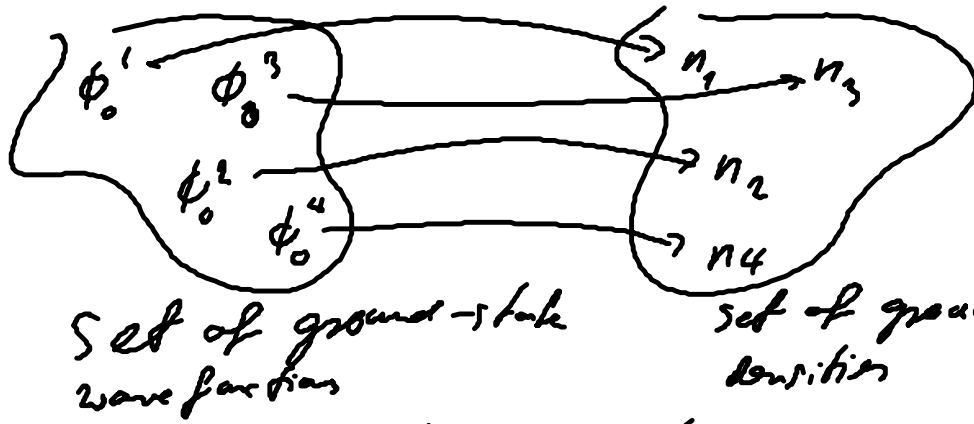


Density-Functional Theory



is there a one-to-one correspondence between ϕ_0 and n ?

can the functional $\phi_0 \rightarrow n$ be inverted

$$n = n[\phi_0] = \langle \phi_0 | \sum \delta(\vec{r} - \vec{r}_i) | \phi_0 \rangle = n(\vec{r})$$

Starting point: two different potentials $v(\vec{r})$, $\tilde{v}(\vec{r})$
 $v(\vec{r}) - \tilde{v}(\vec{r}) \neq \text{const.}$

$\Rightarrow \phi_0$ and $\tilde{\phi}_0$ are different (last lecture)

Assumption: Though ϕ_0 and $\tilde{\phi}_0$ are different they give rise to the same density $n(\vec{r})$

$$E_0^e = \langle \phi_0 | H^e | \phi_0 \rangle < \langle \tilde{\phi}_0 | H^e | \tilde{\phi}_0 \rangle = \langle \tilde{\phi}_0 | H^e + \sum v(\vec{r}) - \sum \tilde{v}(\vec{r}) | \tilde{\phi}_0 \rangle$$

truly larger

$$= \tilde{E}_0^e + \int [v(\vec{r}) - \tilde{v}(\vec{r})] n(\vec{r}) d^3r$$

$$\tilde{E}_0^e = \langle \tilde{\phi}_0 | \tilde{H}^e | \tilde{\phi}_0 \rangle < \langle \phi_0 | H^e | \phi_0 \rangle = \langle \phi_0 | H^e + \sum [\tilde{v} - v] | \phi_0 \rangle$$

$$= E_0^e + \int [\tilde{v}(\vec{r}) - v(\vec{r})] n(\vec{r}) d^3r$$

$$\tilde{E}_0^e + E_0^e < \tilde{E}_0^e + E_0^e = \text{contradiction}$$

\Rightarrow The assumption was wrong — reductio ad absurdum

\Rightarrow If ϕ_0 and $\tilde{\phi}_0$ are different wavefunctions then $n(\vec{r})$ and $\tilde{n}(\vec{r})$ are also different

a) $\phi_0 = \phi_0[n]$ $n(\vec{r})$ determines ϕ_0

and $\langle \phi_0 | H^e | \phi_0 \rangle$ is a functional of the density: $E_0[n]$

$$b) E_0[n] = \int n(\vec{r}) v(\vec{r}) d^3r + F[n]$$

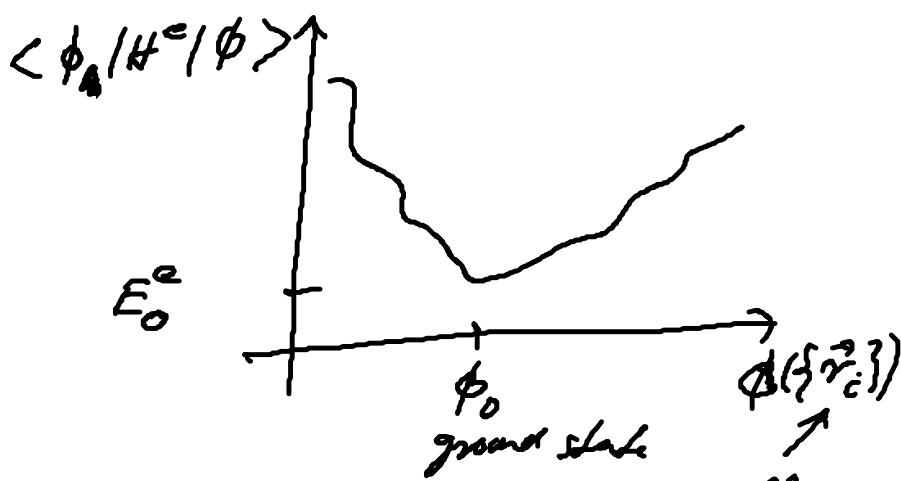
with $F[n] = \langle \phi_0 | \frac{\hbar^2}{2m} \nabla^2 + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{z_i z_j}{|\vec{r}_i - \vec{r}_j|} | \phi_0 \rangle$

c) $E_0[n]$ - under constraint of "particle conservation" - $\int n(\vec{r}) d^3r = N$ has its minimum at the ground state energy: $E_0^e = \text{Min}_{n(\vec{r})} E_0[n]$

$$\delta \left\{ E_0[n] - \mu \left(\int n(\vec{r}) d^3r - N \right) \right\} = 0$$

$$\text{or } \frac{\delta E_0[n]}{\delta n} = \mu$$

Hohenberg
&
Kohn



$\sim 10^{23}$ variables

3 variables

This is exact

We have shown that $E_0[\eta]$. - We don't know how to evaluate it.

Kohn-Sham

$$E_0[\eta] = T_S[\eta] + \int v(\vec{r})n(\vec{r})d^3r + E_{Hartree}[\eta] + E_{xc}[\eta]$$

kinetic of non-interacting particles

$$E_{Hartree} = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \iint \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r d^3r'$$

$T_S[\rho]$ should exist but a closed mathematical expression is not known.

$$T_S[\rho] = \text{Thomas-Fermi} + O(D^2 n(r))$$

$$\frac{1}{5\pi^2} \frac{\hbar^2}{2m} \left(3\pi^2 n(r) \right)^{5/3} \quad \uparrow \quad \uparrow$$

$v, v^2, v^3 \dots$

second term: $\sim v^2$
Weizsäcker

KS Ansatz assume $n(\vec{r}) = \sum_{i=1}^N |\psi_i|^2$

with ψ_i a solution of

$$\left\{ \frac{-\hbar^2}{2m} \nabla^2 + v^{\text{eff}}(\vec{r}) \right\} \psi_i(\vec{r}) = E_i \psi_i(\vec{r})$$

$$T_S[\rho] \stackrel{\text{exact}}{\approx} \sum_i \langle \psi_i | \frac{-\hbar^2}{2m} \nabla^2 | \psi_i \rangle$$

The only unknown is $E^{\text{xc}}[\rho]$

$$E^{\text{xc}}[\rho] = \langle \phi | \hat{H}^e | \phi \rangle - \int v(\vec{r}) n(\vec{r}) d^3r - T_S[\rho] - E^{\text{kin}}[\rho]$$

Hohenberg-Kohn $\frac{\delta E_v[\rho]}{\delta \rho} = \mu = \frac{\delta T_S[\rho]}{\delta \rho} + v^{\text{eff}}(\vec{r})$ Kohn-Sham equation

$$v^{\text{eff}}(\vec{r}) = \frac{\delta \left(\int v(r) n(r) d^3r + E^{\text{kin}}[\rho] + E^{\text{xc}}[\rho] \right)}{\delta \rho}$$

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

The KS must be solved selfconsistently

- a) start with a guess for $n^{(0)}(\vec{r})$ or $v^{\text{eff}}(0)$
- b) calculate ψ_i, E_i from KS-equation
- c) calculate a new $n^{(i+1)}$ and $v^{\text{eff}}(i+1)$

d) get 0 &)
 so for essentially exact. We only accept densities
 $n(\vec{r}) = \sum |\varphi_i|^2$ with $\varphi_i \equiv$ solution of single particle
 Schröd:iff equ. "v-representability"

A very mild approximation

some words $T_S[\rho]$

$$T_S = \sum \langle \varphi_i | \frac{-\hbar^2}{2m} \nabla^2 | \varphi_i \rangle = \sum \epsilon_i - \sum_i \langle \varphi_i | v_{eff} | \varphi_i \rangle$$

\uparrow result from v_{eff} \uparrow result from v_{eff}
 \downarrow input

$T_S[\rho]$
 $\int n^{out} = \int |\varphi_i|^2 =$ output of our KS-equ.

$v_{eff} \equiv$ input

ϵ_i, φ_i, n "output".

we may add terms $\sim (n^{in} - n^{out})$

good & bad at the same time
 1) we tried to use $n(\vec{r})$ (Hohenberg & Kohn) } "bad"
 but we need to calculate T_S , i.e. we
 need ϵ_i, φ_i

2) The $\epsilon_i, \gamma_i(\vec{r})$ tell a lot about the nature of bonding and many other physical properties

essentially exact

$n(\vec{r})$ determines $\phi_0, \phi_0 \rightarrow$ many body hamiltonian, the many-body hamiltonian determines everything.
ground state density determines everything

now !? $E^{xc}[n] = \int \underbrace{E^{xc}[n]}_{\text{xc energy per particle}} n(\vec{r}) d^3r$

$$\frac{\delta E^{xc}}{\delta n} = E^{xc}[n] + \int \frac{\delta E^{xc}}{\delta n} \cdot n(\vec{r}) d^3r$$

$$E^{xc}[n] = E^{xc-jellium}(n) + \begin{matrix} \vdots \\ O(D^2 n(r)) \\ \uparrow \\ D, D^2, D^3, \dots \end{matrix}$$

for jellium we know the results

$E^{xc}[n] \rightarrow E^{xc-jellium} \equiv \text{LDA}$
 local-density approximation
 we evaluate E^{xc} at the local



only for
xc
contribution

replace $n(r)$ by
locally constant
pieces.

if $n(r)$ does not change
much over $\frac{2\pi}{k_F}$ then LDA would be "perfect"

$\frac{2\pi}{k_F} \approx 5 \text{ \AA} \equiv$ interatomic distance.

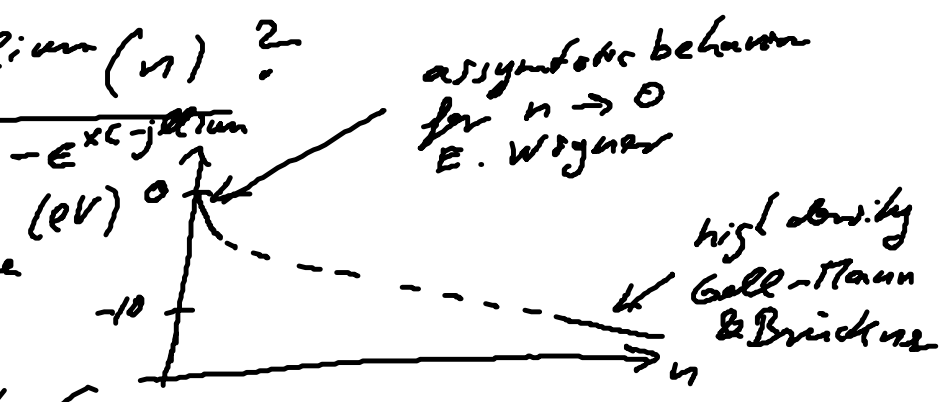
\Rightarrow LDA is NOT well justified.

Still LDA works better than Hartree
or Hartree-Fock.

Nowadays we also include (σ_h) -terms.

How does E^{xc} -jellium (n) ?

- 1938 Wigner
- 1951 Gellman Bruckner
- 1980 Ceperley, Alder

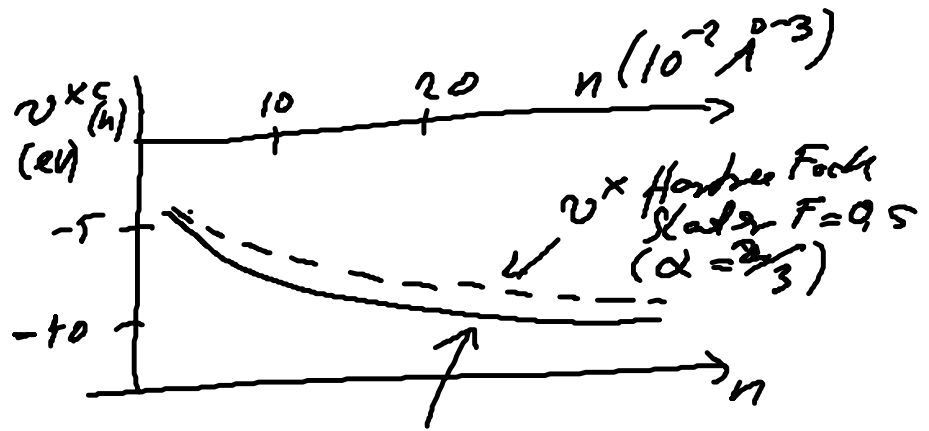


Quantum Monte Carlo

from E^{xc} -jellium we get E^{xc} -LDA

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

$$v^{\text{xc}} = \frac{\delta E^{\text{xc-LDA}}}{\delta n}$$



Interpretation

of v^{xc}

$v^{\text{xc-LDA}}$ =
exact result
for jellium

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

"Correlation": In the electrons the other electrons adjust to the position of the electron.

X \equiv exchange \equiv "Pauli correlation"

$C \equiv$ Coulomb correlation

if an electron sits at point \vec{r}
 the distribution of all other electrons is not

$n(\vec{r})$ but $n(\vec{r}') - n_{xc}(\vec{r}, \vec{r}')$.

In the neighborhood the ~~the~~ net density
 must be reduced

exchange $(n - n_{xc})$

