

typed script, go to <http://www.itp.tu-berlin.de/itp/menue/lehre/lv/ss08/wpfv/tfkp>  
 go to "Webpage at FHI"

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$$H = H^e + T^{\text{ion}} + V^{\text{ion-ion}}$$

$$H^e = T^e + V^{e-\text{ion}} + V^{ee}$$

$$H^e \phi = E \phi; \quad \Psi = \sum \Lambda_\nu(\{\vec{R}_I\}) \phi_\nu(\{\vec{R}_I\} \{z, \alpha\})$$

Expansion of the full many-body wavefunction in terms of eigenfunctions of  $H^e$ .

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$$H \Psi = E \Psi \quad \text{multiply with } \langle \phi_\mu |$$

$$\langle \phi_\mu | H | \sum_\nu \Lambda_\nu \phi_\nu \rangle = E \Lambda_\mu$$

$$- \langle \phi_\mu | H^e | \sum_\nu \Lambda_\nu \phi_\nu \rangle = E_\mu^e \Lambda_\mu$$

$$- \langle \phi_\mu | T^{\text{ion}} | \sum_\nu \Lambda_\nu \phi_\nu \rangle = \text{circled X}$$

$$- \langle \phi_\mu | V^{\text{ion-ion}} | \sum_\nu \Lambda_\nu \phi_\nu \rangle = V^{\text{ion-ion}} \Lambda_\mu(\{\vec{R}_I\})$$

$$\textcircled{Q}: \nabla_{\vec{R}_I}^2 (\Lambda_\nu \phi_\nu) = \vec{\nabla}_{\vec{R}_I} \left[ (\vec{\nabla}_{\vec{R}_I} \Lambda_\nu) \cdot \phi_\nu + \Lambda_\nu \vec{\nabla}_{\vec{R}_I} \phi_\nu \right]$$

$$\begin{aligned} & \underline{(\nabla_{\vec{R}_I}^2 \Lambda_\nu) \cdot \phi_\nu} + (\vec{\nabla}_{\vec{R}_I} \Lambda_\nu) (\vec{\nabla}_{\vec{R}_I} \phi_\nu) + \\ & + (\nabla_{\vec{R}_I} \Lambda_\nu) (\nabla_{\vec{R}_I} \phi_\nu) + \underline{\Lambda_\nu (\nabla_{\vec{R}_I}^2 \phi_\nu)} \end{aligned}$$

$$E \Lambda_\mu = \left( T^{ion} + V^{ion-ion} + E_\mu^e \right) \Lambda_\mu + \sum_\nu \sum_I \frac{-\hbar^2}{2m_I} \left[ \langle \phi_\mu | \nabla_{R_I}^2 | \phi_\nu \rangle \Lambda_\nu + 2 \langle \phi_\mu | \vec{\nabla}_{R_I} \phi_\nu \rangle (\vec{\nabla}_{R_I} \Lambda_\nu) \right]$$

} can we neglect this

if we neglect it:  $H_\mu^{ion} \Lambda_\mu = E \Lambda_\mu$

$$H_\mu^{ion} = T^{ion} + (V^{ion-ion} + E_\mu^e)$$

This is many Schröd. equ.: for every electronic excited state, there is new equation.

for  $\mu=0$   $\equiv$  electronic groundstate

$$V^{ion-ion}(\{R_I\}) + E_{\mu=0}^e(\{R_I\}) = V_{Bo}$$

Born-Oppenheimer potential energy surface.

$\equiv$  energy (potential) on which the ions move.

Q: can we neglect the purple lines?

$\nabla_{R_I}^2 \phi_\nu, \vec{\nabla}_{R_I} \phi_\nu$  are called electron-phonon coupling [phonon  $\equiv$  q.m. name for vibrations]

A: No - not in general. The terms are important e.g. for superconductivity, dynamic Jahn-Teller Effect, Kohn anomaly, Peierls instability (see later!)

Let's do anyhow

- 1) assume that electrons react fast. They always adjust to the current geometry. The atomic motion does not induce electronic excitations.

$$\langle \phi_\mu | \nabla_{\mathbf{R}_I}^2 | \phi_\nu \rangle \text{ and } \langle \phi_\mu | \vec{\nabla}_{\mathbf{R}_I} | \phi_\nu \rangle$$

are zero for  $\mu \neq \nu$

$$2) a) \langle \phi_\mu | \nabla_{\mathbf{R}_I}^2 | \phi_\mu \rangle = \nabla_{\mathbf{R}_I}^2 \frac{1}{2} \underbrace{\langle \phi_\mu | \phi_\mu \rangle}_{\text{normalized} = 1} = 0$$

$$b) |\langle \phi_\mu | \nabla_{\mathbf{R}_I}^2 | \phi_\nu \rangle| \leq |\langle \phi_\mu | \nabla_{\mathbf{R}_I}^2 | \phi_\nu \rangle|$$

$$\left| \frac{\hbar^2}{2M_I} \langle \phi_\mu | \nabla_{\mathbf{R}_I}^2 | \phi_\nu \rangle \right| \leq \frac{m}{M_I} \frac{\hbar^2}{2m} \langle \phi_\mu | \nabla_{\mathbf{R}_I}^2 | \phi_\nu \rangle$$

$\Rightarrow 10^{-4}$  smaller than the kin. energy of electrons

in most cases one studies

$$E_\mu^e \phi = H^e \phi$$

$$\text{and } (T^{\text{ion}} + V_{B0}(\{\mathbf{R}_I\})) \Lambda_0 = E_0 \Lambda_0$$

we should solve

$$-\frac{\Lambda_0(t)}{\partial t} = (T^{\text{ion}} + V_{B0}) \Lambda_0(t)$$

$M_I$  are heavy  $\Rightarrow$  time dep. Schröd. eqn reduces to Newton (classical) equations

O.K. for all atoms except: H  
(already demonstrated behaves essentially like a classical object.)

if BO approx. is acceptable

$$\Psi \rightarrow \Psi^{BO} = \Lambda_0(\{\vec{R}_I\}) \phi_0(\{\vec{R}_I\}, \{\vec{r}_\alpha, \vec{r}_\beta\})$$

At stable or metastable geometries:  $\{\vec{R}_I^0\}$

$$E = E_0^e(\{\vec{R}_I^0\}) + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{\substack{I, J \\ I \neq J}}^{\text{all}} \frac{e^2}{|\vec{R}_I^0 - \vec{R}_J^0|} z_{\alpha I} z_{\beta J}$$

plus vibration

$$\langle \Lambda_0 | T^{vib} + V^{BO}(\{\vec{R}_I - \vec{R}_I^0\}) | \Lambda_0 \rangle$$

classical: the ground state of vibs is zero.

q.m. zero point vibs.

### 1.2.2 An alternative view at the same thing

The static approx.

Now we start from  $H^e(\{\vec{R}_I^0\})$

$\uparrow$  metastable or

The eigenfunctions of  $H^e(\{\vec{R}_I^0\})$  are a good basis

$$\Psi(\{\vec{R}_I\}, \{\vec{r}_{\alpha k}\}) = \sum_{\nu} \hat{\Lambda}_{\nu}(\{\vec{R}_I\}) \phi_{\nu}(\{\vec{r}_{\alpha k}\})$$

hat  $\Lambda$  tells: these are different functions

more on this: see exercises

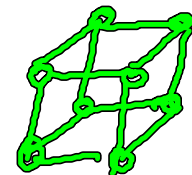
Examples

$$E = E_0^e(\{\vec{R}_I\}) + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum \frac{q^2}{|\vec{R}_I - \vec{r}_j|} z_{Ij} z_{ij} + \underline{9, 14 \text{ vib}}$$

The main challenge is to get  $E_0^e$

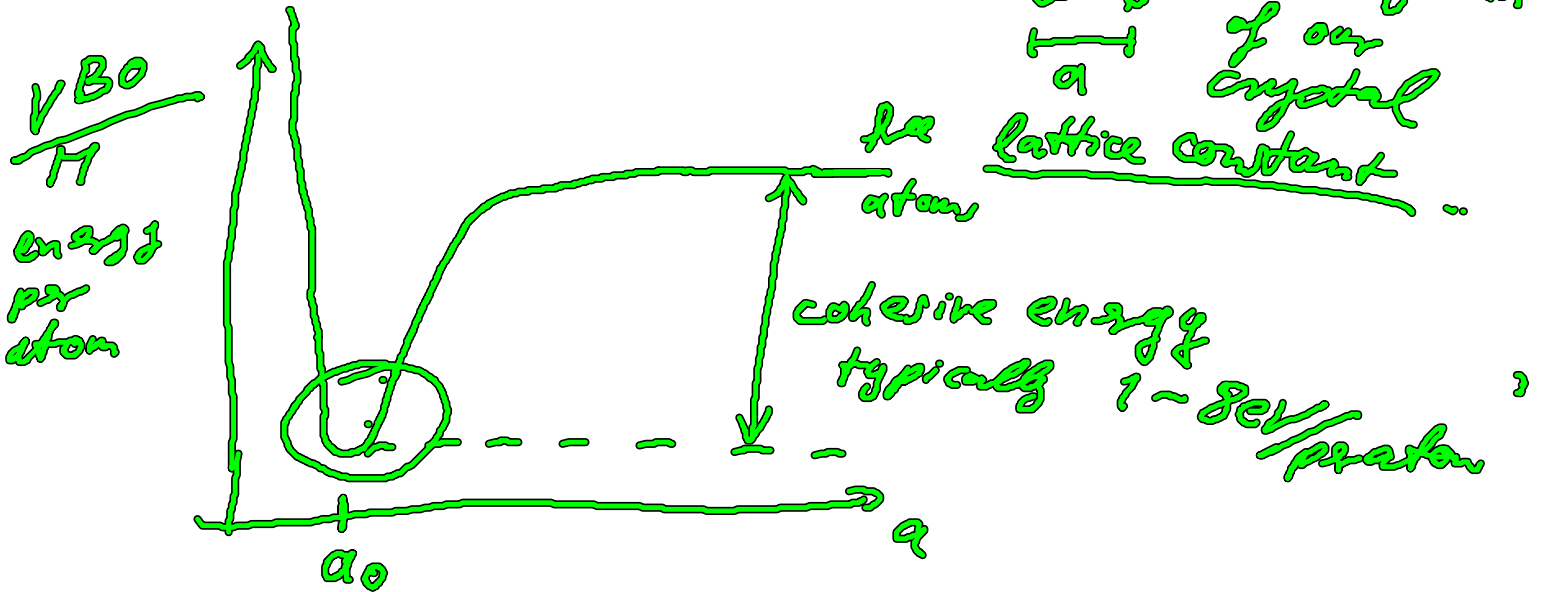
### 1.23 Structure of materials, elastic properties

example for a cubic crystal

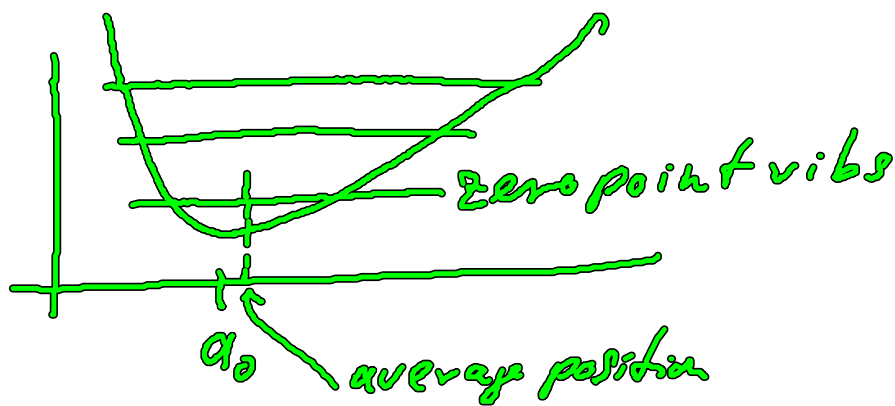


unit cell  
building block  
of our  
crystal

lattice constant



∴



$$\Delta P \Delta X \geq \frac{\hbar}{2}$$

$$\Delta X \approx 0.1 \text{ bohr} \\ \approx 0.05 \text{ \AA}$$

$$\frac{p^2}{2m} \approx 0.02 \text{ eV/Atom}$$

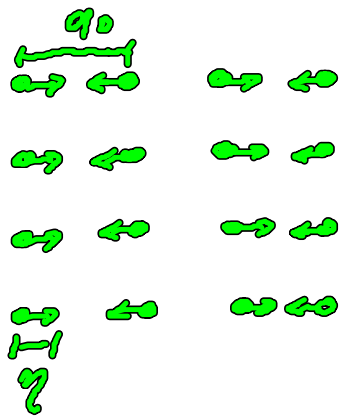
compared to  $a_0$  the average position is  
 $\approx 0.1 - 0.5\%$  larger.

compressibility or bulk modulus

$$B_0 = \frac{1}{K} = V \left. \frac{\partial^2 E(V)}{\partial V^2} \right|_{a=a_0}$$

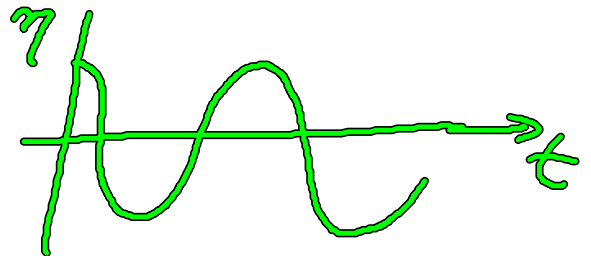
$\Rightarrow$  thermal expansion [warning: in general  
 one has to look free energy; i.e. at entropy]

### 1.2.3 Lattice waves (phonons)



Snapshot at  
a vibrating crystal

periodicity of this phonon:  $2a$ .



calculate such "frozen phonon".

## Chapter 2

### 2.1 Stat. Mech.

$H^e \phi_v = E_v^e \phi_v$  at  $T=0K \Rightarrow E_0^e$   
 $T \neq 0K$  then also excited states play a role

The probability to find the system in state  $E_v^e$  is  $P(E_v^e, T) \sim \exp(-E_v^e/kT)$   
 system is described by density operator

$$\rho = \sum_v P(E_v^e, T) |\phi_v\rangle \langle \phi_v|$$

$$\sum P(E_v^e, T) = 1 = \frac{1}{Z^e} \sum_v e^{-E_v^e/kT}$$

$$Z^e = \sum_v e^{-E_v^e/kT} = \text{Tr} \exp(-H^e/k_B T)$$

"partition function  
(Zustandsumme)

$$-k_B T \ln Z^e = F^e = U^e - T S^e$$

internal energy                      entropy

For system when # particles is fixed and T is given  $F^e =$  Helmholtz free energy is THE relevant quantity

internal energy

$$U^e = \sum_v E_v^e P(E_v^e, T)$$

in general we should discuss  $U = U^e + U^{vib}$   
just replace  $U^e$  in the eq. by  $U$ .

$S^e$  can be calculated from  $U^e$  using

thermodyn. relations

$$\left( \frac{\partial U}{\partial T} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V$$

$$u = \frac{U}{V}$$
$$s = \frac{S}{V}$$

$S^e$  is calculated in exercises

also  $c_v =$  specific heat  $= \frac{1}{V} \left( \frac{\partial U}{\partial T} \right)_V$

$$= \frac{T}{V} \left( \frac{\partial S}{\partial T} \right)_V$$

## 2.2. Fermi Statistics of Electrons



simplified notation

$$E_0^e = \sum_{k=1}^N E_k + \Delta$$

ground state

$k=1$

$\Delta$  many-body correction

true if we would have independent electrons

$E_k$  will solution of 'some' hamiltonian

$$h = \frac{-\hbar^2}{2m} \nabla^2 + \underbrace{V^{\text{eff}}(\vec{r})}_{\text{unknown}}$$

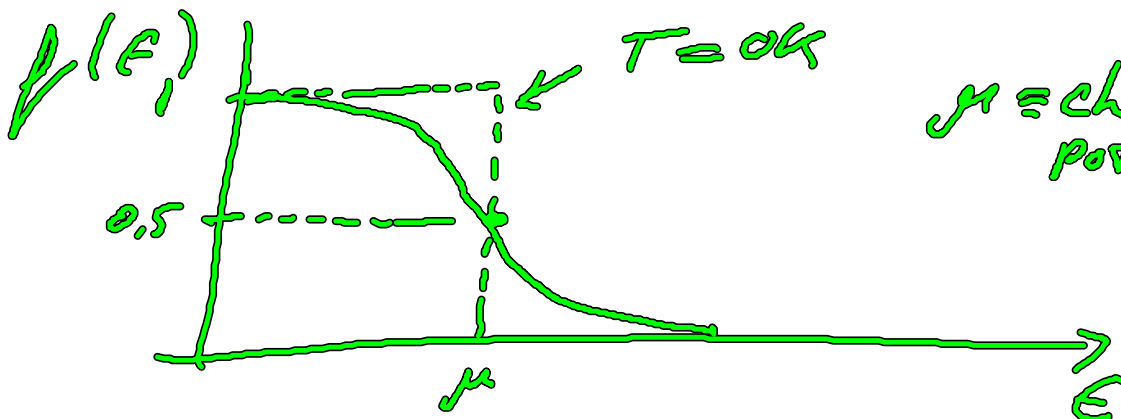
clean proof  
density functional theory

find  $T$

the lowest energy compatible with Pauli principle

$$E^e(T) = \sum_{k=1}^{\infty} E_k \cdot f(E_k, T) + \Delta$$

$$f(E, T) = \frac{1}{\exp[(E - \mu)/k_B T] + 1} \equiv \text{Fermi function}$$



$\mu = \text{chemical potential}$

$\mu \equiv$  the lowest energy to remove a particle (here electron)

$$-\mu = E^e(N-1) - E^e(N)$$

$$N \equiv \text{electrons} = \sum_i f(E_i, T, \mu)$$

Knowing the  $\mathcal{B}_1$ , at given  $T$

left  $N \equiv \text{know}$

right one is known  $\mathcal{B}$

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