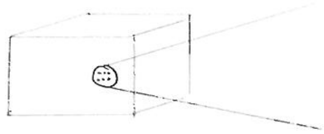
Solid State Theory

0. Introduction

the topic of this lecture:

> theoretical concepts for the description of solids

- what is a solid ?



a piece of solid material ... made out of many (identical) constituents in a regular arrangement

- physical propeties / phenomena observed in solid state materials
  - electrical conductivity → metallic / insulating behaviour
  - specific heat
  - magnetic propeties → ferromagnets, antiferromagnets → phase transitions

  ⋮

  and more exotic phenomena like
  - superconductivity
  - quantum Hall effect

- what is solid state theory based on ?
  - quantum mechanics of many-particle systems

    → why quantum mechanics ? start from the microscopic structure of solids atoms in a unit cell, electrons, ...

    → how to treat the large number of constituents ?

    periodicity simplifies the calculation

    the solid can be viewed as a macroscopic quantum object
  - statistical physics → calculation of thermodynamic propeties

<u>note that</u>: the Hamiltonian is known already

→ find strategie for solving the Hamiltonian

- the fundamental problem:

  → interactions between the constituents

in the lecture: · start with the non-interacting case

· then introduce interactions between electrons, electron and phonons

the interaction via the Coulomb potential is not at all weak!

1. Structure and periodicity

the focus is on crystalline solids (crystals)

$\rightarrow$ regular arrangement of identical building blocks

start with the definition of a point lattice

$\rightarrow$ the points of a Bravais lattice (in dimension $d=3$) are given by

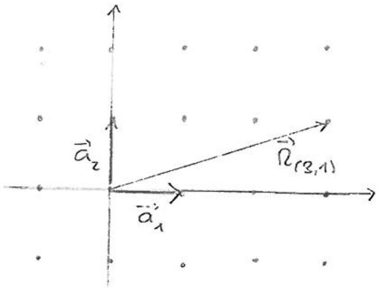
$$\boxed{\vec{R}_{(n_1,n_2,n_3)} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3} \qquad (*)$$

with $n_1, n_2, n_3 \in \mathbb{Z}$

and three non-coplanar vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$ ← the primitive vectors

↳ this means that $\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) \neq 0$

example ($d=2$)



$$\vec{a}_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \vec{a}_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

translational invariance

translation vector $\vec{t}_{(m_1,m_2,m_3)} = m_1\vec{a}_1 + m_2\vec{a}_2 + m_3\vec{a}_3 \qquad m_i \in \mathbb{Z}$

the Bravais lattice – the set of points defined by $(*)$ – is invariant under translation by the vector $\vec{t}$ for any (m_1, m_2, m_3), this means:

$\vec{R}_{(n_1,n_2,n_3)} + \vec{t}_{(m_1,m_2,m_3)}$ is again a point of the same Bravais lattice

$$= (n_1+m_1)\vec{a}_1 + (n_2+m_2)\vec{a}_2 + (n_3+m_3)\vec{a}_3$$

$$= \vec{R}_{(\bar{n}_1,\bar{n}_2,\bar{n}_3)} \quad \text{with} \quad \bar{n}_i = n_i + m_i \in \mathbb{Z}$$

translational invariance only holds for the infinite lattice defined by (*)

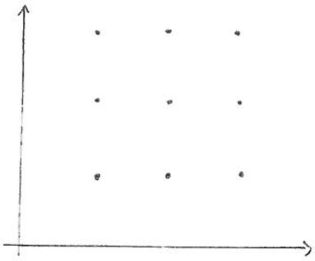
now consider → *finite lattices*

again: $\vec{R}_{(n_1,n_2,n_3)} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$

but with the n_i restricted to a compact region, for example $a_i \le n_i \le b_i$

with $\vec{a}_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $\vec{a}_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

and $n_1 \in \{1,2,3\}$, $n_2 \in \{1,2,3\}$, we have



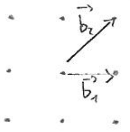
the choice of primitive vectors

example: given a two-dimensional Bravais lattice L_a defined by

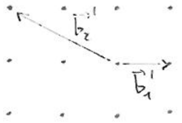
$$L_a = \{ \vec{R}_{(n_1,n_2)} \mid n_1 \in \mathbb{Z}, n_2 \in \mathbb{Z} \}$$

with $\vec{R}_{(n_1,n_2)} = n_1 \vec{a}_1 + n_2 \vec{a}_2$, $\vec{a}_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $\vec{a}_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

the following vectors are primitive vectors of the *same* Bravais lattice

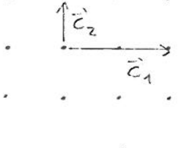


$\vec{b}_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $\vec{b}_2 = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$;



$\vec{b}_1' = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $\vec{b}_2' = \begin{pmatrix} -2 \\ 1 \end{pmatrix}$

while the following vectors are *not* primitive vectors



$\vec{c}_1 = \begin{pmatrix} 2 \\ 0 \end{pmatrix}$, $\vec{c}_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

what distinguishes $\{\vec{b}_1, \vec{b}_2\}$ from $\{\vec{c}_1, \vec{c}_2\}$?

→ define the Bravais lattice $L_b = \{ \vec{R}'_{(\bar{n}_1,\bar{n}_2)} \mid \bar{n}_1 \in \mathbb{Z}, \bar{n}_2 \in \mathbb{Z} \}$

with $\vec{R}'_{(\bar{n}_1,\bar{n}_2)} = \bar{n}_1 \vec{b}_1 + \bar{n}_2 \vec{b}_2$

we have to show that $L_b = L_a$, this means

i, all the elements of L_b are also elements of L_a

$$\rightarrow \quad \vec{R}'_{(\bar{n}_1, \bar{n}_2)} = \bar{n}_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \bar{n}_2 \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \begin{pmatrix} \bar{n}_1 + \bar{n}_2 \\ \bar{n}_2 \end{pmatrix} = \vec{R}_{(\bar{n}_1 + \bar{n}_2, \bar{n}_2)}$$

ok because $\bar{n}_1 + \bar{n}_2 \in \mathbb{Z}$ and $\bar{n}_2 \in \mathbb{Z}$

ii, for each (n_1, n_2), there is a set of integers $(\bar{n}_1, \bar{n}_2)$ such that

$$\bar{n}_1 \vec{b}_1 + \bar{n}_2 \vec{b}_2 = \begin{pmatrix} n_1 \\ n_2 \end{pmatrix} \qquad (*)$$

with $\vec{b}_1 = \begin{pmatrix} b_{11} \\ b_{21} \end{pmatrix}$, $\vec{b}_2 = \begin{pmatrix} b_{12} \\ b_{22} \end{pmatrix}$ and the matrix $B = \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix}$,

eq. $(*)$ can be written as: $\quad B \begin{pmatrix} \bar{n}_1 \\ \bar{n}_2 \end{pmatrix} = \begin{pmatrix} n_1 \\ n_2 \end{pmatrix}$

$$\Rightarrow \quad \begin{pmatrix} \bar{n}_1 \\ \bar{n}_2 \end{pmatrix} = B^{-1} \begin{pmatrix} n_1 \\ n_2 \end{pmatrix} \qquad \text{with} \qquad B^{-1} = \frac{1}{\det(B)} \begin{pmatrix} b_{22} & -b_{12} \\ -b_{21} & b_{11} \end{pmatrix}$$

we have $b_{ij} \in \mathbb{Z}$, therefore $\det(B) \in \mathbb{Z}$,

but to get integer $\bar{n}_1, \bar{n}_2$, we must have $\boxed{\det(B) = 1}$

→ in the above example:

- $B = \begin{pmatrix} 1 & 1 \\ 0 & 1 \end{pmatrix} \Rightarrow \det(B) = 1$ ok

- $C = \begin{pmatrix} 2 & 0 \\ 0 & 1 \end{pmatrix} \Rightarrow \det(C) = 2$ → $\vec{c}_1, \vec{c}_2$ are not primitive vectors

geometrical interpretation of det (B)

in $d = 2$ $\qquad |\det(B)| =$ area spanned by $\vec{b}_1$ and $\vec{b}_2$

$$= |\vec{b}_1 \times \vec{b}_2| = \left| \begin{pmatrix} b_{11} \\ b_{21} \\ 0 \end{pmatrix} \times \begin{pmatrix} b_{12} \\ b_{22} \\ 0 \end{pmatrix} \right| = |\det(B)|$$

in $d=3$: $|\det B| =$ volume spanned by the three vectors $\vec{b}_1, \vec{b}_2, \vec{b}_3$

$$= |\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)|$$

= volume of the unit cell

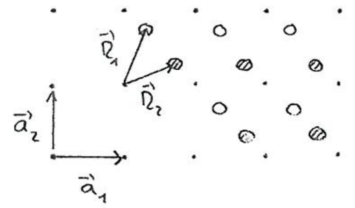
Bravais lattice and basis

consider a Bravais lattice defined by the points $\vec{R}_{\vec{n}} = \vec{R}_{(n_1,n_2,n_3)}$ and add a basis to each unit cell (in particular atoms) located at $\vec{R}_\mu$, $\mu = 1, \dots, M$ (with respect to the origin of the unit cell), so we have for the positions of the atoms:

$$\boxed{\vec{R}_{\vec{n},\mu} = \vec{R}_{\vec{n}} + \vec{R}_\mu}$$

examples:

a)



· : points of the Bravais lattice

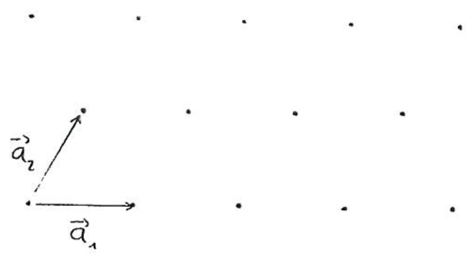
○ : position of atom 1

▨ : — " — 2

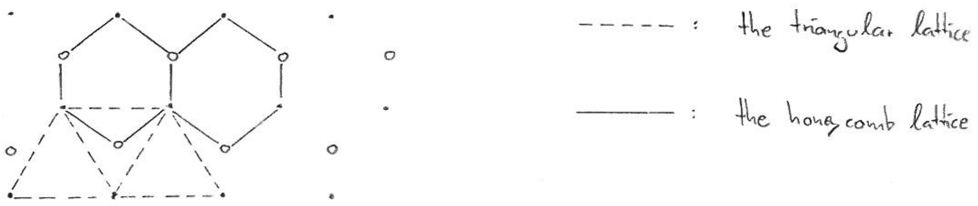
b) the honeycomb lattice

- two-dimensional with $\vec{a}_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $\vec{a}_2 = \frac{1}{2}\begin{pmatrix} 1 \\ \sqrt{3} \end{pmatrix} = \begin{pmatrix} \cos \pi/3 \\ \sin \pi/3 \end{pmatrix}$

  → this defines a triangular lattice



- basis : $\vec{R}_1 = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$, $\vec{R}_2 = \begin{pmatrix} 0 \\ 1/\sqrt{3} \end{pmatrix}$



the honeycomb lattice is not a Bravais lattice !

$L = L_1 \cup L_2$ with $L_\mu = \{ \vec{R}_{\vec{n}} + \vec{R}_\mu \mid n_i \in \mathbb{Z} \}$

↳ the set of points which defines the honeycomb lattice

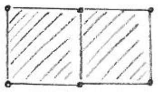
$$\vec{R}_{\vec{n}} = n_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix} + n_2 \frac{1}{2} \begin{pmatrix} 1 \\ \sqrt{3} \end{pmatrix}$$

L cannot be written in the form $L = \{ n_1 \vec{b}_1 + n_2 \vec{b}_2 \mid n_i \in \mathbb{Z} \}$

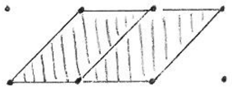
tiling

→ complete filling of the space (complete tiling of the plane) with identical building blocks → the (primitive) unit cell

example : 2d square lattice

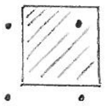


or



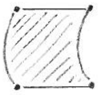
- a common choice : unit cell = the area (the volume) spanned by the primitive vectors $\vec{a}_1, \vec{a}_2$ ($\vec{a}_1, \vec{a}_2, \vec{a}_3$)

note : - the freedom of choice of the origin



- each unit cell contains exactly one lattice point

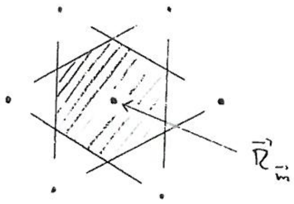
- sides need not be straight



- Wigner-Seitz cell around the lattice point $\vec{R}_{\vec{m}}$ is defined as the area (volume)

$$A = \left\{ \vec{r} \in \mathbb{R}^{2\,(3)} \;\middle|\; |\vec{r} - \vec{R}_{\vec{m}}| < |\vec{r} < \vec{R}_{\vec{n}}| \;\; \forall \vec{n} \neq \vec{m} \right\}$$

example and construction : 2d triangular lattice



//// : Wigner-Seitz cell

symmetries

- translational symmetry → see above
- symmetry under rotation by an angle φ

examples: - 2d square lattice is invariant under rotation by $\varphi = \frac{\pi}{2} = \frac{2\pi}{4}$: 4-fold symmetry

- 2d triangular lattice $\rightarrow \varphi = \frac{\pi}{3} = \frac{2\pi}{6}$: 6-fold symmetry

$\hookrightarrow$ $L = \{ \vec{R}_{\vec{n}} \mid n_i \in \mathbb{Z} \}$ with $\vec{R}_{\vec{n}} = n_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix} + n_2 \frac{1}{2} \begin{pmatrix} 1 \\ \sqrt{3} \end{pmatrix}$

→ show that $D_{\pi/3} \vec{R}_{\vec{n}} \in L$

with D_φ the rotation matrix $D_\varphi = \begin{pmatrix} \cos\varphi & -\sin\varphi \\ \sin\varphi & \cos\varphi \end{pmatrix}$

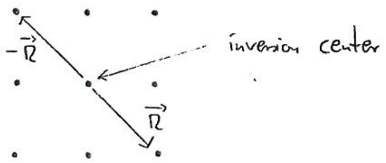
$$D_{\pi/3} \vec{R}_{\vec{n}} = \frac{1}{2} \begin{pmatrix} 1 & -\sqrt{3} \\ \sqrt{3} & 1 \end{pmatrix} \begin{pmatrix} n_1 + \frac{1}{2} n_2 \\ \frac{1}{2} n_2 \sqrt{3} \end{pmatrix} = \frac{1}{2} \begin{pmatrix} n_1 - n_2 \\ \sqrt{3}\,(n_1 + n_2) \end{pmatrix}$$

$$\overset{!}{=} \vec{R}_{\vec{m}} = \begin{pmatrix} m_1 + \frac{1}{2} m_2 \\ \frac{1}{2} m_2 \sqrt{3} \end{pmatrix} \quad \Rightarrow \quad \begin{aligned} m_2 &= n_1 + n_2 \in \mathbb{Z} \\ m_1 &= -n_2 \in \mathbb{Z} \end{aligned}$$

$\Rightarrow \vec{R}_{\vec{m}} \in L$ ok.

- inversion symmetry

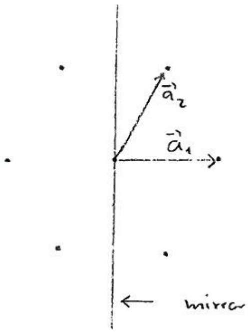
$\rightarrow$ $\vec{R} \in L$, L is symmetric under inversion (with respect to the inversion center $\vec{0}$) if $-\vec{R} \in L$ for all $\vec{R} \in L$



Bravais lattices are always symmetric under inversion

$\rightarrow$ follows directly from $\vec{R}_{\vec{n}} = n_1 \vec{a}_1 + n_2 \vec{a}_2 \rightarrow -\vec{R}_{\vec{n}} = \vec{R}_{(-\vec{n})} \in L$

- mirror symmetry $\rightarrow$ example: the 2d triangular lattice



here: reflection with respect to the y-axis

$$\begin{pmatrix} x \\ y \end{pmatrix} \rightarrow \begin{pmatrix} -x \\ y \end{pmatrix}$$

$$\vec{R}_{\vec{n}} = \begin{pmatrix} n_1 + \frac{1}{2} n_2 \\ \frac{1}{2} n_2 \sqrt{3} \end{pmatrix} \rightarrow \begin{pmatrix} -n_1 - \frac{1}{2} n_2 \\ \frac{1}{2} n_2 \sqrt{3} \end{pmatrix} \overset{!}{=} \begin{pmatrix} m_1 + \frac{1}{2} m_2 \\ \frac{1}{2} m_2 \sqrt{3} \end{pmatrix} = \vec{R}_{\vec{m}}$$

$$\Rightarrow \quad m_1 = -n_1 - n_2 \, , \quad m_2 = n_2 \quad \text{and } \vec{R}_{\vec{m}} \in L$$

1.2 the reciprocal lattice

consider a Bravais lattice $L = \{ \vec{R}_{\vec{n}} \mid n_i \in \mathbb{Z} \}$

with $\vec{R}_{\vec{n}} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$, $\vec{a}_i = \begin{pmatrix} a_{ix} \\ a_{iy} \\ a_{iz} \end{pmatrix}$ $i = 1,2,3$

$\rightarrow$ construct the matrix A:

$$A = \begin{pmatrix} a_{1x} & a_{2x} & a_{3x} \\ a_{1y} & a_{2y} & a_{3y} \\ a_{1z} & a_{2z} & a_{3z} \end{pmatrix} = (\vec{a}_1 \; \vec{a}_2 \; \vec{a}_3)$$

each lattice point can be written as $\vec{R}_{\vec{n}} = A\begin{pmatrix} n_1 \\ n_2 \\ n_3 \end{pmatrix}$

define a matrix B through the relation $\boxed{BA = 2\pi \mathbb{1}}$ $(*)$

with the unit matrix $\mathbb{1}$ and

$$B = \begin{pmatrix} b_{1x} & b_{1y} & b_{1z} \\ b_{2x} & b_{2y} & b_{2z} \\ b_{3x} & b_{3y} & b_{3z} \end{pmatrix} = \begin{pmatrix} \vec{b}_1 \\ \vec{b}_2 \\ \vec{b}_3 \end{pmatrix} \quad \text{with} \quad \vec{b}_i = (b_{ix}, b_{iy}, b_{iz})$$

$(*)$ is equivalent to

$$\begin{pmatrix} \vec{b}_1 \\ \vec{b}_2 \\ \vec{b}_3 \end{pmatrix} (\vec{a}_1\, \vec{a}_2\, \vec{a}_3) = \begin{pmatrix} \vec{b}_1\cdot\vec{a}_1 & \vec{b}_1\cdot\vec{a}_2 & \vec{b}_1\cdot\vec{a}_3 \\ \vec{b}_2\cdot\vec{a}_1 & \vec{b}_2\cdot\vec{a}_2 & \vec{b}_2\cdot\vec{a}_3 \\ \vec{b}_3\cdot\vec{a}_1 & \vec{b}_3\cdot\vec{a}_2 & \vec{b}_3\cdot\vec{a}_3 \end{pmatrix} = 2\pi \mathbb{1}$$

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

this means : $\vec{b}_1$ is perpendicula to the plane spanned by $\vec{a}_2$ and $\vec{a}_3$

($\vec{b}_2, \vec{b}_3$ accordingly)

construction of the vectors $\vec{b}_i$:

set $v = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = \det A$: volume of the unit cell

$$\Rightarrow \quad \boxed{\vec{b}_1 = \frac{2\pi}{v}\, \vec{a}_2 \times \vec{a}_3 \,, \quad \vec{b}_2 = \frac{2\pi}{v}\, \vec{a}_3 \times \vec{a}_1 \,, \quad \vec{b}_3 = \frac{2\pi}{v}\, \vec{a}_1 \times \vec{a}_2}$$

$$\rightarrow \vec{b}_1 \cdot \vec{a}_1 = \frac{2\pi}{v}\, \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = 2\pi \,, \quad \vec{b}_1 \cdot \vec{a}_2 = 0 \,, \text{ etc.}$$

<u>now:</u>

take the $\vec{b}_i$ as primitive vectors of a lattice L_r :

$$L_r = \{ \vec{G}_{\vec{h}} \mid h_i \in \mathbb{Z} \} \quad \text{with} \quad \vec{G}_{\vec{h}} = h_1 \vec{b}_1 + h_2 \vec{b}_2 + h_3 \vec{b}_3$$

$$= (h_1\, h_2\, h_3)\, B$$

L_r : the reciprocal lattice of the original lattice L (= direct lattice)

unit cell of L_r :

- volume : start from $BA = 2\pi \mathbb{1}$

$$\Rightarrow \quad \det(BA) = \underbrace{\det(B)}_{= v_r} \; \underbrace{\det(A)}_{= v} = \det(2\pi \mathbb{1}) = (2\pi)^3$$

$$\Rightarrow \quad v_r = \frac{(2\pi)^3}{v}$$

- Brillouin zone → defined as the Wigner - Seitz cell of the reciprocal lattice

example : the 3d square lattice $\vec{a}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \; \vec{a}_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \; \vec{a}_3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$

$$\Rightarrow \quad \vec{b}_1 = 2\pi \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \vec{b}_2 = 2\pi \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad \vec{b}_3 = 2\pi \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

now conside the scalar product

reciprocal - lattice vector $\vec{G}_{\vec{h}}$ · direct - lattice vector $\vec{R}_{\vec{n}}$

$$\vec{G}_{\vec{h}} \cdot \vec{R}_{\vec{n}} = \Big(\sum_i h_i \vec{b}_i\Big) \cdot \Big(\sum_j n_j \vec{a}_j\Big) = \sum_{ij} h_i n_j \underbrace{\vec{b}_i \cdot \vec{a}_j}_{= 2\pi \delta_{ij}}$$

$$= 2\pi \underbrace{\sum_i h_i n_i}_{= m \in \mathbb{Z}}$$

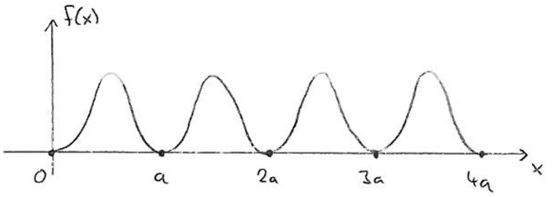
$$\Rightarrow \quad \boxed{e^{i \vec{G}_{\vec{h}} \cdot \vec{R}_{\vec{n}}} = e^{2\pi i m} = 1}$$

1.3 periodic functions

conside a function $f(\vec{r})$ with the following propety

$$\boxed{f(\vec{r}) = f(\vec{r} + \vec{R})} \quad \forall \vec{r} \in \mathbb{R}^3, \; \forall \vec{R} \in L$$

→ f has the translational invariance of the Bravais lattice L in 1d :



→ lattice points at

$R_m = ma \quad , \; m \in \mathbb{Z}$

$\rightarrow \quad f(x) = f(x+ma)$

f(x) can be written as a Fourier series

$$f(x) = \sum_h f_h \, e^{i \frac{2\pi}{a} h x} \quad \text{with} \quad f_h = \frac{1}{a} \int_0^a dx \, f(x) \, e^{-i \frac{2\pi}{a} h x} \; , \; h \in \mathbb{Z}$$

in 3d :

$$\boxed{f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} \, e^{i \vec{G} \cdot \vec{r}}} \; (*)$$

$\sum_{\vec{G}}$: sum over all reciprocal lattice vectors $\vec{G} \in L_r$

with $$\boxed{f_{\vec{G}} = \frac{1}{v} \int_v d^3 r \, f(\vec{r}) \, e^{-i \vec{G} \cdot \vec{r}}}$$

$\int_v d^3 r$: integral over one unit cell of the direct lattice

$$\rightarrow \quad f(\vec{r} + \vec{R}) \overset{(*)}{=} \sum_{\vec{G}} f_{\vec{G}} \underbrace{e^{i \vec{G} \cdot (\vec{r} + \vec{R})}}_{= e^{i \vec{G} \cdot \vec{r}} \underbrace{e^{i \vec{G} \cdot \vec{R}}}_{= 1 \text{ for all } \vec{R} \in L \text{ and } \vec{G} \in L_r}} = f(\vec{r}) \quad \text{ok}$$

eq. (*) in 1d :

$$f(x) = \sum_h f_h \, e^{i g_h x} \quad \text{with } g_h = \frac{2\pi}{a} h$$

$$\Rightarrow \quad g_h R_m = \frac{2\pi}{a} h m a = 2\pi h m$$

2. Separation of lattice and electron dynamics

2.1 the general solid state Hamiltonian

the solid is now viewed as a quantum mechanical system consisting of

N_a atoms (better: ions) : mass M_k, charge $Z_k e$

and N_e electrons : mass m, charge $-e$

charge neutrality requires : $N_e \cdot (-e) + \sum_{k=1}^{N_a} Z_k e = 0$

$\Rightarrow N_e = \sum_{k=1}^{N_a} Z_k$

the coordinates

electrons : $\vec{r}_i = (x_i, y_i, z_i)$, $i = 1, \dots, N_e$, $\{\vec{r}\} = (\vec{r}_1, \dots, \vec{r}_{N_e})$

ions : $\vec{R}_k = (X_k, Y_k, Z_k)$, $k = 1, \dots, N_a$, $\{\vec{R}\} = (\vec{R}_1, \dots, \vec{R}_{N_a})$

the Schrödinger equation (stationary)

$$H \Psi(\{\vec{r}\}, \{\vec{R}\}) = E \Psi(\{\vec{r}\}, \{\vec{R}\})$$

→ the first step : write down the Hamiltonian of the system

(the second step : solution of the SE)

a) kinetic energies

electrons : $T_e = \sum_{i=1}^{N_e} \frac{\vec{p}_i^{\,2}}{2m}$, $\vec{p}_i^{\,2} = -\hbar^2 \Delta_i =$

$= -\hbar^2 \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right)$

ions : $T_a = \sum_{k=1}^{N_a} \frac{\vec{P}_k^{\,2}}{2 M_k}$

b) interactions

$V_{e\text{-}e} = V_{e\text{-}e}(\{\vec{r}\})$: interactions between the electrons

$V_{a\text{-}a} = V_{a\text{-}a}(\{\vec{R}\})$: —— " —— the ions

$V_{e\text{-}a} = V_{e\text{-}a}(\{\vec{r}\}, \{\vec{R}\})$: —— " —— electrons and ions we have two-body interactions of the following form :

$$V_{e\text{-}e} = \sum_{i<j} v_{e\text{-}e}(\vec{r}_i - \vec{r}_j) \qquad\qquad V_{e\text{-}a} = \sum_{i,k} v_{e\text{-}a}(\vec{r}_i - \vec{R}_k)$$

$$V_{a\text{-}a} = \sum_{k<l} v_{a\text{-}a}(\vec{R}_k - \vec{R}_l)$$

in particular : Coulomb interaction

$$\rightarrow \quad v_{e\text{-}e}(\vec{r}_i - \vec{r}_j) = \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \qquad\qquad v_{e\text{-}a}(\vec{r}_i - \vec{R}_k) = \frac{-Z_k e^2}{|\vec{r}_i - \vec{R}_k|}$$

$$v_{a\text{-}a}(\vec{R}_k - \vec{R}_l) = \frac{Z_k Z_l e^2}{|\vec{R}_k - \vec{R}_l|}$$

the general solid state Hamiltonian is of the following form :

$$\boxed{H = T_e + T_a + V_{e\text{-}e} + V_{a\text{-}a} + V_{e\text{-}a}}$$

<u>now</u>: rewrite the Hamiltonian in atomic units

$$\rightarrow \quad \text{Bohr radius} : \quad a_0 = \frac{\hbar^2}{me^2} \quad (= 0{,}5\ \text{Å})$$

define dimensionless vectors $\tilde{\vec{r}} = \frac{1}{a_0}\vec{r}$, $\tilde{\vec{R}} = \frac{1}{a_0}\vec{R}$

$$\rightarrow \quad \text{energy} \quad E_0 = \frac{\hbar^2}{m a_0^2} = \frac{e^2}{a_0} = \frac{me^4}{\hbar^2}$$

consider $\frac{H}{E_0}$, $\frac{T_e}{E_0}$, ... (again dimensionless)

$$\frac{T_e}{E_0} = \frac{1}{E_0}\sum_{i=1}^{N_e}\frac{\vec{p}_i^{\,2}}{2m} = \ldots \qquad\qquad \frac{\partial}{\partial x_i} = \frac{1}{a_0}\frac{\partial}{\partial \tilde{x}_i}$$

$$\ldots = \frac{1}{2}\underbrace{\frac{1}{mE_0a_0^2}}_{=\frac{1}{\hbar^2}}\sum_{i=1}^{N_e}\tilde{\vec{p}}_i^{\,2}$$

$$\frac{T_a}{E_0} = \frac{1}{2\hbar^2}\sum_{k=1}^{N_a}\underbrace{\frac{m}{M_k}}_{\text{of the order } 10^{-5} - 10^{-4}\ !}\tilde{\vec{P}}_k^{\,2}$$

$$\frac{V_{e-e}}{E_0} = \frac{1}{E_0} \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} = \underbrace{\frac{e^2}{E_0 a_0}}_{=1} \sum_{i<j} \frac{1}{|\tilde{\vec{r}}_i - \tilde{\vec{r}}_j|}$$

$\frac{V_{a-a}}{E_0} = \dots$ contains $Z_n Z_e$; $\frac{V_{e-a}}{E_0} = \dots$ contains Z_n

$\Rightarrow$ T_a can be viewed as a perturbation to $H_0 = T_e + V_{e-e} + V_{a-a} + V_{e-a}$

the limit $\frac{m}{M_n} \to 0$

- a simple model : harmonic oscillator in $d=1$

$$H = \underbrace{-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2}}_{\to 0} + \frac{1}{2}kx^2 \quad \longrightarrow \quad \text{what happens when we let the mass } M \text{ go to } \infty \,?$$

$$\Rightarrow \quad H = \frac{1}{2}kx^2$$

Schrödinge equation : $\frac{1}{2}kx^2\,\psi(x) = E\,\psi(x)$

has the following solutions : $\psi_{\bar{x}}(x) = \delta(x-\bar{x}) \;\to\; \frac{1}{2}kx^2\,\psi_{\bar{x}}(x) = \frac{1}{2}k\bar{x}^2\,\psi_{\bar{x}}(x)$

$$\Rightarrow E = \frac{1}{2}k\bar{x}^2$$

this means : the particle is fixed at position $\bar{x}$!

ground state at $\bar{x} = 0$

- and for the solid state Hamiltonian :

> in the limit $\frac{m}{M_n} \to 0$ we can reduce the problem to a purely electronic problem in the background of ions at fixed positions

2.2 Adiabatic Approximation (Born-Oppenheimer-Approximation)

the aim : decouple the dynamics of the electrons from the $\underbrace{\text{dynamics of the ions}}$

later $\to$ lattice vibrations (phonons)

the starting point : assume that the SE for H_0 can be solved

H_0 contains the positions of the ions, $\vec{R}$, as fixed parameters

$\rightarrow$ $\boxed{H_0\, \Phi_\alpha(\vec{r},\vec{R}) = \varepsilon_\alpha(\vec{R})\, \Phi_\alpha(\vec{r},\vec{R})}$ (1) $\{\alpha\}$: complete set of quantum numbers

with the eigenenergies $\varepsilon_\alpha(\vec{R})$ dependent on $\vec{R}$

SE for the full Hamiltonian

$H\, \Psi(\vec{r},\vec{R}) = E\, \Psi(\vec{r},\vec{R})$ $\rightarrow$ expand the wave function $\Psi(\vec{r},\vec{R})$ for each $\vec{R}$ in the complete system of functions $\Phi_\alpha(\vec{r},\vec{R})$

$$\boxed{\Psi(\vec{r},\vec{R}) = \sum_\alpha \chi_\alpha(\vec{R})\, \Phi_\alpha(\vec{r},\vec{R})} \quad (*)$$

insert $(*)$ into $(H-E)\Psi = 0$

$$\rightarrow \quad (H-E)\,\Psi(\vec{r},\vec{R}) = \sum_\alpha \underbrace{(H-E)}_{= H_0 + T_a - E} \chi_\alpha(\vec{R})\, \Phi_\alpha(\vec{r},\vec{R}) = \,'''$$

note that : $H_0\, \chi_\alpha(\vec{R})\, \Phi_\alpha(\vec{r},\vec{R}) = \chi_\alpha(\vec{R})\, \underbrace{H_0\, \Phi_\alpha(\vec{r},\vec{R})}_{= \varepsilon_\alpha(\vec{R})\, \Phi_\alpha(\vec{r},\vec{R})}$

$$''' = \sum_\alpha \left(\varepsilon_\alpha(\vec{R}) + T_a - E \right) \chi_\alpha(\vec{R})\, \Phi_\alpha(\vec{r},\vec{R}) \overset{!}{=} 0$$

$\rightarrow$ analysis of $T_a\, \chi_\alpha(\vec{R})\, \Phi_\alpha(\vec{r},\vec{R})$:

$$T_a = \sum_k \frac{\vec{P}_k^{\,2}}{2M_k} = -\hbar^2 \sum_k \frac{1}{2M_k} \Delta_k \quad \text{with} \quad \Delta_k = \frac{\partial^2}{\partial X_k^2} + \frac{\partial^2}{\partial Y_k^2} + \frac{\partial^2}{\partial Z_k^2}$$

$$\rightarrow \quad \frac{\partial^2}{\partial X_k^2}\left[\chi_\alpha(\vec{R})\, \Phi_\alpha(\vec{r},\vec{R}) \right] = \chi_\alpha(\vec{R}) \frac{\partial^2}{\partial X_k^2} \Phi_\alpha(\vec{r},\vec{R}) + \left[\frac{\partial^2}{\partial X_k^2} \chi_\alpha(\vec{R}) \right] \Phi_\alpha(\vec{r},\vec{R})$$
$$+ 2 \left(\frac{\partial}{\partial X_k} \chi_\alpha(\vec{R}) \right) \left(\frac{\partial}{\partial X_k} \Phi_\alpha(\vec{r},\vec{R}) \right)$$

$$\Rightarrow \quad \Delta_k \left[\chi_\alpha(\vec{R})\, \Phi_\alpha(\vec{r},\vec{R}) \right] = \chi_\alpha(\vec{R})\, \Delta_k\, \Phi_\alpha(\vec{r},\vec{R}) + \left[\Delta_k\, \chi_\alpha(\vec{R}) \right] \Phi_\alpha(\vec{r},\vec{R})$$
$$+ 2\, \vec{\nabla}_k\, \chi_\alpha(\vec{R}) \cdot \vec{\nabla}_k\, \Phi_\alpha(\vec{r},\vec{R})$$

we then have

$$T_a \, \chi_\alpha(\vec{R}) \, \Phi_\alpha(\vec{r},\vec{R}) = \left[T_a \, \chi_\alpha(\vec{R}) \right] \Phi_\alpha(\vec{r},\vec{R}) \; + \text{ remaining terms which will be dropped}$$

$$\Rightarrow \quad \sum_\alpha \left[\left(\varepsilon_\alpha(\vec{R}) + T_a - E \right) \chi_\alpha(\vec{R}) \right] \Phi_\alpha(\vec{r},\vec{R}) = 0$$

the next step: multiply with $\Phi^*_\beta(\vec{r},\vec{R})$ and integrate over $d\vec{r}$

$$\rightarrow \quad \sum_\alpha \int d\vec{r} \, \underbrace{\left[\left(\varepsilon_\alpha(\vec{R}) + T_a - E \right) \chi_\alpha(\vec{R}) \right]}_{\text{does not depend on } \vec{r}} \Phi^*_\beta(\vec{r},\vec{R}) \, \Phi_\alpha(\vec{r},\vec{R}) = \ldots$$

$$\int d\vec{r} \, \Phi^*_\beta(\vec{r},\vec{R}) \, \Phi_\alpha(\vec{r},\vec{R}) = \delta_{\alpha\beta}$$

$$\ldots = \left(\varepsilon_\beta(\vec{R}) + T_a - E \right) \chi_\beta(\vec{R}) = 0$$

so we arrive at

$$\boxed{\left(T_a + \varepsilon_\beta(\vec{R}) \right) \chi_\beta(\vec{R}) = E \, \chi_\beta(\vec{R})} \quad (2)$$

→ eq.(2) has the form of a Schrödinger equation for the wave function $\chi_\beta(\vec{R})$ in the effective potential $\varepsilon_\beta(\vec{R})$

$\chi_\beta(\vec{R})$: the wave function of the ions

<u>the Born-Oppenheimer approximation</u> (adiabatic approximation)

1. solve the electronic SE (1) for fixed position of the ions $\vec{R}$

   → this give the eigenenergies $\varepsilon_\alpha(\vec{R})$

2. solve the ionic SE (2) with the effective potential given by $\varepsilon_\alpha(\vec{R})$, for all α

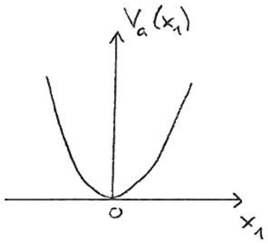
what is the approximation?

→ neglect of the 'remaining terms' (see top of this page)

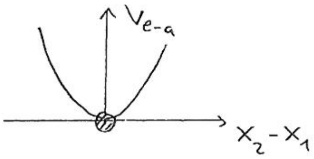
example

- a single ion, mass M, in a 1d harmonic potential: $T_a = \frac{p_1^2}{2M}$

  $V_a = \frac{1}{2} k_1 x_1^2$



- electron, mass $m \ll M$, bounded to the ion via a harmonic potential



$$T_e = \frac{p_2^2}{2m}$$

$$V_{e-a} = \frac{1}{2} k_2 (x_1 - x_2)^2$$

physical consequence of $m/M \ll 1$

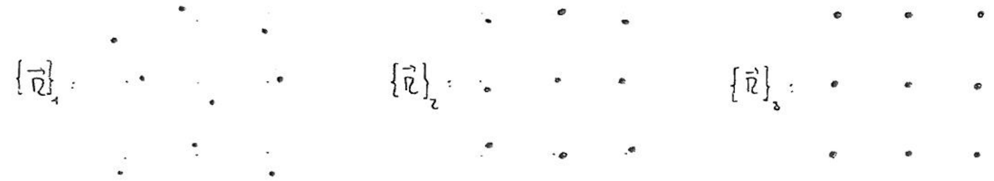
- different time scales of electronic and ionic motion $\tau_e \ll \tau_a$

  $\Rightarrow$ electron (that is the electronic wave function) reacts instantaneously to the displacements of the ion: 'adiabatic' approximation

the effective potential $\varepsilon(\vec{R})$

$\rightarrow$ include $V_{a-a}(\vec{R})$ + the effective potential due to the reaction of the electrons to the ionic positions

in principle: the global minimum of $\varepsilon(\vec{R})$ should correspond to the actual lattice structure of the solid state Hamiltonian



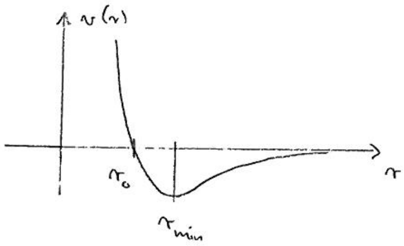
$$\varepsilon(\{\vec{R}\}_1) > \varepsilon(\{\vec{R}\}_2) > \varepsilon(\{\vec{R}\}_3)$$

but: it is impossible to calculate $\varepsilon(\vec{R})$ (and the resulting minima) without further assumptions and approximations

⇒ choose a suitable ansatz for the effective potential

again, a two-body interaction $V^{\text{eff}}_{a-a} = \sum_{k<l} v(|\vec{R}_k - \vec{R}_l|)$

with $v(r)$ of the form



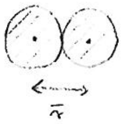
→ $v(r) > 0$ for $r < r_0$: (strongly) repulsive for short distances

→ Coulomb-repulsion of cores

→ —— " —— electrons

→ Pauli principle : for $r \to 0$, electrons have to occupy highe lying energy state

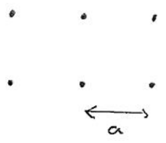
one can set $v(r) = \infty$ for $r < \bar{r}$



"hard-core" potential

→ minimum at $r = r_{min}$ and attractive potential for $r > r_{min}$

↳ of the orde of the lattice constant a



→ $v(r) \to 0$ for $r \to \infty$

3. Phonons

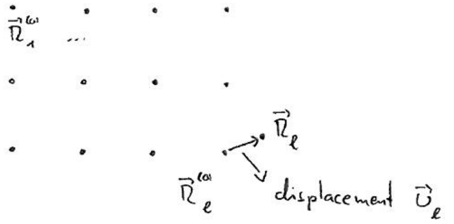
3.1 The harmonic approximation

the starting point : Schrödinge equation for the wave function of the ions

$$H\,\chi(\vec{R}) = E\,\chi(\vec{R}) \qquad \text{with} \qquad H = \sum_{\ell=1}^{N} \frac{\vec{P}_\ell^{\,2}}{2M_\ell} + V_{eff}(\vec{R})$$

for the effective potential, $V_{eff}(\vec{R})$, we assume that there exists an equilibrium position $\{\vec{R}^{(0)}\} = (\vec{R}_1^{(0)}, \dots, \vec{R}_N^{(0)})$, corresponding to the absolute minimum of $V_{eff}(\vec{R})$

$\{\vec{R}^{(0)}\}$:



→ expand $V_{eff}(\vec{R})$ around the equilibrium position for small displacements

$$\vec{u}_\ell = \vec{R}_\ell - \vec{R}_\ell^{(0)}$$

$$V_{eff}(\vec{R}) = V_{eff}(\vec{R}^{(0)}) + \sum_{\ell=1}^{N}\sum_{\alpha=1}^{d} \left.\frac{\partial V_{eff}}{\partial R_{\ell\alpha}}\right|_{\vec{R}^{(0)}} \cdot u_{\ell\alpha}$$

$$+ \frac{1}{2}\sum_{\ell m \alpha\beta} \left.\frac{\partial^2 V_{eff}}{\partial R_{\ell\alpha}\,\partial R_{m\beta}}\right|_{\vec{R}^{(0)}} \cdot u_{\ell\alpha} u_{m\beta} + \underbrace{\dots\dots}_{\text{these terms are dropped in the harmonic approximation}}$$

notation: $\vec{R}_\ell = (R_{\ell 1}, \dots, R_{\ell d})$

we have : $\left.\frac{\partial V_{eff}}{\partial R_{\ell\alpha}}\right|_{\vec{R}^{(0)}} = 0 \implies$ the linear term vanishes

now define the $dN \times dN$ - matrix Φ via

$$\Phi_{\ell\alpha, m\beta} = \left.\frac{\partial^2 V_{eff}}{\partial R_{\ell\alpha}\,\partial R_{m\beta}}\right|_{\vec{R}^{(0)}} \qquad (\text{ the Hesse matrix})$$

now define $\tilde{u}_{l\alpha} = \sqrt{M_l}\, u_{l\alpha}$, $\tilde{p}_{l\alpha} = \frac{1}{\sqrt{M_l}}\, p_{l\alpha}$

and write the Hamiltonian in the harmonic approximation as

$$H_{harm} = \sum_{l=1}^{N}\sum_{\alpha=1}^{d} \underbrace{\frac{p_{l\alpha}^2}{2M_l}}_{=\frac{1}{2}\tilde{p}_{l\alpha}^2} + \underbrace{V_{eff}(\vec{R}^{(0)})}_{\text{can be set to } 0} + \frac{1}{2}\sum_{lm\alpha\beta} \Phi_{l\alpha,m\beta}\, \underbrace{u_{l\alpha}\, u_{m\beta}}_{=\frac{1}{\sqrt{M_l M_m}}\tilde{u}_{l\alpha}\tilde{u}_{m\beta}}$$

definition of the dynamical matrix D

$\rightarrow$ matrix elements $\boxed{D_{l\alpha,m\beta} = \frac{1}{\sqrt{M_l M_m}}\, \Phi_{l\alpha,m\beta}.}$

with the vectors $\vec{\tilde{u}} = \begin{pmatrix} \tilde{u}_{11} \\ \tilde{u}_{12} \\ \vdots \\ \tilde{u}_{Nd} \end{pmatrix}$ and $\vec{\tilde{p}} = \begin{pmatrix} \tilde{p}_{11} \\ \tilde{p}_{12} \\ \vdots \\ \tilde{p}_{Nd} \end{pmatrix}$, we can write

$$\boxed{H_{harm} = \frac{1}{2}\, \vec{\tilde{p}}^{\,t}\, \mathbb{1}\, \vec{\tilde{p}} + \frac{1}{2}\, \vec{\tilde{u}}^{\,t}\, D\, \vec{\tilde{u}}}$$

properties of the matrix D :

- real ✓
- symmetric, because $\frac{\partial^2 V_{eff}}{\partial R_{l\alpha}\partial R_{m\beta}} = \frac{\partial^2 V_{eff}}{\partial R_{m\beta}\partial R_{l\alpha}}$
- positiv definit, because

$$\vec{\tilde{u}}^{\,t}\, D\, \vec{\tilde{u}} > 0 \quad \text{for all } \vec{u} \neq \vec{0}$$ (follows from $\vec{R}^{(0)}$ being an absolute minimum)

$\Longrightarrow$ there exists an orthogonal matrix C with

$C D C^t = \Omega$, with Ω a diagonal matrix with $\Omega_{ii} > 0$

$\rightarrow$ Ω can be written as

$$\Omega = \begin{pmatrix} \omega_1^2 & & & 0 \\ & \omega_2^2 & & \\ & & \ddots & \\ 0 & & & \omega_{Nd}^2 \end{pmatrix}$$ with $\omega_i \in \mathbb{R}\setminus 0$ $\quad i = 1, \dots, Nd$

C is an orthogonal matrix $\rightarrow$ $C^t C = \mathbb{1}$

$\rightarrow$ H_{harm} can be written as:

$$H_{harm} = \frac{1}{2} \vec{\tilde{p}}^{\,t} C^t C \vec{\tilde{p}} + \frac{1}{2} \vec{\tilde{u}}^{\,t} C^t \underbrace{C D C^t}_{= \Omega} C \vec{\tilde{u}}$$

define new vectors: $\vec{p}\,' = C \vec{\tilde{p}}$; $(\vec{p}\,')^t = (C \vec{\tilde{p}})^t = \vec{\tilde{p}}^{\,t} C^t$

$\vec{u}\,' = C \vec{\tilde{u}}$; $(\vec{u}\,')^t = (C \vec{\tilde{u}})^t = \vec{\tilde{u}}^{\,t} C^t$

$$\Rightarrow \quad \boxed{H_{harm} = \frac{1}{2} (\vec{p}\,')^t \mathbb{1} \vec{p}\,' + \frac{1}{2} (\vec{u}\,')^t \Omega \vec{u}\,'}$$

write the Hamiltonian in the components p_i' and u_i', $i = 1, \dots, Nd$

$$H_{harm} = \frac{1}{2} \sum_{i=1}^{Nd} (p_i')^2 + \frac{1}{2} \sum_{i=1}^{Nd} \omega_i^2 (u_i')^2 = \sum_{i=1}^{Nd} H_i$$

with $H_i = \frac{1}{2}(p_i')^2 + \frac{1}{2} \omega_i^2 (u_i')^2$ $\Rightarrow$ H_{harm} describes a set of Nd independent harmonic oscillators

<u>but</u>: what about the commutation relation $[u_i', p_j']$?

$\rightarrow$ start with the conjugate variables $p_i = -i\hbar \frac{\partial}{\partial u_i}$ and u_i

$$[u_i, p_j] = i\hbar \delta_{ij}$$

$\rightarrow$ with $\tilde{u}_i = \sqrt{M}\, u_i$ and $\tilde{p}_i = \frac{1}{\sqrt{M}} p_i$ we still have

$$[\tilde{u}_i, \tilde{p}_j] = i\hbar \delta_{ij}$$

$\rightarrow$ now insert $u_i' = \sum_k C_{ik} \tilde{u}_k$ and $p_j' = \sum_\ell C_{i\ell} \tilde{p}_\ell$ into $[u_i', p_j']$:

$$[u_i', p_j'] = \sum_{k\ell} C_{ik} C_{j\ell} \underbrace{[\tilde{u}_k, \tilde{p}_\ell]}_{= i\hbar \delta_{k\ell}} = i\hbar \sum_\ell C_{i\ell} C_{j\ell} = \dots$$

$$\ldots = i\hbar \sum_{\ell} C_{i\ell} \, (C^t)_{\ell j} = i\hbar \, (\underbrace{C C^t}_{= \mathbb{1}})_{ij} = i\hbar \, \delta_{ij}$$

this means : u'_i, p'_i define a pair of conjugate variables !

now (as in standard quantum mechanics) define operators

$$b_j^{(\dagger)} = \sqrt{\frac{\omega_j}{2\hbar}} \, u'_j \pm i \sqrt{\frac{1}{2\hbar\omega_j}} \, p'_j$$

with the commutation relations

$$[b_j, b_k^\dagger] = \delta_{jk} \quad , \quad [b_j, b_k] = [b_j^\dagger, b_k^\dagger] = 0$$

and we arrive at the final form of H_{harm} :

$$\boxed{H_{harm} = \sum_{j=1}^{Nd} \hbar\omega_j \left(b_j^\dagger b_j + \frac{1}{2} \right)}$$

the remaining question : how to diagonalize the matrix D ?

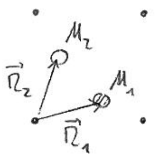
→ numerical diagonalization is limited to $Nd \lesssim 10^5 - 10^6$

=> use translational invariance to simplify the diagonalization of D

3.2 translational invariance

given a Bravais lattice L, with lattice vectors $\vec{R}_{\vec{n}}$

→ add a basis of atoms with mass M_μ at positions $\vec{R}_\mu$, $\mu = 1, \ldots, r$



$$\vec{R}^{(0)}_{\vec{n},\mu} = \vec{R}_{\vec{n}} + \vec{R}_\mu$$

now we assume that the $\vec{R}^{(0)}_{\vec{n},\mu}$ correspond to the equilibrium position of the atoms !

so we have for the actual positions : $\vec{R}_{\vec{n},\mu} = \vec{R}^{(0)}_{\vec{n},\mu} + \vec{u}_{\vec{n},\mu}$

↳ the displacements

with the notation of Sec. 3.1 :

$$l = (\vec{n},\mu) \quad , \quad m = (\vec{n}',\mu')$$

again : harmonic approximation of $V_{\text{eff}}(\vec{R})$

→ Hesse matrix $\Phi_{l\alpha,m\alpha'} = \Phi_{\vec{n}\mu\alpha,\vec{n}'\mu'\alpha'}$

→ dynamical matrix $$D_{l\alpha,m\alpha'} = \underbrace{\frac{1}{\sqrt{M_l M_m}}}_{= \frac{1}{\sqrt{M_\mu M_{\mu'}}}} \Phi_{l\alpha,m\alpha'} = D_{\vec{n}\mu\alpha,\vec{n}'\mu'\alpha'}$$

- what does translational invariance mean for the matrix elements of D ?

→ $D_{\vec{n}\mu\alpha,\vec{n}'\mu'\alpha'}$ only depends on the difference $(\vec{R}_{\vec{n}} - \vec{R}_{\vec{n}'})$
(and not on $\vec{R}_{\vec{n}}$ and $\vec{R}_{\vec{n}'}$ individually)

so we can write : $$D_{\vec{n}\mu\alpha,\vec{n}'\mu'\alpha'} = D'_{\mu\alpha,\mu'\alpha'}(\vec{R}_{\vec{n}} - \vec{R}_{\vec{n}'})$$

with the $D'_{\mu\alpha,\mu'\alpha'}(\vec{r})$ the matrix elements of the $rd \times rd$ matrix D'

$$D'(\vec{r}) = \begin{pmatrix} D'_{11,11}(\vec{r}) & D'_{11,12}(\vec{r}) & \dots & D'_{11,rd}(\vec{r}) \\ \vdots & & \ddots & \\ D'_{rd,11}(\vec{r}) & & & D'_{rd,rd}(\vec{r}) \end{pmatrix}$$

- and how to diagonalize a matrix D with this property ?

→ start with $D\vec{a} = \omega^2 \vec{a}$, corresponding to a system of linear equations :

$$\omega^2 a_{l\alpha} = \sum_{m\alpha'} D_{l\alpha,m\alpha'} a_{m\alpha'}$$

$$\hat{=} \quad \omega^2 a_{\vec{n}\mu\alpha} = \sum_{\vec{n}'\mu'\alpha'} D_{\vec{n}\mu\alpha,\vec{n}'\mu'\alpha'} a_{\vec{n}'\mu'\alpha'} = \sum_{\vec{n}'\mu'\alpha'} D'_{\mu\alpha,\mu'\alpha'}(\vec{R}_{\vec{n}} - \vec{R}_{\vec{n}'}) a_{\vec{n}'\mu'\alpha'}$$

now: a specific ansatz for the components $a_{\vec{n}\mu\alpha}$:

$$\boxed{a_{\vec{n}\mu\alpha} = b_{\mu\alpha}\, e^{i\vec{q}\cdot\vec{R}_{\vec{n}}}}$$

$$\Rightarrow \quad \omega^2 b_{\mu\alpha}\, e^{i\vec{q}\cdot\vec{R}_{\vec{n}}} = \sum_{\vec{n}'\mu'\alpha'} D'_{\mu\alpha,\mu'\alpha'}(\vec{R}_{\vec{n}} - \vec{R}_{\vec{n}'})\, b_{\mu'\alpha'}\, e^{i\vec{q}\cdot\vec{R}_{\vec{n}'}}$$

$$\omega^2 b_{\mu\alpha} = \sum_{\mu'\alpha'} b_{\mu'\alpha'} \sum_{\vec{n}'} D'_{\mu\alpha,\mu'\alpha'}(\vec{R}_{\vec{n}} - \vec{R}_{\vec{n}'})\, e^{-i\vec{q}\cdot(\vec{R}_{\vec{n}} - \vec{R}_{\vec{n}'})} = \ldots$$

substitute $\vec{R}_{\vec{m}} = \vec{R}_{\vec{n}} - \vec{R}_{\vec{n}'}$ and replace $\sum_{\vec{n}'}$ by $\sum_{\vec{m}}$

$$\ldots = \sum_{\mu'\alpha'} b_{\mu'\alpha'} \underbrace{\sum_{\vec{m}} D'_{\mu\alpha,\mu'\alpha'}(\vec{R}_{\vec{m}})\, e^{-i\vec{q}\cdot\vec{R}_{\vec{m}}}}$$

$=: \bar{D}_{\mu\alpha,\mu'\alpha'}(\vec{q})$ this defines the $rd \times rd$ matrix $\bar{D}(\vec{q})$ which has as its matrix elements the Fourier transforms of the matrix elements of D'

this gives the following equation:

$$\boxed{\omega^2 b_{\mu\alpha} = \sum_{\mu'\alpha'} \bar{D}_{\mu\alpha,\mu'\alpha'}(\vec{q})\, b_{\mu'\alpha'}} \quad (*)$$

which can be written as $\omega^2 \vec{b} = \bar{D}(\vec{q})\, \vec{b}$ with $\vec{b} = \begin{pmatrix} b_{11} \\ b_{12} \\ \vdots \\ b_{rd} \end{pmatrix}$

$\Rightarrow$ eq. $(*)$ defines (again) an eigenvalue problem,

but now the ω^2 are eigenvalues of the $rd \times rd$-matrix $\bar{D}(\vec{q})$!

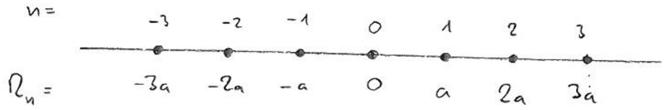
example

- a one-dimensional Bravais lattice $L = \{R_n \mid n \in \mathbb{Z}\}$

  with $R_n = na$ → $d = 1$

  and a mono-atomic basis : $R_{\mu=1} = 0$ → $r = 1$

- the R_n are the equilibrium position of ions of mass M



the effective potential is of the form:

$$V_{eff} = \alpha \sum_n (u_{n+1} - u_n)^2 = \alpha \sum_n (u_{n+1}^2 + u_n^2 - 2 u_{n+1} u_n)$$

$$= 2\alpha \sum_n u_n u_n - \alpha \sum_n u_n u_{n+1} - \alpha \sum_n u_n u_{n-1}$$

$$= \frac{1}{2} \sum_{nm} \Phi_{nm} u_n u_m \qquad \text{with} \quad \Phi_{nn} = 4\alpha$$

$$\Phi_{nn+1} = \Phi_{nn-1} = -2\alpha$$

$$\Rightarrow \quad \Phi = 2\alpha \begin{pmatrix} 2 & -1 & & 0 \\ -1 & 2 & -1 & \\ & -1 & \ddots & \\ 0 & & \ddots & \end{pmatrix}$$

the dynamical matrix $D_{nm} = \frac{1}{\sqrt{M_n M_m}} \Phi_{nm} = \frac{1}{M} \Phi_{nm}$

the system is translationally invariant

$$\Rightarrow \quad D_{nm} = D'(R_n - R_m) \qquad \text{with } D' \text{ a } 1\times1\text{- matrix } (rd=1)$$

the function $D'(r)$ has the following form:

$$D'(r) = \begin{cases} \frac{1}{M} 4\alpha & : r = 0 \\ -\frac{1}{M} 2\alpha & : |r| = a \\ 0 & : \text{otherwise} \end{cases} \quad \hat{=} \quad D'(R_m) = \begin{cases} \frac{1}{M} 4\alpha & : m = 0 \\ -\frac{1}{M} 2\alpha & : |m| = 1 \\ 0 & : \text{otherwise} \end{cases}$$

<u>Fourier transform of $D'(r)$:</u>

$$\bar{D}(q) = \sum_m D'(R_m) e^{-iqR_m}$$

$$= D'(0) + D'(a) e^{-iqa} + D'(-a) e^{iqa}$$

$$= \frac{1}{M} [4\alpha - 2\alpha \underbrace{(e^{-iqa} + e^{iqa})}_{= 2\cos(qa)}] = 4 \frac{\alpha}{M} [1 - \cos(qa)]$$

the eigenvalue, follow from the equation

$$\omega^2 b = \bar{D}(q) b \qquad \Rightarrow \qquad \boxed{\omega(q) = 2\sqrt{\frac{\alpha}{M}(1 - \cos(qa))}}$$

$\omega(q)$: dispersion relation

question : $q \in \mathbb{R}$ arbitrary, or restricted to a specific range ?

- go back to the ansatz (for the 1d-problem)

$$a_n = b e^{iqR_n} = b e^{iqna}$$

- now consider the reciprocal lattice of L

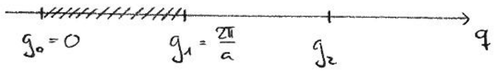
$\rightarrow$ reciprocal lattice vector $g_h = \frac{2\pi}{a} h$, $h \in \mathbb{Z}$

$\Rightarrow$ the function $a_n(q)$ is periodic with respect to the reciprocal lattice !

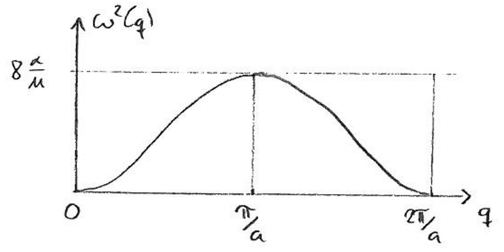
$$a_n(q+g_h) = b e^{i(q+g_h)na} = b e^{iqna} \underbrace{e^{ig_h na}}_{= e^{i\frac{2\pi}{a}hna} = 1} = a_n(q)$$

$\rightarrow$ restrict the q-values to one unit cell of the reciprocal lattice

for example $q \in [0, \frac{2\pi}{a}[$



the dispersion relation has the form :



$\rightarrow$ we have found the eigenvalues of the dynamical matrix D, the ω^2, parametrized as a function $\omega^2(q)$, $q \in [0, 2\pi/a[$

what does this mean for the Hamiltonian $H_{harm} = \sum_{j=1}^{Nd} \hbar\omega_j (b_j^\dagger b_j + \frac{1}{2})$?

- discrete spectrum $\{\omega_j\}$, $j = 1, \dots, Nd$

  vs. continuous spectrum $\omega(q)$, $q \in [0, \frac{2\pi}{a}[$?

- in the limit $N \to \infty$, do we have to replace the $\sum_j$ by $\int dq$?

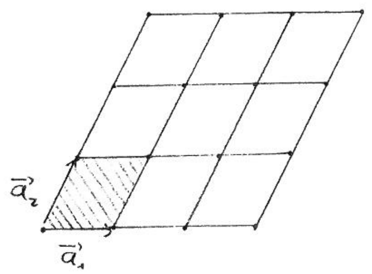
in the following: consider a finite system with appropriate boundary conditions

3.3 boundary conditions

- consider a Bravais lattice $L = \{ \vec{R}_{\vec{n}} \mid n_i \in \mathbb{Z} \}$ with the lattice vectors $\vec{R}_{\vec{n}} = \sum_{i=1}^{d} n_i \vec{a}_i$ and the primitive vectors $\vec{a}_i$

- define the unit cell as the volume spanned by the $\vec{a}_i$

now: construct a finite solid by repeating the unit cell N_i times in the direction of $\vec{a}_i$

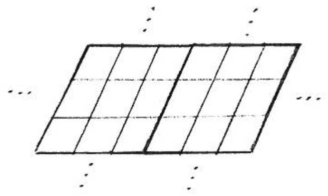


▨ : the unit cell

→ $N_1 = 3$, $N_2 = 3$

the solid consists of $N = \prod_{\alpha=1}^{d} N_\alpha$ unit cells

then: construct an infinite solid by adding identical copies of the finite solid in all d directions



let $f(\vec{R}_n)$ be a function defined on the lattice points $\vec{R}_{\vec{n}}$ of the finite lattice, i.e. $0 \leq n_i < N_i$

- periodic boundary conditions

$$\boxed{f(\vec{R}_{\vec{n}} + N_\alpha \vec{a}_\alpha) = f(\vec{R}_{\vec{n}})} \quad (*)$$

(and now f is defined for all $\vec{R}_{\vec{n}} \in L$)

back to Sec. 3.2 and the ansatz $a_{\vec{n}\mu\alpha} = b_{\mu\alpha} e^{i\vec{q}\cdot\vec{R}_{\vec{n}}}$

→ assume that the $a_{\vec{n}\mu\alpha}$ fulfill the condition (*):

$$\Rightarrow \quad e^{i\vec{q}\cdot\vec{R}_{\vec{n}}} \overset{(*)}{=} e^{i\vec{q}\cdot(\vec{R}_{\vec{n}} + N_\alpha \vec{a}_\alpha)}$$

$$e^{iN_\alpha \vec{q}\cdot\vec{a}_\alpha} = 1$$

the $\vec{q}$-values can be restricted to one unit cell of the reciprocal lattice

$\longrightarrow$ we can write $\vec{q} = \sum_{\beta=1}^{d} c_\beta \vec{b}_\beta$ with: - $\vec{b}_\beta$ the primitive vectors of L_r

- $0 \leq c_\beta < 1$

insert this representation into $N_\alpha \vec{q} \cdot \vec{a}_\alpha = m_\alpha 2\pi \qquad m_\alpha \in \mathbb{Z}$

$$\longrightarrow \quad N_\alpha \sum_{\beta=1}^{d} c_\beta \underbrace{\vec{b}_\beta \cdot \vec{a}_\alpha}_{= 2\pi \delta_{\alpha\beta}} = m_\alpha 2\pi \quad , \quad N_\alpha c_\alpha = m_\alpha \quad , \quad c_\alpha = \frac{m_\alpha}{N_\alpha}$$

with the restriction $0 \leq c_\alpha < 1$ we have for the allowed values of c_α:

$$c_\alpha = \frac{m_\alpha}{N_\alpha} \quad , \quad m_\alpha = 1, 2, \dots N_\alpha - 1$$

and for the set of allowed $\vec{q}$-values

$$\boxed{\vec{q}\,(m_1, \dots, m_d) = \sum_{\beta=1}^{d} \frac{m_\beta}{N_\beta} \vec{b}_\beta \quad , \quad m_\beta = 0, 1, \dots, N_\beta - 1}$$

number of $\vec{q}$-values: $\prod_{\beta=1}^{d} N_\beta = N$ equals the number of unit cells

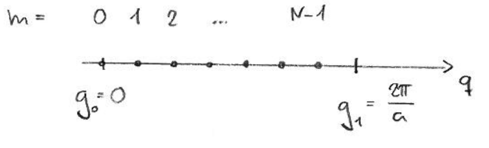
$\Rightarrow$ we now have a discrete spectrum of ω-values

$$\omega_j = \omega(\vec{q}_j) \quad , \quad j = 1, \dots, N$$

and we recover the continuous spectrum in the limit $N \to \infty$

<u>example</u>: $d = 1$, lattice spacing a

$$\longrightarrow \quad q\,(m) = \frac{m}{N} b \qquad \text{with } b = \frac{2\pi}{a} \quad , \quad m = 0, 1, \dots, N-1$$



• : the allowed q-value

important: the specific set of allowed q-values depends on the boundary conditions!

3.4 phonons : quantized lattice vibrations

the Hamiltonian in the harmonic approximation, on a finite lattice with periodic boundary conditions :

$$\boxed{H_{harm} = \sum_{\vec{q}} \sum_{l=1}^{dr} \hbar\omega_l(\vec{q}) \left(b^{\dagger}_{l\vec{q}} b_{l\vec{q}} + \frac{1}{2} \right)}$$

- commutation relations : $[b_{l\vec{q}}, b^{\dagger}_{l'\vec{q}'}] = \delta_{ll'} \delta_{\vec{q}\vec{q}'}$, etc

- $\sum_{\vec{q}}$ is the sum over the N allowed $\vec{q}$-values $\vec{q}_{\vec{m}}$ with $\vec{m} = (m_1, .., m_d)$

  and $m_\alpha = 0, 1, .. N_\alpha - 1$

- for each $\vec{q}$, we have to solve an eigenvalue problem

  $\omega^2 \vec{b} = \bar{D}(\vec{q}) \vec{b}$, with $\bar{D}$ a $\vec{q}$-dependent $rd \times rd$ - matrix

  → this gives rd ω-values for each $\vec{q}$, the $\omega_l(\vec{q})$, $l = 1, .., rd$

  in total : Nrd ω-values

- H_{harm} describes a system of non-interacting bosons

  these bosons are called $\boxed{\text{phonons}}$

  → the first example of 'quasiparticles'

solution of the Schrödinger equation

\+ a few remarks on single-particle vs many-particle levels

the spectrum of single-particle levels : $\{ \hbar\omega_l(\vec{q}) \}$

H_{harm} can be written as $H_{harm} = \sum_{\vec{q}} \sum_{l} H_{\vec{q}l}$ and we have

$$H_{\vec{q}l} | n_{\vec{q}l} \rangle = \hbar\omega_l(\vec{q}) \left(b^{\dagger}_{l\vec{q}} b_{l\vec{q}} + \frac{1}{2} \right) | n_{\vec{q}l} \rangle = \hbar\omega_l(\vec{q}) \left(n_{\vec{q}l} + \frac{1}{2} \right) | n_{\vec{q}l} \rangle$$

with $| n_{\vec{q}l} \rangle$ the eigenstates of the particle number operator $b^{\dagger}_{\vec{q}l} b_{\vec{q}l}$

$n_{\vec{q}l} = 0, 1, 2, ...$

now construct the many-particle eigenstate

$H_{harm} |m\rangle = E_m |m\rangle$ with $|m\rangle$ written as product state of the eigenstates of $H_{\vec{q}l}$: $|m\rangle = \prod_{\vec{q}l} |n_{\vec{q}l}\rangle$

this gives the many-particle energies $$\boxed{E_m = \sum_{\vec{q}l} \hbar\omega_l(\vec{q}) \left(n_{\vec{q}l} + \frac{1}{2} \right)}$$

$\rightarrow$ the spectrum of many-particle levels $\{E_m\}$

phonon branches

- for each l ($l = 1, \dots, dr$), the dispersion relation $\omega_l(\vec{q})$ corresponds to one phonon branch $\rightarrow$ dr phonon branches in total
- (without proof) there are d phonon branches with $\omega_l(\vec{q}) \rightarrow 0$ for $|\vec{q}| \rightarrow 0$

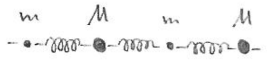
  $\rightarrow$ acoustic phonons

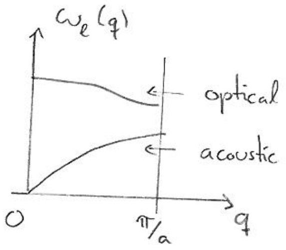
  for the remaining $dr - d$ branches we have $\omega_l(\vec{q}) \rightarrow \bar{\omega}_l \neq 0$ for $|\vec{q}| \rightarrow 0$

  $\rightarrow$ optical phonons

example : $d = 1$, $r = 2$

corresponding to





3.5 Thermodynamics of lattice vibrations

we now have a problem of statistical physics

$\rightarrow$ calculate the partition function of a system of non-interacting bosons (in the same way as for a photon gas)

in the following:

calculate the internal energy E and the specific heat C as a function of temperature T

E is defined as $E = \langle H_{harm} \rangle$

with the expectation value $\langle X \rangle$ of an operator X defined as :

$$\langle X \rangle = \frac{1}{Z} \sum_m e^{-\beta E_m} X$$

with
- $\beta = \frac{1}{k_B T}$, k_B : Boltzmann constant
- the partition function $Z = \sum_m e^{-\beta E_m}$
- $\sum_m$: sum over all many-particle levels

H_{harm} as defined in Sec. 3.4

$$\rightarrow \quad \langle H_{harm} \rangle = \sum_{l\vec{q}} \hbar\omega_l(\vec{q}) \left(\langle b^{\dagger}_{\vec{q}l} b_{\vec{q}l} \rangle + \frac{1}{2} \right)$$

with the expectation value $\langle b^{\dagger}_{\vec{q}l} b_{\vec{q}l} \rangle$ (the mean occupation number of the level $(l,\vec{q})$ at temperature T) given by the Bose function

$$\boxed{\langle n_{\vec{q}l} \rangle = \langle b^{\dagger}_{\vec{q}l} b_{\vec{q}l} \rangle = \frac{1}{e^{\beta\hbar\omega_l(\vec{q})} - 1}}$$

we then get for the internal energy

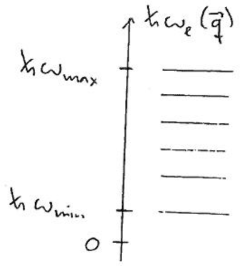
$$\boxed{E = E_0 + \sum_{l\vec{q}} \hbar\omega_l(\vec{q}) \frac{1}{e^{\beta\hbar\omega_l(\vec{q})} - 1}}$$

with the zero-point energy

$$E_0 = \frac{1}{2} \sum_{l\vec{q}} \hbar\omega_l(\vec{q})$$

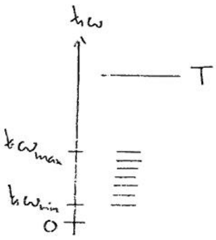
how to evaluate the sum over all $\vec{q}$-values ?

→ the single-particle spectrum :

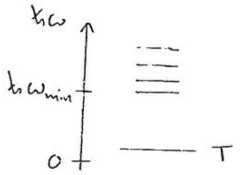


i, the high-temperature limit

$$k_B T \gg \hbar\omega_{max}$$



ii, the low-temperature limit



but : for the acoustic branches we have

$\omega_{min} \rightarrow 0$ for $N \rightarrow \infty$!

i, the high-temperature limit

i.e. $k_B T \gg \hbar\omega_\ell(\vec{q})$ for all $\ell, \vec{q}$

→ expand the exponential in the Bose function up to 1st order in $\frac{\hbar\omega_\ell(\vec{q})}{k_B T}$:

$$\frac{1}{e^{\beta\hbar\omega_\ell(\vec{q})}-1} \approx \frac{1}{1+\beta\hbar\omega_\ell(\vec{q})-1} = \frac{k_B T}{\hbar\omega_\ell(\vec{q})}$$

$$\Rightarrow \quad E \approx \sum_{\ell\vec{q}} \left(\frac{1}{2}\hbar\omega_\ell(\vec{q}) + k_B T \right) = \sum_{\ell\vec{q}} k_B T \left(\frac{1}{2} \underbrace{\frac{\hbar\omega_\ell(\vec{q})}{k_B T}}_{\ll 1} + 1 \right)$$

$$\approx k_B T \sum_{\ell\vec{q}} 1$$

and we arrive at the high-temperature expression for the internal energy :

$$\boxed{E(T) = N d r\, k_B T} \quad \rightarrow \text{ the Dulong-Petit law}$$

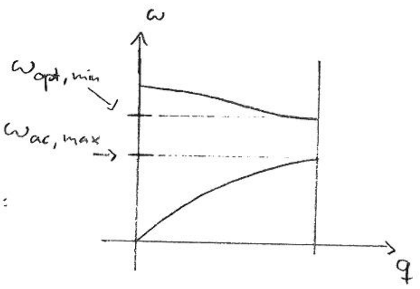
classical statistical physics : each degree of freedom which enters the Hamilton function quadratically, contributes $\frac{1}{2}k_B T$ to the internal energy

⇒ the limit of high T give the classical result for Ndr harmonic oscillators

ii, the low-temperature limit

we cannot expand in $\frac{k_B T}{\hbar\omega_\ell(\vec{q})}$

→ look at the structure of the phonon branches :



we assume that a, $k_B T \ll \hbar\omega_{opt,min}$

b, $k_B T \ll \hbar\omega_{ac,max}$

a, we can drop all the optical branches ! (except for the zero-point energy)

contribution to the internal energy :

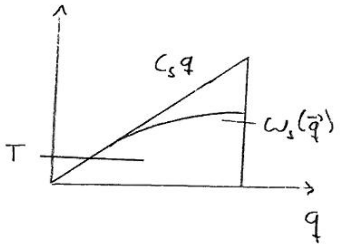
$$\sum_{\ell_0\vec{q}} \hbar\omega_{\ell_0}(\vec{q}) \underbrace{\frac{1}{e^{\beta\hbar\omega_{\ell_0}(\vec{q})}-1}}_{\approx\, e^{-\beta\hbar\omega_{\ell_0}(\vec{q})}} \qquad \sum_{\ell_0} \text{ sum over the optical branches}$$

exponentially suppressed !

b) for the d acoustic branches

$$\longrightarrow \quad \omega_s(\vec{q}) = c_s q \quad \text{for } q \to 0 \;, \quad q = |\vec{q}| \,, \quad s = 1, \dots, d$$

for sufficiently low T, we can approximate $\omega_s(\vec{q}) = c_s q$ for all $\vec{q}$!

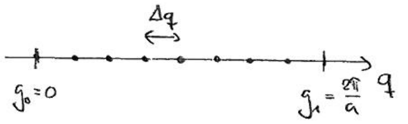


$$\Rightarrow \quad \underset{\substack{\uparrow \\ \text{keep only the acoustic branches}}}{E \approx} \underbrace{E_0}_{\text{does not depend on T and will not be evaluated further}} + \sum_{s\vec{q}} \hbar\omega_s(\vec{q}) \frac{1}{e^{\beta\hbar\omega_s(\vec{q})} - 1} \approx \dots$$

$$\dots \underset{\substack{\uparrow \\ \text{ok for low T}}}{\approx} E_0 + \sum_{s\vec{q}} \frac{\hbar c_s q}{e^{\beta\hbar c_s q} - 1}$$

how to evaluate $\sum_{\vec{q}} f(\vec{q})$?

d = 1 :
$$\sum_n f(q_n) = \frac{1}{\Delta q} \sum_n \Delta q\, f(q_n) \underset{\substack{\uparrow \\ \text{for large N}}}{\approx} \frac{1}{\Delta q} \int dq\, f(q) = \dots$$



$$\to \quad \Delta q = \frac{2\pi}{Na} = \frac{2\pi}{L}$$

$$\dots = \frac{L}{2\pi} \int dq\, f(q)$$

d = 3 :
$$\sum_{\vec{q}} f(\vec{q}) \approx \frac{V}{(2\pi)^3} \int d^3q\, f(\vec{q})$$

$$\Rightarrow \quad E - E_0 \approx \frac{V}{(2\pi)^3} \sum_s \int d^3q \frac{\hbar c_s q}{e^{\beta\hbar c_s q} - 1} = \dots \qquad \int d^3q \to 4\pi \int dq\, q^2$$

$$= \frac{V}{2\pi^2} \sum_s \int dq \frac{\hbar c_s q^3}{e^{\beta\hbar c_s q} - 1} = \dots$$

substitute : $x = \beta\hbar c_s q \quad \to \quad q = \frac{k_B T}{\hbar c_s} x \;, \quad dq = \frac{k_B T}{\hbar c_s} dx$

$$\dots = \frac{V}{2\pi^2}\,(k_B T)^4 \sum_s \frac{1}{(\hbar c_s)^3} \underbrace{\int_0^\infty dx \, \frac{x^3}{e^x - 1}}_{= \frac{\pi^4}{15}}$$

$\int_0^{\infty \to \text{ok}}$ because integrand falls off rapidly

and we arrive at

$$\boxed{E - E_0 = \frac{\pi^2}{30} V \left(\sum_s \frac{1}{(\hbar c_s)^3} \right) (k_B T)^4} \quad (*)$$

the internal energy is proportional to T^4 for low T !

to simplify eq. (*), define $\frac{1}{(\bar{c}_s)^3} = \frac{1}{d} \sum_s \frac{1}{c_s^3}$ (here : $d = 3$)

$$\Rightarrow \quad E - E_0 = \frac{\pi^2}{10} V \frac{1}{(\hbar \bar{c}_s)^3} (k_B T)^4$$

specific heat

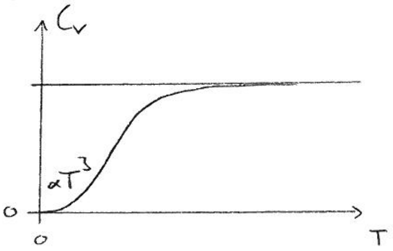
$$\boxed{C_V = \frac{1}{V} \frac{\partial E}{\partial T}} \qquad \text{(specific heat per volume)}$$

i, in the high-temperature limit

$$E(T) = 3 N r k_B T \quad \longrightarrow \quad C_V = 3 \frac{N}{V} r k_B$$

ii, low-temperature limit

$$\longrightarrow \quad C_V = \frac{2}{5} \pi^2 k_B \left(\frac{k_B T}{\hbar \bar{c}_s} \right)^3$$

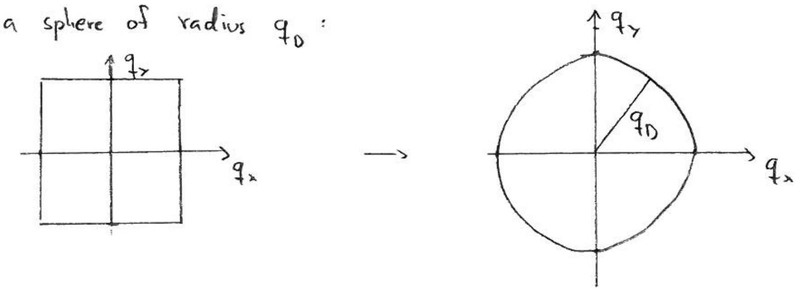


the Debye model

a simplified model which interpolates between the low- and high-T limit

assumptions

a, replace the Brillouin zone (the Wigner-Seitz cell of the reciprocal lattice) by a sphere of radius q_D :



q_D determined such that the sphere contains the same number of $\vec{q}$ - values (= N) as the Brillouin zone :

$$\sum_{\vec{q},\,|q|<q_D} 1 = N = \frac{V}{(2\pi)^3} \int_{|\vec{q}|<q_D} d^3q \; 1 = \frac{V}{(2\pi)^3} \frac{4}{3}\pi q_D^3 = \frac{V}{6\pi^2} q_D^3$$

$$\Rightarrow \quad q_D = \sqrt[3]{6\pi^2 \frac{N}{V}} \qquad q_D : \text{ Debye wave number}$$

b) in the whole sphere assume that $\omega(\vec{q}) = c_s q$ for all branches

we then obtain for the internal energy :

$$E - E_0 = \frac{V}{2\pi^2} (k_B T)^4 \frac{d}{(\hbar c_s)^3} \int_0^{x_D} dx \, \frac{x^3}{e^x - 1} \qquad \text{with} \quad x_D = \beta \hbar c_s q_D$$

now define : - Debye frequency : $\omega_D = c_s q_D$

- Debye temperature Θ_D via $k_B \Theta_D = \hbar \omega_D$

$$\Rightarrow \quad \boxed{E - E_0 = 9N \left(\frac{T}{\Theta_D}\right)^3 k_B T \int_0^{\Theta_D/T} dx \, \frac{x^3}{e^x - 1}} \qquad (\text{here} : d = 3)$$

3.6 phonon density of states

given a single - particle spectrum $\{\varepsilon_\ell\}$, $\ell = 1, \dots, N$

the density of states is defined as :

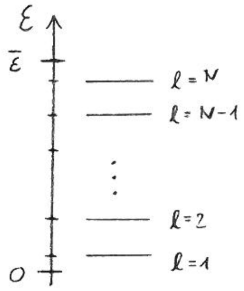
$$\boxed{\rho(\varepsilon) = \sum_{\ell=1}^{N} \delta(\varepsilon - \varepsilon_\ell)} \qquad \text{or} \qquad \boxed{\bar{\rho}(\varepsilon) = \frac{1}{N} \sum_{\ell=1}^{N} \delta(\varepsilon - \varepsilon_\ell)}$$

the total weight in $\rho(\varepsilon)$ corresponds to the number of single - particle levels :

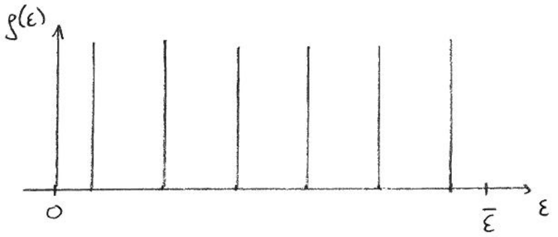
$$\int_{-\infty}^{\infty} \rho(\varepsilon)\, d\varepsilon = \sum_{\ell=1}^{N} \int_{-\infty}^{\infty} d\varepsilon \, \delta(\varepsilon - \varepsilon_\ell) = \sum_{\ell=1}^{N} 1 = N$$

whereas : $\displaystyle\int_{-\infty}^{\infty} \bar{\rho}(\varepsilon)\, d\varepsilon = 1$

example: $\varepsilon_\ell = (\ell - \frac{1}{2})\frac{\bar{\varepsilon}}{N}$, $\ell = 1, \dots, N$



$\Rightarrow$

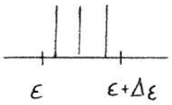


→ $\rho(\varepsilon)$ for a finite system is always a collection of δ-peaks

why 'density' of states

density of states = $\frac{\text{number of states}}{\text{energy interval}}$ → $\Delta\varepsilon \cdot \rho(\varepsilon)$ = number of states in the interval $[\varepsilon, \varepsilon + \Delta\varepsilon]$

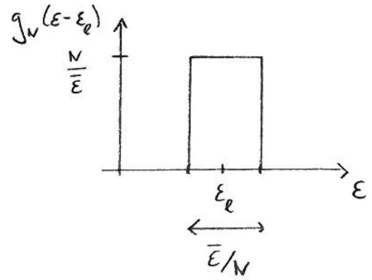
$\Delta\varepsilon \cdot \rho(\varepsilon) \approx \int_{\varepsilon}^{\varepsilon+\Delta\varepsilon} \rho(\varepsilon)\, d\varepsilon$ → counts the δ-peaks



the limit $N \to \infty$

→ representation of the δ-function via a sequence of functions:

$$\delta(x) = \lim_{N\to\infty} g_N(x) \quad , \text{ here we can use } \quad g_N(x) = \begin{cases} \frac{N}{\bar{\varepsilon}} & : \ |x| < \frac{\bar{\varepsilon}}{2N} \\ 0 & : \ \text{otherwise} \end{cases}$$

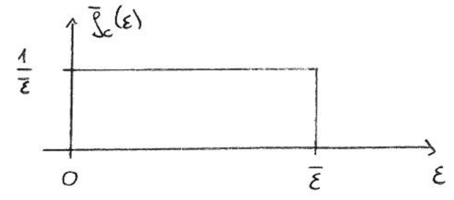


$$\rightarrow \int_{-\infty}^{\infty} g_N(x)\, dx = 1$$

now define: $\bar{\rho}_c(\varepsilon) := \lim_{N\to\infty} \bar{\rho}_N(\varepsilon) = \lim_{N\to\infty} \frac{1}{N} \sum_{\ell=1}^{N} \delta(\varepsilon - \varepsilon_\ell)$

$$\overset{!}{=} \lim_{N\to\infty} \underbrace{\frac{1}{N} \sum_{\ell=1}^{N} g_N(\varepsilon - \varepsilon_\ell)}_{= \begin{cases} N/\bar{\varepsilon} & : \ 0 \leq \varepsilon \leq \bar{\varepsilon} \\ 0 & : \ \text{othewise} \end{cases}} = \begin{cases} \frac{1}{\bar{\varepsilon}} & : \ 0 \leq \varepsilon \leq \bar{\varepsilon} \\ 0 & : \ \text{otherwise} \end{cases}$$

this gives a constant density of states :



$$\rightarrow \int_{-\infty}^{\infty} \bar{\varrho}_c(\varepsilon)\, d\varepsilon = \frac{1}{\bar{\varepsilon}}\, \bar{\varepsilon} = 1$$

in the limit $N \to \infty$, we obtain a continuous density of states

the phonon density of states

defined as $\boxed{n(\omega) = \frac{1}{N} \sum_j \sum_{\vec{q}} \delta(\omega - \omega_j(\vec{q}))}$

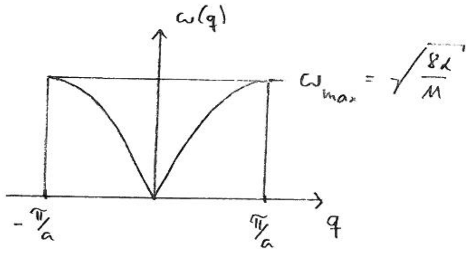
for $d = 1,\ r = 1$: $n(\omega) = \frac{1}{N} \sum_\ell \delta(\omega - \omega(q_\ell))$ with the q_ℓ equally spaced

$$\rightarrow \quad n(\omega) = \frac{1}{N} \frac{1}{\Delta q} \sum_\ell \Delta q\, \delta(\omega - \omega(q_\ell)) \qquad \left(\Delta q = \frac{2\pi}{aN}\right)$$

$$= \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dq\, \delta(\omega - \omega(q)) = \dots$$

evaluate the integral for the dispersion relation calculated in Sec. 3.2

$$\omega(q) = 2\sqrt{\frac{\alpha}{M} \underbrace{(1 - \cos(qa))}_{= 2\sin^2\left(\frac{qa}{2}\right)}} = \sqrt{\frac{8\alpha}{M}} \sin\left(\frac{qa}{2}\right)$$



$$\dots = \frac{a}{2\pi} \sum_{i=1}^{2} \frac{1}{|\omega'(q_i)|} \quad \text{with } q_i \text{ the two zeros of } \omega - \omega(q_i) = 0$$

$$\rightarrow \quad \omega_{max} \sin\left(\frac{q_i a}{2}\right) = \omega \quad \Longrightarrow \quad q_i = \frac{2}{a} \arcsin\left(\frac{\omega}{\omega_{max}}\right)$$

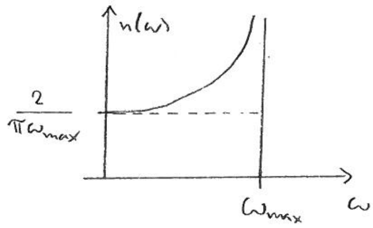
$$\rightarrow \quad \omega'(q) = \frac{a}{2} \omega_{max} \cos\left(\frac{qa}{2}\right)$$

$$\Longrightarrow \quad \omega'(q_i) = \frac{a}{2} \omega_{max} \underbrace{\cos\left(\arcsin\left(\frac{\omega}{\omega_{max}}\right)\right)} \qquad \cos^2 x = 1 - \sin^2 x$$

$$= \sqrt{1 - \sin^2\left(\arcsin\left(\frac{\omega}{\omega_{max}}\right)\right)}$$

$$= \sqrt{1 - \left(\frac{\omega}{\omega_{max}}\right)^2}$$

$$\Rightarrow \quad n(\omega) = \frac{a}{2\pi}\, 2 \, \frac{1}{\frac{a}{2}\,\omega_{max}\sqrt{1-(\omega/\omega_{max})^2}} = \frac{2}{\pi}\,\frac{1}{\sqrt{\omega_{max}^2-\omega^2}} \,, \quad 0 \le \omega < \omega_{max}$$



$\Rightarrow$ $n(\omega)$ diverges for $\omega \to \omega_{max}$!

Van Hove - singularity

density of states of the Debye model

see Sec. 3.5 : $\omega(\vec{q}) = c_s q$ for all branches , $q < q_D$

$$n_D(\omega) = \frac{1}{N}\, d \sum_{\vec{q}} \delta(\omega - \omega(\vec{q}))$$

for $r=1$: $\sum_j$ gives a factor d

$$= \frac{d}{N} \sum_{\vec{q}} \delta(\omega - c_s q)$$

$$= \frac{d}{N}\,\frac{1}{(\Delta q)^3} \sum_{\vec{q}} (\Delta q)^3\, \delta(\omega - c_s q)$$

with $(\Delta q)^3 = \frac{(2\pi)^3}{VN}$

$$= \frac{dV}{(2\pi)^3} \int d^3q\, \delta(\omega - c_s q)$$

with $\int d^3q = 4\pi \int_0^{q_D} \overset{!}{dq}\, q^2$

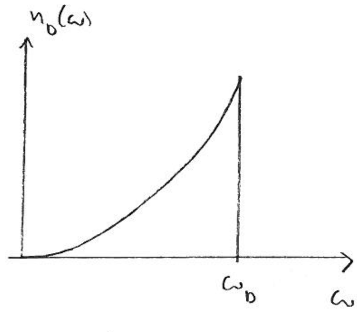
$$= \frac{dV}{2\pi^2} \underbrace{\int_0^{q_D} dq\, q^2\, \delta(\omega - c_s q)}_{= \frac{1}{c_s}\left(\frac{\omega}{c_s}\right)^2}$$

$\int dq\, a(q)\, \delta(f(q)) = \frac{a(q')}{|f'(q')|}$

with $f(q') = 0$

$$\Rightarrow \quad \boxed{n_D(\omega) = \frac{3V}{2\pi^2 c_s^3}\, \omega^2}$$

$0 \le \omega \le \omega_D$



$\propto \omega^2$ in the whole frequency range

internal energy

$\rightarrow$ calculation via the density of state

Sec. 3.5 :

$$E - E_0 = \sum_{l\vec{q}} \underbrace{\hbar\omega_l(\vec{q})\, \frac{1}{e^{\beta\hbar\omega_l(\vec{q})} - 1}}_{= e(\hbar\omega_l(\vec{q}))} = \sum_{l\vec{q}} e(\hbar\omega_l(\vec{q}))$$

with $e(x) = \frac{x}{e^{\beta x} - 1}$

instead of performing the sum $\sum_{\vec{q}}$, the internal energy can also be calculated by a one-dimensional integral:

$$\boxed{E - E_0 = N \int d\omega \; n(\omega)\, e(\hbar\omega) = N \int d\omega \; n(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}}$$

because:

$$N \int d\omega \, n(\omega)\, e(\hbar\omega) = N \int d\omega \, \frac{1}{N} \sum_{\ell} \sum_{\vec{q}} \delta(\omega - \omega_\ell(\vec{q}))\, e(\hbar\omega)$$

$$= \sum_{\ell} \sum_{\vec{q}} \underbrace{\int d\omega \; e(\hbar\omega)\, \delta(\omega - \omega_\ell(\vec{q}))}_{= \; e(\hbar\omega_\ell(\vec{q}))} \qquad \text{ok}$$

4. Electrons on a lattice (non-interacting)

→ Sec. 2.1 the general solid state Hamiltonian

$$H = T_e + T_a + V_{e\text{-}e} + V_{a\text{-}a} + V_{e\text{-}a}$$

in the spirit of Sec. 2.2 (adiabatic approximation), consider the purely electronic problem for fixed positions of the ions $\vec{R}$

$$\Rightarrow \quad H_{ee} = T_e + V_{e\text{-}e} + V_{e\text{-}a}$$

in this section

we assume that the interactions between the electrons can be ignored, i.e. $V_{e\text{-}e} = 0$

⇒ it is sufficient to study the Schrödinger equation for a single electron!

$$T_e = \frac{\vec{p}^{\,2}}{2m} \quad , \quad V_{e\text{-}a}(\vec{r}) = \sum_k v_{e\text{-}a}(\vec{r} - \vec{R}_k)$$

→ assume that the ions are fixed at lattice points $\vec{R}_k$ of a Bravais lattice L

$\sum_k$ is the sum over all lattice points of L

⇒ $V_{e\text{-}a}(\vec{r})$ has the translational invariance of the Bravais lattice L

$$\boxed{V_{e\text{-}a}(\vec{r}) = V_{e\text{-}a}(\vec{r} + \vec{R})} \qquad \forall \vec{r} \in \mathbb{R}^3 , \ \forall \vec{R} \in L$$

$$V_{e\text{-}a}(\vec{r} + \vec{R}) = \sum_k v_{e\text{-}a}(\vec{r} + \vec{R} - \vec{R}_k) \qquad \text{substitute: } \vec{R}_\ell = \vec{R}_k - \vec{R} \in L , \ \sum_k \to \sum_\ell$$

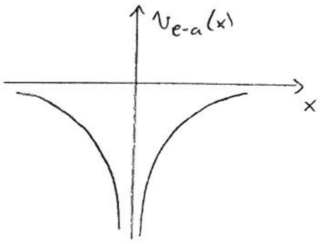
$$= \sum_\ell v_{e\text{-}a}(\vec{r} - \vec{R}_\ell) = V_{e\text{-}a}(\vec{r}) \quad \checkmark$$

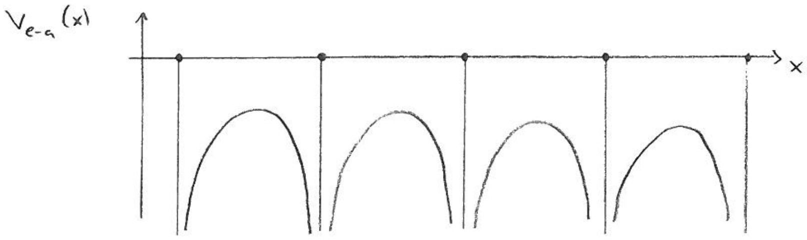
example: take for $v_{e\text{-}a}$ the bare Coulomb repulsion

$$v_{e\text{-}a}(\vec{r} - \vec{R}_k) = \frac{-Z_k e^2}{|\vec{r} - \vec{R}_k|} \quad , \quad \text{and consider } d = 1 \ \rightarrow \ v_{e\text{-}a}(x) = -\frac{Z_k e^2}{|x|}$$

$$\Rightarrow \quad V_{e\text{-}a}(x) = \sum_n v_{e\text{-}a}(x - an)$$

$$(R_n = an , \ n \in \mathbb{Z})$$





now we drop the index 'e-a' and we arrive at the Schrödinger equation of a single electron in a periodic potential $V(\vec{r})$:

$$\boxed{\underbrace{\left(-\frac{\hbar^2}{2m}\Delta + V(\vec{r})\right)}_{=H}\psi(\vec{r}) = E\,\psi(\vec{r})}$$

4.1 Bloch theorem

the Hamiltonian commutes with the translation operator $T_{\vec{R}}$, $\vec{R}\in L$

with $T_{\vec{R}}$ defined as $\boxed{T_{\vec{R}}\,f(\vec{r}) = f(\vec{r}+\vec{R})}$

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

$$T_{\vec{R}}\,H\,f(\vec{r}) = -\frac{\hbar^2}{2m}\underbrace{T_{\vec{R}}\left(\Delta f(\vec{r})\right)}_{\downarrow} + \underbrace{T_{\vec{R}}\,V(\vec{r})\,f(\vec{r})}_{=V(\vec{r}+\vec{R})\,f(\vec{r}+\vec{R})} = \dots$$

$$= \left(\Delta f(\vec{r})\right)\Big|_{\vec{r}+\vec{R}} = \Delta f(\vec{r}+\vec{R}) \qquad \left[\text{as in } f'(x+a) = \frac{d}{dx}f(x+a)\right]$$

$$\dots = \left(-\frac{\hbar^2}{2m}\Delta + \underbrace{V(\vec{r}+\vec{R})}_{=V(\vec{r})}\right)\underbrace{f(\vec{r}+\vec{R})}_{=T_{\vec{R}}\,f(\vec{r})} = H\,T_{\vec{R}}\,f(\vec{r})$$

$$\Rightarrow \quad \underbrace{\left(T_{\vec{R}}H - HT_{\vec{R}}\right)}_{=[T_{\vec{R}},H]} f(\vec{r}) = 0 \qquad ✓$$

$\Rightarrow$ we can choose a system of eigenfunctions $\psi(\vec{r})$ with

$$H\psi(\vec{r}) = E\psi(\vec{r}) \quad \text{and} \quad \boxed{T_{\vec{R}}\,\psi(\vec{r}) = c(\vec{R})\,\psi(\vec{r})}$$

with $c(\vec{R})$ the eigenvalue of the operator $T_{\vec{R}}$

propeties of $T_{\vec{R}}$:

- $T_{\vec{R}}\, T_{\vec{R}'} = T_{\vec{R}+\vec{R}'}$, follows from $T_{\vec{R}}\, T_{\vec{R}'}\, f(\vec{r}) = T_{\vec{R}}\, f(\vec{r}+\vec{R}') =$

$$= f(\vec{r}+\vec{R}+\vec{R}') = T_{\vec{R}+\vec{R}'}\, f(\vec{r}) \qquad ✓$$

- $T_{\vec{R}}\, T_{\vec{R}'} = T_{\vec{R}'}\, T_{\vec{R}} \quad \hat{=} \quad [T_{\vec{R}}, T_{\vec{R}'}] = 0$ ✓

conditions for the eigenvalue $c(\vec{R})$

- $c(\vec{R})\, c(\vec{R}') = c(\vec{R}+\vec{R}')$, follows from $\underbrace{T_{\vec{R}}\, T_{\vec{R}'}\, \psi(\vec{r})}_{= c(\vec{R})\, c(\vec{R}')\, \psi(\vec{r})} = \underbrace{T_{\vec{R}+\vec{R}'}\, \psi(\vec{r})}_{= c(\vec{R}+\vec{R}')\, \psi(\vec{r})}$

- $|c(\vec{R})|^2 = 1$

  → we assume that $\psi(\vec{r})$ can be normalized to 1 : $\int d^3r\, |\psi(\vec{r})|^2 = 1$

  ⇒ we have to consider a finite solid, as in Sec. 3.3, with volume V

  $\int d^3r \;\hat{=}\; \int_V d^3r$

  → now consider $\int_V d^3r\, |\psi(\vec{r}+\vec{R})|^2$ and use periodic boundary conditions

$$\boxed{\psi(\vec{r} + N_\alpha \vec{a}_\alpha) = \psi(\vec{r})} \quad \Rightarrow \quad \int_V d^3r\, |\psi(\vec{r}+\vec{R})|^2 = 1 = \dots$$

$$\dots = |c(\vec{R})|^2 \underbrace{\int_V d^3r\, |\psi(\vec{r})|^2}_{=1} \qquad ✓$$

this means that $c(\vec{R})$ is of the form $c(\vec{R}) = e^{i f(\vec{R})}$

→ insert this into $c(\vec{R})\, c(\vec{R}') = c(\vec{R}+\vec{R}')$:

$$e^{i f(\vec{R})}\, e^{i f(\vec{R}')} = e^{i f(\vec{R}+\vec{R}')} \quad \Rightarrow \quad f(\vec{R}) + f(\vec{R}') = f(\vec{R}+\vec{R}')$$

in particular for $\vec{R}$ and $\vec{R}'$ in the direction of $\vec{a}_1$:

$$\left.\begin{aligned} \vec{R} &= m\vec{a}_1 \\ \vec{R}' &= n\vec{a}_1 \end{aligned}\right\} \quad f(m\vec{a}_1) + f(n\vec{a}_1) = f((m+n)\vec{a}_1)$$

$\Rightarrow$ $f(m_1 \vec{a}_1)$ has to be a linear function of m_1

$\rightarrow$ $f(m_1 \vec{a}_1) = \alpha_1 m_1$

add the othe directions : $f(\vec{R}) = \sum_{i=1}^{3} \alpha_i m_i \overset{!}{=} \vec{k} \cdot \vec{R}$

with $\vec{k} = \sum_{i=1}^{3} \alpha_i \vec{b}_i$

$\hookrightarrow$ the primitive vectors of L_r

so we arrive at

$$c(\vec{R}) = e^{i\vec{k}\cdot\vec{R}} \quad \text{and} \quad \boxed{\psi(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\,\psi(\vec{r})}$$

<u>this means</u>:
- the wave function $\psi(\vec{r})$ is not periodic (for $\vec{k} \neq \vec{0}$)
- but the electron density is periodic : $|\psi(\vec{r}+\vec{R})|^2 = |\psi(\vec{r})|^2$

<u>the vector $\vec{k}$</u> :

the function $a(\vec{k}) = e^{i\vec{k}\cdot\vec{R}}$, $\vec{R} \in L$, is periodic with respect to the reciprocal lattice L_f (as in Sec. 3.3)

$\rightarrow$ restrict the $\vec{k}$-values to one unit cell of L_f

<u>then</u>: periodic boundary conditions give a discrete set of allowed $\vec{k}$-values

$$\vec{k}(m_1, \dots, m_d) = \sum_{\beta=1}^{d} \frac{m_\beta}{N_\beta} \vec{b}_\beta \quad , \quad m_\beta = 0, 1, \dots, N_\beta - 1$$

now define a function

$$\boxed{u_{\vec{k}}(\vec{r}) = e^{-i\vec{k}\cdot\vec{r}}\, \psi_{\vec{k}}(\vec{r})} \quad (*)$$

($\vec{k}$ is used as a label for the eigenstates $\psi_{\vec{k}}(\vec{r})$)

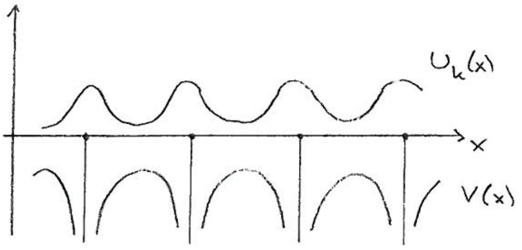
$u_{\vec{k}}(\vec{r})$ ist periodic :

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

$$= e^{-i\vec{k}\cdot\vec{r}} \underbrace{e^{-i\vec{k}\cdot\vec{R}}\, e^{i\vec{k}\cdot\vec{R}}}_{=1} \psi(\vec{r}) = u_{\vec{k}}(\vec{r})$$

this gives the Bloch theorem: $$\boxed{\psi_{\vec k}(\vec r) = e^{i\vec k\cdot\vec r}\, u_{\vec k}(\vec r)}$$

→ the solution of the (single-particle) Schrödinger equation, $H\psi_{\vec k}(\vec r) = E(\vec k)\,\psi_{\vec k}(\vec r)$, can be written as a product of the plane-wave factor $e^{i\vec k\cdot\vec r}$ and a lattice periodic Bloch factor $u_{\vec k}(\vec r)$!



now: derive a differential equation for $u_{\vec k}(\vec r)$

$$H\psi_{\vec k}(\vec r) = \left(-\frac{\hbar^2}{2m}\Delta + V(\vec r)\right) e^{i\vec k\cdot\vec r}\, u_{\vec k}(\vec r) = \dots$$

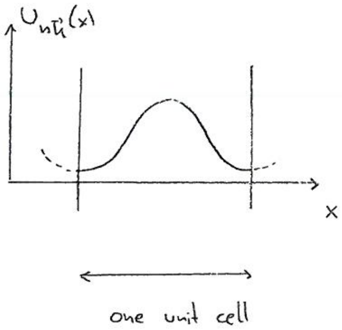
$$\Delta e^{i\vec k\cdot\vec r}\, u_{\vec k}(\vec r) = e^{i\vec k\cdot\vec r}\left(-k^2 + 2i\,\vec k\cdot\vec\nabla + \Delta\right) u_{\vec k}(\vec r)$$

$$\dots = e^{i\vec k\cdot\vec r}\underbrace{\left[\frac{\hbar^2}{2m}\left(k^2 - 2i\,\vec k\cdot\vec\nabla - \Delta\right) + V(\vec r)\right]}_{= h(\vec k)} u_{\vec k}(\vec r) = E(\vec k)\, e^{i\vec k\cdot\vec r}\, u_{\vec k}(\vec r)$$

$$\Rightarrow \quad \boxed{h(\vec k)\, u_{\vec k}(\vec r) = E(\vec k)\, u_{\vec k}(\vec r)} \; (*) \qquad h(\vec k): \text{ effective Hamiltonian}$$

this means:
- we have to solve one partial differential equation for each $\vec k \in$ Brillouin zone
- it is sufficient to solve eq. (*) for $\vec r \in$ one unit cell of the Bravais lattice

  → take care of the boundary conditions !



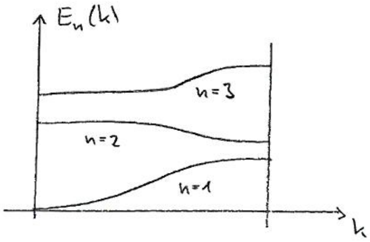
⇒ the eigenvalues of (*) are discrete

$$h(\vec k)\, u_{n\vec k}(\vec r) = E_n(\vec k)\, u_{n\vec k}(\vec r)$$

$$n = 1, 2, \dots \infty$$

→ the quantum number n labels the 'electronic bands'

→ band structure : the dependence of the eigenenergies E_n on $\vec{k}$



the $u_{n\vec{k}}(\vec{r})$ can be normalized within each unit cell of the direct lattice

$$\boxed{\frac{1}{V_{uc}} \int_{V_{uc}} d^3r \; u^*_{n\vec{k}}(\vec{r}) \, u_{n'\vec{k}}(\vec{r}) = \delta_{nn'}}$$

V_{uc} : volume of the unit cell

→ follows directly from the $u_{n\vec{k}}(\vec{r})$ being the solutions of (*)

→ normalization of the full wave functions $\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \, u_{n\vec{k}}(\vec{r})$

$$\int_V d^3r \; \psi^*_{n\vec{k}}(\vec{r}) \, \psi_{n'\vec{k}'}(\vec{r}) = \ldots$$

V : the whole volume → $\int_V d^3r = \sum_{\vec{R}} \int_{V_{uc}(\vec{R})} d^3r$

↳ the unit cell at the lattice vector $\vec{R}$

$$\ldots = \sum_{\vec{R}} \int_{V_{uc}(\vec{R})} d^3r \; e^{i(\vec{k}'-\vec{k})\cdot\vec{r}} \, u^*_{n\vec{k}}(\vec{r}) \, u_{n'\vec{k}'}(\vec{r}) = \ldots$$

for each $\vec{R}$ substitute $\vec{r}\,' = \vec{r} - \vec{R}$ ⇒ $\int d^3r'$ covers the volume $V_{uc}(\vec{0}) = V_{uc}$

$$\ldots = \sum_{\vec{R}} \int_{V_{uc}} d^3r' \; e^{i(\vec{k}'-\vec{k})\cdot(\vec{r}\,'+\vec{R})} \, \underbrace{u^*_{n\vec{k}}(\vec{r}\,'+\vec{R})}_{= u^*_{n\vec{k}}(\vec{r}\,')} \, \underbrace{u_{n'\vec{k}'}(\vec{r}\,'+\vec{R})}_{= u_{n'\vec{k}'}(\vec{r}\,')} =$$

$$= \int_{V_{uc}} d^3r' \; \underbrace{e^{i(\vec{k}'-\vec{k})\cdot\vec{r}\,'}}_{1} \, u^*_{n\vec{k}}(\vec{r}\,') \, u_{n'\overset{\uparrow\,=\vec{k}}{\vec{k}'}}(\vec{r}\,') \underbrace{\sum_{\vec{R}} e^{i(\vec{k}'-\vec{k})\cdot\vec{R}}}_{= N\delta_{\vec{k},\vec{k}'}} =$$

$$= N \underbrace{\int_{V_{uc}} d^3r' \; u^*_{n\vec{k}}(\vec{r}\,') \, u_{n'\vec{k}}(\vec{r}\,')}_{= V_{uc}\,\delta_{nn'}} \, \delta_{\vec{k},\vec{k}'} = N V_{uc} \, \delta_{nn'} \, \delta_{\vec{k}\vec{k}'}$$

the Fourier-transformed Schrödinger equation

the potential $V(\vec{r})$ is periodic : $V(\vec{r}) = V(\vec{r}+\vec{R})$

=> we can write
Sec. 1.3

$$\boxed{V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}}\, e^{i\vec{G}\cdot\vec{r}}} \quad (1)$$

↳ sum over all reciprocal lattice vectors $\vec{G} \in L_r$

the wave function $\psi(\vec{r})$ can be written as a Fourier series :

$$\boxed{\psi(\vec{r}) = \sum_{\vec{q}} c_{\vec{q}}\, e^{i\vec{q}\cdot\vec{r}}} \quad (2)$$

$\psi(\vec{r})$ does <u>not</u> have the translational invariance of L, but it should fulfill periodic boundary conditions (Sec. 3.3)

$\rightarrow \psi(\vec{r}) = \psi(\vec{r} + N_\alpha \vec{a}_\alpha)$ (same notation as in Sec. 3.3)

$$\Rightarrow \quad \vec{q} = \sum_{\beta=1}^{d} \frac{m_\beta}{N_\beta} \vec{b}_\beta$$

$m_\beta \in \mathbb{Z}$ arbitrary

→ $\vec{q}$ is not restricted to the Brillouin zone

insert (1) and (2) into the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\Delta + V(\vec{r})\right)\psi(\vec{r}) = E\,\psi(\vec{r})$$

$$\rightarrow \left(-\frac{\hbar^2}{2m}\Delta + \sum_{\vec{G}} V_{\vec{G}}\, e^{i\vec{G}\cdot\vec{r}}\right) \sum_{\vec{q}} c_{\vec{q}}\, e^{i\vec{q}\cdot\vec{r}} = E \sum_{\vec{q}} c_{\vec{q}}\, e^{i\vec{q}\cdot\vec{r}}$$

acts on

with $\Delta e^{i\vec{q}\cdot\vec{r}} = -q^2 e^{i\vec{q}\cdot\vec{r}}$ the left-hand side gives :

$$\sum_{\vec{q}} \frac{\hbar^2 q^2}{2m} c_{\vec{q}}\, e^{i\vec{q}\cdot\vec{r}} + \underbrace{\sum_{\vec{q}\,\vec{G}} V_{\vec{G}}\, e^{i(\vec{G}+\vec{q})\cdot\vec{r}}\, c_{\vec{q}}} = \dots$$

substitute $\vec{q}\,' = \vec{q} + \vec{G}$ → $\sum_{\vec{q}} \rightarrow \sum_{\vec{q}\,'}$ (ok because the range of $\vec{q}$-values is not restricted)

$$\dots = \sum_{\vec{q}} \left[\frac{\hbar^2 q^2}{2m} c_{\vec{q}} + \sum_{\vec{G}} V_{\vec{G}}\, c_{\vec{q}-\vec{G}} \right] e^{i\vec{q}\cdot\vec{r}} = \underbrace{\sum_{\vec{q}} E\, c_{\vec{q}}\, e^{i\vec{q}\cdot\vec{r}}}$$

include this term in

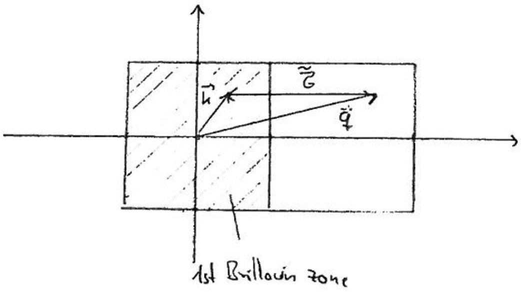
$$\rightarrow \left(\frac{\hbar^2 q^2}{2m} - E\right) c_{\vec{q}} + \dots$$

$$\Rightarrow \quad \left(\frac{\hbar^2 q^2}{2m} - E\right) c_{\vec q} + \sum_{\vec G} V_{\vec G}\, c_{\vec q - \vec G} = 0$$

the vector $\vec q$ can be written as :

$$\vec q + \tilde{\vec G} = \vec k$$

with $\tilde{\vec G} \in L_r$ and $\vec k \in$ Brillouin zone



$$\Rightarrow \quad \left[\frac{\hbar^2}{2m}(\vec k - \tilde{\vec G})^2 - E\right] c_{\vec k - \tilde{\vec G}} + \underbrace{\sum_{\vec G} V_{\vec G}\, c_{\vec k - \tilde{\vec G} - \vec G}}_{\text{substitute } \vec G' = \vec G + \tilde{\vec G}\ ;\ \sum_{\vec G} \to \sum_{\vec G'}} = 0$$

and we arrive at the Fourier-transformed Schrödinger equation :

$$\boxed{\left[\frac{\hbar^2}{2m}(\vec k - \tilde{\vec G})^2 - E\right] c_{\vec k - \tilde{\vec G}} + \sum_{\vec G} V_{\vec G - \tilde{\vec G}}\, c_{\vec k - \vec G} = 0}$$

→ a set of linear equations for the coefficients $c_{\vec k - \vec G}$ with $\vec k \in$ BZ fixed and $\vec G \in L_r$

4.2 the nearly-free electron model

start with free electrons ($V(\vec r) = 0$) ; later : include the potential within perturbation theory

for $V(\vec r) = 0$ we have $\left[\frac{\hbar^2}{2m}(\vec k - \tilde{\vec G})^2 - E^{(0)}\right] c_{\vec k - \tilde{\vec G}} = 0$ (drop the ~)

$$\Rightarrow \quad \boxed{E^{(0)} = E^{(0)}_{\vec G}(\vec k) = \frac{\hbar^2}{2m}(\vec k - \vec G)^2} \qquad (0) : \text{zeroth order in } V(\vec r)$$

→ the reciprocal lattice vector $\vec G$ labels the different bands within the 1st Brillouin zone

Comparison with the free-electron case

$$-\frac{\hbar^2}{2m}\Delta \psi_{\vec q}(\vec r) = \varepsilon(\vec q)\, \psi_{\vec q}(\vec r) \quad \to \quad \psi_{\vec q}(\vec r) = e^{i\vec q\cdot\vec r}$$

and $\varepsilon(\vec q) = \frac{\hbar^2 q^2}{2m}$

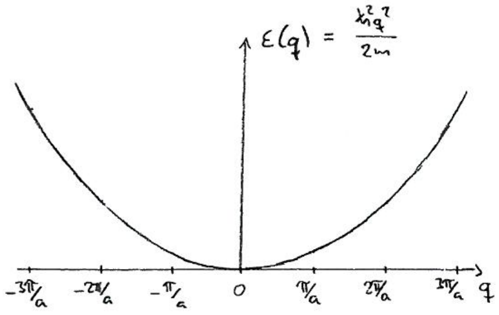
$$\to \quad \varepsilon(\vec k - \vec G) = E^{(0)}_{\vec G}(\vec k)$$

- for each $\vec{G} \in L_r$, the function $E_{\vec{G}}(\vec{k})$ with $\vec{k} \in BZ$, corresponds to one electronic band
- the collection of the $E_{\vec{G}}(\vec{k})$ corresponds to the electronic band structure

band structure for d=1

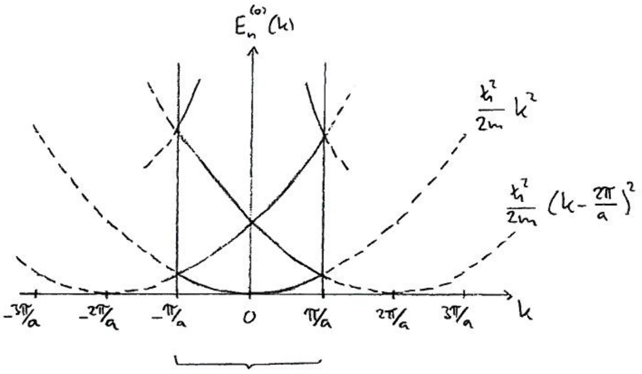
$$\vec{G} \longrightarrow g_n = \frac{2\pi}{a} n \quad , \quad n \in \mathbb{Z} \quad ; \quad k \in \left[-\frac{\pi}{a}, \frac{\pi}{a} \right[$$

$$\Rightarrow \quad \boxed{E_n^{(0)}(\vec{k}) = \frac{\hbar^2}{2m} \left(k - \frac{2\pi}{a} n \right)^2}$$



the extended-zone scheme

$\longrightarrow$ each unit cell of the reciprocal lattice contains one band



the reduced-zone scheme

$\longrightarrow$ all bands are shown within the first Brillouin zone

now: corrections to the band structure for $V(\vec{r}) \neq 0$

start from the Fourie transformed Schrödinge equation:

$$\Big(\underbrace{\frac{\hbar^2}{2m} (\vec{k} - \vec{G}_0)^2}_{= E^{(0)}_{\vec{G}_0}(\vec{k})} - E \Big) c_{\vec{k} - \vec{G}_0} = - \underbrace{V_{\vec{G}_0 - \vec{G}_0}}_{= V_{\vec{0}}} c_{\vec{k} - \vec{G}_0} - \sum_{\vec{G} \neq \vec{G}_0} V_{\vec{G} - \vec{G}_0} c_{\vec{k} - \vec{G}}$$

the Fourie coefficients of the potential $V(\vec{r})$ are defined as:

$$V_{\vec{G}} = \frac{1}{v} \int_v d^3r \, V(\vec{r}) \, e^{-i \vec{G} \cdot \vec{r}}$$

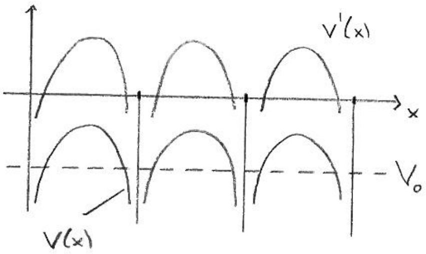
with the integral ove one unit cell of the direct lattice

for late use: $(V_{\vec{G}})^* = \frac{1}{v} \int_v d^3r \, V(\vec{r}) \, e^{i \vec{G} \cdot \vec{r}} = V_{-\vec{G}}$

$V_{\vec{0}} = \frac{1}{v} \int_v d^3r \, V(\vec{r})$ can be set to zero

formally: define a potential $V'(\vec{r}) = V(\vec{r}) - V_{\vec{0}}$

- gives the same eigenstate
- eigenenergie are shifted by $V_{\vec{0}}$



$$\Rightarrow \quad \boxed{\left(E - E^{(0)}_{\vec{G}_0}(\vec{k})\right) C_{\vec{k}-\vec{G}_0} = \sum_{\vec{G} \neq \vec{G}_0} V_{\vec{G}-\vec{G}_0} \, C_{\vec{k}-\vec{G}}} \quad (*)$$

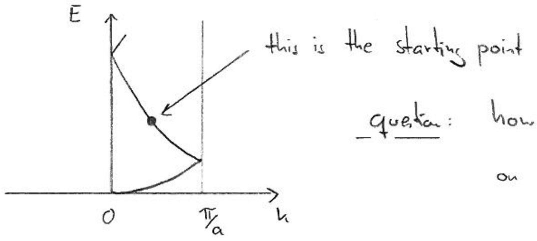
→ start from the limit $V = 0$ of eq. (*), with a given $\vec{k}$ and $\vec{G}_0$:

$$\left(E - E^{(0)}_{\vec{G}_0}(\vec{k})\right) C_{\vec{k}-\vec{G}_0} = 0$$

→ solution of the Schrödinge equation is the wave function $\psi(\vec{r}) = e^{i(\vec{k}-\vec{G}_0)\cdot\vec{r}}$

⇒ we have a single Fourier coefficient $C_{\vec{k}-\vec{G}_0} \neq 0$ (all the othe $C_{\vec{k}-\vec{G}}$ are $= 0$)

and the eigenenegy is $E = E^{(0)}_{\vec{G}_0}(\vec{k})$



questn: how does the energy change, when we switch on the potential?

rewrite eq. (*):

$$E = E^{(0)}_{\vec{G}_0}(\vec{k}) + \frac{1}{C_{\vec{k}-\vec{G}_0}} \sum_{\vec{G} \neq \vec{G}_0} V_{\vec{G}-\vec{G}_0} \underbrace{C_{\vec{k}-\vec{G}}} = \dots$$

$$\text{with eq. } (*) \longrightarrow = \frac{1}{E - E^{(0)}_{\vec{G}}(\vec{k})} \sum_{\tilde{\vec{G}} \neq \vec{G}} V_{\tilde{\vec{G}}-\vec{G}} \, C_{\vec{k}-\tilde{\vec{G}}}$$

$$\dots = E^{(0)}_{\vec{G}_0}(\vec{k}) + \frac{1}{C_{\vec{k}-\vec{G}_0}} \sum_{\vec{G} \neq \vec{G}_0} \frac{1}{E - E^{(0)}_{\vec{G}}(\vec{k})} V_{\vec{G}-\vec{G}_0} \sum_{\tilde{\vec{G}} \neq \vec{G}} V_{\tilde{\vec{G}}-\vec{G}} \, C_{\vec{k}-\tilde{\vec{G}}}$$

↓

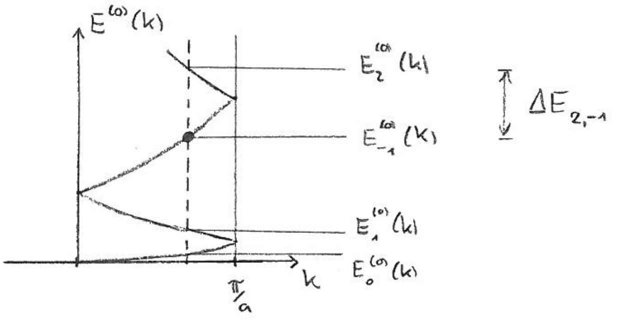
can be replaced by $E^{(0)}_{\vec{G}_0}(\vec{k})$ because the corrections give contibutions of orde $O(V^3)$

decompose the $\sum_{\tilde{\vec{G}} \neq \vec{G}}$:

$$V_{\vec{G}_0 - \vec{G}}\, C_{\vec{k} - \vec{G}_0} + \sum_{\tilde{\vec{G}} \neq \vec{G}_0, \vec{G}} V_{\tilde{\vec{G}} - \vec{G}}\, \underbrace{C_{\vec{k} - \tilde{\vec{G}}}}_{\text{using eq. (*) again gives contributions of order } O(V^3)}$$

$$\ldots = E^{(0)}_{\vec{G}_0}(\vec{k}) + \sum_{\vec{G} \neq \vec{G}_0} \frac{1}{E^{(0)}_{\vec{G}_0}(\vec{k}) - E^{(0)}_{\vec{G}}(\vec{k})} \underbrace{V_{\vec{G} - \vec{G}_0} V_{\vec{G}_0 - \vec{G}}}_{= |V_{\vec{G} - \vec{G}_0}|^2} + O(V^3)$$

$$\Longrightarrow \boxed{E(\vec{k}) = E^{(0)}_{\vec{G}_0}(\vec{k}) + \sum_{\vec{G} \neq \vec{G}_0} \frac{|V_{\vec{G} - \vec{G}_0}|^2}{E^{(0)}_{\vec{G}_0}(\vec{k}) - E^{(0)}_{\vec{G}}(\vec{k})} + O(V^3)} \quad (*)$$



each contribution to the shift of the energies $E^{(0)}_{\vec{G}_0}(\vec{k})$ contains a factor

$$\frac{1}{\Delta E_{\vec{G}_0, \vec{G}}} = \frac{1}{E^{(0)}_{\vec{G}_0}(\vec{k}) - E^{(0)}_{\vec{G}}(\vec{k})}$$

what happens when $\Delta E_{\vec{G}_0, \vec{G}} \to 0$?

that is $E^{(0)}_{\vec{G}}(\vec{k}) \to E^{(0)}_{\vec{G}_0}(\vec{k})$ for $\vec{G} \neq \vec{G}_0$

$\Delta E \to 0$ at the boundaries of the Brillouin zone !

$\longrightarrow$ there is one reciprocal lattice vector $\vec{G}_1 \neq \vec{G}_0$ in the sum $\sum_{\vec{G} \neq \vec{G}_0}$ with

$$|\Delta E_{\vec{G}_0, \vec{G}_1}| \ll |V_{\vec{G}_1 - \vec{G}_0}|^2$$

$\Rightarrow$ go back one step and keep $E(\vec{k})$ instead of replacing it by $E^{(0)}_{\vec{G}_0}(\vec{k})$ in this term :

$$\underbrace{E(\vec{k}) = E^{(0)}_{\vec{G}_0}(\vec{k}) + \frac{|V_{\vec{G}_1 - \vec{G}_0}|^2}{E(\vec{k}) - E^{(0)}_{\vec{G}_1}(\vec{k})}}_{\text{corresponds to a quadratic equation for } E(\vec{k})} + \sum_{\vec{G} \neq \vec{G}_0, \vec{G}_1} \underbrace{\frac{|V_{\vec{G} - \vec{G}_0}|^2}{E^{(0)}_{\vec{G}_0}(\vec{k}) - E^{(0)}_{\vec{G}}(\vec{k})}}_{\text{can be neglected since}} + O(V^3)$$

$E(\vec{k}) - E^{(0)}_{\vec{G}_1}(\vec{k}) \ll E^{(0)}_{\vec{G}_0}(\vec{k}) - E^{(0)}_{\vec{G}}(\vec{k})$

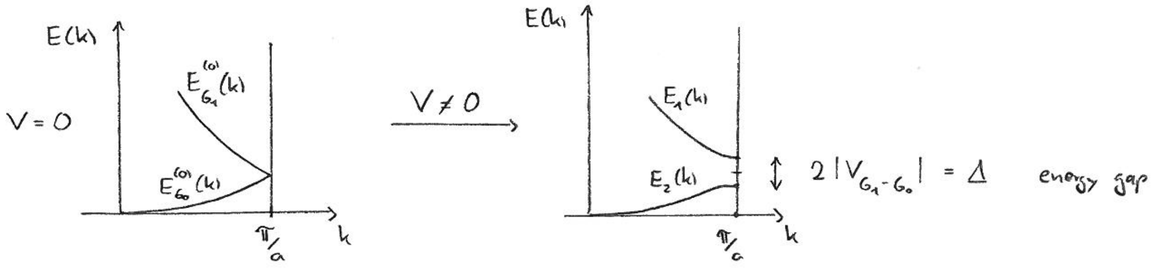
for all $\vec{G} \neq \vec{G}_1$!

solution of the quadratic equation gives:

$$\boxed{E_{1/2}(\vec{k}) = \frac{1}{2}\left(E^{(0)}_{\vec{G}_0}(\vec{k}) + E^{(0)}_{\vec{G}_1}(\vec{k})\right) \pm \frac{1}{2}\sqrt{\left(E^{(0)}_{\vec{G}_0}(\vec{k}) - E^{(0)}_{\vec{G}_1}(\vec{k})\right)^2 + 4\left|V_{\vec{G}_1-\vec{G}_0}\right|^2}}$$

in the limit $E^{(0)}_{\vec{G}_1}(\vec{k}) \longrightarrow E^{(0)}_{\vec{G}_0}(\vec{k})$:

$$E_{1/2}(\vec{k}) = E^{(0)}_{\vec{G}_0}(\vec{k}) \pm \left|V_{\vec{G}_1-\vec{G}_0}\right|$$



→ the potential $V(\vec{r})$ opens a gap $\Delta = 2\left|V_{\vec{G}_1-\vec{G}_0}\right|$ in the bandstructure at the zone boundaries!

4.3 the effective mass

Start from the differential equation for the Bloch factors $u_{n\vec{k}}(\vec{r})$ (Sec. 4.1):

$$h(\vec{k})\, u_{n\vec{k}}(\vec{r}) = E_n(\vec{k})\, u_{n\vec{k}}(\vec{r}) \qquad (*)$$

with the effective Hamiltonian

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

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

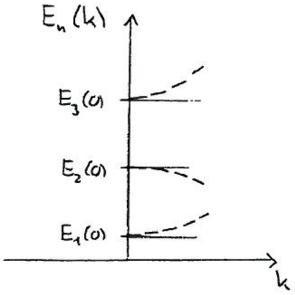
→ we can split up the effective Hamiltonian as:

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

we now assume that eq. (*) has been solved for $\vec{k} = \vec{0}$:

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

with a non-degenerate spectrum $\{E_n(\vec{0})\}$



⟶ treat $h_1(\vec{k})$ as a perturbation (ok for small values of k) to calculate the $\vec{k}$-dependence of $E_n(\vec{k})$ (valid for small k)

the energie up to 2nd order in the perturbation:

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

the 1st order term:

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

(proof see exercise)

the matrix elements in the 2nd order term:

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

$$\Rightarrow \quad E_n(\vec{k}) = E_n(\vec{0}) + \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2}{m^2} \sum_{\alpha\alpha'} k_\alpha k_{\alpha'} \sum_{n' \neq n} \frac{\langle n^{(0)} | p_\alpha | n'^{(0)} \rangle \langle n'^{(0)} | p_{\alpha'} | n^{(0)} \rangle}{E_n(\vec{0}) - E_{n'}(\vec{0})}$$

this means: for small k, $E_n(\vec{k})$ is quadratic in the k_α

the effective-mass tensor

definition:

$$\boxed{\left(\frac{1}{m^*(n)} \right)_{\alpha\alpha'} = \frac{1}{\hbar^2} \frac{\partial^2 E_n(\vec{k})}{\partial k_\alpha \partial k_{\alpha'}}}$$

the free electron part gives:

$$\frac{1}{\hbar^2} \frac{\partial^2}{\partial k_\alpha \partial k_{\alpha'}} \frac{\hbar^2 k^2}{2m} = \frac{1}{2m} \frac{\partial^2}{\partial k_\alpha \partial k_{\alpha'}} (k_x k_x + k_y k_y + k_z k_z)$$

$$= \frac{1}{2m} 2 \delta_{\alpha\alpha'} = \frac{1}{m} \delta_{\alpha\alpha'}$$

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

the 2nd order part gives:

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

$\alpha = \alpha'$: $\frac{2}{m^2} f_{\alpha\alpha}$

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

4.4 the tight-binding model

start from the Schrödinger equation of a single electron in a periodic potential $V(\vec{r})$:

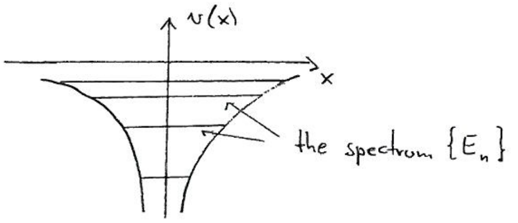
$$H \psi(\vec{r}) = E \psi(\vec{r}) \qquad \text{with} \qquad H = -\frac{\hbar^2}{2m} \Delta + V(\vec{r})$$

$$\text{and} \qquad V(\vec{r}) = \sum_{\vec{R}} v(\vec{r} - \vec{R})$$

now define an atomic problem

$$H_{at} \varphi_n(\vec{r}) = E_n \varphi_n(\vec{r}) \qquad \text{with} \qquad H_{at} = -\frac{\hbar^2}{2m} \Delta + v(\vec{r})$$

assume that the atomic problem has been solved, i.e the $\{E_n\}, \{\varphi_n(\vec{r})\}$ are known



and an atomic problem for each lattice vector $\vec{R}$

$$H_{at,\vec{R}} = -\frac{\hbar^2}{2m} \Delta + v(\vec{r} - \vec{R}) \quad \rightarrow \quad H_{at,\vec{R}} \varphi_n(\vec{r} - \vec{R}) = E_n \varphi_n(\vec{r} - \vec{R})$$

the full Hamiltonian can be decomposed as

$$H = \underbrace{-\frac{\hbar^2}{2m} \Delta + v(\vec{r} - \vec{R})}_{= H_{at,\vec{R}}} + \underbrace{\sum_{\vec{R}' \neq \vec{R}} v(\vec{r} - \vec{R}')}_{=: \Delta V_{\vec{R}}(\vec{r})}$$

we can now construct Bloch states (= wave functions which obey the Bloch theorem) via

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

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

substitute $\vec{R}'' = \vec{R}' - \vec{R} \quad \rightarrow \quad \sum_{\vec{R}'} \rightarrow \sum_{\vec{R}''}$

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

$$= e^{i\vec{k}\cdot\vec{R}} \psi_{n\vec{k}}(\vec{r}) \quad \Rightarrow \quad u_{n\vec{k}}(\vec{r}) = e^{-i\vec{k}\cdot\vec{r}} \psi_{n\vec{k}}(\vec{r}) \text{ is periodic}$$

(see Sec. 4.1)

are the $\varphi_n(\vec{r}-\vec{R})$ eigenstate of H ?

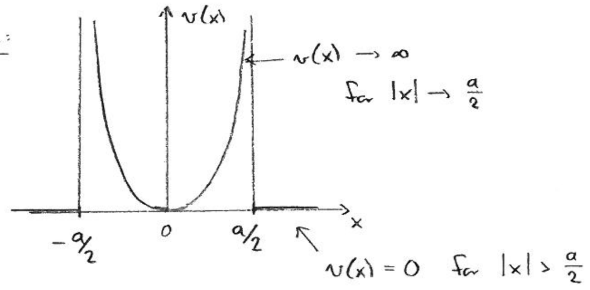
$$H \varphi_n(\vec{r}-\vec{R}) = (H_{at,\vec{R}} + \Delta V_{\vec{R}}(\vec{r}))\, \varphi_n(\vec{r}-\vec{R}) = E_n \varphi_n(\vec{r}-\vec{R}) + \underbrace{\Delta V_{\vec{R}}(\vec{r}) \varphi_n(\vec{r}-\vec{R})}_{= g_{\vec{R}}(\vec{r})}$$

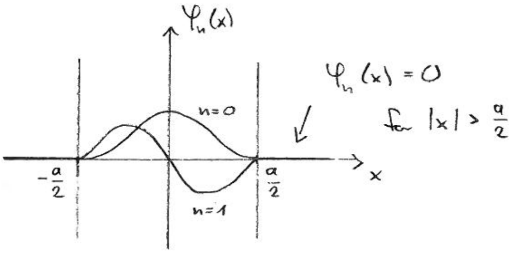
$\rightarrow$ eigenstate if $g_{\vec{R}}(\vec{r}) = 0$ (sufficient condition)

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

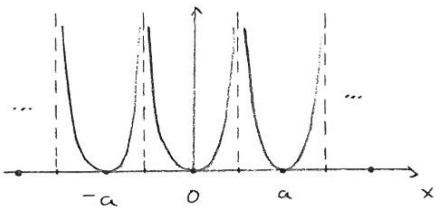
and ii) $\Delta V_{\vec{R}}(\vec{r}) = 0$ — " — inside — " —

example:

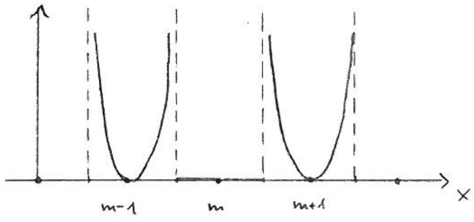




$$\rightarrow V(x) = \sum_n v(x-na)$$



$$\Delta V_m(x) = \sum_{n\neq m} v(x-na)$$



in the case of $g_{\vec{R}}(\vec{r}) = 0$, calculate the band structure $E_n(\vec{k})$

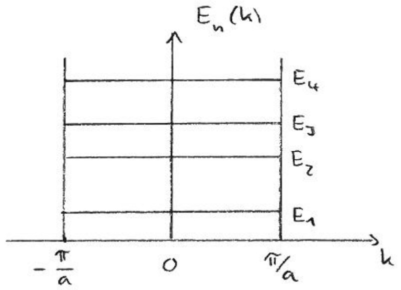
$$\longrightarrow \quad H\,\psi_{n\vec{k}}(\vec{r}) = E_n(\vec{k})\,\psi_{n\vec{k}}(\vec{r})$$

↳ the Blochstate defined above

$$H \underbrace{\frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \varphi_n(\vec{r}-\vec{R})} \underset{\substack{\uparrow \\ \text{for } g_{\vec{R}}(\vec{r})=0}}{=} \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} E_n \varphi_n(\vec{r}-\vec{R}) = E_n\,\psi_{n\vec{k}}(\vec{r})$$

$$\Longrightarrow \quad E_n(\vec{k}) = E_n$$

localized state give rise to dispersionless bands



the general case, $g(\vec{r}) \neq 0$

$$H\,\psi_{n\vec{k}}(\vec{r}) = E_n(\vec{k})\,\psi_{n\vec{k}}(\vec{r}) \qquad \text{no longe valid !}$$

but, as an approximation for $E_n(\vec{k})$, we can use

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

(→ Ritz variational method of quantum mechanics)

a) $\langle \psi_{n\vec{k}} | \psi_{n'\vec{k}} \rangle = \ldots$

$$\ldots = \frac{1}{N} \sum_{\vec{R}_1} \sum_{\vec{R}_2} \int d^3r\, e^{-i\vec{k}\cdot\vec{R}_1} e^{i\vec{k}\cdot\vec{R}_2} \varphi_n^*(\vec{r}-\vec{R}_1)\,\varphi_{n'}(\vec{r}-\vec{R}_2) = \ldots$$

subsitute $\vec{r}\,' = \vec{r} - \vec{R}_2$, $\int d^3r \to \int d^3r'$ the integral is ove the whole volume

$$\ldots = \frac{1}{N} \sum_{\vec{R}_1} \sum_{\vec{R}_2} e^{i\vec{k}\cdot(\vec{R}_2-\vec{R}_1)} \int d^3r'\, \varphi_n^*(\vec{r}\,'+\vec{R}_2-\vec{R}_1)\,\varphi_{n'}(\vec{r}\,') = \ldots$$

substitute $\vec{R} = \vec{R}_1 - \vec{R}_2$, $\sum_{\vec{R}_2} \longrightarrow \sum_{\vec{R}}$

$$\ldots = \frac{1}{N} \sum_{\vec{R}_1} \sum_{\vec{R}} e^{-i\vec{k}\cdot\vec{R}} \int d^3r'\, \varphi_n^*(\vec{r}\,'-\vec{R})\,\varphi_{n'}(\vec{r}\,') = \ldots$$

$\sum_{\vec{R}_1} \dots$ $\hookrightarrow$ does not depend on $\vec{R}_1$ $\Rightarrow$ $\sum_{\vec{R}_1}$ gives a factor N

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

with $\int d^3r\, \varphi_n^*(\vec{r})\, \varphi_{n'}(\vec{r}) = \delta_{nn'}$ and $\alpha_{nn'}(\vec{R}) := \int d^3r\, \varphi_n^*(\vec{r}-\vec{R})\, \varphi_{n'}(\vec{r})$

we arrive at

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

b) $\underline{\langle \psi_{n\vec{k}} | H | \psi_{n\vec{k}} \rangle = \dots}$

$$\dots = \frac{1}{N} \sum_{\vec{R}_1} \sum_{\vec{R}_2} e^{i\vec{k}\cdot(\vec{R}_2-\vec{R}_1)} \int d^3r\, \varphi_n^*(\vec{r}-\vec{R}_1)\, H\, \varphi_n(\vec{r}-\vec{R}_2) = \dots$$

$$H \downarrow$$

$$= H_{at,\vec{R}_2} + \Delta V_{\vec{R}_2}(\vec{r})$$

$$\downarrow$$

gives a factor E_n

$$\dots = E_n \langle \psi_{n\vec{k}} | \psi_{n\vec{k}} \rangle + \frac{1}{N} \sum_{\vec{R}_1} \sum_{\vec{R}_2} e^{i\vec{k}\cdot(\vec{R}_2-\vec{R}_1)} \int d^3r\, \varphi_n^*(\vec{r}-\vec{R}_1) \sum_{\vec{R}_3\neq\vec{R}_2} v(\vec{r}-\vec{R}_3)\, \varphi_n(\vec{r}-\vec{R}_2) \quad (*)$$

$\longrightarrow$ the functions $\varphi_n^*(\vec{r}-\vec{R})$, $v(\vec{r}-\vec{R})$, $\varphi_n(\vec{r}-\vec{R})$ are all localized at $\vec{R}$

$\Rightarrow$ classify the contributions to the triple sum $\sum_{\vec{R}_1} \sum_{\vec{R}_2} \sum_{\vec{R}_3\neq\vec{R}_2}$ according to the number of equal $\vec{R}_i$'s:

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

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

ii) $\vec{R}_1 = \vec{R}_3 \neq \vec{R}_2$

c) $\vec{R}_1 \neq \vec{R}_2 \neq \vec{R}_3 \neq \vec{R}_1$: these terms can be neglected as $\varphi_n^*(\vec{r}-\vec{R}_1)\, v(\vec{r}-\vec{R}_3)\, \varphi_n(\vec{r}-\vec{R}_2)$ is small for all values of $\vec{r} \in V$

$\dashrightarrow$ continue with $\underline{\text{i) } \vec{R}_1 = \vec{R}_2 \neq \vec{R}_3}$

$\sum_{\vec{R}_1} \sum_{\vec{R}_2} \dashrightarrow \sum_{\vec{R}_1}$ as $\vec{R}_2$ is fixed to $\vec{R}_1$

the second term in (*) gives

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

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

and note that

$$\Delta V_{\vec{R}_1}(\vec{r}\,'+\vec{R}_1) = \sum_{\vec{R}_3 \neq \vec{R}_1} v(\vec{r}\,'+\vec{R}_1-\vec{R}_3)$$ does not contain $v(\vec{r}\,') = v(\vec{r}\,'-\vec{0})$

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

$$\dots = \frac{1}{N}\sum_{\vec{R}_1} \underbrace{\int d^3r'\; \varphi_n^*(\vec{r}\,')\, \Delta V_{\vec{0}}(\vec{r}\,')\, \varphi_n(\vec{r}\,')}_{=:\beta_n,\ \text{does not depend on } \vec{R}_1} = \beta_n \quad \rightarrow$$ gives a constant energy shift

ii) $\vec{R}_1 = \vec{R}_3 \neq \vec{R}_2$

the second term in (*) gives

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

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

then substitute $\vec{R} = \vec{R}_1 - \vec{R}_2$, $\sum_{\vec{R}_2\neq\vec{R}_1} \rightarrow \sum_{\vec{R}\neq\vec{0}}$

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

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

and we finally arrive at

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

with $\alpha_n(\vec{R}) = \alpha_{nn}(\vec{R})$ as defined above now assume that $\left|\sum_{\vec{R}\neq\vec{0}} e^{-i\vec{k}\cdot\vec{R}}\alpha_n(\vec{R})\right| \ll 1$

$$\rightarrow \quad E_n(\vec{k}) \approx E_n + \Big(\beta_n + \sum_{\vec{R}\neq\vec{0}} e^{-i\vec{k}\cdot\vec{R}}\lambda_n(\vec{R})\Big)\Big(1 - \sum_{\vec{R}\neq\vec{0}} e^{-i\vec{k}\cdot\vec{R}}\alpha_n(\vec{R})\Big)$$

neglect the product of these two terms

$$\approx \underbrace{E_n + \beta_n}_{c_n} + \sum_{\vec{R}\neq\vec{0}} e^{-i\vec{k}\cdot\vec{R}} \underbrace{\big(\lambda_n(\vec{R}) - \beta_n\alpha_n(\vec{R})\big)}_{=\gamma_n(\vec{R})}$$

general form of the dispersion in the tight-binding approximation:

$$\boxed{E_n(\vec{k}) = c_n + \sum_{\vec{R}\neq\vec{0}} e^{-i\vec{k}\cdot\vec{R}}\gamma_n(\vec{R})}$$

<u>example</u>: one-dimensional lattice, $R_m = ma$

$$\rightarrow \quad E_n(k) = c_n + \sum_{m\neq 0} e^{-ikma}\gamma_n(R_m)$$

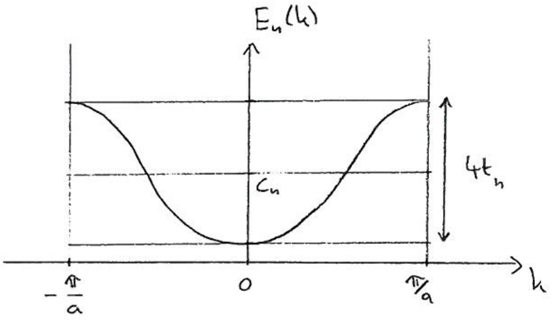
now assume that

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

this means: significant overlap of $\varphi_n(x-R_m)$ and $\varphi_n(x)$ only between site 0 and its nearest neighbours.

$$\Rightarrow \quad E_n(k) = c_n - t_n\left(e^{ika} + e^{-ika}\right)$$

$$\boxed{E_n(k) = c_n - 2t_n\cos ka}$$



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

<u>now</u>: expand $E_n(k)$ around $k=0$:

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

effective mass : $\frac{1}{m^*(n)} = \frac{1}{\hbar^2}\frac{d^2E_n(k)}{dk^2} = \frac{1}{\hbar^2}\,2t_n a^2$

$$\Rightarrow \boxed{m^*(n) = \frac{\hbar^2}{2a^2}\frac{1}{t_n}}$$ the effective mass diverges for $t_n \to 0$

Wannier functions

main idea of the tight-binding method : use wave functions localized at lattice site $\vec{R}$ to construct Bloch states

so far : $\varphi_n(\vec{r}-\vec{R}) \to$ eigenstate of the atomic Hamiltonian $H_{at,\vec{R}}$

but : the $|\varphi_{n,\vec{R}}\rangle$ do not form an orthonormal basis !

$$\to \langle\varphi_{n,\vec{R}}|\varphi_{n',\vec{R}'}\rangle \neq \delta_{nn'}\delta_{\vec{R}\vec{R}'}$$

now define : Wannier functions with the properties

- $w_n(\vec{r}-\vec{R})$ localized at $\vec{R}$
- $\langle w_{n,\vec{R}}|w_{n',\vec{R}'}\rangle = \delta_{nn'}\delta_{\vec{R}\vec{R}'}$

Bloch states can be defined as above :

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

with the property :

$$\langle\psi_{n\vec{k}}|\psi_{n'\vec{k}}\rangle \underset{\substack{\uparrow\\ \text{as on p16/17}}}{=} \sum_{\vec{R}} e^{-i\vec{k}\cdot\vec{R}} \underbrace{\langle w_{n\vec{R}}|w_{n'\vec{0}}\rangle}_{=\delta_{nn'}\delta_{\vec{R},\vec{0}}} = \delta_{nn'}$$

how to construct the Wannier functions ?

start from the solution of the full problem : $H|\psi_{n\vec{k}}\rangle = E_n(\vec{k})|\psi_{n\vec{k}}\rangle$

$\to$ the $\psi_{n\vec{k}}(\vec{r})$ are known and fulfil $\langle\psi_{n\vec{k}}|\psi_{n'\vec{k}'}\rangle = \delta_{nn'}\delta_{\vec{k}\vec{k}'}$

construct the Wannie functions as

$$\boxed{w_n(\vec{r}-\vec{R}) = \frac{1}{\sqrt{N}}\sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}}\, e^{i\varphi_{\vec{k}}}\,\psi_{n\vec{k}}(\vec{r})}$$ $\varphi_{\vec{k}}$: an arbitrary phase

$$\langle w_{n\vec{R}} | w_{n'\vec{R}'}\rangle = \frac{1}{N}\sum_{\vec{k}}\sum_{\vec{k}'} e^{i\vec{k}\cdot\vec{R}}\, e^{-i\varphi_{\vec{k}}}\, e^{-i\vec{k}'\cdot\vec{R}'}\, e^{i\varphi_{\vec{k}'}} \underbrace{\langle \psi_{n\vec{k}} | \psi_{n'\vec{k}'}\rangle}_{=\delta_{nn'}\delta_{\vec{k}\vec{k}'}} =$$

$$= \frac{1}{N}\delta_{nn'} \underbrace{\sum_{\vec{k}} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}}_{=N\delta_{\vec{R}\vec{R}'}} \underbrace{e^{-i\varphi_{\vec{k}}}\, e^{i\varphi_{\vec{k}}}}_{=1} = \delta_{nn'}\delta_{\vec{R}\vec{R}'}$$

↪ the phase drops out

this means: as a basis we can either choose

$\{|\psi_{n\vec{k}}\rangle\}$: Bloch states

or $\{|w_{n\vec{R}}\rangle\}$: Wannier states

but: whether the $w_n(\vec{r}-\vec{R})$ are localized at $\vec{R}$ depends on the choice of the $\varphi_{\vec{k}}$ → this defines a complex optimization problem

4.5 electron density of states and Fermi surface

given a band structure $E_n(\vec{k})$ ($\hat{=}$ a single-particle spectrum $\{E_n(\vec{k})\}$), we define the electron density of states as

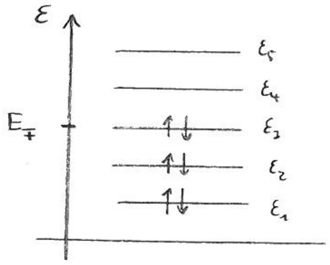
$$\boxed{\rho(E) = \frac{1}{N}\sum_{n\vec{k}\sigma} \delta(E - E_n(\vec{k}))}$$

→ similar to the definition of the phonon density of states

σ: the electron spin, if the bandstructure does not depend on σ, the sum $\sum_\sigma$ gives a factor 2

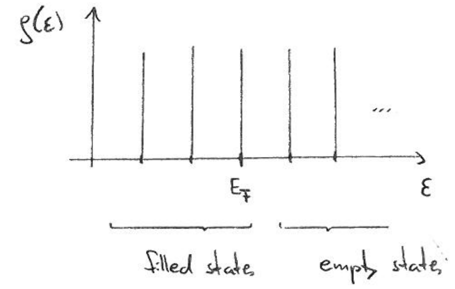
Fermi energy

question: what is the many-particle state with the lowest energy for a single-particle spectrum $\{\varepsilon_n\}$ and a given number of electrons Z_e?

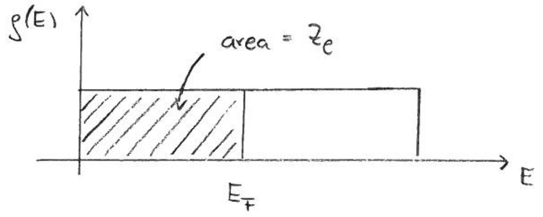


Pauli principle!

→ fill up the single-particle levels starting from the lowest energy up to E_F, the Fermi energy translate this picture into the density of states :



and in the continuous case :



$\rightarrow$ E_F can be defined as $$\boxed{\int_{-\infty}^{E_F} dE\, \varrho(E) = Z_e}$$

<u>example:</u> density of states and Fermi energy of free electrons in d=3

$$E(\vec{k}) = \frac{\hbar^2 k^2}{2m} \quad , \quad \varrho(E) = \frac{2}{N} \sum_{\vec{k}} \delta(E - E(\vec{k}))$$

$\sum_{\vec{k}}$ can be replaced by $\frac{V}{(2\pi)^3} \int d^3k$ (see Sec. 3.5)

and $\int d^3k \rightarrow 4\pi \int_0^\infty dk\, k^2$

$$\Rightarrow \quad \varrho(E) = \frac{2V}{N} \frac{4\pi}{(2\pi)^3} \underbrace{\int_0^\infty dk\, k^2\, \delta\left(E - \frac{\hbar^2 k^2}{2m}\right)} = \ldots$$

$$= \int_0^\infty dk\, f(k)\, \delta(g(k)) = \frac{f(k_0)}{|g'(k_0)|}$$ $\rightarrow$ only one zero of $g(k)$ with $k > 0$

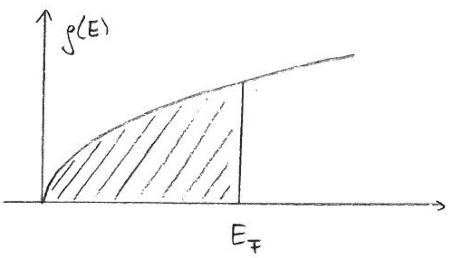
$$\rightarrow \quad g(k) = E - \frac{\hbar^2 k^2}{2m} \quad , \quad k_0 = \frac{1}{\hbar}\sqrt{2mE}$$

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

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

$$\ldots = \frac{2V\, 2mE\, m}{N\, 2\pi^2\, \hbar^2\, \hbar\, \sqrt{2mE}}$$

$$\boxed{\varrho(E) = \frac{Vm}{N\pi^2\hbar^3} \sqrt{2mE}}$$



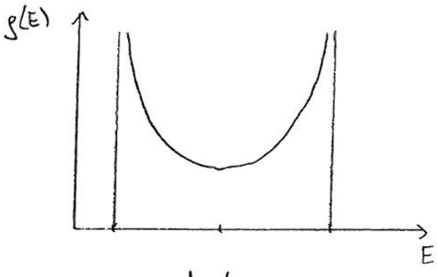
calculate the Fermi energy via

$$Z_e = \int_0^{E_F} dE\, \varrho(E) = \frac{V}{3N\pi^2\hbar^3} (2mE_F)^{3/2}$$

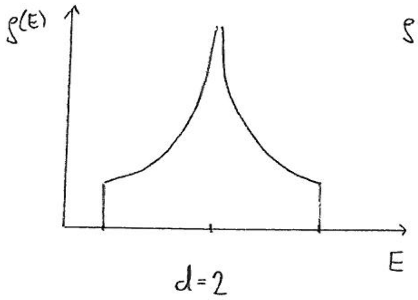
$$\Rightarrow \boxed{E_F = \frac{\hbar^2}{2m}\left(\frac{3N\pi^2 Z_e}{V}\right)^{2/3}}$$

density of state of tight-binding bands

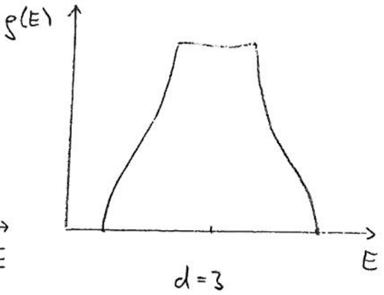
in d dimensions : $E(\vec{k}) = -2t\sum_{i=1}^{d}\cos(k_i a)$



d = 1



d = 2



d = 3

Fermi surface

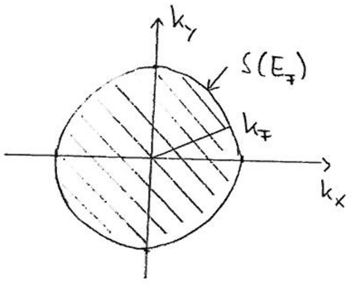
in d = 3 : define S(E) as the area of constant energy in k-space

$$\boxed{S(E) = \left\{\vec{k}\in \text{Brillouin zone} \mid E_n(\vec{k}) = E\right\}}$$

$S(E_F)$: the Fermi surface

example : free electrons in d = 2

$E(\vec{k}) = \frac{\hbar^2}{2m}(k_x^2 + k_y^2)$ → lines of constant energy E are circle with radius $k = \sqrt{2mE}/\hbar$



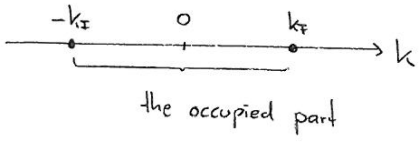
k_F : Fermi wave vector

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

in d = 2 : $S(E_F)$ → Fermi line

$S(E_F)$ separates the $\vec{k}$-space into
- the occupied part : $E \leq E_F$
- the unoccupied part : $E > E_F$

d = 1 :

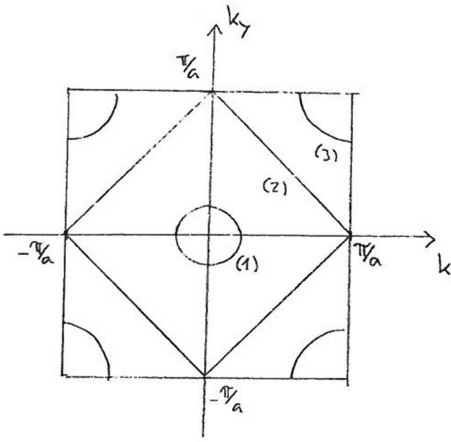


⇒ two Fermi points

2d square lattice

$S(E_F)$ in the tight-binding model

maximum numbe of electrons in each tight-binding band : $Z_m = 2N$



(1) $Z_e \ll Z_m$

- $S(E_F)$ as in the free electron case

(2) $Z_e = \frac{1}{2} Z_m$: half-filling

(3) Z_e close to Z_m : the Fermi line in the 1st Brillouin zone is not simply connected

(4) $Z_e = Z_m$: all the states in the 1st Brillouin zone are filled

4.6 thermodynamics of electrons on a lattice

in Sec. 4 we consider : single-particle levels $E_\ell(\vec{k})$ (the band structure)

the quantum numbers $(\ell, \vec{k}, \sigma)$ label a single-particle state

→ define the occupation $n_{\ell\vec{k}\sigma}$ of this state, with $n_{\ell\vec{k}\sigma} = 0,1$

the set of occupations $\{n_{\ell\vec{k}\sigma}\}$ defines a microstate

total numbe of electrons :

$$N = \sum_{\ell\vec{k}\sigma} n_{\ell\vec{k}\sigma} = N(\{n_{\ell\vec{k}\sigma}\})$$

total enegy :

$$E = \sum_{\ell\vec{k}\sigma} n_{\ell\vec{k}\sigma} E_\ell(\vec{k}) = E(\{n_{\ell\vec{k}\sigma}\}) \quad \hat{=} \text{ many-particle enegy}$$

T = 0 : the ground state is given by the many-particle state with the lowest enegy

$$\rightarrow \quad n_{\ell\vec{k}\sigma} = \begin{cases} 1 & : \ E_\ell(\vec{k}) \leq E_F \\ 0 & : \ E_\ell(\vec{k}) > E_F \end{cases}$$

→ all single-particle states filled up to the Fermi enegy E_F

now move on to $T>0$

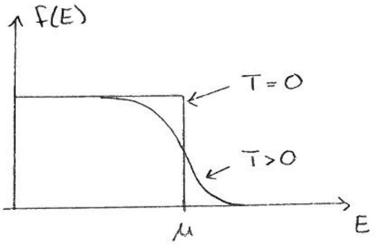
$\longrightarrow$ work with a grand canonical ensemble

partition function: $$Z_{gc} = \sum_{\{n_{\ell\vec{k}\sigma}\}} e^{-\beta\left(E\{n_{\ell\vec{k}\sigma}\} - \underbrace{\mu}_{\text{chemical potential}} N\{n_{\ell\vec{k}\sigma}\}\right)}$$

average quantities are obtained via $$\langle X\rangle = \frac{1}{Z_{gc}} \sum_{\{n_{\ell\vec{k}\sigma}\}} X\, e^{-\beta(E-\mu N)}$$

- the mean occupation number of the state $(\ell, \vec{k}, \sigma)$ is given by the

Fermi distribution: $$\boxed{\langle n_{\ell\vec{k}\sigma}\rangle = f(E_\ell(\vec{k})) = \frac{1}{\exp\left[\beta(E_\ell(\vec{k})-\mu)+1\right]}}$$



$f(E)$: the Fermi function

in the limit $T\to 0$:

$$\mu(T\to 0) = E_F$$

- the average total number of electrons:

$$\langle N\rangle = \sum_{\ell\vec{k}\sigma} \langle n_{\ell\vec{k}\sigma}\rangle \qquad \text{depends on } \beta, \mu$$

$\longrightarrow$ for a given N, adjust μ such that $\langle N\rangle = N$

$$\langle N\rangle = \sum_{\ell\vec{k}\sigma} f(E_\ell(\vec{k})) = \int dE\, g(E)\, f(E)$$

$\hookrightarrow$ see Sec. 3.6

- internal energy

$$U = \sum_{\ell\vec{k}\sigma} \langle n_{\ell\vec{k}\sigma}\rangle E_\ell(\vec{k}) = \int dE\, g(E)\, f(E)\, E$$

Sommerfeld expansion

$\longrightarrow$ approximate calculation of integrals of the form

$$\boxed{\int_{-\infty}^{\infty} dE\, H(E)\, f(E)}$$

define $$K(E) = \int_{-\infty}^{E} dE'\, H(E')$$

partial integration :

$$\int_{-\infty}^{\infty} dE\ H(E)\, f(E) = \underbrace{\Big[k(E)\, f(E) \Big]_{-\infty}^{\infty}}_{} - \int_{-\infty}^{\infty} dE\ k(E) \frac{df}{dE}$$

$= 0$ because $k(E \to -\infty) = 0$ and $f(E \to +\infty) = 0$

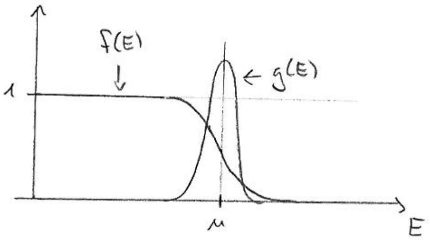
and evaluate $\frac{df}{dE}$:

$$\frac{df}{dE} = -1 \left(e^{\beta(E-\mu)} + 1 \right)^{-2} e^{\beta(E-\mu)} \beta$$

$$= -\frac{1}{k_B T} \frac{1}{\left(e^{\beta(E-\mu)}+1\right)\left(e^{-\beta(E-\mu)}+1\right)} =: -g(E)$$

<u>properties of $g(E)$</u> :

- $g(E)$ is symmetric around μ → $g(\mu + \Delta E) = g(\mu - \Delta E)$
- $\lim_{E\to\infty} g(E) = 0$; $\lim_{E\to-\infty} g(E) = 0$
- $\lim_{T\to 0} g(E) = \delta(E-\mu)$



for the evaluation of $\int dE\ k(E)\, g(E)$ it is sufficient to determine $k(E)$ in a small intervall around μ

→ Taylor expansion of $k(E)$:

$$k(E) = k(\mu) + \sum_{n=1}^{\infty} \frac{1}{n!} (E-\mu)^n \left.\frac{d^n k(E)}{dE^n}\right|_{E=\mu}$$

→ insert this into $\int dE\ k(E)\, g(E)$

$$\Rightarrow \int_{-\infty}^{\infty} dE\ H(E) f(E) = k(\mu) \int_{-\infty}^{\infty} dE\ g(E) +$$

$$+ \sum_{n=1}^{\infty} \frac{1}{n!} \left.\frac{d^n k(E)}{dE^n}\right|_{E=\mu} \int_{-\infty}^{\infty} dE\ (E-\mu)^n g(E) = \ldots$$

now we use : $\int_{-\infty}^{\infty} dE\ g(E) = 1$,

$k(\mu) = \int_{-\infty}^{\mu} dE\ H(E)$, and $\left.\frac{d^n k(E)}{dE^n}\right|_{E=\mu} = \left.\frac{d^{n-1} H(E)}{dE^{n-1}}\right|_{E=\mu}$

and substitute $x = \beta(E-\mu)$ → $dE = \frac{1}{\beta}\,dx$

$$\dots = \int_{-\infty}^{\mu} dE\, H(E) + \sum_{n=1}^{\infty} \left.\frac{d^{n-1}H(E)}{dE^{n-1}}\right|_{E=\mu} \int_{-\infty}^{\infty} dx\, \frac{1}{\beta}\,(k_BT)^n\, \frac{x^n}{n!}\, \beta\, \frac{1}{(e^x+1)(e^{-x}+1)}$$

the integral $\int_{-\infty}^{\infty} dx \dots$ is non zero only for $n = 2m$, $m \in \mathbb{N}$

now define

$$\boxed{a_m = \int_{-\infty}^{\infty} dx\, \frac{x^{2m}}{(2m)!}\, \frac{1}{(e^x+1)(e^{-x}+1)}}$$

can be written as

$$a_m = \left(2 - \frac{1}{2^{2(m-1)}}\right)\zeta(2m)$$

with the Riemann Zeta function $\zeta(x) = \sum_{m=1}^{\infty} \frac{1}{m^x}$

the Sommerfeld expansion then reads:

$$\boxed{\int_{-\infty}^{\infty} dE\, H(E)\, f(E) = \int_{-\infty}^{\mu} dE\, H(E) + \sum_{m=1}^{\infty} \left.\frac{d^{2m-1}H(E)}{dE^{2m-1}}\right|_{E=\mu} (k_BT)^{2m}\, a_m}$$

internal energy

$$U = \int_{-\infty}^{\infty} dE\, \rho(E)\, f(E)\, E \quad \rightarrow \quad H(E) = E\rho(E)$$

→ expansion up to order T^2:

$$U = \int_{-\infty}^{\mu} dE\, E\rho(E) + \underbrace{\left.\frac{dH(E)}{dE}\right|_{E=\mu}}_{=\ \rho(E) + E\rho'(E)} (k_BT)^2\, \underset{\searrow\ =\ \frac{\pi^2}{6}}{a_1} + \mathcal{O}(T^4) =$$

$$= \int_{-\infty}^{\mu} dE\, E\rho(E) + \frac{\pi^2}{6}(k_BT)^2\left(\rho(\mu) + \mu\rho'(\mu)\right) + \mathcal{O}(T^4)$$

total number of electrons

we assume that $\langle N\rangle$ is fixed to N, which results in a T-dependent $\mu \rightarrow \mu(T)$

$$\rightarrow \quad N = \int_{-\infty}^{\infty} dE\, \rho(E)\, f(E)$$

$$\underset{\uparrow}{=} \int_{-\infty}^{\mu} dE\, \rho(E) + \frac{\pi^2}{6}(k_BT)^2\rho'(\mu) + \mathcal{O}(T^4)$$

in the Sommerfeld expansion

for the integral $\int_{-\infty}^{\mu(T)} dE\,\varrho(E)$ we assume that $\mu(T)$ is close to E_F

$$\to \int_{-\infty}^{\mu} dE\,\varrho(E) = \underbrace{\int_{-\infty}^{E_F} dE\,\varrho(E)}_{\overset{!}{=} N} + \underbrace{\int_{E_F}^{\mu} dE\,\varrho(E)}_{\approx \varrho(E_F)(\mu - E_F)} \approx N + (\mu - E_F)\varrho(E_F)$$

↳ this is precisely the expression we get for $T = 0$

and we get:

$$N = N + (\mu - E_F)\varrho(E_F) + \frac{\pi^2}{6}(k_B T)^2 \underbrace{\varrho'(\mu)}_{\approx \varrho'(E_F)}$$

$\Rightarrow$ the temperature dependence of the chemical potential for low T is given by:

$$\boxed{\mu = E_F - \frac{\pi^2}{6}\frac{\varrho'(E_F)}{\varrho(E_F)}(k_B T)^2} \qquad (*)$$

continue with the internal energy:

$$U = \underbrace{\int_{-\infty}^{E_F} dE\,\varrho(E)\,E}_{= U_0} + \underbrace{(\mu - E_F)}_{\text{insert } (*)}\varrho(E_F)E_F + \frac{\pi^2}{6}(k_B T)^2\Big(\varrho(\underset{\underset{E_F}{\downarrow}}{\mu}) + \underset{\underset{E_F}{\downarrow}}{\mu}\,\varrho'(\underset{\underset{E_F}{\downarrow}}{\mu})\Big) + O(T^4)$$

↳ the internal energy for $T = 0$

the term $\frac{\pi^2}{6}(k_B T)^2\varrho'(E_F)E_F$ cancels and we get

$$\boxed{U(T) = U_0 + \frac{\pi^2}{6}\varrho(E_F)(k_B T)^2}$$

Specific heat

$$C_v = \frac{1}{V}\frac{\partial U}{\partial T} \Rightarrow \boxed{C_v(T) = \frac{\pi^2}{3V}\varrho(E_F)k_B^2 T} =: \gamma T$$

this means: if $\varrho(E_F) \neq 0$, the contribution of the electrons to the specific heat is linear in T!

5. Electron - electron interaction

start with the Hamiltonian as used in Sec. 4 and add the interaction between the electrons :

$$H = T_e + V_{e-a} + V_{e-e} \quad \text{with} \quad V_{e-e} = \sum_{i<j} v_{e-e}(\vec{r}_i - \vec{r}_j)$$

5.1 the solid-state Hamiltonian in second quantization

start with a suitable basis of the single-electron problem

→ Bloch state $|\psi_{n\vec{k}}\rangle$ or Wannier state $|w_{n\vec{R}}\rangle$

in general : $|k\rangle$ with $\{k\}$ a complete set of single-particle quantum numbers

now define:

the N-particle Hilbet-space $H_a(N)$, with its basis given
$\hookrightarrow$ antisymmetric

by slater determinants :

$$|\psi_{k_1 k_2 .. k_N}(1,2,..N)\rangle = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} |k_1\rangle^{(1)} & \cdots & |k_1\rangle^{(N)} \\ \vdots & & \\ |k_N\rangle^{(1)} & \cdots & |k_N\rangle^{(N)} \end{pmatrix}$$

$|k_\alpha\rangle^{(m)}$: particle m is in state $|k_\alpha\rangle$

→ exchange of particle coordinate give a minus sign

→ Pauli principle ; $n_k = 0$ or 1

the basis of $H_a(N)$ can be written as :

$$\{ |n_{k_1}, n_{k_2}, \ldots \rangle \} \quad \text{with} \quad \sum_k n_k = N$$

Fock space

defined as the direct sum of the N-particle Hilbet spaces :

$$H_{a,\mp} = H_a(0) \oplus H_a(1) \oplus \ldots \oplus H_a(N) \oplus \ldots$$

and define new operators on the Fock space

→ creation and annihilation operators $C^{+}_{k_\alpha}$, C_{k_α}

with:

$$C_{k_\alpha}\,|n_{k_1},\dots,n_{k_\alpha},\dots\rangle = (-1)^{S_\alpha}\, n_{k_\alpha}\,|n_{k_1},\dots,n_{k_\alpha}-1,\dots\rangle$$

$$C^{+}_{k_\alpha}\,|n_{k_1},\dots,n_{k_\alpha},\dots\rangle = (-1)^{S_\alpha}\,(1-n_{k_\alpha})\,|n_{k_1},\dots,n_{k_\alpha}+1,\dots\rangle$$

$$S_\alpha = \sum_{\sigma=1}^{\alpha-1} n_{k_\sigma}$$

properties of $C^{(+)}_{k_\alpha}$:

- $$\underbrace{C^{+}_{k_\alpha}C_{k_\alpha}}\,|n_{k_1},\dots,n_{k_\alpha},\dots\rangle = n_{k_\alpha}\,|n_{k_1},\dots,n_{k_\alpha},\dots\rangle$$

  $= \hat{n}_{k_\alpha}$: particle number operator

  → operator for the total particle number $\hat{N} = \sum_\alpha \hat{n}_{k_\alpha}$

- $[C_{k_\alpha}, C_{k_\beta}]_+ = 0$, $[C^{+}_{k_\alpha}, C^{+}_{k_\beta}]_+ = 0$

  $[C_{k_\alpha}, C^{+}_{k_\beta}]_+ = \delta_{\alpha\beta}$

field operators

with $\varphi_{k_\alpha}(\vec{r}) = \langle \vec{r}\,|k_\alpha\rangle$ we define

$$\hat{\Phi}(\vec{r}) = \sum_\alpha \varphi_{k_\alpha}(\vec{r})\, C_{k_\alpha} \quad , \quad \hat{\Phi}^{+}(\vec{r}) = \sum_\alpha \varphi^{*}_{k_\alpha}(\vec{r})\, C^{+}_{k_\alpha}$$

with the property:

$$[\hat{\Phi}(\vec{r}), \hat{\Phi}^{+}(\vec{r}\,')]_+ = \delta(\vec{r}-\vec{r}\,') \quad , \text{ due to } \sum_\alpha \varphi^{*}_{k_\alpha}(\vec{r})\,\varphi_{k_\alpha}(\vec{r}\,') = \delta(\vec{r}-\vec{r}\,')$$

operators in particle number representation

a) single-particle operators $A^{(1)} = \sum_{i=1}^{N} \underbrace{A^{(1)}(\vec{r}_i)}_{\text{act only on one particle coordinate}}$

example: T_e, V_{e-a}

$$A^{(1)} = \sum_{i=1}^{N} \hat{1}\, A^{(1)}(\vec{r}_i)\, \hat{1} \qquad \text{with the unity operator } \hat{1} = \sum_\alpha |k_\alpha\rangle^{(i)}\,{}^{(i)}\langle k_\alpha|$$

$$= \sum_{\alpha,\beta} \underbrace{\langle k_\alpha|A^{(1)}(\vec{r})|k_\beta\rangle}_{=A^{(1)}_{k_\alpha,k_\beta}} \sum_{i=1}^{N} |k_\alpha\rangle^{(i)}\,{}^{(i)}\langle k_\beta|$$

with $\sum_{i=1}^{N} |k_\alpha\rangle^{(i)}\,{}^{(i)}\langle k_\beta| = c^\dagger_{k_\alpha} c_{k_\beta}$ we obtain

$$\boxed{A^{(1)} = \sum_{\alpha,\beta} A^{(1)}_{k_\alpha,k_\beta}\, c^\dagger_{k_\alpha} c_{k_\beta}}$$

now set $A^{(1)} = T_e + V_{e-a} = \sum_{i=1}^{N} \frac{-\hbar^2}{2m}\Delta_i + \sum_{i=1}^{N} V(\vec{r}_i)$

$\longrightarrow$ $A^{(1)}(\vec{r}) = -\frac{\hbar^2}{2m}\Delta + V(\vec{r}) \mathrel{\hat{=}} H$ as used in Secs. 4.1 ff

i, Bloch states $|\psi_{n\vec{k}\sigma}\rangle$

$\rightarrow$ eigenstate of H $\Rightarrow$ $\langle k_\alpha|A^{(1)}(\vec{r})|k_\beta\rangle = E_n(\vec{k})\,\delta_{nn'}\,\delta_{\vec{k}\vec{k}'}\,\delta_{\sigma\sigma'}$

and the single-particle terms of the solid state Hamiltonian can be written as:

$$\boxed{\sum_{n\vec{k}\sigma} E_n(\vec{k})\, c^\dagger_{n\vec{k}\sigma} c_{n\vec{k}\sigma}}$$

ii, Wannier states $|w_{\vec{R}\sigma}\rangle$

$\rightarrow$ here for a single band (drop the index n)

$\langle k_\alpha|A^{(1)}(\vec{r})|k_\beta\rangle = \langle w_{\vec{R}\sigma}|A^{(1)}(\vec{r})|w_{\vec{R}'\sigma'}\rangle = -t_{\vec{R}\vec{R}'}\,\delta_{\sigma\sigma'}$

the Wannier state are supposed to be well localized, therefore we assume

$$t_{\vec{R}\vec{R}'} = \begin{cases} t & : \vec{R}' = \vec{R} + \vec{\Delta} \\ 0 & : \text{otherwise} \end{cases}$$ with $\vec{\Delta}$ the vectors to the nearest neighbour of $\vec{R}$

$\Rightarrow$ the single-particle terms read $$\boxed{-t \sum_{\vec{R}\vec{\Delta}\sigma} c^\dagger_{\vec{R}\sigma} c_{\vec{R}+\vec{\Delta}\sigma}}$$

b, two-particle operators

$A^{(2)} = \frac{1}{2}\sum_{i\neq j} A^{(2)}(\vec{r}_i,\vec{r}_j)$ $\rightarrow$ acts on two particle coordinate

example: V_{e-e}

now insert four unity operators: $\hat{1}^{(i)}, \hat{1}^{(j)}$ each twice

and we obtain for the general form of $A^{(2)}$ in particle number representation:

$$\boxed{A^{(2)} = \frac{1}{2}\sum_{\alpha\beta\gamma\delta} A^{(2)}_{k_\alpha k_\beta, k_\gamma k_\delta}\, c^\dagger_{k_\alpha} c^\dagger_{k_\beta} c_{k_\gamma} c_{k_\delta}}$$

with: $$A^{(2)}_{k_\alpha k_\beta, k_\gamma k_\delta} = \overset{(i)}{\langle k_\alpha|}\, \overset{(j)}{\langle k_\beta|}\, A^{(2)}(\vec r_i, \vec r_j)\, |k_\gamma\rangle^{(j)}\, |k_\delta\rangle^{(i)} =$$

$$= \int d^3r \int d^3r'\, \varphi^*_{k_\alpha}(\vec r)\, \varphi^*_{k_\beta}(\vec r')\, A^{(2)}(\vec r, \vec r')\, \varphi_{k_\gamma}(\vec r')\, \varphi_{k_\delta}(\vec r)$$

$A^{(2)}$ in a Wannier state basis

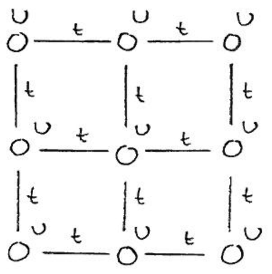
- for a single band only
- assume that the Wannier states $|w_{\vec R\sigma}\rangle$ are localized to an extent that

$$A^{(2)}_{\vec R_\alpha \sigma_\alpha \vec R_\beta \sigma_\beta \dots} \neq 0 \quad \text{only for} \quad \vec R_\alpha = \vec R_\beta = \vec R_\gamma = \vec R_\delta$$

after properly dealing with the spin indices, we obtain the single-band Hubbard model

$$\boxed{H = \sum_{\vec R \vec\Delta \sigma} t\, c^\dagger_{\vec R\sigma} c_{\vec R + \vec\Delta \sigma} + U \sum_{\vec R} c^\dagger_{\vec R\uparrow} c_{\vec R\uparrow} c^\dagger_{\vec R\downarrow} c_{\vec R\downarrow}}$$

for a 2d square lattice:



now: start with a few simple models and move on to increasingly complex models

- ○ no U
- ○ ○ ○ ○ ... $U=0,\ t=0$
- ○ $U \neq 0$
- ○—○ $U=0,\ t\neq 0$
- ○—○—○—○ ... $U=0,\ t\neq 0$

more complex models require advanced analytical / numerical tools

→ see the lecture on computational many-body physics, advanced solid state theory
quantum field theory