

# CHM 673

## Lecture 18: Density Functional Theory, part 3

---

Suggested reading:

Chapter 6.5-6.8 from Jensen

# DFT summary

---

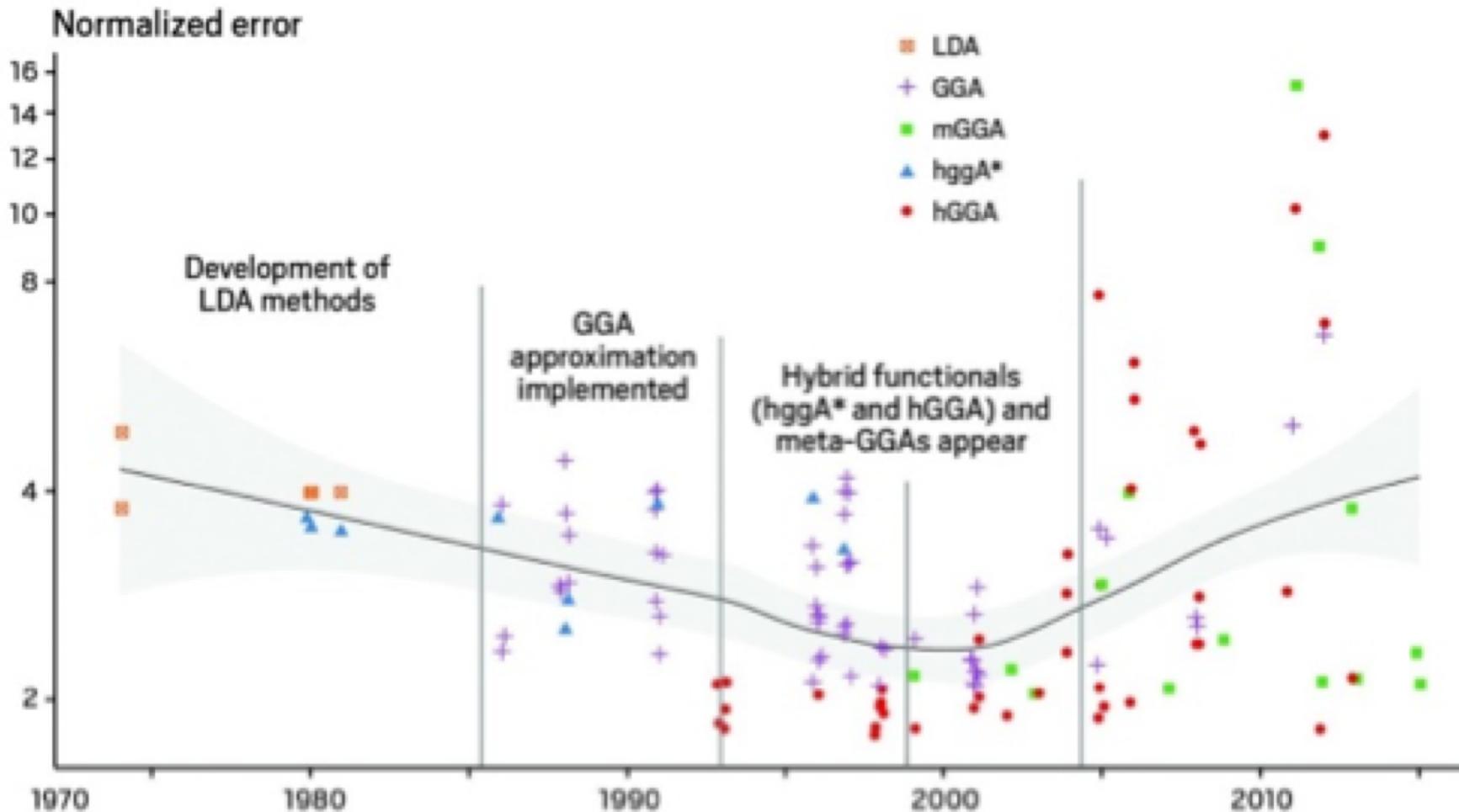
## Pros

- Computational cost & scaling: similar to Hartree-Fock
- Superb geometries and frequencies
- Good energetics for covalent systems
- Smaller spin-contamination in open-shell systems

## Cons

- Every functional goes nuts on some system or other
- Missing long-range correlation (van der Waals interactions) → functionals with D (dispersion) corrections
- Non-dynamical (multireference) correlation is not treated correctly  
(e.g. DFT should not be applied to metals without careful benchmarking!)
- Errors due to electron self-interaction (loosely bound electrons in anions, destabilized transition states, charge-transfer states) → hybrid and long-range corrected functionals
- States of different multiplicities (HF favors high spin, DFT favors low spin) → hybrid functionals might help

# DFT development: errors in the density

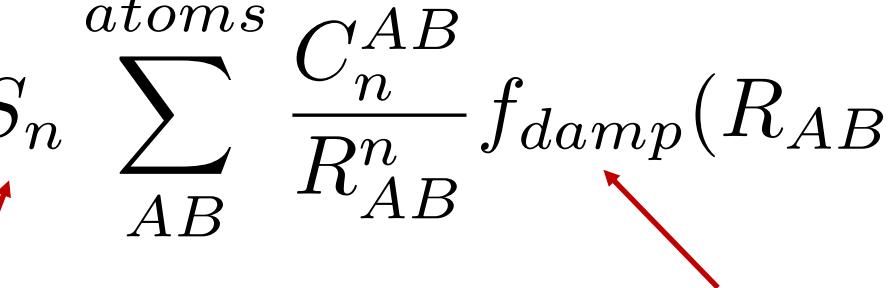


# Partial solutions to DFT problems: long-range correlation

Due to their local nature, DFT correlation functionals describe short-range (dynamic) but not long-range correlation → **description of weakly bound complexes dominated by dispersion interactions is unreliable**

Idea: describe dispersion as in force fields, assigning each atom with (semi)empirical  $C_n$  coefficients (Stefan Grimme):

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



Functional-dependent scaling coefficient

Damping function ensures correct short-range behavior

Several generations of dispersion corrections: D, D2, D3...

Functionals: B3LYP-D3, wB97x-D, etc

# Partial solutions to DFT problems: long-range correlation

---

$\Delta E_{disp}$  - additive correction to KS energy → does not depend on density

Concerns:

- Dispersion correction does not depend on density: not sensitive to multiplets (e.g. singlets versus triplets), excited states, etc
- $f_{damp}$  might be not accurate for highly strained complexes → large errors at short separations

Other ideas for incorporating dispersion into KS-DFT:

- use polarizability (instead of  $C_n$  coefficients), either from experiment (Tkatchenko functionals) or computed (Johnson)
- add dependence on density

## Partial solutions to DFT problems: long-range corrected functionals

---

Self-interaction error tends to over-delocalize electrons → errors in dissociation energies of anions, excitation energies of charge-transfer and Rydberg states

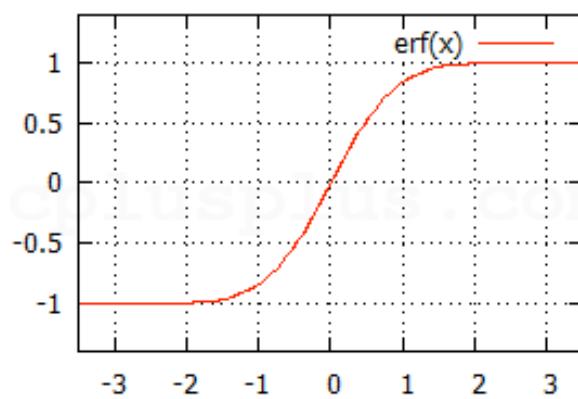
# Partial solutions to DFT problems: long-range corrected functionals

Fix: range-separated (or long-range corrected) functionals

Use different exchange functionals for short-range and long-range parts

$$\frac{1}{|r_1 - r_2|} = \frac{1}{r_{12}} = \frac{1 - \operatorname{erf}(\omega r_{12})}{r_{12}} + \frac{\operatorname{erf}(\omega r_{12})}{r_{12}}$$

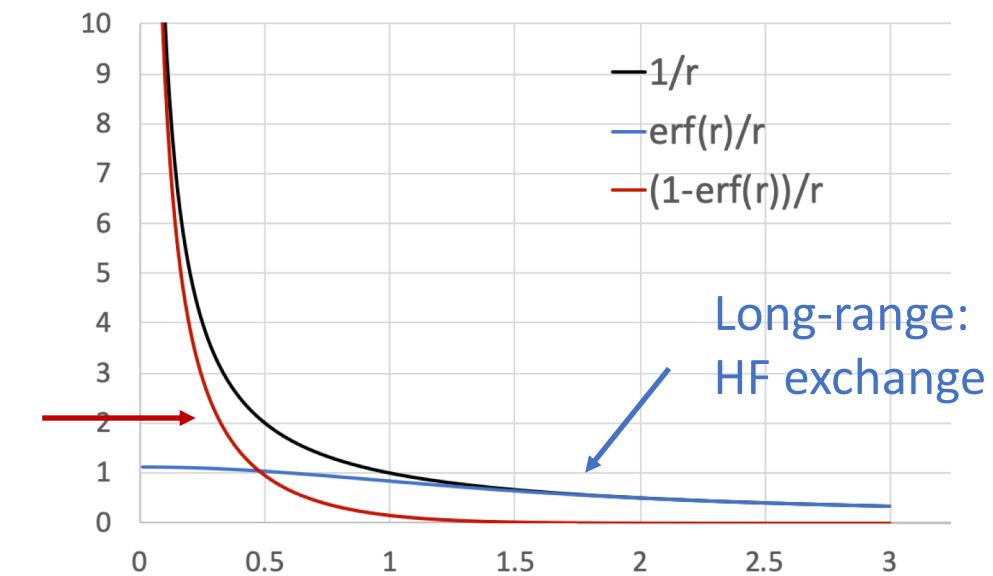
$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$



short-range:  
DFT exchange

$\omega$  – parameter,  $\omega \sim 0.3\text{-}0.5$  Bohr

$\omega$  is both system- and functional-dependent



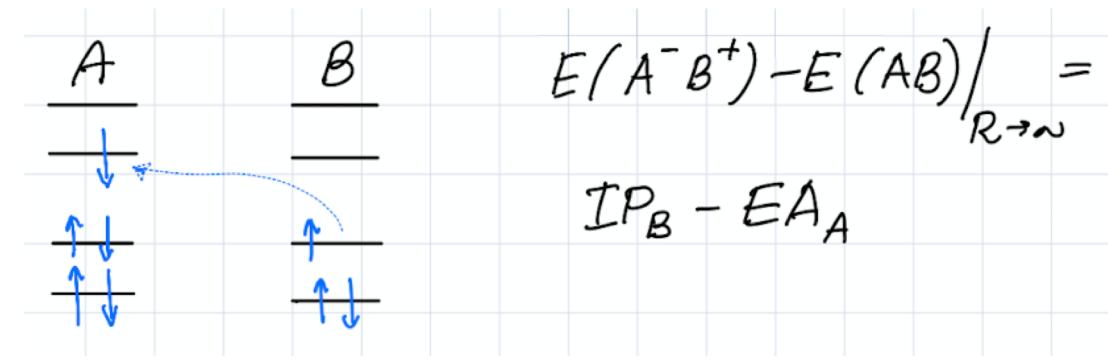
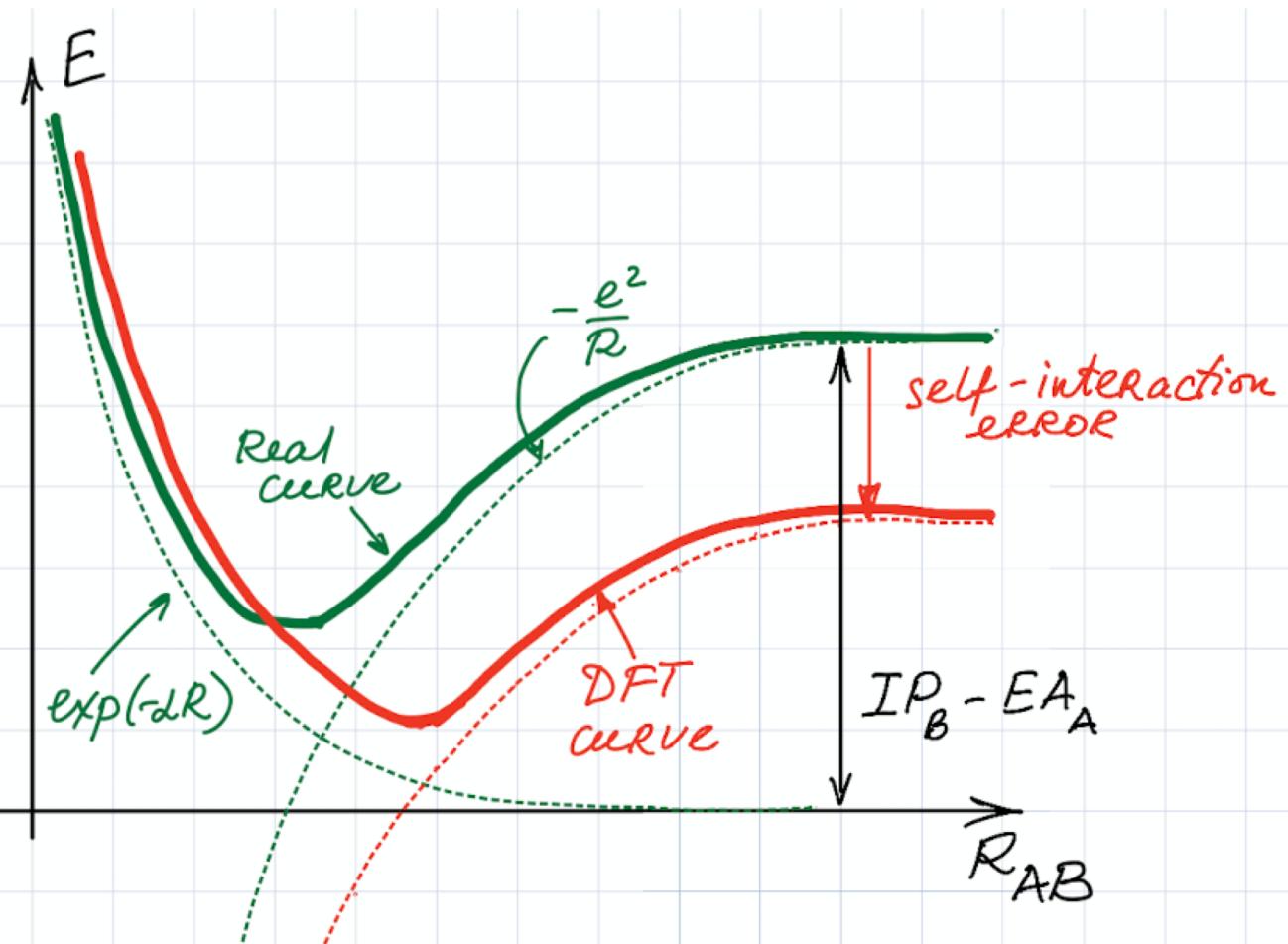
Common functionals:

LC: LC-BLYP

$\omega$ :  $\omega$ B97x

CAM: CAM-B3LYP

# Charge-transfer states in DFT



# Performance of DFT functionals (RMSDs in kcal/mol)

Molecular Physics, 115:19, 2315-2372

# Computational cost

Kohn-Sham equations are similar to Hartree-Fock equations:

- Diagonalization of KS matrix  $\sim K^3$  ( $K$  - # of basis functions)
- Coulomb integrals  $\sim K^4$

Different from HF, in KS theory we need to compute integrals of exchange-correlation potential:

$$\int \chi_i^*(r) V_{xc}[\rho(r), \nabla \rho(r)] \chi_i(r) dr$$

As those do not have analytical formulas, numerical integration on the grid is used:

$$\sum_k^{\text{Grid}} V_{xc}[\rho(r_k), \nabla \rho(r_k)] \chi_i^*(r_k) \chi_i(r_k) dV_k \quad \begin{matrix} \sim GK^2 \\ \text{linear with system size} \end{matrix}$$

spherical grid around nuclei: 1000-10,000 points per atom

- grid is similar to basis set: tighter grid gives more accurate energy
- geometry optimization & frequencies require tighter grid than energy calculations

# KS DFT and HF: comparison

DFT: can be an exact theory

HF is exact only for 1-electron systems or non-interacting electrons

## Orbital energies

HF: occupied orbitals – IPs  
virtual orbitals - EAs

DFT: occupied orbitals  
are still related to IPs  
(Janak theorem)  
virtual orbitals – correspond to exciting an  
electron (not attaching an electron as in HF!)

$$\varepsilon_i = \frac{\partial E}{\partial n_i}$$

DFT virtuals are lower than HF virtuals!

# HF model: orbital energies

$$\hat{f}_i |\chi_i\rangle = \varepsilon_i |\chi_i\rangle$$

$$\hat{f}_i = \hat{h}_i + \sum_j^{N_{elec}} (\hat{J}_j(i) - \hat{K}_j(i))$$

For occupied orbital k:

$$\hat{f}_k = \hat{h}_k + \sum_j^{N_{elec}} (\hat{J}_j(k) - \hat{K}_j(k)) = \hat{h}_k + \sum_{j \neq k}^{N_{elec}} (\hat{J}_j(k) - \hat{K}_j(k))$$

(Red arrow pointing to the term  $(\hat{J}_k(k) - \hat{K}_k(k))$ )

$$(\hat{J}_k(k) - \hat{K}_k(k))=0$$

→ Electron on occupied orbital k experiences field from (N-1) other electrons

For virtual orbital a:

$$\hat{f}_a = \hat{h}_a + \sum_j^{N_{elec}} (\hat{J}_j(a) - \hat{K}_j(a))$$

→ Electron on virtual orbital a experiences field from N other electrons

$\varepsilon_a$  corresponds to electron attachment to orbital a

# Kohn-Sham model: orbital energies

---

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

$$\hat{f}^{KS}(r) = \hat{h}(r) + \int \frac{n(r')}{|r - r'|} dr' + V_{xc}(r)$$

exchange-correlation potential       $V_{xc} = \frac{\delta E_{xc}}{\delta n}$

Electrons placed either on occupied or virtual orbitals experience a field of (N-1) electrons

$$\varepsilon_a - \varepsilon_i \approx \omega_{ia} \quad \omega_{ia} \text{ - excitation energy}$$

true for non – hybrid functionals only