

SBM CDT 2020

Computational Module

Day 2

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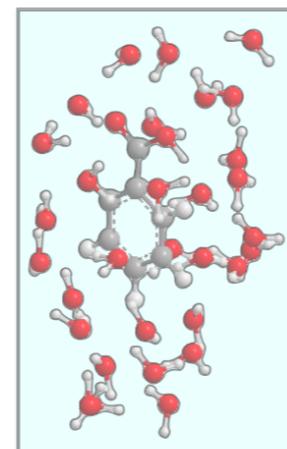


Github: duartegroup

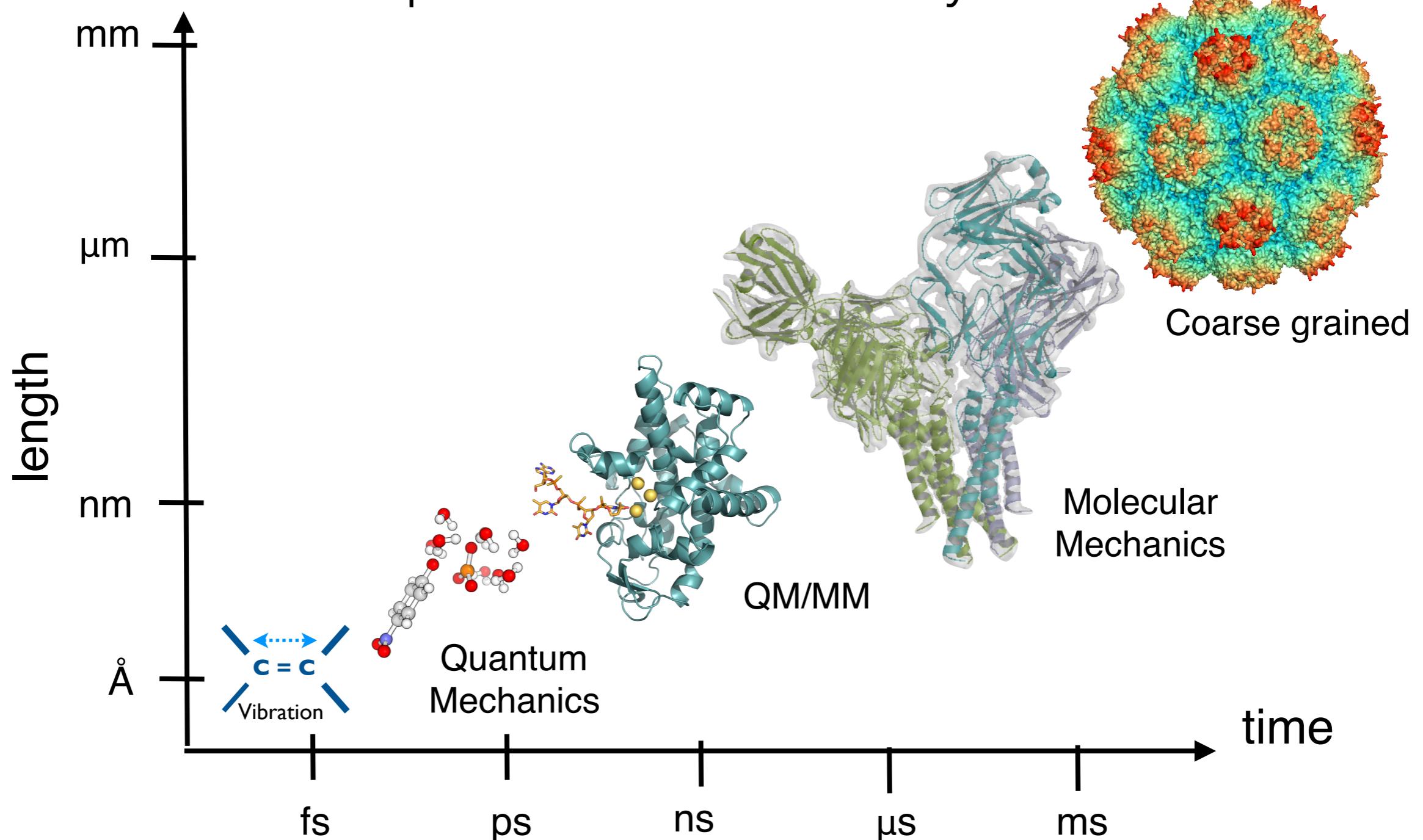
Lecture 2

Outline

- Recap of Day 1
- The zoo of DFT functionals
- Basis sets
- Solvent effect



Computational Chemistry



“Everything should be made as simple as possible, but not simpler.”

How do we use it?

Which System Do I Have?



What Do You Want to Compute (and Why)?



Which Model /Method Should I Choose?



Verify Approach (vs. Experiment)



Interpret/Analyse

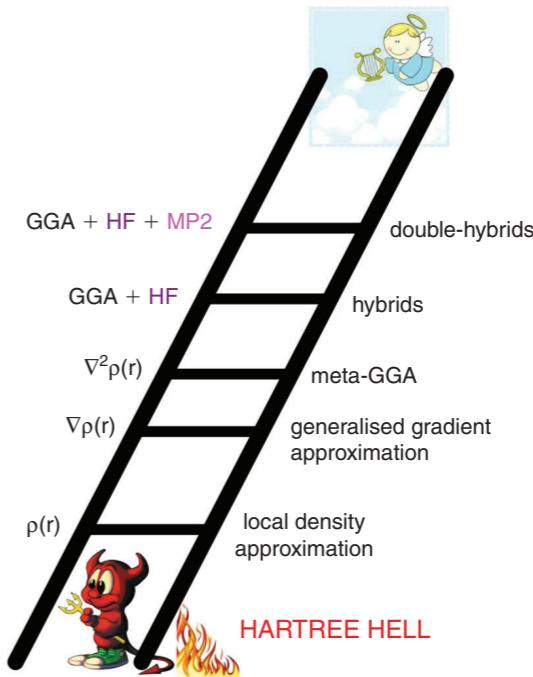
Useful References

A Trip to the Density Functional Theory Zoo: Warnings and Recommendations for the User

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

<https://doi.org/10.1071/CH19023>

HEAVEN OF CHEMICAL ACCURACY



Thirty years of density functional theory in computational chemistry: an overview and extensive assessment of 200 density functionals

Mol. Phys. **2017**, 115, 2315

<https://doi.org/10.1080/00268976.2017.1333644>

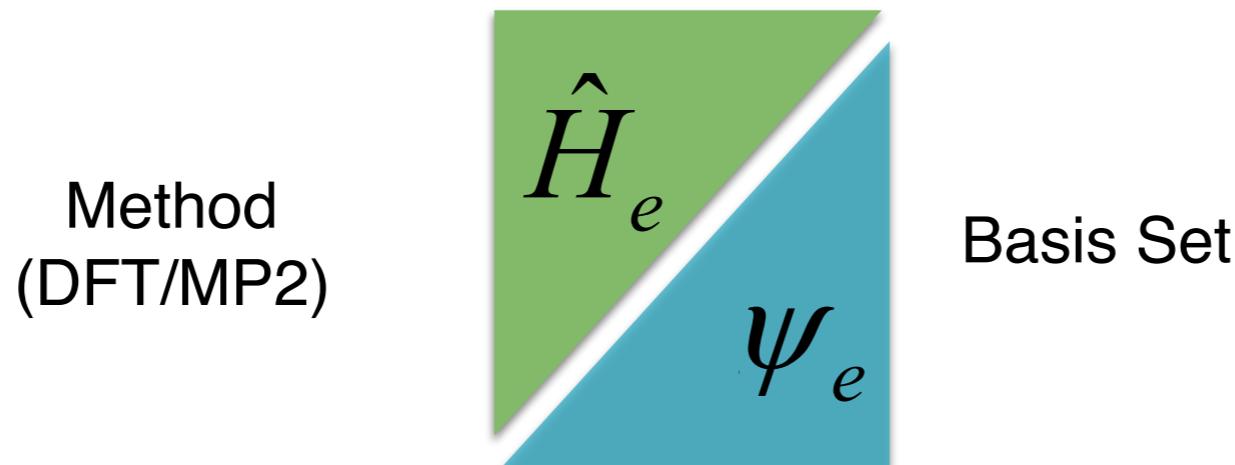


Functional/Basis Sets

Electronic Schrödinger Equation

$$\hat{H}_e \psi_e = E_e \psi_e$$

$$\hat{H}_e = \frac{-\hbar^2}{2m} \sum_i^{electrons} \nabla_i^2 - \sum_i^{electrons} \sum_A^{nuclei} \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \sum_{i < j}^{electrons} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$



Functional/Basis Sets

The foundation of DFT is the **Hohenberg–Kohn theorem**, it states that the density determines everything about the system

second H-K theorem states that the electron density that minimises the energy of the functional is the true electron density corresponding to the solutions of the Schrödinger equation

Variational principle

$$E_0[\Psi_0] = \min_{\Psi} E[\Psi] = \min_{\Psi} \langle \Psi | T + V_{Ne} + V_{ee} | \Psi \rangle$$

$$E_0[\rho_0] = \min_{\rho} E[\rho] = \min_{\rho} T[\rho] + E_{Ne}[\rho] + E_{ee}[\rho]$$

Functional/Basis Sets

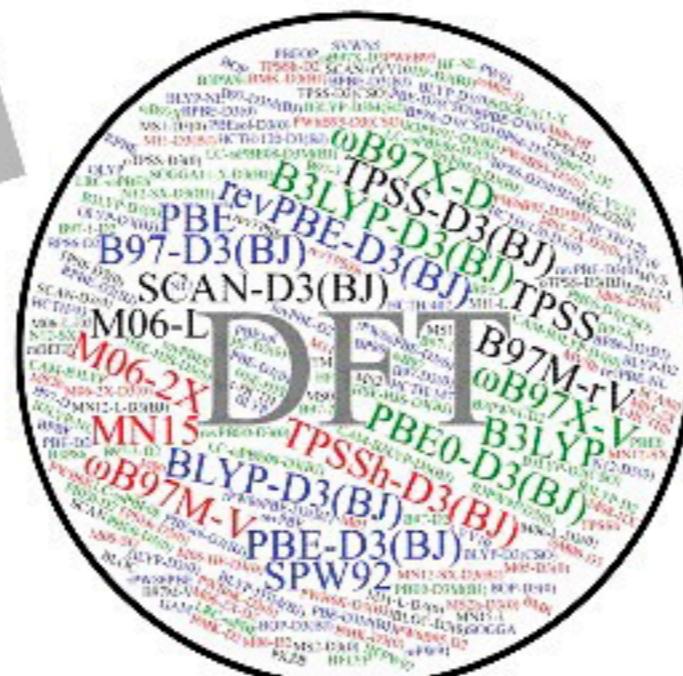
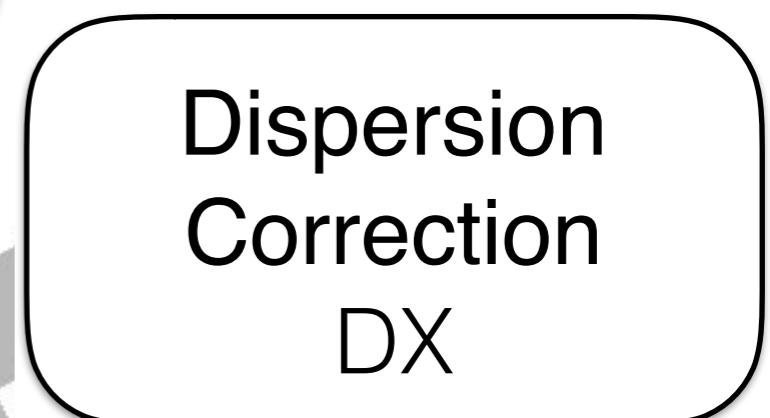
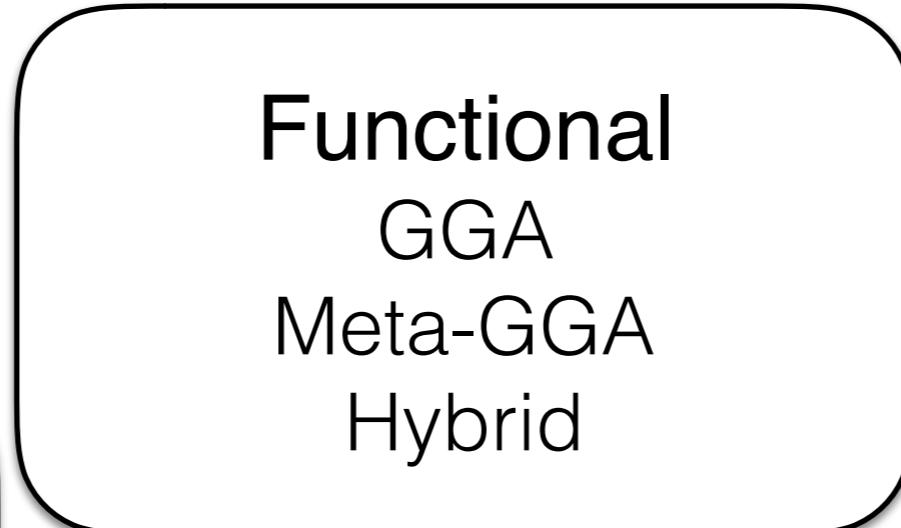
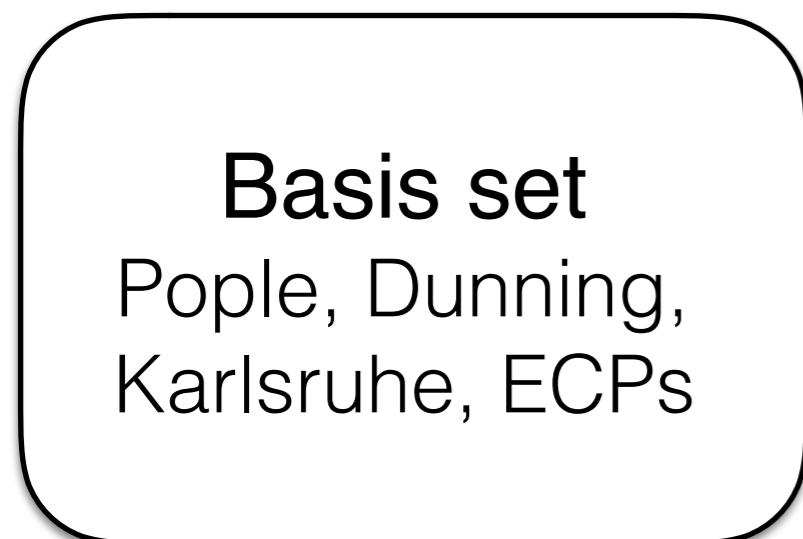
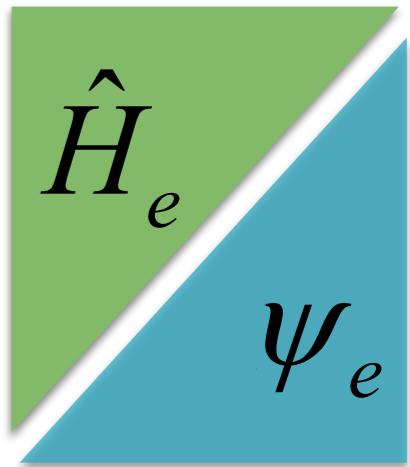
The system is replaced by a **fictitious non-interaction system** with same density as the real system.

$$E[\rho] = T[\rho] + E_{Ne}[\rho] + E_H[\rho] + E_x[\rho] + E_c[\rho]$$

$$T[\rho] = -\frac{1}{2}\langle\psi|\nabla^2|\psi\rangle$$

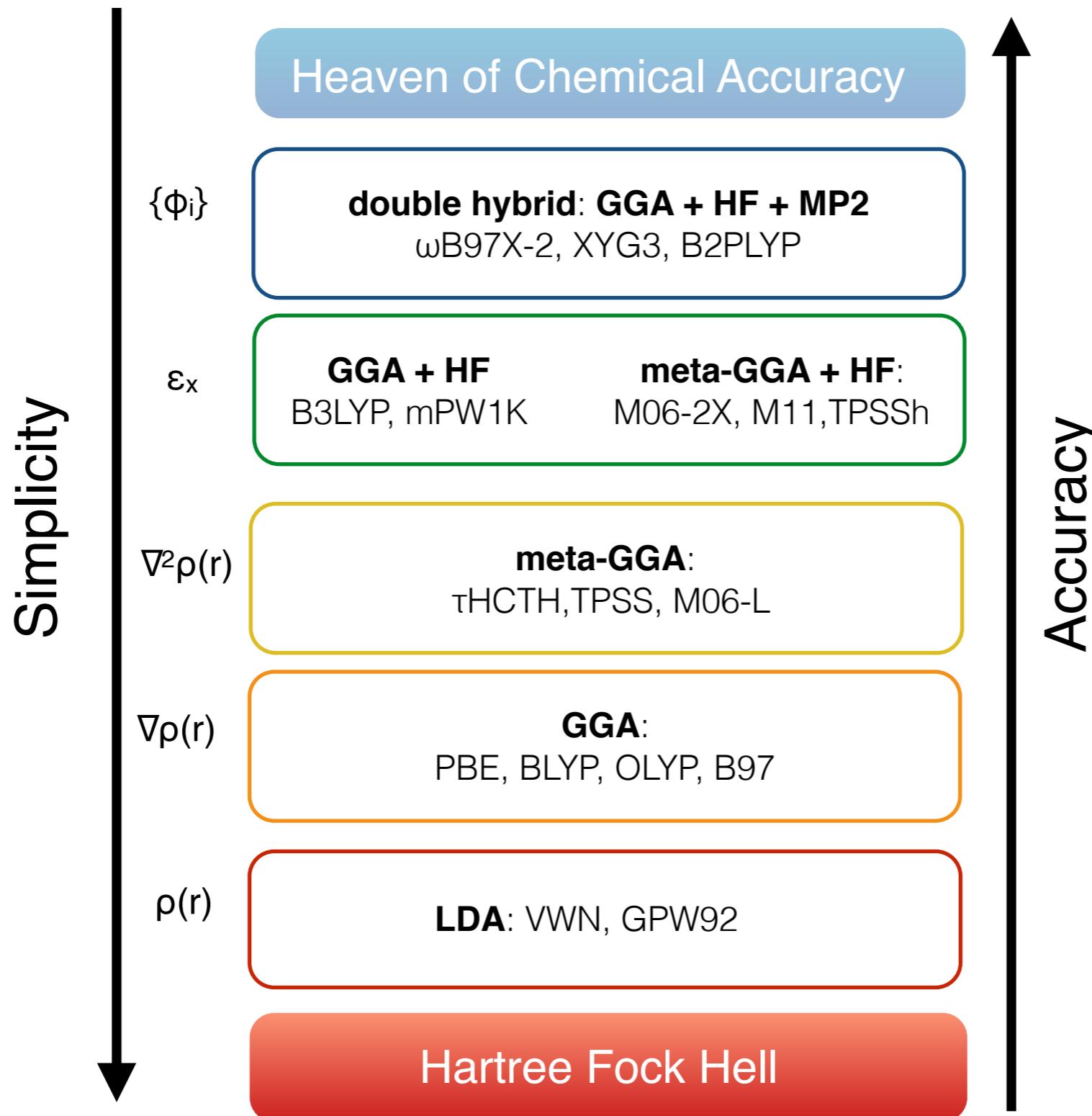
$$E_{Ne}[\rho] + E_H[\rho] = Z \int \frac{\rho(r)}{r} dr - \frac{1}{2} \int \rho(r_1)\rho(r_2) dr_1 dr_2$$

Functional/Basis Set



Functional/Basis Sets

\hat{H}_e



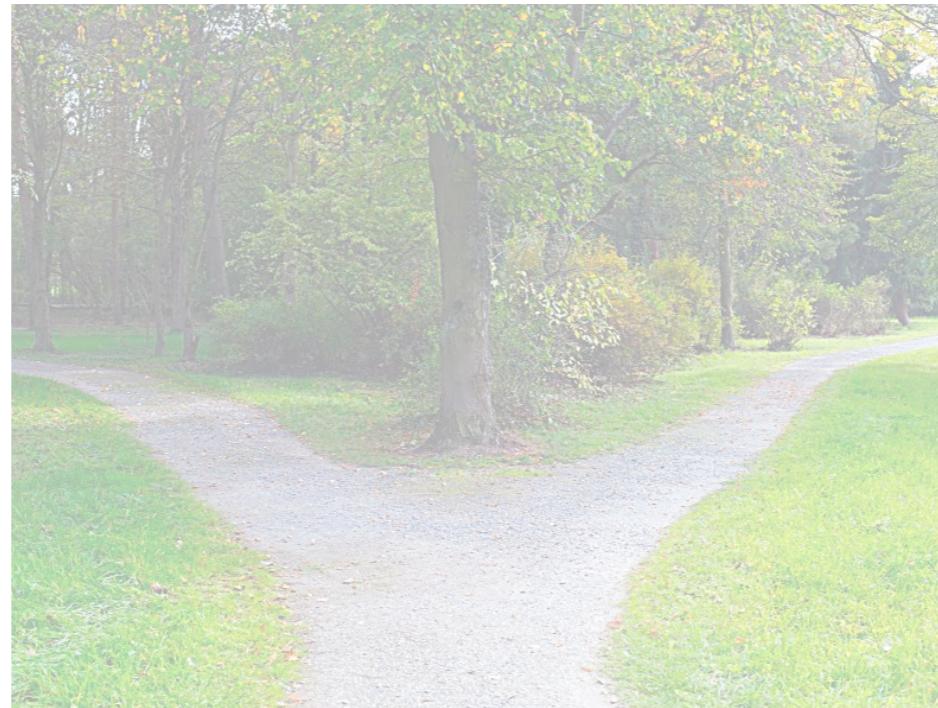
Theoretical Method (Functional)

\hat{H}_e

Non-Empirical

John Perdew

PBE, TPSS, etc.



Semi-Empirical

Axel Becke

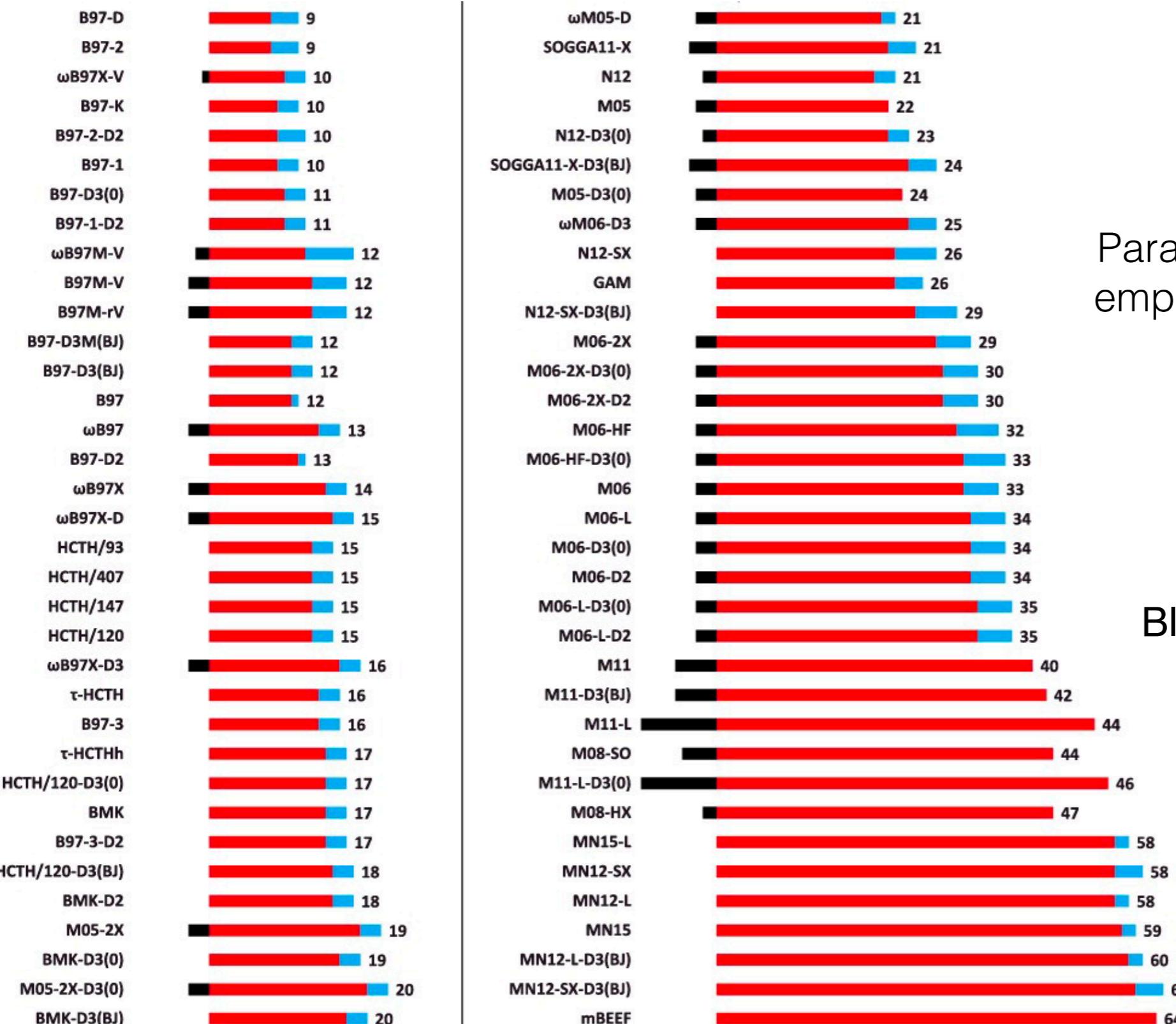
B3LYP, B97, etc.

... modern functionals are ‘sacrificing physical rigor for the flexibility of empirical fitting’...

as a result DFT is in need of new strategies for functional development’

Perdew *et al.* *Science* 2017, 6320,49

Theoretical Method (Functional)



Parameter counting in semi-empirical density functionals

Red: fitted parameters
Blue:borrowed or preset parameters

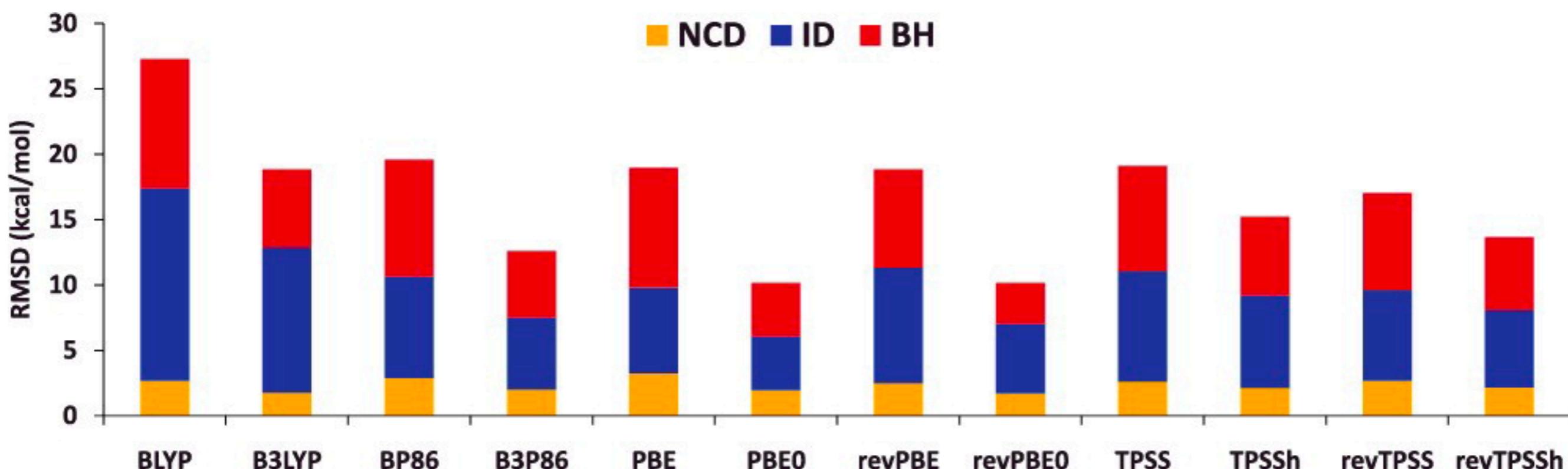
Black:number of constraints

Theoretical Method (Functional)

\hat{H}_e

Which Functional is Best for ...?

NCD 91 non-covalent inter. **ID** 155 isomerisation energies **BH** 206 barrier heights

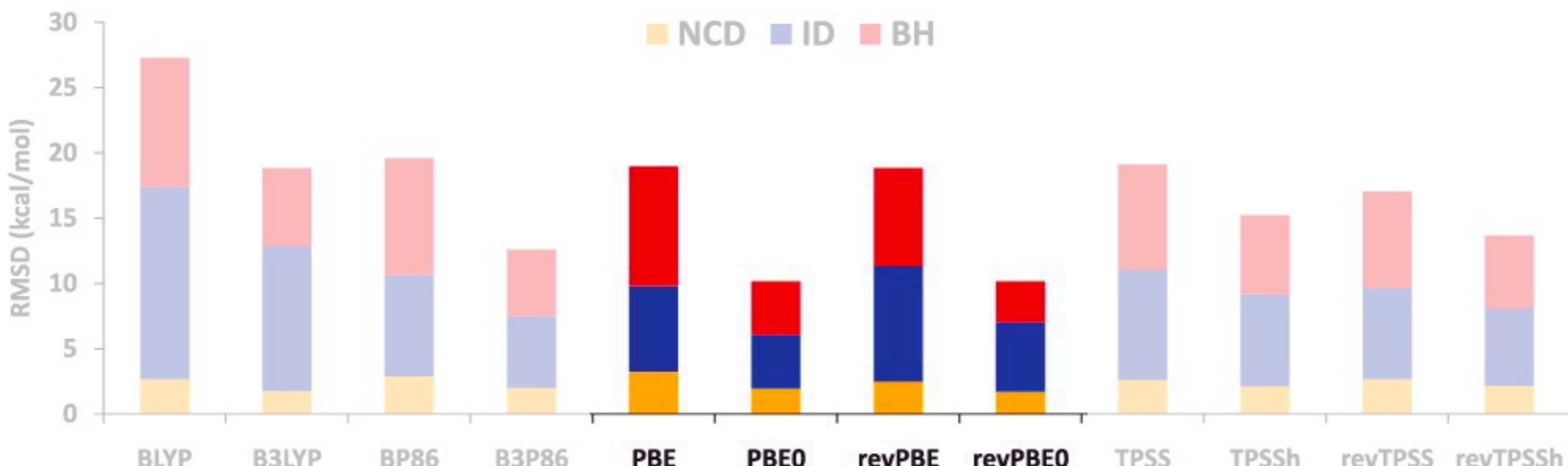


Theoretical Method (Functional)

\hat{H}_e

Which Functional is Best for ...?

NCD 91 non-covalent inter. **ID** 155 isomerisation energies **BH** 206 barrier heights



PBE: Perdew-Burke-Ernzerhof (GGA)

PBE0 (hybrid: GGA + HF)

revPBE: increase of the gradient contribution to the exchange

14

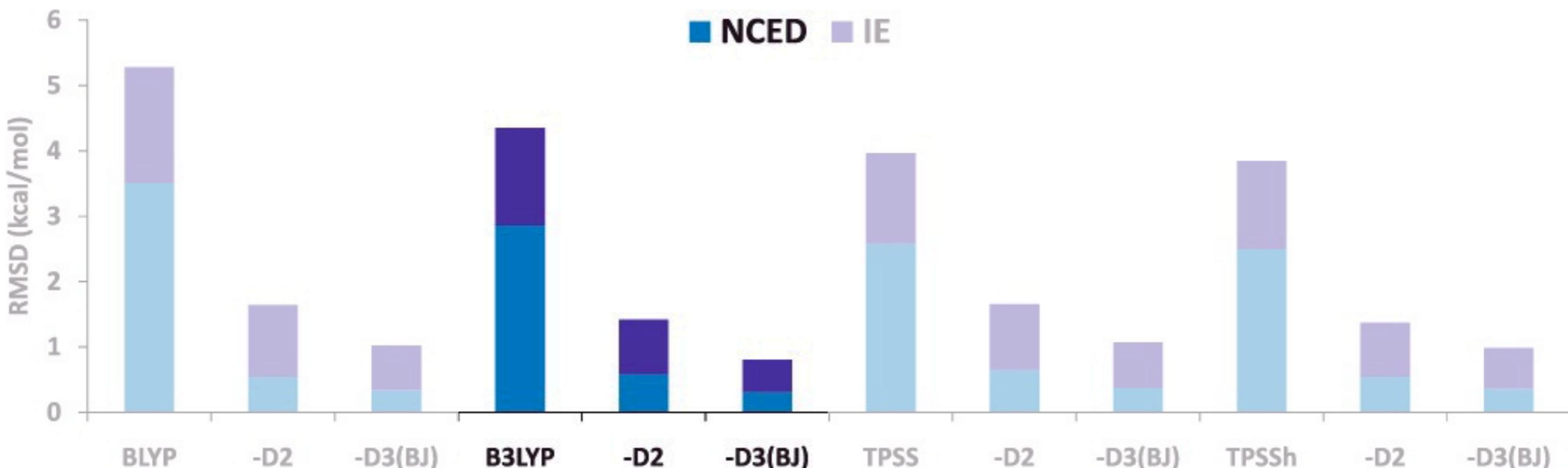
Theoretical Method (Functional)

\hat{H}_e

Which Functional is Best for ...?

NCED 91 1744 non-covalent dimer interactions

IE 755 isomerisation energies

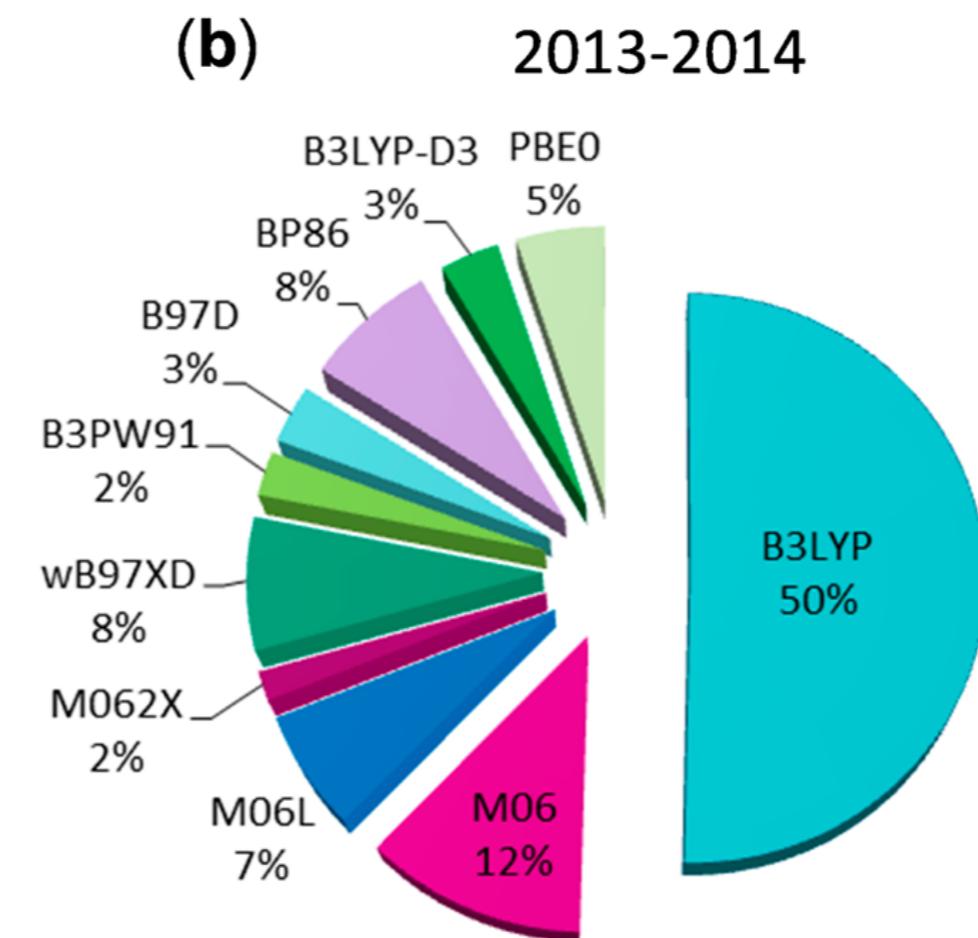
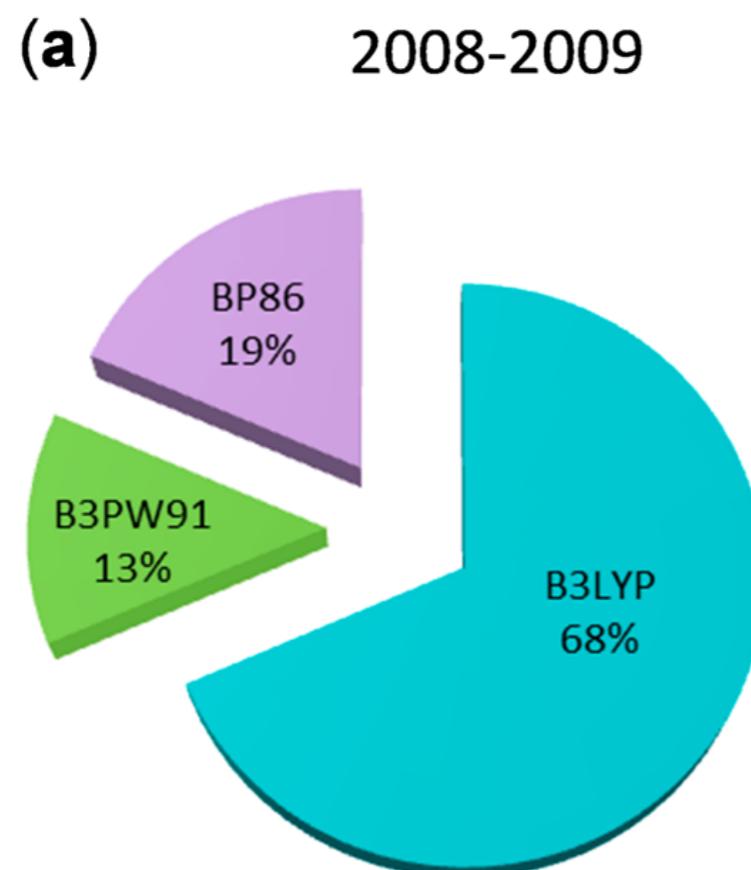


Theoretical Method (Functional)

\hat{H}_e

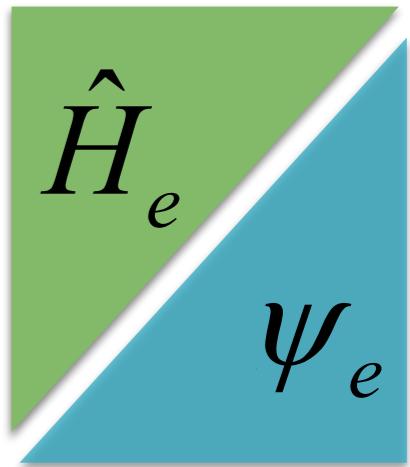
Which Functional is Best for Geometry Optimisation?

Popular DFT methods used for Pd, Ni, Rh, and Ir



the dominance of B3LYP appears to be fading...(more later)

Functional/Basis Set



Basis set
Pople
Dunning
ECPs

Functional
GGA
Meta-GGA
Hybrid

Dispersion
Correction
DX



Basis Set

Collection of vectors which defines a space in which a problem is solved

ψ_e

Physicists

like plane wave basis sets

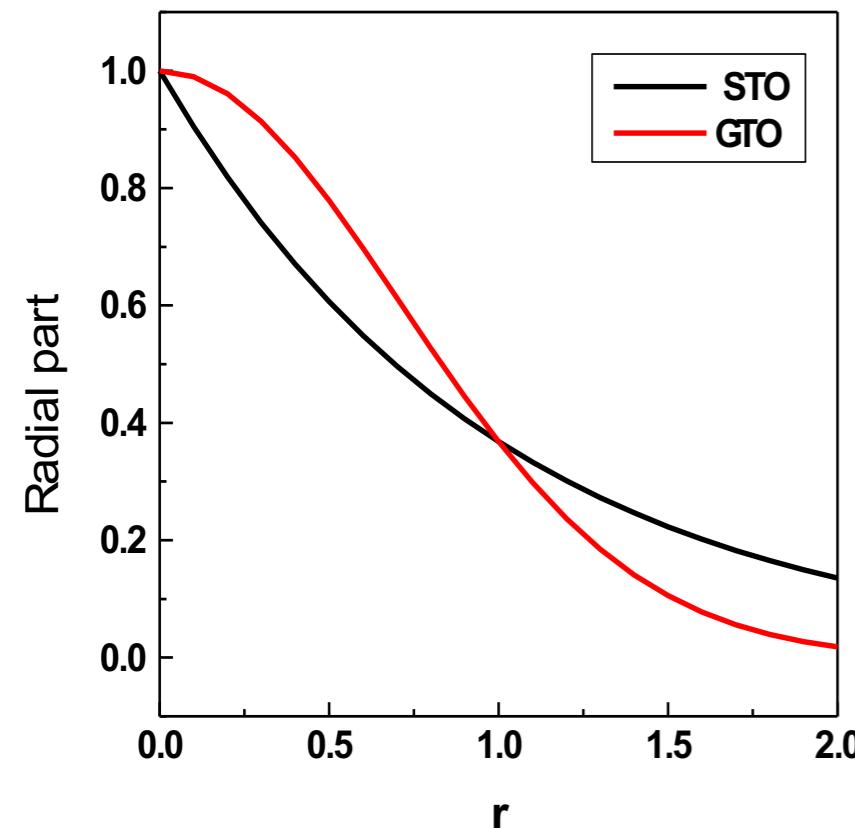
Chemists

LCAO-MO approximation

Basis Set

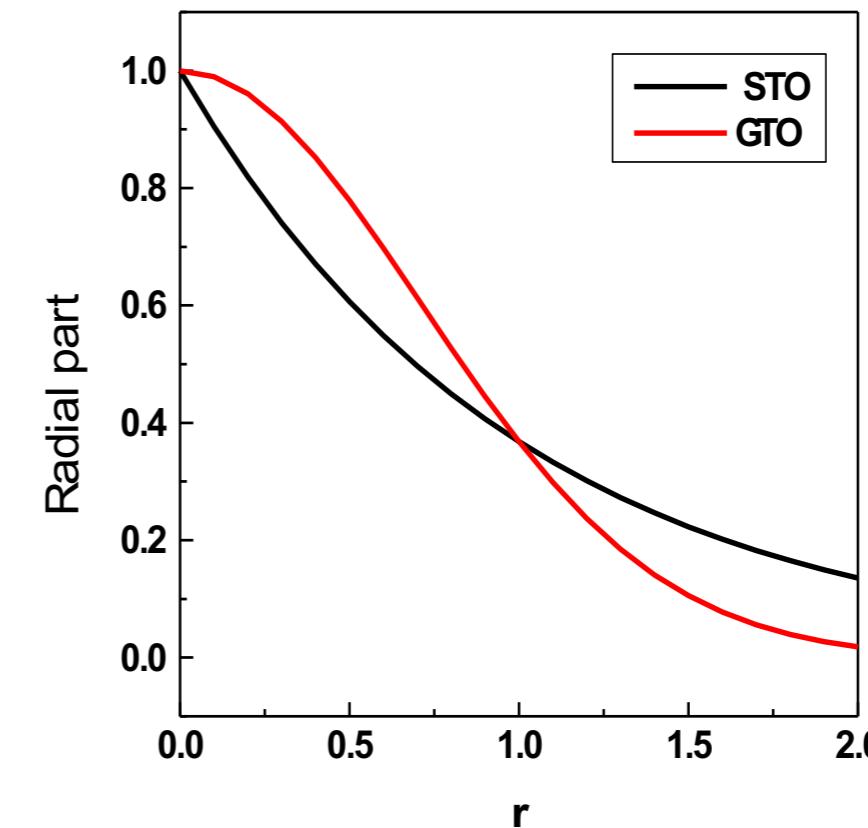
ψ_e

Slater type orbitals (STOs)



$$\phi_{nlm_l}^{STO} = N_\xi r^{n-1} e^{-\xi r} Y_{lm_l}$$

Gaussian type orbitals (GTOs)



$$\phi_{nlm_l}^{GTO} = N_\xi r^{n-1} e^{-\xi r^2} Y_{lm_l}$$

Hydrogen atom orbitals

3/4-centre integrals can't be performed analytically. Numerically expensive

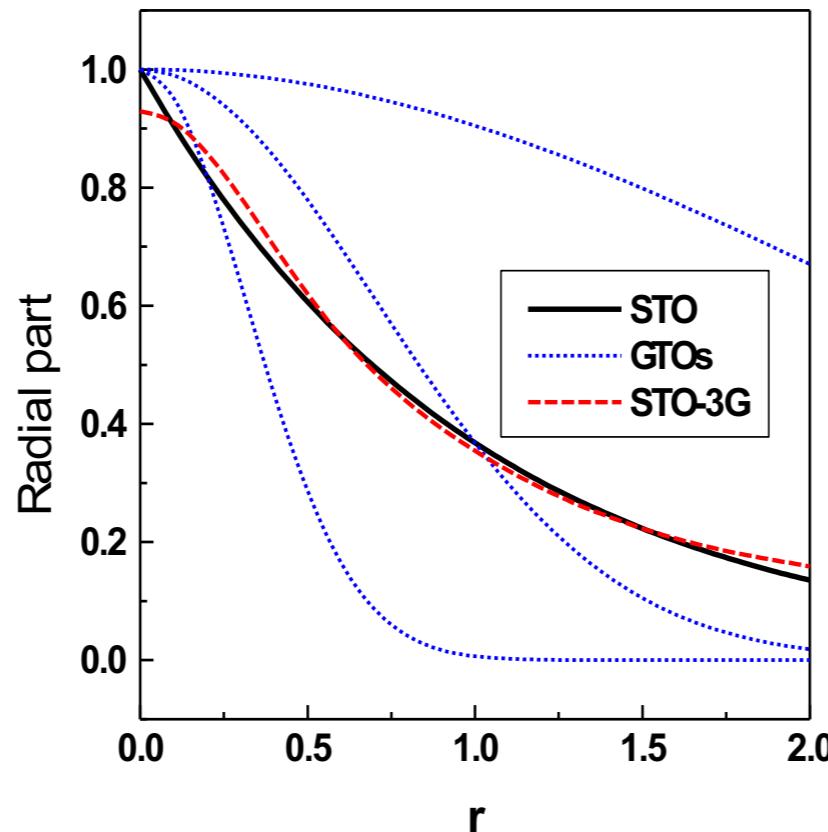
Known analytic form, more efficient

Basis Set

ψ_e

STOs vs GTOs

At the nucleus a GTO has zero slope, in contrast to a STO which has a cusp



Linear combination of gaussians to model one STO.

This gave rise to the STO-nG family of basis sets (n = gaussians used to model STO's)

Classification of basis sets

 ψ_e

Type	Description	Example
Minimal Basis Sets	1 STO for each atomic shell, core or valence	C: 1s, 2s, 2px, 2py, 2pz (5 AO's -> 5 basis functions)
Double Zeta (DZ)	2 STOs per AO	C: 10 basis functions
Triple Zeta (TZ)	3 STOs for each AO	C: 15 basis functions
Split-valence basis	1 STO for each core AO at least 2 STOs for valence AO's	C atom: 9 basis functions

...Having different-sized functions allows the orbital to get bigger or smaller when other atoms approach it

Classification of basis sets

split-valence basis

ψ_e

Pople split valence	Dunning (correlation consistent)	Karlsruhe
3-21G	cc-pvdz	aug-cc-pvdz
6-31+G*	cc-pvtz	aug-cc-pvtz
6-311++G**	cc-pvqz	aug-cc-pvqz

3 primitives assigned for each AO

valence AO described by 2 basis, one made of 2 primitives and the other of 1

3-21G

13 basis functions, 21 primitive gaussians, 13 cartesian basis functions
5 alpha electrons 5 beta electrons

O $1s^2 2s^2 2p^2 2p^1 2p^1 (3 \times 5 = 15P)$; $1 + 2 \times 4 = 9$ basis

H $1s^1 (2 \times 3 = 6P)$; $2 \times 2 = 4$ basis

Classification of basis sets

Ψ_e

Type	Description	Example
Diffuse functions	Very small ζ exponents	Improve the description of the density at large distances anions, H-bonds, polarizability
Polarisation functions	Flexibility in angular $(\ell \rightarrow \ell+1)$	Improve the description of bonding

Functional/Basis Sets

h2o_bad_geometry.inp

```
! BP86 def2-SVP SP

*xyz 0 1
H -1.0 0.0 0.0
O 0.0 0.0 0.0
H 1.5 0.0 0.0
*
```

BP86 is a GGA functional composed of:
Becke 1988 exchange functional & Perdew 1986 correlation
functional

def2-svp: Split valence polarization basis set

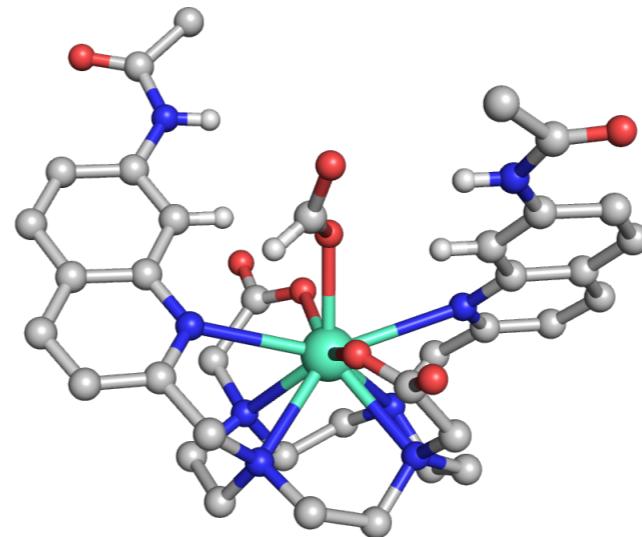
Classification of basis sets

ψ_e

- Electrostatic core potentials (ECP) e.g. lanl2dz or SDD

Cu $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s$

Pd $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^8$

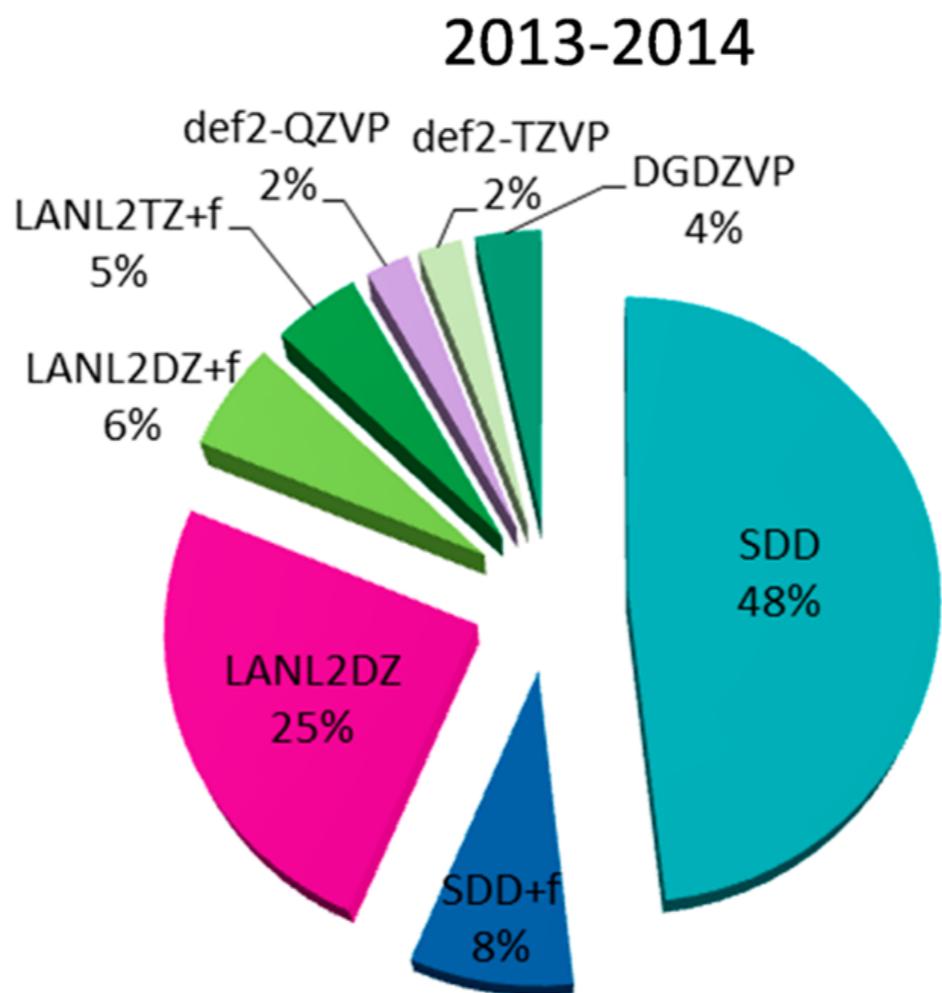


- Relativistic Effect:
 - For heavy elements, ECPs are chosen to reproduce all-e relativistic calculations
 - Other effects may (or may not) be included: e.g. spin-orbit coupling

Classification of basis sets

ψ_e

Popular DFT methods used for Pd, Ni, Rh, and Ir



Basis set superposition error (BSSE)

interaction energy of molecular complexes = $E(AB) - E(A) - E(B)$

ψ_e

Small basis

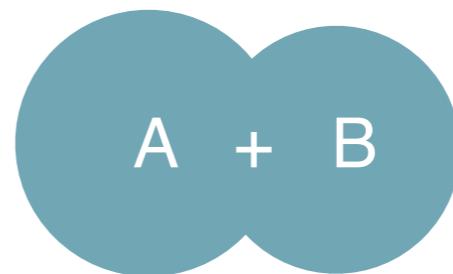
Poor description of A (anion)
Higher energy



$E(A)$

$E(B)$

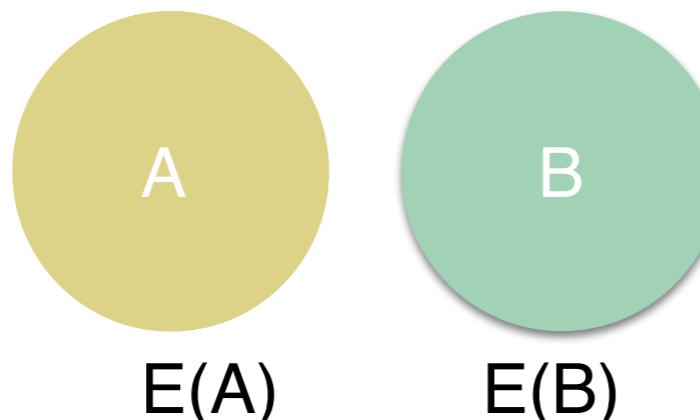
description of A is improved by the
basis from B (overstabilisation)



$E(AB)$

Large basis

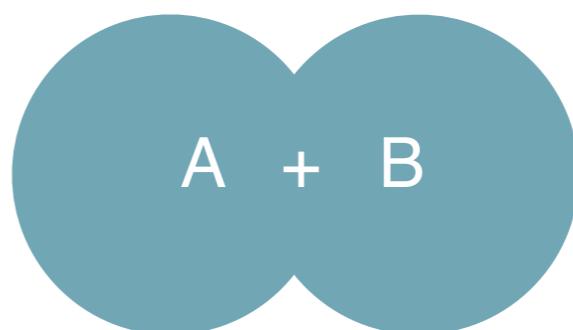
Good description of A (anion)



$E(A)$

$E(B)$

Good description of A in the complex



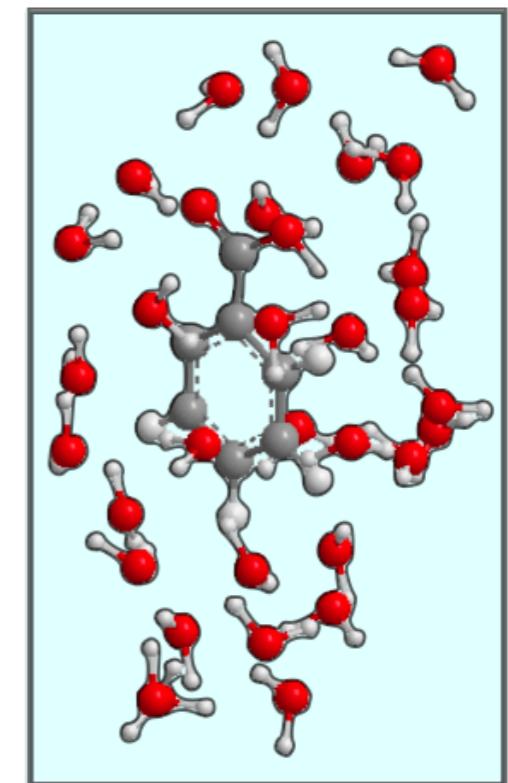
$E(AB)$

a spurious attractive contribution that arises from an improved description of the fragments in the combined basis rather than from a true physical interaction between the fragments

What is DFT useful for?

Solvent Models: Explicit vs. Implicit Solvation

Model	Explicit	Implicit
Solvent	solvent molecules	dielectric constant
Interaction	Specific non-bonded interactions	Field effect only
Comp. cost	Expensive	Relatively cheap



Break