Web pages www.itp. ...
and th.fhi-berlin.mpg.de ...
see exercise sheet.

Grades: a) why?
b) active participation in the exercises plus presenting a solution (with discussion).

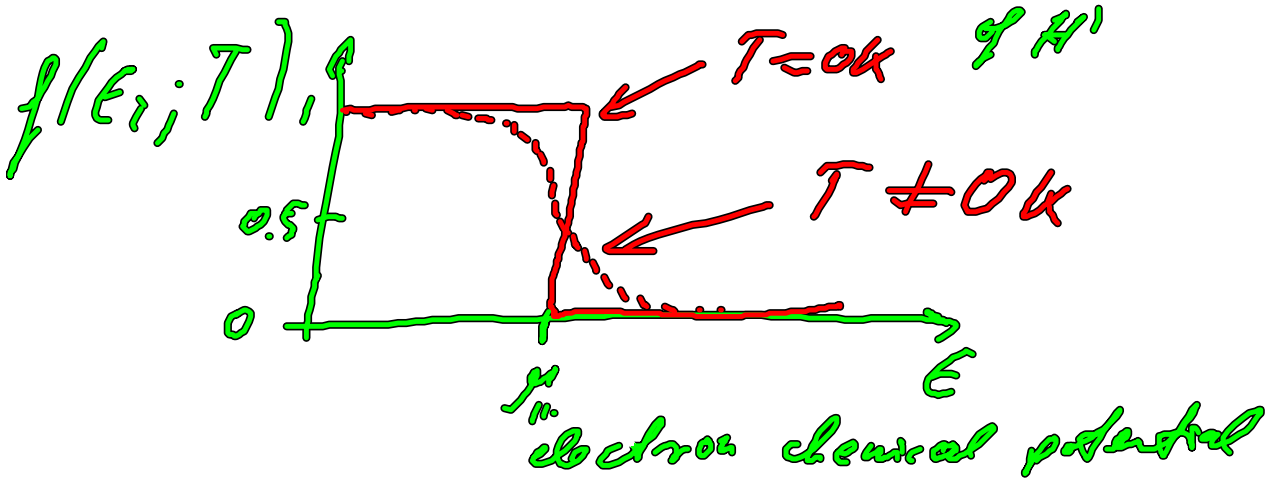
2.2. Fermi Statistics of the Electrons (a reminder)

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

$$H^e = \sum_{k=1}^{N} h_k + H'$$

$$U^e(T) = \sum_{i=1}^{N} \epsilon_i \, f(\epsilon_i, T) + \Delta$$

Δ = expect. value of H'



$$f(\epsilon_i, T) = \frac{1}{\exp[(\epsilon - \mu)/k_B T] + 1}$$

number of electrons:

$$N = \sum_{i=1}^{\infty} f(\epsilon_i, T)$$

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

= ionisation energy

2.3 Definition (needed again & again ...)

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

$V^{e\text{-}ion}$ = const. in space

$\Rightarrow V^{e\text{-}e}$ = const.

$V^{e\text{-}ion} - V^{e\text{-}e} \equiv$ energy zero

$$\rightarrow H^e = T^e = \sum_{k=1}^{N} \frac{-\hbar^2}{2m} \nabla_{\vec{r}_k}^2$$

$$-\frac{\hbar^2}{2m}\nabla^2 \varphi_j(\vec{r}) = \epsilon_j \varphi_j(\vec{r})$$

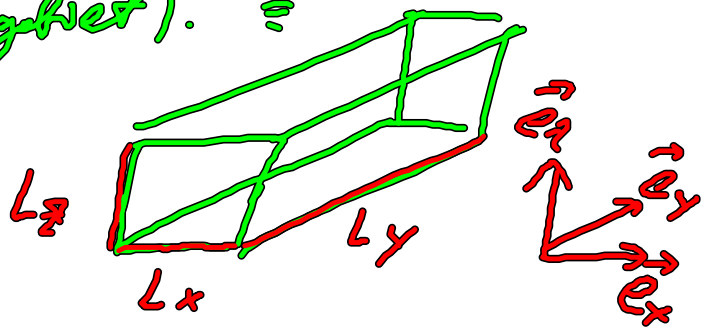
$$\varphi_{\vec{k}} = e^{i\vec{k}\vec{r}}$$

$$\epsilon_{\vec{k}} = \epsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m}$$

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

$$\lambda = \frac{2\pi}{|\vec{k}|}$$

Often we "constrain" the electrons to a base region (Grundgebiet). =



→ big

box contains
N electrons
M nuclei

size must be so that physics must not depend on the size.

Born-von Karman:

$$\varphi(\vec{r}) = \varphi(\vec{r} + L_x\vec{e}_x) = \varphi(\vec{r} + L_y\vec{e}_y)$$
$$= \varphi(\vec{r} + L_z\vec{e}_z)$$

$$\int_{V_g} \varphi^*_{\vec{k}}(\vec{r})\, \varphi_{\vec{k}'}(\vec{r})\, d^3\vec{r} = \delta_{\vec{k},\vec{k}'}$$

$$\varphi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V_g}}\, e^{i\vec{k}\vec{r}}$$

$\vec{k}$ is no longer continuous; it is now discrete:

$$\vec{k} = \left(\frac{2\pi n_x}{L_x}, \frac{2\pi n_y}{L_y}, \frac{2\pi n_z}{L_z} \right)$$

with n_x, n_y, n_z integer

$\vec{k}$ is discrete = allowed values of $\vec{k}$ correspond to a volume $\frac{(2\pi)^3}{V}$

$\varepsilon(\vec{k}) = \frac{\hbar^2}{2m} k^2$ depends only on $|\vec{k}|$

number of all electrons: highest occupied state k_F; $\varepsilon(k_F)$

$$N = 2 \cdot \frac{4}{3}\pi k_F^3 \cdot \frac{V_g}{(2\pi)^3}$$

2: spin; $\frac{4}{3}\pi k_F^3$: sphere; $\frac{V_g}{(2\pi)^3}$: density of k-point

$$= \frac{1}{3\pi^2} k_F^3 V_g$$

electron density

$$n(\vec{r}) = \frac{N}{V_g} = \frac{1}{3\pi^2} k_F^3$$

$$\boxed{k_F = \sqrt[3]{3\pi^2 n(\vec{r})}}$$

$$\epsilon_F = \frac{\hbar^2}{2m} k_F^2 = \frac{\hbar^2}{2m} (3\pi n(r))^{2/3}$$

another important quantity:

Density of electronic states ≡ number of states in an energy interval $[\epsilon, \epsilon + d\epsilon]$

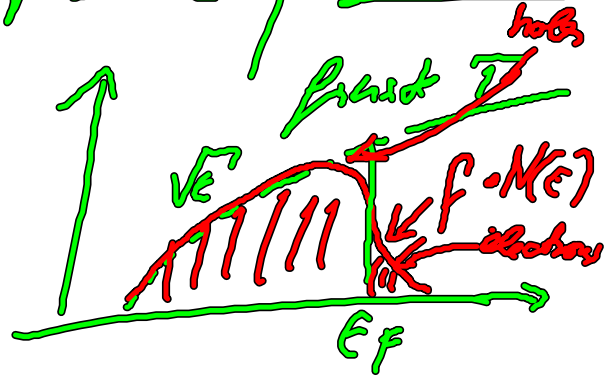
$$= \underbrace{N(\epsilon)}_{\text{density of states}} d\epsilon$$

total number of electrons

$$N = \int_{-\infty}^{+\infty} N(\epsilon) f(\epsilon, T) d\epsilon \quad \left\{ \text{jellium} \right.$$

$$N(\epsilon) = 2 \frac{V_g}{(2\pi)^3} \left\{ d^3k \; \delta(\epsilon - \epsilon(k)) \right.$$

$= \dots$ $\frac{m V_q}{\pi^2 \hbar^3} \sqrt{2mE}$ 3-dim



Chapter 3

Electron - electron interactions

still an active field = new concepts
new ideas are published every few months.

Challenge: How to deal with

$$V^{e-e} \equiv \frac{1}{2} \frac{1}{4\pi\varepsilon_0} \sum_{k,k'}^{N,N} \frac{e^2}{|\vec{r}_k - \vec{r}_{k'}|}$$

Three classes of approaches

1) Many - body perturbation theory
(also Green function / self energy methods)
not practical for total energies (yet).
The method to deal with excited states.

2) Effective single particle theory

$$H^e = \sum_k h_k + H'$$

$\Rightarrow$ find the best choice = make the effect of H' small.

Hartree
Hartree-Fock
density functional theory

3) Quantum Monte Carlo method

ansatz for many body wavefunction
(ϕ = several parameters)

$$\frac{\langle \phi | H^e | \phi \rangle}{\langle \phi | \phi \rangle} = \text{minimum}$$

3.1 Hartree approximation

* example how and why a theory is being developing
* basis of even the most advanced developments

Hartree: $V^{e-e} = \frac{1}{2} \frac{1}{4\pi\varepsilon_0} \sum_{k,k'}^{N,N} \frac{e^2}{|\vec{r}_k - \vec{r}_{k'}|}$

$$= \cdots \sum_{\substack{k=1 \\ k \neq k'}}^{N} \{ \text{electrostatic potential of all other electrons} \}$$

$$v^{Hartree}(r) = \frac{e^2}{4\pi\varepsilon_0} \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \; v^{Hartree}(\vec{r}_k)$$

"average" mean field description

$$H^e = \sum_{k=1}^{N} h(\vec{r}_k)$$

$$h = \frac{-\hbar^2}{2m} \nabla^2_{\vec{r}_k} + v(r) + v^{Hartree}(\vec{r})$$

"potential due to nuclei"

Mathematical Derivation

$$H^e \phi_\nu = E^e_\nu \phi_\nu \,, \quad \phi_\nu(\{\vec{r}_k, \sigma_k\})$$

H^e does not couple spins.

$$\phi_\nu(\{\vec{r}_i, \sigma_i\}) = \phi_\nu(\{\vec{r}_i\}) \chi_\nu(\{\sigma_i\})$$

$\nu \equiv$ quantum numbers $\equiv$ two types

$= (O_\nu, S_\nu)$ — spin quantum number

↑ orbital quantum number

Reminder: $\sigma_v = (k_x, k_y, k_z)$

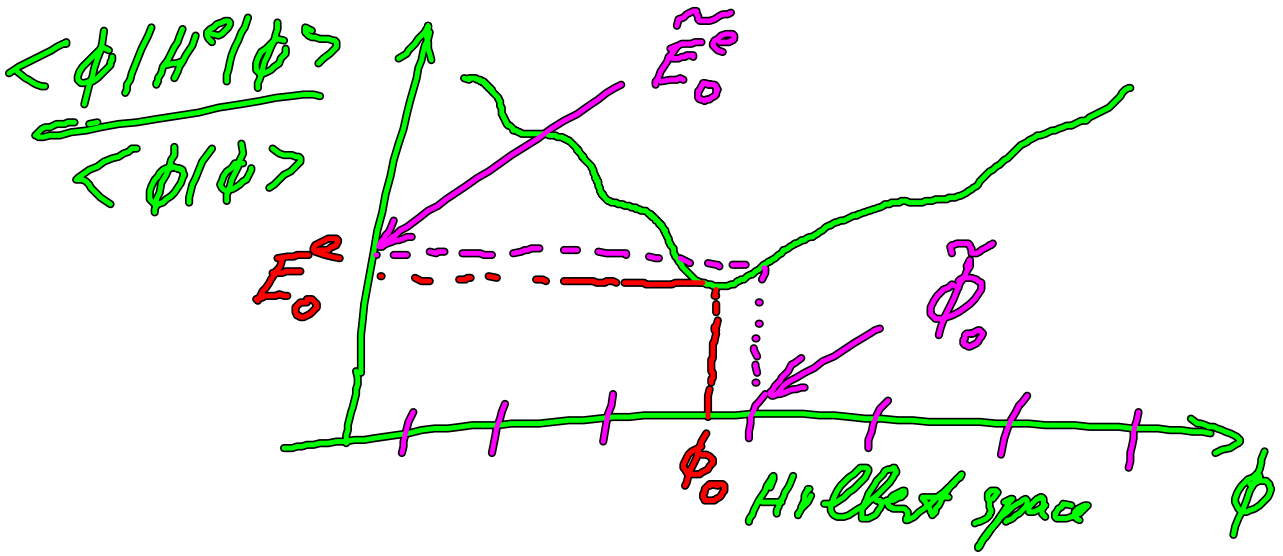
s_v = spin up or spin down

back to H^e

$$E_0^e \leq \frac{\langle \phi | H^e | \phi \rangle}{\langle \phi | \phi \rangle}$$

for any vector ϕ of the Hilbert space of H^e. The lowest energy is the ground state

schematic picture



Restrict the admitted functions ϕ to a subspace of Hilbert space of H^e.

$\Rightarrow$ the energy may be good

the wavefunction $\tilde{\phi}_0$ may not be o.k.

Hartree's restriction:

$$\phi(\vec{r}_i) \approx \phi^{Hartree}(\{\vec{r}_i\})$$

$$= \varphi_{a_1}(\vec{r}_1)\,\varphi_{a_2}(\vec{r}_2)\cdots\varphi_{a_N}(\vec{r}_N)$$

with $\langle \varphi_{a_i} | \varphi_{a_i} \rangle = 1$

This ansatz is equivalent to

$$H^e = \sum_{k=1}^{N} h(\vec{r}_k)$$

↑ how do these look?