Density Functional Theory 2

Hohenberg - Kohn theorem 1964

The ground state density $\rho(\vec{r})$ uniquely determines the external potential, up to a constant

$$V_{ext} = \hat{H}_{ne}$$

Proof: assume there are V_{ext_1}, V_{ext_2} that result in the same ρ

$$V_{ext,1} \rightarrow \hat{H}_1 \rightarrow \Psi_1 \rightarrow \rho \leftarrow \Psi_2 \leftarrow \hat{H}_2 \leftarrow V_{ext,2}$$

$$\langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle > E_1$$

$$\langle \Psi_2 | \hat{H}_2 | \Psi_2 \rangle + \langle \Psi_2 | \hat{H}_1 - \hat{H}_2 | \Psi_2 \rangle > E_1$$

$$E_2 + \langle \Psi_2 | \hat{V}_{ext_1} - \hat{V}_{ext2} | \Psi_2 \rangle > E_1$$

$$E_2 + \int \rho(r) (V_{ext_1} - V_{ext2}) dr > E_1$$

from the other side:

$$+ \quad \langle \Psi_1 | \hat{H}_2 | \Psi_1 \rangle > E_2$$

$$\vdots$$

$$E_1 + \int \rho(r)\,(V_{ext_2} - V_{ext_1})\,dr > E_2$$

$$E_1 + E_2 > E_1 + E_2 \quad \text{Wrong!}$$

Exchange and correlation holes

Reduced density matrix

$$\gamma_1(r_1, r_1') = N_{elec} \int \Psi^*(r_1', r_2 \ldots r_N)\,\Psi(r_1, r_2, \ldots r_N)\, d\sigma_2\, dr_3\, dr_N$$

first order RDM

$$\rho(r_1) = \gamma_1(r_1, r_1) \quad \text{electron density}$$

Second-order RDM:

$$\gamma_2(r_1, r_2, r_1', r_2') = N(N-1) \int \Psi^*(r_1', r_2' \ldots r_N)\,\Psi(r_1, r_2, \ldots r_N)\, dr_3 \ldots dr_N$$

$$\rho_2(r_1, r_2) = \gamma_2(r_1, r_2, r_1, r_2) \quad \text{electron pair-density}$$

$$V_{ne} = -\sum_A^{N_{atoms}} \frac{Z_A\,\gamma_1(r_1, r_1)}{|R_A - r_1|}\,dr_1 = -\sum_A^{N_{atom}} \frac{Z_A\,\rho_1(r)}{|R_A - r|}\,dr$$

$$V_{ee} = \frac{1}{2} \int \frac{\gamma_2(r_1, r_2, r_1, r_2)}{|r_1 - r_2|}\,dr_1\,dr_2 = \frac{1}{2} \int \frac{\rho_2(r_1, r_2)}{|r_1 - r_2|}\,dr_1\,dr_2$$

$$J = \frac{1}{2} \int \frac{\rho_1(r_1)\,\rho_1(r_2)}{|r_1 - r_2|}\,dr_1\,dr_2$$

$$T = -\frac{1}{2}\int \nabla^2 \gamma_1(r_1, r_1')\Big|_{r=r'} dr'$$

$$\Psi \underset{?}{\rightleftarrows} \rho$$

how to ensure antisymmetry of w.f. from density :
N-representability problem

$$\rho_2(r_1, r_1) = 0$$

probability to find 2 electrons in the same space is zero

Non-interacting electrons:

$$\rho_2^{indep}(r_1, r_2) = \frac{N-1}{N}\rho_1(r_1)\,\rho_1(r_2) = \Big(1 - \underbrace{\frac{1}{N}}_{\text{self-interaction}}\Big)\rho_1(r_1)\rho_1(r_2)$$

Interacting electrons:

$$\rho_2(r_1, r_2) = \rho_1(r_1)\,\rho_1(r_2) + \rho_1(r_1)\,h_{xc}(r_1, r_2)$$

$$h_{xc}(r_1, r_2) = \frac{\rho_2(r_1, r_2)}{\rho_1(r_1)} - \rho_1(r_2)$$

h_{xc} represents reduced probability to find el. 2 @ r_2 if el. 1 is @ r_1

$$h_{xc} = h_x + h_c$$

$$h_x = h_x^{\alpha\alpha} + h_x^{\beta\beta}$$ Exchange or Fermi hole

$$h_c = h_c^{\alpha\alpha} + h_c^{\beta\beta} + h_c^{\alpha\beta}$$ correlation hole

$$\int h_{xc}(r_1, r_2)\, dr_2 = \int \frac{\rho_2(r_1, r_2)}{\rho_1(r_1)} dr_2 - \int \rho_1(r_2)\, dr_2 =$$

$$= \frac{N(N-1)}{N} \int \frac{\int \Psi^*(r_1, r_2 ..)\Psi(r_1, r_2) dr_3 .. dr_N}{\int \Psi^*(r_1, r_2 .. r_N)\Psi(r_1, .. r_N) dr_2\, dr_N} dr_2 \to 1$$

$$- N = \frac{N(N-1)}{N} - N = N - 1 - N = -1$$

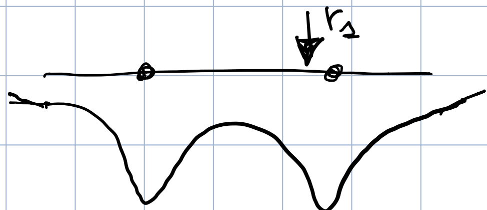
$$\int h_x\, dr_2 = -1$$ from analyzing spin densities

$$\int h_c\, dr_2 = 0$$

$$h_x(r_2 \to r_1, r_1) = -\rho(r_1)$$

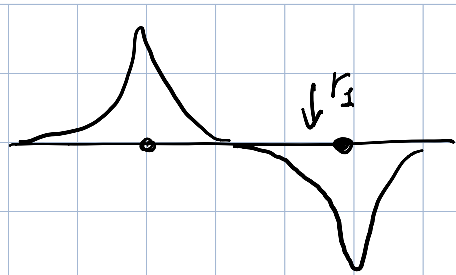
H_2 molecule $\quad h_x^{\alpha}(r_1, r_2) = -\rho^{\alpha}(r_1) = -\frac{1}{2}\rho(r_1)$

$$= -\frac{1}{2}|\sigma|^2$$

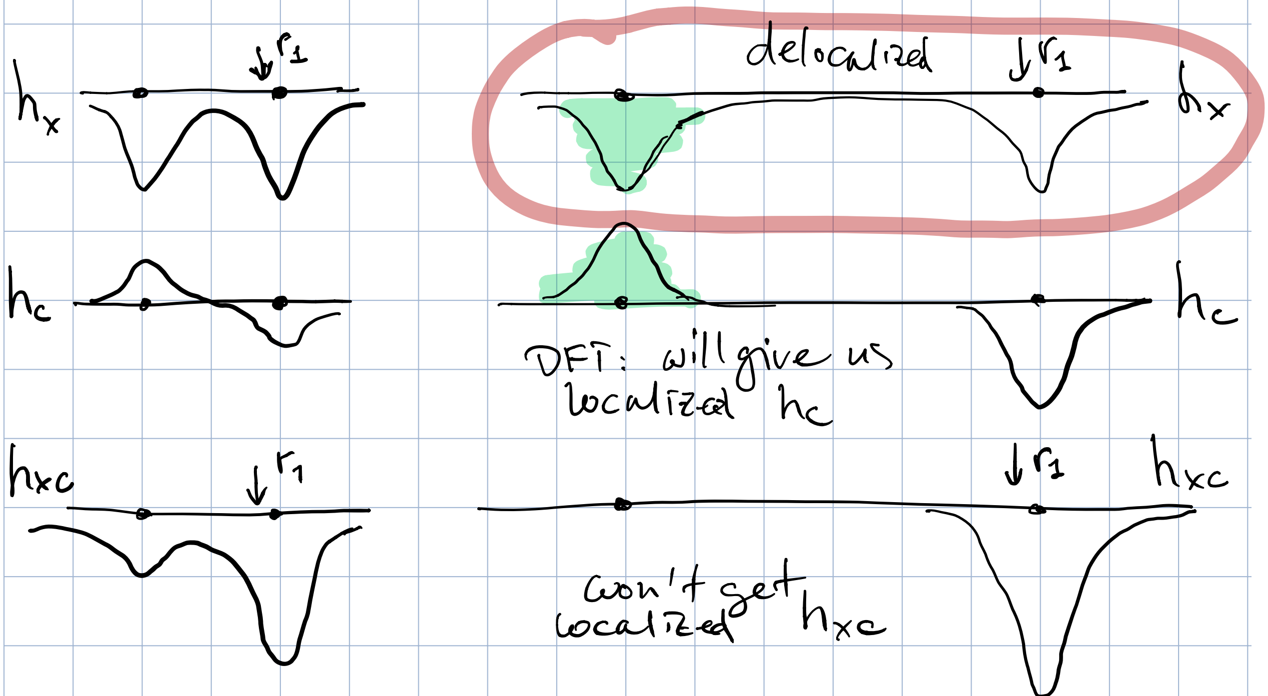


h_x delocalized over all molecule

creates charge depletion of half electron in vicinity of each nucleus



$h_c \qquad \int h_c \, dr_2 = 0$



Why not to use HF exchange term in Kohn-Sham DFT?

W.f. methods: delocalized h_c, delocalized h_x can cancel each other to get localized h_{xc}

DFT: localized h_c, localized h_x
$\rightarrow$ Localized h_{xc}

if mix HF h_x and DFT h_c
$\rightarrow$ delocalized h_{xc}