

W.f. methods:

h_x is delocalized

h_c is delocalized

DFT models:

h_x is local

h_c is local

hard to mix DFT & HF exchange functionals

Self-interaction

$$\text{HF: } J - K = \int \chi_i^*(1) \chi_j^*(2) \frac{1}{r_{12}} \chi_i(1) \chi_j(2) d\mathbf{r}_1 d\mathbf{r}_2 - \int \chi_i^*(1) \chi_j^*(2) \frac{1}{r_{12}} \chi_i(2) \chi_j(1) d\mathbf{r}_1 d\mathbf{r}_2$$

$$\text{if } i=j \rightarrow J - K = 0$$

$$\text{DFT: } J[\rho] = \frac{1}{2} \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \neq 0$$

↓
self-interaction

for 1 electron

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

energy of more delocalized electron is more favorable (electron hates itself less)

Chemical problems:

transition states are too low (too stable)

anions - loose electrons

charge-transfer states - too low

Functionals

ladder of approximation →

$$\rho \rightarrow D\rho \rightarrow D^2\rho \rightarrow \dots$$

1) Local density approximation

LDA

LSDA

spin

use functionals from UEG

$$E_x^{LDA} = -C_x \int \rho^{4/3}(r) dr$$

E_c^{LDA} analytic expressions for
low-density and high-density UEG,
interpolate in the middle

VWN

PW Perdew, Wang

Remember: Kohn-Sham approximation

→ kinetic energy from orbitals!

accuracy ~ HF

10% error in exchange

correlation ~ about twice bigger

fonds are too tight
 LDA is exact for UEG!

2) Gradient-corrected methods

non-local methods : $\rho, \nabla\rho$

$$K_2[\rho] = \dots \int \frac{(\nabla\rho)^2}{\rho^{4/3}(r)} dr$$

but breaks properties of holes:

$$\int h_h dr \neq -1 \quad \begin{matrix} \text{performance worse} \\ \text{than in LDA} \end{matrix}$$

GGA: generalized gradient appr.

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

Axel Becke: (1988)

$$E_x[\rho] = \int \rho(r) \mathcal{E}_x[\rho] dr \quad \begin{matrix} \nwarrow \\ \text{energy per particle} \end{matrix}$$

$$\mathcal{E}_x^{B88} = \mathcal{E}_x^{LDA} + \Delta \mathcal{E}_x^{B88}$$

$$\Delta \mathcal{E}_x^{B88} = -\beta \rho^{1/3} \frac{x^2}{1 + 6\beta x \sinh^{-1} x}$$

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

fitted on rare gases

reduces error in exchange by 2 orders!

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

BLYP

PW86, PW91 Perdew, Wang

PBE

Perdew, Burke,
 Ernzerhof

3) Meta-GGA

include Laplacian $D^2\rho$
 or orbital kinetic energy density
 $T = \frac{1}{8}\rho^{1/2}$

BR

B95, HCTH, TPSS...

not a significant improvement in accuracy

Back to self-interaction problem :

4) Hybrid or hyper-GGA functionals

adiabatic connection formula

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

$$\text{non-interacting : } E_0 = \langle \psi_0 | \hat{T} | \psi_0 \rangle + \int \rho(r) V_{ext}(r) dr$$

$$\begin{aligned} \text{interacting } E_1 &= \langle \psi_0 | \hat{T} | \psi_0 \rangle + \int \rho(r) V_{ext}(r) dr \\ &\quad + \int_0^1 \langle \psi_\lambda | V_{ee} | \psi_\lambda \rangle d\lambda \end{aligned}$$

$$\langle \psi_\lambda | V_{ee} | \psi_\lambda \rangle = \frac{1}{2} \left(\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho_2(\lambda, r_1, r_2) dr_1 dr_2 \right)$$

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

define $V_{xc}^{\text{hole}}(\lambda, r) = \frac{1}{2} \int \frac{h_{xc}(\lambda, r_1, r_2)}{(r_1 - r_2)} dr_1 dr_2$

$$E_{xc} \approx \frac{1}{2} \left(\langle \psi_0 | V_{xc}^{\text{hole}}(0) | \psi_0 \rangle + \langle \psi_1 | V_{xc}^{\text{hole}}(1) | \psi_1 \rangle \right)$$

linear in λ no interaction
 exchange = HF exchange (unknown)
 DFT ex.-corr.

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

$$\begin{aligned} E_{xc}^{\text{B3LYP}} &= (1-a) E_x^{\text{LDA}} + a E_x^{\text{HF}} + b \Delta E_x^{\text{B88}} + \\ &\quad + (1-c) E_c^{\text{LDA}} + c E_c^{\text{LYP}} \end{aligned}$$

$$\text{B3LYP : } a = 0.20, \quad b = 0.72, \quad c = 0.81$$

PBE₀

HF & LDA produce error cancellation

5) double hybrid methods

add MP2 correlation

high computational cost

+

Problems in DFT:

- long-range correlation (dispersion)
vdW interactions
 - loosely bound electrons (anions, TS) ←
Self-interaction error
 - CT states and systems ↗
 - states with different multiplicities
HF favors high spin, DFT favors low spin
-

Affination energies, ionization energies,
electron & proton affinities

~ 400 molecules

Functional	Type	RMS (kJ/mol)	MAD (kJ/mol)
HF	-	649	885
LDA	local density, ρ	439	510
PW91	GGA	80	99
PBE		87	93
BLYP	ρ , $D\rho$	41	40
B3LYP	hybrid, ρ , $D\rho$	40	21

Advantages of DFT:

- scaling : similar to HF
- geometries & frequencies - similar to MP2
- systems with MR character ~ similar to CC
- Smaller spin-contamination (el. correlation)

(' multi-reference is included)