

3.8 DFT

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

T_S = kinetic energy of non interacting particles

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

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

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

↑ effective single particle eqn. because we need to know the final result for $n(\vec{r})$ in order to solve it.

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

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

↑
the result of solving the

Schrödinger equ.

T_s can be evaluated exactly

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

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

So far no approximation

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

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

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

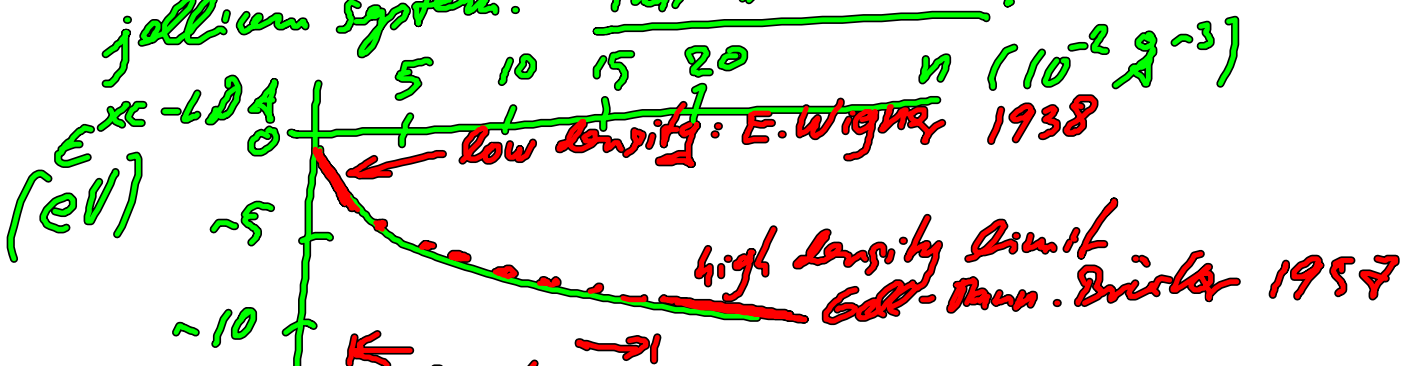
$E^{xc}[n] = E^{xc-LDA}[n] + O[\nabla n]$

LDA = local-density approximation

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

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

$E^{xc-LDA} \equiv xc$ 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 $E^{xc-LDA}(n)$.

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

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

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

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

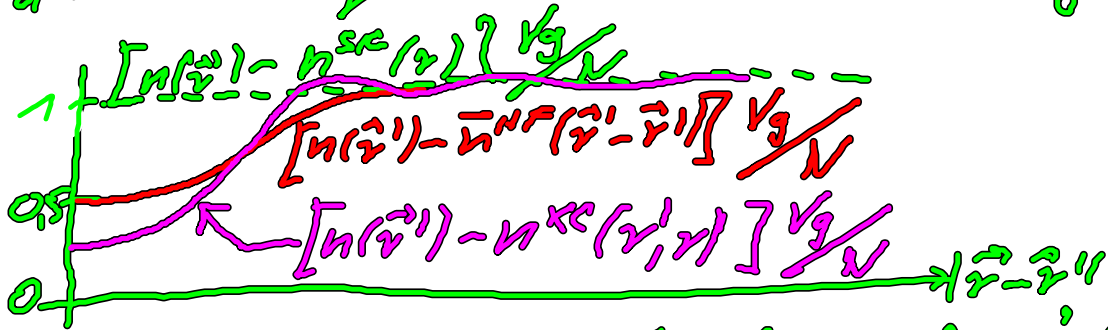
Interpretation

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

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

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

discussion of Hohen & HF theory



The exchange correlator hole for jellium

3.8.1 Training of KS single-particle energies

Only 2 quantities have a safe meaning:

$n(\vec{r})$, electron-chemical potential μ : $\frac{\delta E_0}{\delta n} + v_{ext} = \mu$

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

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

O.k. for metals.

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

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

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

$$\begin{aligned} \Delta E_0[n] &= \sum_{i=1}^{N+m} \epsilon_{o_i} - \int v_{eff} (n + \delta n) d^3\vec{r} \\ &\quad - \sum_{i=1}^N \epsilon_{o_i} + \int v_{eff} n d^3\vec{r} \\ &\quad + \int v(\vec{r}) \delta n d^3\vec{r} \\ &\quad + \frac{e^2}{4\pi\epsilon_0} \left\{ \int \frac{n \delta n}{|\vec{r}-\vec{r}'|} d^3\vec{r}', \right. \\ &\quad \left. + \frac{e^2}{4\pi\epsilon_0} \int \frac{\delta E^{xc}}{\delta n} d^3\vec{r} \right\} \end{aligned}$$

$$= m \cdot \epsilon_N = m \epsilon_F$$

$$\frac{\delta E_0}{\delta n} = \frac{m \cdot \epsilon_F}{m} = \epsilon_F = \epsilon_N = \mu$$

\Rightarrow the highest occupied state equals the ionization energy.

Other states?

Analog to Koopmans' theorem.

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

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

Let's admit functional numbers

$$T_s = \sum_{i=1}^N f_{0i} E_{0i} - \int v \text{d}^3 \vec{r} h(\vec{r}) \text{d}^3 \vec{r}$$

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

$$\frac{\partial E_v}{\partial f_{0i}} = \int \frac{\delta E_v[u]}{\delta u} \frac{\partial u}{\partial f_{0i}} \text{d}^3 \vec{r}$$

$$\frac{\partial u}{\partial f_{0i}} = |\varphi_{0i}(\vec{r})|^2$$

$$\frac{\partial E_v}{\partial f_{0i}} = \int \left[\frac{\delta T_s}{\delta u} + v \text{d}^3 \vec{r} \right] |\varphi_{0i}(\vec{r})|^2 \text{d}^3$$

$$\int \frac{\delta T_s}{\delta u} |\varphi_{0i}(\vec{r})|^2 \text{d}^3 \vec{r} = \frac{\partial T_s}{\partial f_{0i}}$$

$$= E_{0i} - \int v \text{d}^3 \vec{r} |\varphi_{0i}|^2 \text{d}^3 \vec{r}$$

$$\boxed{\frac{\partial E_v}{\partial f_{0i}} = E_{0i}}$$

Ionisation energies

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

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

mid value
slater - theorem
of transition state

3.8.2 Spin polarization

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

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

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

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

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

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

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

... the same as before

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

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

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

\equiv description of exchange-correlation

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 structures
- intratomic distances
- common tangent \pm pressure phase transitions.

B) The earth core

calculate the melting curve of iron

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