

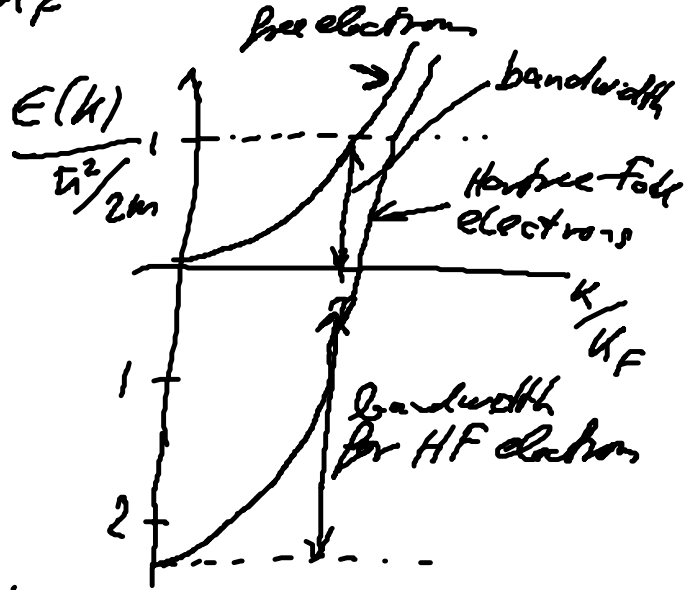
Hartree-Fock theory for $v^{ion}(\vec{r}) = \text{const. i.e. jellium}$

e : spin value

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



average value



Q: May 2
RD

No lecture



Hartree Fock

- 1) For small k also HF eigenvalues are parabolic but with different curvature: $E(k) = \frac{\hbar^2}{2m^*} k^2 + \epsilon_0$

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

$$r_s = 2 \dots 4 \text{ bohr}$$

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

- 2) bandwidth of HF electrons is significantly larger (Fig. now 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) $v^x(\vec{k}) = \frac{-e^2}{4\pi\epsilon_0} \frac{2k_F}{\pi} F\left(\frac{k}{k_F}\right)$

- ϵ^{HF} is lower than ϵ free electron

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

1) 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;
→ economics; 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) ϕ = single Slater determinant \equiv Hartree Fock
- 3) Removing an electron from ϕ will not affect the other single particle k states.

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

ϵ_k have the approximate meaning of ionization energies

excitations

$$\Delta E_{i \rightarrow j} = \epsilon_j - \epsilon_i$$

Koopman's theorem works well for delocalized states

The X_α Method (Slater, 1951)

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

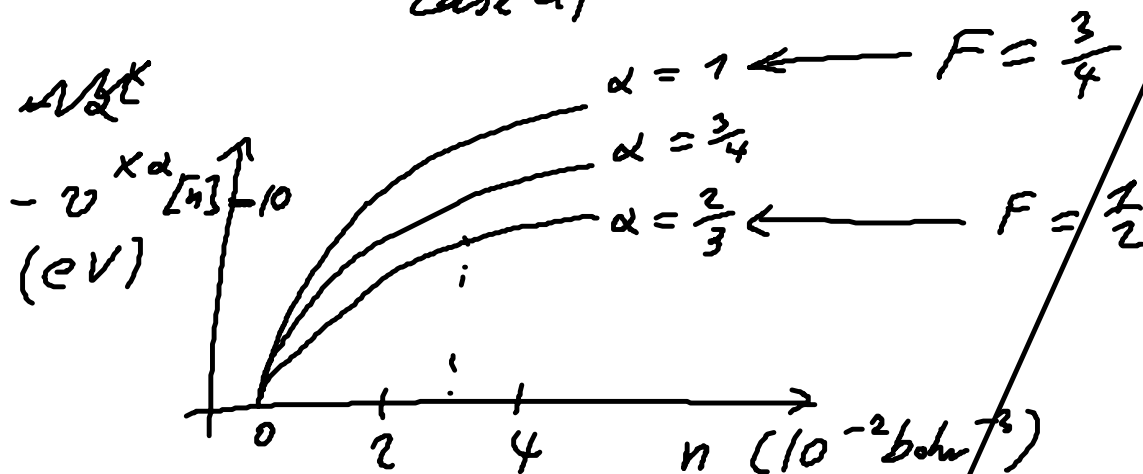
for jellium

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

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

with $\frac{2}{3} < \alpha < 1$
 ||| case a) ||| case b)



Thomas-Fermi Theory & the Concept of Screening

$$\phi \rightarrow n(r) = \langle \phi | \sum \delta(r - r_i) | \phi \rangle$$

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

can we get $n(\vec{r})$ directly; without ϕ

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

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^{eff} and not the expectation value; called "quasi-classical approx."

use this for k_F

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

$$k_F = \sqrt{\frac{2m(\mu - v^{\text{eff}})}{\hbar^2}}$$

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

T F
equation

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: $v^{\text{eff}} \rightarrow v^{\text{eff}} + \Delta v^{\text{eff}}$
 μ shall 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 $\alpha = \mu$

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

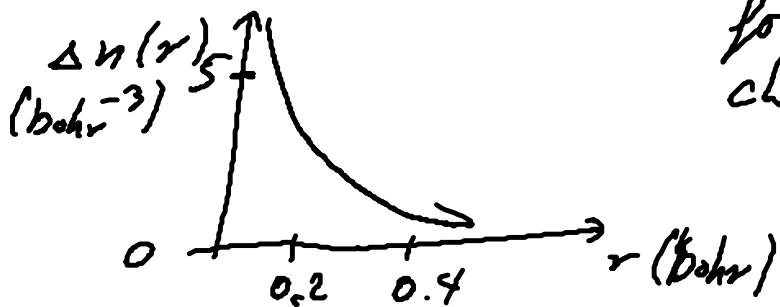
$$\Delta n(\vec{r}) = \tilde{n} - n = - \left. \frac{\partial F_1}{\partial \alpha} \right|_{\alpha = \mu} \Delta v^{\text{eff}} + O(\Delta v^{\text{eff}^2})$$

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

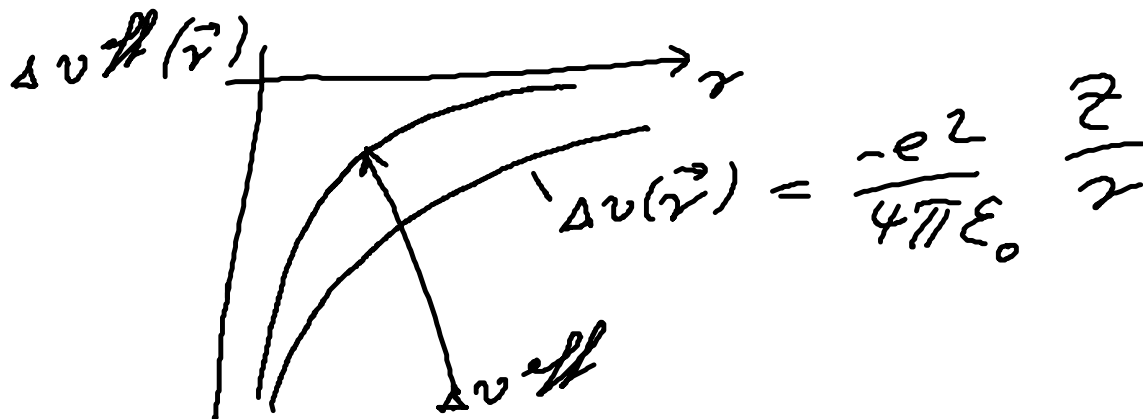
we really want $\Delta v \rightarrow \Delta v^{\text{eff}} \rightarrow \Delta n(\vec{r})$

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

more see exercises

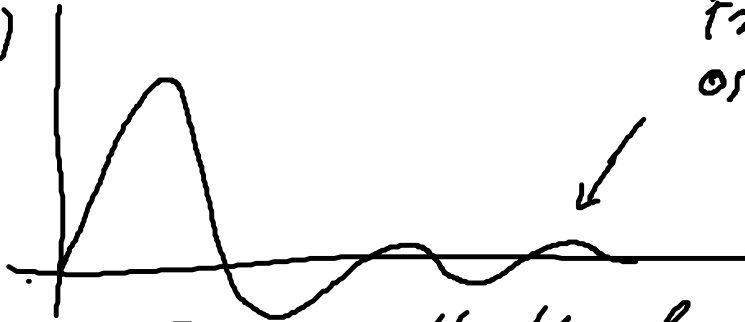


for a point charge in a solid



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.

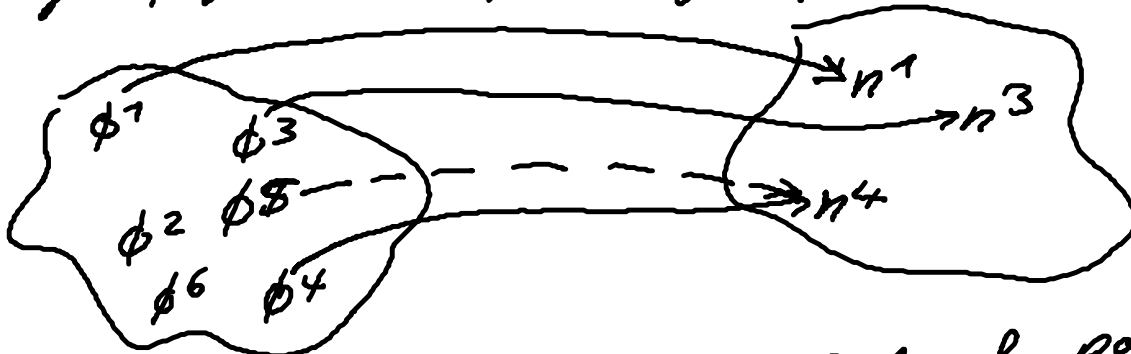
" " $n_{\uparrow} = n_{\downarrow} = \frac{1}{2} n(\vec{r})$ non magnetic

Ansatz: Hohenberg & Kohn

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

?! E is a functional of the density

$F = \langle \phi | T^e + V^e - e | \phi \rangle$ it is a functional of ϕ ; 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 functions the hamiltonians have the same potentials.