A Trip to the Density Functional Theory Zoo
(ground states)

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THE UNIVERSITY OF MELBOURNE

RACI Phys Chem Division Webinar Series 2021

1. DFT basics

2. The Jacob's Ladder classification

3. The London-dispersion problem

4. Finding a way through the DFT zoo

(5. Self interaction error; optional)

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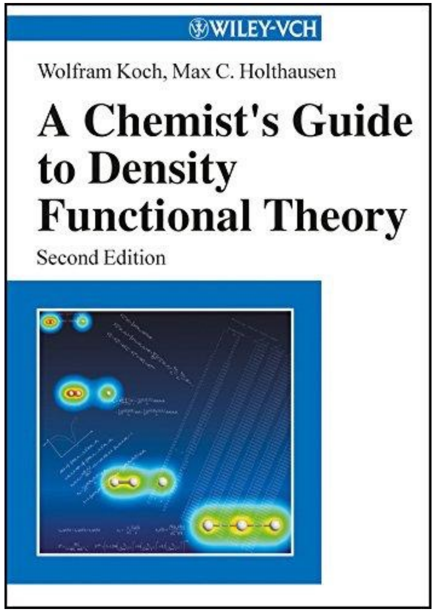
Everyone has heard of and can easily use DFT … … … really?

see presentation for content

Recommended reading for people new to this field

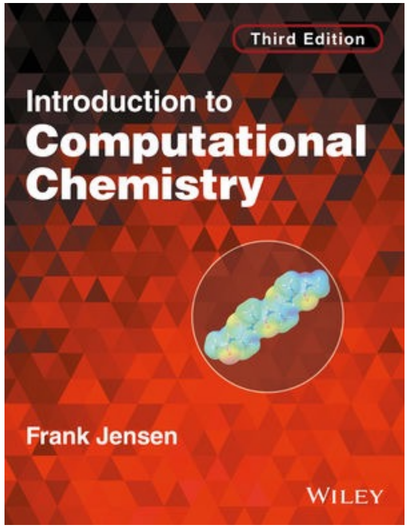


W. Koch and M. C. Holthausen
A Chemist's Guide to Density Functional Theory
2nd edition, Wiley

(Chapters 1-7; the other chapters may no longer be that relevant)

F. Jensen
Introduction to Computational Chemistry
3rd edition, Wiley

(Chapter 6)



The electronic wave function and the electron density

electronic coordinates ("r" stands for a general coordinate; could be x, y, z)

$$\boldsymbol{\Psi}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}, \ldots, \mathbf{r_N})$$

In Cartesian coordinates: wave function depends on 3N spatial variables! 4N if you also consider spin.

We cannot observe the wave function!

The ***square of the wave function*** is a probability distribution.
The wave function is normalised because the probability of finding all N electrons anywhere in space must be 1:

$$\int |\, \boldsymbol{\Psi}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}, \ldots, \mathbf{r_N}) \,|^2 \, \mathbf{dr_1 dr_2 dr_3 \ldots dr_N} = 1$$

The ***square of the wave function*** is related to the electron density.
The electron density is the probability of finding any of the N electrons at position r_1, while the remaining electrons have arbitrary positions represented by the wave function:

number of electrons

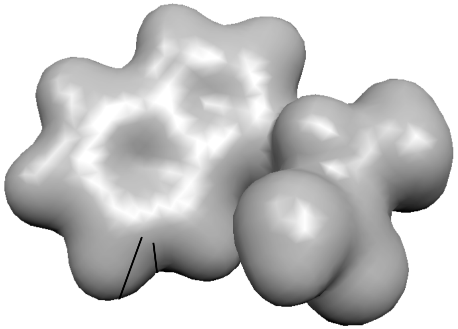
$$\rho(\mathbf{r_1}) = \mathrm{N} \int |\, \boldsymbol{\Psi}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}, \ldots, \mathbf{r_N}) \,|^2 \, \boxed{\mathbf{dr_2 dr_3 \ldots dr_N}}$$

The electron density is observable (X-ray scattering)!

Properties of the electron density

isosurface plots (constant electron density)

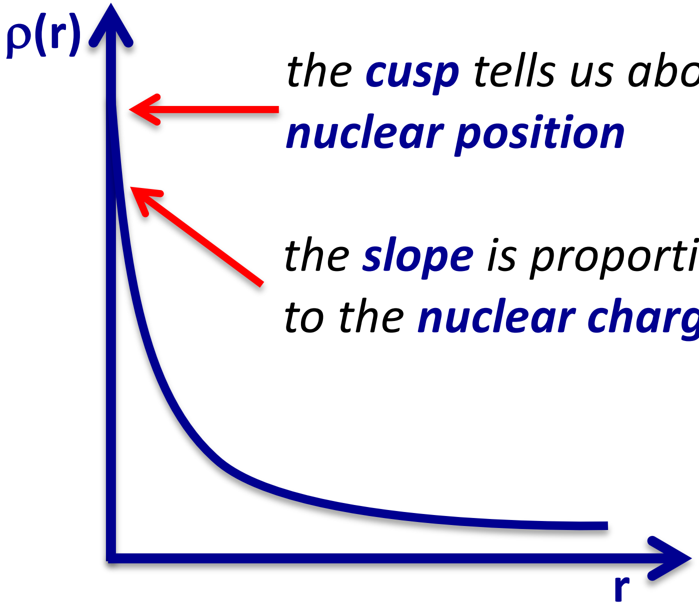
tryptophan



water

relief map for water
(values of the density projected onto a plane)

see presentation for image



*the **cusp** tells us about the **nuclear position***

*the **slope** is proportional to the **nuclear charge***

$$\rho(\mathbf{r_1}) = \mathrm{N}\int |\,\mathbf{\Psi}(\mathbf{r_1},\mathbf{r_2},\mathbf{r_3},...,\mathbf{r_N})\,|^2\, \mathbf{dr_2dr_3...dr_N}$$

$$\int \rho(\mathbf{r_1})\mathbf{dr_1} = \mathrm{N}\underbrace{\int\int |\,\mathbf{\Psi}(\mathbf{r_1},\mathbf{r_2},\mathbf{r_3},...,\mathbf{r_N})\,|^2\, \mathbf{dr_1dr_2dr_3...dr_N}}_{=1}$$

$$\boxed{\int \rho(\mathbf{r_1})\mathbf{dr_1} = \mathrm{N}}$$

Properties of the electron density

Positions of nuclei → cusps in ρ(r)

nuclear charges → slopes of ρ(r) at nuclear positions

number of electrons → ρ(r) integrated over the entire space

↓

ρ(r) contains all information needed to describe a molecule

↓

Can we formulate a theory based entirely on ρ(r)?

Advantages:

- **no need for Ψ!**
- **ρ only depends on three variables (x,y,z)!**

A theory without wave functions?

conventional Wave Function Theory (WFT)

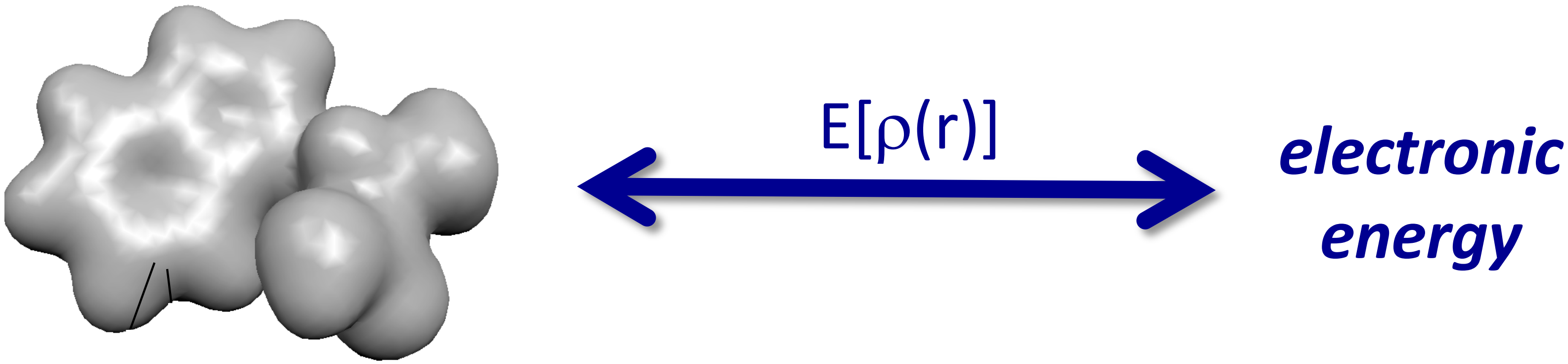
prescription to obtain the electronic energy

$$\begin{tikzcd}
 & \Psi \arrow[dr] & \\
\hat{\mathrm{H}} \arrow[ur] \arrow[rr, leftrightarrow] & & \rho \propto |\Psi|^2
\end{tikzcd}$$

Is there a direct connection between the two observables "electron density" and "electronic energy" ?

Density Functional Theory (DFT)

- 1st Hohenberg-Kohn Theorem (1964): the electronic ground-state energy of a system depends uniquely on its electron density ρ(r).



E[ρ(r)]

electronic energy

- DFT is an *exact* theory and the *true* E[ρ(r)] gives us an energy equivalent to the exact solution of the Schrödinger Equation.

Hohenberg, Kohn *Phys. Rev.* **1964**, *136*, B864.

Significance and limitations of the Hohenberg-Kohn Theorems

- The true functional solves the Schrödinger Equation exactly at a negligible cost compared to electron-correlation wavefunction theory (WFT) methods.

➡ **DFT is an exact theory!**

- The true functional does not rely on the wave function of the system.

➡ **There are no orbitals in pure DFT!**

- The true functional is universal.

➡ **Problem: The theorems do not tell us what the true functional looks like.**

General form of the energy functional

electron-nucleus interaction

known expression:

nuclei

$$-\sum_{\mathbf{I}}^{\mathbf{M}}\int\frac{\mathbf{Z_I}\rho(\mathbf{r})}{|\mathbf{R_I}-\mathbf{r}|}\mathbf{dr}$$

non-classical effects

exchange, correlation, correction for self interaction

unknown expression:

needs to represent the exchange-correlation hole (see textbooks for more information)

$$\mathbf{E}[\rho]=\mathbf{V_{ne}}[\rho]+\mathbf{V_{ee}}[\rho]+\mathbf{T}[\rho]+\mathbf{E_{XC}}[\rho]$$

classical Coulomb energy

known expression:

$$+\frac{1}{2}\int\int\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathbf{drdr}'$$

➡ ***suffers from self interaction***

kinetic energy

unknown expression:

*example: the **Thomas-Fermi model** (see textbooks for more information)*

➡ **The main problem of orbital-free DFT is to find an accurate approximation to the kinetic-energy functional**

Interlude: Energy expressions in wave function theory

The energy is expressed as an expectation value of an operator

$$\mathbf{\hat{H}\Psi(r) = E\Psi(r)} \quad \Rightarrow \quad \int \mathbf{\Psi^*(r)\hat{H}\Psi(r)dr} = \left\langle \mathbf{\Psi} \mid \mathbf{\hat{H}} \mid \mathbf{\Psi} \right\rangle = \mathbf{E}$$

bra-ket notation

The electronic Hamiltonian is a sum of separate operators:

$$\mathbf{\hat{H} = \hat{T} + \hat{V}_{ne} + \hat{V}_{ee}}$$

With the kinetic energy operator:

$$\mathbf{\hat{T}} = -\frac{\mathbf{1}}{\mathbf{2}}\sum_{\mathbf{i}}^{\mathbf{N}} \nabla_{\mathbf{i}}^{\mathbf{2}}, \qquad \mathbf{with} \qquad \nabla^{\mathbf{2}} = \frac{\mathbf{d^2}}{\mathbf{dr^2}}$$

The kinetic energy in an *N*-electron system is therefore:

$$\left\langle \mathbf{\Psi} \mid \mathbf{\hat{T}} \mid \mathbf{\Psi} \right\rangle = \mathbf{T}$$

Interlude: Hartree-Fock (HF) theory

- By describing the wave function with one-particle functions (MOs), we break the N-electron Schrödinger Equation down into ***N*** separate, effective one-electron equations (**independent particle model**).

$$\begin{aligned}\hat{\mathbf{f}}\phi_{\mathbf{1}}\left(\mathbf{r_1}\right) &= \epsilon_{\mathbf{1}}\phi_{\mathbf{1}}\left(\mathbf{r_1}\right)\\ \hat{\mathbf{f}}\phi_{\mathbf{2}}\left(\mathbf{r_2}\right) &= \epsilon_{\mathbf{2}}\phi_{\mathbf{2}}\left(\mathbf{r_2}\right)\\ &\vdots\\ \hat{\mathbf{f}}\phi_{\mathbf{N}}\left(\mathbf{r_N}\right) &= \epsilon_{\mathbf{N}}\phi_{\mathbf{N}}\left(\mathbf{r_N}\right)\end{aligned}$$

Fock operator

MO energies

- The **Fock operator** contains the same terms as the normal electronic Hamiltonian (kinetic energy, eN-interaction) plus an *effective ee-interaction term* (*see next slide*). In other words, the equations all depend a bit on one another, as we will see shortly.

- Despite relying on an average ee-interaction term, which leads to the bad description of electron correlation with HF, HF theory has an accurate exchange component, i.e.

➡ ***HF theory obeys the Pauli principle.***

Interlude: The Fock operator

The **Fock operator** is an effective one-electron operator as it acts on one electron at a time:

kinetic energy and electron-nucleus interaction: $-\frac{1}{2}\nabla^2 + \hat{\mathbf{V}}_{\mathbf{ne}}$

$$\hat{f}(1)\phi_i(1) = \left[\hat{h}(1) + \sum_j^N \hat{J}_j(1) - \sum_j^N \hat{K}_j(1)\right]\phi_i(1) = \epsilon_i\phi_i(1)$$

Coulomb operator:

note how the Coulomb operator introduces other MOs

$$\hat{J}_j(1)\phi_i(1) = \left[\int dr_2 \phi_j^*(2)\frac{1}{r_{12}}\phi_j(2)\right]\phi_i(1)$$

Exchange operator:

note how this operator introduces other MOs and induces the exchange of two orbitals

$$\hat{K}_j(1)\phi_i(1) = \left[\int dr_2 \phi_j^*(2)\frac{1}{r_{12}}\phi_i(2)\right]\phi_j(1)$$

HF describes electrons as independent particles. However, the sums involving the Coulomb and Exchange operators run over all MOs (i.e. electrons). Those sum expressions represent an averaged potential that interacts with the "independent" electron (**mean field approximation**)

Kohn-Sham DFT (KS-DFT) (1965)

Kohn, Sham *Phys. Rev.* **1965**, *140*, A1133.

Imagine a ***fictional reference system*** in which ***the electrons do not interact***.
This system must have ***exactly the same density*** as the real system.
We can calculate this density by ***reintroducing MOs*** (KS orbitals):

$$\rho = \sum_{\mathbf{i}}^{\mathbf{N}} \mid \phi_{\mathbf{i}}^{\mathbf{KS}} \mid^{\mathbf{2}}$$

The KS orbitals allow us to calculate the ***kinetic energy*** for this reference system of non-interacting electrons ***in the same was as we do in Hartree-Fock (HF) theory***:

$$\mathbf{T^{KS}} = -\frac{\mathbf{1}}{\mathbf{2}} \sum_{\mathbf{i}}^{\mathbf{N}} \langle \phi_{\mathbf{i}}^{\mathbf{KS}} \mid \nabla_{\mathbf{i}}^{\mathbf{2}} \mid \phi_{\mathbf{i}}^{\mathbf{KS}} \rangle$$

$$\boxed{\nabla^{\mathbf{2}} = \frac{\mathbf{d^2}}{\mathbf{dr^2}}}$$

This kinetic energy term is more accurate than the previous orbital-free ones.
We are now left with just ***one unknown component***:

same expressions as on slide 14

$$\mathbf{E^{KS}}[\rho] = \mathbf{V_{ne}}[\rho] + \mathbf{V_{ee}}[\rho] + \mathbf{T^{KS}} + \mathbf{E_{XC}^{KS}}[\rho]$$

The Exchange-Correlation Functional (unknown):

contains exchange and correlation; corrects for self interaction;
corrects for the difference between $\boldsymbol{T^{KS}}$ *and the exact* $\boldsymbol{T}$ *for interacting electrons*

The Kohn-Sham Equations

Describing our molecule with the help of a reference system of non-interacting electrons and reintroducing orbitals allows us to make use of the same underlying “machinery” that is used in HF theory. The Kohn-Sham Equations assume the form of effective one-electron equations:

KS-MO energy

$$\begin{aligned} \hat{\mathbf{f}}^{\mathbf{KS}} \phi_{\mathbf{1}}^{\mathbf{KS}}(\mathbf{r_1}) &= \epsilon_{\mathbf{1}}^{\mathbf{KS}} \phi_{\mathbf{1}}^{\mathbf{KS}}(\mathbf{r_1}) \\ \hat{\mathbf{f}}^{\mathbf{KS}} \phi_{\mathbf{2}}^{\mathbf{KS}}(\mathbf{r_2}) &= \epsilon_{\mathbf{2}}^{\mathbf{KS}} \phi_{\mathbf{2}}^{\mathbf{KS}}(\mathbf{r_2}) \\ &\vdots \\ \hat{\mathbf{f}}^{\mathbf{KS}} \phi_{\mathbf{N}}^{\mathbf{KS}}(\mathbf{r_N}) &= \epsilon_{\mathbf{N}}^{\mathbf{KS}} \phi_{\mathbf{N}}^{\mathbf{KS}}(\mathbf{r_N}) \end{aligned}$$

Kohn-Sham operator

KS-MO

Comparing the Kohn-Sham and Fock operators:

$$\begin{array}{lclclcl} \hat{\mathbf{f}}^{\mathbf{KS}} = & \overbrace{-\frac{1}{2}\nabla^2 + \hat{\mathbf{V}}_{\mathbf{ne}}}^{\hat{\mathbf{h}}} & + & \sum_{\mathbf{j}}^{\mathbf{N}} \hat{\mathbf{J}}_{\mathbf{j}} & + & \mathbf{V_{XC}}[\rho] \\ & \updownarrow \qquad\quad \updownarrow & & \updownarrow & & \not\updownarrow \\ \hat{\mathbf{f}} = & -\frac{1}{2}\nabla^2 + \hat{\mathbf{V}}_{\mathbf{ne}} & + & \sum_{\mathbf{j}}^{\mathbf{N}} \hat{\mathbf{J}}_{\mathbf{j}} & - & \sum_{\mathbf{j}}^{\mathbf{N}} \hat{\mathbf{K}}_{\mathbf{j}} \end{array}$$

Exchange-Correlation Potential:

$$\mathbf{V_{XC}}[\rho] = \frac{\delta \mathbf{E_{XC}}[\rho]}{\delta \rho}$$

The KS equations give us the exact energy for the true V_{xc}!

The HF equations do not give us the exact energy!

Solving the KS equations

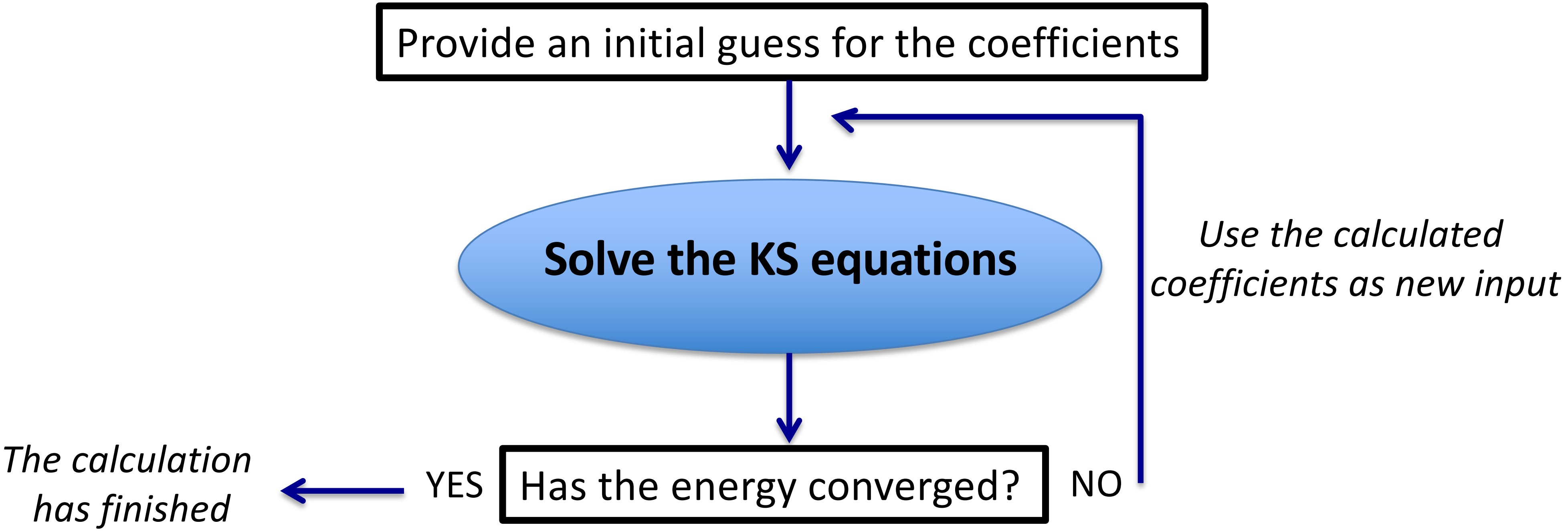
- The KS-MOs are described by a linear combination of known AOs (LCAO):

AOs (they define the basis set)

$$\hat{\mathbf{f}}^{\mathbf{KS}}\sum_{\mathbf{i}}\mathbf{c_i}\chi_{\mathbf{i}} = \epsilon_{\mathbf{N}}^{\mathbf{KS}}\sum_{\mathbf{i}}\mathbf{c_i}\chi_{\mathbf{i}}$$

input: a set of coefficients ⟷ *output: a set of coefficients*

- The KS equations are then solved with an iterative **self-consistent-field (SCF)** approach



Provide an initial guess for the coefficients

Solve the KS equations

Use the calculated coefficients as new input

Has the energy converged?

NO

YES

The calculation has finished

→ Each iteration lowers the energy until we reach a minimum.

Pros and cons of the Kohn-Sham approach

👍 Computational techniques similar to HF can be used.

👍 Unlike HF, correlation is included.
(“the orbitals are correlated”)

👍 Exact for the true exchange-correlation potential.

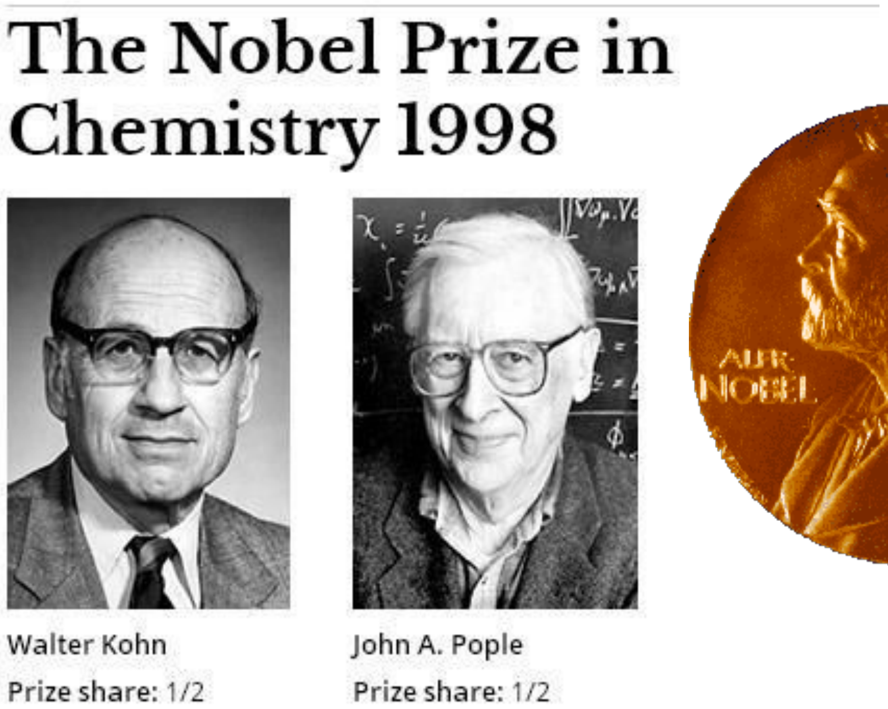
👎 More costly than orbital-free DFT.

👎 The true exchange-correlation potential is unknown.

👎 Unlike WFT, KS-DFT is not systematically improvable.

👎👎👎 **We have HUNDREDS of density functional approximations!**

(KS-)DFT has become the workhorse of quantum chemistry



The Nobel Prize in Chemistry 1998

Walter Kohn
Prize share: 1/2

John A. Pople
Prize share: 1/2

1. DFT basics

2. The Jacob's Ladder classification

3. The London-dispersion problem

4. Finding a way through the DFT zoo

(5. Self interaction error; optional)

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The zoo of DFT approximations

see presentation for content

Some notes on exchange-correlation functionals

- Sometimes we use the acronym DFA (Density Functional Approximation)
- The exchange-correlation functional is usually broken down into two separate exchange and correlation contributions:

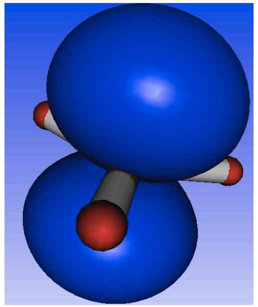
$$\mathbf{E_{XC}}[\rho] = \mathbf{E_{X}}[\rho] + \mathbf{E_{C}}[\rho]$$

- XC functionals are often expressed as energy densities:

$$\mathbf{E_{XC}} = \int \epsilon_{\mathbf{XC}}[\rho(\mathbf{r})]\rho(\mathbf{r})\mathbf{dr}$$

- In open-shell systems (unpaired electrons), these functionals do not only depend on the total electron density, but also on the spin density ρ^{α}-ρ^{β}:

Example: spin density of the methyl radical



- Density functional development usually involves a trial-and-error approach
- Density functional approximations may depend on parameters that are either adjusted by:
  - ➢ fulfilling theoretical boundary conditions: **"non-empirical"**
  - ➢ fitting to atomic/molecular properties: **"(semi-)empirical"**

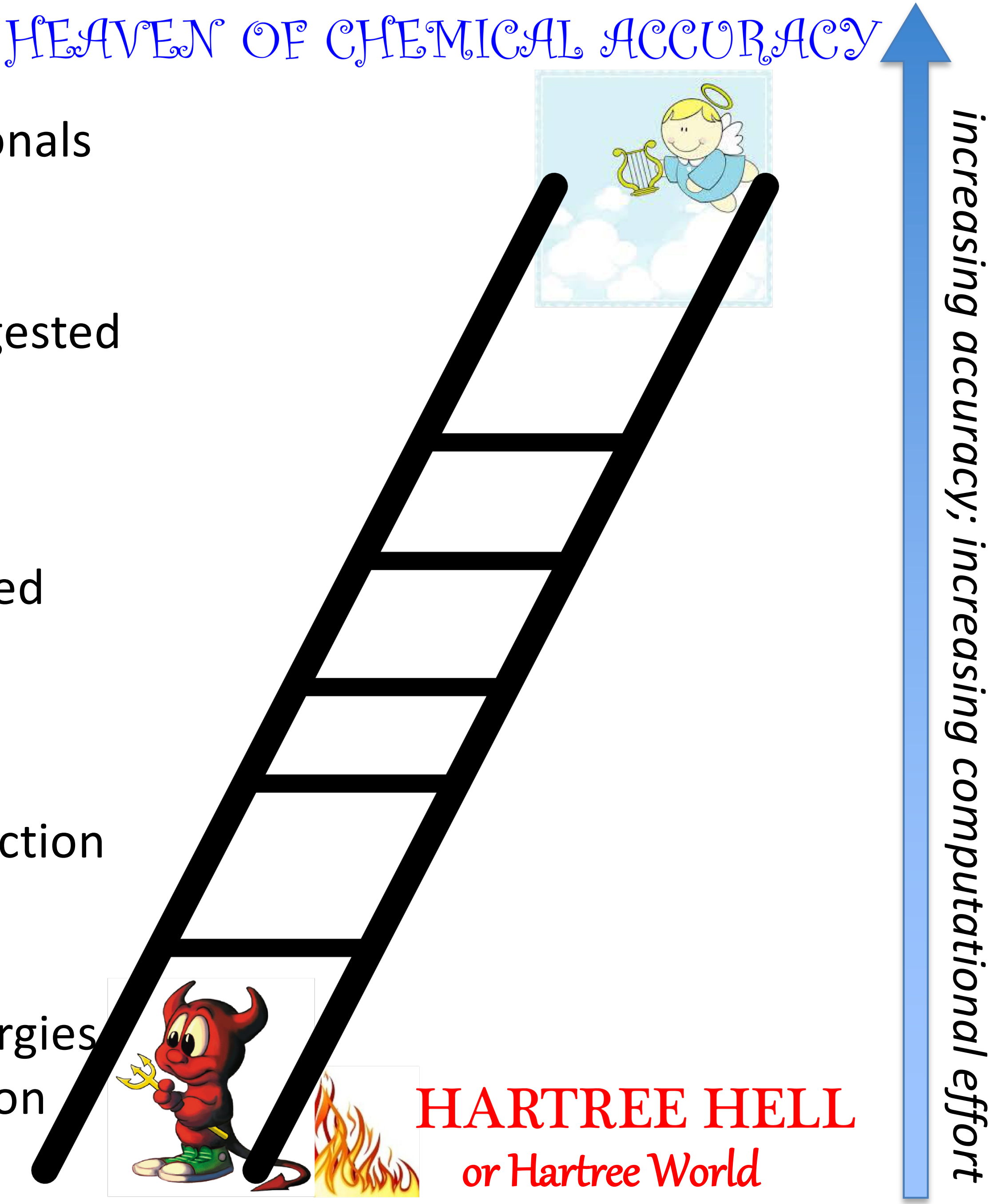
Bringing order into chaos: Perdew's Jacob's Ladder (modified)

- Exchange and correlation functionals contain different components

- Perdew and Schmidt (2001) suggested to classify functionals by these components

- Each functional class is interpreted as a "rung" on a ladder

- ***Chemical accuracy limit:***
  - 4 kJ/mol (1 kcal/mol) for reaction energies
  - 0.4 kJ/mol (0.1 kcal/mol) for noncovalent interaction energies
  - 0.1 eV for electronic excitation energies



Climbing Jacob’s Ladder

Local Density Approximation (LDA):

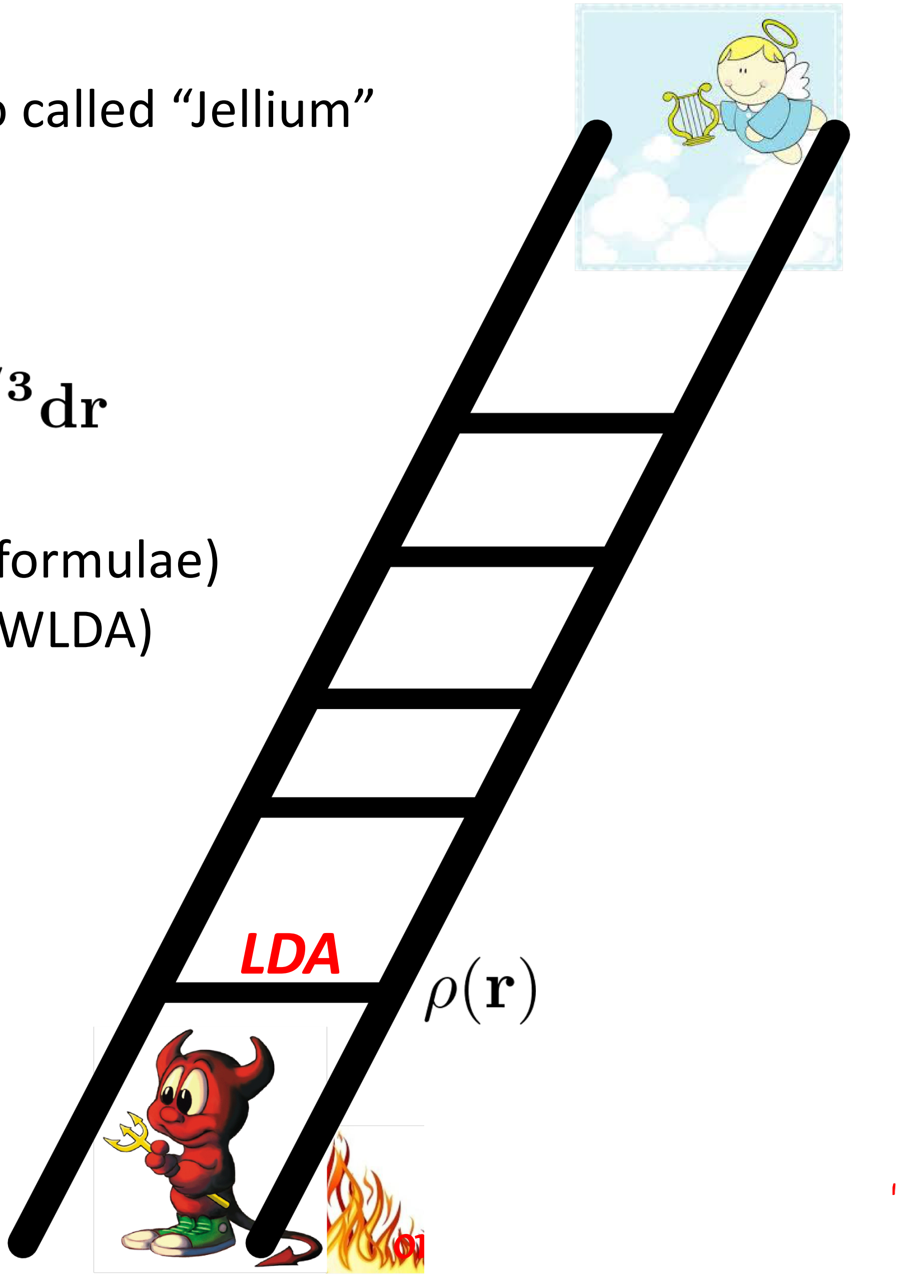
- Based on the Uniform Electron Gas (UEG), also called “Jellium”

- Slater Exchange:

$$\mathbf{E_X^S}[\rho] = -\mathbf{C_x} \int \rho(\mathbf{r})^{\mathbf{4/3}} \mathbf{dr}$$

- Correlation (based on analytical interpolation formulae)

VWN (Vosko-Will-Nusair) or Perdew-Wang LDA (PWLDA)



Local Density Approximation (LDA)

- LDA functionals tend to overbind systems.

- LDA functionals are still very popular in solid-state physics, but they are basically useless for chemical systems.

Why do LDA functionals fail for most chemical systems?

see presentation for image

Climbing Jacob's Ladder

Generalized Gradient Approximation (GGA):

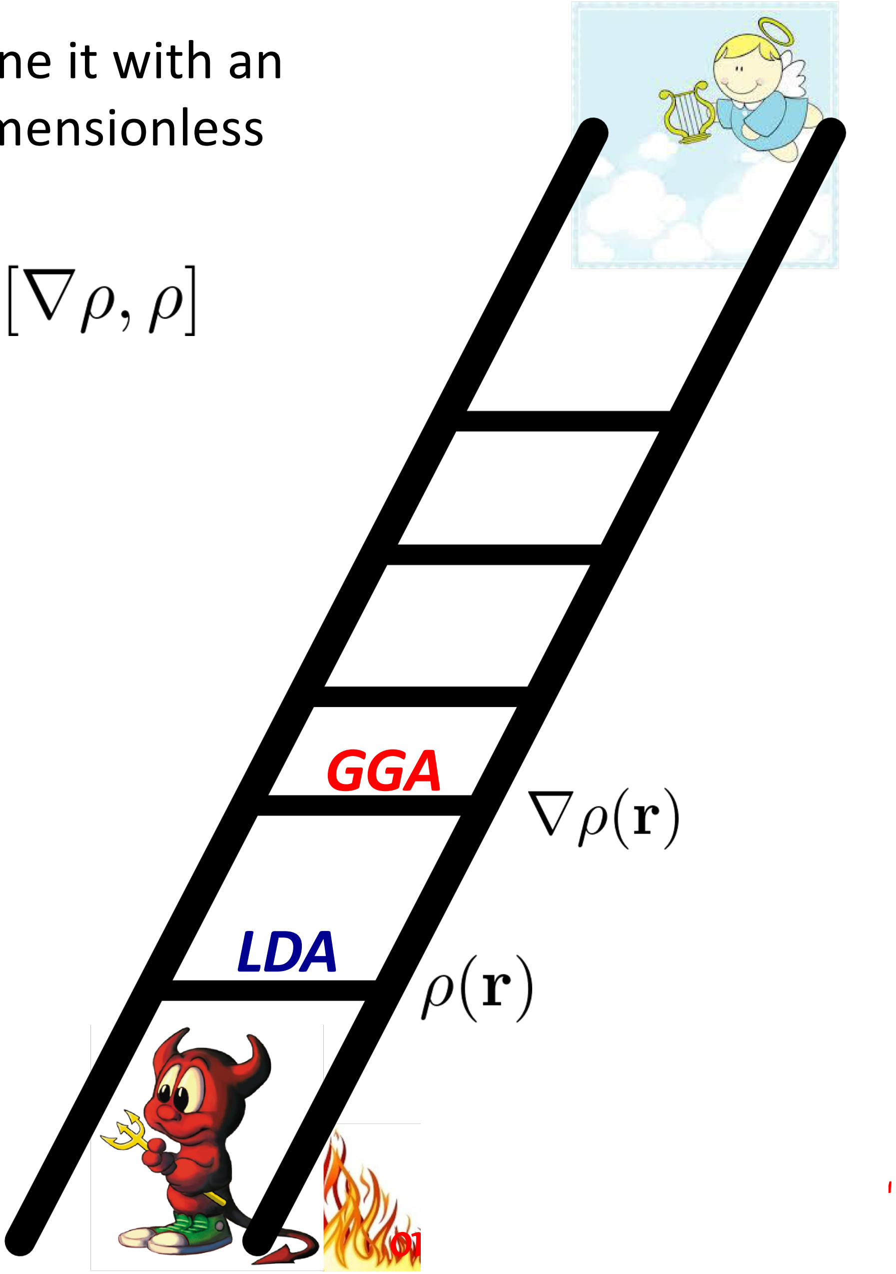
- Most GGA functionals use the LDA and combine it with an "enhancement factor F" that depends on the (dimensionless reduced) density gradient.

$$\epsilon_{\mathbf{XC}}^{\mathbf{GGA}} = \epsilon_{\mathbf{XC}}^{\mathbf{LDA}}[\rho]\mathbf{F}_{\mathbf{XC}}^{\mathbf{GGA}}[\nabla\rho, \rho]$$

- GGAs are ***"semi-local"*** functionals

- Popular exchange functionals:
  - Becke 88 (B)
  - Perdew-Burke-Ernzerhof (PBE)

- Popular correlation functionals:
  - PBE
  - Lee-Yang-Parr (LYP)
  - Perdew 86 (P86)



Examples for DFT expressions:

$$E_X^{B88} = E_X^{LDA} - \beta \sum_\sigma \int \rho_\sigma^{\frac{-4}{3}} \frac{\mid \nabla \rho_\sigma \mid^2}{1 + \frac{6\beta|\nabla\rho_\sigma|}{\rho_\sigma^{\frac{4}{3}}} sinh^{-1}\left(\frac{|\nabla\rho_\sigma|}{\rho_\sigma^{\frac{4}{3}}}\right)} d^3r$$

$$\begin{aligned} E_C^{LYP} = & - a \int \frac{4}{1 + d\rho^{-\frac{1}{3}}} \frac{\rho_\alpha \rho_\beta}{\rho} - ab \int \omega\{\rho_\alpha\rho_\beta[2^{\frac{11}{3}} C_F \left(\rho_\alpha^{\frac{8}{3}} + \rho_\beta^{\frac{8}{3}}\right) \\ & + \left(\frac{47}{18} - \frac{7}{18}\delta\right) \mid \nabla\rho \mid^2 - \left(\frac{5}{2} - \frac{1}{18}\delta\right) (\mid \nabla\rho_\alpha \mid^2 + \mid \nabla\rho_\beta \mid^2) \\ & - \frac{\delta - 11}{9} \left(\frac{\rho_\alpha}{\rho} \mid \nabla\rho_\alpha \mid^2 + \frac{\rho_\beta}{\rho} \mid \nabla\rho_\beta \mid^2\right)] - \frac{2}{3}\rho^2 \mid \nabla\rho \mid^2 \\ & + (\frac{2}{3}\rho^2 - \rho_\alpha^2) \mid \nabla\rho_\beta \mid^2 + (\frac{2}{3}\rho^2 - \rho_\beta^2) \mid \nabla\rho_\alpha \mid^2\} \end{aligned}$$

meta-GGAs

- In principle, meta-GGAs are ***semi-local*** functionals based on LDA that contain $\nabla\rho(\mathbf{r})$ and also higher-order derivates of ρ(r). In practice, these higher-order terms are expressed through the so-called ***kinetic-energy density*** τ, which is calculated with the help of KS orbitals:

$$\tau = \frac{1}{2}\sum_{\mathbf{i}}^{\mathbf{N}} |\nabla\phi_{\mathbf{i}}^{\mathbf{KS}}|^{\mathbf{2}}$$

- meta-GGAs yield better geometries than GGAs, but they are not automatically better for thermochemistry.

- Typical meta-GGAs: Tao-Perdew-Scuseria-Staroverov (***TPSS***) and revised TPSS (***revTPSS***) exchange and correlation; Becke95 (***B95***) correlation, ***M06-L*** (a so-called Minnesota functional), ***SCAN***, ***B97M-V***

- ***Minnesota functionals*** have been developed by Prof. Don Truhlar from 2005 onwards. They usually contain many separate terms that depend on a large number of parameters (up to 50) that have been empirically adjusted to covalent and noncovalent properties.

Climbing Jacob's Ladder

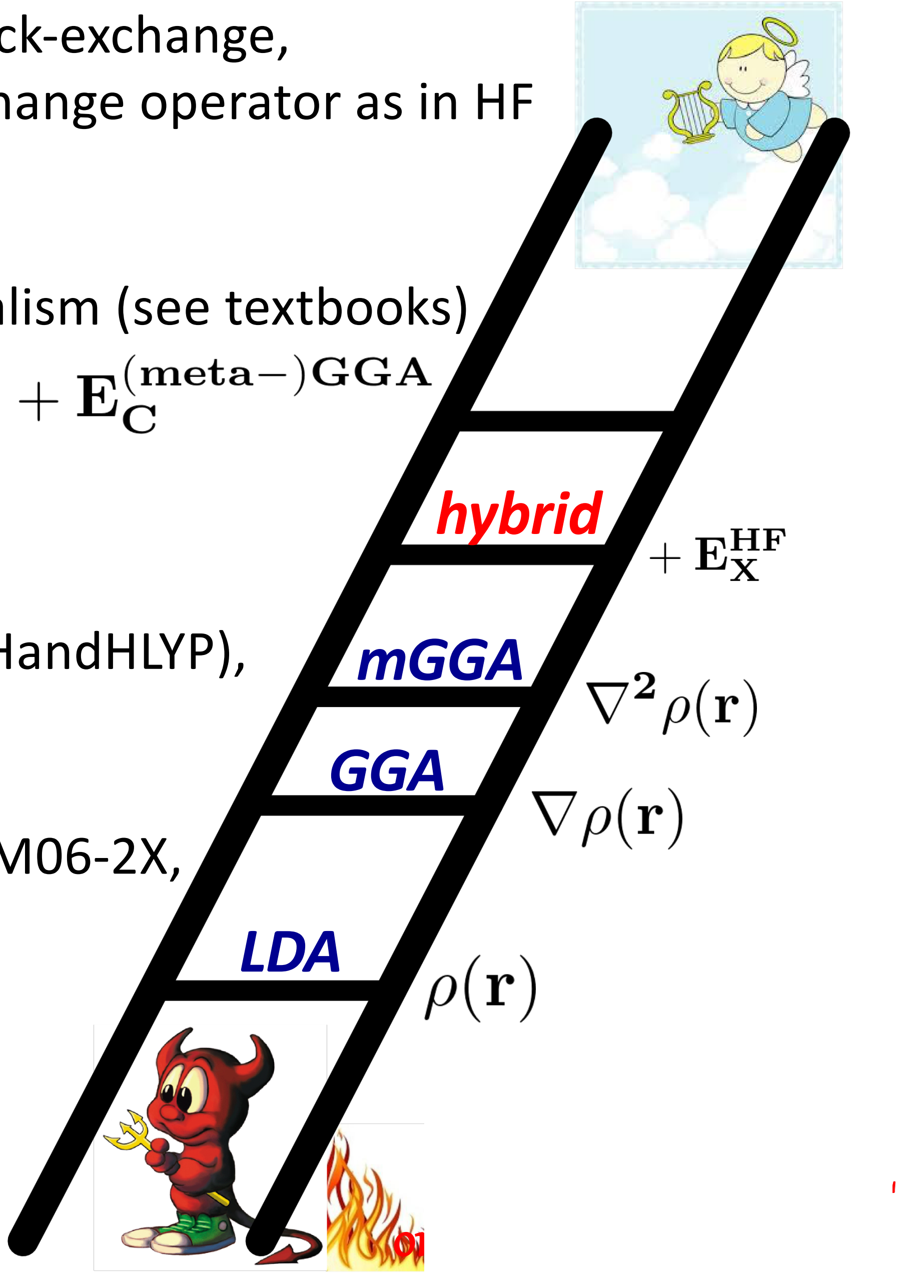
Hybrid functionals:

- ***Replace*** parts of the approximate DFT with Fock-exchange, sometimes also called ***exact exchange*** (same exchange operator as in HF theory)

- Formally based on adiabatic connection formalism (see textbooks)

$$\mathbf{E_{XC}^{hybrid} = (1 - a_X)E_X^{(meta)-GGA} + a_X E_X^{HF} + E_C^{(meta-)GGA}}$$

- Common hybrid functionals:
  - based on GGA: B3LYP, B3PW91, BHLYP (BHandHLYP), PBE0 (PBE1PBE)
  - based on meta-GGA: TPSSh, PW6B95, Minnesota functionals (M05, M05-2X, M06, M06-2X, M11, MN12-SX, ...), ωB97X-V, ωB97M-V



Climbing Jacob's Ladder

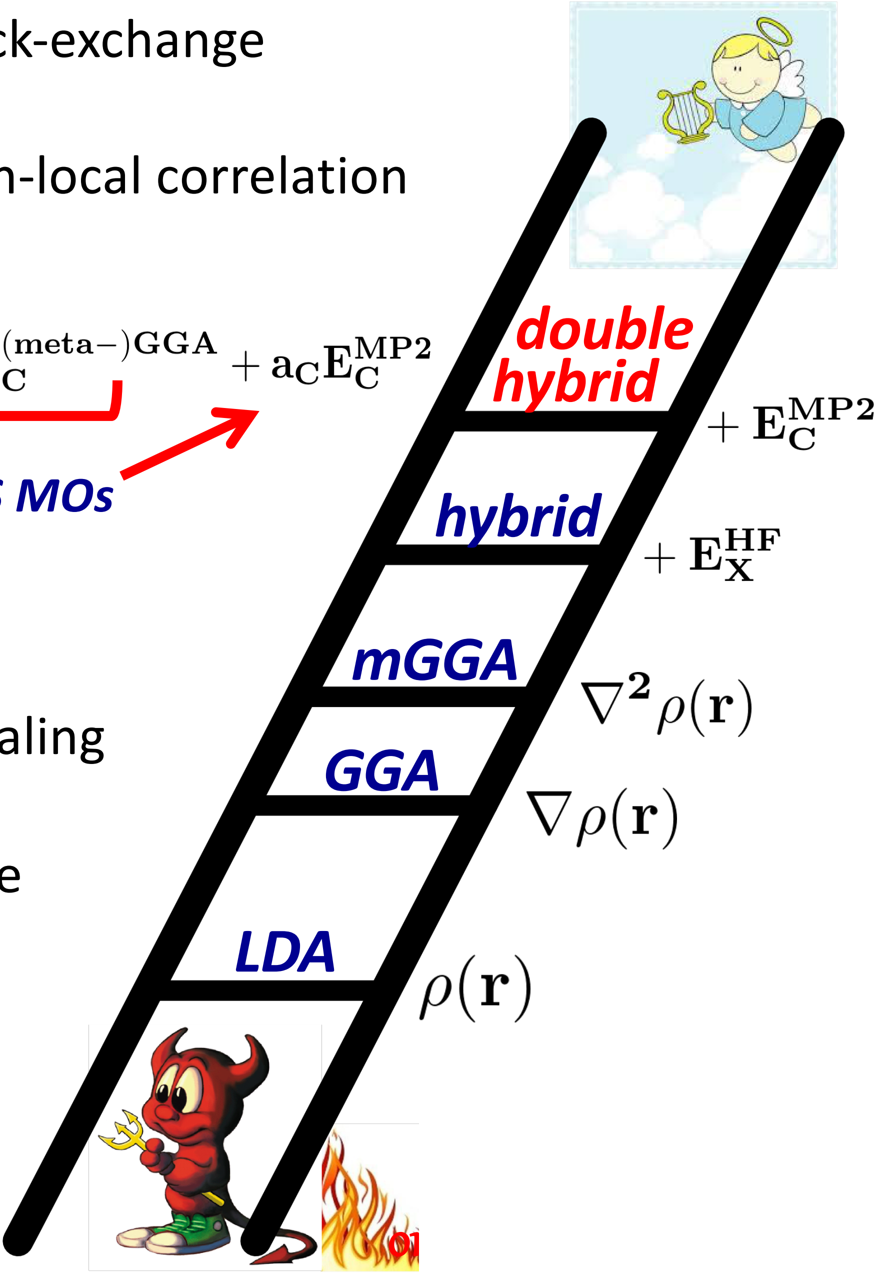
Note: The 5th rung encompasses all methods that rely on unoccupied orbitals

Double-Hybrid functionals (as defined in 2006):

Grimme *J. Chem. Phys.* **2006**, *124*, 034108.

- ***Replace*** parts of the approximate DFT with Fock-exchange (same as in hybrid DFT)
- ***Replace*** parts of the approximate DFT with non-local correlation (basically an MP2-type term)

$$\mathbf{E_{XC}^{double-hybrid}} = \underbrace{(1-a_X)E_X^{(meta)-GGA} + a_X E_X^{HF} + (1-a_c)E_C^{(meta-)GGA}}_{\textit{hybrid-DFT SCF} \rightarrow \textit{KS MOs}} + a_C E_C^{MP2}$$



- Typical Fock-exchange contribution: 50-80%
- Typical MP2-type contribution: 16-50%
- MP2 term can also include spin-component-scaling or spin-opposite-scaling (SCS/SOS)
- Techniques to speed up MP2 term are available
- Some (of the many) double-hybrids:
  - B2PLYP (the first double hybrid)
  - DSD and DOD methods (with SCS/SOS)
  - PBE-QIDH ("non-empirical")
  - ωB97X-2, ωB97M(2)

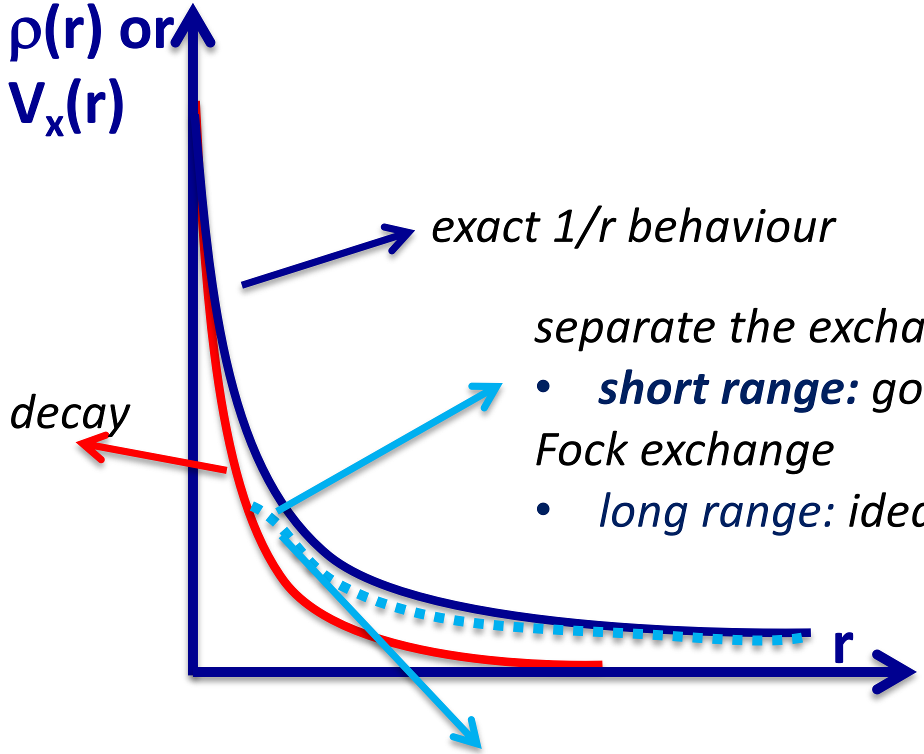
Range-separation (RS) in DFT

- In conventional functionals, the exchange potential has the wrong asymptotic behaviour

➡ **The electron density decays at too short distances!**

➡ **Long-range excitations (CT and Rydberg) are red-shifted**

see, e.g.: Dreuw, Head-Gordon, *JACS* **2004**, *126*, 4007.



exact 1/r behaviour

wrong exponential decay

separate the exchange potential into two parts:

- ***short range:*** *governed by a DFT term and Fock exchange*
- *long range: ideally 100% Fock exchange*

the range-separation parameter ω (or μ) controls the interplay between short- and long-range components

Leininger, Stoll, Werner, Savin, *Chem. Phys. Lett.* **1997**, *275*, 151.

Iikura, Tsuneda, Yanai, Hirao, *J. Chem. Phys.* **2001**, *115*, 3540.

Range-separation (RS) in DFT

- The exchange component of a functional, then becomes:

$$E_X(\omega) = \overbrace{a_x E_X^{HF,SR}(\omega) + a_{x,DFA} E_X^{DFA,SR}(\omega)}^{\substack{\textit{short range}\\ \textit{(usually } a_{x,DFA} = 1-a_x\textit{)}}} + \underbrace{E_X^{HF,LR}(\omega)}_{\substack{\textit{long range}\\ \textit{(usually 100\% Fock exchange,}\\ \textit{but not always)}}}$$

- Names of some range-separated hybrids:
  - CAM-B3LYP (*does not have 100% Fock exchange at asymptotic limit*)
  - LC-PBE,LC-wPBE, LC-BLYP
  - ωB97X, ωB97X-D, ωB97X-D3, ωB97X-V/D4/D3(BJ)
  - ωB97M-V/D3(BJ)/D4
- Names of some range-separated double hybrids (RS in exchange part):
  - ωB97X-2, ωB97M(2)
  - RSX-QIDH, ωDSD$_{72}$-PBEP86-D4, ωDSD3-PBEP86-D4
  - ωB2PLYP, ωB2GP-PLYP (*optimised for excited states*)

(*For double hybrids for excited states, incl. our RS ones, see Aust. J. Chem* **2021**, *74*, 3; ***free access***)

1. DFT basics

2. The Jacob’s Ladder classification

3. The London-dispersion problem

one of the many problems of density functional approximations one could talk about

4. Finding a way through the DFT zoo

(5. Self interaction error; optional)

The London-dispersion problem

- London-dispersion (van-der-Waals) forces are non-local electron-correlation effects:

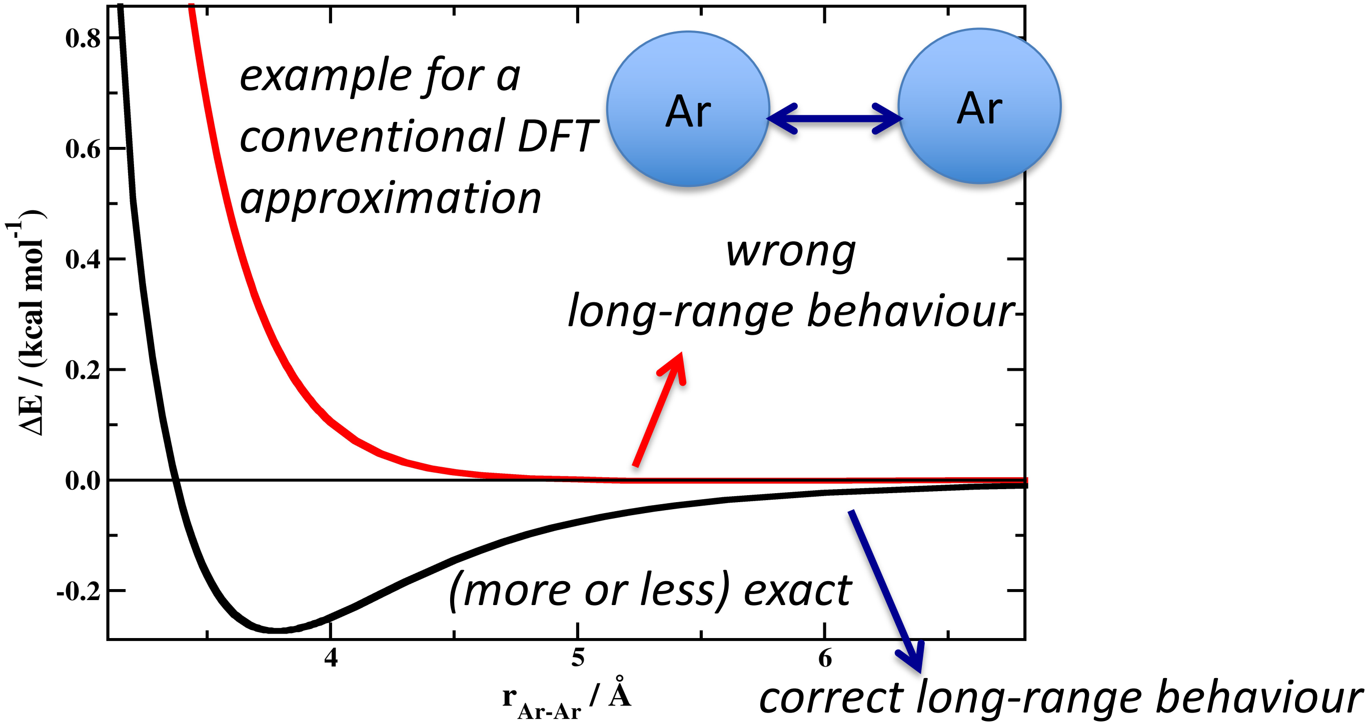
$$E_{disp} \propto \frac{C_6}{R^6}$$

system-specific dispersion coefficient

Fritz London (1900-1954)

- Conventional correlation functional approximations are only (semi-)local

➡ **They fail to describe London-dispersion effects!**



example for a conventional DFT approximation

wrong long-range behaviour

(more or less) exact

correct long-range behaviour

Dispersion-corrected DFT

Many solutions to the London-dispersion problem have been developed:

For a review, see: Grimme, Hansen, Brandenburg, Bannwarth, *Chem. Rev.* **2016**, *9*, 5105.

1) Additive corrections:

- Perform a conventional DFT calculation; then perform an additional calculation that estimates the dispersion contribution and add it to the DFT result.
- Many examples exist (DFT-D2, DFT-D4, XDM, vdw-TS, dDsC,…); Grimme's ***DFT-D3***

Combined, nearly 25,000 citations!

Grimme, Ehrlich, Antony, Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
Grimme, Ehrlich, Goerigk, *J. Chem. Phys.* **2011**, *32*, 1456.

$$\mathbf{E^{DFT-D3} = E_{XC}^{DFT} + E_{disp}^{DFT-D3}}$$

- ○ Takes geometry and chemical environment of each atom into account
- ○ 2-3 empirical parameters fitted to each functional
- ○ goes through every possible atom pair; three-body correction is available
- ○ Works for energies, geometries, and frequencies
- ○ Comes in three flavours; generally the variant with Becke-Johnson damping [DFT-D3(BJ)] should be used, otherwise use zero-damping [DFT-D3(0)]
- ○ The newer DFT-D4 takes charges and total spin into consideration. Works better for metals and different oxidation states.

Dispersion-corrected DFT

Many solutions to the London-dispersion problem have been developed:

For a review, see: Grimme, Hansen, Brandenburg, Bannwarth, *Chem. Rev.* **2016**, *9*, 5105.

2) Van-der-Waals-DFT

- Functionals that contain a density-dependent non-local (NL) term with the correct asymptotic behaviour (***more costly than additive corrections***)
- Usually only 2-body interactions; can be combined with DFT-D3's 3-body term

$$\mathbf{E}_{\mathbf{XC}}^{\mathbf{vdW-DFT}} = \underbrace{\underbrace{\mathbf{E}_{\mathbf{X}}^{\mathbf{DFT}}[\rho(\mathbf{r})] + \mathbf{E}_{\mathbf{C}}^{\mathbf{DFT}}[\rho(\mathbf{r})]}_{} + \mathbf{E}_{\mathbf{C}}^{\mathbf{NL}}[\rho(\mathbf{r}), \rho(\mathbf{r}')]}_{}$$

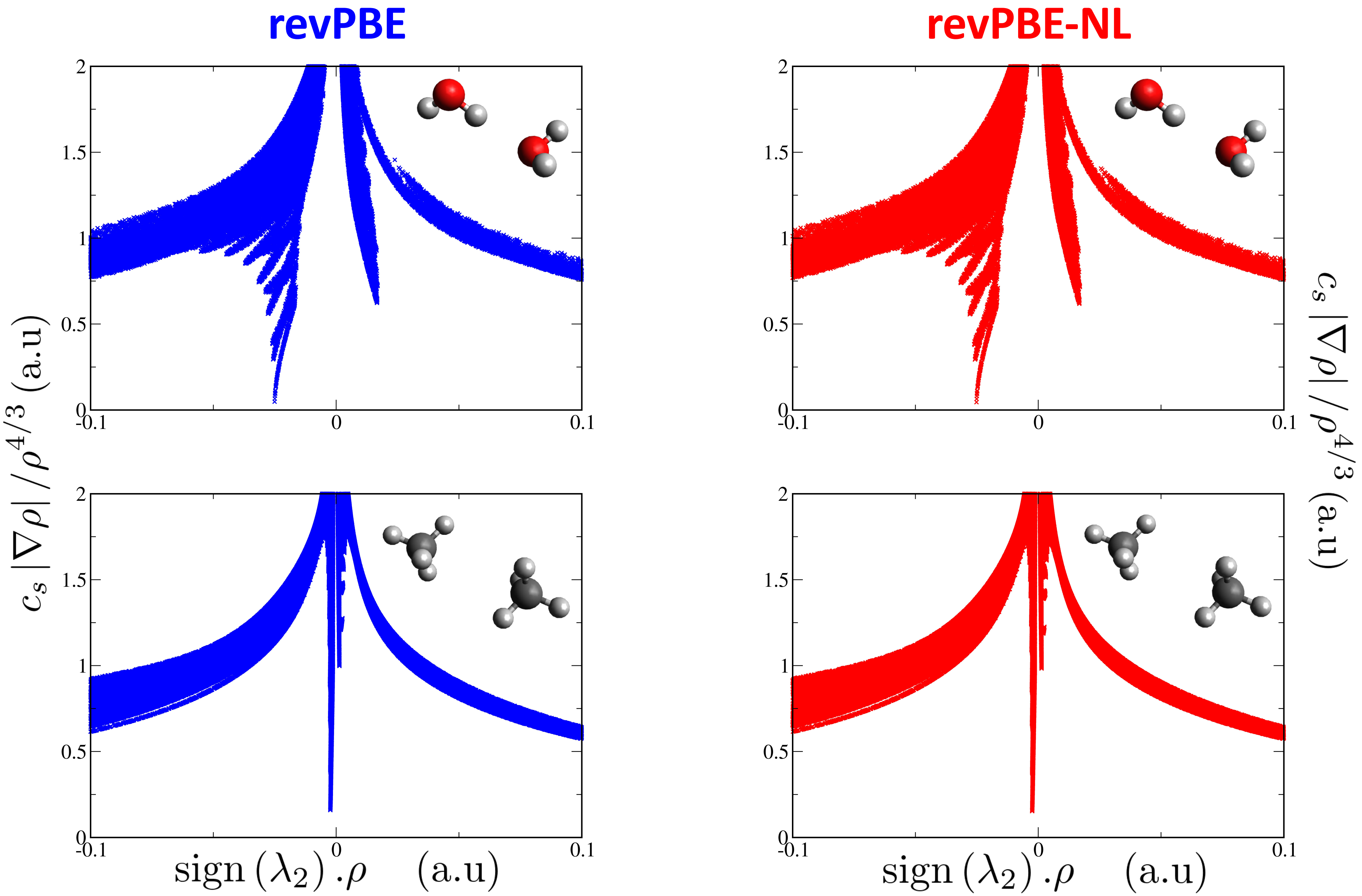
Option 1: Solve everything fully self-consistently ('true vdW-DFT')

Option 2: SCF for semi-local XC part, post SCF for NL part (halves computational effort without loss of accuracy: Najibi, Goerigk, *JCTC* **2018**, *14*, 5725.

- Currently, the most popular NL term is the VV10 term:
  Vydrov, van Voorhis, *J. Chem. Phys*. **2010**, *133*, 244103.

  Usage of VV10 term implied by using the suffix "-NL" or "-V"

Density changes in vdW-DFT? (NCIPLOTs)



Najibi, Goerigk, *JCTC* **2018**, *14*, 5725.

Dispersion-corrected DFT

3) Effective core potentials

- Part of every QM program to mimic core electrons incl. basic relativistic effects
- Fitted to interaction energies in dimers to mimic dispersion interactions (e.g. DCACP; LAP; DCP [Torres, DiLabio *J. Phys. Chem. Lett.* **2012**, *3*, 1738.])
- Conceptual problem: Those potentials are Gaussian functions; they do not have the correct R^{-6} tail
- The DCP approach breaks down for intramolecular dispersion (e.g. conformers) and general thermochemistry (Goerigk *JCTC* **2014**, *10*, 968.)
- Effective core potential development has moved away from dispersion.

4) Conventional functionals fitted to noncovalent interaction energies:

- ***Minnesota functionals*** **(**e.g. Peverati, Truhlar, *Philos. Trans. R. Soc. A* **2014**, *372*, 20120476) are an example for approximations that were fitted

against "covalent" and "noncovalent properties.

(Do they really describe dispersion?)

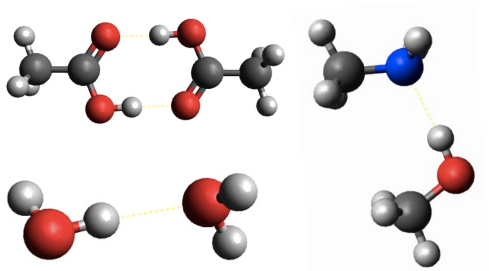
🤔

Dispersion-corrected DFT for typical dimers

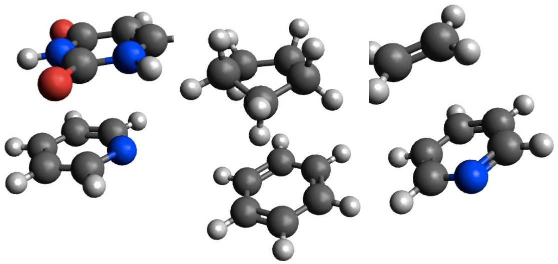
Hobza's S22 benchmark set for 22 noncovalently bound dimers:

Jurecka, Sponer, Cerny, Hobza, *PCCP* **2006**, *8*, 1985.

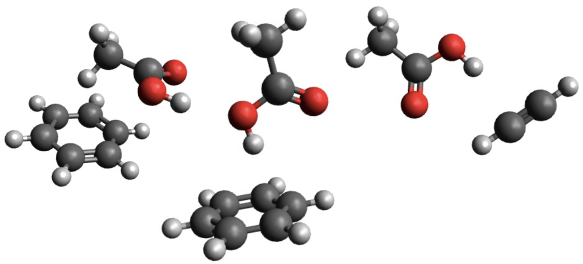
electrostatic interactions



dispersion dominated



dispersion and electrostatics



method*	Mean absolute deviation/(kcal mol^{-1})
B3LYP	**3.78**
B3LYP-D3(BJ)	**0.31**
M06	**1.03**
M06-D3(0)	**0.27**

* Values taken from:
Goerigk, Hansen, Bauer, Ehrlich, Najibi, Grimme, *PCCP* **2017**, *19*, 32184.
Najibi, Goerigk, *JCTC* **2018**, *14*, 5725.
Najibi, Goerigk *J. Comput. Chem.* **2020**, *41*, 2562.

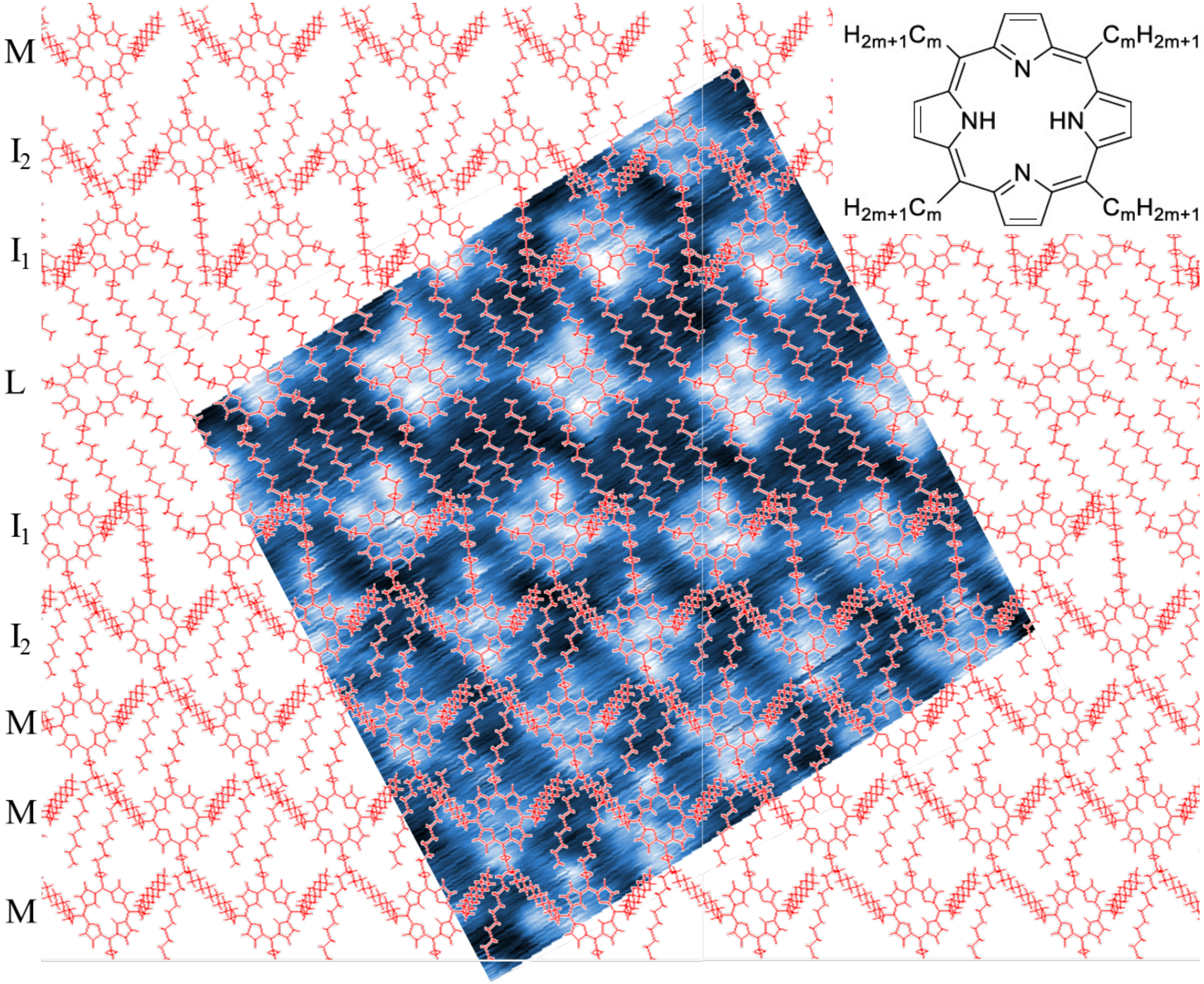
* def2-QZVP basis set

Conventional vs. dispersion-corrected DFT

London dispersion is often ignored in Computational Chemistry DFT applications!

Misconception #1: "London dispersion is small"

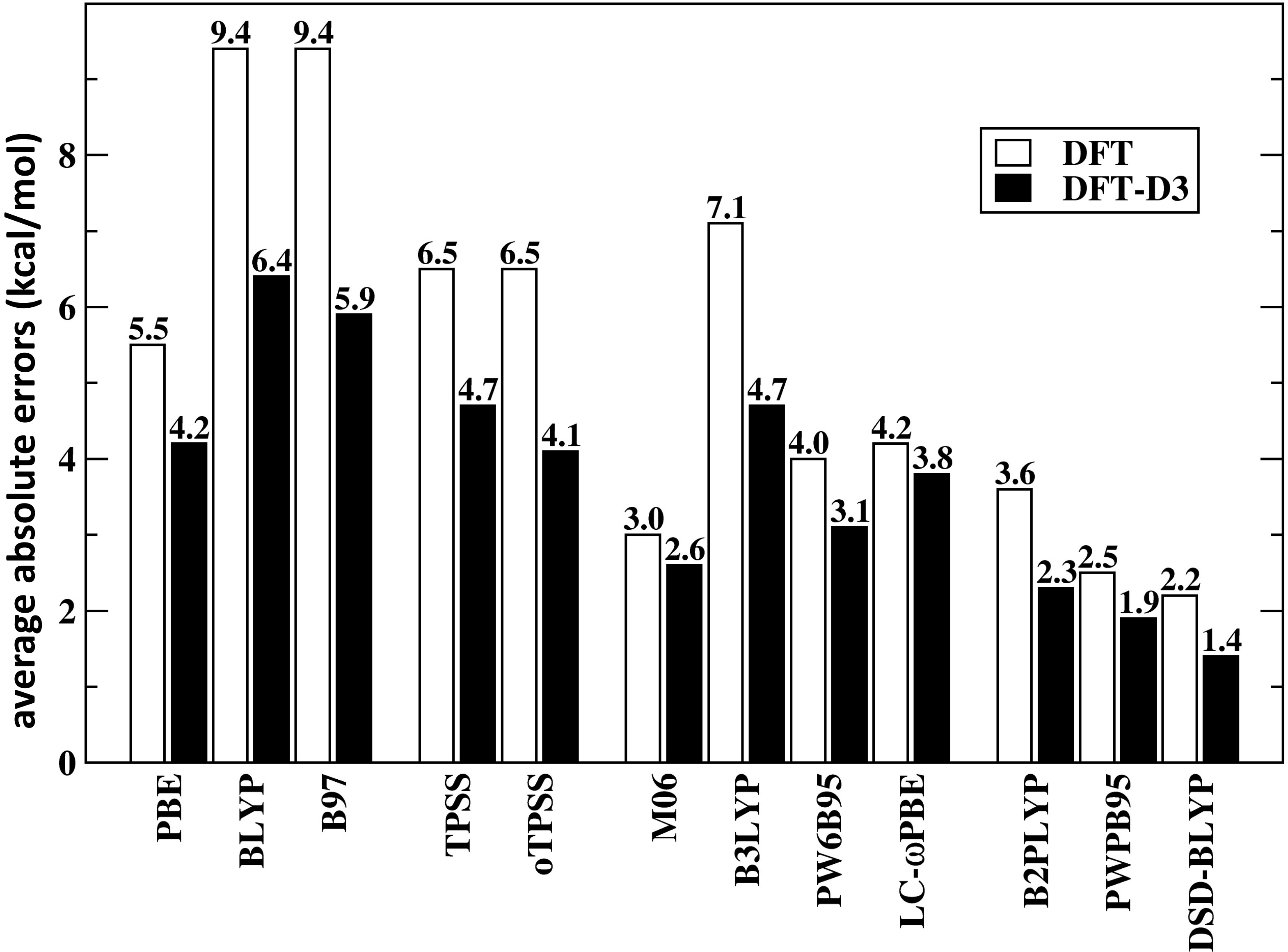
Tetraalkylporphyrin monolayers on graphite:



➡ **dispersion-induced substrate-monolayer interactions are between** **400 and 600 kJ/mol** *(with DFT-D3)*

Reimers et al., *PNAS* **2015**, *112*, E6101.

Misconception #2: “London dispersion is irrelevant in reactions”

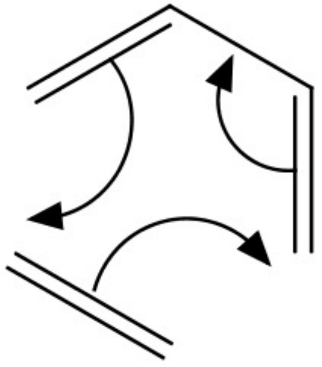


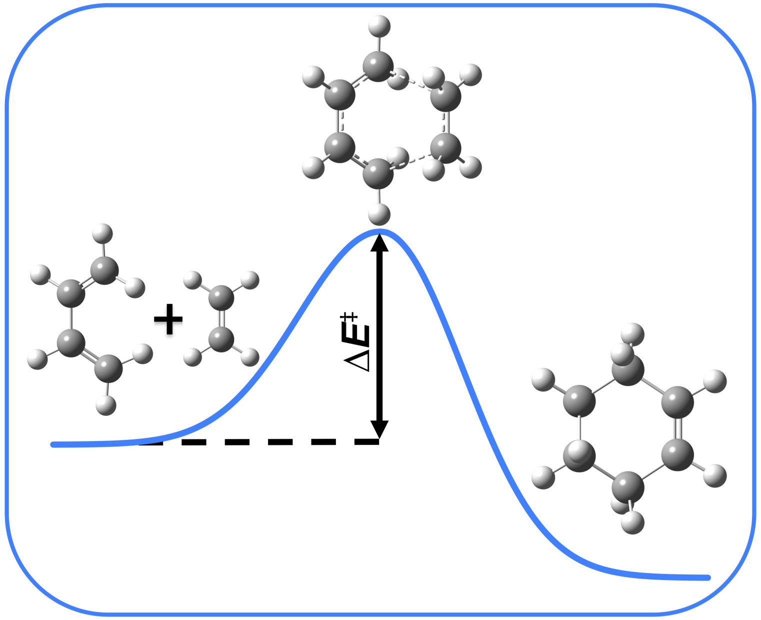
- average absolute errors (kcal/mol) for a large set of reaction energies with conventional DFT methods and DFT-D3 correction

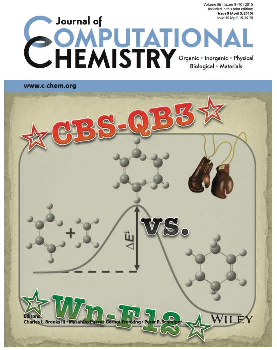
Goerigk, Grimme, *PCCP* **2011**, *13*, 6670.

Misconception #2: “London dispersion is irrelevant in reactions”

Barrier in pericyclic reactions







Barrier height in kcal/mol (QZ basis)

	DFT		DFT-D3
B3LYP	26.5	→	19.8
PW6B95	22.9	→	20.9
PWPB95	23.1	→	21.6

Ref (W2-F12): 22.3 kcal/mol

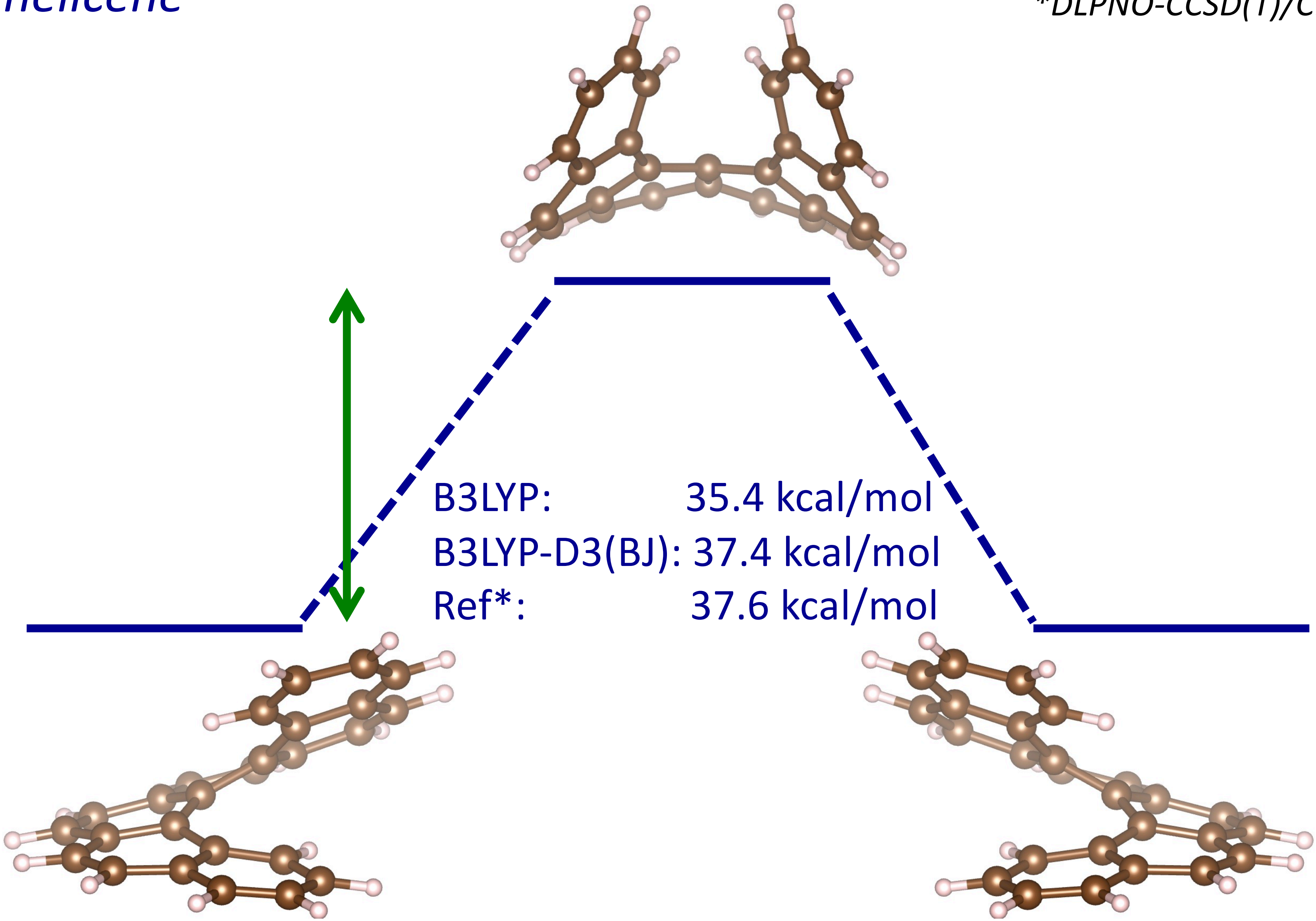
Karton, Goerigk, *J. Comput. Chem.* **2015**, *36*, 622.

Misconception #2: “London dispersion is irrelevant in reactions”

Inversion and racemization barriers:

Hexahelicene

**DLPNO-CCSD(T)/CBS*



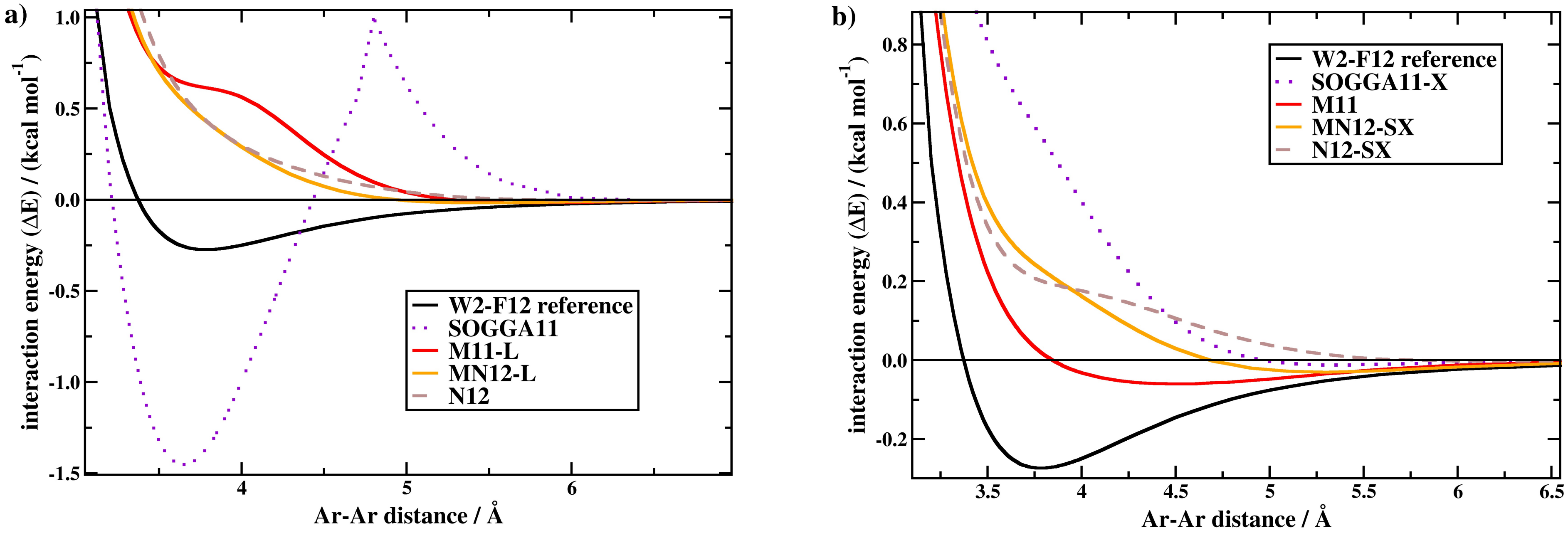
B3LYP: 35.4 kcal/mol

B3LYP-D3(BJ): 37.4 kcal/mol

Ref*: 37.6 kcal/mol

Goerigk, Sharma, Can. J. Chem. **2016,** *94*, 1133. (***Open Access***)

Misconception #3: "Minnesota functionals capture dispersion"



Can be made more robust with a dispersion correction, e.g. DFT-D3 *(usually zero damping has to be used)* or DFT-NL/VV10.

Goerigk *J. Phys. Chem. Lett.* **2015**, *6*, 3891.

Misconception #3: "London dispersion is irrelevant in geometries"

The hexaphenylethane riddle, solved by Grimme and Schreiner:

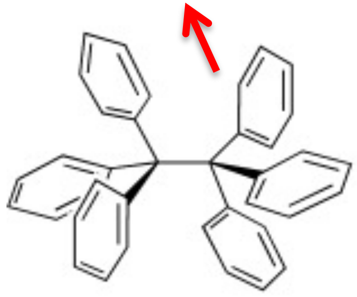
(*Angew. Chem. Int. Ed.* **2011**, *50*, 12639.)

(all images copyright Wiley VCH, reproduced with permission by S. Grimme)

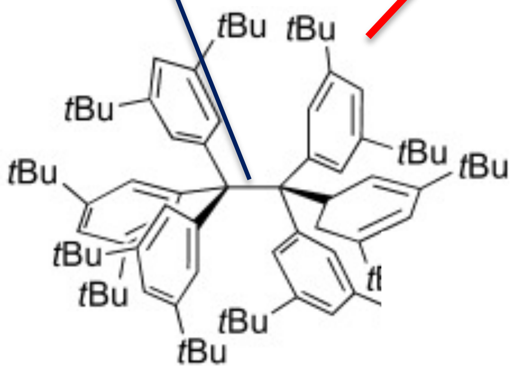
unusually long C-C single bond (1.67 Å)

stable despite being very crowded!

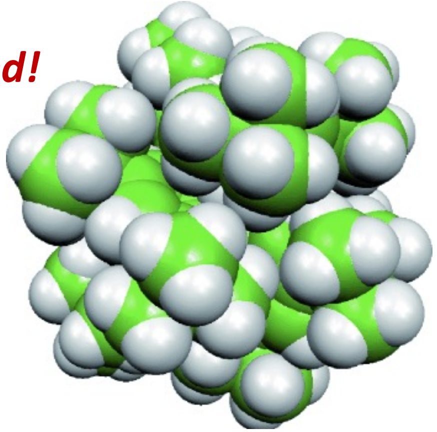
unstable (why?)



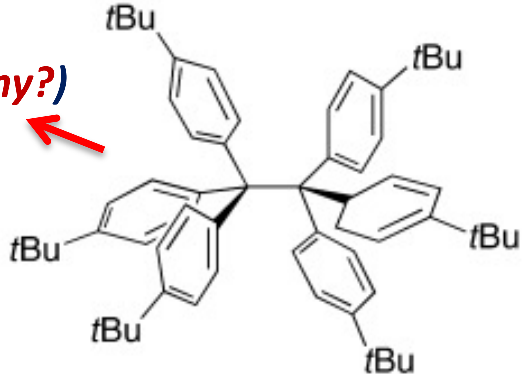
1



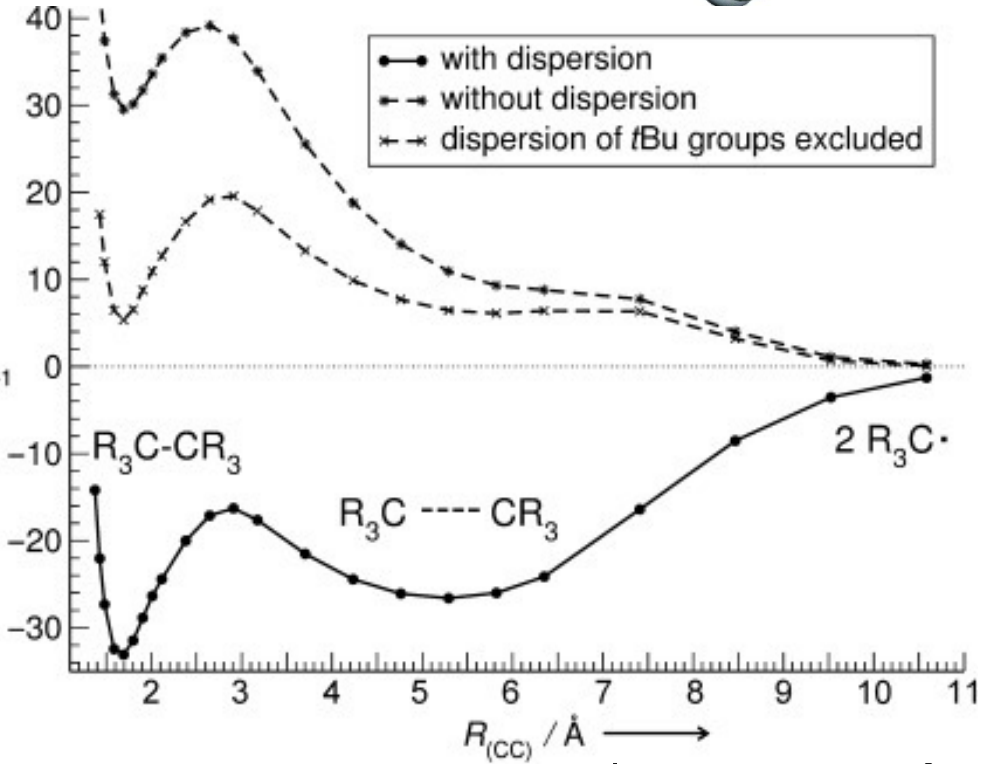
2



unstable (why?)



3



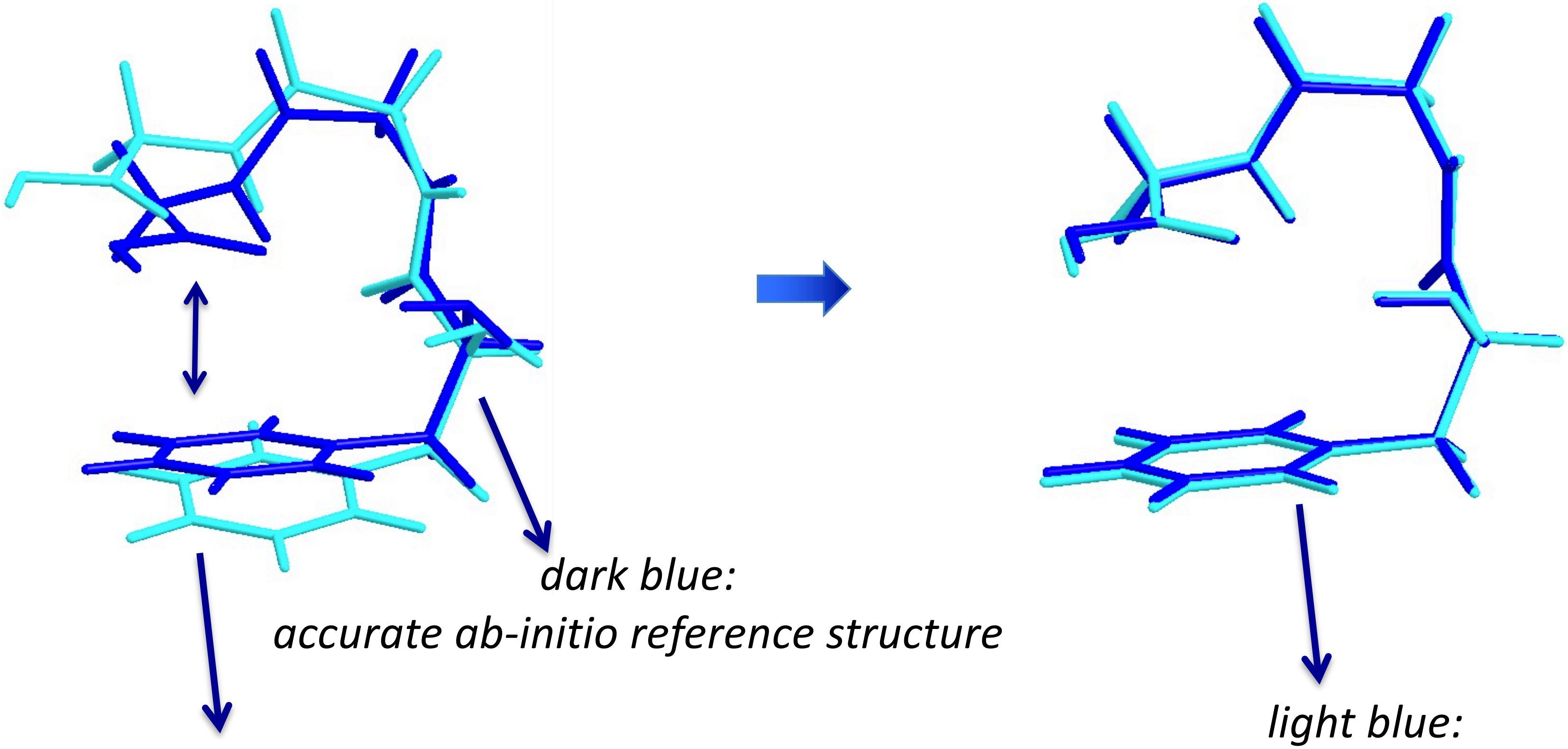
*(TPSS-D3/TZV2P//PBE-D3/TZVP potential energy curves for **2**)*

Also see this blog:

http://www.compchemhighlights.org/2012/04/steric-crowding-canstabilize-labile.html

Misconception #4: “London dispersion is irrelevant in geometries”

A folded conformer of the tripeptide phenylalanyl-glycyl-glycine:



dark blue:
accurate ab-initio reference structure

light blue:
BP86-optimised structure (very popular approach)

light blue:
BP86-D3-optimised structure

Goerigk, Reimers, *JCTC* **2013**, *9*, 3240.

Conventional vs. dispersion-corrected DFT: recommendations

➡ **Always use a dispersion correction!**

➡ **If the result gets worse after including dispersion: change the functional!**

1. DFT basics
2. The Jacob's Ladder classification
3. The London-dispersion problem
4. Finding a way through the DFT zoo

(5. Self interaction error; optional)

Main-group thermochemistry, kinetics, and noncovalent interactions

The GMTKN55 database

basic properties and reaction energies for small systems
18 sets

reaction energies for large systems and isomerisations
9 sets

GMTKN55
55 sets
2462 single point calculations
1505 relative energies

intramolecular noncovalent interactions
9 sets

barrier heights
7 sets

intermolecular noncovalent interactions
12 sets

>350 variations of dispersion-corrected and -uncorrected functionals

about **250 CPU years**

provides insights for method developers and users

Goerigk, Hansen, Bauer, Ehrlich, Najibi, Grimme, *PCCP* **2017**, *19*, 32184 (***Open Access, 2017 Hot Article, top 1% Chemistry papers on Web of Science***); Mehta, Casanova-Páez, Goerigk, *PCCP* **2018**, *20*, 23175 (***2018 Hot Article***); Najibi, Goerigk, *JCTC* **2018**, *14*, 5725 and *J. Comput. Chem*. **2020**, *41*, 2562; Najibi, Casanova-Páez, Goerigk, *JPCA* **2021**, DOI: 10.1021/acs.jpca.1c02549.

The best dispersion-corrected double-hybrids for ground states

DSD-PBEP86-NL/-D3(BJ)
ωB97X-2-D3(BJ)
DSD-BLYP-NL/-D3(BJ)
B2NC-PLYP-D3(BJ)
B2GPPLYP-D3(BJ)

latest updates: **ωB97M(2)**
ωDSD$_{72}$-PBEP86-D4
ωDSD3-PBEP86-D4
DOD-SCAN-D3(BJ)/D4
revDOD-PBEP86D3(BJ)/D4

Martin and co-workers: *JPCA* **2019**, *123*, 5129; **2021**, arXiv:2102.04943.

➡ **Much better than MP2!**

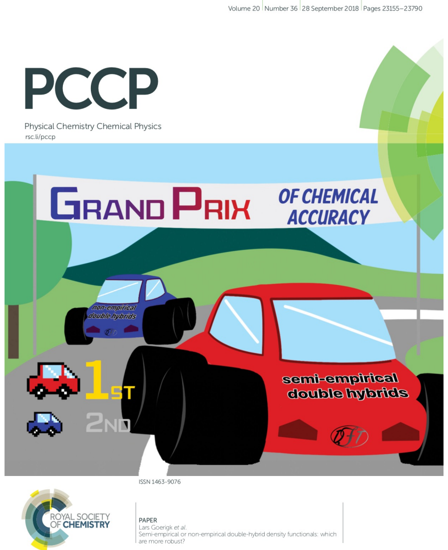

Volume 19 | Number 48 | 28 December 2017 | Pages 32147–32744

PCCP
Physical Chemistry Chemical Physics
rsc.li/pccp

ISSN 1463-9076

ROYAL SOCIETY OF CHEMISTRY

PAPER
Lars Goerigk, Stefan Grimme *et al.*
A look at the density functional theory zoo with the advanced GMTKN55 database for general main group thermochemistry, kinetics and noncovalent interactions


Volume 20 | Number 36 | 28 September 2018 | Pages 23155–23790

PCCP
Physical Chemistry Chemical Physics
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ISSN 1463-9076

ROYAL SOCIETY OF CHEMISTRY

PAPER
Lars Goerigk *et al.*
Semi-empirical or non-empirical double-hybrid density functionals: which are more robust?

Goerigk, Hansen, Bauer, Ehrlich, Najibi, Grimme, *PCCP* **2017**, *19*, 32184 (***Open Access, 2017 Hot Article, top 1% Chemistry papers on Web of Science***); Mehta, Casanova-Páez, Goerigk, *PCCP* **2018**, *20*, 23175 (***2018 Hot Article***); Najibi, Goerigk, *JCTC* **2018**, *14*, 5725 and *J. Comput. Chem*. **2020**, *41*, 2562; Najibi, Casanova-Páez, Goerigk, *JPCA* **2021**, DOI: 10.1021/acs.jpca.1c02549.

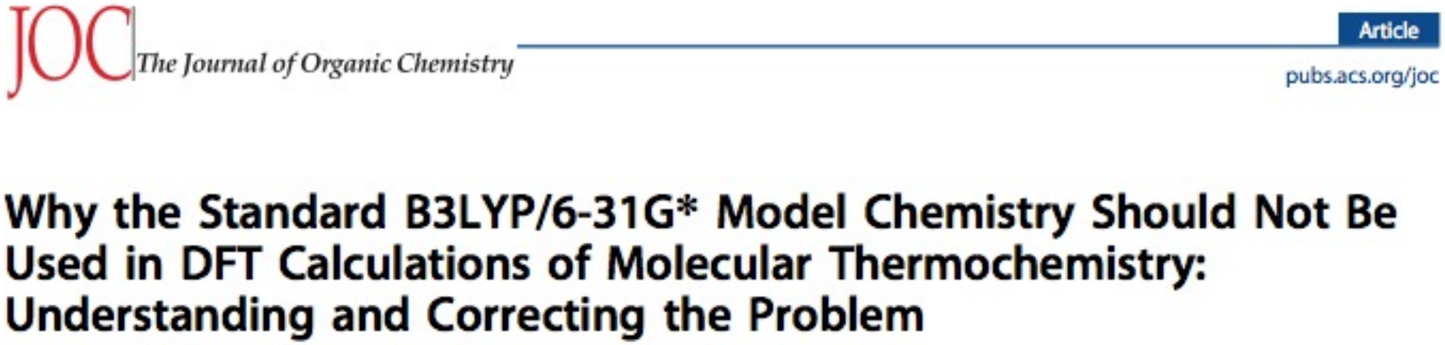
The (omnipresent) B3LYP functional

$$\mathbf{E_{XC}^{B3LYP} = 0.8E_X^{S} + 0.72E_X^{B88} + 0.2E_X^{HF} + 0.19E_C^{VWN} + 0.81E_C^{LYP}}$$

Stephens, Devlin, Chabalowski, Frisch *J. Phys. Chem.* **1994**, *98*, 11623.

- **nearly 14,500 citations; highly popular**
- a great contribution to the field of Chemistry
- **BUT:**
  - **Popularity does not imply reliability**
  - Always question your choice of functional
  - GMTKN55: B3LYP ranks in **197th position**; B3LYP-D3(BJ) in **72nd**.

    Goerigk et al., *PCCP* **2017**, *19*, 32184; *PCCP* **2018**, *20*, 23175; *JCTC* **2018**, *14*, 5725.
  - Much earlier, we already recommended other alternatives:



JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Why the Standard B3LYP/6-31G* Model Chemistry Should Not Be Used in DFT Calculations of Molecular Thermochemistry: Understanding and Correcting the Problem

Kruse, Goerigk, Grimme, *JOC* **2012**, *77*, 10824.

Summary of other findings

- Despite numerous claims and the hype around non-empirical double hybrids, they are not better than semi-empirical double hybrids

  Mehta, Casanova-Páez, Goerigk, *PCCP* **2018**, *20*, 23175 (***2018 Hot Article***)

- Many non-empirical lower-rung functions (rungs 2-4) are also outperformed by semi-empirical functionals

  (*see references on the GMTKN55 slide*)

- While some range-separated functionals belong to the best, range separation itself is no guarantee that a functional is better for general thermochemistry, kinetics, and noncovalent interactions compared to its non-RS counterpart (also called "global hybrid/double hybrid")

  Najibi, Casanova-Páez, Goerigk, *JPCA* **2021**, DOI: 10.1021/acs.jpca.1c02549.

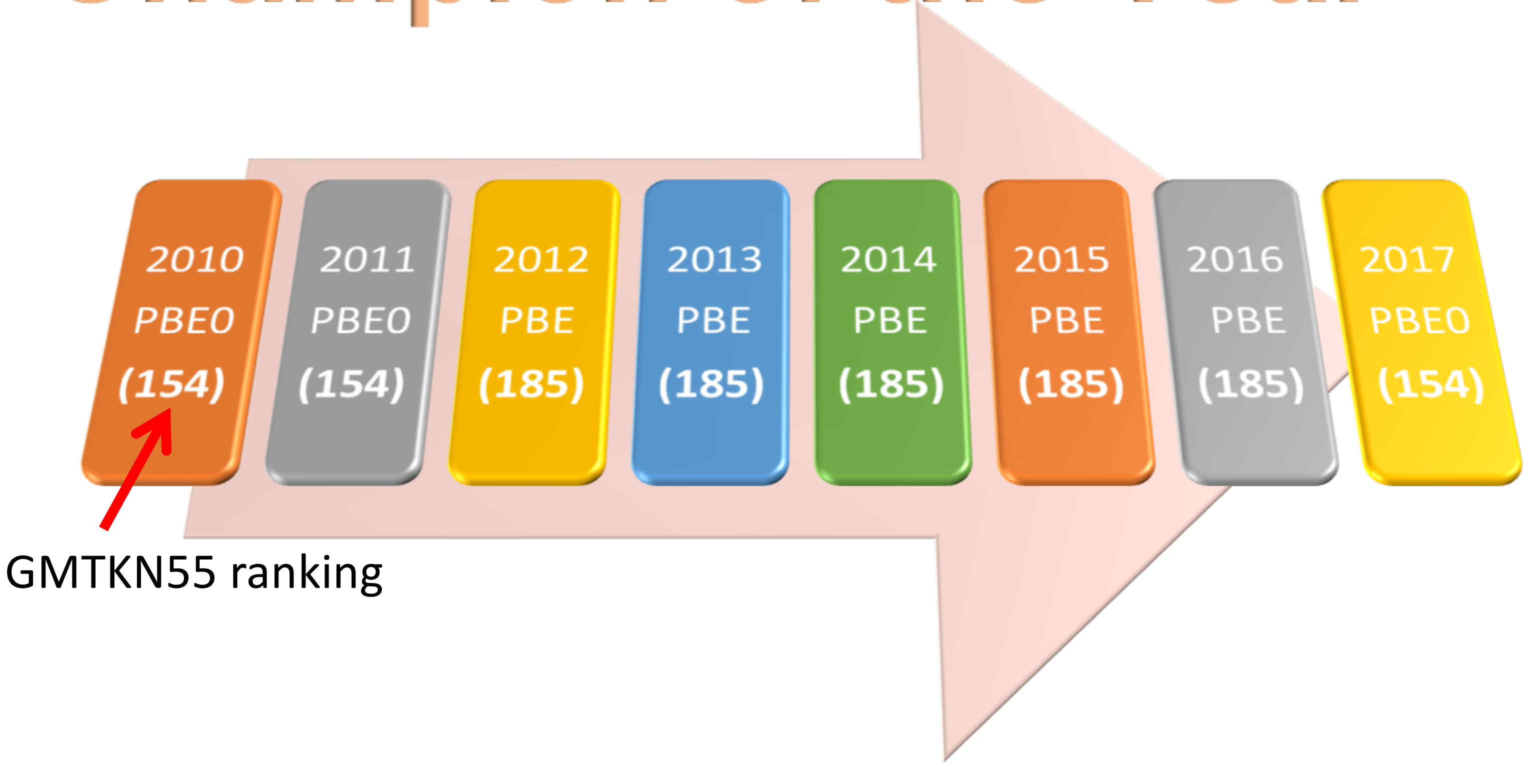
Popularity vs. accuracy

DFT Popularity Poll by Swart, Bickelhaupt, Solà

(see M. Swart's website)

DFT Poll

Champion of the Year



2010	2011	2012	2013	2014	2015	2016	2017
PBE0	PBE0	PBE	PBE	PBE	PBE	PBE	PBE0
(154)	(154)	(185)	(185)	(185)	(185)	(185)	(154)

GMTKN55 ranking

Goerigk, Mehta, *Aust. J. Chem.* **2019**, *72*, 563 (**free access**)

Popularity vs. accuracy

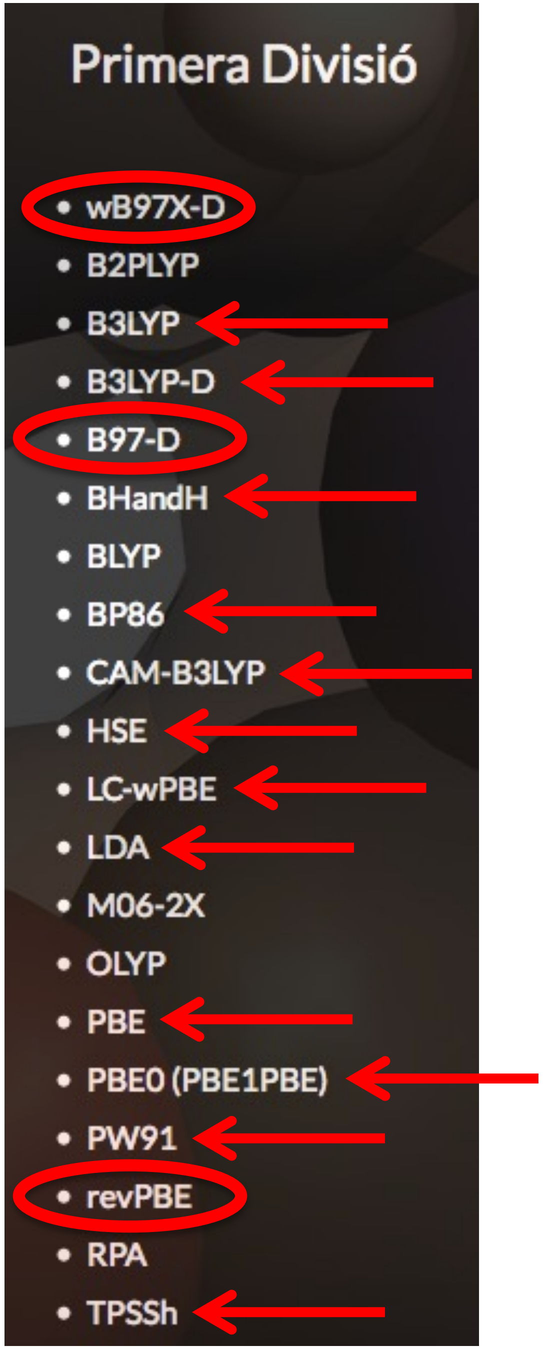
DFT Popularity Poll 2017 by Swart, Bickelhaupt, Solà

(see M. Swart’s website)

- Only **three** of our recommended methods made it into the **TOP20** (**without any or with outdated dispersion corrections**)

- **12 methods did not perform very well** for GMTKN55 (or the GMTKN30 predecessor)

Goerigk, Mehta, *Aust. J. Chem.* **2019**, *72*, 563 (**free access**)



Primera Divisió

- wB97X-D
- B2PLYP
- B3LYP
- B3LYP-D
- B97-D
- BHandH
- BLYP
- BP86
- CAM-B3LYP
- HSE
- LC-wPBE
- LDA
- M06-2X
- OLYP
- PBE
- PBE0 (PBE1PBE)
- PW91
- revPBE
- RPA
- TPSSh

Most robust functionals per rung (for main-group problems)

Rung	Functional
double hybrid	See slide 55
hybrid	ωB97M-V
	ωB97X-V
	ωB97M-D3(BJ)
mGGA	B97M-V
	B97M-D4
	B97M-D3(BJ)
GGA	revPBE-D3(BJ)
	revPBE-NL
	B97-D3(BJ)
LDA	**Do not use!**

Do NOT use rungs 1-3 for barrier heights (self-interaction error too large)

Get our free-access account written for students and (non-expert) users

Goerigk, Mehta, *Aust. J. Chem.* **2019**, *72*, 563.

Our latest GMTKN55 publications:

Najibi, Goerigk, *J. Comput. Chem*. **2020**, *41*, 2562; Najibi, Casanova-Páez, Goerigk, *JPCA* **2021**, DOI: 10.1021/acs.jpca.1c02549.

Additional open-access must-read:

Mardirossian, Head-Gordon, *Mol. Phys.* **2017**, *115*, 2315.

Final thoughts

Take-home messages

- Work your way from **the top of Jacob's Ladder to the bottom** (but no LDA)
- Avoid rungs 2&3 for barrier heights.
- **Always use a dispersion correction!**

- Don't base your choice of functional on what is popular. For a new problem, follow the discussed recommendations. Try two or three functionals to separate genuine trends from artifacts.

- For specific cases, look up GMTKN55 recommendations in the ESIs of the articles.
- **Don't use small basis sets!** (something like def2-TZVPP or def2-TZVPPD should usually be good enough)
- **Always include your level of theory on slides in your presentations!**

Thoughts on geometry optimisations

- **Hybrids or meta-GGAs** are often good enough, such as PW6B95, PBE0, even B3LYP, TPSS, B97M-V/D3/D4

… Usually, no need for double hybrids.

- **Always use a dispersion correction!**
- Use a basis set of triple-ζ quality. If you have to use a double-ζ basis set, use an intramolecular BSSE correction, such as gCP. Other alternatives are special approaches, such as PBEh-3c or B97-3c.

Transition metal compounds

There's still much to do in this space, but:

- **Avoid high amounts of Fock exchange**, double hybrids probably won't work, but you can give PWPB95 a try. PW6B95 may be a good hybrid, M06 most likely too.
- **Always use a dispersion correction and at least a triple-ζ basis set!**

Everyone has heard of and can easily use DFT … … … really?

see presentation for content

1. DFT basics

2. The Jacob's Ladder classification

3. The London-dispersion problem

4. Finding a way through the DFT zoo

(5. Self interaction error; optional)

Electron self interaction (HF vs. approximate DFT)

$$\hat{f}(1)\phi_i(1) = \left[\hat{h}(1) + \sum_j^N \hat{J}_j(1) - \sum_j^N \hat{K}_j(1)\right]\phi_i(1) = \epsilon_i\phi_i(1)$$

Fock operator

The two sums run over all electrons/MOs. This means we calculate integrals with i=j. In other words, we introduce the artefact of **self interaction**, i.e. an orbital/electron interacts with itself.

If i=j, the Coulomb and exchange expressions from slide 17 become identical.

Because we have a minus sign in front of the exchange term, the spurious self-interaction components cancel each other.

Hartree-Fock theory is therefore **self-interaction free.**

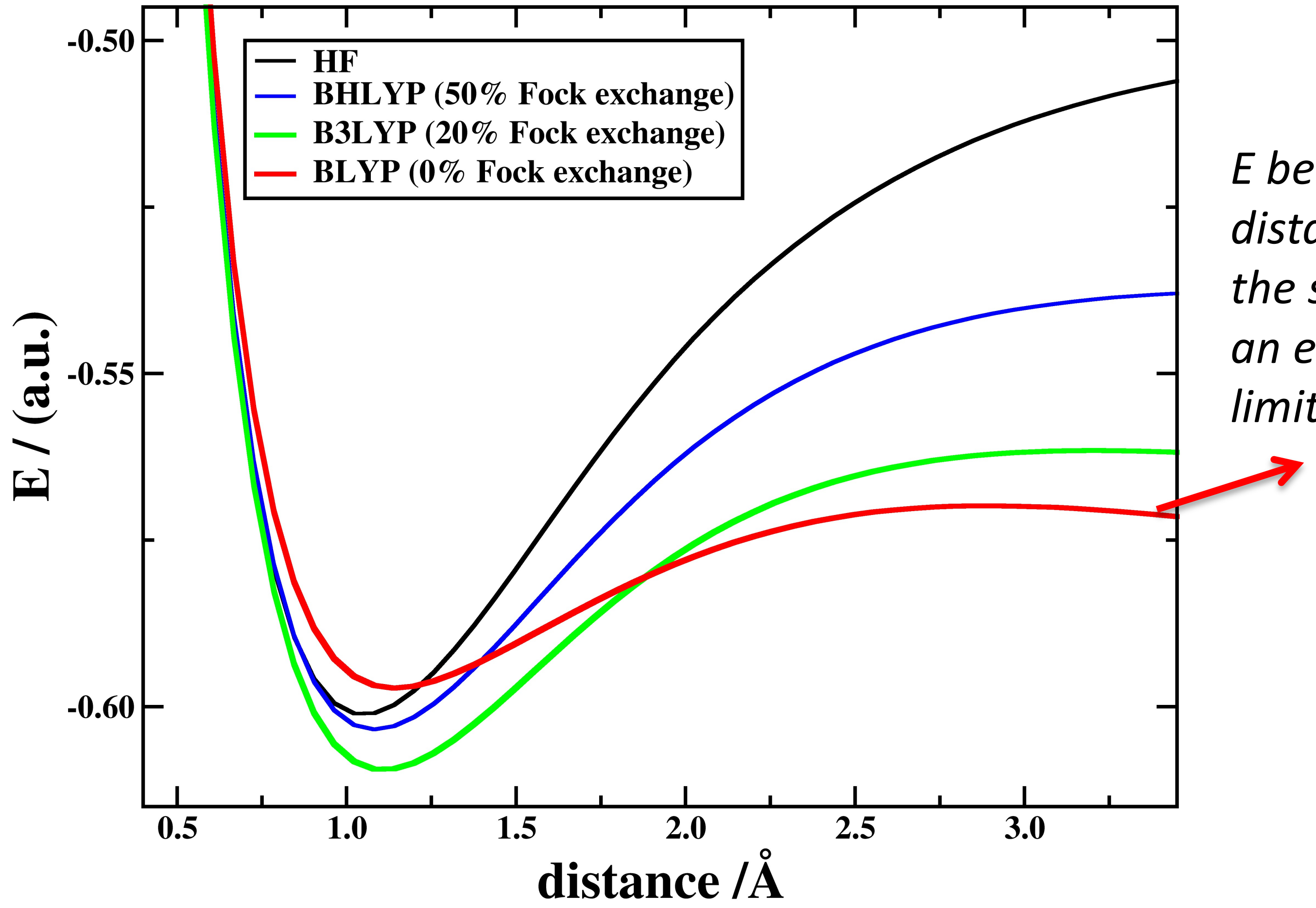
Kohn-Sham operator

$$\mathbf{\hat{f}^{KS} = -\frac{1}{2}\nabla^2 + \hat{V}_{ne} + \sum_j^N \hat{J}_j + V_{XC}[\rho]}$$

no automatic cancellation of the SIE. The true V_{xc} is SIE-free *but in an approximate V_{xc}* ***this cannot be automatically guaranteed***

SIE example: dihydrogen cation dissociation

For a given basis set, HF provides the exact solution of the Schrödinger Eq. for one-electron systems



E becomes more negative at large distances. Artificial stabilisation of the system.Each nucleus shares half an electron at the dissociation limit (SIE = delocalisation error)

- Higher Fock exchange = less SIE
- However, functionals with 100% in applications are no ideal solution either.

Some SIE-related problems and tips/my thoughts

- Elongated bonds, such as in **transition states**: reaction barriers often underestimated

➡ Often a hybrid functional with 50% Fock exchange is good (or a double hybrid)

- Impact on **HOMO-LUMO gaps**: *Example: octatetraene [6-311+G(2d,p) basis]*

➡ Gaps depend on amount of Fock exchange

➡ Trying to predict or quantify such gaps is a useless exercise. At best we can provide trends for a series of molecules

➡ The same problem also exists for band gaps in solids

method	gap /eV
HF	9.16
BHLYP	5.73
B3LYP	3.76
BLYP	2.51

- Little known consequence of the gap problem: treating **polypeptides/proteins** with (meta-)GGAs often leads to SCF convergence problems, see:

Rudberg *J. Phys.: Condens. Matter* **2012**, *24*, 072202.
Goerigk, Collyer, Reimers *JPCB* **2014**, *118*, 14612.

Some SIE-related problems and tips/my thoughts

- Wrong decay of density, can lead to **unbound electrons in negatively charged systems**. *Example: occupied orbitals peroxide anion* O_2^{2-} *[6-311+G(2d,p) basis]*

orbital #	energy /(a.u.)
1	-18.58535
2	-18.58533
3	-0.38964
4	-0.24122
5	0.17649
6	0.21408
7	0.21408
8	0.30710
9	0.30710

Positive MO energies for occupied orbitals are unphysical! Unbound electrons in a molecule!!!

- **Transition metal compounds**:
  - Splitting between different spin states often wrong
  - Spin densities (and therefore unpaired electrons) can be too delocalised

- Many more problems for ground and excited states ...

A few formal definitions around the SIE

- SIE = SIE(one-e^-) + SIE (many-e^-)
  - Hard to separate the two in many-electron systems.
  - Many-electron SIE is often investigated with the help of fractional electron numbers, but we won't discuss this here.
  - A functional that is one-electron SIE-free is not necessarily free from the many-electron SIE

- We can also separate the SIE into other components, for instance into a component that shows the SIE contribution from the exchange part of the functional and another looking at the correlation contribution to the SIE (self correlation)
- There is one more useful separation that we'll discuss later.

- Perdew and Zunger (PZ) developed a one-electron correction that removes the SIE on an orbital-by-orbital basis: Perdew, Zunger *Phys. Rev. B: Condens. Matter Mater. Phys.* **1981**, *23*, 5048.
  - Improves on some many-electron problems
  - Increased computational effort
  - Energy varies with unitary rotation of orbitals.
  - People have attempted improved corrections based on the PZ one.

The largest study of the one-electron SIE

Lonsdale, Goerigk *PCCP* **2020**, *22*, 15805 (**2020 Hot Article**, Emerging Investigator Themed Collection)

Volume 22
Number 28
28 July 2020
Pages 15775–16434

PCCP

Physical Chemistry Chemical Physics
rsc.li/pccp

ISSN 1463-9076

ROYAL SOCIETY OF CHEMISTRY

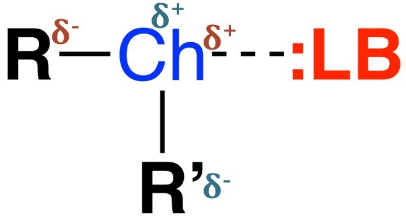
PAPER
Dale R. Lonsdale and Lars Goerigk
The one-electron self-interaction error in 74 density functional approximations: a case study on hydrogenic mono- and dinuclear systems

- one-electron atoms/ions ranging from Z=1-36
- Heteronuclear and homonuclear one-electron diatomics with nuclei having Z=1-6
- 74 density functionals

Main findings (w/o showing you any plots or tables)

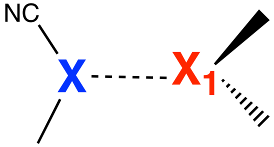
- Some functionals are truly one-electron SIE free for the mononuclear systems, but not for the dinuclear ones: TPSS, revTPSS, SCAN, hybrids based on those
- PBE is one-SIE free for H atom, but relies on error compensation between exchange and correlation SIE.
- Erratic behaviour for some Minnesota functionals
- Van-der-Waals functionals (VV10 based) have spurious self dispersion
- Range separation is no guaranteed solution for the one-electron SIE
- One-electron SIE is linear in Z

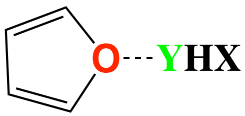
How SIE affected our own research: chalcogen bonding

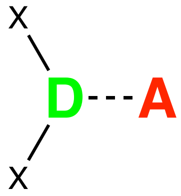


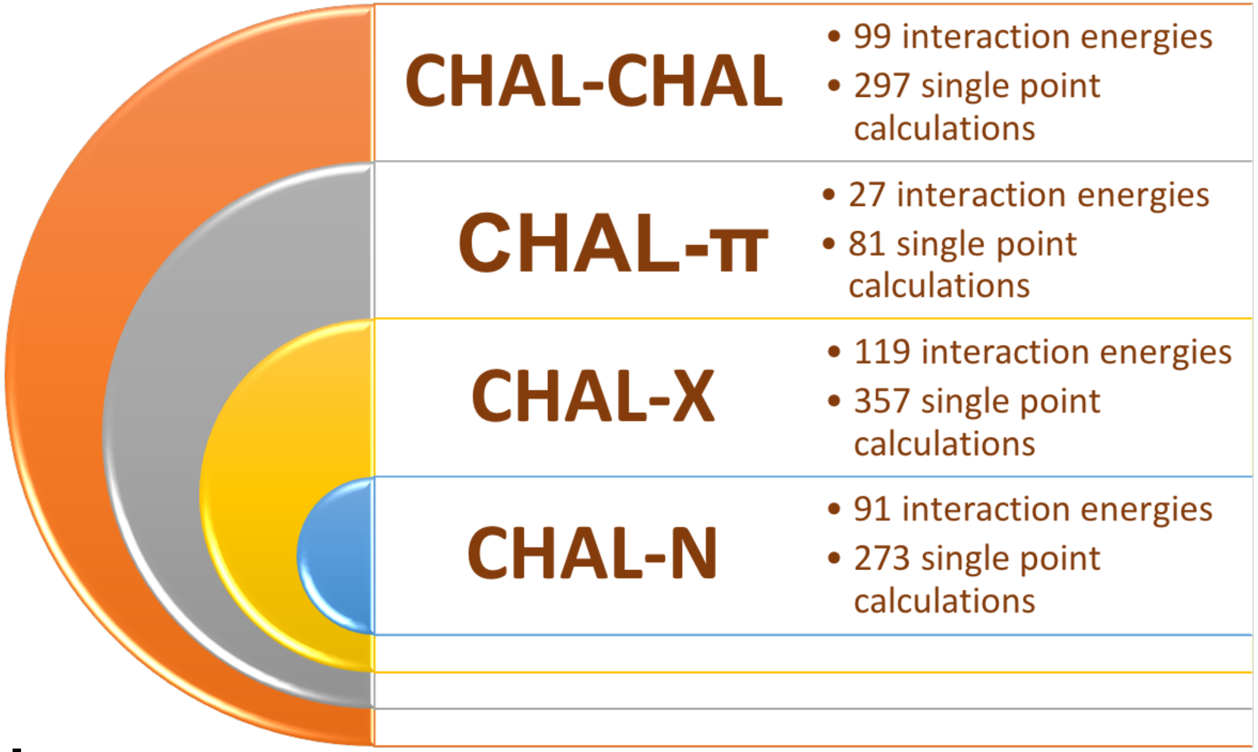
CHAL336 Benchmark Set

1008 single point calculations
336 interaction energies







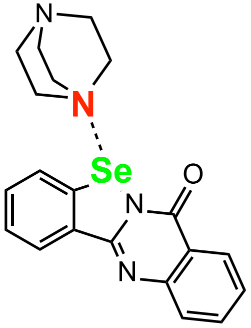


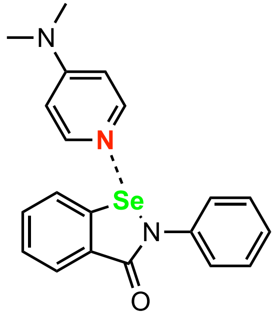
CHAL-CHAL
- 99 interaction energies
- 297 single point calculations

CHAL-π
- 27 interaction energies
- 81 single point calculations

CHAL-X
- 119 interaction energies
- 357 single point calculations

CHAL-N
- 91 interaction energies
- 273 single point calculations





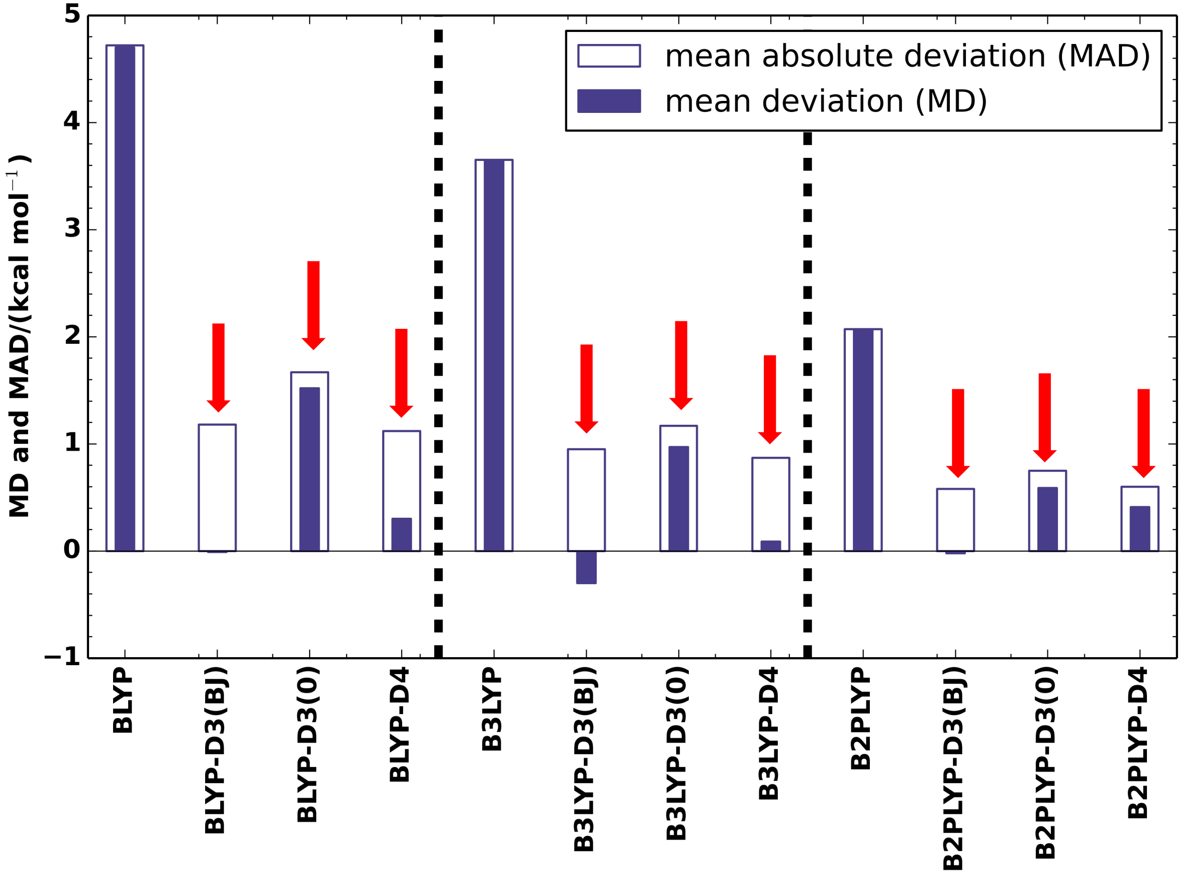
$O{=}C{=}Y\cdots NH_3$

$O_3Y - - - - NH_3$

Mehta, Fellowes, White, Goerigk *JCTC* **2021**,
DOI: 10.1021/acs.jctc.1c00006.

Impact of London dispersion corrections

- ❖ A negative mean deviation (MD) signifies overestimation
- ❖ ma-def2-QZVPP basis set



Mehta, Fellowes, White, Goerigk *JCTC* **2021**, *DOI:* 10.1021/acs.jctc.1c00006.

Impact of London dispersion corrections

	MAD	MD
PBE	1.81	0.98
PBE-D3(BJ)	1.49	-1.24
PBE-D4	1.54	-1.31
PBE-D3(0)	1.14	-0.58
PBE-NL	1.96	-1.85

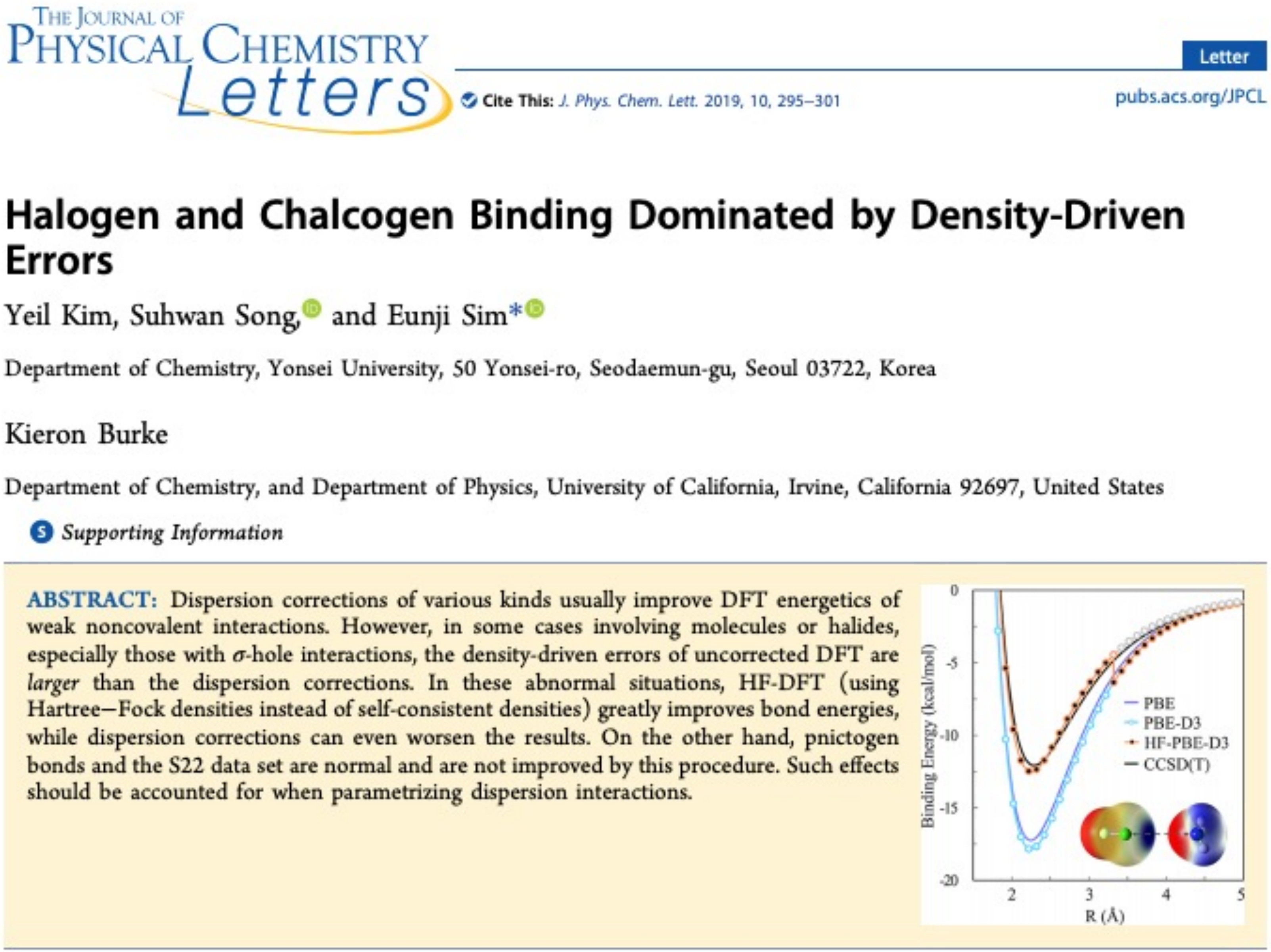
- A negative mean deviation (MD) signifies overestimation
- ma-def2-QZVPP basis set
- We made the observations on the left also for other functionals

~~**Dispersion corrections make things worse!!!!!**~~

➡ **No, it seems to depend on the functional. Something else is going on.**

Mehta, Fellowes, White, Goerigk *JCTC* **2021**, *DOI:* 10.1021/acs.jctc.1c00006.

It seems to be the density-driven error



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Letter
Cite This: J. Phys. Chem. Lett. 2019, 10, 295−301
pubs.acs.org/JPCL

Halogen and Chalcogen Binding Dominated by Density-Driven Errors

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Supporting Information

ABSTRACT: Dispersion corrections of various kinds usually improve DFT energetics of weak noncovalent interactions. However, in some cases involving molecules or halides, especially those with σ-hole interactions, the density-driven errors of uncorrected DFT are *larger* than the dispersion corrections. In these abnormal situations, HF-DFT (using Hartree−Fock densities instead of self-consistent densities) greatly improves bond energies, while dispersion corrections can even worsen the results. On the other hand, pnictogen bonds and the S22 data set are normal and are not improved by this procedure. Such effects should be accounted for when parametrizing dispersion interactions.

Functional and density errors

- SIE = (functional error) + (density error)

ρ : exact density (results from SCF with true functional)
$\tilde{\rho}$: approximate density (results from SCF with approximate functional)

Functional error: arises from the fact that we use an approximate functional

$$\Delta E_{\mathrm{F}} = E_{\mathrm{XC}}^{\mathrm{DFA}}[\rho] - E_{\mathrm{XC}}^{\mathrm{exact}}[\rho]$$

Density error: arises from the fact that the approximate functional ”contaminates” the density during the SCF procedure

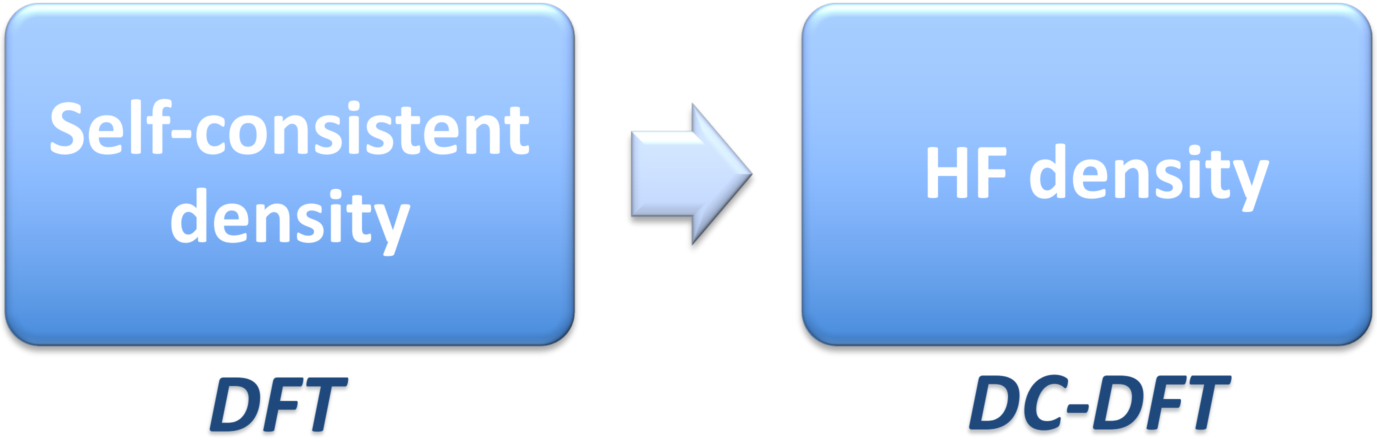
$$\Delta E_{\mathrm{D}} = E^{\mathrm{DFA}}[\tilde{\rho}] - E^{\mathrm{DFA}}[\rho]$$

Lee, Furche, Burke *J. Phys. Chem. Lett.* **2010,** *1*, 2124.
Kim, Sim, K. Burke *J. Chem. Phys.* **2014**, *140*, 18A528.
Sim, Song, Burke *J. Phys. Chem. Lett.* **2018**, *9*, 6385.
Kim, Song, Sim, Burke *J. Phys. Chem. Lett.* **2019**, *10*, 295.

Density-corrected DFT (DC-DFT)

$$\Delta E_{\mathrm{D}} = E^{\mathrm{DFA}}[\tilde{\rho}] - E^{\mathrm{DFA}}[\rho]$$

- Using the exact density with our approximate functional in a non-SCF step would eliminate the density error
- As a proxy for the unknown exact density, we use a HF density (SIE free)



Self-consistent density

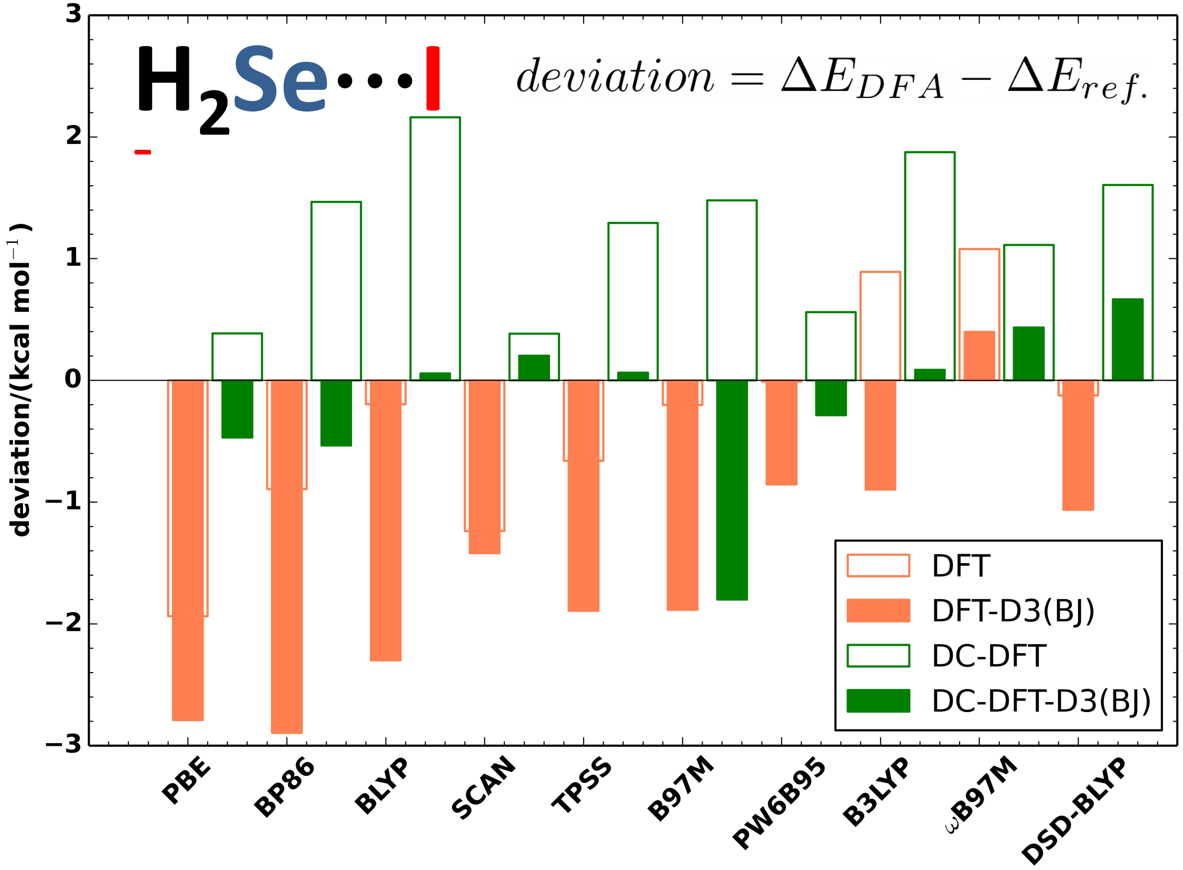
HF density

DFT

DC-DFT

Lee, Furche, Burke *J. Phys. Chem. Lett.* **2010,** *1*, 2124.
Kim, Sim, K. Burke *J. Chem. Phys.* **2014**, *140*, 18A528.
Sim, Song, Burke *J. Phys. Chem. Lett.* **2018**, *9*, 6385.
Kim, Song, Sim, Burke *J. Phys. Chem. Lett.* **2019**, *10*, 295.

DFT vs DC-DFT for chalcogen bonding



Average deviation (**kcal/mol**)

DFT -0.33

DFT-D3(BJ) -1.56

DC-DFT 1.23

DC-DFT-D3(BJ) -0.16

Mehta, Fellowes, White, Goerigk *JCTC* **2021**, *DOI:* 10.1021/acs.jctc.1c00006.

DFT vs DC-DFT for chalcogen bonding (10 select systems)

	DFT-D3(BJ)	DC-DFT-D3(BJ)
PBE	1.00 (-1.00)	0.51 (0.42)
BP86	1.21 (-1.09)	0.54 (0.38)
BLYP	1.29 (0.27)	1.59 (1.59)
SCAN	0.82 (-0.72)	0.68 (-0.35)
TPSS	0.83 (-0.78)	0.39 (0.38)
B97M	2.85 (-2.84)	1.80 (-1.80)
PW6B95	0.56 (-0.48)	0.29 (0.07)
B3LYP	0.41 (-0.04)	0.71 (0.68)
ωB97M	0.83 (0.83)	1.11 (1.11)
DSD-BLYP	0.97 (-0.97)	0.69 (0.23)

- MADs (and MDs in parenthesis) are in kcal mol^{-1}.
- A negative mean deviation (MD) signifies overestimation.
- ma-def2-QZVPP basis set.

Mehta, Fellowes, White, Goerigk *JCTC* **2021**, *DOI:* 10.1021/acs.jctc.1c00006.

Now we're talking about dispersion again: very final thoughts

- Only because a result is worse when using a dispersion correction, it does not automatically mean we can blame the correction:
  - ➢ We know that many approximate functionals do not describe dispersion
  - ➢ There might be some error compensation that contributes to a seemingly good result without a dispersion correction
  - ➢ adding the correction ruins that error compensation, but provides a "truer" picture of the functional

- Ultimately, we always rely on some inherent error cancellation, but we can reduce the reliance on it by trying to address as many inherent problems as possible.

- Based on benchmarking (general or specific problems), we can identify the most robust or suitable functionals until we have fixed more of the current problems.

- DFT development is still important. **Don't shy away from new approaches**.

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