^4}{10!} \]
Lifting of degeneracy:
- Coulomb interaction + Pauli principle
  (\(=\) intra-atomic exchange interaction)
- spin-orbit coupling

2D Hund's rules

for weak SO coupling we have

1) maximum \( \hat{S} \)
2) max \( \hat{L} \) for given \( \hat{S} \)

\( \hat{S} \) \( \hat{L} \) \( \hat{I} \) \( \hat{J} \)

ferromagnetic
intra atomic exchange, see below

paramagnetic response of isolated atoms

ions align in external field:

\[ \uparrow \vec{B} \]
for simplicity, consider \( J = \frac{1}{2} \) \( \vec{\mu} = \vec{\gamma} J \):

average magnetization:

\[
M = n \langle \vec{\mu} \rangle \quad n: \text{ density}
\]

\[
\langle \vec{\mu} \rangle = \frac{\sum_{\mu = -J}^{J} \mu B \chi_{\mu} e^{\beta \mu B \chi_{\mu} B}}{\sum_{\mu = -J}^{J} e^{\beta \mu B \chi_{\mu} B}}
\]

\[
= \mu B \frac{1}{J} \tanh \left( \frac{\beta \mu B \chi_{\mu} B}{2} \right)
\]

for \( X \rightarrow 1 \), i.e. either \( T \rightarrow 0 \) or \( B \) large: saturation

\[
\langle \mu \rangle \sim \mu B \delta^{1/2}
\]

linear response

\[
\langle \mu \rangle \sim \frac{\mu B \delta^{2}}{4k_{B}T} B
\]
susceptibility of isolated magnetic moments

\[ \chi = \frac{\partial M}{\partial B} = \frac{\mu_B^2 g^2}{4} \frac{1}{k_B T} \] \hspace{1cm} \text{Curie law}

\[ \chi^{-1} \]

\[ \chi \propto \frac{1}{T} \quad \text{indication of isolated moments} \]

Behavior of interacting moments?

interaction

\[ H = -J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \]

\( \text{physical origin: } \)
\[ \text{see below.} \]

exchange interaction, \( |J_1| > 0 \)

favors parallel alignment of spins
mean field description of response:
\[ \chi = \frac{\partial M}{\partial B} \quad M = \sum_j \langle S_j \rangle \quad \text{average moment} \]

\[ gH \sim \chi_{\text{free}} (B + \text{Induced}) \]

mean field response of free moments \[ \sim \frac{1}{4} \]

\[ \text{Induced} = \sum_i \text{J}_{ij} \langle S_j \rangle = \frac{J_0}{\sum \langle S_j \rangle} \]
(at ion \# i)

\[
\begin{bmatrix}
\chi = \frac{\chi_{\text{free}}}{1 - J_0 \chi_{\text{free}}} \sim \frac{1}{T - T_c}
\end{bmatrix}
\]

where \( T_c \sim J_0 \)

instability of the system for \( T < T_c \): ordering of moments for infinitesimally small field! Ferromagnetic transition
Ferromagnetic state, long-range order.
Exchange interaction

**General principle:**

Pauli principle \( \Rightarrow \) \( n \)-electron wave function symmetric under exchange of both spin (\( \tau \)) and position (\( \bar{\tau} \)).

Symmetric under exchange of \( \tau_i \) \( \Rightarrow \) anti-symmetric under exchange of \( \bar{\tau}_i \)

Anti-symmetric under exchange of \( \tau_i \) \( \Rightarrow \) symmetric under exchange of \( \bar{\tau}_i \)

Effective interaction between spins \( \hat{\xi} \)

Coulomb energy depends on this form of the wave function.

Exchange interaction is "not a fundamental force"

\( \Rightarrow \) 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

\[
H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + V(r_1) + V(r_2) + \frac{e^2}{r_{12}}
\]

Basis:
- Wannier orbitals \( \psi^{(1)} \), \( \psi^{(2)} \) (localized at nuclear positions \( R_1, R_2 \))
- Highly bound electrons, \( \psi^{(i)} \approx \) atomic orbitals, take into account only one orbital per site (others are at "high energy").
- Neglect hopping \( T = \sum_{i} \psi^{(i)*} \left( \frac{p_i^2}{2m} + V(r_i) \right) \psi^{(i)} \)
  \( \approx \) leads to different type of exchange, see below

goal: find ground state

\[
\Phi(\vec{r}_1, \vec{r}_2, \sigma_1, \sigma_2) = \psi(\vec{r}_1, \vec{r}_2) \chi(\sigma_1, \sigma_2)
\]

excluding ionized states (both electrons in \( \psi^{(1)} \) or \( \psi^{(2)} \))
possible combinations

\[ \chi(\sigma_1, \sigma_2) = \chi^\pm(\sigma_1, \sigma_2) = \frac{1}{\sqrt{2}} \left( \sigma_{\uparrow} \sigma_{\downarrow} - \sigma_{\downarrow} \sigma_{\uparrow} \right) \]

\[ \equiv \text{singlet } \quad S_{\text{tot}} = 0 \quad \text{(i.e. } (S_1^2 + S_2^2) = 0) \]

\[ \text{antisymmetric under } \quad 1 \leftrightarrow 2 \quad \Rightarrow \]

orbital part \[ = \Phi^\pm(\gamma_1, \gamma_2) \propto \left( \phi^{(1)}(\gamma_1) \phi^{(2)}(\gamma_2) + \phi^{(2)}(\gamma_1) \phi^{(1)}(\gamma_2) \right) \]

\[ \chi(\sigma_1, \sigma_2) = \begin{cases} 
\chi^{(t, +1)}(\sigma_1, \sigma_2) = \sigma_{\uparrow} \uparrow \downarrow \\
\chi^{(t, 0)}(\sigma_1, \sigma_2) = \frac{1}{\sqrt{2}} \left( \sigma_{\uparrow} \uparrow \sigma_{\downarrow} \downarrow + \sigma_{\downarrow} \downarrow \sigma_{\uparrow} \uparrow \right) \\
\chi^{(t, -1)}(\sigma_1, \sigma_2) = \sigma_{\downarrow} \downarrow \sigma_{\uparrow} \uparrow 
\end{cases} \]

\[ \equiv \text{triplet } \quad S_{\text{tot}} = 1 \quad , \quad (S_1^2 + S_2^2) = S_{\text{tot}} (S_{\text{tot}} + 1) = 2 \]

\[ \text{symmetric under } \quad 1 \leftrightarrow 2 \quad \Rightarrow \]

orbital part \[ = \Phi^-(\gamma_1, \gamma_2) \propto \left( \phi^{(1)}(\gamma_1) \phi^{(2)}(\gamma_2) - \phi^{(2)}(\gamma_1) \phi^{(1)}(\gamma_2) \right) \]
Energy expectation value: \( (+ \equiv \text{singlet} / \text{triplet}) \)

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

\(= \int \prod_{i=1}^{n} d^3 \vec{r}_i \, \varphi^{\pm}(\vec{r}_1, \vec{r}_2) \, H(\vec{r}_1, \vec{r}_2) \, \varphi^{\pm}(\vec{r}_1, \vec{r}_2) \)

\(= E_1 + E_2 + C_1 \pm C_2 \) (neglect hopping!)

\[
E^{(\pm)}_{1,2} = \int \prod_{i=1}^{n} d^3 \vec{r}_i \, \varphi^{(\pm)}(\vec{r}_i) (\vec{p}_i^2 + V(\vec{r}_i)) \, \varphi^{(\pm)}(\vec{r}_i)
\]

\[
C_1 = \int \prod_{i=1}^{n} d^3 \vec{r}_i \, \frac{e^2}{\pi \Delta^2} \frac{|\varphi^{(1)}(\vec{r}_1)|^2 |\varphi^{(2)}(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|} \]

\[
C_2 = \int \prod_{i=1}^{n} d^3 \vec{r}_i \, \frac{e^2}{\pi \Delta^2} \frac{\varphi^{(1)}(\vec{r}_1) \varphi^{(2)}(\vec{r}_2) \varphi^{(1)}(\vec{r}_1) \varphi^{(2)}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}
\]

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

\[
H_{\text{eff}} = -J \vec{S}_1 \cdot \vec{S}_2 \quad J = \frac{2C_2}{\hbar^2}
\]
proof: Heff acts only on spin

\[ \langle \Phi^+ | H_{\text{eff}} | \Phi^+ \rangle = \langle \chi^{\frac{1}{2}} | H_{\text{eff}} | \chi^{\frac{1}{2}} \rangle \]

\[ = -J \left( \langle \chi^{\frac{1}{2}} | \left[ \left( S_1 + S_2 \right)^2 - S_1^2 - S_2^2 \right]^{\frac{1}{2}} | \chi^{\frac{1}{2}} \rangle \right) \]

\[ \frac{\hbar^2}{8} S_{\text{tot}} \left( S_{\text{tot}} + 1 \right) \]

\[ \frac{\hbar^2 J^3}{4}, \text{ for spin-}\frac{1}{2}, \quad S = \frac{1}{2} (\frac{3}{2} + 1) \]

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

\[ E^+ - E^- = \frac{1}{2} \left( E^{(1)} - E^{(2)} \right) = \hbar^2 J \]

Notes:
- "direct exchange": directly related to Coulomb matrix element
- depends on overlap of \( \psi^{(1)} \) and \( \psi^{(2)} \) =
- decays exponentially with distance
- Let \( \psi^{(1)} \), \( \psi^{(2)} \) be atomic orbitals of some atom and calculation can be seen as model calculation for intra-atomic exchange
- \( \equiv 1.5 \)th Hund's rule (maximal \( S \) favored)
• in solids: not often other exchange mechanisms relevant (see below)
• argument for localized electrons ⇒ applies to insulators.

Superexchange (Kinetic Exchange)

Many magnetic oxides (\(\text{MnO, NiO}...\)) have well defined magnetic moments ("localized electrons") but their distance is too large for direct exchange. ⇒ Exchange mechanism involving hopping of electrons between ions, or between oxygen and ions. ⇒ 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)
\[ H = -t \sum_{\sigma} (c_{i\sigma}^+ c_{2\sigma} + h.c.) + U \sum_{i \neq j} n_{i\uparrow} n_{i\downarrow} \]

hopping

intra-orbital
Coulomb energy

occupation number basis: (sign!)

\[ |n_{i\uparrow} n_{i\downarrow} n_{j\uparrow} n_{j\downarrow}\rangle = (c_{i\uparrow}^\dagger)^{n_{i\uparrow}} (c_{i\downarrow}^\dagger)^{n_{i\downarrow}} (c_{j\uparrow}^\dagger)^{n_{j\uparrow}} (c_{j\downarrow}^\dagger)^{n_{j\downarrow}} |0\rangle \]

\[ \Rightarrow \text{6 states for two electrons:} \]

\[ |10 10\rangle \equiv |\uparrow, \uparrow\rangle \]
\[ |10 10\rangle \equiv |\uparrow, \downarrow\rangle \]
\[ |10 01\rangle \equiv |\uparrow, \downarrow\rangle \]
\[ |10 10\rangle \equiv |\downarrow, \uparrow\rangle \]

\[ |11 00\rangle \equiv |\uparrow, \downarrow\rangle \]
\[ |11 00\rangle \equiv |\downarrow, \uparrow\rangle \]
\[ |00 11\rangle \equiv |10, \downarrow\rangle \]

\[ \text{low energy states} \]

\[ \text{high-energy states} \quad (E \approx U) \]
\[
H = \begin{pmatrix}
2\varepsilon & 0 & 0 & 0 & 0 & 0 \\
0 & 2\varepsilon & 0 & 0 & 0 & 0 \\
0 & 0 & 2\varepsilon & -t & -t & 0 \\
0 & 0 & 0 & 2\varepsilon & t & t \\
0 & 0 & -t & t & 2\varepsilon + U & 0 \\
0 & 0 & -t & t & 0 & 2\varepsilon + U \\
\end{pmatrix}
\]

analytic diagonalization possible, noting that

- \((1\uparrow, \downarrow\uparrow + 1\downarrow, 1\uparrow\downarrow) \frac{1}{\sqrt{2}} \equiv (0, 0, 1, 1, 0, 0)^+ \sqrt{12}
\]

\(1\uparrow, \downarrow\uparrow\) \text{ are eigenstates with energy } E_t = 2\varepsilon

- \((1\uparrow, 0\downarrow - 1\downarrow, 0\uparrow\downarrow) \frac{1}{\sqrt{2}} \) eigenstate energy \(2\varepsilon + U\)

remaining 2x2 matrix:

Ground state \(E_s = 2\varepsilon + \frac{U}{2} - \sqrt{\left(\frac{U}{2}\right)^2 + 4t^2}\) \text{ singlet}
result important for \( t < U \).

\[ \begin{align*}
12,0 \rightarrow 10,12 \rightarrow U \\
(12,0) + (10,12) / \sqrt{2} \\
12,0 \rightarrow 12,0 \rightarrow (12,0) - (10,12) / \sqrt{2}
\end{align*} \]

states, for \( (t=0) \)

\[ \begin{align*}
\text{high energy states} \\
X \rightarrow 3
\end{align*} \]

\[ J_{\text{eff}} = \mathbf{J} \mathbf{S}_1 \cdot \mathbf{S}_2 \]

\[ J = \frac{4 t^2}{2U} = E_t - E_s \text{ else above} \]

- Singlet lowered due to virtual hopping processes (kinetic energy). Virtual hopping excluded for triplet due to Pauli principle.
Spin-orbital exchange (Kugel-Khomskii model KCuF3)

Cu 3d orbitals
9 electrons

eg orbitals

t2g orbitals

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

Orbital pseudospin:
\[ \tau_z = \frac{1}{2} \quad \tau_z = -\frac{1}{2} \quad \tau_z = \frac{1}{2} \quad \tau_z = -\frac{1}{2} \]

Spin:
\[ s_z = \frac{1}{2} \quad s_z = \frac{1}{2} \quad s_z = -\frac{1}{2} \quad s_z = -\frac{1}{2} \]

Interaction: intra-orbital Coulomb, inter-orbital Coulomb, Hunds-Coupling
Orbital-orbital exchange, and mixed orbital-spin exchange
Super exchange via oxygen ion

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

Simple cluster model:

\[ \text{Mn}^{2+} \quad \text{O}^{2-} \quad \text{Mn}^{2+} \]

\[ 3d \]

half-filled shell \( (↑↑↑↑↑↑) \) \( S = \frac{5}{2} \) due to Hund's rule

\( \rightarrow \) an electron which hops from \( \text{O}^{2-} \) to \( \text{Mn}^{2+} \) must be anti-parallel to spin at \( \text{Mn}^{2+} \)

- possible states for anti-parallel alignment of Mn spins:

\[ |1\rangle = \uparrow \downarrow \]
\[ |2\rangle = \uparrow \uparrow \downarrow \]
\[ |3\rangle = \uparrow \downarrow \downarrow \]
\[ |4\rangle = \uparrow \uparrow \uparrow \downarrow \]

\[ \langle \text{H} | H | \text{H} \rangle = \begin{pmatrix} 0 & t & t & t & 0 \\ t & U & 0 & t \\ t & 0 & t & 0 \\ t & t & 0 & 0 \end{pmatrix} \]

Large spin, like classical variable
for parallel alignment:

\[ k_j = \uparrow \circ \downarrow \]
\[ \langle 11 H 1 j \rangle = \begin{pmatrix} 0 & t & t \\ t & u & 0 \\ t & 0 & u \end{pmatrix} \]

Again, "singlet" (a.k.a. parallel Mn\(^{3+}\) spins) lower in energy, because \(O^2^-\) electrons more delocalized, i.e.: lower kinetic energy.
(Difference in first order perturbation theory)

Double exchange

e.g. mixed valence Mn\(^{3+}\)/Mn\(^{4+}\)

3d  \equiv  \text{Crystal eg} \xrightarrow{\text{hex}} \text{eg of Mn}^{4+} \text{Mn}^{3+} \leftarrow \text{parallel spins due to Hund's rule}

If Mn-spins are parallel \(\Rightarrow\) extra eg electron can move freely (without violating Hund's rule) \(\Rightarrow\) lower kinetic energy \(\Rightarrow\) ferromagnetic exchange
Itinerant ferromagnetism (e.g. Fe): only brief summary...

Response of band electrons (paramagnetism)

Density of state $N(s)$

$B = 0$ shift of chemical potential of $\uparrow, \downarrow$ electrons due to Zeeman energy $= 0$

$$X = \frac{\partial \mu}{\partial B} \sim N(\varepsilon_F)$$

Local Coulomb interaction (density-density)

$$U n_\uparrow (\vec{r}) n_\downarrow (\vec{r}) = \frac{U}{4} \left[ n(\varepsilon) n(\varepsilon) - \frac{4}{2} \left< S_{\vec{r}}^x \right|^2 \right]$$

Because of Pauli principle only electrons with opposite spin interact locally

$$\frac{n_\uparrow - n_\downarrow}{2} = \frac{1}{2}$$

Local magnetization
Local interaction leads to induced magnetic field \( \propto U(H) \) in mean field description.

\[
\chi = \frac{\chi_{\text{free}}}{1 - UN(C_F)}
\]

Instability \( \Rightarrow \) magnetic ordering for

\( UN(C_F) = 1 \)

Stoner criterion

\[ \uparrow \]

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

\[ N(C_F) \]

Large DCW \( \Leftrightarrow \)

Ferromagnetic instability