

# CHM 673

## Lecture 17: Density Functional Theory, part 2

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Suggested reading:

Chapter 6.2, 6.4, 6.5 from Jensen

# Kohn-Sham DFT

Solution: **Kohn & Sham approach**

Represent **kinetic energy** as two terms:

one will be exact through orbitals (Slater Determinant term,  $T_{SD}$ ),  
second – small correction

Price:

- back to orbitals (from 3 to 4N coordinates)
- correlation functional reappears as a separate term  $E_{xc}$

**Kohn-Sham functional:**  $E_{KS}[n] = T_{SD}[n] + E_{ne}[n] + J[n] + E_{xc}[n]$

where  $E_{xc}$  is defined as:

$$E_{xc}[n] = \underbrace{(T[n] - T_{SD}[n])}_{\text{kinetic correlation energy}} + \underbrace{(E_{ee}[n] + J[n])}_{\text{potential correlation \& exchange energies}}$$

# Kohn-Sham DFT

Kohn-Sham functional:

$$E_{KS}[n] = T_{SD}[n] + E_{ne}[n] + J[n] + E_{xc}[n]$$

compare with Hartree-Fock energy:

$$E_{HF}[\{\chi\}] = T + E_{ne} + J - K$$

Using variational principle, Kohn-Sham functional results in a self-consistent problem

$$\hat{f}^{KS} \chi_i = \varepsilon_i \chi_i$$

with

$$\hat{f}^{KS}(x_1) = \hat{h}(x_1) + \Sigma_j \hat{J}_j(x_1) + V_{xc}(x_1)$$

exchange-correlation potential

$$V_{xc} = \frac{\delta E_{xc}}{\delta n}$$


Kohn-Sham theory is exact if  $V_{xc}$  is known

# Pair density

Electron density  $\rho(r) = \rho_1(r) = N \int |\Psi(r_1, r_2, r_3, \dots, r_N)|^2 dr_2 dr_3 \dots dr_N$

A related more general property: **electron pair-density  $\rightarrow$  probability to find an electron at position  $r_1$  and another electron at position  $r_2$**

$$\rho_2(r_1, r_2) = N(N - 1) \int |\Psi(r_1, r_2, r_3, \dots, r_N)|^2 dr_3 \dots dr_N$$

 integrates to the number of electron pairs

Pair-electron density contains information about electron correlation. In particular:

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

$\rho_2(r_1, r_1) = 0$       probability to find 2 electrons in the same space is zero

# Exchange-correlation hole

Assume non-interacting electrons (electrons do not have charge and spin). Then:

$$\rho_2^{indep}(r_1, r_2) = \frac{N-1}{N} \rho_1(r_1) \rho_1(r_2) = \left(1 - \frac{1}{N}\right) \rho_1(r_1) \rho_1(r_2)$$

self-interaction factor

Since real electrons have charge and spin, there is a reduced probability to find an electron near another electron. We can account for this reduced probability with **exchange-correlation hole**  $h_{xc}$

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

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

The exchange-correlation hole represents the reduced probability of finding electron 2 at a position  $r_2$  given that electron 1 is located at  $r_1$

# Exchange-correlation hole

The exchange-correlation hole represents the reduced probability of finding electron 2 at a position  $r_2$  given that electron 1 is located at  $r_1$

Repulsion due to electron charge (dynamical correlation) → Coulomb hole  $h_c$

Repulsion due to electron spin (exchange) → Fermi hole  $h_x$

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

$$h_x = h_x^{\alpha\alpha} + h_x^{\beta\beta}$$

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

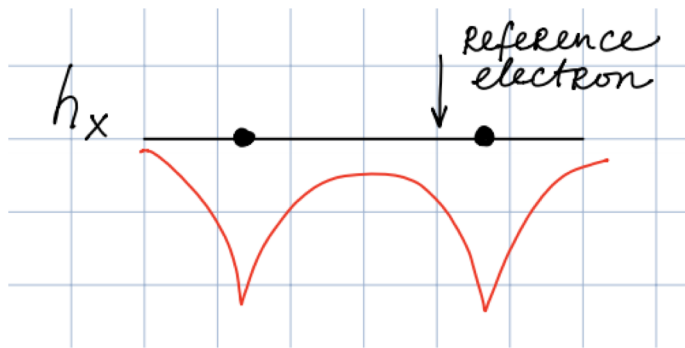
# Exchange and correlation holes

$$\int h_{xc}(r_1, r_2) dr_2 = \int \frac{\rho_2(r_1, r_2)}{\rho_1(r_1)} dr_2 - \int \rho_1(r_2) dr_2 = \frac{N(N-1)}{N} - N = -1$$

The integral of the total exchange-correlation hole is -1  $\rightarrow$  this is electron self-repulsion

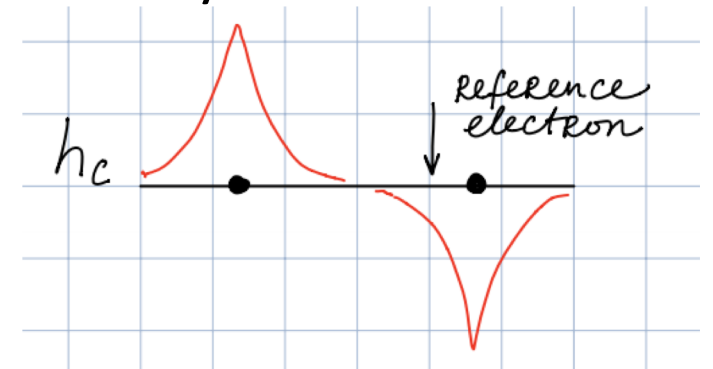
$$\int h_x(r_1, r_2) dr_2 = -1$$

exchange hole is negative everywhere:  
static reduction in a probability to find  
one electron near another



$$\int h_c(r_1, r_2) dr_2 = 0$$

Coulomb hole reduces the probability of  
finding an electron near the reference  
electron, but increases the probability of  
finding it further away



# Exchange and correlation holes

From definition of the hole 
$$h_{xc}(r_1, r_2) = \frac{\rho_2(r_1, r_2)}{\rho_1(r_1)} - \rho_1(r_2) \quad \rightarrow$$

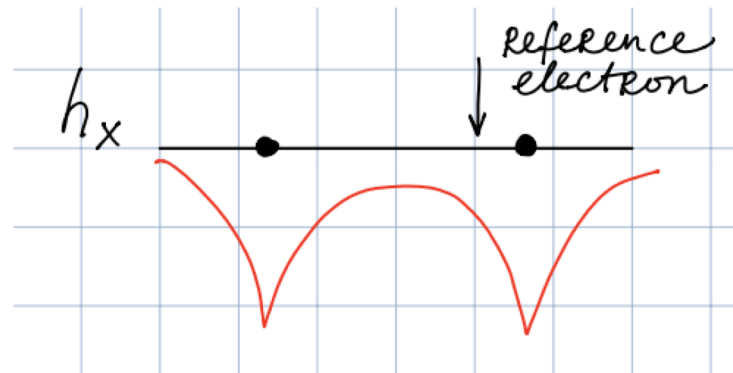
$$h_{xc}(r_1, r_2 \rightarrow r_1) = -\rho_1(r_1)$$

Consider H<sub>2</sub> molecule at the Hartree-Fock level (no correlation)

$$h_x(r_1, r_2 \rightarrow r_1) = -\rho_1(r_1)$$

$$h_x^\alpha(r_1, r_2) = -\rho_1^\alpha(r_1) = -\frac{1}{2}\rho_1(r_1)$$

There is only one electron of each spin, so the exchange hole is fully due to self-interaction!





# Electron self-interaction energy

Hartree-Fock electron-electron interaction:

$$J - K = \int dx_1 dx_2 \chi_i^*(x_1) \chi_j^*(x_2) \frac{1}{r_{12}} \chi_i(x_1) \chi_j(x_2) - \int dx_1 dx_2 \chi_i^*(x_1) \chi_j^*(x_2) \frac{1}{r_{12}} \chi_i(x_2) \chi_j(x_1)$$

if  $x_1 = x_2 \rightarrow J - K = 0$

Electron self-interaction energy in HF model is zero!

DFT: electron-electron interaction is given by

$$E_{ee} = J[\rho] + E_{xc}[\rho] = \frac{1}{2} \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 + \frac{1}{2} \int \frac{\rho(r_1)h_{xc}(r_1, r_2)}{|r_1 - r_2|} dr_1 dr_2$$

$\neq 0$  for 1 electron!

It is hard to cancel self-interaction with non-HF exchange functional

DFT infamous self-interaction error: each electron interacts with itself (repels itself)

# DFT self-interaction error

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In most modern density functionals, there is a repulsive electron self-interaction

→ Electrons tend to be more delocalized

Chemical consequences:

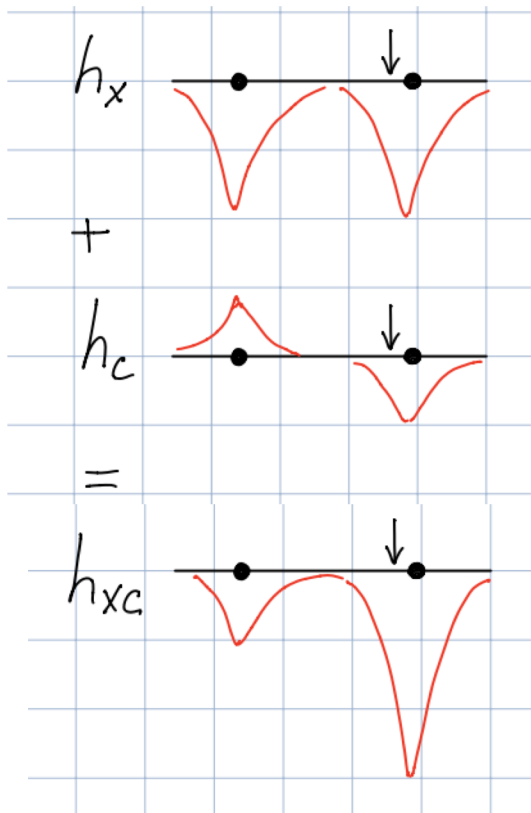
- transition states are too low (too stable)
- loose electrons in anions
- charge-transfer states are too low
- small band gaps
- dissociation energies of ions are too low
- Rydberg states are too low

# Why not to use the HF exchange in DFT?

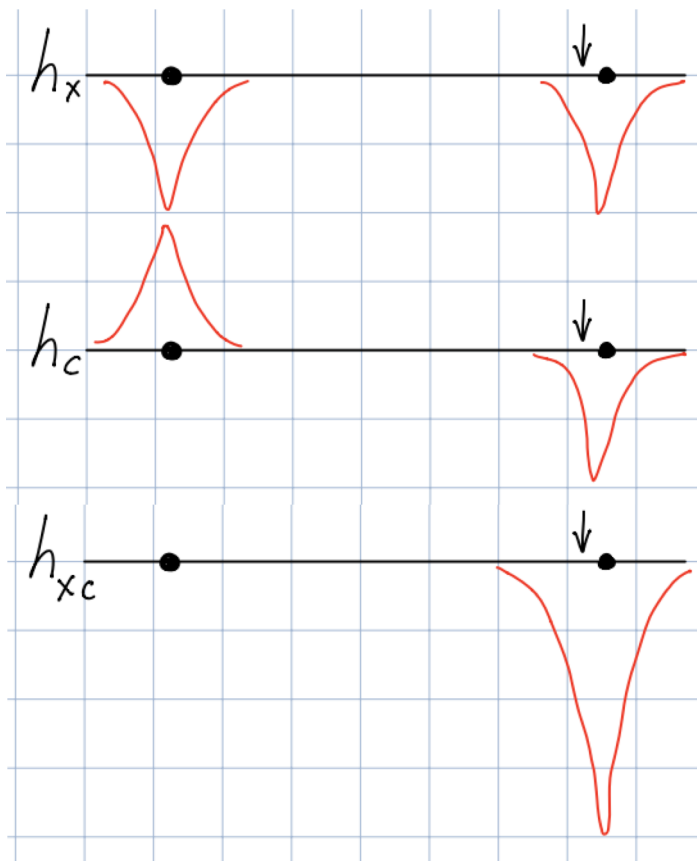
If the Hartree-Fock exchange so nicely cancels out electron self-interaction, why not use it in DFT, and add a correlation functional to describe correlation?

Consider  $H_2$  modeled with FCI

Near equilibrium



large separation



wave function methods:

delocalized  $h_x$  +  
delocalized  $h_c \rightarrow$   
might cancel to produce  
localized  $h_{xc}$

DFT:

localized  $h_x$  +  
localized  $h_c \rightarrow$   
localized  $h_{xc}$

delocalized HF  $h_x$  +  
Localized DFT  $h_c \rightarrow$   
delocalized  $h_{xc}$  **BAD**

# Functionals. LDA

Perdew-Jacob's ladder of approximations:  $n \rightarrow \nabla n \rightarrow \nabla^2 n \rightarrow \dots$

1. **Local density approximation (LDA)**: functionals depend on density only

- often called LSDA (local spin density approximation)
- exchange from the uniform electron gas model:  $E_x^{LDA} = -c_X \int n^{\frac{4}{3}}(r) dr$
- correlation  $E_c^{LDA}$  : analytic expressions for low-density and high-density UEG, interpolated in the middle (Vosko-Wilk-Nusair (VWN), Perdew-Wang (PW))
- recall: Kohn-Sham approximation  $\rightarrow$  kinetic energy from Slater determinant
- accuracy similar to Hartree-Fock
- ~10% underestimation in exchange energy
- correlation is overestimated (often ~twice)
- bonds are too tight (by ~100 kJ/mol)
- LDA is exact for UEG!

# Functionals. GGA

2. **Gradient-corrected methods:** functionals depend on density and density derivatives  
non-local methods

Let's improve exchange functional with  $K_2[n] = -\frac{5}{216}(3\pi^5)^{-\frac{1}{3}} \int \frac{|\nabla n(r)|^2}{n^{\frac{4}{3}}(r)} dr$

and similarly for correlation. But these corrections break properties of holes (integrals are not -1 and 0 for  $h_x$  and  $h_c$ )

→ **Performance worse than LDA** 😞

Solution: Generalized Gradient Approximation (GGA)

$\nabla n$  becomes a variable + condition on  $h_x$  and  $h_c$

# Functionals. GGA

**Generalized Gradient Approximation (GGA)** :  $\nabla n$  becomes a variable + condition on  $h_x$  and  $h_c$

$$E_x[n] = \int n(r) \varepsilon_x[n(r)] dr$$

energy per particle (energy density)

Axel Becke (1988):

$$\varepsilon_x^{B88} = \varepsilon_x^{LDA} + \Delta\varepsilon_x^{B88}$$

$$\Delta\varepsilon_x^{B88} = -\beta n^{\frac{1}{3}} \frac{x^2}{1 + 6\beta x \sinh^{-1} x}$$

fitted to rare gases

$$x = \frac{|\nabla n|}{n^{\frac{4}{3}}}$$

**Reduces error in exchange energy by 2 orders! for the cost of 1 parameter**

GGA correlation: LYP (Lee, Yang, Parr) – 4 parameters fitted to He

**BLYP**, PW86, PW91 (Perdew, Wang), **PBE** (Perdew, Burke, Ernzerhof)

# Functionals. Meta-GGA

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## 3. Meta-GGA

include Laplacian  $\nabla^2 n$  or orbital kinetic energy density

BR, B95, HCTH, TPSS, ...

Not a significant improvement in accuracy

# Functionals. Hybrid or Hyper-GGA

4. Back to self-interaction problem: **hybrid or hyper-GGA functionals** include a portion of the Hartree-Fock exchange

adiabatic connection formula (slowly turning on the interaction between electrons):

$$E_{xc} = \frac{1}{2}E_x^{HF} + \frac{1}{2}(E_x^{LDA} + E_c^{LDA})$$

$$E_{xc}^{B3LYP} = (1 - a)E_x^{LDA} + aE_x^{HF} + b\Delta E_x^{B88} + (1 - c)E_c^{LDA} + cE_c^{LYP}$$

**B3LYP**:  $a=0.20$ ,  $b=0.72$ ,  $c=0.81$

**PBE0**

HF & LDA exchange produce error cancelation



# Functionals. Double hybrid methods

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## 5. Double hybrid methods:

- add MP2 (perturbation theory) correlation

- high computational cost