

01.09.22

Tahke koha ja pooljähtide püsisika

193. 40. 252. 77 (VASP)

Remote IP address

11. sept // Vaata läbi 1. loeng

12. sept Küsimused (3) 10.00

13. sept 12.00 antakse vastavate alg

Ruumat PARSEK server lõpus

Kunstes lõppeb eksamiiga

Järgmine kord loeng nr 3

ssh -l sipuga 193. 40. 252. 77

Password : jamesbond1

parsek.yf.ttu/~physics

Lecture 3. Vibrations of lattice



N - total number of atoms

What capacity per certain volume
 $C_V(T) = ?$

Correct part from CP $N_A \sim 6,02 \cdot 10^{23} \text{ mol}^{-1}$



$$C_V = \frac{\partial E_{\text{tot}}}{\partial T}$$

// CP can't explain low temp

$$0 \quad T$$

$$1d \quad C_V \sim T$$

$$2d \quad C_V \sim T^2$$

$$3d \quad C_V \sim T^3$$

$$C_V \rightarrow R$$

$$C_V \rightarrow R^2$$

$$C_V \rightarrow R^3$$

$$T \rightarrow \infty$$

$$E_{\text{tot}} = E_{\text{kin}} + E_{\text{pot}}$$

- displacement from the equilibrium state

$$u_k(t) = ?$$

$$u_k(t) = \dot{u}_k(t) = \frac{\partial u_k(t)}{\partial t}$$

$$E_{\text{kin}} = \frac{1}{2} m \sum_{k=1}^N \dot{u}_k^2$$

$$= \frac{1}{2} m \sum_{k=1}^N \dot{u}_k^2$$

$$E_{\text{pot}} = \frac{1}{2} g \sum u^2$$

$$\bar{E}_{\text{pot}} = \frac{1}{2} g \sum_{k=1}^N (u_k - u_{k-1})^2$$

$$\bar{E}_{\text{tot}} = \frac{1}{2} m \sum_{k=1}^N \dot{u}_k^2 + \frac{1}{2} g \sum_{k=1}^N (u_k - u_{k-1})^2$$

- In the equilibrium state $u_k = 0$ and
 $u_k - u_{k-1} = 0$
 so $E_{\text{tot}} = 0$.

- For a linear lattice

$$F \sim u$$

- Which parameter depends on temp.? Ans: u_k^i
- So finally we need to introduce the harmonic oscillator model
- But firstly let's look at it classically

$$\bar{E}_{\text{tot}} = \bar{E}_{\text{kin}} + \bar{E}_{\text{pot}}$$

(+) (+) - average

- depend on time

$$\bar{E} = \frac{\alpha T}{2} N$$

$$\bar{E}_{\text{pot}} = \frac{\alpha T}{\omega} \cdot N$$

- dependence on temperature

$$\bar{E}_{\text{tot}} = kT \cdot N$$

$$C_V = \frac{\partial E_{\text{tot}}}{\partial T} = k \cdot N \quad (\text{doesn't depend on } T \text{ at all})$$

$$\approx [N = N_A] = k \cdot N_A \Rightarrow R$$

$$E_{\text{tot}} = \frac{1}{2} m \sum_k \dot{u}_k^2 + \boxed{\frac{1}{2} g \sum_i (u_i - u_{i-1})^2}$$

$$a = \frac{F}{m} \Rightarrow \ddot{u}_i = \frac{F_i}{m} \quad F_i = -\frac{\partial E_{\text{pot}}}{\partial u_i}$$

\downarrow \downarrow \downarrow

$$\frac{1}{2} g \left\{ (u_i - u_{i-1})^2 + (u_{i+1} - u_i)^2 \right\}$$

i - directed process.

Why $u_{i+2} - u_{i+1}$ can be ignored?

• Bc its derivative is eq. to 0.

why i - "area"? *

$$\textcircled{z} - \frac{1}{2} g \left\{ 2(u_i - u_{i-1}) - 2(u_{i+1} - u_i) \right\} \leftarrow$$

$$\begin{aligned} & \frac{\partial}{\partial u_i} (u_{i+1} - u_i)^2 = \frac{\partial}{\partial u_i} (u_{i+1}^2 - 2u_{i+1}u_i + u_i^2) \\ & \text{constant} \quad \text{variable} \quad \text{the " - " sign} \\ & = -2u_{i+1} + 2u_i = -2(u_{i+1} - u_i) \end{aligned}$$

$$\textcircled{z} \quad g(u_{i+1} - 2u_i + u_{i-1})$$

$$F_i = g(u_{i+1} - 2u_i + u_{i-1})$$

$$\left\{ \begin{array}{l} \ddot{u}_k = \frac{g}{m} (u_{k+1} - 2u_k + u_{k-1}) \\ \vdots \\ \vdots \\ \vdots \end{array} \right.$$

This can be described through the harmonic function

Harmoic function / wave

wave vector
pos vec for downard.

$$u_k(t) = A_q \cdot e^{i(\omega t + q^\circ R_k)}$$

R_k = dist between atoms "k · a"

$$R_k = k \cdot a$$

in of atoms

$$w(q) = ?$$

$$|q| = \frac{2\pi}{\lambda}$$

wavelength



A_q - specific amplitude for $q \neq 0, \dots$

$$u_h(t) = \frac{2}{m} (u_{k+1} - 2u_k + u_{k-1})$$

~~$$- A_q \omega^2 e^{i(wt + q \cdot a \cdot k)} = \frac{2}{m} (A_q \cdot e^{i(wt + qa(k))})$$~~

$$- 2A_q e^{i(wt + qa(k))} + A_q e^{i(wt + qa(k-1))} =$$

$$= \frac{A_q}{m} e^{i(wt + qa(k))} (e^{iqa} - 2 + e^{-iqa}) =$$

$$= \frac{A_q}{m} e^{i(wt + qa(k))} (-2 + 2 \cos(qa))$$

$$-\omega^2 = -\frac{2q}{m} (1 + \cos(qa))$$

$$\omega^2 = \frac{2g}{\pi k} (1 - \cos(ga))$$

$$\omega^2 = \left(\frac{4g}{\pi k}\right) \cdot \sin^2\left(\frac{ga}{2}\right)$$

$$(1 - \cos \alpha) = 2 \sin^2\left(\frac{\alpha}{2}\right)$$

$$w(q) = w_0 \cdot |\sin\left(\frac{ga}{2}\right)|$$

$$u_k(t) = A_q \cdot e^{i(w(q)t + ga \cdot k)}$$

- We find q : given parabolic boundary condition:

$$| u_k = u_{k+N} |$$

$$A_q \cdot e^{i(w(q)t + ga \cdot k)} = A_q \cdot e^{i(w(q)t + ga \cdot (k+N))}$$

$$1 = e^{igaN}$$

$$q = \frac{2\pi}{a} \cdot \frac{n}{N}, n \in \mathbb{Z} [1 \dots N]$$

N is quite a big number
so discreteness is not very important

Once more time

$$F_i = g(u_{i+1} - 2u_i + u_{i-1})$$

$$R_k = k \cdot a$$

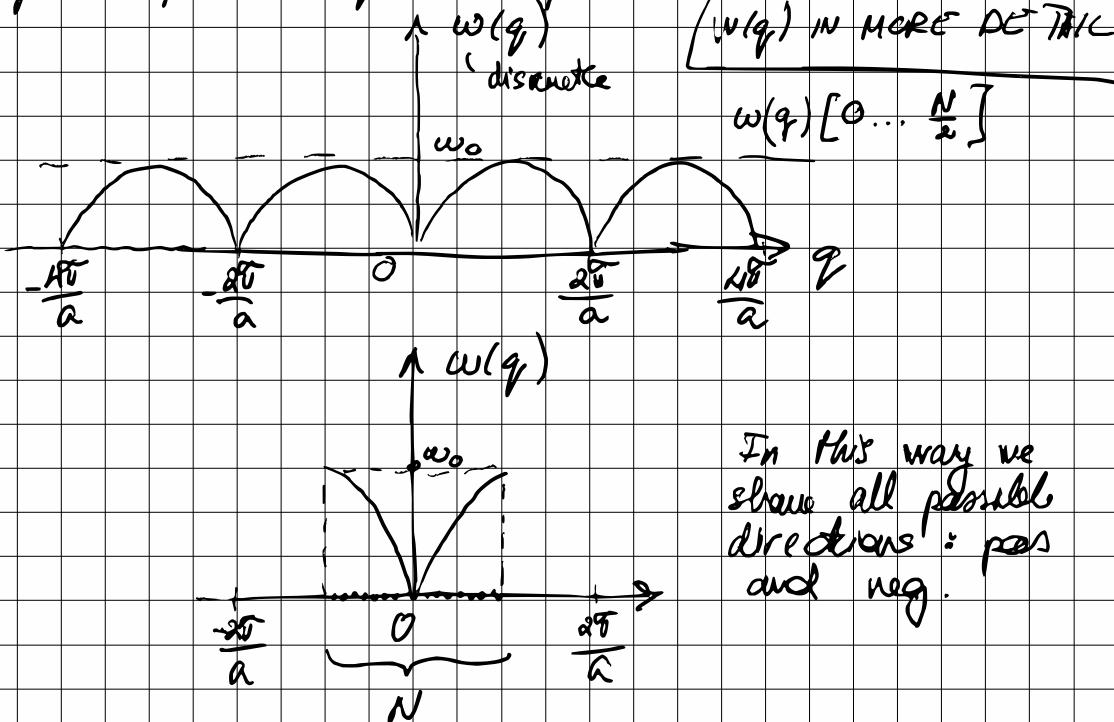
$$u_e(x) = Aq \cdot e^{i(\omega q + qax)} \rightarrow \sum_q e^{i(\omega q) + qax}$$

$$\omega(q) = \omega_0 / \sin\left(\frac{qa}{a}\right)$$

$$q = \frac{2\pi}{(aN)} \cdot n = \frac{2\pi}{L} \cdot n, n \left[-\frac{N}{2}, \dots, \frac{N}{2} \right]$$

total length of lattice L

If $n = 1, 2, \dots, N$ then q is pos and propagates
deam left to right. If q is neg, the wave propagates
deam right to left.



$(w(q))$ IN MORE DETAIL

$$w(q) [0 \dots \frac{N}{a}]$$

In this way we show all possible directions: pos and neg.

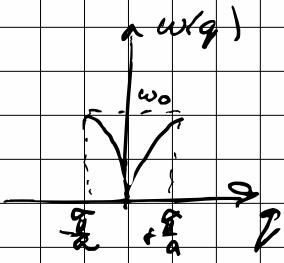
DOS - Density of states (in literature)
 gives us it's more like density of waves (DW)

$$g(\omega) = \frac{dn}{d\omega}$$

$d\omega$ - no of waves.
 waves that have
 different waves

$$dn = g(\omega)d\omega \quad [\omega, \omega + d\omega]$$

$$\int g(\omega)d\omega = N_{12}$$



The no of different
 waves from
 ω_1 to ω_2

$$\int g(\omega)d\omega = N$$

$$q = \frac{\partial \theta}{L} \cdot n \Rightarrow dq = \frac{\partial \theta}{L} \cdot dn$$

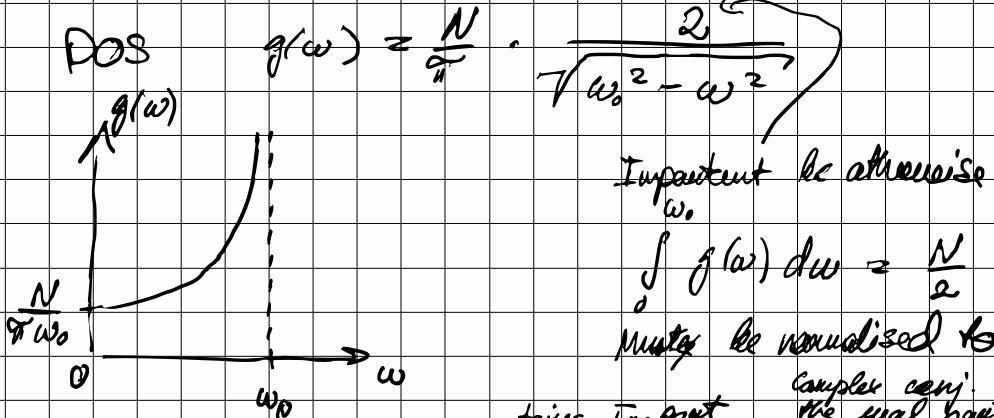
$$g(\omega) = \frac{L}{2\pi} \cdot \frac{dq}{d\omega} =$$

$$= \frac{L}{2\pi} \cdot \frac{1}{\frac{dq}{d\omega}} \quad (\text{E})$$

$$\frac{d\omega}{dq} = \frac{d}{dq} \left(\omega_0 / \sin \left(\frac{qa}{2} \right) \right) = \omega_0 \cdot \frac{q}{2} \cos \left(\frac{qa}{2} \right)$$

$$(2) \frac{L}{2\pi} \cdot \frac{1}{\omega_0 \cdot q \cdot \cos \left(\frac{qa}{2} \right)} = \frac{N}{\pi} \cdot \frac{1}{\omega_0 \sqrt{1 - \sin^2 \left(\frac{qa}{2} \right)}} =$$

$$= \frac{N}{q} \cdot \frac{1}{\sqrt{\omega_0^2 - \omega_0^2 \sin^2 \left(\frac{qa}{2} \right)}}$$



$$E_{kin} = \frac{1}{2} m \sum_k i\omega_k^2 = \frac{1}{2} m \sum_k i\omega_k i\omega_k^*$$

$$u_q(t) = \frac{1}{TN} A_q \cdot e^{i(\omega(q)t + qak)} =$$

$$= \frac{1}{TN} A_q \cdot e^{i(\omega(q)t)} \cdot e^{iqak} = \sum_{q=-\frac{N}{2}}^{\frac{N}{2}} \frac{1}{TN} A_q(t) \cdot e^{iqak} =$$

$A_q(t)$

$$= \frac{1}{2} m \sum_{q=-\frac{N}{2}}^{\frac{N}{2}} \sum_{q'} \dot{A}_q \cdot e^{iqak} \cdot \sum_{q'} \dot{A}_{q'}^* e^{-iq'ak} =$$

$$= \frac{1}{2} m \sum_{q, q'} \dot{A}_q \dot{A}_{q'}^* \cdot \sum_a e^{ia k (q - q')} =$$

$\sum_{q, q'} \cdot N$

$$= \frac{1}{2} m \sum_{q, q'} \dot{A}_q \dot{A}_{q'}^* \delta_{qq'} \cdot N = \frac{1}{2} m \sum_{q, q'} \dot{A}_q \dot{A}_{q'}^* =$$

$$= \frac{1}{2} m \sum_{q=-\frac{N}{2}}^{\frac{N}{2}} \dot{A}_q^2 \quad // \text{total nr. of comp. is } N$$

$$\text{Real} \quad \epsilon_{\text{part}} = \frac{1}{2} g \sum_k (u_k - u_{k-1})^2 =$$

$$= \frac{1}{2} g \sum_k (u_k - u_{k-1})(u_k - u_{k-1})^* =$$

each attains coop. conj. form

$$= \frac{1}{2} g \sum_k \{ u_k u_k^* + u_{k-1} u_{k-1}^* - u_{k-1} u_k^* - u_k u_{k-1}^* \} =$$

$$= \frac{1}{2} g \sum_k \{ u_k u_k^* + u_{k-1} u_{k-1}^* - 2 \operatorname{Re} \{ u_{k-1} u_k^* \} \}$$

$$u_n(t) = \sum_q \frac{A_q}{\sqrt{N}} e^{i(\omega t + q a k)}$$

$$i) \frac{1}{2} g \sum_k u_k u_k^* = \frac{1}{2} g \sum_k \sum_q \frac{A_q}{\sqrt{N}} \cdot e^{i(\omega t + q a k)}.$$

$$\cdot \sum_q \frac{A_q^*}{\sqrt{N}} e^{-i(\omega t + q' a k)} = \frac{1}{2} \frac{g}{N} \sum_{q,q'} A_q A_{q'}^*.$$

$$\underbrace{\sum_k e^{i(q-q')ak}}_{N\delta_{qq'}} = \frac{1}{2} g \sum_q A_q^2$$

$$ii) \frac{1}{2} g \sum_k u_{k-1} u_{k-1}^* = \frac{1}{2} g \sum_k u_k u_k^* = \frac{1}{2} g \sum_q A_q^2$$

Once more time x 2

$$E_{\text{kin}} = \frac{1}{2} M \sum_q \dot{A}_q^2 \quad E_{\text{pot}} = \frac{1}{2} M \sum_q w(q) \cdot A_q^2$$
$$w(q) = \omega_0 / \sin^2 \left(\frac{\pi q}{L} \right)$$

$$E_{\text{tot}} = \sum_q \left\{ \frac{1}{2} M \dot{A}_q^2 + \frac{1}{2} w(q) \cdot A_q^2 \right\}$$

Fact. en. harmonic osc. for CP:

$$\frac{1}{2} M \dot{c}_i^2 + \frac{1}{2} M \omega^2 c_i^2 \quad // \text{For 1 osc. wave}$$

// Periodically the same

In QM

$$\frac{\hbar \omega}{2} (2n+1) = \hbar \omega \left(n + \frac{1}{2} \right)$$

quantum no. $n = [0, \dots, +\infty]$

In quantum mechanics, harm. osc is always in motion:

$$E_0 = \frac{\hbar \omega}{2} \quad \text{zero energy state}$$

/ different quantum no. for diff quantum state

$$E_{\text{tot}} = \sum_{q=-\frac{\pi}{a}}^{\frac{\pi}{a}} \hbar w(q) \left(\tilde{n}_q + \frac{1}{2} \right)$$

/ averaged

$$E_0 = \sum_q \frac{\hbar w(q)}{2}, \quad n = 0$$

[Planapay]

Python package: *visualine properties of lattice*

\bar{n}_q - can be found from the Bose-Einstein distribution

$$\bar{n}_q = \frac{1}{e^{\frac{\hbar\omega(q)}{kT}} - 1}$$

$$E = \sum_q \frac{\hbar\omega(q)}{e^{\frac{\hbar\omega(q)}{kT}} - 1} = \begin{cases} \Sigma \rightarrow S \\ \text{bc } N \text{ is sufficiently large} \end{cases}$$

$$\sum_q \rightarrow \frac{L}{\pi a^3} \int dq \quad 1d$$

, total volume

$$\sum_q \rightarrow \frac{V}{(a^3)^3} \int dq^3 \quad 3d$$

$$E = \frac{L}{2\pi} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} \frac{\hbar\omega(q)}{e^{\frac{\hbar\omega(q)}{kT}} - 1} dq =$$

$$= \frac{L}{2\pi} \int_0^{\frac{\pi}{a}} \frac{\hbar\omega(q)}{e^{\frac{\hbar\omega(q)}{kT}} - 1} dq = \begin{cases} dq \rightarrow d\omega \\ \text{using the DOS funct} \end{cases}$$

$$g(\omega) = \frac{dn}{d\omega}; q = \frac{\omega}{L} \cdot n$$

$$dn = \frac{L}{\omega} d\varphi$$

$$g(\omega) = \frac{L}{\omega} \frac{d\varphi}{d\omega}$$

$$d\varphi = \frac{\omega}{L} g(\omega) d\omega$$

$$\textcircled{2} \quad \frac{dN}{d\varphi} \int_0^{\omega_0^2} \frac{\omega}{\sqrt{\omega_0^2 - \omega^2}} \left(e^{\frac{i\omega}{kT}} - 1 \right) d\omega; \quad \omega_0 = \sqrt{\frac{4\pi}{m}}$$

$$x = \frac{\hbar \omega}{kT} \quad (\text{dimensionless parameter})$$

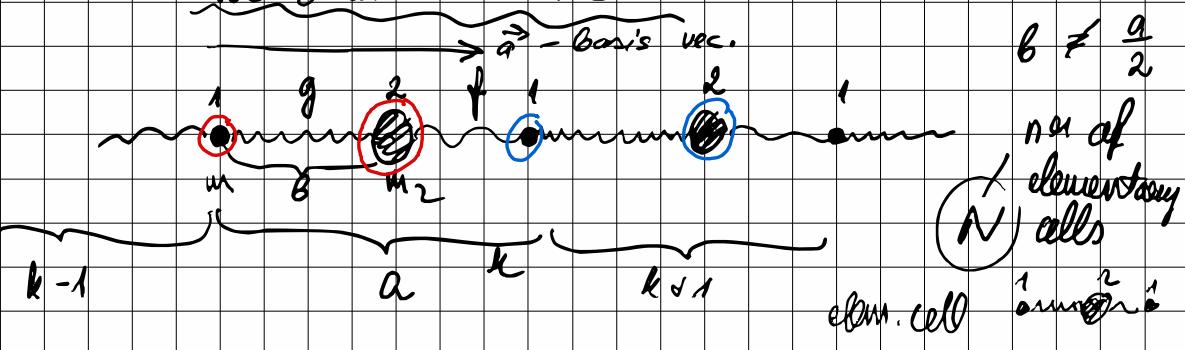
$$C_V = \frac{\partial E}{\partial T} = k \cdot N \cdot \frac{2}{\pi} \int_0^{x_0} \frac{x^2 e^x}{\sqrt{x_0^2 - x^2} (e^x - 1)^2} dx$$

$$x_0 = \frac{\hbar \omega_0}{kT}$$

So now we can calculate the near zero we can
for C_V only thanks to quantum mechanics.

L 3.2 Harmonic vibration of 1D + two atomic lattice

15.09.22



q, f are not equal b/c no have different stiffness / deformation from electron clouds.

What params. we need

(1.) frequency of vibration

We consider
2 atoms in 1
1 elem. cell

$$\omega(q, ?) \quad \alpha = [1, N]$$

(2.) displacement from equilibrium position

$$u_k^s - [x \text{ or } z] \\ u_k^s - [\text{any integer}]$$

$$R_k^s = R_a + a_k^s = a_k + u_k^s + u_k^s(t)$$

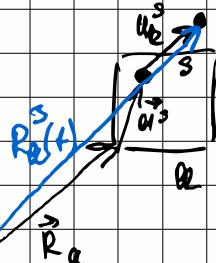
$$s = 1, 2$$

$$a_1^s = 0 \\ a_2^s = \beta$$

$$R_k^s = a \cdot k + a^s$$

$$a^s = (0, \beta)$$

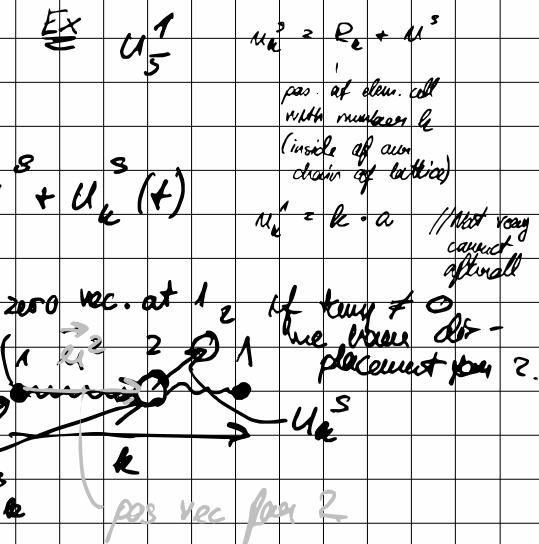
u_k^s
real no.



In 3-D

Let a, β be
predefined

Main question is
how do we calculate
 $u_k^s(t)$?



In classical phys. to calculate to position
phase only known law: Newton's II Law
vectors can be ignored in 1-D.

$$a = \frac{F}{m}$$

, bc $u_a^s(t)$ depends on time

$$a_a^s = \ddot{r}_a^s(t) = 0 + 0 + \ddot{u}_a^s$$

$$\ddot{u}_a^s = \frac{F_a^s}{m_s}$$

$$F_a^s = -\frac{\partial E_{\text{pot}}}{\partial u_a^s}$$

$$E_{\text{pot}} = \frac{g}{2} \sum_n (u_n^1 - u_n^2)^2$$

$$+ \frac{g}{2} \sum_n (u_n^1 - u_{n-1}^2)$$

not squared last term

^{2nd order}
^{2nd order}

Answer can be found
from Lect 3 notes

n - index of summation

a - fixed

$$m_1 \ddot{u}_a^1 = -g(u_a^1 - u_a^2) - g(u_a^1 - u_{a-1}^2)$$

$$m_2 \ddot{u}_a^2 = -g(u_a^2 - u_a^1) - g(u_a^2 - u_{a-1}^1)$$

•
•
•

2N

$$N \approx 10^{23}$$

We can do this numerically but
analytically?

We take our equations from classical mechanics

$$F \sim u \text{ linear propagation}$$

Because we have linear dependence, use the harmonic waves.

Wave propagating in one lattice

$$u_a^s(t) = \frac{A}{\sqrt{m_s N}} e^{i(\omega t + q \cdot R_a^s)}$$

ω ?

$$R_a^s = a \cdot a + a^s$$

$$m_1 u_a^1 = -g(u_a^1 - u_{a-1}^1) - f(u_a^1 - u_{a-1}^1) u^s = (0, \theta); s=1, 2$$

$$u_a^1(t) = \frac{A}{\sqrt{N m_1}} e^{i(\omega t + q(R_a))}$$

$$u_a^2(t) = \frac{A^2}{\sqrt{N m_2}} e^{i(\omega t + q(R_a + a))}$$

$$-\omega^2 \cdot \frac{m_1}{\sqrt{m_1}} A^1 e^{i(\omega t + qak)} =$$

$$= -\frac{(g+f) \dot{u}_a^1}{\sqrt{m_1}} + \frac{(g u_a^2 + f u_{a-1}^2)}{\sqrt{m_2}}$$

$$-\omega^2 \cdot A^1 e^{i(\omega t + qak)} = -\frac{(g+f) \dot{u}_a^1}{m_1} + \frac{(g u_a^2 + f u_{a-1}^2)}{\sqrt{m_1 m_2}}$$

$$-\omega^2 \cdot A^1 e^{i(\omega t + qak)} = -\frac{(g+f)}{m_1} A^1 e^{i(\omega t + qak)} \quad (\textcircled{+})$$

$$\textcircled{+} \quad \frac{A^2 / g e^{i(\omega t + q(\alpha_0 + \theta))}}{\sqrt{m_1 m_2}} + q C e^{i(\omega t + q(\alpha_{k-1} + \theta))}$$

Divide by $e^{i(\omega t + q\alpha_0)}$

$$-\omega^2 A^1 = -\frac{(g + \ell)}{m_1} A^1 + \frac{A^2}{\sqrt{m_1 m_2}} (g e^{iq\theta} + q e^{iq\theta} \cdot C e^{-iq\theta})$$

$$-\omega^2 A^1 = -\frac{(g + \ell)}{m_1} A^1 + \frac{A^2}{\sqrt{m_1 m_2}} e^{iq\theta} (g + q \cdot C e^{-iq\theta})$$

↑ we have an additional wave shift. So we shall combine it with A^2 to get rid of the waves

$$-\omega^2 A^1 = -\frac{(g + \ell)}{m_1} A^1 + \frac{A^2}{\sqrt{m_1 m_2}} (g + q \cdot C e^{-iq\theta})$$

$$\left(\omega^2 - \frac{(g + \ell)}{m_1} \right) A^1 + \left(\frac{g + q e^{-iq\theta}}{\sqrt{m_1 m_2}} \right) A^2 = 0$$

$$\left(\frac{g + q e^{iq\theta}}{\sqrt{m_1 m_2}} \right) A^1 + \left(\omega^2 + \frac{(g + \ell)}{m_2} \right) A^2 = 0$$

All elementary cells are equivalent, so in the cell $k+1, k-1$ an whatever we have the same equations of motion.

Have the determinant looks like

$$\begin{vmatrix} \omega^2 - \frac{(g+f)}{m_1} & \frac{g+f e^{-iqa}}{\sqrt{m_1 m_2}} \\ \frac{g+f e^{iqa}}{\sqrt{m_1 m_2}} & \omega^2 - \frac{(g+f)}{m_1^2} \end{vmatrix}$$

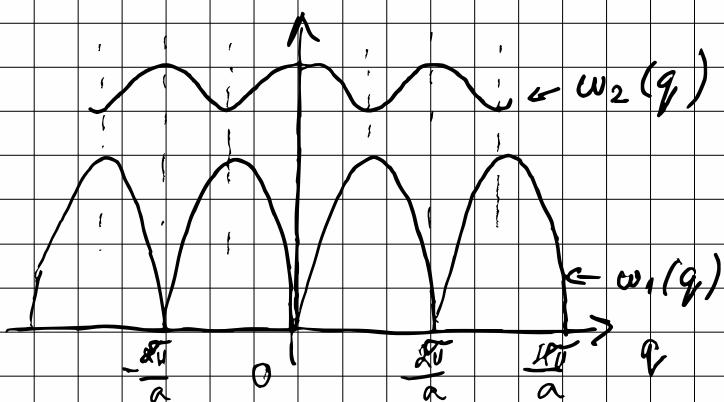
With this we get a quadratic equation

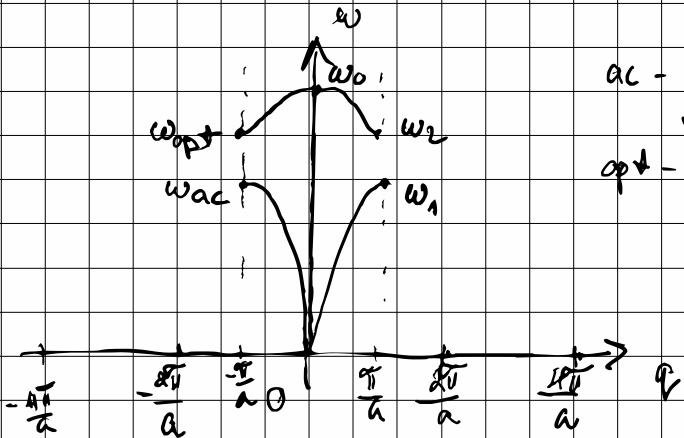
$$\omega_1^2(q) = \frac{1}{2} \omega_0^2 \left(1 - \sqrt{1 - f^2 \sin^2 \left(\frac{qa}{a} \right)} \right)$$

$$\omega_2^2(q) = \frac{1}{2} \omega_0^2 \left(1 + \sqrt{1 - f^2 \sin^2 \left(\frac{qa}{a} \right)} \right)$$

$$\omega_0^2 = \frac{(g+f)(m_1 + m_2)}{m_1 m_2}$$

$$f = 16 \frac{gf}{(g+f)^2} \cdot \frac{m_1 m_2}{(m_1 + m_2)}$$





ac - acoustic waves
opt - optical branches of propagation

To find q we need to apply periodic boundary conditions

$$u_n^1 = u_{n+N}^1; e^{iqNa} = 1$$

$$qNa = 2\pi n$$

$$q = \frac{2\pi}{Na} \cdot n = \frac{2\pi}{a} \cdot \frac{n}{N}, n \in \left\{ \frac{N}{2}, \frac{N}{2} \right\}$$

q is defined from $-\frac{\pi}{a}$ to $\frac{\pi}{a}$ see $n = \frac{-N}{2}$ or

$$n = \frac{N}{2} \text{ bc } q = \frac{2\pi}{a} \cdot \frac{n}{N} = \frac{2\pi}{a} \cdot \frac{N}{q} \cdot \frac{1}{N} = \frac{\pi}{a}$$

with eight bands

The waves acoustic and optic

Acoustic waves propagate at a certain speed, the speed of sound

$$\omega_1 \sim q$$

Optical waves

$$u_k^1 \quad u_k^2 \quad \cancel{q = 0} \quad \omega_2 = \omega_0$$

$$u_k^1 = \frac{A'}{\sqrt{m_1}} e^{i(\omega t + q k a)}$$

$$M_k^1 = \frac{A}{\sqrt{m_2}} e^{i\omega_0 t}$$

$$u_k^2 = \frac{A^2}{\sqrt{m_2}} e^{i\omega_0 t}$$

Amplitude can be found from
 $(\dots) A_1 + (\dots) A_2 = 0$

$$(\dots) A_1 + (\dots) A_2 = 0$$

$$|q| = \frac{q}{\lambda}$$

For the harmonic appear.

It is impossible to simultaneously calculate A_1 and A_2 , but we can calculate the ratio A_1 / A_2 .

$$\left(\frac{(q + \ell)(m_1 + m_2)}{m_1 + m_2} + \frac{q + \ell}{m_1} \right) A' + \left(\frac{0 + e^0}{\sqrt{m_1 m_2}} \right) A^2 = 0$$

$$\left(\frac{m_1 + m_2}{m_1 m_2} - \frac{1}{m_1} \right) A' + \left(\frac{1}{\sqrt{m_1 m_2}} \right) A^2 = 0$$

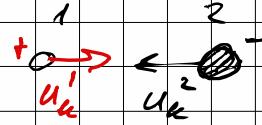
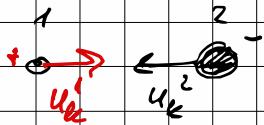
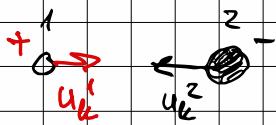
$$u_k^1 = \frac{A'}{\sqrt{m_1}}$$

$$\frac{A'}{A^2} = \sqrt{\frac{m_1}{m_2}}$$

$$u_k^1 = \frac{A^2}{\sqrt{m_2}}$$

$$\frac{u_k^1}{u_k^2} = \frac{m_2}{m_1}$$

$$U_k^1 M_1 + U_k^2 M_2 = 0$$



of charged atoms

This movement creates dipole momentums, which makes it able to absorb and emit EM waves. That is why this type of wave is called an optic waves.

But if the atoms are not charged, they are acted in Raman spectrum (space scattering)

* Raman spectroscopy

L. 3.3 Vibrations of 3D crystals

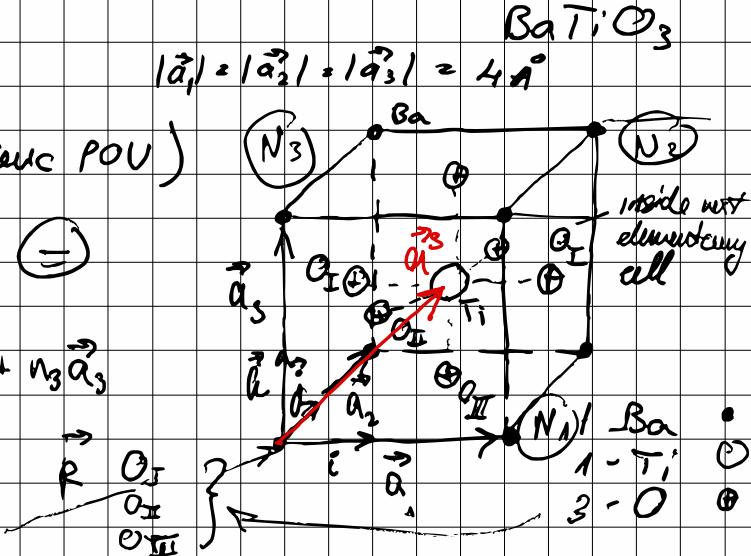
O-atoms are the same chemically but not the same in sense of crystallography (from the symmetric POV)

$$\vec{R}_n = \vec{R}_n + \vec{\alpha}_1^3 \quad (=)$$

$$|\vec{\alpha}_1| = |\vec{\alpha}_2| = |\vec{\alpha}_3| = 4.9^\circ$$

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

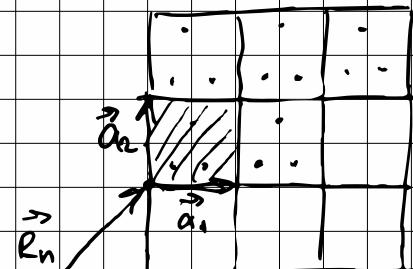
$$n_1, n_2, n_3 \in \mathbb{Z}$$



	x	y	z	a	
1 Ba	0	0	0	(\AA)	All chem. cell are equivalent. (for $T = 0$)
1 Ti	2	2	2		
1 O _I	0	2	2		S - no af different atoms
1 O _{II}	2	0	2		
1 O _{III}	2	2	0		n - nr af chem. cell

$$\begin{matrix} \vec{a}_1 & 4 & 0 & 0 \\ \vec{a}_2 & 0 & 4 & 0 \\ \vec{a}_3 & 0 & 0 & 4 \end{matrix}$$

(2) $\vec{R}_{n_1, n_2, n_3}^s + \vec{a}^s$



\vec{R}_n - vec. af
tænus lasteren

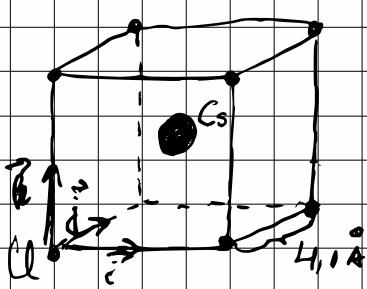
$$\vec{R}_n^s = \vec{R}_{\alpha,n} + \vec{a}_{\alpha}^s + \vec{u}_{\alpha,n}^s (+)$$

$$N = N_1 N_2 N_3$$

N - total nr af
different chem. cells

$$\vec{R}_{\alpha,n}^s = \vec{R}_{\alpha,n} + \vec{a}_{\alpha}^s + \vec{u}_{\alpha,n}^s (+) \quad T \neq 0$$

$$\vec{R}_{n_1, n_2, n_3}^s = \vec{R}_{\alpha,n_1, n_2, n_3} + \vec{a}_{\alpha}^s + \vec{u}_{\alpha,n_1, n_2, n_3}^s (+)$$

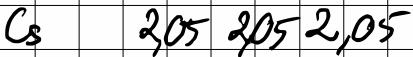


$s = \text{Cl}, \text{Cs}$
 $s = 1, 2$

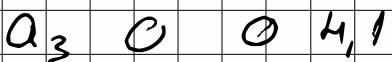
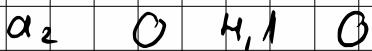
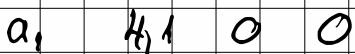
$T = 0$

$$\vec{R}_{n_1, n_2, n_3}^s = \vec{R}_{n_1, n_2, n_3} + \vec{a}^s$$

$$\vec{a}^{\pm} \quad x \quad y \quad z \quad 1 \text{ \AA} = 10^{-10} \text{ m}$$



$$\vec{a} \quad x \quad y \quad z$$



In VASP:

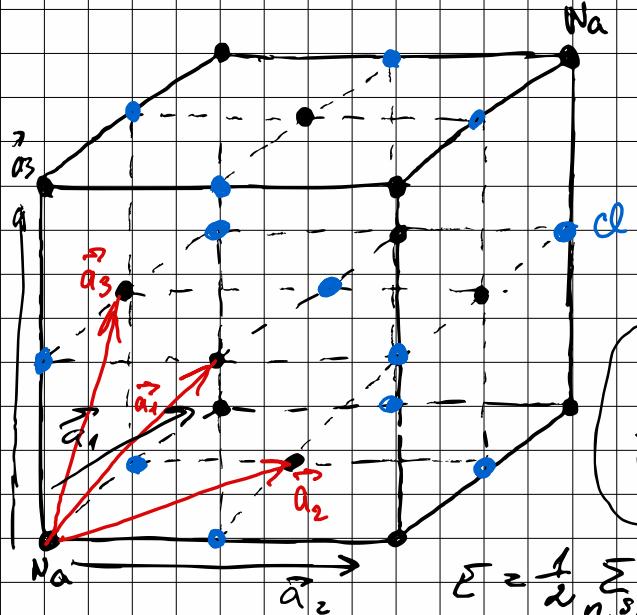
POSCAR // Position

- 1 Cs Cl
- 2 1.0 - multiplying factor
- 3 4,1 ↘ 0. ↘ 0.
- 4 0. ↘ 4,1 ↘ 0.
- 5 0. ↘ 0. ↘ 4,1
- 6 Cs ↘ Cl
- 7 1 ↘ 1 // have many columns
- 8 Cartesian
- 9 2,05 ↘ 2,05 ↘ 2,05
- 10 0. ↘ 0. ↘ 0. ↘

POSCAR

- 1 Ba Ti O 3
- 2 1.0
- 3 4. w 0. w 0.
- 4 0. w 4 w 0.
- 5 0. w 0. w 4.
- 6 Ba ↘ Ti ↘ O ~~halo de 0,06~~
- 7 1 ↘ 1 ↘ 3 // 1 ↘ 1 ↘ 1
- 8 Cartesian
- 9 0. w 0. w 0. / also halo
- 10 2. ↘ 2. ↘ 2.
- 11 0. ↘ 2. ↘ 2.
- 12 2 ↘ 0. ↘ 2
- 13 2 ↘ 2. ↘ 0. ↘

Na Cl



The basis vectors are very strange but it is easier to solve the Schrödinger eq with 2 atoms and 22 electrons. We can also use 8 atoms but we would need 120 electrons. So the choice of coordinates is very important.

$$\vec{R}_n^s = \vec{R}_n + \vec{a}_1^s$$

$$\vec{R}_{\alpha,n}^s = \vec{R}_{\alpha,n} + \vec{a}_{\alpha}^s + u_{\alpha,n}^s(r)$$

$$\Sigma = \frac{1}{2} \sum_{n,s,\alpha} m_s (u_{\alpha,n}^s(r))^2 + V_{\text{part}}(R_n^s)$$

ε Force

$$V(R) = V(0) + \sum_{\alpha,n,s} \frac{\partial V}{\partial u_{\alpha,n}^s} \Big|_{u=0} u_{\alpha,n}^s +$$

in equilibrium state

$$+ \frac{1}{2} \sum_{\alpha,n,s, \beta,n',s'} \frac{\partial^2 V}{\partial u_{\alpha,n}^s \partial u_{\beta,n'}^{s'}} \Big|_{u=0} \cdot u_{\alpha,n}^s \cdot u_{\beta,n'}^{s'}$$

$$F_{\alpha,n}^s = - \frac{\partial V}{\partial u_{\alpha,n}^s} \Big|_{u=0} = 0$$

$$V(R) = V(0) + \frac{1}{2} \sum_{\alpha,n,s} \frac{\partial V}{\partial u_{\alpha,n}^s} \Big|_{u=0} u_{\alpha,n}^s +$$

$$\cdot u_{\alpha,n}^s \cdot u_{\beta,n'}^{s'} \quad \left| \quad \varphi_{\alpha,\beta}^{(s s')}_{(n n')} = \frac{\partial V}{\partial u_{\alpha,n}^s \partial u_{\beta,n'}^{s'}} \right|_{u=0}$$

Now try this with

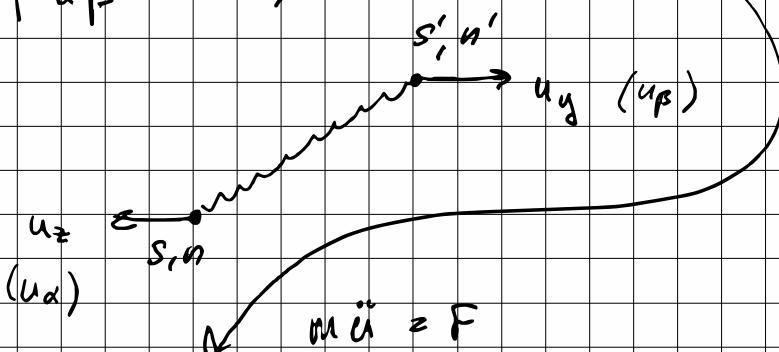
$$E = \frac{1}{2} \sum_{n,s,\alpha} m_s (\dot{u}_{\alpha,n}^s(r))^2 + V_{pot}(\vec{r}_n^s)$$

$$N = N_1 N_2 N_3 \approx 10^{23}$$

$$V(R) = V(0) + \frac{1}{2} \sum_{\alpha, n, s} \sum_{\beta, n', s'} \Phi_{\alpha\beta}^{ss'} (n n') u_{\alpha,n}^s \cdot u_{\beta,n'}^{s'}$$

$$\Phi_{\alpha\beta}^{ss'} (n n')$$

α, β -directions



$$m \ddot{u} = F$$

$$F_{\alpha,n}^s = - \frac{\partial V}{\partial u_{\alpha,n}^s} = - \sum_{\beta, n', s'} \Phi_{\alpha\beta}^{ss'} (n n') u_{\beta,n'}^{s'}$$

$3sN \times 3sN$

$$F_{\alpha,n}^s = - \sum_{\beta, n', s'} \Phi_{\alpha\beta}^{ss'} (n n') u_{\beta,n'}^{s'}$$

$F \sim u$
Hooke's law

$$m_s \ddot{u}_{\alpha,n}^s = - \sum_{\beta, n', s'} \Phi_{\alpha\beta}^{ss'} u_{\beta,n'}^{s'}$$

$3 \cdot 3 \cdot N$

Too fucking many
equations

Previous p. 9

\vec{q} - wave vector

$$u_{\alpha, n}^s(t) = \frac{1}{\sqrt{N M_s}} \cdot A(\vec{q}) \cdot e_\alpha^s(\vec{q}) \cdot e^{i(\omega(\vec{q}) \cdot t + \vec{q} \cdot \vec{R}_n^s)}$$

$$\omega^2 \cdot \sqrt{M_s} \cdot A(\vec{q}) e_\alpha^s(\vec{q}) e^{i\vec{q} \cdot \vec{R}_n^s} =$$

$$= \sum_{\beta, s', n'} \langle \rangle_{\alpha \beta} \begin{pmatrix} s & s' \\ n & n' \end{pmatrix} e^{i\vec{q} \cdot \vec{R}_n^s} \cdot \frac{A(\vec{q})}{\sqrt{M_{s'}}} \cdot e_\beta^{s'}(\vec{q})$$

$$\left\{ \omega^2(\vec{q}) e_\alpha^s(\vec{q}) = \sum_{\beta, s'} D_{\alpha \beta}^{ss'}(\vec{q}) e_\beta^{s'}(\vec{q}) \right.$$

$G = SS'$

CSCl
 $s = 1, 2$

$$D_{\alpha \beta}^{ss'}(\vec{q}) = \sum_{n, n'} \langle \rangle \begin{pmatrix} s & s' \\ n & n' \end{pmatrix} e^{i\vec{q} \cdot (\vec{R}_n^s - \vec{R}_{n'}^{s'})}$$

$$D_{\alpha \beta}^{ss'} = (3s \times 3s) \quad D_{\alpha \beta}^{ss'} = D_{\beta \alpha}^{s's}$$

dynamical matrix

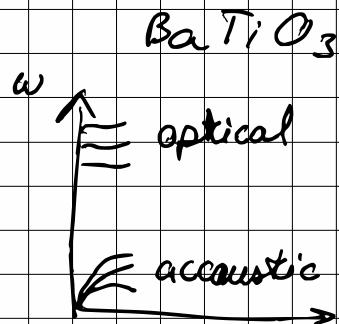
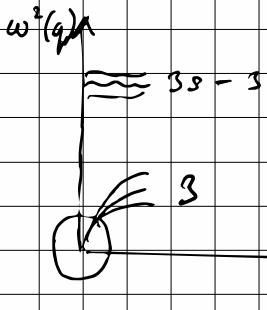
$$\omega^2 e = De$$

$$(\omega^2 I - D)e = 0$$

$$|\omega^2 \cdot I - D| = 0 \xrightarrow{(3s \times 3s)} 3s \xrightarrow{\omega^2(\vec{q})} 0$$

$$D_{\alpha \beta}^{ss'} = (6 \times 6)$$

$$\omega_i^2(\vec{q}) \approx 1 \dots 33 \quad \text{CsCl} \quad \omega_i^2(\vec{q}) \quad i=1 \dots 6$$



Periodic boundary conditions

$$u_n = u_{n+N}$$

$$u_{\alpha, n_1, n_2, n_3}^s = u_{\alpha, n_1 + N, n_2, n_3}^s$$

$$= u_{\alpha, n_1, n_2 + N, n_3}^s = u_{\alpha, n_1, n_2, n_3 + N}^s$$

$$e^{i q_1 N_1 a_1} = 1$$

a_1 - first basis vector

$$q_1 N_1 a_1 = 2\pi l_1, \quad l_1 \in \mathbb{Z}$$

$$q_1 = \underbrace{\frac{2\pi}{N_1 a_1}}_{L_1 - \text{total length in } x\text{-dir}} \cdot l_1 = \frac{2\pi}{a_1} \cdot \frac{l_1}{N_1}$$

L_1 - total length in x -dir

$$q_2 = \frac{2\pi}{a_2} \cdot \frac{l_2}{N_2} \quad q_3 = \frac{2\pi}{a_3} \cdot \frac{l_3}{N_3}$$

csd

$$\omega_i^2(\vec{q})$$

$$j = 1 \dots 6$$

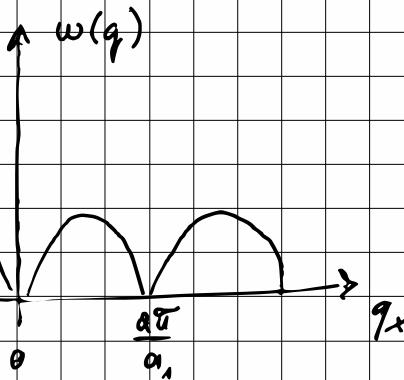
$$\omega_i^2(\vec{q})$$

$$f = 1 \dots 6$$

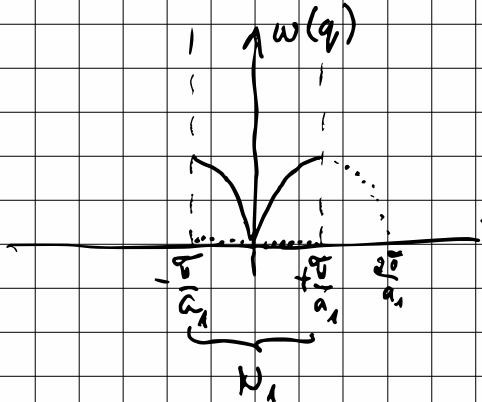
$$x \frac{2\pi}{a_1}$$

$$y \frac{2\pi}{a_2}$$

$$z \frac{2\pi}{a_3}$$



To symmetrize



q_x - disc. func

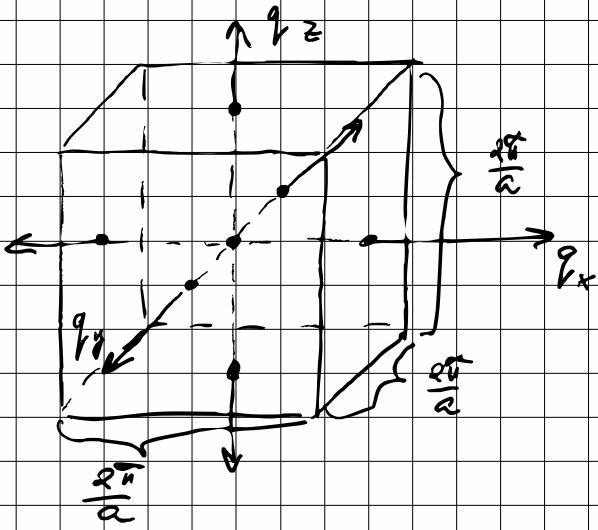
$$\vec{q} = (q_x, q_y, q_z)$$

$$q_x = \frac{2\pi}{a_x} \cdot \frac{N_x}{N_x}$$

$$l_\alpha = \left[-\frac{N_\alpha}{2}, \dots, \frac{N_\alpha}{2} \right]$$

$$N_x = N_y = N_z = N_\alpha$$

$$N = N_\alpha^3$$



CsCl

$$\Phi_{\alpha\beta}^{ss'}(u u') \rightarrow D_{\alpha\beta}^{ss'} \xrightarrow{\omega^2(\vec{q})} e_\alpha^s(\vec{q}) \rightarrow \epsilon_{\text{ext}}$$

matrices
form

$$\boxed{F} = \boxed{Q} \boxed{U}$$

↓
calculated by VASP

Packag
PHONOOPY

D

↓
diagonal

$$e_\alpha^s(\vec{q}) \quad \omega(\vec{q})$$

$$u_{\text{pat}} = u(0) + \frac{1}{2} \sum \phi u$$

L4. Adiabatic approximation

$$\hat{H} \Psi = E \Psi$$

10^{23} - no. of nuclei

In ground state,
no don't have
dependence on
time.

$$\Psi(x_1, x_2, \dots, y_1, \dots, z_1, \dots, t_1, \dots, t_2, \dots, t_3, \dots)$$

Number of particles counts is way too many (10^{23})
so we need some simplifications

$$H = \hat{T}_e + \hat{T}_n + U_{ee} + U_{en} + U_{nn}$$

$$\hat{T}_e = -\frac{\hbar^2}{2m} \sum_i \hat{\Delta}_i$$

$$\hat{T}_n = -\frac{\hbar^2}{2} \sum_n \frac{\hat{\Delta}_n}{H_n}$$

$$U_{ee} = \frac{e^2}{4\pi\epsilon_0} \sum_{i,j} \frac{1}{r_{i,j}}$$

$r_{i,j}$ - dist between electrons
 i and j

$$U_{nn} = \frac{e^2}{4\pi\epsilon_0} \sum_{j,k} \frac{z_j z_k}{R_{j,k}}$$

z - dim-less charge
of particles

$$U_{en} = \frac{e^2}{4\pi\epsilon_0} \sum_{i,k} \frac{z_k}{R_{i,k}}$$

wave function and total energy from Sch. eq.

$$\Psi(\alpha, R)$$

Quantity of any physical particle

$$\int \psi^* \hat{A} \psi d\sigma^3 dR^3 = A$$

What about the normalizing property?

some multiplying factor - mass and nuclei technically

$$10 \frac{M_p}{m_e} \approx 20000$$

$$\frac{v_n}{v_e} \approx \sqrt{\frac{m_e}{m_n}} \approx$$

$$\approx \sqrt{\frac{1}{20000}} \approx \frac{1}{140}$$

Boltzmann law

$$\frac{3kT}{2} \approx \frac{mv^2}{2}$$

$$1\bar{v} \approx \sqrt{\frac{3kT}{m}}$$

$$\boxed{T_1} > \boxed{T_2}$$

Temp must be equalized

$$v_e \approx 100 v_n$$

- from descr. electrons

$$\Psi(a, R) = \psi(a, R) \cdot \varphi(R)$$

1
total wave function
function

from nuclei

we separate electrons from the nuclei

$$\hat{A}_i (\psi(a, R) \cdot \varphi(r)) = \varphi(r) \hat{A}_i \psi(a, R)$$

$$\hat{A}_i = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$$

R - loc of nuclei

$$\hat{T}_1 \cdot \psi(a, R) \psi(R) = \psi(R) \hat{T} \psi(a, R)$$

$$\begin{aligned}
& \hat{\Delta}_n \psi(a, R) \psi(R) = \hat{\nabla}_n \hat{\nabla}_n \psi(a, R) \psi(R) = \\
& = \hat{\nabla}_n (\psi(a, R) \hat{\nabla}_n \psi(R) + \psi(R) \hat{\nabla}_n \psi(a, R)) = \\
& = \psi(a, R) \hat{\Delta}_n \psi(R) + \hat{\nabla}_n \psi(r, R) \hat{\nabla}_n \psi(R) + \\
& + \hat{\nabla}_n \psi(R) \hat{\nabla}_n \psi(a, R) + \psi(R) \hat{\Delta}_n \psi(a, R) = \\
& = \psi(a, R) \hat{\Delta}_n \psi(R) + 2 \cdot \hat{\nabla}_n \psi(a, R) \cdot \hat{\nabla}_n \psi(R) + \\
& + \psi(R) \hat{\Delta}_n \psi(a, R)
\end{aligned}$$

$$\begin{aligned}
& \hat{T}_n \psi(a, R) \psi(R) = -\frac{\hbar^2}{2} \sum_n \left\{ \psi(a, R) \hat{\Delta}_n \psi(R) + \right. \\
& \left. + 2 \hat{\nabla}_n \psi(R) \hat{\nabla}_n \psi(a, R) + \psi(R) \hat{\Delta}_n \psi(a, R) \right\} \frac{1}{M_n} \\
& M - masses \text{ af nuclei}
\end{aligned}$$

$$\hat{H} =$$

$$\begin{aligned}
& = \psi(R) \hat{T}_e \cdot \psi(a, R) + V_{ee} \psi(a, R) \psi(R) + \\
& + V_{en} \psi(a, R) \psi(R) - \frac{\hbar^2}{2} \sum_n \frac{1}{M_n} \left\{ \psi(a, R) \hat{\Delta}_n \psi(R) + \right. \\
& \left. + 2 \hat{\nabla}_n \psi(a, R) \hat{\nabla}_n \psi(a, R) + \psi(R) \hat{\Delta}_n \psi(a, R) \right\} + \\
& + V_{nn} \psi(a, R) \psi(R) = E \cdot \psi(a, R) \psi(R)
\end{aligned}$$

Neue Sch. Eq.

$$\psi(R) \hat{\tau}_e \varphi(a, R) + V_{ee} \varphi(a, R) \psi(R) + V_{ea} \varphi(e, R) \psi(R) = \\ = E_e \cdot \varphi(a, R) \psi(R)$$

$$\int \psi^*(R) \psi(R) dR^3 = 1$$

$$\int (\varphi^*(a, R) \varphi(a, R) d\alpha^3 = 1$$

$$\int \underbrace{\{ \psi^*(\psi(R) \hat{\tau}_e \varphi(a, R) + V_{ee} \varphi(a, R) \psi(R) + V_{ea} \varphi(e, R) \psi(R) \})}_{= E_e \cdot \varphi(a, R) \int \psi^*(R) \psi(R) d\alpha^3} d\alpha^3 = \\ = E_e \cdot \varphi(a, R) \int \psi^*(R) \psi(R) d\alpha^3$$

$$i) \hat{\tau}_e \varphi(a, R) \underbrace{\int \psi^* \psi d^3 R}_{\text{1}} = \hat{\tau}_e \varphi(a, R)$$

$$ii) \dots \text{and so on}$$

Left-hand side is therefore

$$\hat{\tau}_e \varphi(a, R) + (V_{ee} + V_{ea}) \varphi(a, R) = E_e \varphi(a, R)$$

Once again

$$-\frac{\hbar^2}{2} \sum_n \frac{1}{M_n} \left\{ \psi(R) \Delta_n \psi(R) + 2 \hat{\tau}_n \psi(n, R) \hat{\tau}_n \psi(R) + \right. \\ \left. + \psi(R) \Delta_n \varphi(a, R) \right\} + V_{ea} \varphi(a, R) \psi(R) + E_e \varphi(a, R) \psi(R) =$$

$$= E \psi(a, R) \Psi(R)$$

$$\int \left(\psi^*(a, e) - \frac{e^2}{2} \sum_n \frac{1}{\Delta_n} \left((\psi_{nR}(a, R) \Delta_n \psi(R) + 2 \hat{\nabla}_n \psi(a, e) \hat{\nabla}_n \psi(e) + \psi(R) \Delta_n \psi(a, R) \right) + V_{nn} \psi(a, e) \psi(e) + E_e \psi_{nR}(e) \psi(e) \right) d\alpha^3 =$$

$$= E \psi(R) \underbrace{\int \psi^*(a, R) \psi(a, R) d\alpha^3}_{\text{''1''}}$$

Simplifying 1st member:

$$i) \int \psi^*(a, R) \psi(a, R) \Delta_n \psi(R) d\alpha^3 =$$

$$= \Delta_n \psi(R) \underbrace{\int \psi^*(a, R) \psi(a, R) d\alpha^3}_{\text{''1''}} = \Delta_n \psi(R)$$

$$ii) 2 \int (\psi^*(a, R) \hat{\nabla}_n \psi(a, R)) \cdot \hat{\nabla}_n \psi(e) d\alpha^3 =$$

$$= 2 \hat{\nabla}_n \psi(e) \int (\psi^*(a, e) \hat{\nabla}_n \psi(a, e)) d\alpha^3 = 0$$

We assume that electric current from our case doesn't exist. So $\psi = \psi^*$.

$$\vec{j} = \frac{i\epsilon\hbar}{2m} (\psi \cdot \hat{\nabla} \psi^* - \psi^* \cdot \hat{\nabla} \psi) \xrightarrow{\psi \rightarrow R} \text{check under } \text{mag write other}$$

$$\int \psi^* \psi d\alpha^3 = \int \psi^2 d\alpha^3 = 1 \quad \text{may}$$

$$\hat{\nabla}_n (\psi^2) = \nabla_n (\psi \cdot \psi) = 2\psi \nabla \psi$$

$$\hat{\nabla}_n \int \psi^2 d\alpha^3 = 0 = 2 \int \psi(\alpha, R) \hat{\nabla}_n \psi(\alpha, R) d\alpha^3 = 0$$

nonadiabaticity

$$\hat{T}_n \psi(R) - \frac{\hbar^2}{2} \sum_n \frac{1}{m_n} \left\{ \int \langle \psi^*(\alpha, R) \psi(R) \rangle_{in} \psi(\alpha, R) d\alpha^3 \right\} +$$

ϵ_n

$$+ V_{nn} \psi(R) = (\underbrace{E - \epsilon_e}_{\text{can be ignored}}) \psi(R)$$

bc of our simplification

E - total energy ; ϵ - energy per electron
 $(E - \epsilon_e) = \epsilon_n$ - energy per nuclei

$\Delta_n \psi(\alpha, R)$ - shows us the influence of electrons on the system electron subsystem atom

$$\Delta_n \psi(\alpha, R) = \frac{\partial^2 \psi(\alpha, R)}{\partial X_n^2} + \dots$$

Bc the atoms is much more massive than electrons the ratio of charge to so little mass is basically zero

$$\begin{cases} \hat{T}_e \psi(x, R) + (V_{ee} + V_{en}) \psi(\alpha, R) = \epsilon_e \psi(\alpha, R) \\ T_n \psi(R) + V_{nn} \psi(R) = (E - \epsilon_e) \psi(R) \end{cases}$$

$$T_n \psi(R) + V_{nn} \psi(R) + \epsilon_e \psi(R) = E \psi(R)$$

$$\hat{T}_n \psi(r) + V_{nn} \psi(r) = E_n \psi(r)$$

$$-\frac{\hbar^2}{2} \sum_n \hat{\Delta}_n \psi(r) + V_{nn} \psi(r) = E_n \psi(r)$$

Taylor series

$$V = V(0) + \sum_n \left. \frac{\partial V}{\partial u_n} \right|_{u_n=0} \cdot u_n +$$

$$+ \frac{1}{2} \sum_{n,n'} \left. \frac{\partial^2 V}{\partial u_n \partial u_{n'}} \right|_0 u_n u_{n'} + \dots$$

can be ignored for harmonic approx.

$$V = V(0) + \frac{1}{2} \sum_{n,n'} C_{nn'} u_n u_{n'}$$

$$\downarrow$$

$$w(q)$$

$$D \rightarrow$$

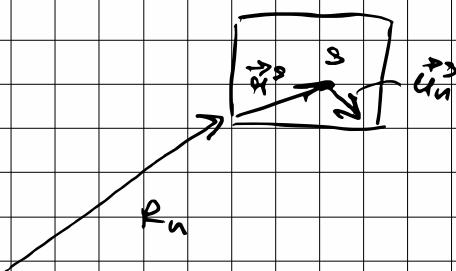
diagonalisierung

Why linear term in Taylor exp is zero?

V

$$F_n = - \frac{\partial V}{\partial u_n}$$

$U_{\alpha,n}^s$



CCl; $\alpha = 1, 2$

V - direction of dep; n - pos cl. cell; s - atom index

$$\vec{R}_n^s = \vec{R}_n + \vec{s}_1^s + \underbrace{\vec{u}_n^s}_{\text{displacement results from cell in}}$$

For $T = 0$, can be ignored

For equilibrium position ($\Rightarrow T = 0$)

$$F = -\frac{\partial V}{\partial u_n} = 0$$

$$\hat{T}_e \varphi + (U_{ee} + U_{en}) \varphi = E_e \varphi$$

Why repulsion can be ignored? bc it is compensated by attractions of pos. particles

①.

$$\hat{T} \varphi = E \varphi$$

$$N = 10^{23}$$

$$E \sim \epsilon - N$$

$$-\frac{\hbar^2}{2m} \hat{\Delta} \varphi = E \cdot \varphi$$

$$\varphi(x, y, z) = \varphi_x(x) \cdot \varphi_y(y) \cdot \varphi_z(z)$$

This is possible bc b^y all these movements are equiv.

$$E = E_x + E_y + E_z$$

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \varphi}{\partial x^2} + \frac{\partial^2 \varphi}{\partial y^2} + \frac{\partial^2 \varphi}{\partial z^2} \right) =$$

$$= (E_x + E_y + E_z) \varphi$$

$$\left\{ \begin{array}{l} -\frac{\hbar^2}{2m} \frac{\partial^2 \varphi_x(x)}{\partial x^2} = E_x \varphi_x(x) \\ -\frac{\hbar^2}{2m} \frac{\partial^2 \varphi_y(y)}{\partial y^2} = E_y \varphi_y(y) \\ -\frac{\hbar^2}{2m} \frac{\partial^2 \varphi_z(z)}{\partial z^2} = E_z \varphi_z(z) \end{array} \right. \quad \begin{array}{l} \text{can be} \\ \text{ignored} \\ \text{bc all wave-} \\ \text{functions are even} \end{array}$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \varphi_x(x)}{\partial x^2} = E_x \varphi_x(x) \quad \begin{array}{l} \varphi_x(x) = ? \\ E_x = ? \end{array}$$

$$\frac{\partial^2 \varphi_x(x)}{\partial x^2} + \frac{2m E_x}{\hbar^2} \cdot \varphi_x(x) = 0$$

$$\int_{-\infty}^{+\infty} \varphi_x(x)^* \varphi_x(x) dx = 1$$

$k = \text{const}$

$$\frac{\partial^2 \varphi_x(x)}{\partial x^2} + k^2 \varphi_x(x) = 0$$

$$\varphi_x(x) = e^{-kx}$$

E_x - kin en. always positive

$$\lambda^2 + k^2 = 0 \quad \lambda_{1,2} = \pm ik$$

$$\varphi_x(x) = A e^{+ikx} + B e^{-ikx} \quad \vec{p} = \hbar \vec{k}$$

/ /

electron moving
in pos. direction

electron moving
in neg. direction

We take the positive solution but this is anti-symmetric

$$\varphi_x(x) = A e^{+ikx}$$

So we apply boundary conditions

$$\psi_x(x) = \psi_x(x + L_x)$$

$$\vec{k} = (k_x, k_y, k_z)$$

$$A e^{i k_x L_x} = A$$

$$e^{i k_x L_x} = 1$$

$$k_x L_x = 2\pi \cdot n_x, n_x \in \mathbb{Z}$$

$$\psi_{n_x}(x) = A_x e^{-i \frac{2\pi}{L_x} n_x x}$$

$$k_x = \frac{2\pi}{L_x} n_x$$

To find A_x , we use the normalizing property
 Periodic boundary conditions mean that
 for $\int_{-\infty}^{\infty} \psi_x(x)^* \psi_x(x) dx = 1$ over int. tracks due

$$\int_0^{L_x} (\psi_{n_x}^*(x) \psi_{n'_x}(x)) dx = \delta_{n_x, n'_x}$$

$$A_x^2 \int_0^{L_x} e^{-i \frac{2\pi}{L_x} n_x x} e^{i \frac{2\pi}{L_x} n'_x x} dx = 1$$

$$A_x^2 \cdot L_x = 1$$

$$A_x = \frac{1}{\sqrt{L_x}}$$

$$\psi_{n_x} = \frac{1}{\sqrt{L_x}} e^{i \frac{2\pi}{L_x} n_x x}, n_x \in \mathbb{Z}$$

$$E_x = \frac{q_m E_x}{\hbar^2}$$

$$P_x = \hbar \cdot k_x$$

$$E_x = \frac{\hbar^2 k_x^2}{2m}$$

$$E_x = \frac{\hbar^2 k_x^2}{2m} = \frac{P_x^2}{2m}$$

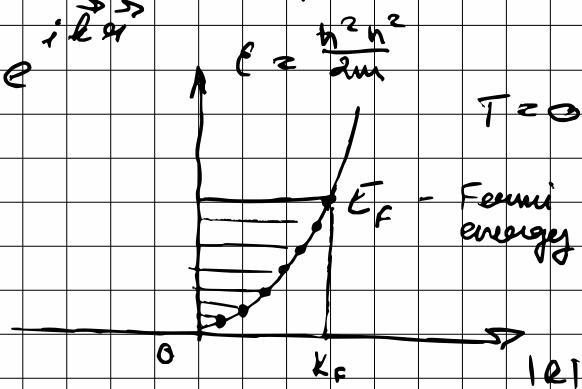
$$\Psi(x, y, z) = \varphi_x(x) \varphi_y(y) \varphi_z(z)$$

$$E = E_x + E_y + E_z = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 k^2}{2m}$$

$$\Psi = \frac{1}{\sqrt{k_x k_y k_z}} e^{i(\frac{\hbar k_x}{L_x} n_x x + \frac{\hbar k_y}{L_y} n_y y + \frac{\hbar k_z}{L_z} n_z z)} =$$

$$= \frac{1}{\sqrt{V}} e^{i(k_x \cdot x + k_y \cdot y + k_z \cdot z)}$$

$$\Psi(x, y, z) = \frac{1}{\sqrt{V}} e^{i \vec{k} \vec{r}}$$



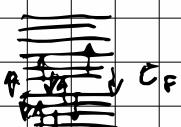
Is k continuous or discrete?

Discrete parameter

Electrons are Fermi particles, that means it can occupy only one state.

E_F - maximum energy occupied by electrons

$$N=10$$



What if $T \neq 0$? Elec can then occupy all possible energy levels and is not limited to E_F .

$$f(\epsilon, T) = \frac{1}{e^{\frac{\epsilon - \mu}{kT}} + 1} \quad \mu - \text{chemical potential}$$

Fermi-Dirac Equation

$$T \ll \mu \approx E_F$$

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

$$E_F = \frac{\hbar^2 n e}{2m}$$

For $T = 0$ all levels up to Fermi energy must be occupied and all other levels below must be empty.

$$E_F() \neq T$$

$$\mu(T) = E_F \left(1 - \frac{\pi^2}{12} \cdot \frac{T}{T_F} \right)$$

No dependence on temperature

$$T_F = \frac{E_F}{k} \approx 50\ 000 \text{ K} \quad (\text{class. model})$$

μ and E_F are very different parameters!!!

$$\frac{T}{T_F} \ll 1$$

Also for semi-conductors we have very different μ E_F dependences.

1 5. 1

$$\hat{H}\psi = E\psi, \quad E = E_x + E_y + E_z$$

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2$$

$$\psi(x, y, z) = \varphi_x(x)\varphi_y(y)\varphi_z(z)$$

$$x : -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \varphi_x(x) = E_x \varphi_x(x)$$

$$\varphi_x(x) = \frac{1}{\sqrt{L_x}} e^{ik_x x}$$

$$\vec{k} = k_x \cdot \vec{i} + k_y \cdot \vec{j} + k_z \cdot \vec{k} = \\ = (k_x, k_y, k_z)$$

$$\psi(x, y, z) = \psi(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}}$$

$$\vec{r} = x \cdot \vec{i} + y \cdot \vec{j} + z \cdot \vec{k}$$

$$V = L_x L_y L_z$$

$$E(k_x, k_y, k_z) = E(\vec{k}) = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 |\vec{k}|^2}{2m} = \frac{p^2}{2m}$$

Periodic
boundary
condition

$$\varphi_x(x) = \varphi_x(x + L_x)$$

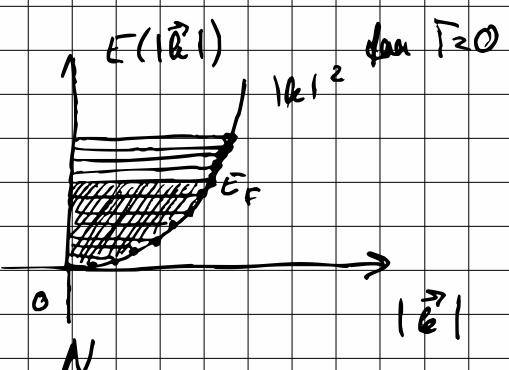
$$k_\alpha = \frac{2\pi}{L_\alpha} \cdot n_\alpha, \quad n_\alpha \in \mathbb{Z} \quad -\infty \leq n_\alpha \leq +\infty$$

$$n_x, n_y, n_z$$

$$(\psi_{n_x, n_y, n_z} (\vec{k})) = \frac{1}{\sqrt{V}} e^{i \vec{k} \cdot \vec{r}} \left(\frac{n_x}{L_x} x + \frac{n_y}{L_y} y + \frac{n_z}{L_z} z \right)$$

$$n_\alpha = [-\infty, +\infty]$$

$$\vec{p} = m \vec{v} = \hbar \vec{R}$$



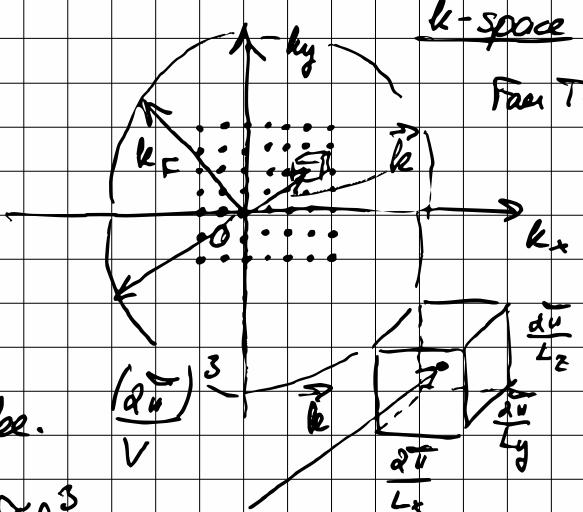
Fermi particles can occupy only one state

E_F - Fermi energy

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

k-space

For $T=0$



For each allowed \vec{k} we have a specific cube.

Volume of the sphere $\frac{4}{3} \pi k_F^3$

$$\frac{(2\pi)^3}{V}$$

$$\frac{4}{3} \pi k_F^3$$

Total number of occupied states

$$N_{\text{states}} = \frac{\frac{4}{3} \pi k_F^3}{(2\pi)^3/V}$$

$$N_{\text{states}} = \frac{k_F^3 \cdot V}{6 \pi^2} \quad k_F = \left(\frac{16 \pi^3 \cdot N_{\text{states}}}{V} \right)^{\frac{1}{3}}$$

$N = 2 N_{\text{states}}$ // number of free electrons

$$k_F = \left(\frac{3 \pi^2}{V} N \right)^{\frac{1}{3}} = (2 \pi^2 n)^{\frac{1}{3}}$$

$$n = \frac{N}{V} \quad // \text{concentration}$$

$$E_F = \frac{t_0^2 k_F^2}{2m} = \frac{(3 \pi^2 t_0^3)^{\frac{2}{3}}}{2m} \cdot n^{\frac{2}{3}} \quad // \text{so now we only need } n$$

If temperatures are not zero

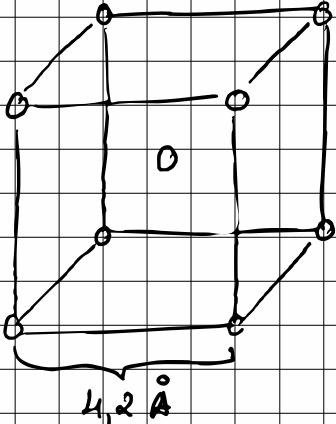
$$E = \frac{t_0^2 k^2}{2m} \quad // \text{this will lead to the assumption that speed will propagate faster than light, in vacuum velocity is impossible}$$

$$E \rightarrow \infty$$

$$T = 0$$

$$1 \text{ \AA} = 10^{-10} \text{ m}$$

Na



$$n = \frac{N}{V}$$

// Only need to take into account 1 electron

Total number of Na atoms in elementary cell is only 2.

$$\frac{n_A}{\text{atoms}} \approx \frac{n_{\text{fe}}}{\text{free electrons}}$$

$$n = \frac{2}{V} = 2 \cdot 10^{23} \text{ cm}^{-3}$$

Estimating heat capacity

$$C_V = \frac{\partial E}{\partial T}$$

Total number of atoms

$$E_a = \underbrace{\frac{3}{2} kT \cdot N}_{\text{Boltzmann kin. en.}} + \underbrace{\frac{3}{2} kT \cdot N}_{\text{part. en.}} = 3kT \cdot N$$

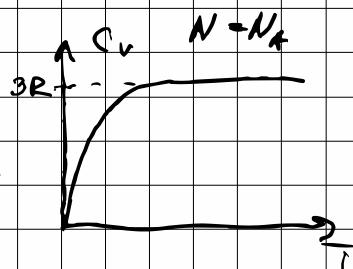
Energy

$$N = N_A$$

Atoms $E_A = 3k \cdot T \cdot N_A = 3RT$

electrons

$$E_{fe} = \underbrace{\frac{3}{2} kT \cdot N}_{R} = \frac{3}{2} RT$$



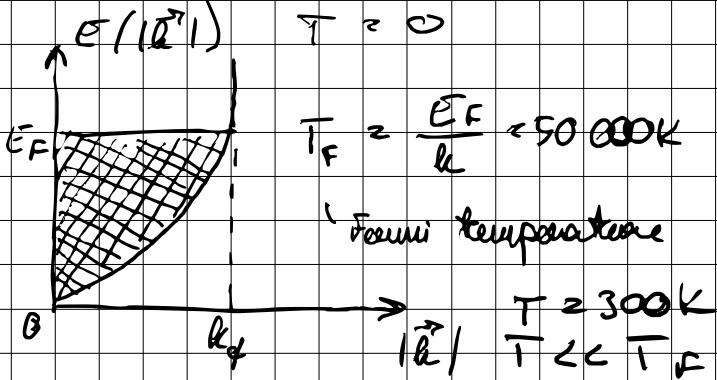
$$E = 4,5RT \quad C_V = 4,5R \quad C_{V,\text{exp}} \approx 3R$$

Free electron part is currently wrong

Why must the electrons be ignored?

$$N_{fe} \ll N_A$$

To fix this problem, we must $\propto m$.



(Na)

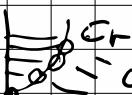
$$n \approx 2 \cdot 10^{23} \text{ cm}^{-3}$$

$$k_F \approx 1 \text{ Å}$$

$$E_F = 4 \text{ eV}$$

$$1 \text{ eV} = 1.6 \cdot 10^{-19} \text{ J}$$

Electron wave



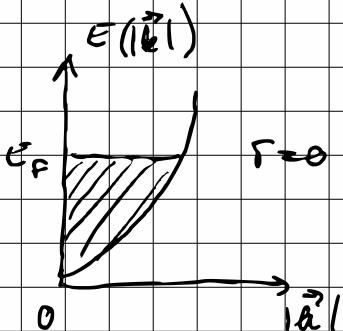
can't take these states bc they are already occupied. Only possible location would be for $T \neq 0$ to be higher than E_F . But what temperature would this new state have?

activates electrons

$$N_{Ae} \approx 0.01 N_A$$

$$T_F = \frac{E_F}{k}$$

$$E = \frac{3}{2} \cdot kT \cdot N_{Ae}$$



Fermi - Dirac

$$f(E, T) = \frac{1}{e^{\frac{E-\mu}{kT}} + 1}$$

μ - chemical potential

$$T \ll T_F$$

$$\mu = E_F$$

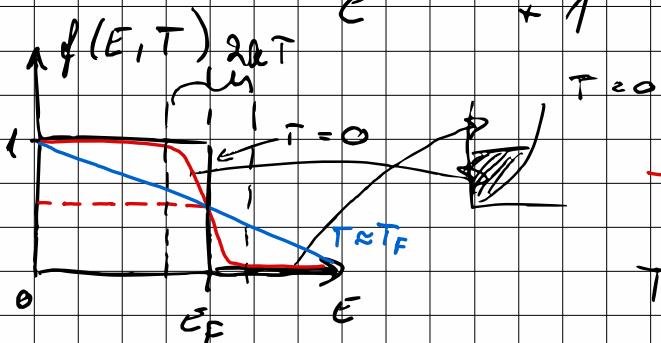
$$\mu(T) = E_F \left(1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 + \dots \right)$$

$$T \ll T_F$$

Two regimes:

$$f(E, T) = \frac{1}{e^{\frac{E-E_F}{kT}} + 1}$$

$$\begin{aligned} E < E_F & \rightarrow T \rightarrow 0 \\ E > E_F & \rightarrow T \rightarrow \infty \end{aligned}$$



$$T_F \gg T > 0$$

$$T \approx T_F$$

$$\sum_{\text{all states}} f(E, T) = N_{\text{states}}$$

$$2 \sum_{\text{all states}} f(E, T) = N \quad \text{no. of electrons}$$

$$2 \sum_{\text{all states}} \frac{1}{e^{\frac{E-E_F}{kT}} + 1} = N$$

$$2 \sum_{n_x, n_y, n_z} \frac{1}{e^{\frac{E_{n_x, n_y, n_z} - M}{kT}} + 1} = N$$

Density of States - DOS

$$g(E) \approx \frac{dN_{\text{states}}}{dE}$$

$$2 \int_0^{E_F} g(E) dE = N$$

$$E = \frac{(3\pi^2 \frac{n}{h^3})^{\frac{2}{3}}}{2m} \left(\frac{N}{V}\right)^{\frac{1}{3}}$$

$$g(E) = \frac{\sqrt{2}}{2\pi^2} \frac{m}{h^3} V \cdot \sqrt{E} = V \cdot G(E)$$

$$N = 2N_{\text{states}}$$

$$E \sim (N_{\text{states}})^{\frac{2}{3}}$$

$$N_{\text{states}} \sim N^{\frac{3}{2}}$$

$$G(E) = \frac{g(E)}{V}$$

$$2 \int_0^{E_F} G(E) dE = n$$

$$2 \int_0^{E_F} g(E) dE = N$$

$$E = C_{\text{kin}} \cdot n^{\frac{5}{3}}, T=0$$

DOS

$$g(E) = V \cdot G(E) = \frac{\sqrt{2}}{2\pi^2 h^3} \frac{m}{V} \sqrt{E}$$

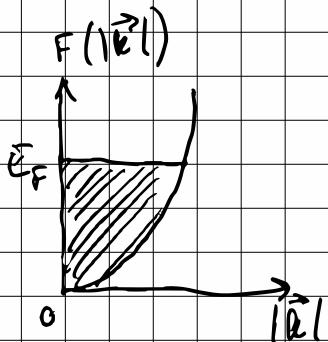
For $T=0$

$$2 \int_0^{E_F} g(E) dE = N$$

$$2 \int_0^{E_F} G(E) dE = n$$

$$E_{\text{total}} = 2 \int_0^{E_F} E \cdot G(E) dE =$$

$$= \frac{3 \pi^2}{40 m} \cdot \left(\frac{3}{\pi}\right)^{\frac{2}{3}} \cdot n^{\frac{5}{3}}$$



$T \neq 0$

$$n = 2 \int_0^{+\infty} G(E) \cdot f(E, T) dE$$

$$G(E) = \left(\frac{\sqrt{2}}{2\pi^2} \frac{m}{h^3} \right)^{\frac{3}{2}} E^{\frac{3}{2}} = \alpha E^{\frac{3}{2}}$$

$$\alpha \int_0^{+\infty} f(E, T) \cdot E^{\frac{3}{2}} dE =$$

Perform integration by parts $\int u dv = uv - \int v du$

$$= \frac{2}{3} \alpha \cdot f(E, T) \Big|_0^{+\infty} - \frac{2}{3} \alpha \int_0^{+\infty} E^{\frac{1}{2}} \left| \frac{\partial f(E, T)}{\partial E} \right| dE$$



$$f(E, T) \left| \frac{\partial f}{\partial E} \right| \quad T \ll 0$$

'bc otherwise it would be negative'

Think of a derivative of a function. Pos. derivatives shows increasing values, neg. decreasing.

$$n = \frac{2\alpha}{3} \int_0^{+\infty} E^{\frac{1}{2}} \cdot \underbrace{\left| \frac{\partial f(E, T)}{\partial E} \right|}_{\delta(E-\mu)} dE \Rightarrow$$

$$\Rightarrow n = \frac{(\alpha m)^{\frac{3}{2}}}{2\pi^2 h^3} \mu^{\frac{1}{2}} \Rightarrow \mu = \frac{(\alpha m)^2}{\alpha^2 m} \cdot \frac{(3n)^{\frac{2}{3}}}{8\pi^2}$$

Conclusion: $T \approx 0 \quad \mu = E_F$

For $T \ll 0 \quad \mu = E_F$. Doesn't work for high temp regions.

$$C_V = \frac{\partial E}{\partial T}, \quad E_{\text{tot}} = 2 \int_0^{+\infty} E \cdot G(E) \cdot f(E, T) dE$$

$$E_{\text{tot}}' = 2 \int_0^{+\infty} (E - E_F) G(E) f(E, T) dE // \text{Not correct}$$

$T \ll 0$

$$\mu = E_F$$

$$= 2 \int_0^{+\infty} E G(E) f(E, T) dE - (2E_F) \int_0^{+\infty} G(E) f(E, T) dE =$$

"But binds ps

"as well ??

i) For $T = 0$

$$2 \int_0^{E_F} G(E) dE = n$$

$$= 2 \int_0^{E_F} E G(E) f(E, T) dE = E_F \cdot n$$

$$\frac{\partial E_{\text{tot}}'}{\partial T} = \frac{\partial E_{\text{tot}}}{\partial T} - \underbrace{\frac{\partial}{\partial T} (E_F \cdot n)}_0$$

$$\frac{\partial E_{\text{tot}}'}{\partial T} = \frac{\partial E_{\text{tot}}}{\partial T} \delta(E - E_F), \quad T \ll T_F$$

$$C_V = 2 \int_0^{+\infty} (E - E_F) \cdot G(E) \underbrace{\frac{\partial f(E, T)}{\partial T} dE}_0 \approx$$

$$= k \cdot G(E_F) \int_{-\infty}^{+\infty} \frac{x^2 e^x}{(e^{x+1})^2} dx \approx \frac{\pi^2}{2} \cdot \underbrace{k \cdot N_A}_{R} \cdot \frac{T}{T_F} \approx$$

$$x = \frac{E - E_F}{kT}$$

$$\approx R \cdot \frac{\pi^3}{2} \cdot \frac{T}{T_F}$$

What is the physical interpretation of this equation?

$$T = 300 \text{ K} \quad \frac{\pi^3}{2} \cdot \frac{T}{T_F} \approx 0,093018 \approx 0$$

$$\frac{T_F}{T} = 50000 \text{ K}$$

This is why free electrons
can be ignored.

L.5.2 Electron in a wave external potential

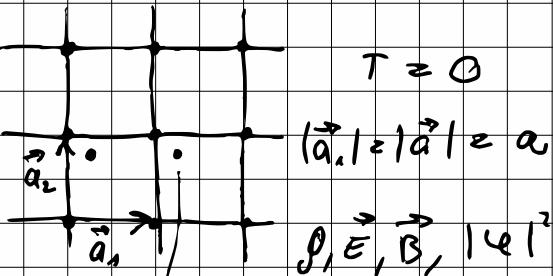
$$T = 0$$

$$U(\vec{a}) = U(\vec{a} + \vec{R}_n)$$

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

$$\hat{H} \psi_0 = E_0 \psi_0$$

for free electron
 $V = 0$



$$\hat{H} = -\frac{\hbar^2}{2m} \hat{\Delta}, \quad \hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad (10)$$

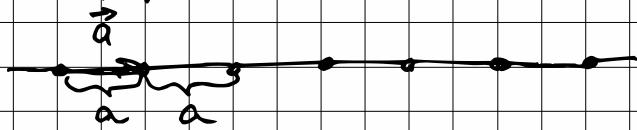
$$\psi_0(x, y, z) = \frac{1}{\sqrt{V}} e^{ikz} \quad \text{for 1d} \quad \psi_0(x) = \frac{1}{\sqrt{L}} e^{ikx}$$

$$\psi_0(\vec{a})$$

at same location same properties due to periodicity

$$E_0(\vec{k}) = \frac{\hbar^2 k}{2m} \quad \text{and} \quad E_0(k) = \frac{\hbar^2 k^2}{2m}$$

A simplified model



Are periodic cells and periodic boundary conditions the same thing? Are they equal?

$$U(x) = U(x + na)$$

$$U(x) = U(x + c) = U(x + Na)$$

Periodic boundary conditions are a subset of periodicity, periodical potential

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \varphi}{\partial x^2} + U(x) \varphi(x) \stackrel{\text{root equal}}{\equiv} E \varphi(x)$$

Solving this is quite hard. But if $U(x)$ is low we can simplify by saying $E_{\text{kin}} > E_{\text{pot}}$. To solve this, we can use the perturbation theory.

For 1st order perturbation theory we can write φ as φ_0 but $\varphi \neq \varphi_0$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \varphi_0}{\partial x^2} + U(x) \varphi_0(x) = (E + E') \varphi_0(x) \quad \text{1st order perturb. th.}$$

$$\underline{U(x) = U(x + na)}$$

$$\varphi_0(x) =$$

$$|\psi_0(x)|^2 = |\psi_0(x+a)|^2$$

\uparrow
 $n=1$

Block theorem. Wave functions for periodical structures.

$$\psi = A U(k) e^{ikx} \quad e^{ikx} = e^{i k (x+a)} \text{ NOT OK!}$$

$$U(k) = U(k + R) \text{ OK!}$$

$$\psi = A \cdot U(k) \cdot e^{ikx}, \quad U(k) = e^{i \frac{2\pi}{a} g \cdot x}, \quad g \in \mathbb{Z}$$

Check:

$$U(k) = e^{i \frac{2\pi}{a} g \cdot x} = e^{i \frac{2\pi}{a} g (x+a)} = \\ = e^{i \frac{2\pi}{a} g x} \cdot \underbrace{e^{i \frac{2\pi}{a} g}}_{1} = e^{i \frac{2\pi}{a} g x}$$

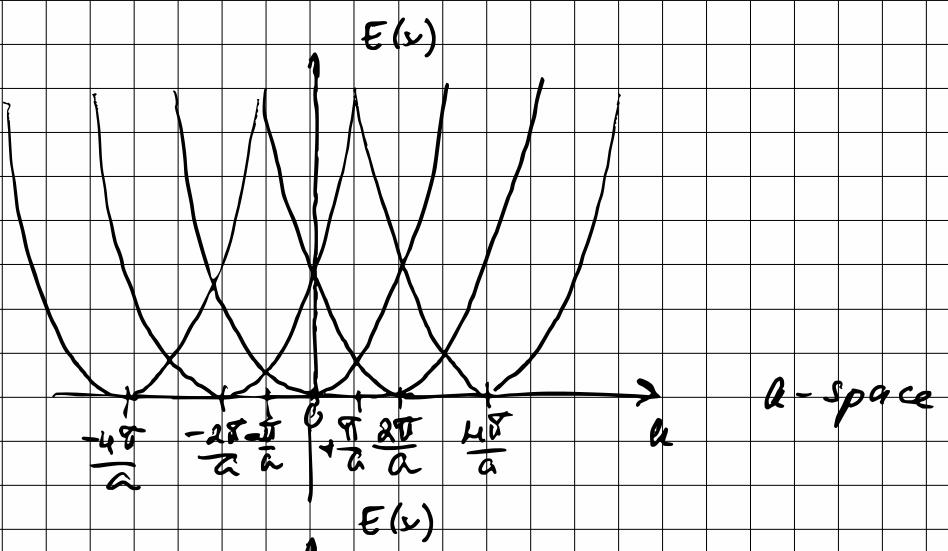
Therefore

$$\psi_0(x) = A c^{i \frac{2\pi}{a} g \cdot x} e^{ikx} = \frac{1}{\sqrt{L}} e^{i((k + \frac{2\pi}{a} g) x)}$$

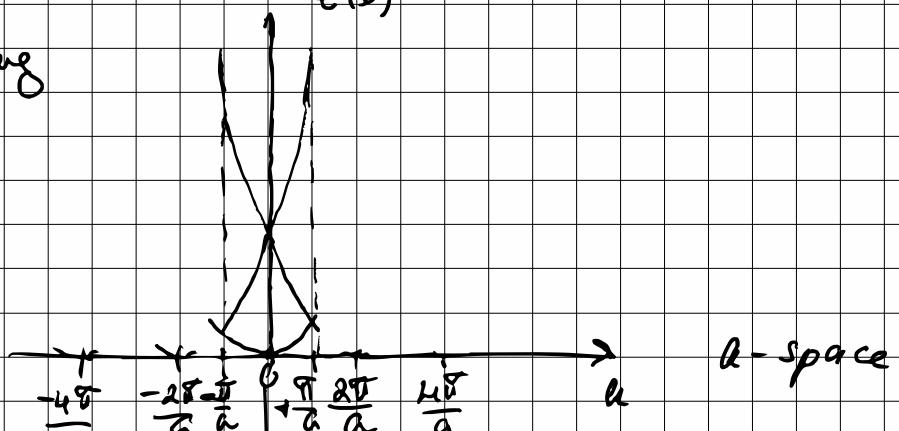
$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_0(x)}{\partial x^2} = E_0 \psi_0$$

$$\psi(x) = A \cdot U(k) e^{ikx} = \frac{1}{\sqrt{L}} e^{i[(k + \frac{2\pi}{a} g) x]}$$

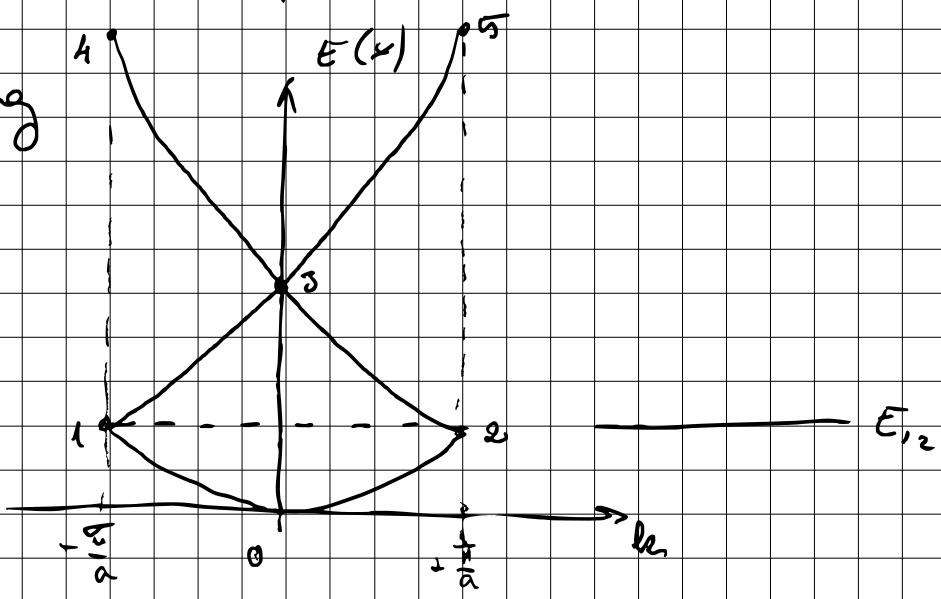
$$E(x) = \frac{\hbar^2 / (k + \frac{2\pi}{a} g)^2}{2m}$$



Simplifying



Resizing



$$\psi_0 = \frac{1}{\sqrt{L}} e^{ikx}$$

$$\psi_1 = \frac{1}{\sqrt{L}} e^{-i\frac{q}{a}x}$$

$$\psi_2 = \frac{1}{\sqrt{L}} e^{+i\frac{q}{a}x}$$

Two different states
with the same energy.
 (E_{12})

$$\text{Also } \psi_1^* = \psi_2$$

$$\psi_2^* = \psi_1$$

$$\begin{vmatrix} V_{11} - E' & V_{12} \\ V_{21} & V_{22} - E' \end{vmatrix} = 0$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_0}{\partial x^2} + U \psi_0 = (E_0 + E') \psi_0$$

$$U(x) = U_0 \cdot \cos\left(\frac{2\pi}{a}x\right)$$

$$V_{11} = \int_0^L \psi_1^* U(x) \psi_1 dx$$

$$V_{22} = \int_0^L \psi_2^* U(x) \psi_2 dx$$

$$V_{12} = \int_0^L \psi_1^* U(x) \psi_2 dx$$

Keep in mind that

$$\psi_1^* = \psi_2, \psi_2^* = \psi_1$$

$$V_{21} = \int_0^L \psi_2^* U(x) \psi_1 dx = \int_0^L \psi_1 U(x) \psi_2^* dx =$$

$$= \int_0^L \psi_1^* U(x) \psi_2 dx, \quad V_{12} = V_{21}$$

$$V_{11} = \frac{1}{a} \cdot U_0 \int_0^a e^{-i\frac{\omega}{a}x} \cos\left(\frac{d\omega}{a}x\right) e^{-i\frac{\omega}{a}x} dx \approx$$

total in ^o at cells

$$= \frac{U_0}{a} \int_0^a \cos\left(\frac{d\omega}{a}x\right) \left(\cos\left(\frac{d\omega}{a}x\right) - i \sin\left(\frac{d\omega}{a}x\right) \right) dx =$$

$$= \frac{U_0}{a} \int_0^a \cos^2\left(\frac{d\omega}{a}x\right) - i \cos\left(\frac{d\omega}{a}x\right) \sin\left(\frac{d\omega}{a}x\right) dx =$$

$$= \frac{U_0}{a} \int_0^a \cos^2\left(\frac{d\omega}{a}x\right) dx = \left[\frac{1}{2} \cos^2(x) + \frac{\sin(2x)}{4} \right]_0^a$$

later

$$= \int \left[\begin{array}{l} y = \frac{d\omega}{a}x \\ dx = \frac{dy}{d\omega} d\omega \end{array} \right] \frac{U_0}{a} \int_0^{d\omega} \cos^2(y) \frac{a}{d\omega} dy =$$

$$= \frac{U_0}{a} \int_0^{2\pi} \cos^2(y) dy = \frac{U_0}{a} \left[\frac{y}{2} + \frac{\sin(2 \cdot y)}{4} \right]_0^{2\pi} =$$

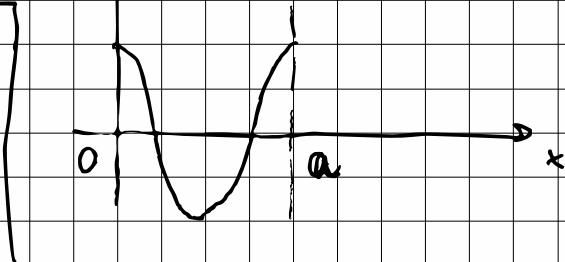
$$= \frac{U_0}{a} \left[\frac{2\pi}{2} + 0 - 0 - 0 \right] = \frac{U_0}{a}$$

$$V_{12} = \frac{U_0}{a} \int_0^a \cos\left(\frac{d\omega}{a}x\right) e^{-i\frac{\omega}{a}x} \cdot e^{+i\frac{\omega}{a}x} dx = 0$$

$$= \frac{U_0}{a} (1 - 1) = 0$$

$$V_{22} = V_{11} = \frac{U_0}{2}$$

$$V_{12} = V_{21} = 0$$



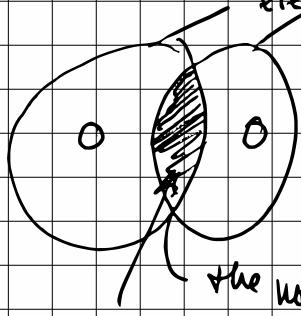
$$\left| \begin{array}{cc} \frac{U_0}{2} - E' & 0 \\ 0 & \frac{U_0}{2} - E' \end{array} \right| z \quad 0, \quad E' = \pm \frac{U_0}{2}$$

Here the conduction
bandgap look like
based on this picture?

Few isolators the
energy levels for the
forbidden zones are much
larger.

If the width of the zone is $> 2eV$, then we have
an isolator.

If it is smaller, we have semiconductors. (I. I S.)
electron clouds
(S 0.74 eV)



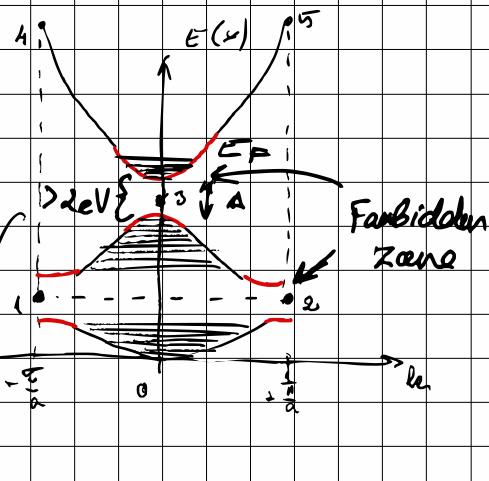
$$V \uparrow \Delta \uparrow$$

the more these areas overlap, the higher the Δ .

$$V$$

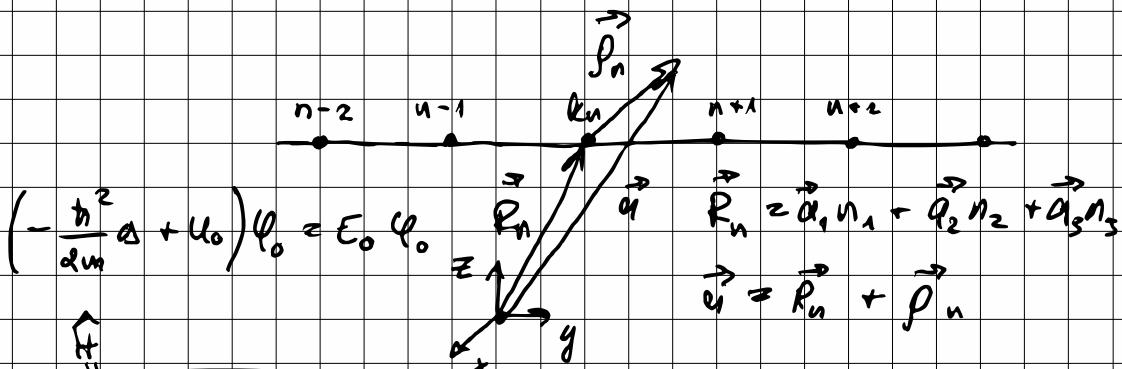
But why from high temp very Δ small?

We have thermal expansion, and the distance between
atoms increases.



If the electrons are moving close to the nuclei, U cannot be ignored and also perturbation theory won't be sufficient. Therefore we must calculate the Schrödinger eq. exactly.

L. 5.2 Tight Binding approximation



$$\left(-\frac{t^2}{2m} \Delta + V \right) \psi = E \psi$$

$U_0 > V$ - pot. en per interacting atoms
↓
pot. en. of isolated atoms

These two eq.s can be equal if and only if the distance between the particles is sufficiently large.

Meaning individual U_0 can be combined and be part of a stable lattice. For this V must have a smaller energy than the combination of U_0 's for this change to happen.

$$E = E_{kin} + U_0$$

$$V$$

$$E = E_{kin} + V$$

$$(e^* \cdot \hat{H} \psi = E \psi \Rightarrow \psi^* \hat{H} \psi = \psi^* e^* \hat{H} \psi \Rightarrow)$$

$$\int_V \psi^* \hat{H} \psi dV = \int_V E \psi^* \psi dV = E \int_V \psi^* \psi dV$$

$$E = \frac{\int_V \psi^* \hat{H} \psi dV}{\int_V \psi^* \psi dV}$$

Since we have periodical structures, we can apply Bloch theorem.

$$\psi = A U(\vec{a}) e^{i \vec{k} \cdot \vec{r}}$$

$$U(\vec{a}) = U(\vec{a} + \vec{R}_n)$$

$$U(\vec{a}) = \sqrt{A} U(\vec{a}) e^{i \vec{k} \cdot \vec{a}} \quad (\textcircled{2})$$

\Rightarrow This is all but $\int_V \psi^* \psi dV$ must be calculated separately bc it's probably not eq. to 1 anyways.

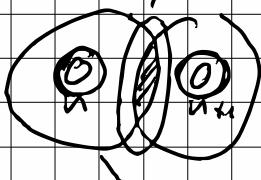
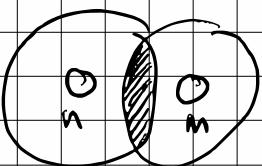
$$\textcircled{2} e^{i \vec{k} \cdot \vec{R}_n} \sum_{n=0}^N \psi_0(\vec{P}_n) e^{-i \vec{k} \cdot \vec{P}_n} = U(\vec{a})$$

$$= \sum_{n=0}^N \psi_0(\vec{S}_n) e^{i \vec{k} \cdot \vec{R}_n}$$

$$\int (\psi_0^*(\vec{P}_n) \psi_0(\vec{P}_m)) dV = \delta_{nm}$$

/ this is ignored

Basically means that the overlapping area doesn't exist. BC



$n+m$

so we exclude external electrons

$$\int_V \psi^* \psi dV = \int \sum_{n=1}^N \psi_0^*(\rho_n) e^{-ik\vec{R}_n} \cdot \underbrace{\sum_{m=1}^N \psi_0(\rho_m) e^{-ik\vec{R}_m}}_{\delta_{nm}}.$$

$$\sum_{m=1}^N \psi_0(\rho_m) e^{-ik\vec{R}_m} dV = \sum_n \sum_m e^{ik(\vec{R}_n - \vec{R}_m)}.$$

$$\int_V \psi_0^*(\rho_n) \psi_0(\rho_m) dV = \sum_n \sum_m \delta_{nm} = N$$

n, m - summation indices

Conclusion

$$\int_V \psi^* \psi dV = N$$

$$\int \sum_n \psi_0^*(\rho_n) e^{-ik\vec{R}_n} \left(-\frac{\hbar^2}{2m} \Delta + V \right) \sum_m \psi_0(\rho_m) e^{ik\vec{R}_m} dV$$

$$= \sum_{n,m} e^{ik(\vec{R}_m - \vec{R}_n)} \int \psi_0^*(\rho_n) \left(-\frac{\hbar^2}{2m} \Delta + V \right) \psi_0(\rho_m) dV =$$

$$= \sum_{n,m} e^{ik(\vec{R}_m - \vec{R}_n)} \left\{ \int \psi_0^*(\rho_n) \left(-\frac{\hbar^2}{2m} \Delta \right) \psi_0(\rho_m) dV + \right.$$

$$+ \left. \int \psi_0^*(\rho_n) V \psi_0(\rho_m) dV \right\} = \int \left[-\frac{\hbar^2}{2m} \Delta \psi_0 = E_0 \psi_0 - U_0 \psi_0 \right] dV$$

$$\approx \sum_{n,m} e^{ik(\vec{R}_m - \vec{R}_n)} \int \psi_0^*(\rho_n) (E_0 + V - U_0) \psi_0(\rho_m) dV =$$

doesn't depend on V and U_0 depend on ρ .

(we assume E_0 is pre-calculated)

$$= \sum_{n,m} e^{ik(\vec{R}_m - \vec{R}_n)} \int \psi_0^*(\rho_n) E_0 \psi_0(\rho_m) dV \quad \oplus$$

$$\begin{aligned} & \oplus \sum_{n,m} e^{i\vec{k}(\vec{R}_m - \vec{R}_n)} \int \varphi_0^*(\vec{p}_n) (V - U_0) \varphi_0(\vec{p}_m) dV = \\ & = E_0 N + \sum_n e^{i\vec{k}(\vec{R}_n - \vec{R}_0)} \int \varphi_0^*(\vec{p}_n) (V - U_0) \varphi_0(\vec{p}_0) dV = \end{aligned}$$

* Remember that atoms are eqv. therefore we only take single summation, in the example's And in we take eq to zeros. so then we get R_0 which we can set to the beginning of coordinate axes ($0, 0, 0$). So now that we only take only 1 into account, to consider all by multiplying by N .

$$= E_0 N + N \cdot \sum_n e^{i\vec{k}\vec{R}_n} \int \varphi_0^*(\vec{p}_n) (V - U_0) \varphi_0(\vec{p}_m) dV$$

$$E = \frac{N (E_0 + \sum_n e^{i\vec{k}\vec{R}_n} \langle \varphi_0^* | V - U_0 | \varphi_0 \rangle)}{N}$$

$$\boxed{E = E_0 + \sum_n e^{i\vec{k}\vec{R}_n} \int \varphi_0^*(\vec{p}_n) (V - U_0) \varphi_0(\vec{p}_m) dV}$$

$$E = E_0 -$$

20. 10. 22

$$- \sum_{n=0}^N \left\{ \int \varphi_0^*(\vec{p}_n) (V - U_0) \varphi_0(\vec{p}_n) dV \right\} \cdot e^{i\vec{k}(\vec{R}_n - \vec{R}_0)} =$$

$$= E_0 - \int \varphi_0^*(\vec{p}_0) (V - U_0) \varphi_0(\vec{p}_0) dV -$$

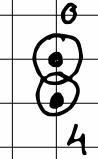
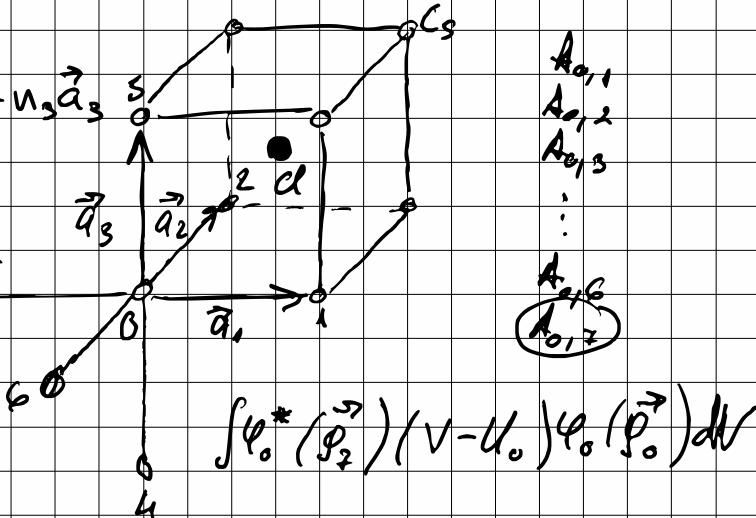
$$-\sum_{n \neq 0}^N \int \varphi_0^*(\vec{p}_n) (V - U_0) \varphi_0(\vec{p}_0) dV \cdot e^{ik(\vec{R}_n - \vec{R}_0)}$$

$$\hat{H}_0 \varphi_0 = E_0 \varphi_0 \quad V < U_0$$

$$E = E_0 - C - \sum_{n \neq 0}^N A_{0,n} \cdot e^{ik(\vec{R}_n - \vec{R}_0)}$$

$$\vec{R}_n = u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3$$

$$\vec{p}_0 = (0, 0, 0)$$



$$\vec{R} = (R_x, R_y, R_z); \quad R_x = -\frac{a}{2} a_1 + \frac{a}{2} a_1;$$

$$R_y = -\frac{a}{2} a_2 + \frac{a}{2} a_2$$

$$R_z = -\frac{a}{2} a_3 + \frac{a}{2} a_3$$

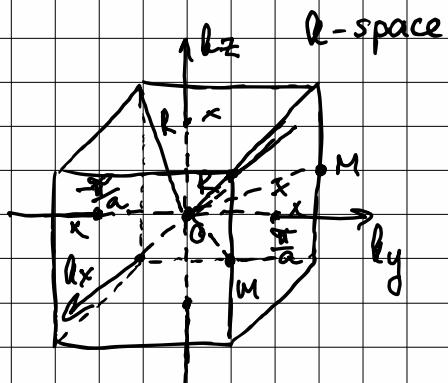
$$E = E_0 - C - \sum_{n=1 \dots 6} A e^{ik R_n} =$$

$$= E_0 - C - A \sum_{n=1 \dots 6} C^{i(R_x R_{xn} + R_y R_{yn} + R_z R_{zn})}$$

$$E = E_0 - C - A \left\{ e^{ik_x a} + e^{-ik_x a} + e^{ik_y a} + e^{-ik_y a} + e^{ik_z a} + e^{-ik_z a} \right\}$$

$$= E_0 - C - 2A \left\{ \cos(k_x a) + \cos(k_y a) + \cos(k_z a) \right\}$$

$$E = E_0 - C - 2A \left\{ \cos(k_x a) + \cos(k_y a) + \cos(k_z a) \right\}$$



$$\Gamma \vec{k} = (0, 0, 0)$$

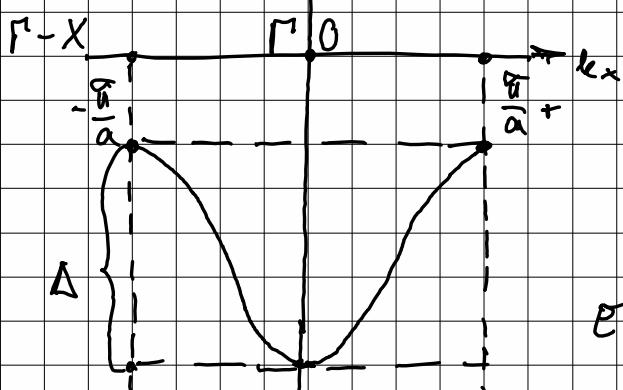
$$X \vec{k} = (0, \frac{\pi}{a}, 0) = (0, \frac{1}{2}, 0) \left(\frac{2\pi}{a} \right) \times 6$$

$$M \vec{k} = (\frac{\pi}{a}, \frac{\pi}{a}, 0) = (\frac{1}{2}, \frac{1}{2}, 0) \times 12$$

$$E(k_x, k_y, k_z)$$

$$E(k_x, k_y, k_z = 0) \quad \Gamma \vec{k} = (\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a}) =$$

$$= (\frac{1}{a}, \frac{1}{a}, \frac{1}{a}) \times P$$



$$E(k_x) = -2A \{ \cos(k_x a) + 2 \}$$

$$k_x = -\frac{\pi}{a}, \dots, +\frac{\pi}{a}$$

$$E(\frac{\pi}{a}) = -2 \cdot A \cdot 1$$

$$E(0) = E(\Gamma) = -6 \text{ eV}$$



$$\Delta \approx 4 \text{ eV}$$

• Δ is very little
for internal electrons

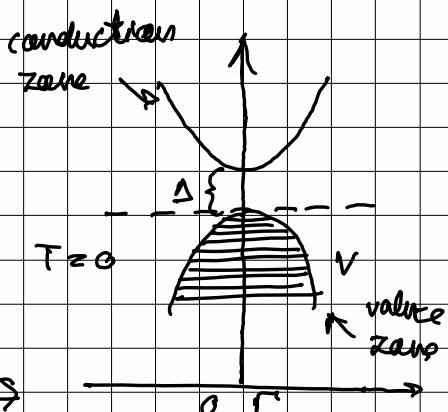
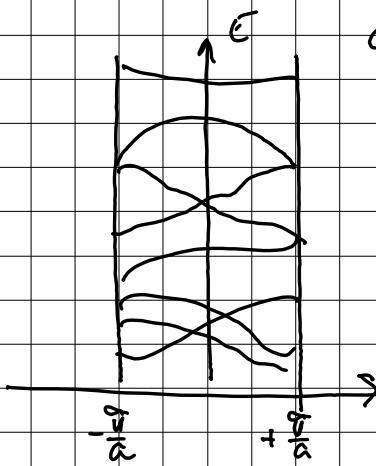
L.5.4. Effective mass approximation

$$E(k_x, k_y, k_z)$$

$$\Delta < 2eV$$

$$\Delta \approx kT$$

$$T \approx \frac{\Delta}{k}$$



$$\Delta < 2eV \text{ semicon.}$$

Free electrons don't depend on temperature.

We have electric charge when the electron jumps from lower to upper zone

How can we increase conductivity? By adding more electrons. When all levels are filled the only available levels are available in the conduction zone

$$\hat{H} \psi = E \psi$$

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

$$\nabla(\vec{\psi}) = \nabla(\vec{\psi} + \vec{R}_n) \quad \vec{R}_n = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

$E_n(k_x, k_y, k_z)$ / Expand into Taylor series

$$E_n(\vec{k}) = E_n(k_{ox}, k_{oy}, k_{oz}) +$$

$$+ \sum_{\alpha=x,y,z} \frac{\partial E_n}{\partial k_\alpha} \Big|_{\vec{k}=\vec{k}_0} (k_\alpha - k_{ox}) +$$

$$+ \frac{1}{2} \sum_{\alpha, \beta} \frac{\partial^2 E}{\partial k_\alpha \partial k_\beta} \Big|_{\vec{k}=\vec{k}_0} (k_\alpha - k_{ox})(k_\beta - k_{oy}) +$$

ignore 3rd power terms

$$E_n(\vec{n}) = \frac{1}{2} \sum_{\alpha, \beta} \frac{\partial^2 E}{\partial k_\alpha \partial k_\beta} \Big|_{\vec{k}=0} k_\alpha k_\beta =$$

= $\begin{pmatrix} A \text{ square matrix will be diagonalized means } \\ \text{elements not on the main diagonal will be zero} \\ \text{and we have new k-vectors on the main diagonal} \end{pmatrix}$

$$= \frac{1}{2} \sum_{\alpha} \frac{\partial^2 E}{\partial k_\alpha^2} k_\alpha^2 \quad (\Rightarrow)$$

$$\vec{k} = T \vec{l}$$

$$T A T^{-1} = A'$$

$$A = \begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & \dots & \dots \\ \dots & \dots & \dots \end{pmatrix}$$

$$E_n(\vec{k}) \approx \frac{1}{2} \Rightarrow \frac{\hbar^2}{m^*} = \frac{\partial^2 E}{\partial k_y^2} \Rightarrow m_y^* = \frac{\hbar^2}{\frac{\partial^2 E}{\partial k_y^2}}$$

$$\textcircled{e} \quad \frac{\hbar^2}{2} \sum_{\vec{k}} \frac{k_y^2}{m_y^*}$$

$$E(\vec{k}) = \frac{\hbar^2 k^2}{2m} - \text{mass of free el.}$$

en. of free electron

$$\Gamma_c = \frac{\hbar^2 k^2}{2m^*}$$

'not mass but pure mathematical object'

m^* - effective mass

- can be used to define the molecule of electrons

For real crystal

Instead of
this \rightarrow

$$(-\frac{\hbar^2}{2m} \Delta + V) \psi = E \psi$$

\uparrow ignored

$$-\frac{\hbar^2}{2m} \Delta \psi = E \psi \quad E = \frac{\hbar^2 k^2}{2m}$$

Fix it possible to write it for E \uparrow again?

$$-\frac{\hbar^2}{2m^*} \Delta \psi = E \psi$$

Yes

Solution to this is very trivial

$$E = \frac{\hbar^2 k^2}{2m^*}$$

$$\psi = \frac{1}{\sqrt{\pi}} e^{i \vec{k} \cdot \vec{r}}$$

We can use
these

Why it's so important to calc. mobility?

$$E = \frac{t^2 k^2}{2m^*} = \frac{P^2}{2m^*}$$

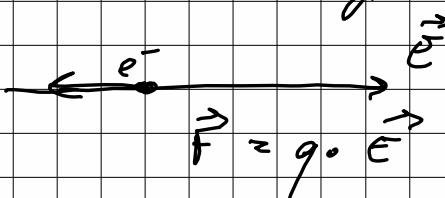
$$P = t k = v \cdot m^*$$

Effective mass can have negative values.

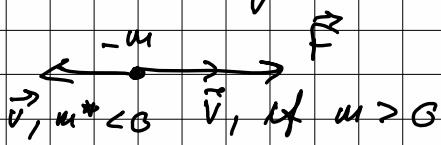
$$\tau = \frac{t k}{m^*}$$

(mobility depends on m^*)

How does the el. charge make it move?



Now think of neg. mass



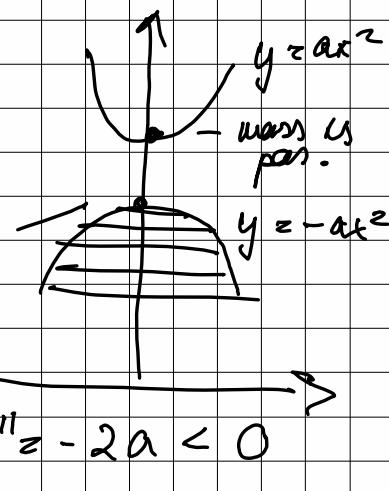
very strange but possible in semiconductors.

Once more: let's assume

Basically in upper part we can have ordinary electron with neg. charge.

$$y = ax^2$$

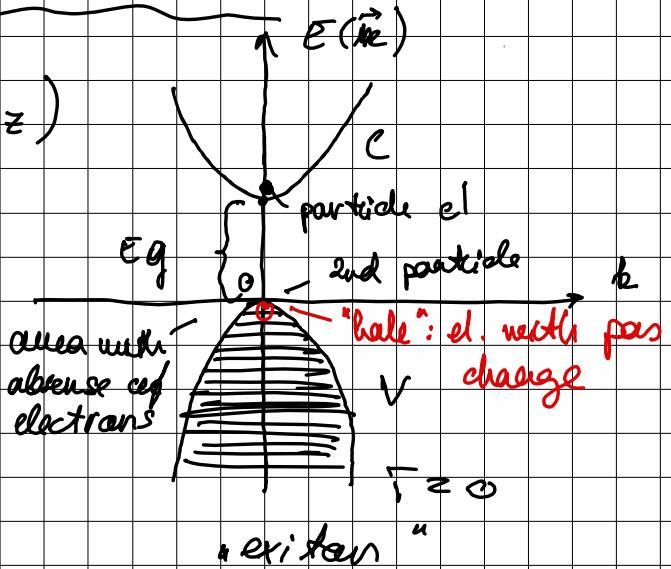
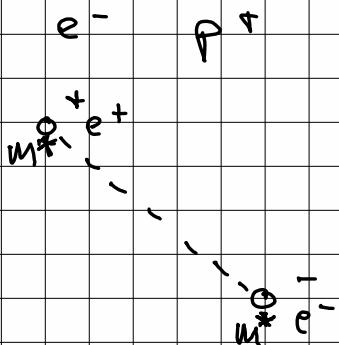
We can have neg. values.



But in the bottom part there exists a quasi-particle like electron but with positive charge.

L. 5.4 Excitation

$$E_n(u_x, u_y, u_z)$$



In this case we can neglect the pot. energy for the particle only if we use effective mass for particles near the extremum points.

$$\left(\frac{\hbar^2}{2m_e} \Delta + V \right) \psi = E \psi$$

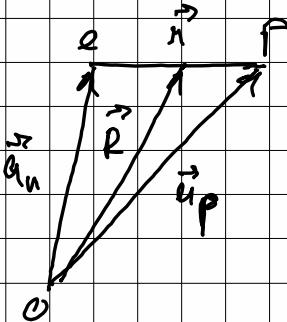
$$\frac{\hbar^2}{2m^*} \Delta \psi = E \psi$$

$$\left(-\frac{\hbar^2}{2m_n^*} \Delta e - \frac{\hbar^2}{2m_p^*} \Delta p - \frac{ke^2}{\epsilon(\vec{r}_n - \vec{r}_p)} \right) \psi(\vec{r}_n, \vec{r}_p) \approx$$

$$\approx (E - E_y) \psi(\vec{r}_n, \vec{r}_p)$$

$$\vec{R} \approx \frac{m_n^* \vec{r}_n + m_p^* \vec{r}_p}{m_n^* + m_p^*}; \vec{r}_1 = \vec{r}_n - \vec{r}_p$$

$$R = \frac{1}{4\pi\epsilon_0}$$



$$\left\{ -\frac{\hbar^2}{2m} \Delta_R - \frac{\hbar^2}{2\mu} \Delta_\alpha - \frac{k e^2}{\epsilon |q|} \right\} \psi(R, \alpha) = E - E_g$$

μ - reduced mass

$$M = m_p^* + m_n^*$$

$$M = \frac{m_n^* m_p^*}{m_n^* + m_p^*}$$

$$\psi(R, \alpha) = X(R) \psi(\alpha)$$

$$-\frac{\hbar^2}{2M} \Delta_R X(R) = W \cdot X(R)$$

kinetic energy of electron

$$W = \frac{\hbar^2 k^2}{Q \cdot M}$$

$$-\frac{\hbar^2}{2\mu} \Delta_\alpha \psi(\alpha) - \frac{k e^2}{\epsilon |q|} \psi(\alpha) = (E - E_g - W) \psi(\alpha)$$

Schödinger eq for hydrogen

$$-\frac{\hbar^2}{2m} \Delta \psi - \frac{k e^2}{|q|} \psi(\alpha) = E \psi(\alpha)$$

$$E_n = E_g - \frac{\mu e^2}{\epsilon^2 8\epsilon_0^2 h^2} \cdot \frac{1}{n^2}$$

E_g



$$E_n = E_g - \frac{me^2}{\epsilon^2 8\pi_0^2 h^2} \cdot \frac{1}{n^2}$$
$$n \rightarrow \infty$$

Ionized exciton



Basically if $n \rightarrow \infty$ radius is increased so much that we get two free particles: electron and hole

Missing lect

Faetee = Fock approximation

03.11.22

$$\hat{H} \psi = E \psi \quad \text{Adiabatic approx.}$$

$$\begin{array}{c} 2 \\ \bullet \\ \hline 2 \end{array} \quad \begin{array}{c} 1 \\ \bullet \\ \hline 2 \end{array} \quad \begin{array}{c} \hat{H} = \hat{T} + \hat{U}_{\text{ex}} + \hat{U}_{\text{ee}} \\ \hline \end{array}$$

$$\begin{array}{c} 1 \\ \bullet \\ \hline 1 \\ 2 \end{array}$$

For oversimplified approx
ignore the spin of atom
(some multiplied by $\frac{1}{2}$)

(This is impossible bc electrons are fermi particles
and will decide by the Pauli exclusion principle)

// Example that was deleted :)

$$\begin{array}{c} \bullet \\ \hline 2 \\ 1 \\ 2 \end{array}$$

$\psi(\vec{x}_1, \vec{x}_2) \rightarrow$ how this exactly looks like,
 $\psi_1(\vec{x}_1)$ nobody knows

$$\psi_1(\vec{x}_1) = \psi_1(1)$$

Total wave function

$$\Psi(1, 2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_1(1) & \psi_1(2) \\ \psi_2(1) & \psi_2(2) \end{vmatrix}$$

$$\psi_1(1)$$

$$\psi_2(2)$$

$$\psi_1(1)$$

$$\psi_2(2)$$

$$\int \psi_i^*(1) \psi_j(1) dV_1 = \delta_{ij}$$

$$\int \Psi^*(1, 2) \Psi(1, 2) dV = 1$$

orthonormalized functions

$$\Psi(1, 2) = \frac{1}{\sqrt{2!}} (\psi_1(1) \psi_2(2) - \psi_2(1) \psi_1(2))$$

$$\hat{H}\psi = E\psi$$

$$\int \psi^* \hat{H} \psi dV = \int E \psi^* \psi dV$$

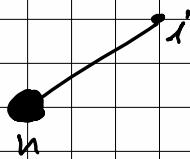
$$E = \int \psi^* \hat{H} \psi dV$$

repulsion

$$\hat{H} = -\frac{\hbar^2}{2m} \hat{\Delta}_1 - \frac{\hbar^2}{2m} \hat{\Delta}_2 + U_{\text{en}}(1) + U_{\text{en}}(2) + \frac{e^2}{4\pi\epsilon_0} \frac{1}{a_{1,2}}$$

$$\hat{\Delta}_1 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}$$

$$U_{\text{en}} = -\frac{e^2}{4\pi\epsilon_0} \sum_{n,i} \frac{z_n}{a_{n,i}} =$$



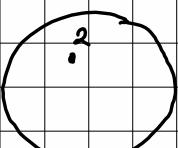
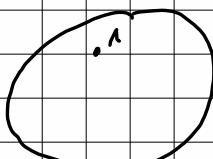
attraction
between pos. nuclei
and neg. electrons

$$= -\frac{e^2}{4\pi\epsilon_0} \left[\sum_{n,i=1} \frac{z_n}{a_{n,i}} + \sum_{n,i=2} \frac{z_n}{a_{n,i}} \right]$$

$$\hat{H} = -\frac{\hbar^2}{2m} \hat{\Delta}_1 + U_{\text{en}}(1) + \underbrace{-\frac{\hbar^2}{2m} \hat{\Delta}_2}_{\hat{H}_2} + U_{\text{en}}(2) + \frac{e^2}{4\pi\epsilon_0} \frac{1}{a_{1,2}}$$

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \frac{e^2}{4\pi\epsilon_0} \frac{1}{a_{1,2}}$$

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + U_{\text{eff}}(1) + U_{\text{eff}}(2) \quad \begin{cases} \text{Staaten-Fock} \\ \text{approx} \end{cases}$$



What does $U_{\text{eff}}(1)$ give us?

$U_{\text{eff}}(1)$ - effective potential
 coordinate
 of el. w.r.t.

$$\hat{H} = \hat{H}_1 + U_{\text{eff}}(1) + \hat{H}_2 + U_{\text{eff}}(2)$$

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + e^2 \frac{1}{a_{12}}$$

$$E = \int \psi^* \hat{H}_1 \psi dV + \int \psi^* \hat{H}_2 \psi dV +$$

$$dV = d^3 u_1 d^3 u_2$$

$$+ e^2 \int \psi^* \frac{1}{a_{12}} \psi dV$$

$$\int \psi^* \hat{H}_1 \psi dV = \frac{1}{2} \sum_{i=1}^2 \int \psi_i^*(1) \hat{H}_1 \psi_i(1) dV_1$$

$$\begin{aligned} \int \psi^* \hat{H}_2 \psi dV_1 dV_2 &= \frac{1}{2} \left[\overbrace{\left(\psi_1^*(1) \psi_2^*(2) - \psi_2^*(1) \psi_1^*(2) \right)}^{\text{III}} \right] \\ &\quad - \left(\psi_2^*(1) \psi_1^*(2) \right) \hat{H}_2 \left(\psi_1(1) \psi_2(2) - \psi_2(1) \psi_1(2) \right) dV_1 dV_2 \end{aligned}$$

I

$$\int \psi_1^*(1) \psi_2^*(2) \hat{H}_2 \psi_1(1) \psi_2(2) dV_1 dV_2 =$$

$$= \int \psi_1^*(1) \psi_1(1) dV_1 \int \psi_2^*(2) \hat{H}_2 \psi_2(2) dV_2 =$$

$$= \int \underline{\varphi_2^*(z)} \hat{H}_2 \underline{\varphi_2(z)} dV_2$$

$$\text{II} - \int \underline{\varphi_1^*(z)} \underline{\varphi_2^*(z)} \hat{H}_2 \underline{\varphi_1(z)} \varphi_2(z) dV_1 dV_2 =$$

$$= - \int \varphi_1^*(z) \varphi_2(z) dV_1 \underbrace{\int \varphi_2^*(z)}_u \hat{H} \varphi_1(z) dV_2 \underset{\textcircled{C}}{=} 0$$

$$\text{III} - \int \varphi_2^*(z) \varphi_1^*(z) H_2 \varphi_1(z) \varphi_2(z) dV_1 dV_2 =$$

$$= - \int \varphi_\alpha^*(z) \varphi_1(z) dV_1 \int \varphi_1^*(z) H_2 \varphi_2(z) dV_2 \underset{\textcircled{C}}{=} 0$$

$$\text{IV} \frac{1}{2} \int \varphi_2^*(z) \varphi_1^*(z) \hat{H}_2 \varphi_2(z) \varphi_1(z) dV_1 dV_2 =$$

$$= \frac{1}{2} \int \varphi_2^*(z) \varphi_2(z) dV_1 \underbrace{\int \varphi_1^*(z) \hat{H}_2 \varphi_1(z) dV_2}_{u_1} =$$

$$= \frac{1}{2} \int \varphi_1^*(z) \hat{H}_2 \varphi_1(z) dV_2$$

$$\int \psi^* H_2 \psi dV_1 dV_2 = \frac{1}{2} \sum_i \int \varphi_i^*(z) \hat{H}_2 \varphi_i(z) dV_2$$

Is it correct to say that these are equal?

$$\int_L \psi_i^*(1) \hat{H}_1 \psi_i(1) dV_1$$

||

$$\int_L \psi_i^*(2) \hat{H}_2 \psi_i(1) dV_2$$

$$\sum_{i=1}^N \int \psi_i^*(1) \hat{H}_1 \psi_i(1) dV_1 \Rightarrow$$

$$\Rightarrow \sum_{i=1}^N \int \psi_i^*(1) \hat{H}_1 \psi_i(1) dV_1 \quad \text{For } N \text{ particles}$$

$$(1) \quad e^2 \int \underbrace{\psi_1^*(1) \psi_2^*(2)}_{\rho_{12}} \frac{1}{a_{12}} \underbrace{\psi_1(1) \psi_2(2)}_{\rho_{12}} dV_1 dV_2 \quad (2)$$

$(\psi_i(1)) = \psi_i^*(1) \psi_i(1)$ — modulus of complex number
gives the density of ch.

$$z = x + iy$$

$$z^* = x - iy$$

$$|\psi_1(1)|^2 e^2 = f_1(1)$$

$$\Rightarrow z^* z = (x + iy)(x - iy) \quad z^* z = x^2 + y^2 \approx |z|^2$$

$$(2) \quad e^2 \int |\psi_1(1)|^2 \frac{1}{a_{12}} e^2 |\psi_2(2)|^2 dV_1 dV_2$$

$$\operatorname{div} \vec{E} = -\frac{\rho_1(1)}{\epsilon_0}, \quad \hat{v} \cdot \vec{E} = -\frac{\rho_1(1)}{\epsilon_0}$$

$$\frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{\partial z} = -\frac{\rho_1(1)}{\epsilon_0}$$

They are, but
the answer is
quite mathematical.

EXPLAN

$$\text{I} \int e |\psi_1(1)|^2 \frac{1}{a_{12}} e |\psi_2(2)|^2 dV_1 dV_2$$

$\underbrace{\psi_1(1)}$
 $\underbrace{\psi_2(2)}$
 $\underbrace{\frac{e^2}{a_{12}}}$ Coulomb force

$$\text{IV} \int \underbrace{\psi_2^*(1) \psi_1^*(2)}_{\text{1st el. in 2nd state}} \frac{1}{a_{12}} \underbrace{\psi_2(1) \psi_1(2)}_{\text{2nd el. in 1st state}} dV_1 dV_2 =$$

$$= \int \underbrace{|\psi_2(1)|^2}_{\text{1st el. in 2nd state}} \frac{1}{a_{12}} \underbrace{|\psi_1(2)|^2}_{\text{2nd el. in 1st state}} dV_1 dV_2$$

$$\text{V} - e^2 \int \underbrace{\psi_1^*(1) \psi_2^*(2)}_{\text{strange mixed state}} \frac{1}{a_{12}} \underbrace{\psi_2(1) \psi_1(2)}_{\text{but can't be eq. to 0 or off } a_{12}} dV_1 dV_2$$

$$\text{VI} - e^2 \int \psi_2^*(1) \psi_1^*(2) \frac{1}{a_{12}} \psi_1(1) \psi_2(2) dV_1 dV_2$$

* exchange energy // CP cannot explain it.

$$E = \sum_{i=1}^2 \int \psi_i^*(1) \hat{H}_1 \psi_i(1) dV_1 +$$

$$\frac{e^2}{2} \sum_{i \neq j} \int |\psi_i(1)|^2 \frac{1}{a_{12}} |\psi_j(2)|^2 dV_1 dV_2 -$$

$$-\frac{e^2}{2} \sum_{i \neq j} \int \psi_i^*(1) \psi_j(1) \frac{1}{u_{12}} \psi_i(2) \psi_j^*(2) dV_1 dV_2$$

$$U \rightarrow c\epsilon + \delta c\epsilon$$

Calculations take quite long time. Check it out:
 "Theory of Semiconductors"

System of independently moving electrons

$$H_1 = -\frac{\hbar^2}{2m} \Delta_1 + U_{\text{eff}}(1)$$

$$\left[\hat{H}_1 + \sum_{j \neq i} \frac{e^2 | \psi_j(2) |^2}{u_{12}} dV_2 - \right. \\ \left. - \sum_{j \neq i} \frac{\psi_j(1)}{\psi_i(1)} \int \frac{e^2 \psi_i(2) \psi_j(2)}{u_{12}} dV_2 \right] \psi_i(1) = E_i \psi_i(1)$$

$$U_{\text{eff}} = \sum_i \int \frac{e^2 | \psi_i(2) |^2}{u_{12}} - \sum_i \frac{\psi_i(1)}{\psi_i(1)} \int \frac{e^2 \psi_i(2) \psi_i(2)}{u_{12}}$$

Cell consistent cycle

$$① U_0$$

$$② U_{\text{eff}}$$

$$③ E, \psi_1$$

The Schrödinger eq. gives us :

Wave functions and Energy

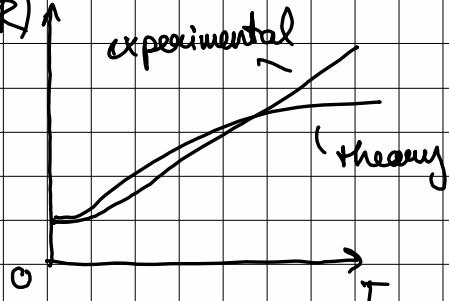
When do we stop
this cycle?

$$E_0 \cup E_1 \cup E_2 \dots$$

$$\psi_0 \quad \psi_1, \quad \psi_2 \dots$$

The cycle step only when

$$|E_{n+1} - E_n| \leq 10^{-6} \text{ eV}$$



$$R = \rho \frac{l(t)}{S(t)}$$

For example

velocity of
electric field

$$j = e \cdot n \cdot v_m$$

$$\alpha = v_+ + v_m$$

$$v_+ = \sqrt{\frac{3kT}{m}} \approx$$

$$\approx \sqrt{\frac{3 \cdot 1,38 \cdot 10^{-23} \cdot 300}{9,109 \cdot 10^{-31}}} \approx 1,17 \cdot 10^5 \frac{\text{m}}{\text{s}}$$

$$v_m$$

$$v_m \approx 10 \text{ cm/s}$$

/ conductivity

$$\sigma = \frac{1}{\rho}$$

$$j = e \cdot n \cdot v_m \sim \sigma \cdot E = \frac{1}{\rho} \cdot E$$

resistivity prop.

Starting with classical physics

as dir. is same

$$m_i + e$$



$$\vec{F} = q_i \vec{E}$$

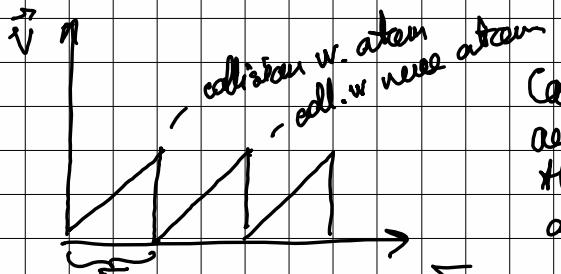
$$F = q \cdot E$$

$$\vec{E}$$

$$am = q \cdot E$$

$$\text{cancel} - \alpha = \frac{q \cdot E}{m}$$

$$V = \alpha \cdot t$$



Collisions with atoms
or scattering cause
the velocity to suddenly
drop

$$\bar{v} = \frac{1}{\tau} \int v dt = \frac{1}{\tau} \int a t dt =$$

$$= \frac{1}{\tau} \cdot a \cdot \frac{t^2}{2} \Big|_0^\tau$$

$$= \frac{a \tau^2}{2\tau} = \frac{a \tau}{2}$$

time between the collision
of two sequential atoms

$$\bar{v} = \frac{a \tau}{2} = \frac{e E \tau}{m}$$

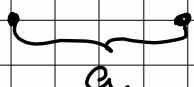
$$j = \frac{e^2 n \tau}{m} \cdot E$$

$$j = \sigma E; \quad \sigma = \frac{e^2 n \tau}{m}$$

distance between nearest
atoms

$$l = a \tau; \quad a = v_\tau \cdot \tau \Rightarrow \tau = \frac{a}{v_\tau} \sim \frac{\alpha}{T}$$

$$\sigma = \frac{a \tau}{e^2 n \tau}$$



$$\tau \sim \frac{1}{T} \sim \frac{1}{P}$$

Incorrect dependence $\leftarrow P \sim \sqrt{T}$

$$\text{In CM : } \rho = n(\tau) \tilde{\epsilon}$$

\const

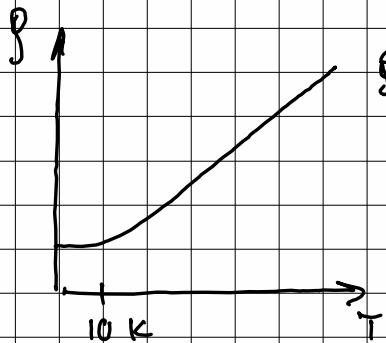
$$\text{In QM : } \rho(\tilde{\epsilon}) = n_e \cdot \tilde{\epsilon}(\tau)$$

very strange : distance dependence
at temperatures

In QM centerum of scattering to not the atom.

Number of centerum $\uparrow - \rho(\tilde{\epsilon}) \downarrow$

Next time we shall see how this works in Quantum Mechanics.



$$\rho \sim T \text{ exp.}$$

10, 11, 12

conductivity

$$j = e \cdot n \cdot v = \sigma \cdot E$$

$n = \text{const}$

all electrons in metals are free \Rightarrow CM electrons near Fermi level are accounted for

Exponentially small resistivity

$$\rho = \frac{1}{\sigma}$$

$$\sigma_c = \frac{e^2 n}{T} \sqrt{\frac{3kT}{m}}$$

$$v = v_c + v_m$$

chaotic / thermal

$$v_m \ll v_c, v_m = 10 \text{ cm/s}$$

$$R = \rho \frac{l}{s}$$

$$\rho(T) = \frac{2m}{e^2 \tilde{\epsilon} n}$$

$$G = v_c \cdot \tilde{\epsilon}$$

$T \ll ?$

ℓ , free path length $\bar{\ell} = a$

$$\text{if } \bar{\ell} = 0, \bar{r} = \infty \quad \bar{\ell} \sim \frac{1}{\sqrt{T}}$$

which means that

particles are fixed, which is not correct.

$$f(\vec{v}, \vec{r}, t)$$

$$dN = f(\vec{v}, \vec{r}, t) d^3 v d^3 r$$



$$dV = d^3 v$$

$$\begin{cases} v_x + dv_x, v_x \\ v_y + dv_y, v_y \\ v_z + dv_z, v_z \end{cases}$$

$$N = \iint f(\vec{v}, \vec{r}, t) d^3 v d^3 r$$

(a) v

$$f \sim e^{-\frac{E}{kT}}$$

$$f = \frac{1}{e^{\frac{E - \mu}{kT}} - 1}$$

$$j_x = \int v_x \cdot f(\vec{v}, \vec{r}, t) d^3 v$$

$$j_\alpha = \sigma_{\alpha\beta} \cdot \vec{v}_\beta$$

$$\sigma_{\alpha\beta} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} = \sigma \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

For equilibrium state total energy

$$f = f_0(E) + f_1(\vec{v}, \vec{v}, \pm)$$

$$E = \frac{mv^2}{2} + U$$

$$\int_x = \int v_x (f_0 + f_1) d^3 v =$$

$$= \underbrace{\int v_x f_0 d^3 v}_{\substack{\text{add} \\ \uparrow \\ \text{even}}} + \underbrace{\int v_x f_1 d^3 v}_{\substack{\text{non-equilibrium} \\ \text{part}}} = \int v_x f_1 d^3 v$$

why in equilibrium state we don't have any currents?

Hence to take into account all values of v_x (pos. and neg.)

How does the f_1 function look like?

$$f_1(\vec{v}, \vec{v}, \pm) = f_+(\vec{v}) + f_-$$

$$N = 0 \Rightarrow f_+(\vec{v}, \vec{v}, \pm) = f'(x, v_x, \pm)$$

$$\frac{\partial f}{\partial t} = \underbrace{\frac{\partial f}{\partial x} \cdot \frac{\partial x}{\partial t}}_{\text{kinetic}} + \frac{\partial f}{\partial v_x} \cdot \frac{\partial v}{\partial t} \rightarrow \left(\frac{\partial f}{\partial t} \right) =$$

$$= \vec{v} \hat{\nabla}_x f + \frac{\vec{F}}{m} \hat{\nabla}_0 f + \left(\frac{\partial f}{\partial t} \right) = 0 \quad \text{kinetic Boltzmann equations}$$

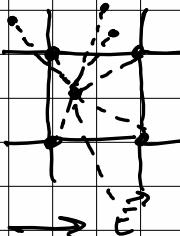
$$\vec{a} \left(= \frac{d\vec{v}}{dt} \right) = \frac{\vec{F}}{m} - \text{all external forces} / \text{in our case } \hat{\nabla}_0 f = \frac{\vec{a}}{m} \cdot f$$

What kind of forces do we have to take into account?

$\vec{a} = \frac{\vec{F}}{m}$ - specifically, the total force acting upon the particle

$$\vec{F}_c = e \vec{E}$$

Internal forces can be neglected, when we use the effective mass.



$$\left(\frac{\partial f}{\partial t} \right) = \int \underbrace{\{ f(v') w(v', v) - f(v) w(v, v') \}}_{w(v', v)} d^3 v$$

dist. func. probability

$w(v', v)$ scattering term
 v' "skate" ring term

Ideal crystal

1. Inf. large
2. Resistivity is equal to 0
3. No clustering of scattering

In CM we have internal collisions, but in QM it turns out that we don't have to take them into account.

$$\frac{df}{dt} = \underbrace{\vec{v} \cdot \hat{\nabla}_v f + \frac{\vec{F}}{m} \cdot \hat{\nabla}_v f}_{\text{field terms}} =$$

$$= - \underbrace{\{ f(v') w(v', v) - f(v) w(v, v') \}}_{\text{direct and inverse scattering}} d^3 v$$

$$f = f_0 + f_1, \quad f_0(E)$$

$$f = f_0$$

$$E = \frac{mv^2}{2} + U(x, y, z)$$

$$\vec{v} \cdot \hat{\nabla}_u f_0(E) = f_0(E)$$

$$P_0 = A e^{-\frac{E}{kT}}$$

$$= \vec{v} \cdot \left(-\frac{1}{kT} \right) \hat{\nabla}_u u =$$

$$F = -\hat{\nabla}_u u$$

$$= -\frac{\vec{v} \cdot f_0}{kT} \cdot \hat{\nabla}_u u =$$

$$= -\frac{\vec{v} \cdot f_0}{kT} \cdot \vec{F}$$

$\nabla \cdot$ terms

$$\frac{3}{m} \vec{\nabla}_v f_0(E) = \frac{\vec{F}}{m} \left(A e^{-\frac{E}{kT}} \right) \left(-\frac{1}{kT} \right) \cdot \frac{1}{\vec{k}} \cdot \vec{v} =$$

$$= -\frac{\vec{v} \cdot f_0}{kT} \cdot \vec{F}$$

Hence but with minus

$$\int \{ f_0(v') w(v', v) - f_0(v) w(v', v) \} d^3 v =$$

$$= f_0 \int \{ w(k', u) - w(u, k') \} d^3 v$$

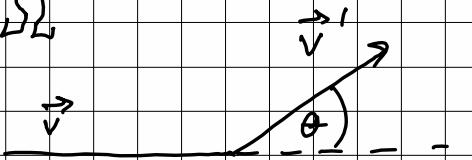
Elastic scattering $w(k', u) = w(u, k')$

Reaktion

$$\int \left\{ f_0(v') w(v', v) - f_0(v) w(v', v) \right\} d^3 v =$$

solid angle

$$= \int w(\theta) (1 - \cos(\theta)) d\Omega$$



for elastic scattering

Last part

deflection from equilibrium pos
from equilibrium pos $|v| = |v'|$

$$\left(\frac{\partial f}{\partial t} \right) = \frac{\Delta f}{\Delta t} \approx \frac{f - f_0}{\tau}$$

time between sequential collisions, with impurities
- vibrations
- other actions

$$\vec{r} \vec{F}_x f + \frac{\vec{F}}{m} \vec{J}_{rx} f = - \frac{f_1}{\tau} \quad j_x = \int v_x f_1 d^3 v =$$

$$\frac{1}{\tau} = \int w(\theta) (1 - \cos(\theta)) d\Omega = \sigma E$$

for elastic stability

$$j_x = \int v_x f_1 d^3 v$$

$$(1) \vec{F} = e \vec{E}$$

$$\vec{T} \varphi + U \varphi = E \varphi$$

$$(2) U = 0$$

$$-\frac{\hbar^2 \varphi}{2m^*} = E \varphi \quad \begin{array}{l} \text{e.g.} \\ \text{free particle} \end{array}$$

effective mass

$$(3) f \rightarrow f_0(E)$$

$$f = f_0 + f_1 =$$

~~$$\vec{v} \cdot \hat{\vec{f}}_0 + \frac{\vec{F}}{m} \hat{\vec{v}} \cdot \hat{\vec{f}}_0 = -\frac{f'_1}{\epsilon}$$~~

bc there is no $U(\vec{r})$ (i) $f \cdot f_0 \approx 0$

(i) $\frac{eE}{kT} \cdot f_0 \left(-\frac{mv_x}{kT} \right) = -\frac{f'_1}{\epsilon}$

$$\frac{eE}{kT} f_0 v_x = \frac{f'_1}{\epsilon} \quad \rightarrow f_0 = e \int v_x f_1 d^3v$$

$$f_1 = \frac{e f_0 v_x \epsilon}{kT} \cdot E$$

$$j_x = \frac{e^2}{m} \int \tilde{\epsilon}(T) \cdot v_x^2 \cdot f_0(E) d^3v \cdot E \neq 0$$

no idea even even Not exact,
"rather
qualitative"

$$j_x = \sigma E$$

$$\sigma = \frac{e^2}{kT} \int \tilde{\epsilon}(\epsilon) \cdot n_x^2 f_0(\epsilon) d^3v =$$

$$\sigma_{kp} = \frac{q^2 m^* e^3}{2 \pi^3 h^3} \int \tilde{\epsilon}(v, \tilde{v}) \frac{\partial f_0}{\partial E} \cdot n_x \cdot n_p d^3v$$

$$\frac{\partial f_0}{\partial E} = \delta(E - E_F), T \ll$$

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

$$P_F = m v_F^2 = \hbar u_F$$

$$R_F = \sqrt{\frac{Qm E_F}{\hbar}}$$

$$M_F = \frac{\tau u_F}{m} = \sqrt{\frac{dm E_F}{m}} = \sqrt{\frac{2 E_F}{m}}$$

$$\sigma_{\alpha\beta} = \frac{q \cdot m^*}{4\pi^3 h^3} \tilde{\epsilon}(v_F, T) \cdot \tau \alpha_F N_F \rho_F$$

$$\sigma_{\alpha\beta} = \frac{q^2 \cdot m^*}{4\pi^3 h^3} \int \tilde{\epsilon}(v, T) \cdot \frac{\partial \phi}{\partial v} \cdot \alpha \cdot \rho_\beta d^3 v$$

Harmonic approximation / linear approximation

$$F \sim u_N$$

$$E = \sum_n \frac{1}{2} m_n \ddot{u}_n^2 + \frac{1}{2} \sum_n g_n (u_n - u_{n-1})^2 / \text{spring constant CM}$$

$$\left\{ \begin{array}{l} m_n \ddot{u}_n = F_n \\ u_n = A e^{i(\omega t + \vec{q} \cdot \vec{a}_n)} \end{array} \right.$$

$N = 1$ used
equations

$$u_n = \sum_q A_q e^{i(\omega(q)t + \vec{q} \cdot \vec{a}_n)}$$

quantum mech.

$$E = \sum_q \left(\frac{1}{2} A_q^2 + \frac{1}{2} m \omega^2(q) \cdot A_q^2 \right) = \underbrace{\sum_q \frac{\hbar \omega(q)}{2} (2u_q + 1)}$$

sum of harmonic oscillations
classical mechanics

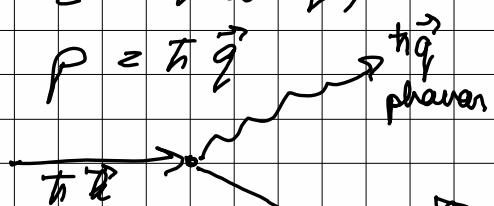
$$E = \sum_q \frac{\hbar \omega(q)}{2} (2u_q + 1) \quad u_q \in [0, \dots, +\infty]$$

photon

Creation of photon

$$E = \hbar \omega(\vec{q})$$

$$\vec{P} = \hbar \vec{q}$$



$$E = \frac{\hbar^2 k^2}{2m^*}$$

$$\hbar \vec{k}'$$

same electron

$\hbar \vec{q}$

photon

quasiparticle - a particle that doesn't actually exist but can be used to simplify existing problems

1. set of vibrating particles

2. set see boom waves

3. quasiparticle

Direct scattering $w(k, k')$

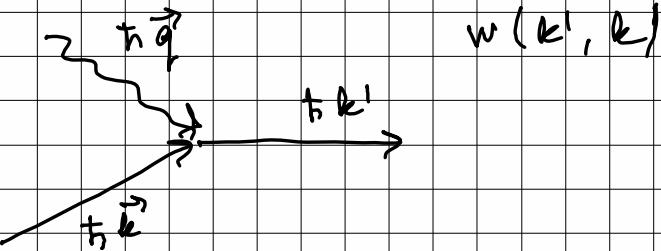
$\hbar \vec{k}'$

$\hbar \vec{k}$

creates a wave

specifically a photon

Inverse scattering / Destruktion of photon



Creation

$$\left\{ \begin{array}{l} \vec{u} = \vec{q}_i + \vec{u}' \\ \frac{\hbar^2 k^2}{2m^*} = \hbar w(\vec{q}_i) + \frac{\hbar^2 u'^2}{2m^*} \end{array} \right.$$

Destruction

$$\left\{ \begin{array}{l} \vec{k} = \vec{k}' - \vec{q} \\ \frac{\hbar^2 k^2}{2m^*} + \hbar w(\vec{q}) = \frac{\hbar^2 k'^2}{2m^*} \end{array} \right.$$

$$w(k, \omega) = w(q) (N_q + 1) \delta(E_{k+q} - E_k - \hbar\omega(q))$$

$$w(k, \omega') = w(q) (N_q) \delta(E_{k+q} - E_k - \hbar\omega(q))$$

'no of phonons'

$$N_q = \frac{1}{e^{\frac{\hbar\omega}{kT}} - 1}$$

$$\omega = 1 \text{ THz}$$

But... what about
the physical interpre-
tation?

$$l = \alpha \cdot \tilde{\epsilon}$$

$$\alpha = \alpha(T) \cdot \tilde{\epsilon}$$

$$\text{and } l = n_F \cdot \tilde{\epsilon}$$

Very strange result $l \sim \frac{v_F}{T}$ for low T , $l \rightarrow \infty$

$T \rightarrow \infty$, no of phonons $\rightarrow \infty$, $\tilde{\epsilon} \rightarrow 0$, $l \rightarrow 0$

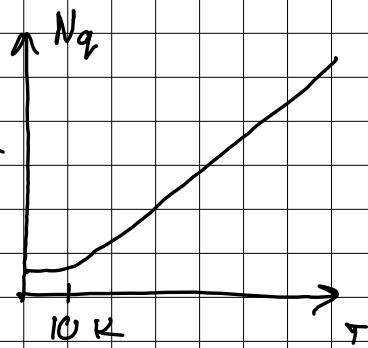
If $l \rightarrow 0$, bc we have too many phonons.

L. 5. 6. 22

What's the difference between
Fermi and Bose particles?

T. 11. 22

Bose p. - all particles are in one state
Fermi p. - one particle for each energy level



$T \approx C$

$$f(E, T) = \frac{1}{e^{\frac{E-\mu}{kT}} + 1}$$

μ - chemical potential
 f - probabilities

$$K = 2 \int_0^{+\infty} G(E) f(E, T) dE$$

$$\begin{aligned} G(E) dE \\ E, E + dE \\ G(E) \sim \sqrt{E} \end{aligned}$$

$$\mu = E_F \left(1 - \frac{\pi^2}{12} \left(\frac{kT}{E_F} \right)^2 \right)$$

$$E_F = \frac{\pi^2 e^2 k_F^2}{2m}$$

$$k_F \sim n^{\frac{1}{3}}$$

$$\begin{array}{|c|} \hline \text{total energy} \\ \hline \boxed{E_F \sim n^{\frac{2}{3}}} \\ \hline \end{array}$$

Fermi en -
all energy levels
are occupied

from 0 to E_F . ($\text{for } T=0$)

$$E_F = 2 \int_0^{E_F} E G(E) dE \sim n^{\frac{5}{3}}$$

$$\text{Exact eq. } E_F = 2 \int_0^{+\infty} E G(E) f(E, T) dE$$

$$f(E, T) = \begin{cases} 1, & 0 < E \leq E_F \\ 0, & E > E_F \end{cases} \quad \text{for } T=0$$

Total (kinetic) energy of free electrons: $E_{ke} \sim n^{\frac{5}{3}}$

What if temp is sufficiently large, but concentration is low?

$$f \sim e^{-\frac{E}{kT}}$$

Boltzmann - Maxwell distribution

For conductors:

$$\mu = E_F \left(1 - \frac{\pi^2}{12} \left(\frac{kT}{E_F} \right)^2 \right) \quad (1)$$

Why the dependence on temp is not so strong

$$T_F = \frac{E_F}{k} \approx 50 \text{ 000 K} \text{ // for potassium}$$

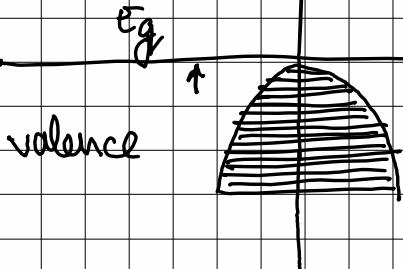
$$(2) \quad E_F \left(1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right) \quad \begin{matrix} \uparrow \\ T_F \text{ so large; } (T_F) \text{ neglected} \end{matrix}$$

Fermi energy does not depend on temperature!

$$\mu \neq E_F ; \mu(T) \neq E_F \text{ other cases}$$

$$f(E, T) = \frac{1}{e^{\frac{E-\mu}{kT}} + 1} \quad E(\vec{k}) = E(k_x, k_y, k_z)$$

Band gap Δ



conducting zone

$T=0$



$$n_f(T=0) = 0$$

$E_g < 2 \text{ eV}$ Semiconductor

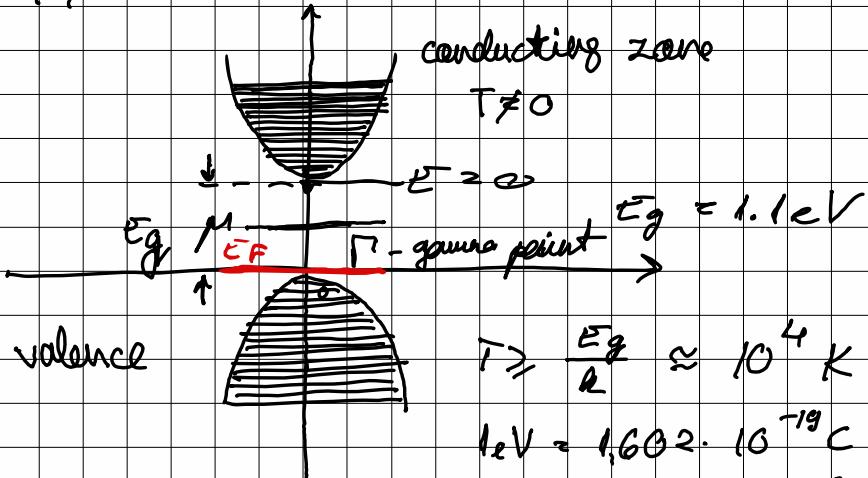
$E_g > 2 \text{ eV}$ Insulator

In semiconductors

Concentration of free electrons for zero temperature:

zero

For $T \neq 0$



For low temp $T \approx 300 K$
is it possible for electrons
to jump to the conducting
zone?

$$T \geq \frac{E_g}{k} \approx 10^4 K$$

$$1eV = 1.602 \cdot 10^{-19} C$$

$$k = 1,38 \cdot 10^{-23} \frac{J}{K}$$

$$T \approx 300 K \ll 10^4 K$$

No electrons in valence zone - hole.

$$m_e^* \geq m_p^*$$

low temperature
case.

$$n \approx 0$$

(low concentration for)

$$T \gg$$

$$\mu \sim n^{\frac{2}{3}}$$

$$E \gg \mu \quad (e^{\frac{E}{kT}} \gg 1)$$

μ is excluded bc
schmal

$$f(E, T) = \frac{1}{e^{\frac{E-\mu}{kT}} + 1} = e^{-\frac{E}{kT}}$$

$$= Ae^{-\frac{E}{kT}}, A = e^{\frac{\mu}{kT}}$$

$$n = \int_0^{+\infty} G(E) \cdot e^{-\frac{E}{kT}} dE \quad // \text{simplified case}$$

$$\mu(T) = kT \ln \left(\frac{4\pi^3 \hbar^3 n}{(2\pi m^* kT)^{\frac{3}{2}}} \right) \quad \begin{array}{l} \text{semi-} \\ \text{conductor} \end{array}$$

$$n = 2 \int_0^{+\infty} G(E) \cdot f(E/T) dE \quad // \text{General case:}$$

Dependence on temp. is linear
but very strong

$$e(E) = e_n(k_x, \theta_y, k_z)$$

$$f(E, T) = \frac{4\pi^3 \hbar^3 n}{(2\pi m^* kT)^{\frac{3}{2}}} \cdot e^{-\frac{E}{kT}}$$

$$E_F = \frac{\hbar^2 k^2}{2m^*} \quad \begin{array}{l} \text{me} \\ | \\ \text{constant} \end{array}$$

$$\text{Exact eq.} \quad -\frac{\hbar^2}{2m} \Delta \psi + V\psi = E\psi \quad // \text{can be found but very difficult}$$

$$\text{NB!} \quad -\frac{\hbar^2}{2m^*} \Delta \psi \approx E\psi \quad // \text{for free electrons}$$

k must be near the minimum
minimum \uparrow
zones! \rightarrow

$$E = \frac{\hbar^2 k^2}{2m^*}$$

m^* - hides the properties
of periodical potential,
can be calculated

Only then we can derive the simplified Sch. eq.
energy of hole near Γ point.

$$E_p = -E_g - \frac{\hbar^2 k^2}{2m_p^*}$$

$$f_p = \frac{1}{e^{\frac{E_p - E_F}{kT}} + 1}$$

$$f_p = 1 - f_e \approx \frac{1}{e^{\frac{m_e - E_p}{kT}} + 1} \approx e^{-\frac{(E_p - \mu)^2 k^2}{2 m_e^* kT}} = e^{-\frac{(E_p - \mu)^2}{2 kT}}$$

and

$$\int G(E) f_e(E_e, T) dE = \int G(E) f_p(E, T) dE$$

ne

valence

Minimal possible energy for H:

$$\int_{E_{\min}}^{E_{\text{ionization}}} \frac{dN}{dE}$$

electrons
recomers
free

Final result:

$$\mu(T) = -\frac{E_g}{2} + \frac{3}{4} kT \ln \left(\frac{m_p^*}{m_e^*} \right)$$

hole
electrons

Fermi en. can be defined only for 0 temp.

If $m_p^* = m_e^*$ ln(1) = 0, so μ won't depend on temperature. In that case, E_F is located in band gap

$$\mu = -\frac{E_g}{2}$$

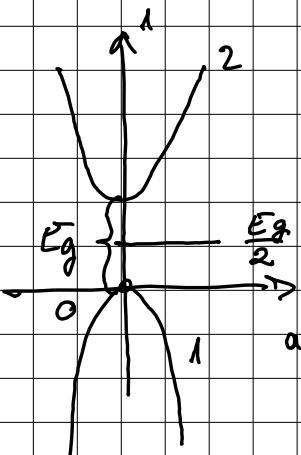
$$\mu - E_F = \frac{E_g}{2}$$

generally not eq. but can be

For 300 K concentrations cannot be very high in the conducting zone.

Conductivity is not high in semi-conductors and the resistance is also high as well.

We can see this when we compare $300K \ll 10^4 K$



$$n = \frac{2\pi}{h^3} \cdot \frac{(m_p^* m_e^* - kT)^{3/2}}{2\pi^2} e^{-\frac{E_g}{kT}}$$

$$\rho(T) = \frac{m}{e^2 \epsilon(-T) \cdot n(T)}$$

resistivity
between segments
between electrons and phonons

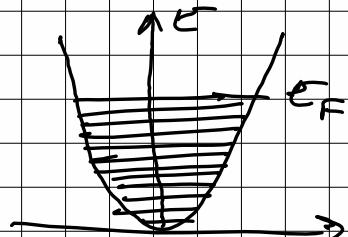
$$\epsilon \sim \frac{1}{T} \quad / \ln QM$$

conduct

$$\epsilon(T) \sim \frac{1}{T}$$

$n \propto T$
no dependence
on temperature

If $T \ll T_F$
activation temp
warm temp



We only have to consider electrons near the E_F so the concentration of el. does not depend on T .

$$T \ll T_F \rightarrow \rho \sim T$$

Electrons near the E_F are activated.

Only

Semicond

In QM electrons collide with the vibrations of atoms, unlike in CM where el. collide with ~~just~~ atoms.

In semicond., we only take into account free electrons in the conducting zone. Similarly to conductors

$$\gamma \sim \frac{1}{T}$$

$$n(T) \sim e^{-\frac{E_g}{kT}} \cdot T^{\frac{3}{2}}$$

main part of temp dependence

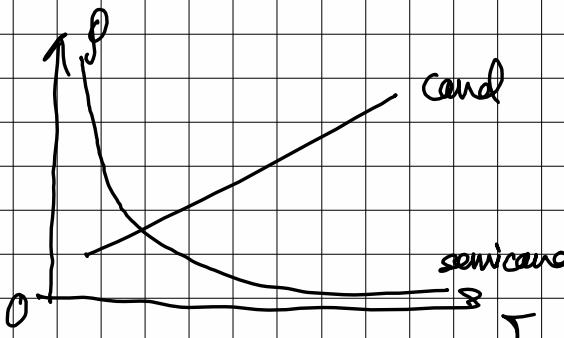
$$\rho(T) \sim \frac{T e^{-\frac{E_g}{kT}}}{T^{\frac{3}{2}}} = T^{-\frac{1}{2}} e^{-\frac{E_g}{kT}}$$

main dependence

$$T \rightarrow \infty$$

$$\frac{E_g}{kT} \rightarrow 0$$

$$e^0 = 1$$



E_g can be calculated from $\rho(T)$.

L. 5.7. Paramagnetic properties of free electrons

24. 11. 22

$\vec{\mu}_0$ - magnetic moment of particle

SI CGS

\vec{H} - strength vector for mag. field $(\frac{A}{m}) (G)$

gauss

$$T = 0$$

$$\vec{m} = \vec{\mu}_0 \cdot n \quad \vec{\mu}_0 \uparrow \uparrow \vec{H}$$

total magnetic flux
inside one m^3 .
(magnetization vector)

$$T \neq 0$$

$$\vec{m}(T) =$$

$$\chi = \frac{M(T)}{H} = \chi(T) \sim \frac{1}{T} \quad \text{Curie's law}$$

magnetic susceptibility

Free electrons:

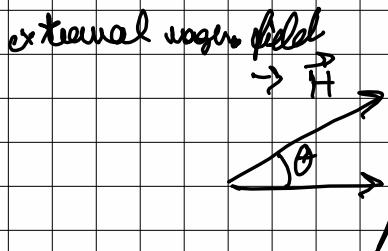
$$\chi \sim \frac{1}{T} \quad \chi = (T) \approx 0$$

Let's check the truthfulness on these relations.

Classical theory of paramagnetism

$$\vec{M} (T)$$

$$X = \frac{A}{T}$$



$$dW = A e^{-\frac{E_P}{kT}} \sin(\theta) d\theta$$

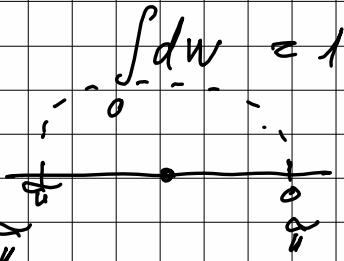
$\theta, \theta + d\theta$

$$E_P = -\vec{\mu}_0 \cdot \vec{H} = \mu_0 H \cos \theta$$

real numbers

$$\mu_0 H \cos \theta$$

$$dW = A e^{-\frac{\mu_0 H \cos \theta}{kT}} \sin(\theta) d\theta$$



dW - probability

(The probability of μ_0 to be located in ext. mag. field H)

$$\int_0^{\pi} dW = A \int_0^{\pi} e^{-\frac{\mu_0 H \cos \theta}{kT}} \sin(\theta) d\theta \approx$$

$$\Rightarrow A = \mu_0 \cdot \int_{-1}^{+1} e^{\alpha x} dx = 1, \quad \alpha = \frac{\mu_0 H}{kT}$$

average magnetization

$$\langle M \rangle = \mu_0 \cdot \frac{\int_{-1}^{+1} x e^{\alpha x} dx}{\int_{-1}^{+1} e^{\alpha x} dx}$$

$$x = \cos \theta$$

$$\alpha = \frac{\mu_0 H}{kT}$$

Lengerichter funktion

$$\langle M \rangle = \mu_0 L \left(\frac{(\mu_0 H)}{kT} \right) n$$

then 1 partikel per lm³

$$L(\alpha) = \coth(\alpha) - \frac{1}{\alpha}$$

Simplifications

$$H \ll 1$$

$$\alpha \ll 1$$

$$\langle M \rangle = \mu_0 L \left(\frac{\mu_0 H}{kT} \right) n$$

$$\sinh(\alpha) = \frac{e^\alpha - e^{-\alpha}}{2}$$

$$\cosh(\alpha) = \frac{e^\alpha + e^{-\alpha}}{2}$$

$$\coth(\alpha) = \frac{\cosh \alpha}{\sinh \alpha} - \frac{1}{\alpha} =$$

$$= \frac{e^\alpha + e^{-\alpha}}{e^\alpha - e^{-\alpha}} - \frac{1}{\alpha}$$

Taylor expansion:

$$e^\alpha = 1 + \frac{1}{1!} \cdot \alpha + \frac{1}{2!} \cdot \alpha^2 + \frac{1}{3!} \cdot \alpha^3 \quad (\text{we exclude other terms})$$

$$e^{-\alpha} = 1 - \alpha + \frac{\alpha^2}{2} - \frac{\alpha^3}{6} \quad [+ \dots \quad (\text{exclude all other terms})]$$

$$\frac{1 + \alpha + \frac{\alpha^2}{2} + \frac{\alpha^3}{6} + 1 - \alpha + \frac{\alpha^2}{2} - \frac{\alpha^3}{6}}{1 + \alpha + \frac{\alpha^2}{2} + \frac{\alpha^3}{6} - 1 + \alpha - \frac{\alpha^2}{2} + \frac{\alpha^3}{6}} - \frac{1}{\alpha} =$$

$$\frac{\alpha + \alpha^2}{2\alpha + \frac{\alpha^3}{3}} - \frac{1}{\alpha} = \frac{\alpha + \alpha^2}{\alpha \left(2 + \frac{\alpha^2}{3} \right)} - \frac{1}{\alpha} =$$

$$= \frac{1}{\alpha} \left(\frac{\alpha + \alpha^2}{2 + \frac{\alpha^2}{3}} - 1 \right) = \frac{1}{\alpha} \left(\frac{\alpha + \alpha^2/2 - \frac{\alpha^2}{3}}{2 + \frac{\alpha^2}{3}} \right)$$

*only interested
in linear terms*

$$= \frac{1}{\alpha} \cdot \frac{\frac{2}{3} \alpha^2}{2 + \frac{\alpha^2}{3}} \approx \frac{\frac{2\alpha}{3}}{3 \cdot 2} = \frac{\alpha}{3}$$

will be excluded

$$\langle M \rangle = \mu_0 \cdot \frac{\mu_0 \cdot hn}{kT} \cdot \frac{1}{3} = \frac{\mu_0^2 hn}{3kT}$$

$$N(\tau) = \frac{M}{H} \approx \frac{\mu_0^2 n}{3kT} \quad (\text{if } N \sim \frac{1}{T} \text{ holds})$$

$$M_j = M_B \cdot j \cdot \vec{J}$$

Basis magneton

$$M_B = \frac{e\hbar}{4m_e}$$

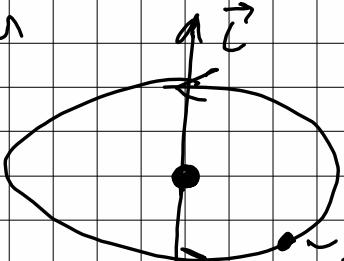
*j - total ang. mom.
l - orbital quantum no.
s - spin*

Landé parameter

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l-1)}{2j(j+1)}$$

What kind of motion add. to spin
spin - rotation of axis
around its axis

1. Orbital motion
2. Spin



localized electron

$$\vec{p}_e = \sqrt{Bc e} \vec{v} \quad (\text{negative})$$

\vec{L} - angular momentum
 \vec{S} - spin

$$\vec{J} = \vec{L} + \vec{S}$$

$$\vec{j} \rightarrow j$$

$$\vec{l} \rightarrow l$$

$$\vec{s} \rightarrow s$$

$(l=0)$

But how does μ look like for free electrons?

$$\vec{j} = 0 + \vec{s} \Rightarrow \vec{j} = \vec{s}$$

$$l=0; j=s$$

$$\mu = \mu_B \cdot g \cdot 2 = \underline{\underline{2\mu_B \cdot s}}$$

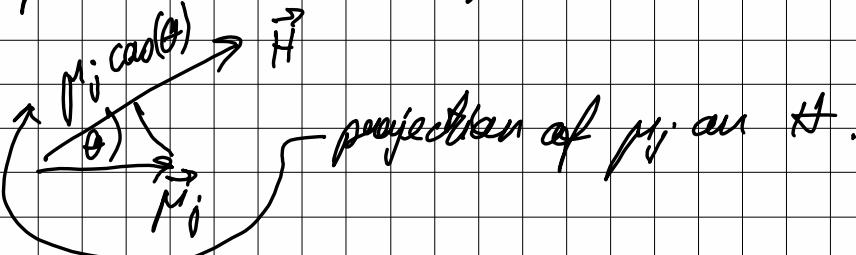
$$g = 1 + \frac{s(s+1) + s(s+1)}{2s(s+1)} =$$

$$= 1 + \frac{\cancel{2s(s+1)}}{\cancel{2s(s+1)}} = \underline{\underline{2}}$$

ang. ac $\Gamma \neq 0$

$$\langle \mu \rangle - ?$$

$$E_p = -\vec{\mu}_j \cdot \vec{H} = -\mu_j \cdot H \cdot \cos(\theta)$$

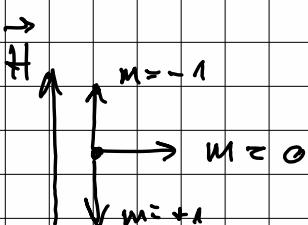


$$\boxed{E_p = -\mu_B \cdot H \cdot g \cdot m}$$

 n

$$\begin{aligned} l &= 0, \dots, n-1 \\ m &= -l, \dots, 0, \dots, +l \end{aligned}$$

Angular/azimuthal quantum no.
magnetic quantum no.

 E_F .

$$\begin{array}{ll} n = 1 & n = 2 \\ l = 0 & l = 0, m = 0 \\ m = 0 & l = 1, m = -1, 0, +1 \end{array}$$

What is the relation between j and m ?

$$j \quad m = -J, \dots, 0, \dots, +J$$

$$\begin{aligned} \langle \mu \rangle &= \frac{\sum_{m=-j}^{+j} M_i \cos(\vec{j} \cdot \vec{M}) e^{-\frac{E_p}{kT}}}{\sum_{m=-j}^{+j} e^{-\frac{E_p}{kT}}} = \\ &\qquad \alpha = \frac{\mu_B \cdot g \cdot H}{kT} \\ &= \mu_B \cdot g \cdot \frac{\sum_{m=-j}^{+j} m e^{\alpha m}}{\sum_{m=-j}^{+j} e^{\alpha m}} \end{aligned}$$

$$\langle \mu \rangle = \frac{\mu_B^2 g^2 j(j+1)}{k n T} \cdot H$$

$$\langle M \rangle = \frac{\mu_B^2 g^2 j(j+1)}{3kT} \cdot H \cdot n$$

$$\chi = \frac{\mu_B^2 g^2 j(j+1) n}{3kT}, \quad \chi \approx \frac{1}{T}$$

But, the other terms in the equations above cancel even $1/T$ on χ in this case, which means that $\chi \approx 0$.

Schrodinger equation for free electrons :

$$\hat{H}\psi = E\psi$$

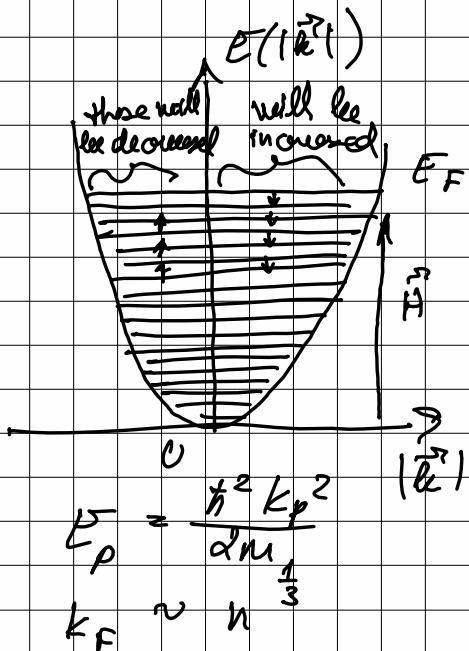
$$\hat{H} = -\frac{\hbar^2 \Delta}{2m}$$

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}}$$

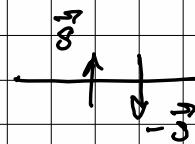
$$E = \frac{\hbar^2 k^2}{2m}$$

$$\vec{k} = (k_x, k_y, k_z)$$

$$|\vec{k}| = \sqrt{k_x^2 + k_y^2 + k_z^2}$$



In each state can be located only 2 electrons which are directed in opposite directions.



Fermi particles

$$\begin{aligned} \vec{m}_s &= \mu_B \cdot \vec{j} \cdot \vec{s} = \\ &= \alpha \mu_B \cdot \vec{s} \end{aligned}$$

k_1, k_2, k_3

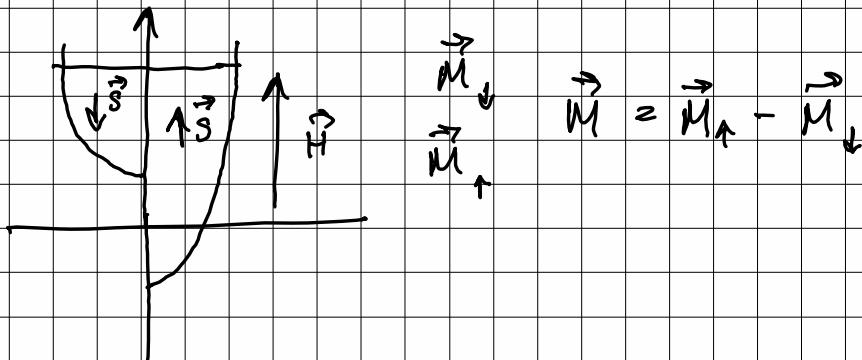
$$\begin{array}{c} \uparrow \vec{s} \\ \uparrow \vec{H} \\ \cos(0) = 1 \end{array} \quad \begin{array}{c} \uparrow \vec{s} - \vec{m}_s \vec{H} \\ \uparrow \vec{s} + \vec{m}_s \vec{H} \\ \cos(180^\circ) = -1 \end{array}$$

Does the external magen. field change the energy?

$$E = -\vec{m}_s \cdot \vec{H} = -\vec{\mu}_s \cdot \vec{H} \cdot \cos(\theta)$$

External field decreases the energy, if $\theta = 0^\circ$.

External field increases the energy, if $\theta = 180^\circ$



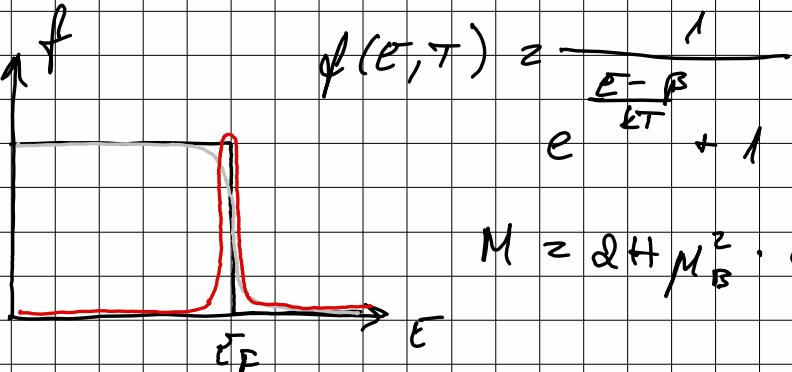
$$M_{\uparrow} = \mu_B \int f(E - \mu_B H) G(E) dE$$

$$M_{\downarrow} = \mu_B \int f(E + \mu_B H) G(E) dE$$

Final result $H \ll$

$$M = 2H \mu_B^2 \int \left(-\frac{\partial f}{\partial E} \right) G(E) dE$$

f - Fermi - Dirac distribution function



$$M = 2H \mu_B^2 \cdot G(E)$$

$$M = \mu_B^2 H G(E_F) \left(1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right)$$

$$\chi = \mu_0^2 G(E_F) \left(1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right) \quad T_F = \frac{E_F}{k} \approx 50000 K$$

As T_F is so large, there is no sufficient dependence on temperature.

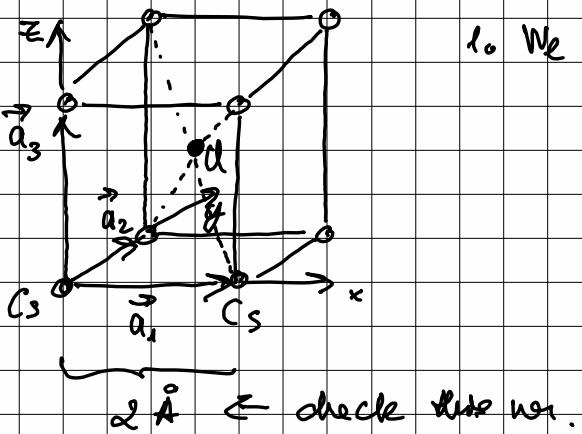
VASP

+ Homework

POSCAR

C₆₀

Total no of files needed to start calc. is 4. First is POSCAR



POSCAR

1	Structure: C ₆₀
2	1.
3	$2. \sqcup \emptyset. \sqcup \emptyset. 4 a_1$
4	$\emptyset. \sqcup 2. \sqcup \emptyset. 4 a_2$
5	$\emptyset. \sqcup \emptyset. \sqcup 2. 4 a_3$
6	C ₆₀ C
7	1 1
8	C
9	$\emptyset. \sqcup \emptyset. \sqcup \emptyset.$
10	1. \sqcup 1. \sqcup 1.

1 comment line

// real numbers 1., used for multiplying basis vectors

// have many atoms in molecule,
// C - Cartesian (cartan sys)

// peers enter to close file

8) D

A D - Direct; pos. def. by Coss's vec

9) $\emptyset \cup \emptyset \cup \emptyset$ 10) $0.5 \cup 0.5 \cup 0.5$

$$\vec{r}_{Cs} = a_1 \cdot \vec{a}_1 + a_2 \cdot \vec{a}_2 + a_3 \cdot \vec{a} \quad (3)$$

in Cartesian:

$$\vec{r}_{Cs} = x_{Cs} \cdot \vec{i} + y_{Cs} \cdot \vec{j} + z_{Cs} \cdot \vec{k}$$

$$\vec{r}_{el} = 1 \cdot \vec{i} + 1 \cdot \vec{j} + 1 \cdot \vec{k}$$

Eq. from conservation

$$(2) u_1 (a_{1x} \cdot \vec{i} + a_{1y} \cdot \vec{j} + a_{1z} \cdot \vec{k}) + u_2 (a_{2x} \cdot \vec{i} + a_{2y} \cdot \vec{j} + a_{2z} \cdot \vec{k}) +$$

$$+ u_3 (a_{3x} \cdot \vec{i} + a_{3y} \cdot \vec{j} + a_{3z} \cdot \vec{k}) =$$

$$= i (u_1 a_{1x} + u_2 a_{2x} + u_3 a_{3x}) +$$

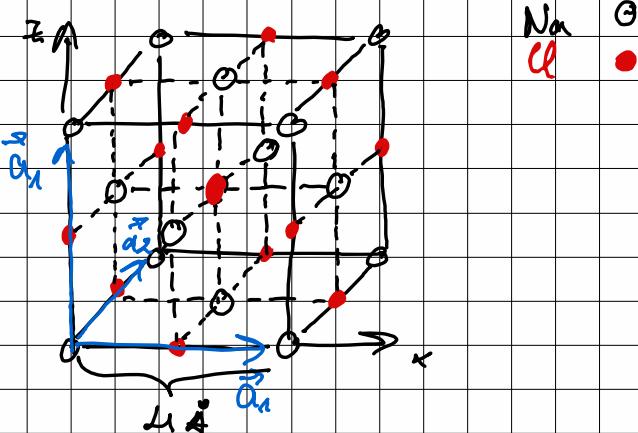
$$+ j (u_1 a_{1y} + u_2 a_{2y} + u_3 a_{3y}) +$$

$$+ k (u_1 a_{1z} + u_2 a_{2z} + u_3 a_{3z})$$

$$\begin{cases} u_1 a_{1x} = x_{Cs} \\ u_1 = \frac{x_{Cs}}{a_{1x}} = \frac{1}{2} \end{cases}$$

VESTA (software, that can be used for POSCAR files to convert Cartesian \rightarrow Direct)

NaCl



POSCAR

1. Structure \hookrightarrow NaCl
2. 1.
3. $4. \sqcup \emptyset. \sqcup \emptyset.$
4. $\emptyset. \sqcup 4. \sqcup \emptyset.$
5. $\emptyset. \sqcup \emptyset. \sqcup 4.$
6. Na \sqcup Cl
7. H \sqcup H
8. C
9. $\emptyset. \sqcup \emptyset. \sqcup \emptyset.$ // &
10. $\emptyset. \sqcup 2. \sqcup 2.$ // \emptyset
11. $2. \sqcup \emptyset. \sqcup 2.$ //
12. $2. \sqcup 2. \sqcup \emptyset.$ // end of Na atoms
13. $2. \sqcup 2. \sqcup 2.$ // start of Cl atoms
14. $\emptyset. \sqcup \emptyset. \sqcup 2.$
15. $\emptyset. \sqcup 2. \sqcup \emptyset.$
16. $2. \sqcup \emptyset. \sqcup \emptyset.$ end of Cl atoms

My homework : Silicon crystal structure

Preferably in Direct coordinates,
write the POSCAR file

In linux command line write

\rightarrow mpi4f90

If it says "files are not specified" as
seen above these lines, everything is configured
correctly.

Copyin:

\rightarrow SCP test.txt srujan@193.40.252.77:

test.txt

\rightarrow [password]

\rightarrow Contains k-vectors .

POSCAR
K-POINTS

$E_n(\vec{k})$

5 5 5

0 0 0

Instead of Monkhorst Pack
Grasses

125 different parts

so 125 lines needed overall

125 k-vectors

1 shift of k work

INCA

- optimisation of structure
- frequency of structure
- charge of atoms

- Optimized parameters can be compared with ex
- Band gap width can be calc

SYSTEM = Si

PREC = High

// Precision of calculation

ENCUT ?

$$Y(k) = \sum_k C_k e^{ik \vec{r}} = \text{Fourier series}$$

maximum

possible cut

on stepping

parameter for

the Fourier

series

$$= \sum_{k_x, k_y, k_z} C_{k_x, k_y, k_z} e^{i(k \vec{r})}$$

$$E = \frac{\pi^2 k^2}{2m}$$

TBTRON - for
optimizing crystal
structure

$$E_{\text{cut}} = \frac{\pi^2 k^2}{2m} \leq E_{\text{encut}}$$

$$k_{\text{cut}}^2 \leq \frac{2m E_{\text{encut}}}{\pi^2}$$

(more allowed values for k vector)

ISIE - without limit of
charge must be low during optimization

positions - position of ions

cell shape - during the opt. process is changed
or not

ISMEAR

+ smearing

0.

EDIFF

energy difference

$$\psi \rightarrow V_{eff} \rightarrow \hat{H} \rightarrow$$

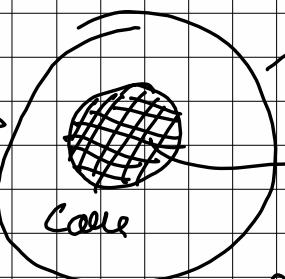
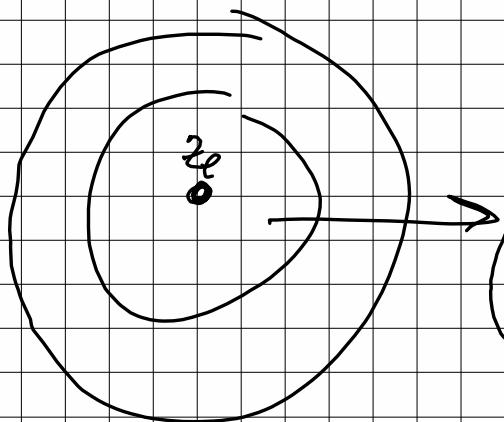
$$\hat{H} \psi = E \psi$$

$$E_{t+1} - E_t \leq EDIFF$$

E_t

) calculations are finished

POTCAR file



- valence electron

pseudopotential

potential of created
by the core

$$V = \frac{1}{4\pi G} \cdot \frac{Ze}{r}$$

NSW - optimization
step

ZVAL = number of valence electrons

DON'T use MORE THAN 2 CORES

user/local/loc

mpnnum -np 2 vasp-P

POS

TOT FORCE

OUTCAR

CONT CAR

external pressure \Rightarrow makes off-k-point ($0, 0, 0$)

> PS

! OUTCAR E-perm

8/18

0

3 Band gap

5,6

2

PID

, kill process

> kill [PID no.]

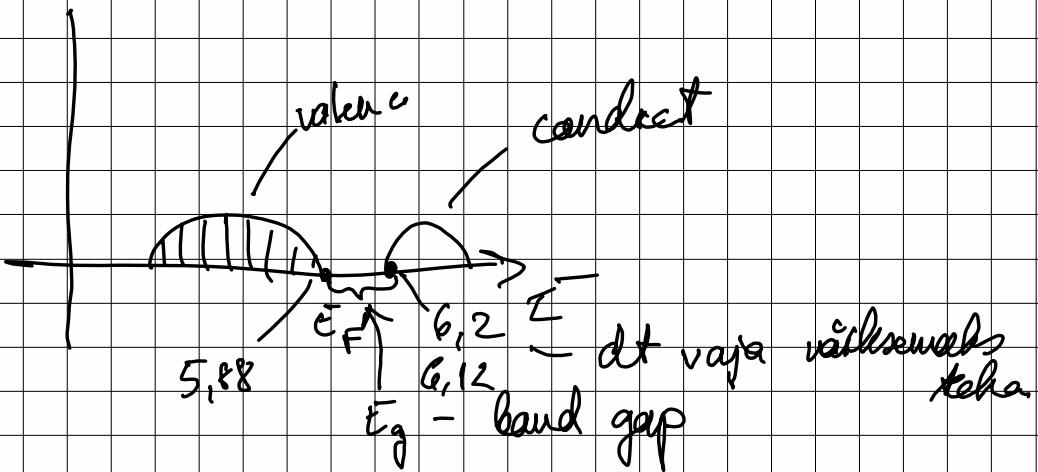
① Basis vectors and compose unitcell

② EF, Eg DOSCAR file

③ DOS of (E) # good if you have plot of this
for example space

You're free submission!

Hobby - F. Vass
last acc



$$E_g = 6,12 - 5,88 = 0,36 \text{ eV}$$

1.12 V

Kurdes DOS sätter
avtagat

DOS
 5,88 6,12
 PHONO P4
 > python3 -m venv venv
 > source ~/venv/bin/activate
 (venv) > pip3 install phonopy
 -.. ? phonopy --symmetry (Generates POSCAR
 files)

generated: POSCAR

POSCAR - same as

VASPKIT - for plotting

calculator seal has on DOS plot

→ Installation (Futurent)

$$E_n(\vec{k})$$

(band number)

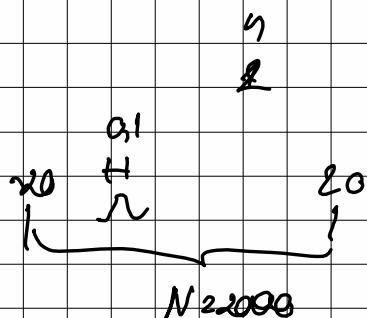
$$n = 1 \dots 8$$

EIGENVAL

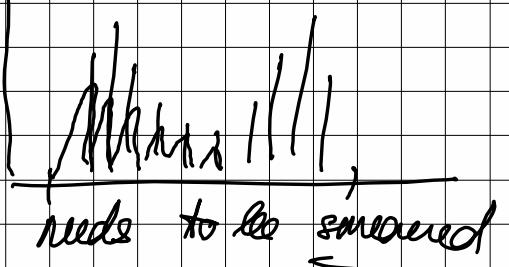
$$\text{DOS}(E) =$$

$$= \sum_{n,\vec{k}} \delta(E - E_n(\vec{k}))$$

DOS(E)



$$E \\ 21,85$$



TDOS.dat

≈ k-mesh size

soh -> -& signs ...

> xms size

TDOS.dat

and C.8.v

CONTCAR

5,833 : 0,712

DOSCAR Results 1.1ev

5,27

0.000
0.000

5,183 → 5,285

Fluor vaspent POSCAR.dat

part

\$ cat POSCAR.dat | awk '{\\$1 "" \\$2}'
| xunzip -pipe

FS → Shell Link → \$ipage@193.. .

cdn | osmat
POSCAR | ...

FO

POSCAR

> scp ' \$ipage@193. . - . 77 : poscar