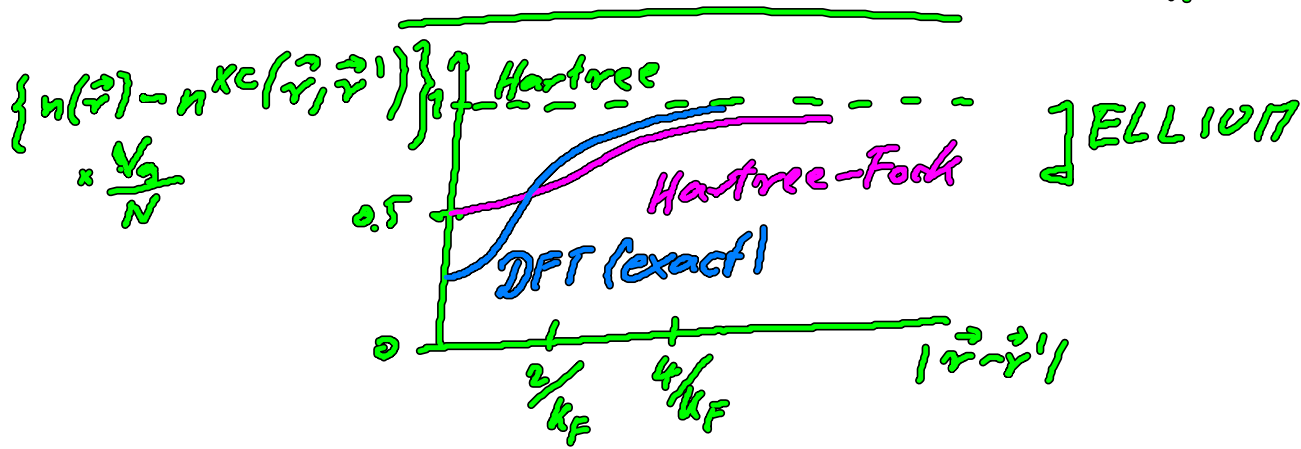


$$\text{Correction: } v^{xc-LDA} = \frac{\partial}{\partial n} \left(n E^{xc-jellium}(n) \right) \Big|_{n=n(\vec{r})}$$

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



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 $r = \vec{r}'$ should be zero. Q.17. unintended 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} must fulfill this condition.

For jellium the LDA is exact.

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

physical meaning. $n(\vec{r})$, $E_0 = M m_{\vec{r}} E_V [A]$

what about $\varphi_i(\vec{r})$, ϵ_i

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

Meaning of the Kohn-Shan single Particle Energies

- The DFT Analogy of Koopmans' theorem -

"Koopmans' theorem does not apply to DFT"

True! However this 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 factor $f(\epsilon_i)$

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

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

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

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

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

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

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

$$\boxed{I_k \approx - \epsilon_k(f_k = \frac{1}{2})}$$

Slater-Janak
fractional state

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

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

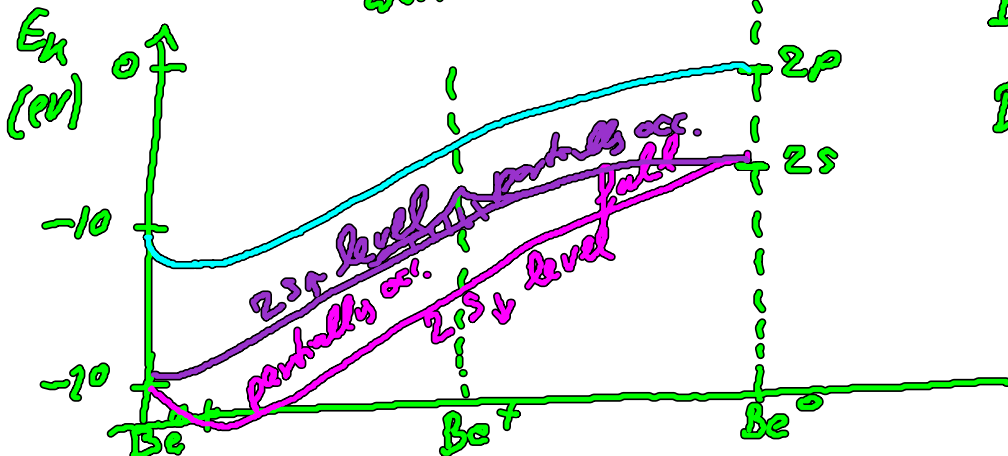
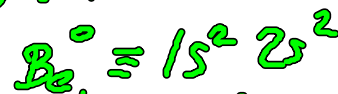
$$E(\psi_k) = E(1) = E(0) = E(\frac{1}{2})$$

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

same eqn. as Koopman's theorem

How does E_k change with occupation?

worst case: Be atom



2 problem with the LDT

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

b) $E^{xc}[4] \equiv$ the correct one \equiv as function of
 f_k : E^{xc} has kinks at integer particle
numbers (analog to E_k or $T_S[4]$)

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

The LDT does not have such property.

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

calculated I_k - 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?

$$\text{DFT: } \left(-\frac{\hbar^2}{2m} \nabla^2 + \frac{-e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r' + v_{xc} \right) \psi_i$$

most to zero in the correct theory $= E_i \psi_i$

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

$$\text{exact: } -\frac{\partial E_n}{\partial \vec{R}_k} = \vec{F}_k = -\int \frac{\partial v(\vec{r}, \{\vec{R}_i\})}{\partial \vec{R}_k} n(\vec{r}, \{\vec{R}_i\}) d^3r$$

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 ...

$$n_{\uparrow\uparrow} = n_{\uparrow}(\vec{r}) = \langle \phi | \sum_{i=1}^N \int_{\vec{r}_i} \delta(\vec{r}-\vec{r}_i) | \phi \rangle$$

$$n_{\downarrow}(\vec{r}) = \langle \dots \sum_{i=1}^N \delta(\vec{r}-\vec{r}_i) \dots \rangle$$

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

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

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

... same procedure as standard DFT

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

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

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

$$v_{\text{xc}} = \frac{\delta E_{\text{xc}}}{\delta n_{\text{xc}}}$$

$$n_{\text{xc}}(\vec{r}) = \sum_{\alpha} \delta_{\alpha} | \varphi_{\alpha}(\vec{r}) |^2$$

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

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

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