CHM 673, Quiz 7 Name_____

1. Formulate the Hohenberg-Kohn theorem.

2. Which term is the least accurate in the Thomas-Fermi-Dirac (orbital-free) density functional theory?

3. What is the main idea of the Kohn-Sham DFT?

4. What is the origin of the self-interaction error in the Kohn-Sham DFT?

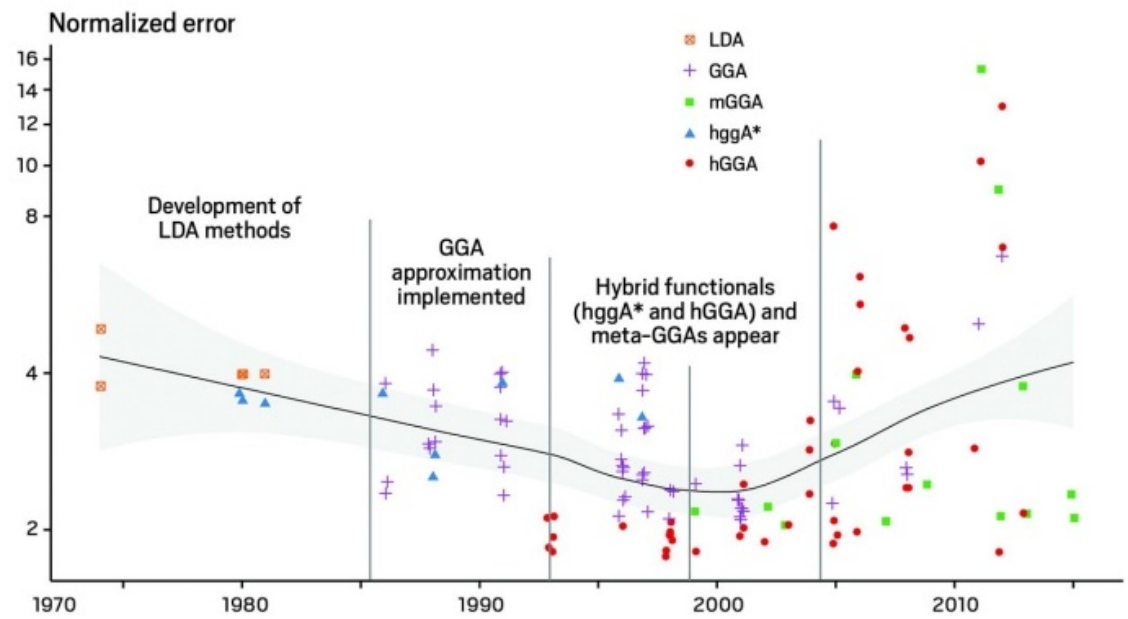
?

5. Why are KS-DFT calculations typically much faster than correlated wave function methods?

a. They yield accurate densities
b. They only solve a non-interacting problem ← ?
c. They use perturbation theory
d. They use empirical information about the system

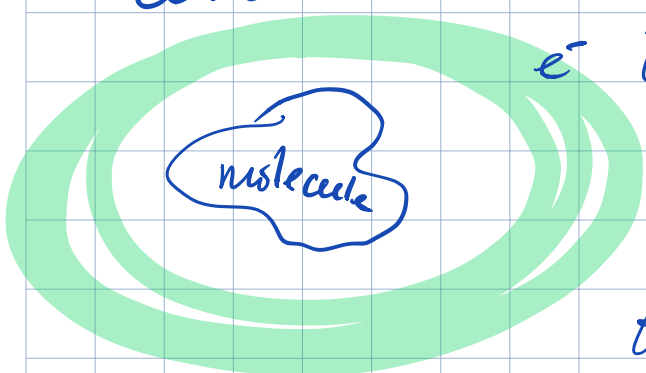
world

functional is empirical



Self-interaction error tends to over-delocalize electrons

anion



e^- becomes unbound

$\varepsilon_{HOMO} > 0$

Especially in diffuse basis sets electron is not bound

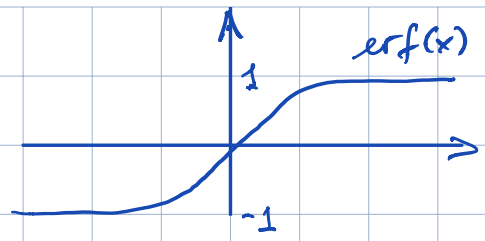
Fix: use range-separated functionals

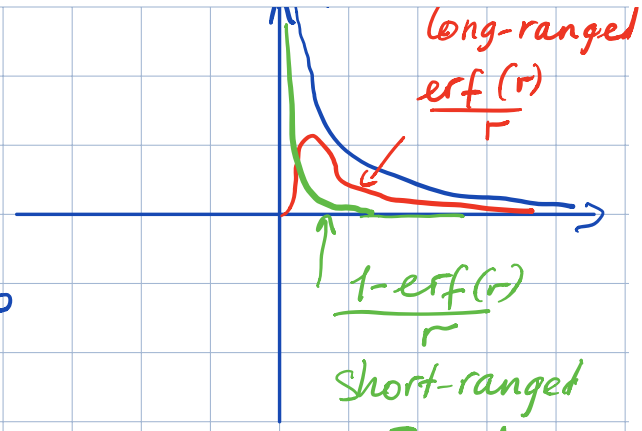
$$\frac{1}{r_{12}} = \frac{1-\mathrm{erf}(\omega r_{12})}{r_{12}} + \frac{\mathrm{erf}(\omega r_{12})}{r_{12}} \leftarrow \text{exact}$$

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$

HF exchange

$\sim 1/r$



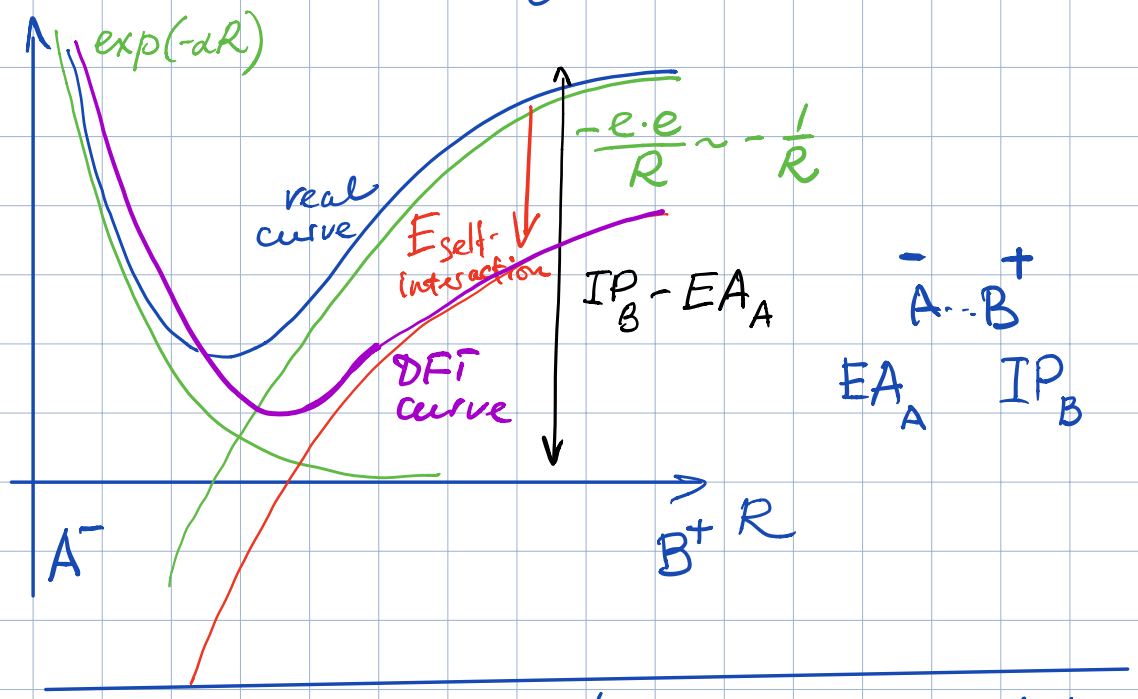


LC	LC-BLYP
ω	ωB97x
CAM	CAM-B3LYP

ω - parameter, ω ~ 0.3-0.5 Bohr

ω is both system dependent & functional dependent

Problem of charge-transfer states



$A^- \cdots B^+$

EA_A IP_B

How to describe long-range correlation?

DFT correlation functional accounts for dynamic correlation aka dispersion

$$E_{disp} \sim \frac{C_6}{R^6} + \frac{C_8}{R^8} + \frac{C_{10}}{R^{10}} + \dots$$

vdW

$C_6 \sim f(\alpha_A \alpha_B)$ α - polarizability

vdW in force fields is described as $\frac{C_{12}}{R^{12}} - \frac{C_6}{R_6}$

$C_6 = \sqrt{C_A C_B}$ ← coefs. on atoms A and B

DFT:

$$\Delta E_{disp} = -\sum_{n=6(8,10)} S_n \sum_{A-B}^{atoms} \frac{C_n^{AB}}{R_{AB}^n} f_{damp}(R_{AB})$$

functional-dependent coeff.

ensures correct short-range behavior

D / D2 / D3

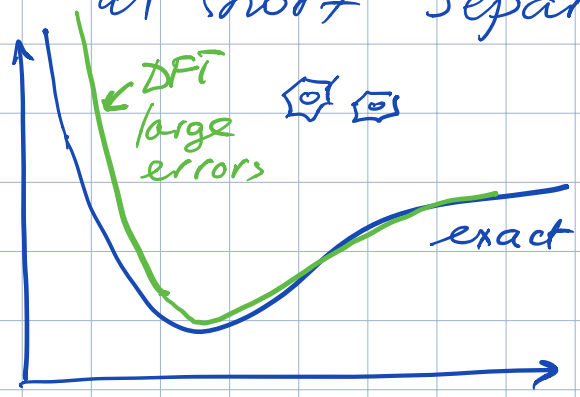
B3LYP-D2

ΔE_{disp} - additive correction to KS energy → does not depend on density

Concerns: - no dependence on density (not sensitive to multiplets, excited states)

- f_{damp} not accurate for strained complexes → large errors

at short separations



Other ideas: use polarizabilities either expt. (Tkatchenko f-ns) or computed (Johnson), add dependence on density

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Computational cost

KS eq-ns are similar to Fock eq-ns

diagonalization of KS matrix $\sim K^3$

K # of basis functions

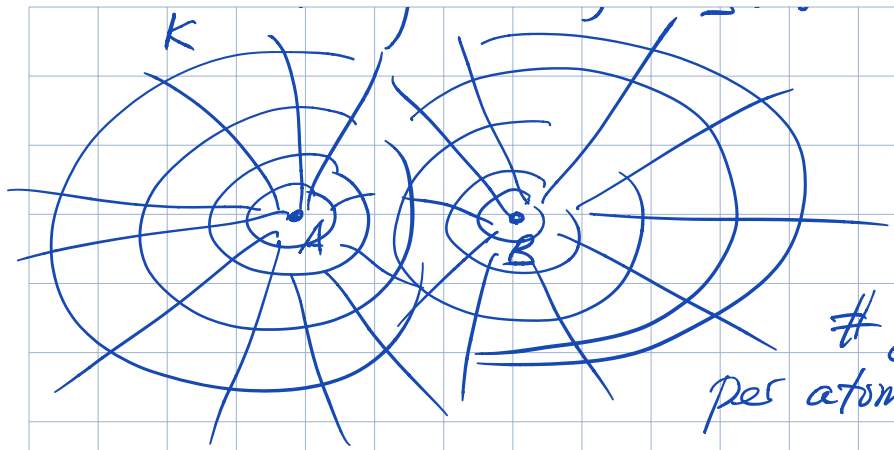
Coulomb integrals K^4

$$V_{xc}[\rho(r), \nabla\rho(r), \nabla^2\rho(r)]$$

$$\int \chi_i(r)\, V_{xc}[\rho(r), \nabla\rho(r)]\, \chi_i(r)\, dr$$ no analitical formulas

Numerical integration:

$$\sum^{\text{Grid}} V_{xc}[\rho(r_k), \nabla\rho(r_k)]\, \chi_i(r_k)\, \chi_i(r_k)\, \Delta V_k \sim$$



volume

$G \cdot K^2$

↳ linear with system size

grid points per atom: 1000 ÷ 10,000

Grid is similar to basis set, tighter grid gives more accurate energy

Geom. opt. and frequencies need tighter grid than energy calcs.

Differencies between DFT & HF

DFT can be exact theory,

HF - no way

<u>Orbital energies</u>

HF: occ. orbitals - IP

vir. orbitals - EA (N electron)

DFT: occ. orbitals $\varepsilon_i = \frac{\partial E}{\partial n_i}$

(Janak theorem) occupation number of the orbital

still ~ related to IP

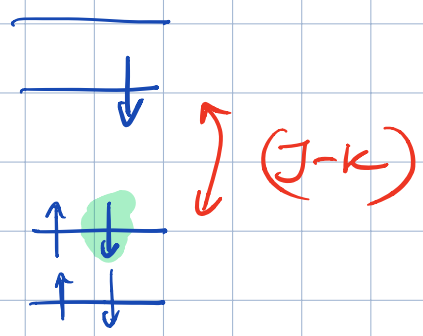
virtual orbitals are computed in field of N-1 electrons →

correspond to exciting (rather than attaching) an electron

DFT virtuals are lower than HF virtuals

DFT: occ-vir gap ~ excitation energy

HF : ~ $+(J-K)$



Project presentations: April 28, 30