

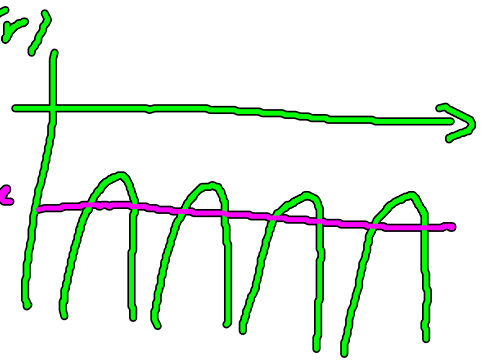
Hartree-Fock theory for  $v^{ion}(\vec{r}) = \text{const.}$  i.e. jellium

$c$ : spin value

$$E(\vec{k}) = \frac{\hbar^2}{2m} k^2 - \frac{e^2}{4\pi\epsilon_0} F\left(\frac{k}{k_F}\right)$$

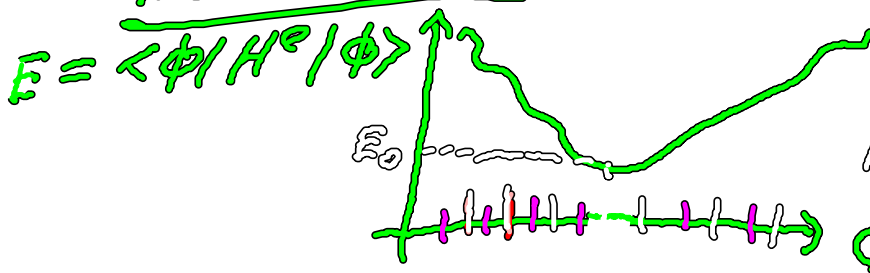


average value

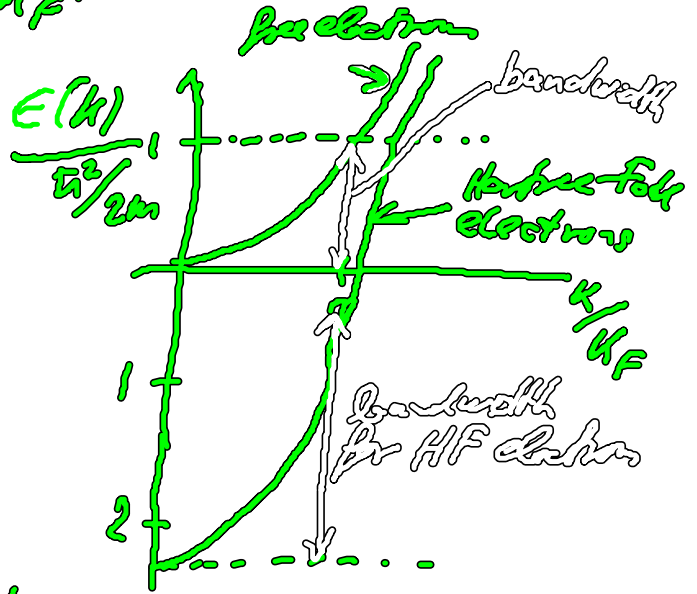


Q: May 2  
RD

No lecture



Hartree  
Hartree Fock



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# Hartree Fock

- 1) For small  $k$  also HF eigenvalues are parabolic but with different curvature:  $E(k) = \frac{\hbar^2 k^2}{2m^*} + C$   
 evaluate the  $F$  function

$$\frac{m^*}{m} = \frac{1}{1 + 0.22 \left( \frac{r_s}{a_0} \right)^2} \text{ for } k \rightarrow 0$$

For metals

$$\frac{4}{3} \pi r_s^3 \stackrel{!}{=} \frac{1}{n}$$

$r_s = 2 \dots 4$  bohr

- 2) bandwidth of HF electrons is significantly larger (Fig. 200 for  $r_s = 4$  bohr)

- 3) For  $k = k_F$  the result is unphysical  $\frac{\partial E}{\partial k} \rightarrow \infty$  at  $k \rightarrow k_F$   
 Bad consequences for calculated conductivity. heat capacity

$$4) v^x(\vec{k}) = \frac{-e^2}{4\pi\epsilon_0} \frac{2k_F}{\pi} F\left(\frac{k}{k_F}\right)$$

-  $\epsilon_{HF}$  is lower than  $\epsilon$  free electron

-  $v^x$  is typically in the range 5 - 15 eV

Many phenomena in condensed matter systems are actuated by energy differences of

0.1 - 0.5 eV.

Are the  $\epsilon(k)$  meaningful (i.e. measurable) energies?

Koopmans' theorem [T. C. Koopmans;  
→ economist; Nobel in economy  
in 1975]

Ionization energies

$$I_k = E_k^{N-1} - E^N = \langle \phi_k^{N-1} | H^{e,N-1} | \phi_k^{N-1} \rangle - \langle \phi^N | H^{e,N} | \phi^N \rangle$$

Assumptions

- 1) removing one electron will not affect the lattice geometry. (Franck Condon principle)
- 2)  $\phi$  = single Slater determinant  $\equiv$  Hartree Fock
- 3) Removing an electron from  $\phi$  will not affect the other single particle states

$$I_k = \dots \approx -\epsilon_k = \text{Lagrange multiplier}$$

$\epsilon_k$  have the approximate meaning of ionization energies

excitations

$$\Delta E_{i \rightarrow j} = E_j - E_i$$

Koopmans' theorem works well for delocalized states

### The X $\alpha$ Method (Slater, 1951)

$$v_k^x = -\frac{e^2}{4\pi\epsilon_0} \frac{2k_F}{\pi} F\left(\frac{k}{k_F}\right) \quad \text{with } k_F = \sqrt[3]{3\pi^2 n}$$

for jellium

average over  $k$  (between  $k=0$  and  $k_F$ )

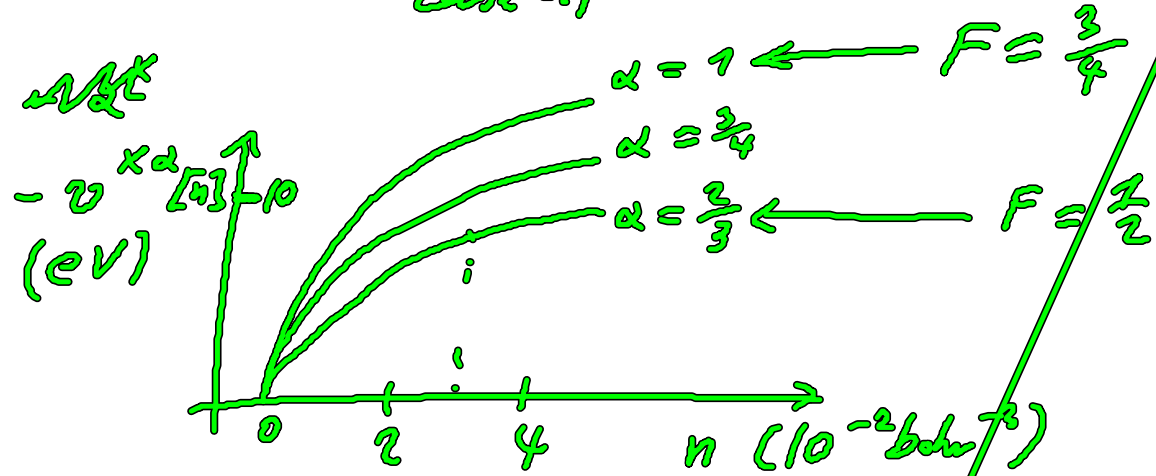
a) average over  $F \Rightarrow \bar{F} = 0.75$

b)  $\Rightarrow F = 0.5 \equiv$  value of  $F$  at  $k_F$

$$v^{X\alpha}(\vec{r}) = -N \frac{3}{2\pi} \frac{e^2}{4\pi\epsilon_0} \sqrt[3]{3\pi^2 n(\vec{r})}$$

with  $\frac{2}{3} < \alpha < 1$

||| case a) ||| case b)



### Thomas-Fermi: Theory & the Concept of Screening

$$\phi \rightarrow n(\vec{r}) = \langle \phi | \sum \delta(\vec{r} - \vec{r}_i) | \phi \rangle$$

in Hartree & Hartree-Fock  $n(\vec{r}) = \sum_{i=1}^N |\psi_i|^2$

can we get  $n(\vec{r})$  directly, without  $\phi$

$$\left[ \frac{-\hbar^2}{2m} \nabla^2 + v_i^{\text{eff}}(\vec{r}) \right] \varphi_i(\vec{r}) = \epsilon_i \varphi_i$$

expectation value for jellium

$$\frac{\hbar^2}{2m} k_i^2 + v^{\text{eff}} = \epsilon_i$$

↳ correctly this should be  $\langle e^{i\vec{k}\cdot\vec{r}} | v^{\text{eff}} | e^{i\vec{k}\cdot\vec{r}} \rangle$   
using  $v^{\text{eff}}$  and not the expectation  
value, called "quasi-classical approx."

use this for  $k_F$

$$\frac{\hbar^2}{2m} k_F^2 + v^{\text{eff}}(\vec{r}) = \epsilon_F = \mu$$

T F  
equation

$$k_F = \sqrt[3]{3\pi^2 n}$$

can be also derived from a variational principle.

### Screening

How do electrons react, when we introduce a localized perturbation? e.g. P atom in Si crystal

$$\text{T-F } n(\vec{r}) = \frac{1}{3\pi^2} \left[ \frac{2\pi}{\hbar^2} (\mu - v^{\text{eff}}) \right]^{\frac{3}{2}} = F_1[v^{\text{eff}}; \mu]$$

perturbation:  $v^{\text{eff}} \rightarrow v^{\text{eff}} + \Delta v^{\text{eff}}$   
 $\mu$  still be unchanged

$$\tilde{n}(\vec{r}) = F_1[v^{\text{eff}} + \Delta v^{\text{eff}}; \mu] = F_1[v^{\text{eff}}; \underbrace{\mu - \Delta v^{\text{eff}}}_{\alpha}]$$

Taylor expansion at  $\alpha = \mu$

$$\tilde{n}(\vec{r}) = F_1[v^{\text{eff}}; \alpha] \Big|_{\alpha=\mu} - \frac{\partial F_1}{\partial \alpha} \Big|_{\alpha=\mu} \Delta v^{\text{eff}} + \dots$$

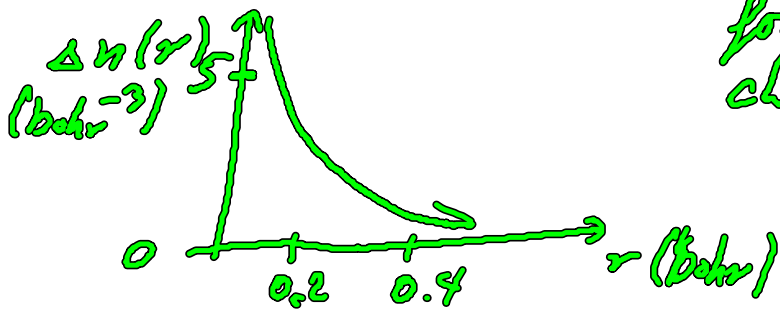
$$\Delta n(\vec{r}) = \tilde{n} - n = - \frac{\partial F_1}{\partial \alpha} \Big|_{\alpha=\mu} \Delta v^{\text{eff}} + O(\Delta v^{\text{eff}^2})$$

$$\Delta v^{\text{eff}} \rightarrow \Delta n(\vec{r})$$

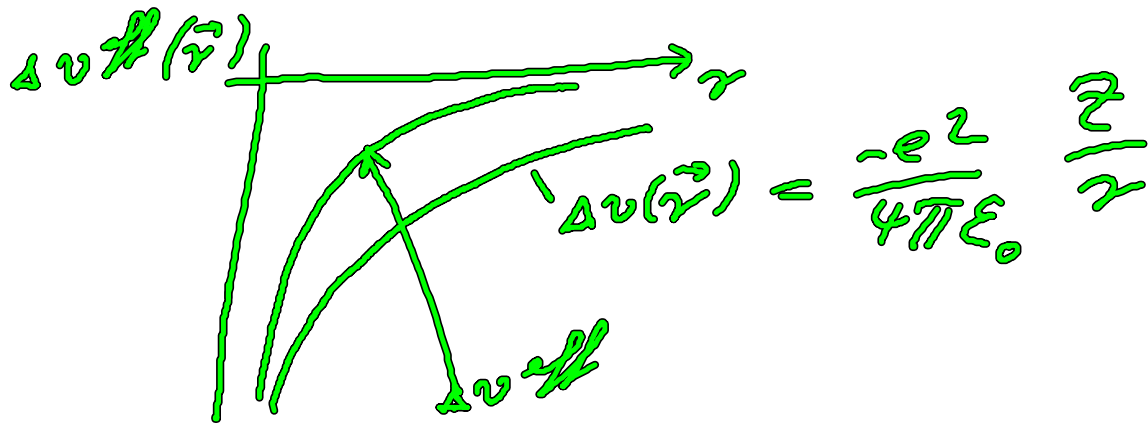
we really want  $\Delta v \rightarrow \Delta v^{\text{eff}} \rightarrow \Delta n(\vec{r})$

$$\Delta v^{\text{eff}} = \Delta v(\vec{r}) + \frac{e^2}{4\pi\epsilon_0} \int \frac{\Delta n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r'$$

more see analysis

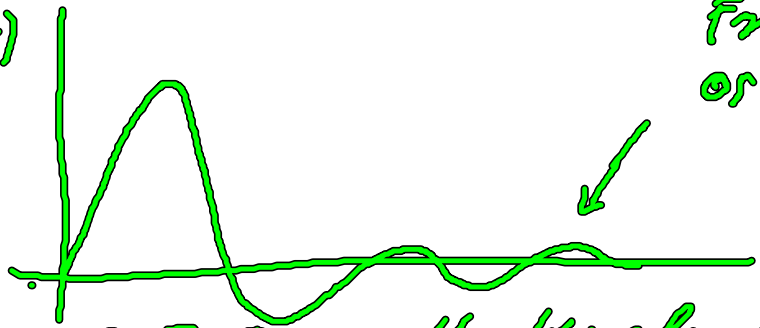


for a point  
change in a solid



the true picture

$\Delta n(r)$



Friedel oscillations

main problem of T-F is the kinetic energy

Density Functional Theory

$$H^e \phi = E \phi$$

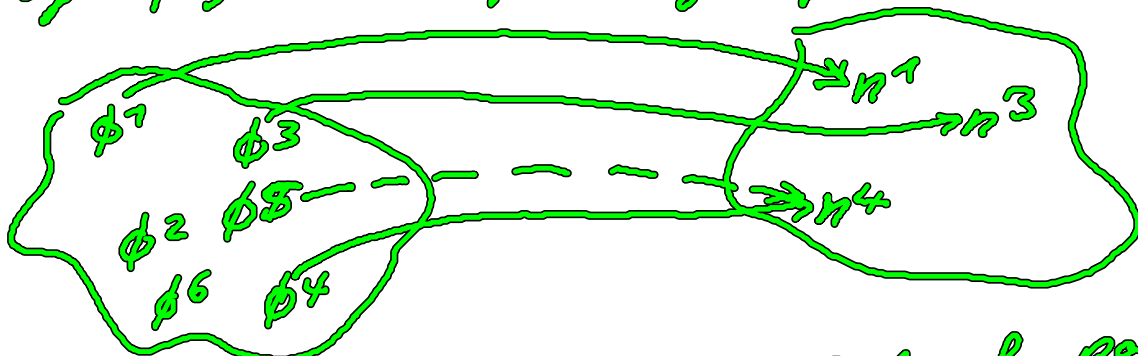
assume that ground state is not degenerate  
 " "  $n_{\uparrow} = n_{\downarrow} = \frac{1}{2} n(\vec{r})$  non magnetic

Ansatz: Hohenberg & Kohn

$$\langle \phi | H^e | \phi \rangle \stackrel{?}{=} E_0[n] = \int v(\vec{r}) n(\vec{r}) d^3\vec{r} + F[n]$$

?!  $E$  is a functional of the density

$F = \langle \phi | T^e + V^e - e | \phi \rangle$  it is a functional of  $\phi$ ; not explicitly dependent on  $v(\vec{r})$



The set of all non degenerate ground-states of arbitrary hamiltonians of the  $N$ -electron problem

set of particle density which belong to non degenerate ground states of the  $N$ -particle problem

2 is the dashed line possible?

Starting point

$v(\vec{r})$  and  $\tilde{v}(\vec{r})$  shall be two physically different potentials:  $v(\vec{r}) - \tilde{v}(\vec{r}) \neq \text{const.}$

$$v(r) \rightarrow H^e \quad \tilde{v} \rightarrow \tilde{H}^e$$

Assumption  $H^e$  and  $\tilde{H}^e$  have the same ground state

$$(\tilde{H}^e - H^e)\phi_0 = \left( \sum_{i=1}^N \tilde{v}(\vec{r}_i) - v(\vec{r}_i) \right) \phi_0 = (\tilde{E}_0 - E_0)\phi_0$$

$$\Rightarrow \sum_{i=1}^N \tilde{v}(\vec{r}_i) - v(\vec{r}_i) = \underbrace{\tilde{E}_0 - E_0}_{\text{const.}}$$

$\Rightarrow$  If 2 hamiltonians have the same ground state wave function, the hamiltonians have the same potential.