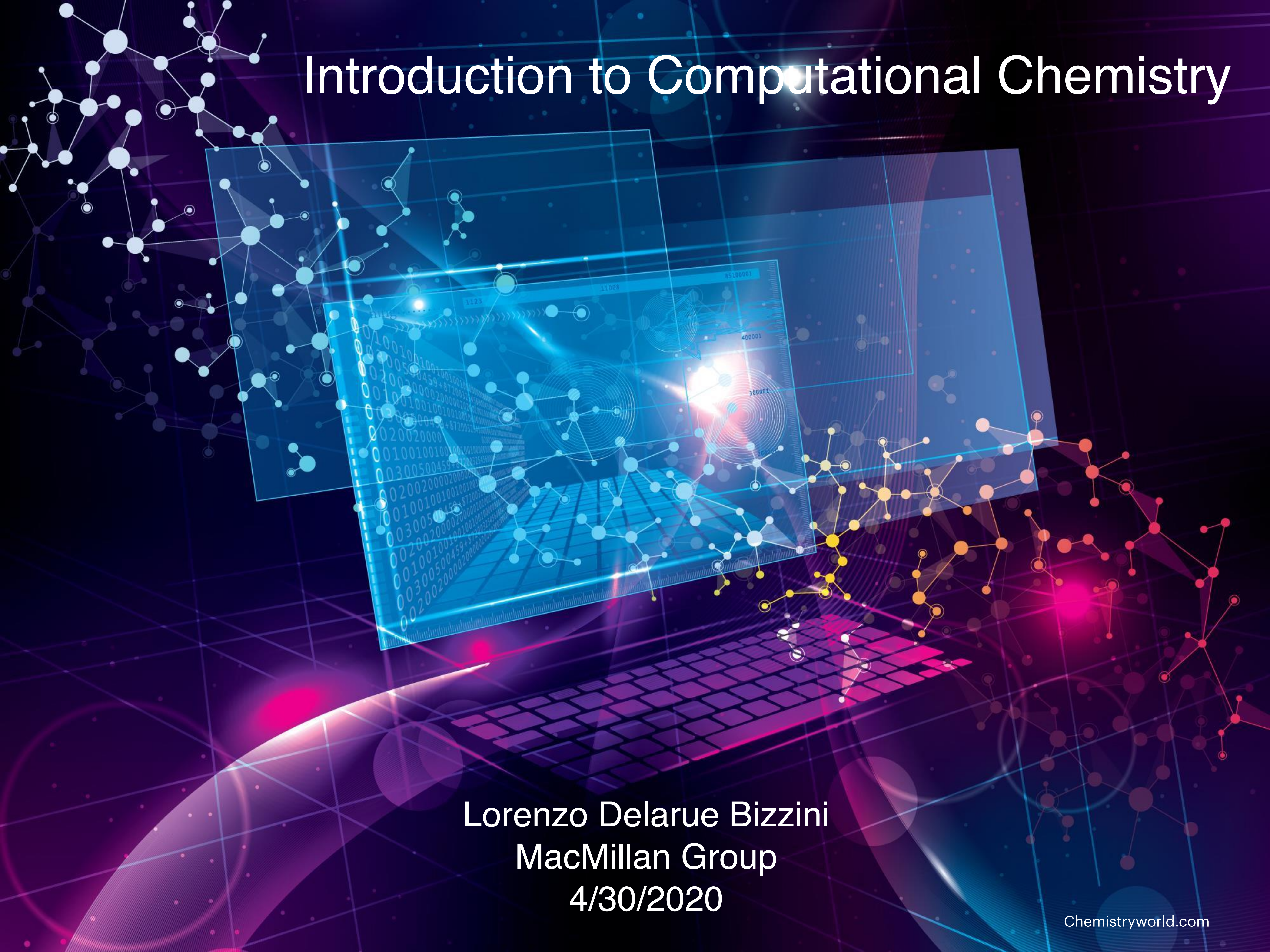
Introduction to Computational Chemistry



Lorenzo Delarue Bizzini
MacMillan Group
4/30/2020

Chemistryworld.com

Goal of this Presentation

General physical background (understanding what goes into calculation)

Understanding which parameter exist and what they do (aimed at Gaussian)

Uses Of Electronic Structure Theory

- Equilibrium geometries
- Vibrationalfrequencies (IR spectra)
- Excited states (UV/VIS spectra)
- NMR spectra
- CD spectra
- Dipole moment, polarizability, spin density, etc.
- Barrier heights and reaction paths
- With transition state theory or dynamics studies, can estimate reaction rates
- With statistical mechanics, can estimate thermodynamics properties

The One Equation for QM Description of a Molecule

$$\hat{H}\Psi = E\Psi$$

Wave Function: Contains the information about any property of the system.

Hamilton Opeator: Acts on the wave function returning the energy

Energy: The total energy of a system described by the wave function

Variational Principle

- Method for approximating the lowest energy of a system.

$$\hat{H}\Psi = E\Psi$$

Wave Function: Parametrized “trial wave function”

Energy: can not go lower than the “true” energy

Converging E leads to the “true wave function”

Ther Hamilton Operator

$$\hat{H} = -\frac{\hbar}{2M_I}\sum_{I}\nabla_I^2 - \frac{\hbar}{2m_e}\sum_{i}\nabla_i^2 \;-\sum_{i,J}\frac{Z_J e^2}{\left|r_i - R_J\right|} + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{\left|R_I - R_J\right|} + \sum_{i\neq j}\frac{e^2}{\left|r_i - r_j\right|}$$

nuclear kinetic E	electron kinetic E	elec/nuc attraction	nuc/nuc repulsion	elec/elec repulsion

Very complex many body problem! We can not even solve classical cases!

Born-Oppenheimer Approximation

- In the time frame of electrons, nuclei motion can be neglected (1800 times heavier)
- Decoupling of the nuclear and electronic energy

$$E = E_{el} + E_{nuc}$$

$$\hat{H}_{el}\Psi_{el} = E_{el}\Psi_{el}$$

- Nuclear kinetic energy becomes zero
- Nuclei repulsion becomes a constant

$$\hat{H}_{el} = -\frac{\hbar}{2m_e}\sum_i \nabla_i^2 - \sum_{i,J}\frac{Z_J e^2}{|r_i - R_J|} + \boxed{\sum_{i\neq j}\frac{e^2}{|r_i - r_j|}}$$

electron kinetic E

elec/nuc attraction a.k.a “external potential”

elec/elec repulsion

→ Still intractable!

Hartree-Fock

- Hartree-Fock approximation: e/e repulsion is replaced by an effective field

$$\hat{H}_{el} = -\frac{\hbar}{2m_e}\sum_i \nabla_i^2 - \sum_{i,J}\frac{Z_J e^2}{|r_i - R_J|} + \boxed{\sum_{i\neq j}\frac{e^2}{|r_i - r_j|}}$$

electron
kinetic E

elec/nuc
attraction
a.k.a
“external potential”

elec/elec
repulsion

$$\hat{H}_{el}^{HF} = K + V_{eN} + V_i^{eff}$$

effective field is produced from the averaged position of all other electrons

$$\hat{H}_{el}^{HF}\,\Psi_{el} = E_{el}^{HF}\,\Psi_{el}$$

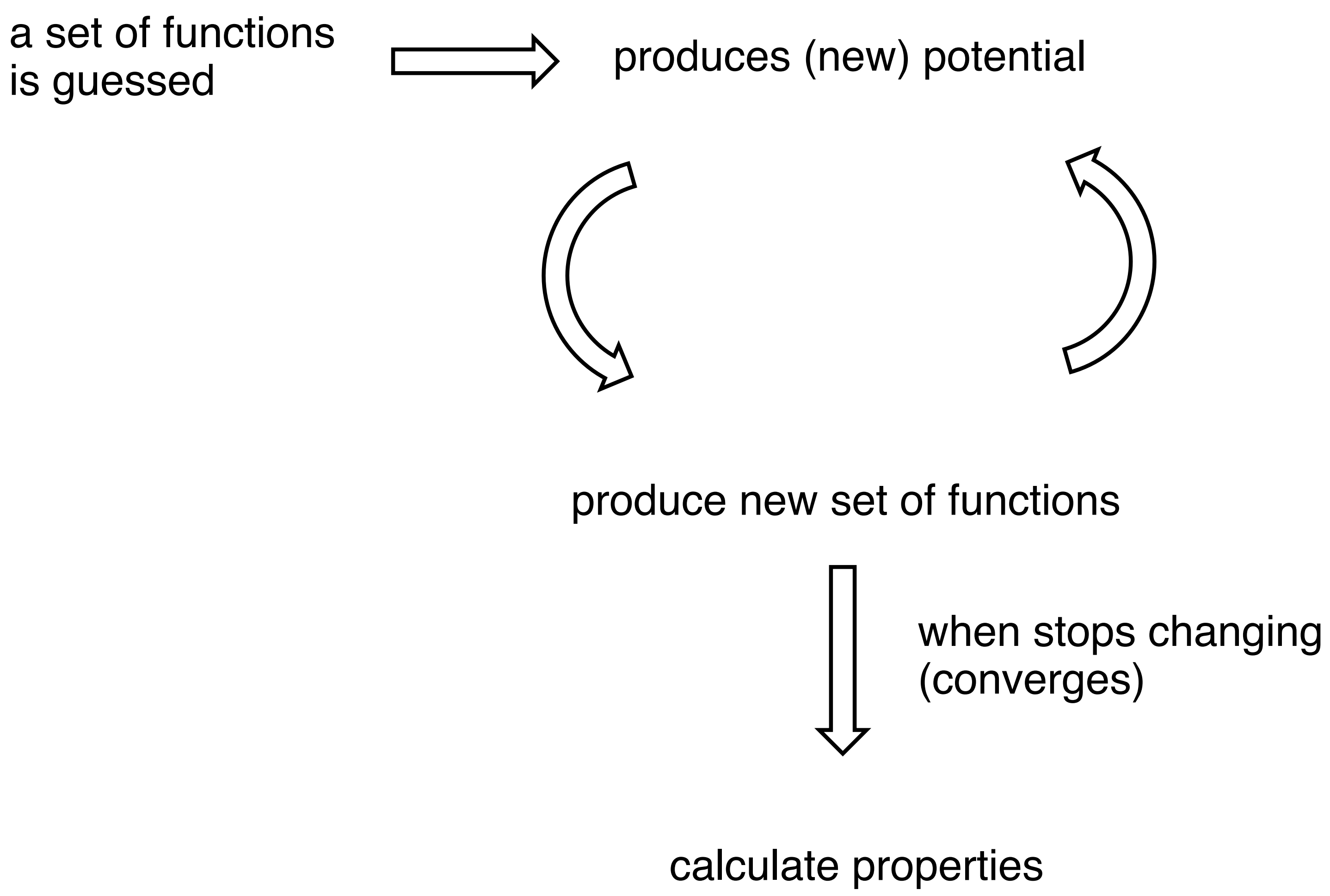
if every electron is depend on the position of all others, where do we start?

$$\Psi_{(r_1,\ldots r_n)} = \phi_{(r_1)}, \phi_{(r_2)}\ldots\phi_{(r_n)}$$

molecular wave function can be expressed as the product of individual on e^- wave function

Self-Consistent Field (SCF)

- Iterative method starting from a guessed set of functions.



a set of functions
is guessed

produces (new) potential

produce new set of functions

when stops changing
(converges)

calculate properties

Slater vs Gaussian-type orbital

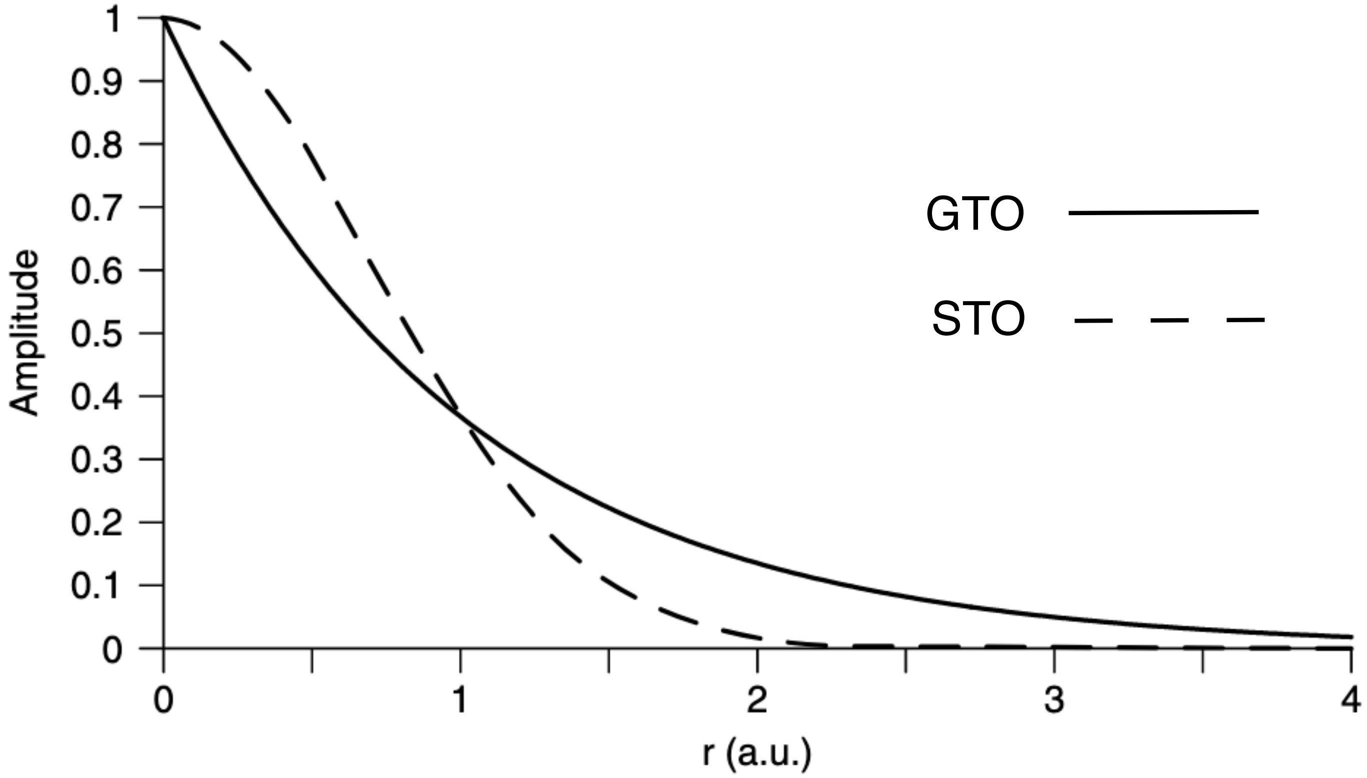
- What function to use?

Slater-type orbital

$$\phi_{1s} = \left(\frac{\zeta}{\pi}\right)^{1/2} e^{-\zeta \cdot r}$$

Gaussian-type orbital

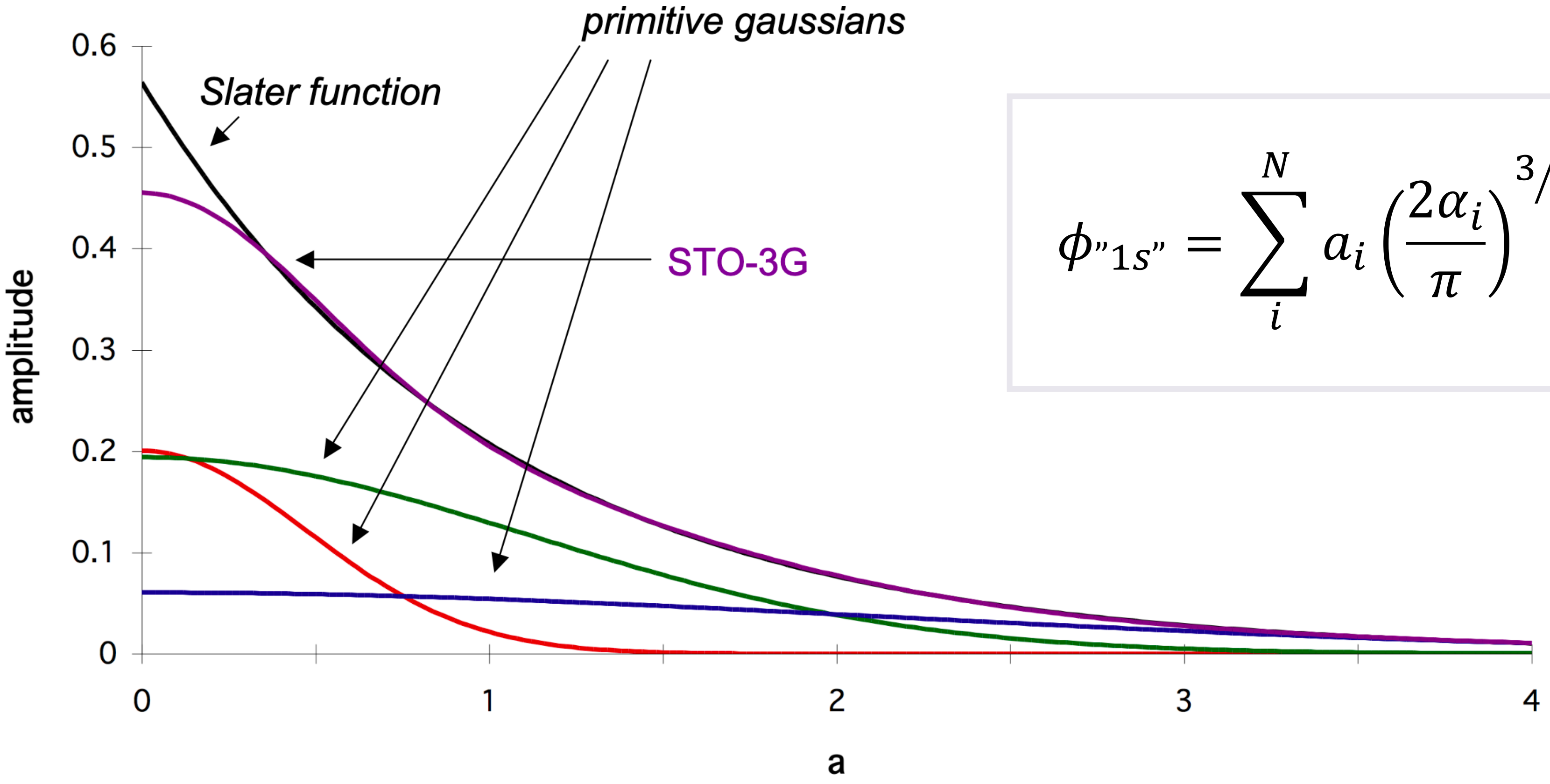
$$\phi_{``1s"} = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha \cdot r^2}$$



Cramer, C.J. Essentials of Computational Chemistry: Theories and Models

Basis Function

- Approximating STO with an linear combination of GTO — contracted basis function



$$\phi_{"1s"} = \sum_{i}^{N} a_i \left(\frac{2\alpha_i}{\pi}\right)^{3/4} e^{-\alpha_i \cdot r^2}$$

STO-*N*G — minimal basis — single ζ (zeta)

Pople optimized a and α values for elements

minimal basis set contais one basis fucntion for each filled and partially filled orbital

H: $1s^1$, contains 1 s-type basis function
C: $1s^2 2s^2 2p^2$, two s-type basis function, three p-type basis functions (p_x, p_y and p_y)

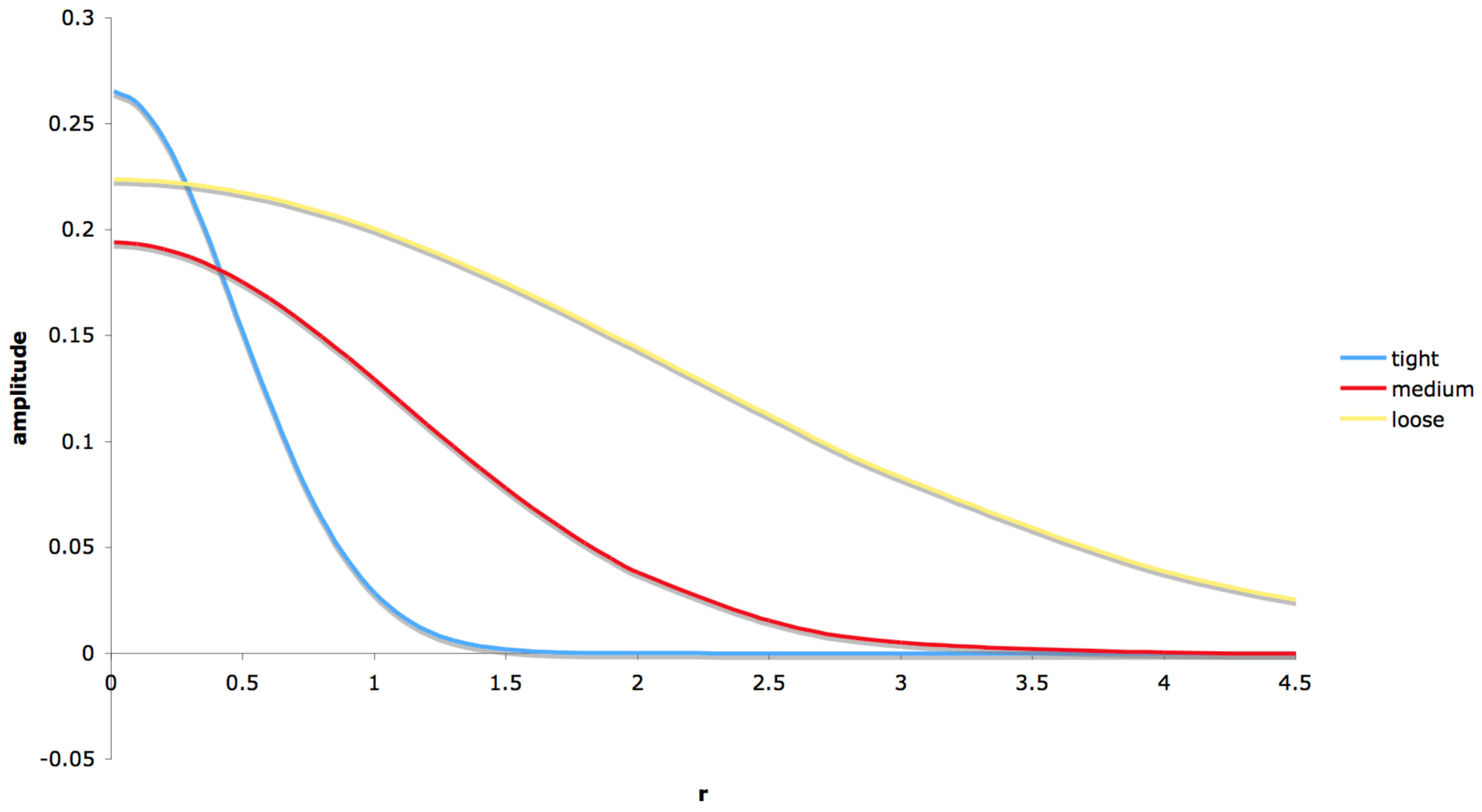
usually not adequate

http://pollux.chem.umn.edu/8021/Lectures/AI_HF_6.pdf

Split Valence Baseis Set

- Atoms may be engaged in different bonding situations — multiple ζ basis set

H—F H—H

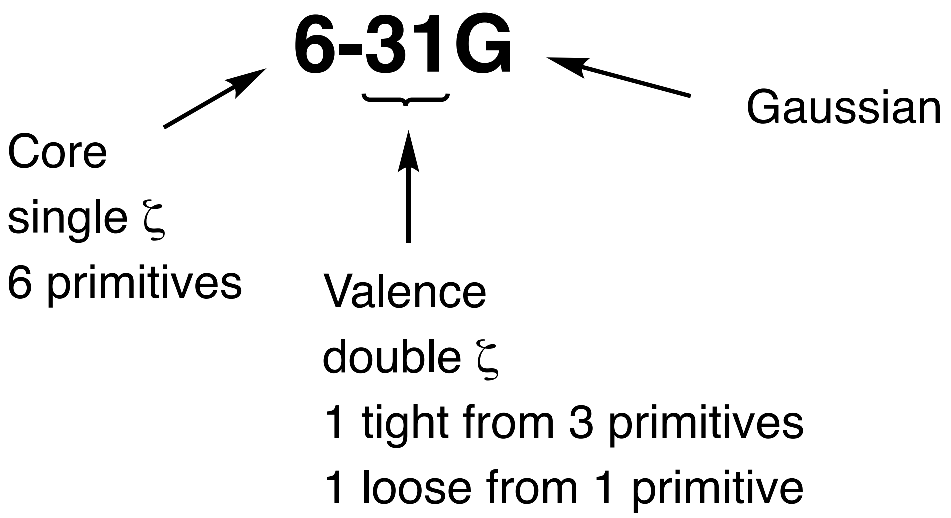


Adds flexibility to the bonding
Usually only applied to valence orbitals

http://pollux.chem.umn.edu/8021/Lectures/AI_HF_6.pdf

Split Valence Baseis Set

- Pople basis set notation — X-YZG



6-31G

Gaussian

Core
single ζ
6 primitives

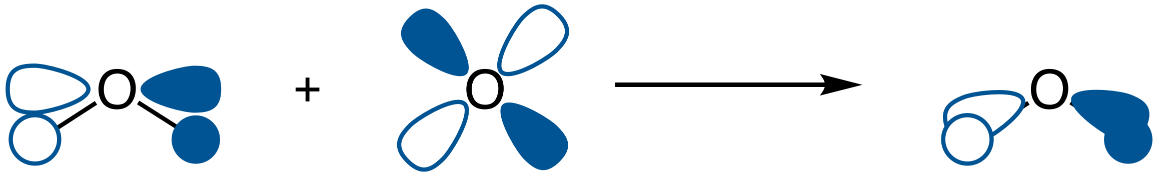
Valence
double ζ
1 tight from 3 primitives
1 loose from 1 primitive

CH_4 6-31G

atom	# atoms	AOs	degeneracy	basis fxn	primitives	total basis fxns	total primitives
C	1	1s(core)	1	1	6	1	6
		2s(val)	1	2	3 + 1 = 4	2	4
		2p(val)	3	2	3 + 1 = 4	6	12
H	4	1s(val)	1	2	3 + 1 = 4	8	16
					total =	17	38

Polarization Functions

- GTO still lack flexbility — add a set of polarization function



6-31G(d): adds six d-type function on heavy atoms (non hydrogen)
6-31G(d,p): adds six d-type to heavy atoms and three p-type function to hydrogen

recomended to keep things balenced:

ζ	polarization
2	d,p
3	2df,2pd
4	3d2fg,3p2df

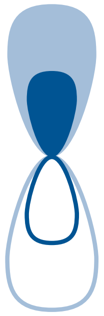
Dunning's basis set adopted
same balance scheeme:

cc-pV*nZ* *n*= D,T,Q,5,6

"correlation-consistent polarized Valence *n* Zeta"

Diffuse Functions

- Anions, excited electronic states, long range interactions, hydrogen boding



valence basis function
augmented with diffuse function
of the same type to allow flexibility when necessary

e.g. CH_4
6-31+G(d): adds one s-type and three p-type diffuse function to carbon (non-H in general)
6-31G++(d,p): adds one s-type and three p-type diffuse function to carbon
and one s-type diffuse function to each proton

Dunning's basis sets family:
Diffuse function on all atoms indicated by prefix 'aug'
Added for all angular momentum allready present

aug-cc-pVTZ: diffuse f, d, p and s functions on all heavy atoms and diffuse d, p, and s on H

Effective Core Potential

- Heavy elements have a large number of electrons thus requiring a multitude of basis functions

Solution:

replace the elctrons with a function representing
the combination of the nuclear and electronic core
Effective Core Potential (ECP)

- ECP also take relativistic effective of the inner electrons of very heavy electrons into account

LANL2DZ (Los Alamos Nat. Lab.)

- ECP for Na and heavier
- double zeta for valence
- uses old Dunning set D95V for H-Ne
- no polarization

SDD (Stuttgart/Dresden)

- ECP for K and heavier
- all double zeta
- uses old Dunning D95 for H-Ar
- no polarization

Def2SVP (Ahlrich's group)

- ECP for Rb and heavier
- valence DZ and TZ
- polarization available (P, PP)

For metal complexes usually
separate basis function are used

LANL2DZ for transition metal
6-31+G(d,p) for C,N,O,H

Post Hartree-Fock methods

- Methods employing increasingly accurate description of the electron correlation term

ab initio Hartree-Fock (HF)
    averaged repulsion
Møller-Plesset (MP2,MP3, etc)
    pertubation theory
Configuration Interaction (CI,CISD,CISDT, etc.)
    considers excitation space
Coupled Cluster (CC, CCSD, CCSD(T), etc.)
    Cluster operator

higher accuracy/
computational cost

scalling behaviour	method(s)
N^3	DFT
N^4	HF
N^5	MP2
N^6	MP3, CISD, CCSD, QCISD
N^7	MP4, CCSD(T), QCISD(T)
N^8	MP5, CISDT, CCSDT
N^9	MP6
N^{10}	MP7, CISDTQ, CCSDTQ

DFT accuracy is less dependent
on basis set size than
wave function methods

post-HF methods require
higher quality basis sets:
  cc-pVDZ
  aug cc-pVDZ
  cc-pVTZ, cc-pVQZ…

Post Hartree-Fock methods

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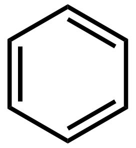
scalling behaviour	method(s)
N^3	DFT
N^4	HF
N^5	MP2
N^6	MP3, CISD, CCSD, QCISD
N^7	MP4, CCSD(T), QCISD(T)
N^8	MP5, CISDT, CCSDT
N^9	MP6
N^{10}	MP7, CISDTQ, CCSDTQ

method	accuracy	max atoms
HF	medium	~500
DFT	medium/High	~500
MP2	high	~100
CISD	high	~30
CCSD(T)	very high	~30

Density Functional Theory (DFT)



Erwin Schrödinger 1925 — wave function theory

All the information is contained in the wave function, an antisymmetric function of 126 coordinates and 42 electronic spin components

Pierre Hohenberg and Walter Kohn 1964 — density functional theory

All the information contained in the density, a function of only 3 coordinates.

Density Functional Theory (DFT)

1st Hohnberg-Kohn Theorem

The ground state electronic energy is determined completely by the electron density $\rho(r)$

2nd Hohenberg-Kohn Theorem

The density $\rho(r)$ which minimizes $E[\rho(r)]$ is the ground-state density, and minimization of this functional alone is enough to fully determine the exact ground-state energy and density $\rho_0(r)$.

Density functional theory (DFT) is an exact reformulation of many-body quantum mechanics in terms of the electron density rather than the wave function
— equivalent independent single-particle problem

The Nobel Prize in Chemistry 1998
Walter Kohn "for his development of the density-functional theory"
and John A. Pople "for his development of computational methods in quantum chemistry."

Density Functional Theory (DFT)

$$E[\rho(r)] = T_e[\rho(r)] + V_{ne}[\rho(r)] + V_{ee}[\rho(r)] + E_{XC}[\rho(r)]$$

T_e = non-interacting kinetic energy

V_{ee} = classical electron electron repulsion

V_{ne} = classical Coulomb interaction with nuclei

E_{XC} = Catch-all term
all we know about the functional E_{XC} that it exists, however, its form is unknown

The Alphabet Soup of Desnity Functionals

“The Big Three”

B3LYP

- Becke’s 3 parameter exchange functional and Lee-Yang-Paar correlation functional
- Developed by Axel Becke in 1993
- 8th most cited paper with over 43’000 citation (2020)
- Per se not dispersion corrected
- Takes only short range into account

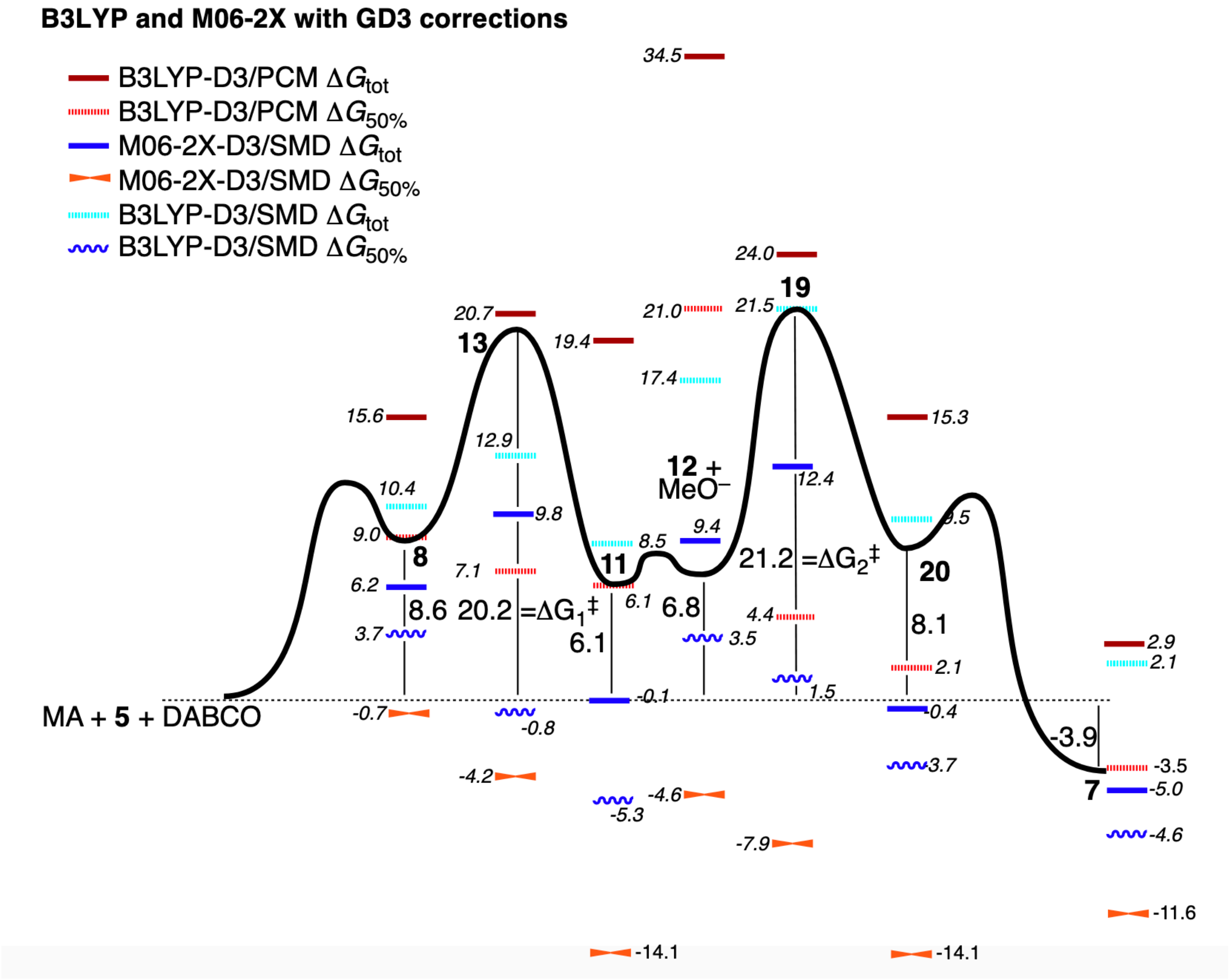
M06

- Develepod by the Truhlar Group
- Latest member of the family MN15
- Per se not dispersion corrected

ωB97X-D

- Developed by Head-Gordon an coworkers
- Latest member of the Family ωB97M-V
- Takes dispersion into account
- Captures long- and short-range interaction

Which Functional to Use?



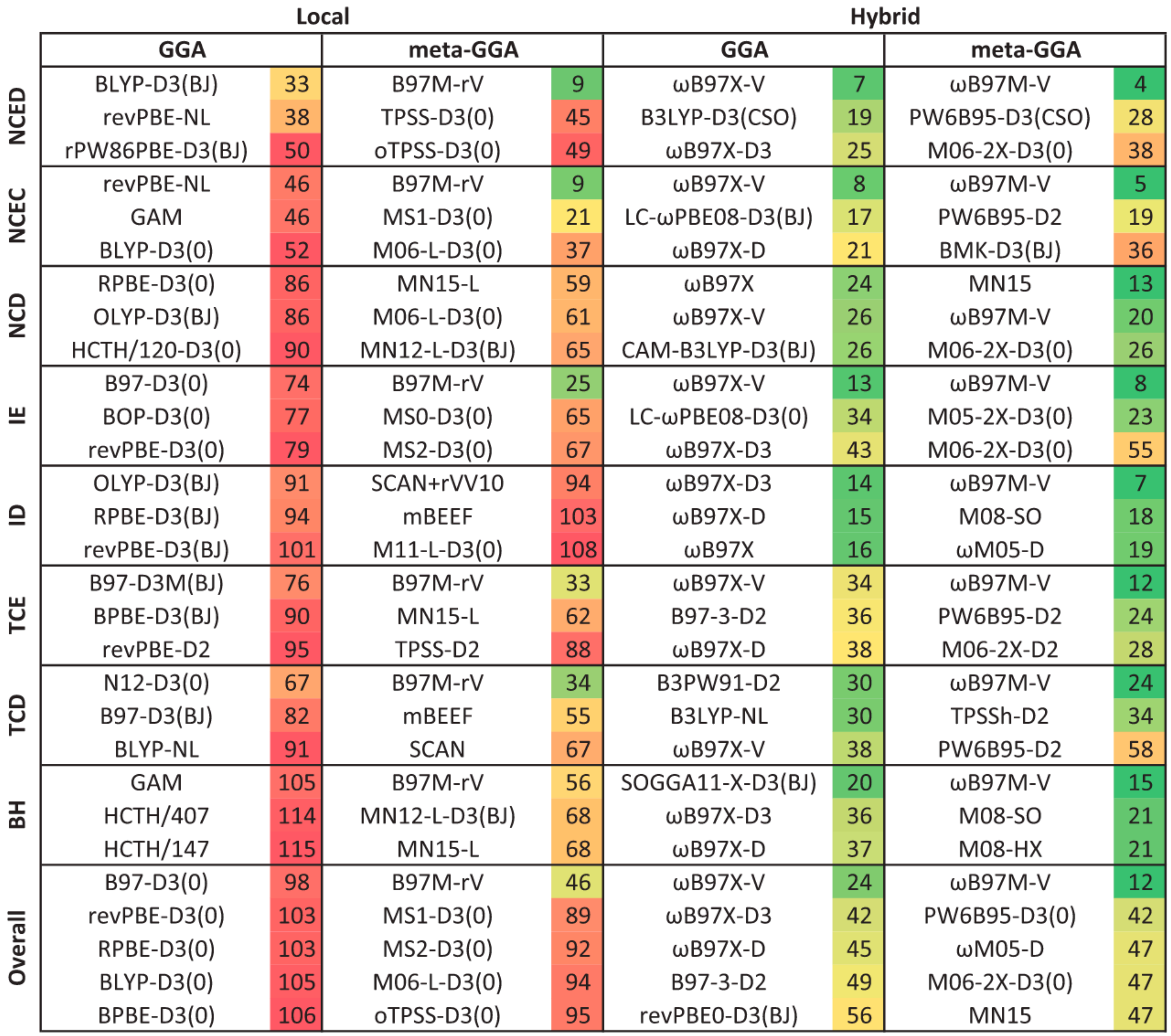
"The computations aid in interpreting observations but fail utterly as a replacement for experiment."

"…there is neither a consensus best-choice method nor acommon view on the right way to choose a method."

Singleton, D. A. *J. Am. Chem. Soc.* **2015**, *137*, 3811.

Benchmarking

- Methods employing increasingly accurate description of the electron correlation term

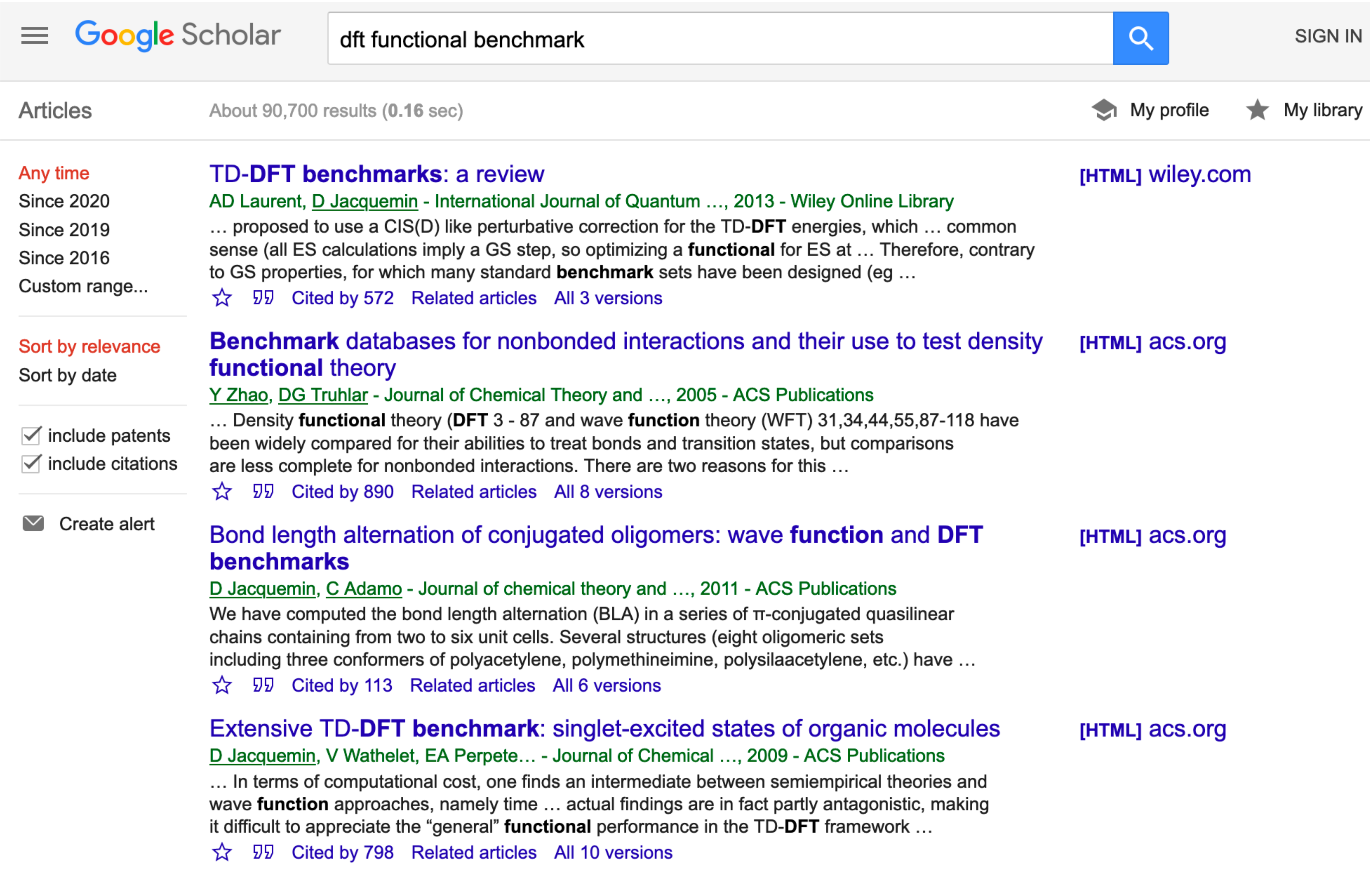


	Local				**Hybrid**			
	GGA		**meta-GGA**		**GGA**		**meta-GGA**	
NCED	BLYP-D3(BJ)	33	B97M-rV	9	ωB97X-V	7	ωB97M-V	4
	revPBE-NL	38	TPSS-D3(0)	45	B3LYP-D3(CSO)	19	PW6B95-D3(CSO)	28
	rPW86PBE-D3(BJ)	50	oTPSS-D3(0)	49	ωB97X-D3	25	M06-2X-D3(0)	38
NCEC	revPBE-NL	46	B97M-rV	9	ωB97X-V	8	ωB97M-V	5
	GAM	46	MS1-D3(0)	21	LC-ωPBE08-D3(BJ)	17	PW6B95-D2	19
	BLYP-D3(0)	52	M06-L-D3(0)	37	ωB97X-D	21	BMK-D3(BJ)	36
NCD	RPBE-D3(0)	86	MN15-L	59	ωB97X	24	MN15	13
	OLYP-D3(BJ)	86	M06-L-D3(0)	61	ωB97X-V	26	ωB97M-V	20
	HCTH/120-D3(0)	90	MN12-L-D3(BJ)	65	CAM-B3LYP-D3(BJ)	26	M06-2X-D3(0)	26
IE	B97-D3(0)	74	B97M-rV	25	ωB97X-V	13	ωB97M-V	8
	BOP-D3(0)	77	MS0-D3(0)	65	LC-ωPBE08-D3(0)	34	M05-2X-D3(0)	23
	revPBE-D3(0)	79	MS2-D3(0)	67	ωB97X-D3	43	M06-2X-D3(0)	55
ID	OLYP-D3(BJ)	91	SCAN+rVV10	94	ωB97X-D3	14	ωB97M-V	7
	RPBE-D3(BJ)	94	mBEEF	103	ωB97X-D	15	M08-SO	18
	revPBE-D3(BJ)	101	M11-L-D3(0)	108	ωB97X	16	ωM05-D	19
TCE	B97-D3M(BJ)	76	B97M-rV	33	ωB97X-V	34	ωB97M-V	12
	BPBE-D3(BJ)	90	MN15-L	62	B97-3-D2	36	PW6B95-D2	24
	revPBE-D2	95	TPSS-D2	88	ωB97X-D	38	M06-2X-D2	28
TCD	N12-D3(0)	67	B97M-rV	34	B3PW91-D2	30	ωB97M-V	24
	B97-D3(BJ)	82	mBEEF	55	B3LYP-NL	30	TPSSh-D2	34
	BLYP-NL	91	SCAN	67	ωB97X-V	38	PW6B95-D2	58
BH	GAM	105	B97M-rV	56	SOGGA11-X-D3(BJ)	20	ωB97M-V	15
	HCTH/407	114	MN12-L-D3(BJ)	68	ωB97X-D3	36	M08-SO	21
	HCTH/147	115	MN15-L	68	ωB97X-D	37	M08-HX	21
Overall	B97-D3(0)	98	B97M-rV	46	ωB97X-V	24	ωB97M-V	12
	revPBE-D3(0)	103	MS1-D3(0)	89	ωB97X-D3	42	PW6B95-D3(0)	42
	RPBE-D3(0)	103	MS2-D3(0)	92	ωB97X-D	45	ωM05-D	47
	BLYP-D3(0)	105	M06-L-D3(0)	94	B97-3-D2	49	M06-2X-D3(0)	47
	BPBE-D3(0)	106	oTPSS-D3(0)	95	revPBE0-D3(BJ)	56	MN15	47

Mardirossian, N.; Head-Gordon, M. *Mol. Phys.* **2017**, *115*, 19, 2315.

Benchmarking

- Chances are good to find benchmark for your indivudual case



dft functional benchmark

About 90,700 results (**0.16** sec)

TD-**DFT benchmarks**: a review — [HTML] wiley.com
AD Laurent, D Jacquemin - International Journal of Quantum …, 2013 - Wiley Online Library
… proposed to use a CIS(D) like perturbative correction for the TD-**DFT** energies, which … common sense (all ES calculations imply a GS step, so optimizing a **functional** for ES at … Therefore, contrary to GS properties, for which many standard **benchmark** sets have been designed (eg …
☆ 99 Cited by 572 Related articles All 3 versions

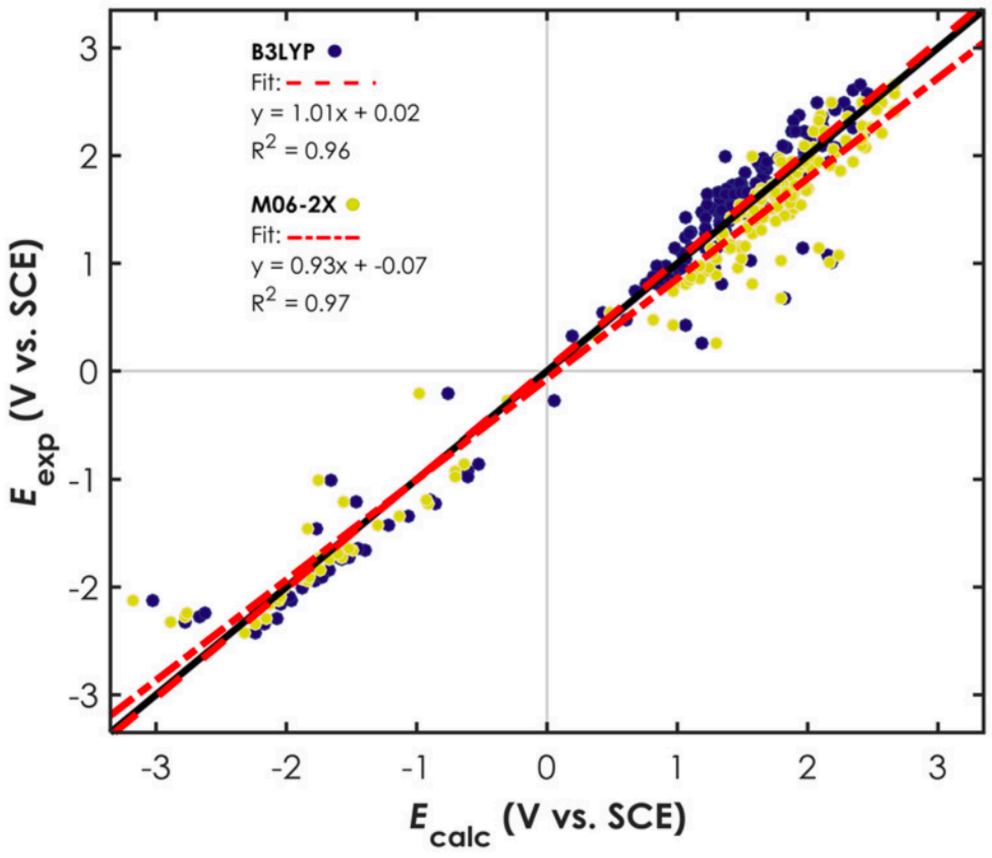
Benchmark databases for nonbonded interactions and their use to test density **functional** theory — [HTML] acs.org
Y Zhao, DG Truhlar - Journal of Chemical Theory and …, 2005 - ACS Publications
… Density **functional** theory (**DFT** 3 - 87 and wave **function** theory (WFT) 31,34,44,55,87-118 have been widely compared for their abilities to treat bonds and transition states, but comparisons are less complete for nonbonded interactions. There are two reasons for this …
☆ 99 Cited by 890 Related articles All 8 versions

Bond length alternation of conjugated oligomers: wave **function** and **DFT benchmarks** — [HTML] acs.org
D Jacquemin, C Adamo - Journal of chemical theory and …, 2011 - ACS Publications
We have computed the bond length alternation (BLA) in a series of π-conjugated quasilinear chains containing from two to six unit cells. Several structures (eight oligomeric sets including three conformers of polyacetylene, polymethineimine, polysilaacetylene, etc.) have …
☆ 99 Cited by 113 Related articles All 6 versions

Extensive TD-**DFT benchmark**: singlet-excited states of organic molecules — [HTML] acs.org
D Jacquemin, V Wathelet, EA Perpete… - Journal of Chemical …, 2009 - ACS Publications
… In terms of computational cost, one finds an intermediate between semiempirical theories and wave **function** approaches, namely time … actual findings are in fact partly antagonistic, making it difficult to appreciate the “general” **functional** performance in the TD-**DFT** framework …
☆ 99 Cited by 798 Related articles All 10 versions

Benchmarking

- Calculated vs experimental properties

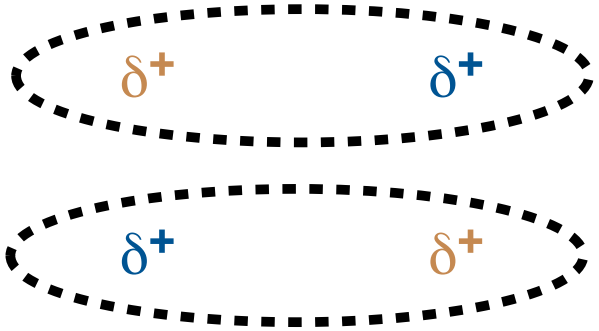


- Benchmark level of theory vs experimental values
- If known molecules are well described similar molecules should be OK

Roth, H .G.; Romero, N. A.; Nicevicz, D. A. *Synlett.* **2015**, *27*, 714.

Dispersion

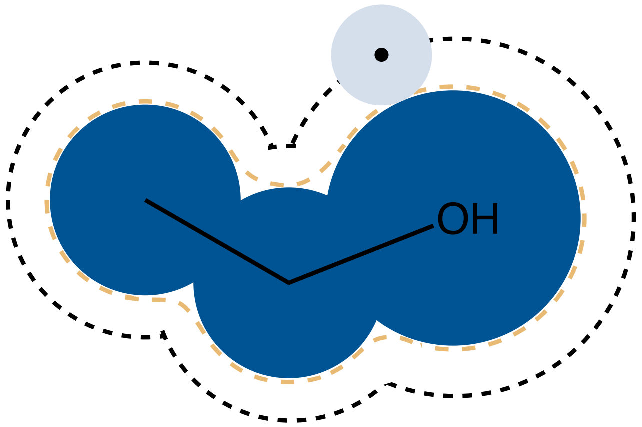
- Consequence of electronic correlation between molecules



- B3LYP and M06 do not threat dispersion by default
- Dispersive interaction important to several chemical phenomena
- ωB97x-D threats dispersion semi-empirically
- Grimme’s D3 dispersion functional can be added to calculation if required

Solvation

- Polarizable Continuum Model (PCM) is the most popular model for solvation effects



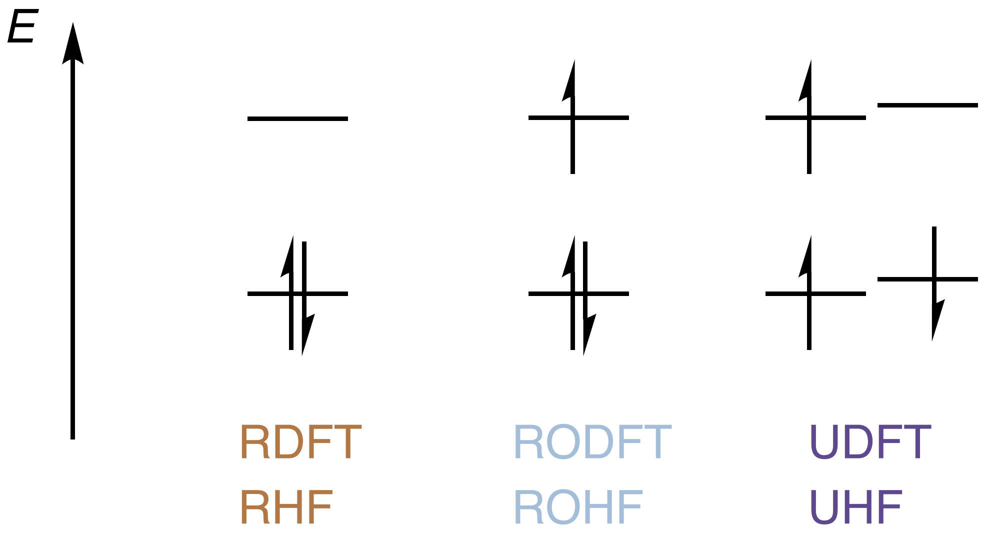
- Polarizable continuum interacts with polar moities of solute
- IEFPCM (default SCRF, called PCM in Gaussian) and CPCM most commonly used.
- It matters most that you are using a modern solvation model than which one
- In Gaussian SMD model used to obtain ΔG_{solv}

- Often little corrections on the energy, sometimes vital (e.g. redox)

- Fails to describe hydrogen bonding and reorientation

Open Shell Calculations

- Two ways of hadling unpaired electrons — Restricted Open-Shell and Unrestricted



Restricted Closed-Shell

- default in Gaussian for closed-shell molecules
- fails to describe di-and biradicals

Restricted Open-Shell

- physically incorrect (prevents spin polarization)
- no spin-contamination issue
- gives higher energies (less accurate) than UDFT/UHF

Unrestricted Open-Shell

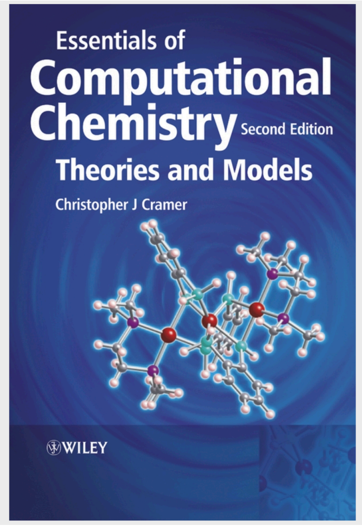
- default in Gaussian for open-shell molecules
- allows to model spin polarization
- gives lower energy than RODFT/ROHF (more accurate)
- spin contamination! Less common in UDFT

$\langle S^2 \rangle = S(S+1)$
0.75 for radical S=1/2
2 for triplets S=1

$\langle S^2 \rangle$ for unrestricted open-shell are higher than the correct value (S(S+1))

5% deviation is acceptable

Resources


Essentials of
Computational
Chemistry Second Edition
Theories and Models
Christopher J Cramer
WILEY

Cramer, C.J. *Essentials of Computational Chemistry: Theories and Models*

Gaussian website: www.gaussian.com

Great on line lectures (Prof. David Sherril and Prof. Chris Cramer) on YouTube