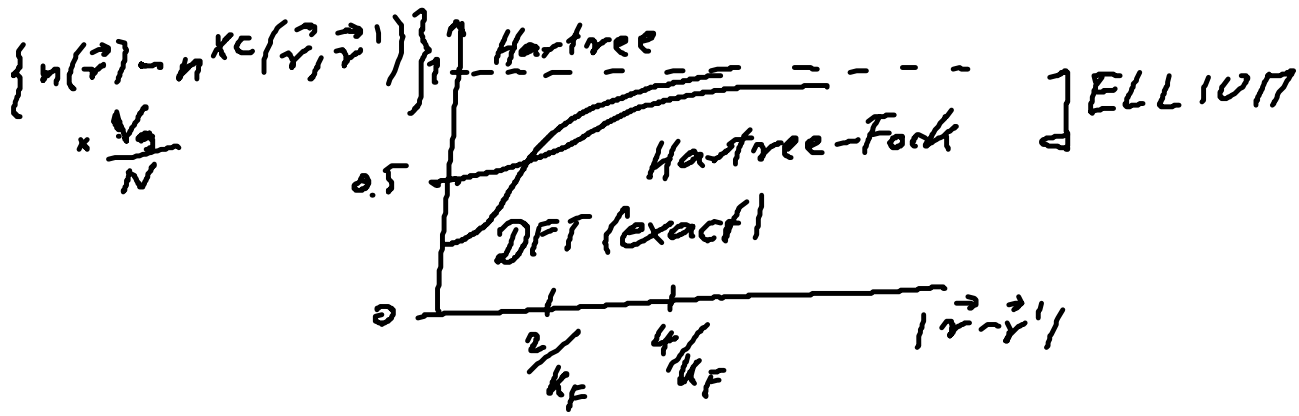




$$\text{Correction: } v^{xc-LDA} = \frac{\partial}{\partial n} \left( n E^{xc-jellium}(n) \right) \Big|_{n=n(\vec{r})}$$

$$= E^{xc-jellium}(n) + n \cdot \frac{\partial E^{xc-jellium}}{\partial n} \Big|_{n=n(\vec{r})}$$



Reduction of electron density at  $\vec{r} = \vec{r}' =$  at the position of the considered electron (Pauli + Coulomb), in classical physics  $n - n^{xc}$  at  $r = r'$  should be zero. Q. 07. weakened due to uncertainty principle

A. electron should interact with the  $N-1$  other

$$\text{electron } j \int n(\vec{r}) d^3r = N$$

$$\Rightarrow \int n^{xc}(\vec{r}, \vec{r}') d^3r' = 1 \quad \text{Any reasonable approx. to } E^{xc} \text{ must fulfil this condition.}$$

For jellium the LDA is exact.

In general LDA is an approximation. What enters is  $E^{xc}$  or  $v^{xc}$  is the integral over  $n^{xc} \equiv$  LDA is approx. to the shape of the xc hole.

physical meaning:  $n(\vec{r})$ ,  $E_0 = \text{Min}_{n(\vec{r})} E_0[n]$

what about  $\varphi_i(\vec{r})$ ,  $\epsilon_i$

$$n(\vec{r}) = \sum |\varphi_i|^2$$

Meaning of the Kohn-Sham single Particle Energies

- The DFT Analog of Koopmans' theorem -

"Koopmans' theorem does not apply to DFT"

True! However there is something very much alike.

Occupation number:

$$n(\vec{r}) = \sum_{i=1}^N |\varphi_i(\vec{r})|^2 = \sum_{i=1}^{\infty} f_i |\varphi_i(\vec{r})|^2$$

$$\text{at } T=0K \quad f_i = \begin{cases} 1 & \text{for } i=1 \dots N \\ 0 & \text{otherwise} \end{cases}$$

at  $T \neq 0K$

$f_i =$  Fermi function  $f(\epsilon_i)$

$$T_s[n] = \sum_{i=1}^{\infty} f_i \epsilon_i - \int v_{\text{eff}}(\vec{r}) n(\vec{r}) d^3r$$

$$\frac{\partial E_v[\psi]}{\partial f_k} = \int \frac{\delta E_v(\psi)}{\delta \psi} \frac{\partial \psi}{\partial f_k} d^3r = ?$$

$$\frac{\delta E_v[\psi]}{\delta \psi} = \frac{\delta T_S[\psi]}{\delta \psi} + \underbrace{v(r) + v_{\text{Hartree}} + v_{xc}}_{v^{\text{eff}}}$$

$$\frac{\partial \psi}{\partial f_k} = |\psi_k(r)|^2$$

$$\frac{\partial E_v[\psi]}{\partial f_k} = \int \frac{\delta T_S[\psi]}{\delta \psi} |\psi_k|^2 d^3r + \int v^{\text{eff}} |\psi_k|^2 d^3r$$

$$\boxed{\frac{\partial E_v[\psi]}{\partial f_k} = \epsilon_k}$$

also true for highest occupied state:

$$\frac{\partial E_v}{\partial f_N} = \epsilon_N = \epsilon_F \quad \text{Fermi level} \quad \frac{\delta E_v}{\delta \psi} = \mu$$

Ionization  $I_k = E_k^{N-1} - E^N = - \int \frac{\partial E_v}{\partial f_k} df_k$

"  $= - \int \epsilon_k(f_k) df_k \approx \epsilon_k(f_k = \frac{1}{2})$   
mid value theorem

$$\boxed{I_k \approx - \epsilon_k(f_k = \frac{1}{2})} \quad \text{Slater-Janak transition state}$$

Assumption (same as in Koopmans)  
 the atoms don't — or: atoms move with significant delay (Franck-Condon principle)

If  $\varphi_k(\vec{r})$  are extended and  $\psi(\vec{r})$  and also  $v_{eff}(\vec{r})$  do not change noticeably upon removal of one out of  $N$  electrons then

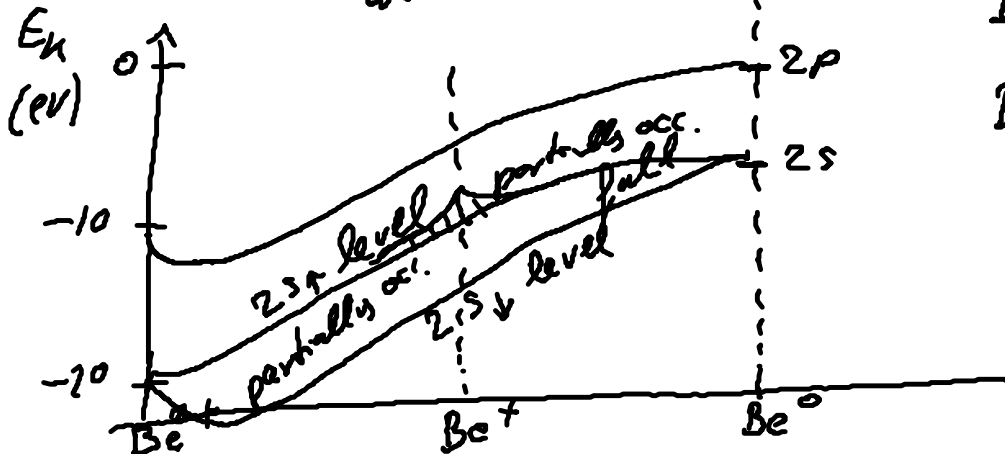
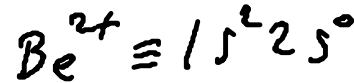
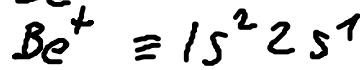
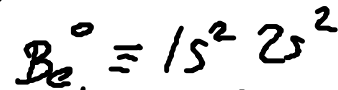
$$E(f_k) = E(1) = E(0) = E\left(\frac{1}{2}\right)$$

$$\Rightarrow \boxed{I_k = -E_k}$$

same equ.  
as Koopmans' theorem

How does  $E_k$  change with occupation?

worst case: Be atom



2 problem with the LDA

a) poor correction of self-interaction  
(wrong shape of xc hole)

b)  $E^{xc}[N] \equiv$  the correct one  $\equiv$  as function of  
 $f_N$ :  $E^{xc}$  has kinks at integer particle  
numbers (analog to  $E_N$  or  $T_S[N]$ )

$\Rightarrow \frac{\delta E^{xc}}{\delta N} = v^{xc} \equiv$  will change discontinuously  
at integer number of particles.

The LDA does not have such property.

(later  $\approx$  July we get back to  
this "excited states")

calculated  $I_N$  - how good are they?

Hydrogen:  $I = 13.6 \text{ eV}$

$N=1$  not many

still an example how good or bad is

the Slater-Janak transition state 2

$$\text{DFT: } \left( -\frac{\hbar^2}{2m} \nabla^2 + \frac{-e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{e^2}{4\pi\epsilon_0} \left( \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + v_{xc} \right) \right) \psi_i$$

must be zero in the correct theory.

exact:  $E_1 = -13.6 \text{ eV}$  It not zero in LDA

LDA:  $E_1 = -6.4 \text{ eV}$

$$E_1\left(\frac{1}{2}\right) = -12.4 \text{ eV}$$

⇒ total energy difference errors cancel to some extent.

In general: Kohn-Sham orbitals/eigenvalues of occupied states are higher than exact DFT

Reason: Self-interaction.

### Hellmann - Feynman theorem

already in 1933 one was very close to DFT

$$\text{exact: } -\frac{\partial E_n}{\partial \vec{R}_k} = \vec{F}_k = -\int \frac{\partial v(\vec{r}, \{\vec{R}_I\})}{\partial \vec{R}_k} n(\vec{r}, \{\vec{R}_I\}) d\vec{r}$$

$\vec{R}_k$   
position of atom k

Forces on atoms are purely electrostatic — between the nuclei and the electron density

1933 Hellmann (Z. f. Physik)

1937 Quantum chemistry text book

1939 Feynman

now with DFT the proof  
is simple  $\Rightarrow$  excite

## Spin Polarization & Magnetism

In principle: the ground state density  $n(\vec{r})$  determines  
everything.  $\Rightarrow$  also magnetic properties.

In practice:  $E^{xc}$  is probably very complicated  
 $\Rightarrow$  use a less periodic approach

density matrix

$$n_{s,s'}(\vec{r}) = \langle \Phi | \psi_s^\dagger(\vec{r}) \psi_{s'}(\vec{r}) | \Phi \rangle$$

$\Phi \equiv$  ground state wave function

$\psi_s^\dagger(\vec{r}) \equiv$  creation operator  $\equiv$  creates electron  
at position  $\vec{r}$  and spin  $s$ .

$\psi_s(\vec{r}) \equiv$  annihilation

$$n_{\uparrow\uparrow} = n_{\uparrow}(\vec{r}) = \langle \Phi | \sum_{i=1}^N \delta_{s_i,\uparrow} \delta(\vec{r}-\vec{r}_i) | \Phi \rangle$$

$$n_{\downarrow}(\vec{r}) = \langle \dots \sum_{s_i,\downarrow} \dots \rangle$$



$$n(\vec{r}) = n_{\uparrow}(\vec{r}) + n_{\downarrow}(\vec{r})$$

$$m(\vec{r}) = \mu_B (n_{\uparrow}(\vec{r}) - n_{\downarrow}(\vec{r}))$$

$$\mu_B \text{ Bohr magneton} = \frac{e\hbar}{2mc}$$

... same procedure as in standard DFT

$$\text{for } n_{\uparrow}, n_{\downarrow} \quad E_0[n_{\uparrow}, n_{\downarrow}] = [n, m]$$

$$\Rightarrow \left\{ \frac{-\hbar^2}{2m} \nabla^2 + v_{Si}^{\text{eff}}(\vec{r}) \right\} \varphi_{\sigma_i s_i}(\vec{r}) = \epsilon_{\sigma_i s_i} \varphi_{\sigma_i s_i}(\vec{r})$$

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

$$v_{Si}^{\text{xc}} = \frac{\delta E^{\text{xc}}}{\delta n_{SiN}}$$

$$n_{Sk}(\vec{r}) = \sum_{i=1} \delta_{\sigma_i s_i} |\varphi_{\sigma_i s_i}(\vec{r})|^2$$

$$E^{\text{xc-LDA}}[n, m] = \int E^{\text{xc-jellium}}(n, m) n(\vec{r}) d^3r$$

with  $E^{\text{xc-jellium}}(n, m) \equiv$  exchange correlation energy per particle of a homogeneous electron system of density  $n$  and magnetization  $m$ .

if  $n_{\uparrow} = n_{\downarrow}$  then Spin-Density-Functional Theory  $\hat{=} DFT$