

3.8 DFT

$$\frac{\delta T_s[n]}{\delta n} + v^{\text{eff}}(\vec{r}) = \mu \quad \text{non-interacting particles}$$

T_s = kinetic energy of non interacting particles

$$n(\vec{r}) = \sum_{i=1}^N |\varphi_{o_i}(\vec{r})|^2 \quad \text{"approximation"}$$

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

$$\Rightarrow \left[\frac{-\hbar^2}{2m} \nabla^2 + v^{\text{eff}} \right] \varphi_{o_i}(\vec{r}) = \epsilon_{o_i} \varphi_{o_i}(\vec{r}) \quad \text{Kohn-Sham eq.}$$

we need to know the final result for $n(\vec{r})$ in order to solve it.

$$T_s[n] = \sum_{i=1}^N \langle \varphi_{o_i} | \frac{-\hbar^2}{2m} \nabla^2 | \varphi_{o_i} \rangle$$

$$= \sum_{i=1}^N \epsilon_{o_i} - \int v^{\text{eff}}[n] n(\vec{r}) d^3r$$

↑
the result of solving the

Schrödinger equ.

T_S can be evaluated exactly

$$E^{xc}[n] \text{ and } v^{xc}(\vec{r}) = \frac{\delta E^{xc}}{\delta n}$$

rewrite: $E^{xc}[n] = \int E^{xc}[n] n(\vec{r}) d^3r$
xc energy per particle

So far no approximation

(except: $n(r) = \sum |p|^2$)

In Hartree & Hartree-Fock we started with a approx. As second step we used variational principle

DFT: first functional derivative and only now we discuss approx.

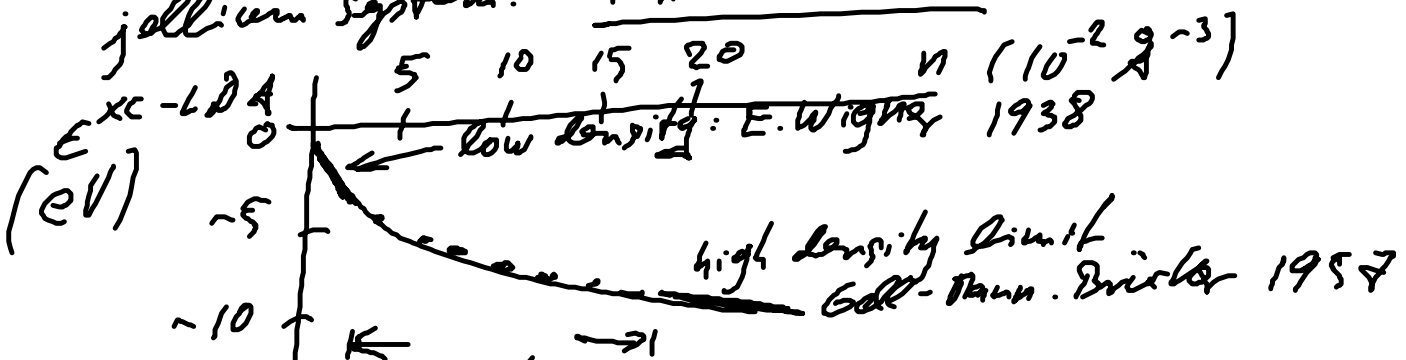
$$E^{xc}[n] = E^{xc-LDA}[n] + O[\nabla n]$$

LDA = local-density approximation

Analog to Thomas-Fermi Theory. There we used the jellium approx. for every-thing. Now: only for E^{xc} .

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

$E^{xc-LDA} \equiv$ xc energy per particle of a jellium system. This is known!



Quantum
Monte Carlo
Ceperley - Alder
1980

realistic material: for every point \vec{r} , get $n(\vec{r})$ and from the figure get $\epsilon^{xc-LDA}(n)$.

LDA were good if $O[dn]$ were small. For real materials this is not true. Still LDA is good.

Today LDA is still used. But there are better treatments: $O[dn]$

$$E^{xc-LDA} \rightarrow v^{xc}(\vec{r}) = \frac{\delta E^{xc}}{\delta n} = \frac{\partial}{\partial n} [\epsilon^{xc-LDA}(n) \cdot n]$$

$$= \left[\epsilon^{xc-LDA}(n) + n \cdot \frac{\partial \epsilon^{xc}(n)}{\partial n} \right]_{n=n(\vec{r})}$$

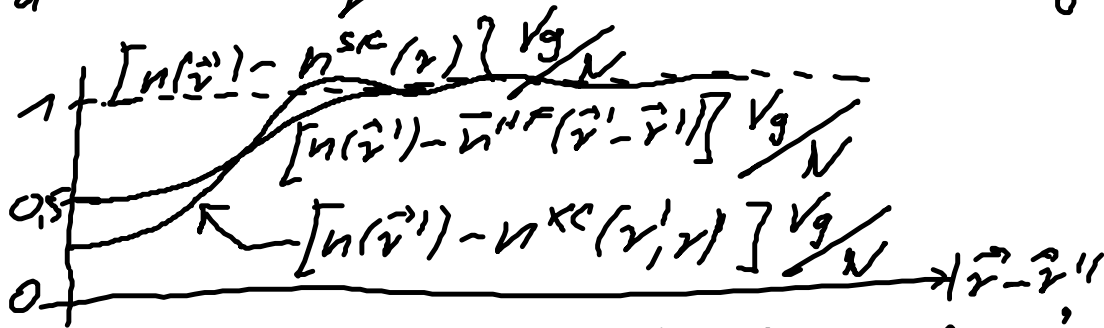
Interpretation

$e-e$ interaction
Hartree $v^{xc} =$

$$\frac{e^2}{4\pi\epsilon_0} \int \frac{(n(\vec{r}') - n^{xc}(\vec{r}, \vec{r}'))}{|\vec{r} - \vec{r}'|} d^3\vec{r}'$$

$n(\vec{r}') - n^{xc}(\vec{r}, \vec{r}')$ = analog to

discussion of Hartree & HF theory



The exchange correlator hole for jellium

3.8.1 meaning of KS single-particle energies

Only 2 quantities have a safe meaning:

$n(\vec{r})$, electron-chemical potential μ : $\frac{\delta T_S}{\delta n} + v_{\text{ext}} = \mu$

In TF-theory: $\mu = \epsilon_N$ true also true for DFT?

Proof: $n(\vec{r}) \rightarrow n(\vec{r}) + \delta n(\vec{r}) \leftarrow$ "small", should not change v_{ext} .

$$\begin{aligned} \Delta E_0[\psi] &= T_S[\psi + \delta\psi] - T_S[\psi] \\ &+ \int v(\vec{r}) \delta n \, d^3r \\ &+ E^{\text{Hartree}}[\psi + \delta\psi] - E^{\text{Hartree}}[\psi] \\ &+ E^{\text{xc}}[\psi + \delta\psi] - E^{\text{xc}}[\psi] \end{aligned}$$

metals: at E_N there are in other states that are empty. ϵ level is degenerate

$$\delta n = \sum_{i=N+1}^{N+m} |\varphi_{o_i}(\vec{r})|^2; \quad m \ll N$$

$$\Delta E_0[n] = \sum_{i=1}^{N+m} \epsilon_{o_i} - \int v^{\text{eff}}(n + \delta n) d^3r$$

$$- \sum_{i=1}^N \epsilon_{o_i} + \int v^{\text{eff}} : n \quad d^3r$$

$$+ \int v(\vec{r}) \delta n \quad d^3r$$

$$+ \frac{e^2}{4\pi\epsilon_0} \int \frac{n \delta n}{|\vec{r} - \vec{r}'|} d^3r'$$

$$+ \frac{e^2}{4\pi\epsilon_0} \int \frac{\delta E^{\text{xc}}}{S_n} d^3r$$

$$= m \cdot E_N = m E_F$$

$$\frac{\delta E_0}{\delta n} = \frac{m \cdot E_F}{m} = E_F = E_N = \mu$$

\Rightarrow the highest occupied state equals the ionisation energy.

Other states?

Analogy to Koopmans' theorem.

$$n(\vec{r}) = \sum_{i=1}^{\infty} f_{o_i} |\varphi_{o_i}(\vec{r})|^2$$

so for

$$f_{o_i} = \begin{cases} 1 & \text{for occupied states} \\ 0 & \text{for empty states} \end{cases}$$

Let's admit fractional numbers

$$T_s = \sum_{i=1}^N f_{oi} E_{oi} - \int v \text{alt } h(\vec{r}) d^3 \vec{r}$$

for $E^{xc}[n]$ we don't know.

$$\frac{\partial E_v}{\partial f_{oi}} = \int \frac{\delta E_v[n]}{\delta n} \frac{\partial n}{\partial f_{oi}} d^3 \vec{r}$$

$$\frac{\partial n}{\partial f_{oi}} = |\varphi_{oi}(\vec{r})|^2$$

$$\frac{\partial E_v}{\partial f_{oi}} = \int \left[\frac{\delta T_s}{\delta n} + v \text{alt } \vec{r} \right] |\varphi_{oi}(\vec{r})|^2 d^3$$

$$\int \frac{\delta T_s}{\delta n} |\varphi_{oi}(\vec{r})|^2 d^3 \vec{r} = \frac{\partial T_s}{\partial f_{oi}}$$

$$= E_{oi} - \int v \text{alt } |\varphi_{oi}|^2 d^3 \vec{r}$$

$$\boxed{\frac{\partial E_v}{\partial f_{oi}} = E_{oi}}$$

Ionisation energies

$$\begin{aligned} \overline{I}_k &= E_k^{N-1} - E^N \\ &= - \int_0^1 \frac{\partial E_0[\eta]}{\partial f_{0k}} d f_{0k} \\ &= - \int_0^1 E_k(f_{0k}) d f_{0k} \end{aligned}$$

$$\approx - E_k(f_{0k} = \frac{1}{2})$$

mid value
Slater - Janak
theorem
transition state

3.8.2 Spin polarization

Strictly: the density $n(\vec{r})$
determines everything. Also magnetism

$E^{xc}[\eta] \equiv$ very complicated

$n_{\uparrow}(\vec{r}), n_{\downarrow}(\vec{r})$ as independent quantities

$$n_{\uparrow} = \sum_{i=1}^N \delta_{S_i \uparrow} |\psi_{0i}|^2$$

$$n_{\downarrow} = \text{analog}$$

$$n(\vec{r}) = n_{\uparrow} + n_{\downarrow} \equiv \text{electron density}$$

$$m(\vec{r}) = \mu_B (n_{\uparrow} - n_{\downarrow}) \equiv \text{magnetization density}$$

... the same as before

$$\Rightarrow \left[\frac{-\hbar^2}{2m} \nabla^2 + v_{Si}^{\text{eff}} \right] \psi(\vec{r}) = E \psi$$

$$v_{Si}^{\text{eff}}(\vec{r}) = v(\vec{r}) + v_{\text{Hartree}}(\vec{r}) + v_{Si}^{\text{xc}}(\vec{r})$$

$$v_{Si}^{\text{xc}} = \frac{\delta E^{\text{xc}}[n_{\uparrow}, n_{\downarrow}]}{\delta n_{Si}}$$

\equiv description of magnetism

3.8.3 Two Examples

since 1980 good quality DFT work

became possible

- 1) algorithms
- 2) computers

since 1980 significant advances in methodology & algorithms.

+ Moore's law (1971)
every second year the # transistors double \Rightarrow

since 1980: a factor of 65,536.
we need completely different codes.

A) equation of state of S_i

- lowest energy structure
- intratomic distances
- common tangent \approx pressure phase transition

B) The earth core

calculate the melting curve of iron

outer core: Fe + (a little O, S, Se)