

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

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

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

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

Expansion of the full many-body wave function in terms of eigenfunctions of H^e .

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

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

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

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

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

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

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

$$+ (\nabla_{\vec{R}_I} \Lambda_\nu) (\nabla_{\vec{R}_I} \phi_\nu) + \underline{\Lambda_\nu (\nabla_{\vec{R}_I}^2 \phi_\nu)}$$

$$E \Lambda_\mu = \left(T^{\text{ion}} + V^{\text{ion-ion}} + E_\mu^e \right) \Lambda_\mu$$

$$+ \sum_\nu \sum_I \frac{-\hbar^2}{2M_I} \left[\langle \phi_\mu | \nabla_{R_I}^2 | \phi_\nu \rangle \Lambda_\nu \right. \\ \left. + 2 \langle \phi_\mu | \vec{\nabla}_{R_I} \phi_\nu \rangle (\vec{\nabla}_{R_I} \Lambda_\nu) \right]$$

} can we neglect this

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

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

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

for $\mu=0 \equiv$ electronic ground state

$$V^{\text{ion-ion}}(\{\vec{R}_I\}) + E_{\mu=0}^e(\{\vec{R}_I\}) = V_{B0}$$

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 $\mu \neq \nu$

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

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

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

$\Rightarrow 10^{-4}$ smaller than
the Kin. Energy of electrons

in most cases one studies

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

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

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

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

If BO approx. is acceptable

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

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

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

plus vibration

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

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
 \uparrow stable geometry

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

hat Λ tell: these are different functions

more on this: see exercises

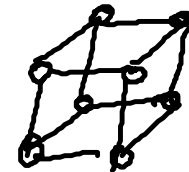
Examples

$$E = E_0^e(\{\vec{R}_I\}) + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{I \neq J} \frac{e^2}{|\vec{R}_I - \vec{R}_J|} z_I z_J + \underline{9, \text{M. -vibs}}$$

The main challenge is to get E_0^e

1.2.3 Structure of materials, elastic properties

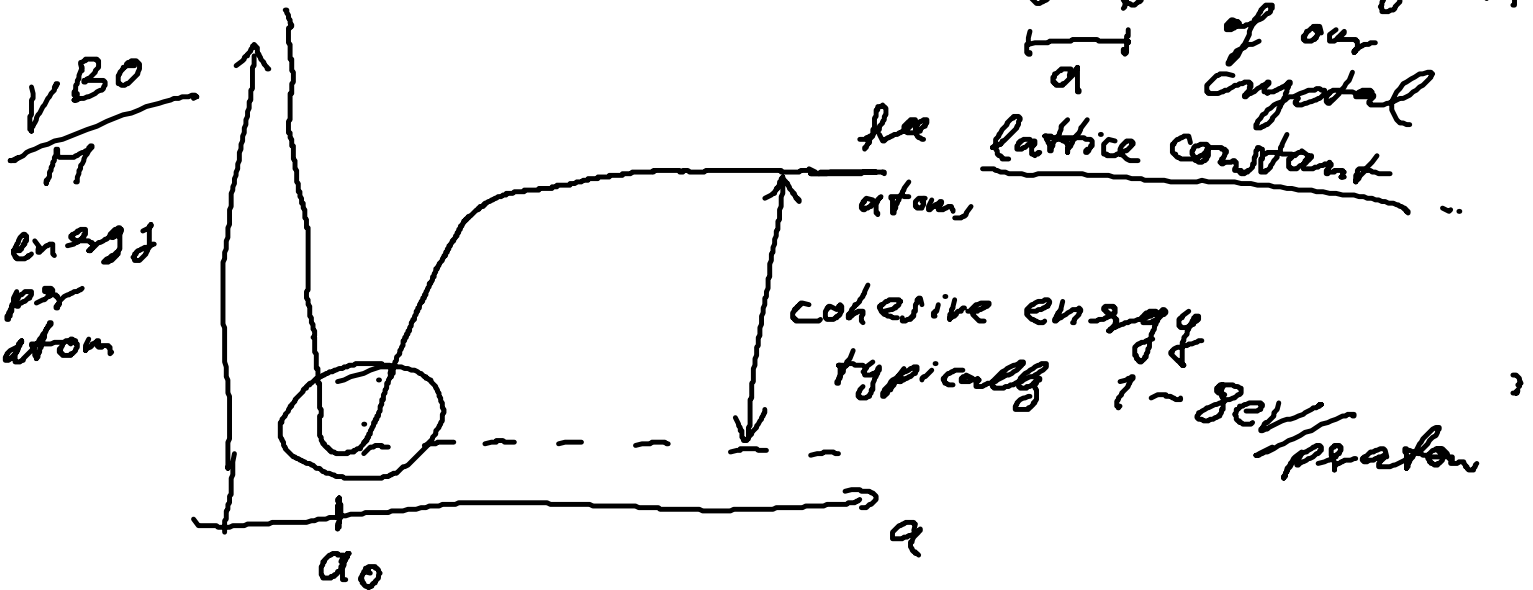
example for a cubic crystal

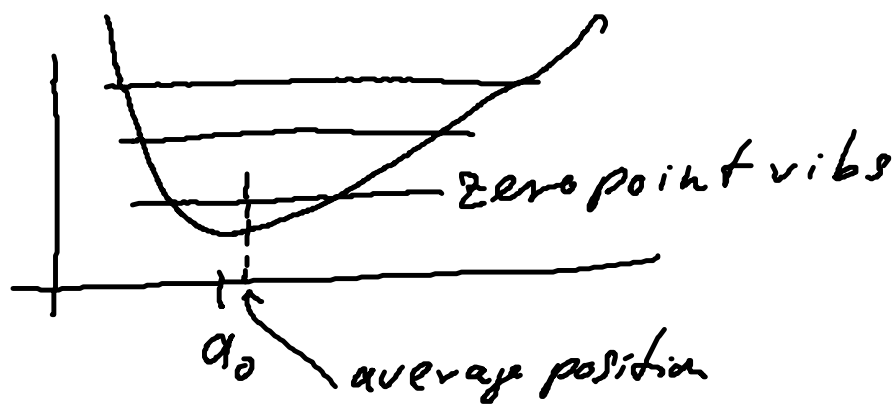


unit cell

building block
of our
crystal

lattice constant





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

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

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

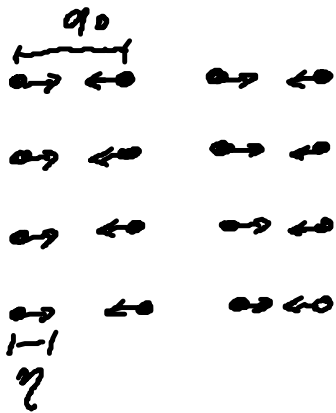
compared to a_0 the average position is
 $\approx 0.1 - 0.5\%$ larger.

compressibility or bulk modulus

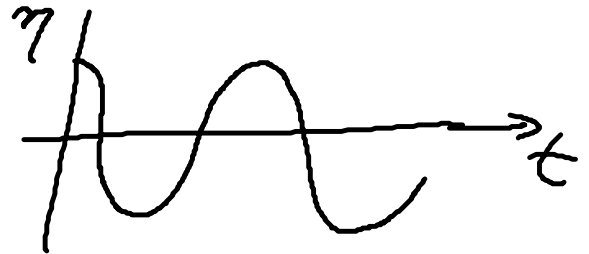
$$B_0 = \frac{1}{K} = V \left. \frac{\partial^2 E(V)}{\partial V^2} \right|_{a=a_0}$$

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

1.2.3 Lattice waves (phonons)



Snapshot at
a vibrating crystal



calculate such "frozen phonon".

Chapter 2

2.1 Stat. Mech.

$$H^e \phi_\nu = E_\nu^e \phi_\nu \text{ at } T=0K \Rightarrow E_0^e$$

$T \neq 0K$ then also excited states play a role

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

$$\rho = \sum_\nu P(E_\nu^e, T) |\phi_\nu\rangle \langle \phi_\nu|$$

$$\sum_\nu P(E_\nu^e, T) = 1 = \frac{1}{Z^e} \sum_\nu e^{-E_\nu^e/k_B T}$$

$$Z^e = \sum_\nu e^{-E_\nu^e/k_B T} = \text{Tr} \exp(-H^e/k_B T)$$

"partition function
(Zustandsumme)

$$-k_B T \ln Z^e = F^e = \underbrace{U^e}_{\text{internal energy}} - T \underbrace{S^e}_{\text{entropy}}$$

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

internal energy

$$U^e = \sum_{\nu} E_{\nu}^{\circ} P(E_{\nu}^{\circ}, T)$$

in general we should discuss $U = U^e + U^{\text{vib}}$
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

$k=1$

↳ many-body correction

true if we would have independent electrons

E_k will be solution of "some" Hamiltonian

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

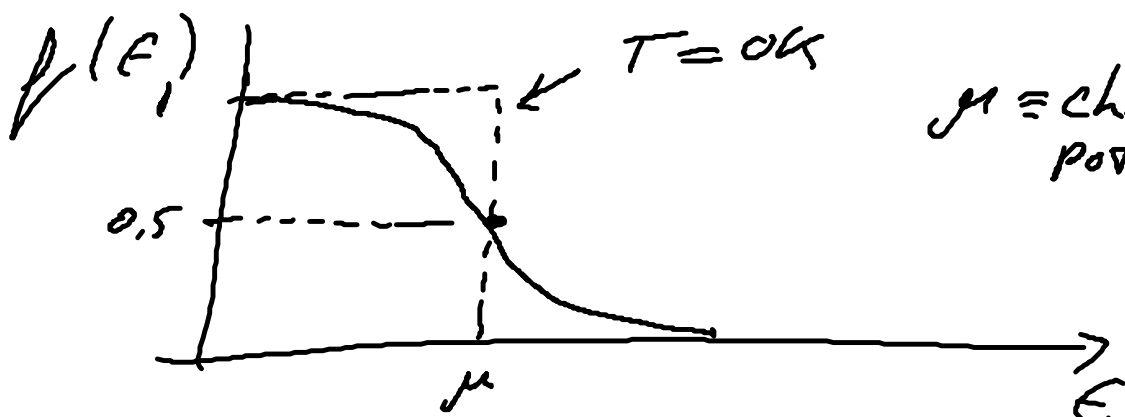
clean proof is density functional theory

finite T

the lowest energy compatible with Pauli principle

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

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



$\mu \equiv$ 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 \mathbb{E}_1 , at given T

left $N \equiv \text{know}$

right one unknown μ

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