

Hohenberg - Kohn theorem

Ground state energy  $E_{gr}$  is completely determined by electronic density  $\rho$

$$\rho \longleftrightarrow E_{gr}$$

but connection is not known

Density?

$$\rho(\vec{r}) = |4(\vec{r})|^2 \text{ for 1 particle}$$

$$\text{for 2 particles } \rho(\vec{r}) = 2 \int |4(\vec{r}_1, \vec{r}_2)|^2 d\vec{r}_2$$

normalization  
# of electrons

$$N \text{ electrons: } \rho(\vec{r}) = N \int |4(x_1, x_2, \dots x_N)|^2 \times$$

$ds dx_2, dx_3, \dots dx_N$

spin↑ of the first particle

density depends on 3 coords

wavefunction depends on  $4N$  coords.

The goal of DFT is to find a functional connecting electronic density and energy

function: produces a number from a set of variables

$$\mathcal{F} = \mathcal{F}(x_1, x_2, \dots x_n)$$

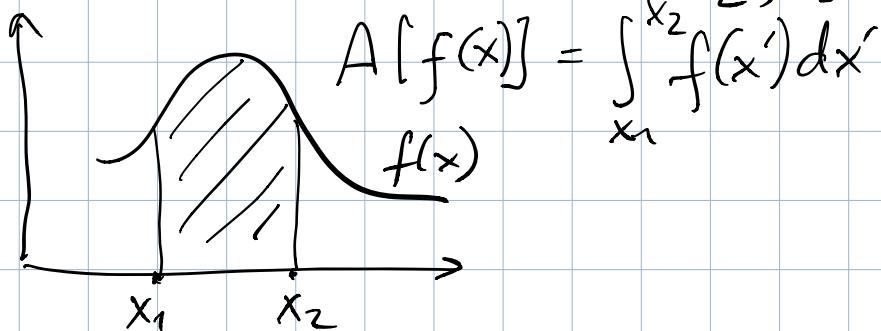
$$\rho = \rho(\vec{\sigma})$$

functional: produces a number from

1

a function

$$F[f] : F[\rho]$$



Why density is sufficient to know properties of the system?

$$\Rightarrow \int \rho(r) dr = N$$

- \* cusps of density define positions of nuclei
- \* heights of cusps define nuclear charges

Orbital-free DFT

$$E[\rho] = ?$$

uniform electron gas

Electron-nuclear attraction:

$$E_{ne}[\rho] = \sum_A^{\text{nuclei}} \int \frac{Z_A(R_A)}{|R_A - r|} \rho(r) dr \quad \textcircled{1}$$

$$\langle \psi | V_{ne} | \psi \rangle = \sum_A^{\text{nuclei}} \int \psi^*(r) \frac{Z_A(R_A)}{|R_A - r|} \psi(r) dr$$

Electron-electron interaction

$$E_{ee}[\rho] \rightarrow \text{Coulomb} \quad J[\rho] = \frac{1}{2} \int \frac{\rho(r) \rho(r') dr dr'}{|r-r'|}$$

↓ exchange

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$$K[\rho] = ?$$

Uniform electron gas:

$$T_{TF}[\rho] = G \int \rho^{5/3}(r) dr, \quad C_F = \frac{3}{10} (3\pi^2)^{1/3}$$

kinetic energy functional

Thomas & Fermi 1927

$$K_D[\rho] = -C_X \int \rho^{4/3}(r) dr, \quad C_X = \frac{3}{4} \left(\frac{8}{3\pi}\right)^{1/3}$$

exchange functional

Block & Dirac 1929/30

Thomas-Fermi-Dirac:

$$E_{TFD}[\rho] = T_{TF}[\rho] + E_{ne}[\rho] + J[\rho] + K_D[\rho]$$

Exact for UEG  
but does not predict bonding in molecules

TFD can be improved by adding derivatives of el. density ( $\sim$  Taylor expansion)

$$T[\rho] = T_0[\rho] + T_1[\rho] + T_2[\rho] + \dots$$

$$T_2[\rho] = \lambda \int \frac{|\nabla \rho(r)|^2}{8\rho(r)} dr$$

von Weizsäcker  
 $\lambda = \frac{1}{9}$

exact for 1 & 2 electrons

$$T_4[\rho] = (540(3\pi)^{2/3})^{-1} \int \rho^{1/3}(r) \left\{ \left( \frac{\nabla^2 \rho}{\rho} \right)^2 - \frac{9}{8} \frac{\nabla^2 \rho}{\rho} \left( \frac{\nabla \rho}{\rho} \right)^2 + \frac{1}{3} \left( \frac{\nabla \rho}{\rho} \right)^4 \right\} dr$$

$T_{TF}$  underestimates by  $\sim 10\%$

$T_2$  underestimates by  $\sim 1\%$

$T_4$  overestimates by  $\sim 1\%$

$T_6, T_8$  - diverge

$$K[\rho] = K_D[\rho] + K_2[\rho] + K_4[\rho]$$

$$K_2[\rho] = -\frac{5}{216} (3\pi^5)^{-1/3} \int \frac{|\nabla \rho|^2}{\rho^{4/3}} dr$$

bonding is allowed, but accuracy is still bad

Cheap theory!  
 Work in progress!

Nobel prize is waiting here

N<sub>2</sub> atom:

$E_{kin} = 128.9 \text{ au.}$

$$E_{\text{exchange}} = -12.1 \text{ a.u.}$$

$$E_{\text{corr.}} = -0.4 \text{ a.u.}$$

Kinetic density functional is the biggest problem!

### Kohn-Sham approach.

Idea: Represent  $\hat{T}$  as 2 terms:  
one is exact through orbitals,  
second - small correction

Price: back to orbitals ( $3 \rightarrow 4N$ ):  
correlation functional reappears as  
a separate term.

Consider  $\hat{H}_\lambda = \hat{T} + \hat{V}_{\text{ext}}(\lambda) + \lambda \hat{V}_{\text{ee}}$

$$\lambda = 0, 1$$

$$\lambda = 1 \text{ real system } (\hat{V}_{\text{ext}}|_{\lambda=1} = \hat{V}_{\text{ne}})$$

$$\lambda = 0 \text{ non-interacting electrons}$$

$V_{\text{ext}}$  is adjusted such that  $\rho$  is the same for all  $\lambda$

for  $\lambda = 0$  (non-interacting electrons)  $\rightarrow$   
exact solution of SF is given by a  
Slater determinant of  $X$ ,

exact kinetic energy :

$$T_S = \sum_{i=1}^{N_{\text{elec}}} \left\langle \chi_i \left[ -\frac{1}{2} \nabla^2 / \chi_i \right] \right\rangle$$

$\uparrow$  Slater determinant

for  $\lambda=1$   $T_S$  is only approximation, but a good one

$$E_{\text{DFT}}[\rho] = T_S[\rho] + E_{\text{ne}}[\rho] + J[\rho] + E_{\text{xc}}[\rho]$$

if  $E_{\text{exact}}$   $\rightarrow$

$$E_{\text{xc}}[\rho] = (T[\rho] - T_S[\rho]) + (E_{\text{ex}}[\rho] - J[\rho])$$

$\uparrow$  Kinetic correlation energy       $\uparrow$  potential correlation & exchange energies

$$E[\rho(r)] = T_S[\rho] + E_{\text{ne}}[\rho] + J[\rho] + E_{\text{xc}}[\rho] =$$

$$= T_S[\rho] + \int V_{\text{ne}} \rho(r) dr + \frac{1}{2} \iint \frac{\rho(r) \rho(r')}{|r-r'|} dr dr' +$$

$$+ E_{\text{xc}}[\rho] =$$

$$= -\frac{1}{2} \sum_{i=1}^{N_{\text{elec}}} \left\langle \chi_i \left[ -\frac{1}{2} \nabla^2 / \chi_i \right] \right\rangle - \sum_{i=1}^{N_{\text{elec}}} \sum_{A=1}^{N_{\text{atom}}} \int_{r_{1A}}^{\infty} Z_A |\chi_i(r)|^2 dr,$$

$$+ \frac{1}{2} \sum_{ij} \int \int |X_i(r_1)|^2 \frac{1}{r_{12}} |X_j(r_2)|^2 dr_1 dr_2 +$$

$$+ E_{xc}(P)$$

continue with  $L = E + \lambda(\langle \chi_i / \chi_j \rangle) \delta$

$\delta L = 0 \rightarrow$  Kohn-Sham eqn

$$\left( -\frac{1}{2} \nabla^2 + \left[ \frac{P(r_2)}{r_{12}} dr_2 - \sum_A \frac{z_A}{r_{1A}} + V_{xc}(r_1) \right] \right) \chi_i = E_i \chi_i$$

$$\underline{V_{xc} = \frac{\delta E_{xc}}{\delta P}}$$

exchange-correlation potential

KS theory is exact if  $V_{xc}$  is known