Density Functionals
Basis Sets

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Density Functional Theory

Introductory notes

$$|\Psi(\mathbf{x_1}, \mathbf{x_2}, \ldots \mathbf{x_N})|^2 d\mathbf{x_1} d\mathbf{x_2} \ldots d\mathbf{x_N}$$

▸ Probability of finding electron 1 in $d\mathbf{x}_1$, electron 2 in $d\mathbf{x}_2$ etc

▸ Integrate over spin-space coordinates of electrons 2–N and spin of 1:

$$\left(\int \cdots \int |\Psi(\mathbf{x_1}, \mathbf{x_2}, \ldots \mathbf{x_N})|^2 ds_1 d\mathbf{x_2} \cdots d\mathbf{x}_N \right) d\mathbf{r_1}$$

▸ Probability of finding electron 1 in volume element $d\mathbf{r}_1$ (other electrons can be anywhere)

$$\left(N \int \cdots \int |\Psi(\mathbf{x_1}, \mathbf{x_2}, \ldots \mathbf{x_N})|^2 ds_1 d\mathbf{x_2} \cdots d\mathbf{x}_N \right) d\mathbf{r_1} = \rho(\mathbf{r_1}) d\mathbf{r_1}$$

▸ Probability of finding any electron in $d\mathbf{r}_1$

$$\rho(\mathbf{r_1}) = N \int \cdots \int |\Psi(\mathbf{x_1}, \mathbf{x_2}, \ldots \mathbf{x_N})|^2 ds_1 d\mathbf{x_2} \cdots d\mathbf{x}_N$$

▸ $\rho(\mathbf{r})$ is the electron density

Density

▸ Wave function: a complicated function of 4 x N_{el} variables. Not a physical "object". Wave function based methods scale poorly with system size and have high requirements on basis sets to properly describe the electron–electron cusp.

▸ Density: a much simpler function of three variables. Experimental observable. If we can use it directly, we might be able to come up with a simpler theory…

DFT: a quantum mechanical theory where the density is the central quantity

Isovalue surfaces (electrons per unit volume)
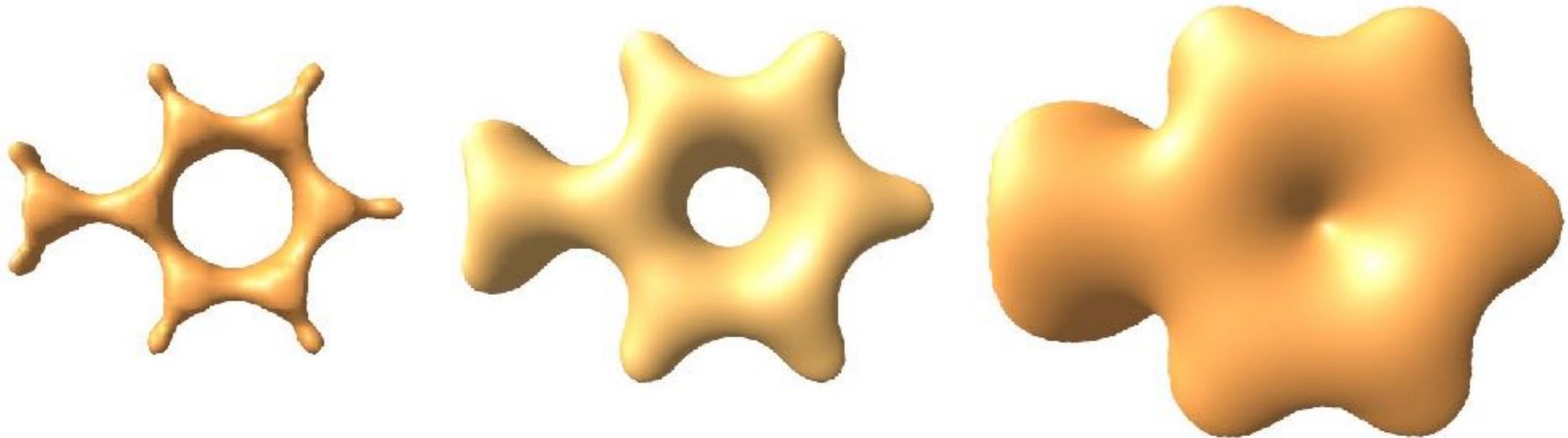
Information from the density

The density has **cusps** at the positions of the nuclei.
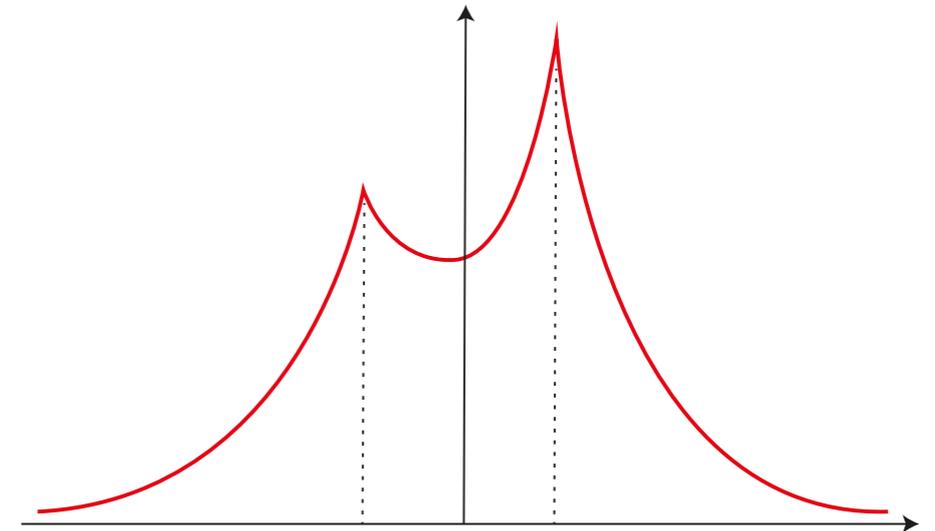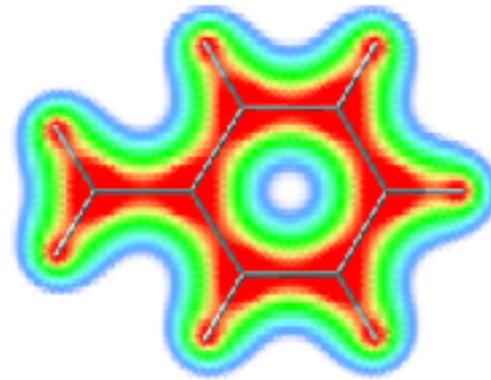
The **shape** of the cusps is directly related to the atomic number Z.

$$\frac{d\rho}{d\mathbf{r}}\bigg|_{\mathbf{r}=\mathbf{R}_\alpha} = -2Z_\alpha \rho(\mathbf{R}_\alpha)$$

By **integrating** the density we get the total number of electrons.

$$N_{\mathrm{el}} = \int \rho(\mathbf{r})d\mathbf{r}$$

We can fully define the Hamiltonian of the system simply by examining the density!

Information from the density

Define Hamiltonian

Find positions of
nuclei, atomic
charges, N_{el}

Solve Schrödinger
equation

Density

Determine
Wavefunction

DFT

Calculate energy
and other
properties

Energy, etc
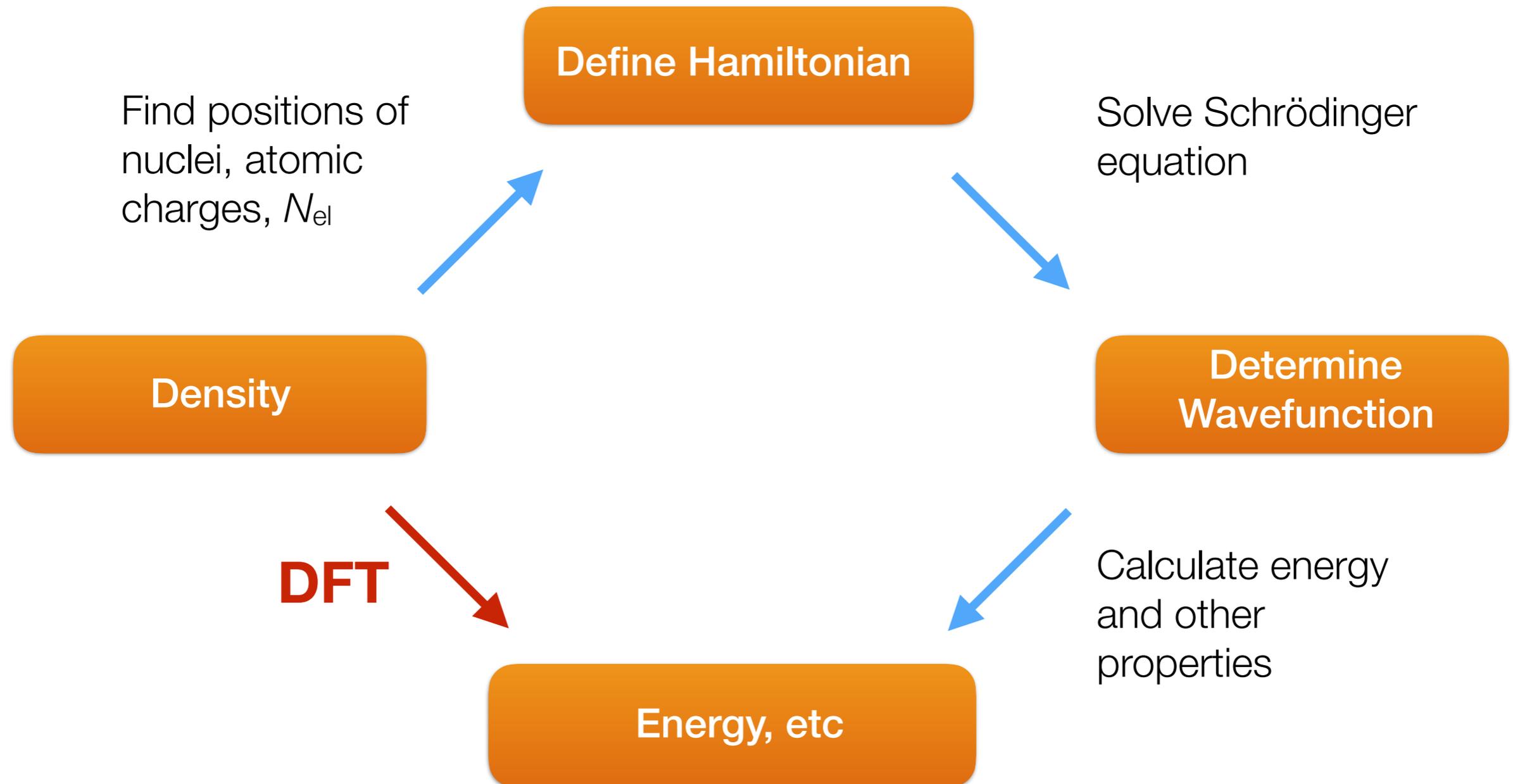
In principle the ground state density contains everything there is to know.
What is needed to make the connection (conceptually and practically)?

Density Functional Theory

A function $f(x)$ maps a number to another number.
A functional $F[f]$ takes a function as input and returns a number.

We need a way to go from the density $\rho(\mathbf{r})$ to the energy E,
i.e. we need to express the energy as a functional of the density, $E[\rho]$

Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}_{\text{ee}} + \hat{V}_{\text{en}} = -\sum_i^N \frac{1}{2}\nabla_i^2 + \sum_{i<j}^N \frac{1}{r_{ij}} + \sum_i^N v(\mathbf{r}_i)$$

External potential

$$v(\mathbf{r}_i) = -\sum_A \frac{Z_A}{r_{Ai}}$$

Owing to the Born–Oppenheimer approximation we perform a quantum calculation only on electrons; nuclei are "external" fixed objects which exert their potential to the electrons.

Hohenberg–Kohn theorems

1st HK theorem: a universal density functional exists

The electron density determines the external potential.

There is a one-to-one correspondence between densities and external potentials (different external potentials always correspond to different densities)

$\Rightarrow$ the electronic energy can be expressed completely as a functional of the density

$$E[\rho] = F_{\mathrm{HK}}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

2nd HK theorem: variational principle for the density

only the exact ground-state density $\rho(\mathbf{r})$ of H minimizes the value of its ground-state energy functional

$$E_{\mathrm{el}}^{(1)}[\rho^{(1)}] \leq E_{\mathrm{el}}^{(1)}[\rho]$$

$\Rightarrow$ One can already use all of the above to do calculations!

Minimize the energy with respect to var. density by constraining $\quad \int \rho(\mathbf{r})d\mathbf{r} = N_{\mathrm{el}}$

Kohn–Sham DFT

Evaluation of kinetic energy has been a central problem.

Assume a fictitious system of independent (non-interacting) electrons that have *precisely* the same density $\rho(\mathbf{r})$ as the real physical system.

Non-interacting system: decoupled coordinates, separable Hamiltonian.

$\Rightarrow$ Slater determinant: we are back to calculating **orbitals**!

$$\hat{H} = -\sum_i^N \frac{1}{2}\nabla_i^2 + \sum_i^N v_{\text{eff}}(\mathbf{r}_i) \qquad \left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r})\right)\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_i^N \varphi_i^2(\mathbf{r}) \qquad T_{\text{s}}[\rho] = \sum_i^N \langle\varphi_i| -\frac{1}{2}\nabla^2|\varphi_i\rangle$$

$$E[\rho] = F_{\text{HK}}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \qquad \text{Write F as} \quad F[\rho] = T_{\text{s}}[\rho] + J[\rho] + E_{\text{XC}}[\rho]$$

Because $\quad F[\rho] = T[\rho] + V_{\text{ee}}[\rho] \quad$ it follows that $\quad E_{\text{XC}}[\rho] = T[\rho] - T_{\text{s}}[\rho] + V_{\text{ee}}[\rho] - J[\rho]$

$\Rightarrow$ E_{XC} is the magic ingredient that corrects other errors, self-interaction, correlation…

$\Rightarrow$ guess E_{XC} functionals, use them in the Kohn–Sham orbital optimization procedure

Kohn–Sham DFT

NOTE: Kohn–Sham DFT is **exact**. No approximations made.

- Importance: problem is shifted from optimizing densities to optimizing orbitals

- Kohn–Sham orbitals are "special"…

- Is Kohn–Sham DFT a "single determinant method"?

How to approximate the exact functional?

One way is to exploit **known limits**. Example: the *Uniform Electron Gas*

No nuclei but a uniform background of positive charge. The electrons move in this homogeneous medium forming a Uniform Electron Gas (UEG). In the UEG there is a very large number of electrons in a large volume V, so that the electronic density $\rho(\mathbf{r})$ **is constant**. The kinetic energy of the electrons in this system is proportional to $\rho(\mathbf{r})^{5/3}V$.

Local Density Approximation (LDA/LSDA)

$$E_{XC} = \int F(\rho)d\mathbf{r}$$

Depends only on the scalar value of the density.
Assumes that the exchange-correlation energy at every position in space for the molecule *is the same as it would be for the uniform electron gas* (UEG) having the same density as found at that position.

Kinetic energy directly derived, similarly straightforward expression for exchange.

$$T = C_F \int \rho^{5/3}(\mathbf{r})d\mathbf{r} \qquad\qquad E_X = C_X \int \rho^{4/3}(\mathbf{r})d\mathbf{r}$$

Several different expressions for the correlation energy:
VWN (Vosko, Wilk, and Nusair), **PW** (Perdew and Wang), …

LDA is exact only for constant-density systems, yet it is already more accurate than Hartree–Fock as a general electronic structure theory.

Generalized Gradient Approximation (GGA)

$$E_{\mathrm{XC}}[\rho] = \int F(\rho, \nabla\rho)d\mathbf{r}$$

Introduces additional dependence on the gradient of the density at a given point ("non-local functionals")
Most GGA functionals are created as "add-ons" to LDA.

And this is where the fun begins!

Do **not** contain empirical parameters: (focus on satisfying constraints and norms)

Exchange: B86, PBE, … | *Correlation*: PW91

Do contain empirical parameters: (focus on reproducing known quantities)

Exchange: B, CAM, O, PW, mPW, X, … | *Correlation*: B88, P86, LYP

2 Schools of DFT

The historical tension between the "first principles" and the fitting approaches continues to this day and shows no signs of resolution!

GGA functionals first enabled real computational chemistry to be done!
Still an excellent choice for many tasks in quantum chemistry.

BP86 usually fine for geometry optimizations!

Meta-GGA

$$E_{\mathrm{XC}} = \int F(\rho, \nabla\rho, \nabla^2\rho)d\mathbf{r}$$

Try to achieve further improvement by including dependence on the Laplacian of the density (in practice: kinetic energy density).

Examples: B95, B98, TPSS, VSXC, M06-L, SCAN

Usually limited improvement compared to GGAs.

Hybrid functionals

$$E_{XC} = \int F(\rho, \nabla\rho)d\mathbf{r} + \xi E_X^0$$

Also known as Adiabatic Connection Method (ACM) functionals.They include fractions of exact Hartree-Fock exchange energy, calculated as a functional of the Kohn-Sham MOs. Controlled error cancellation.

Most famous example: **B3LYP** (20% HF exchange).
Probably Hundreds of other functionals in this part of the DFT supermarket!

In combination with meta-GGAs: hybrid meta-GGA functionals, e.g. **TPSSh** (10% HF).

Range-separated functionals, variable exchange, e.g. **CAM-B3LYP**, **ωB97**.

Often superior for **spin state** problems and **spectroscopic** properties.

HF exchange as adjustable parameter: a blessing or a curse?

- Low-spin/high-spin energy splittings for Fe complexes

- Cu-O_2 adducts

- Reaction barriers

- Valence isomerism and bonding in transition metal clusters
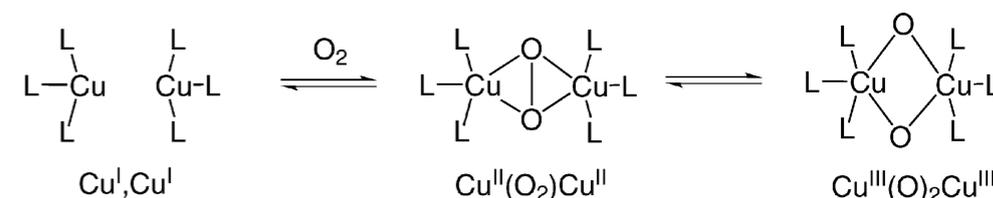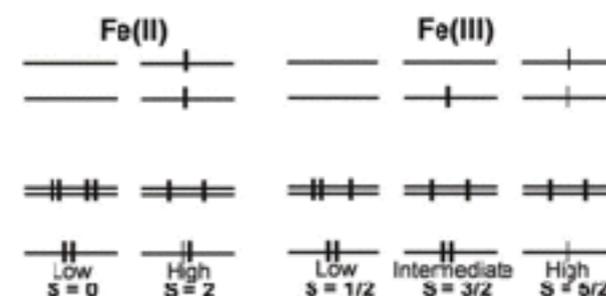
Example - effect of exact exchange on relative energies
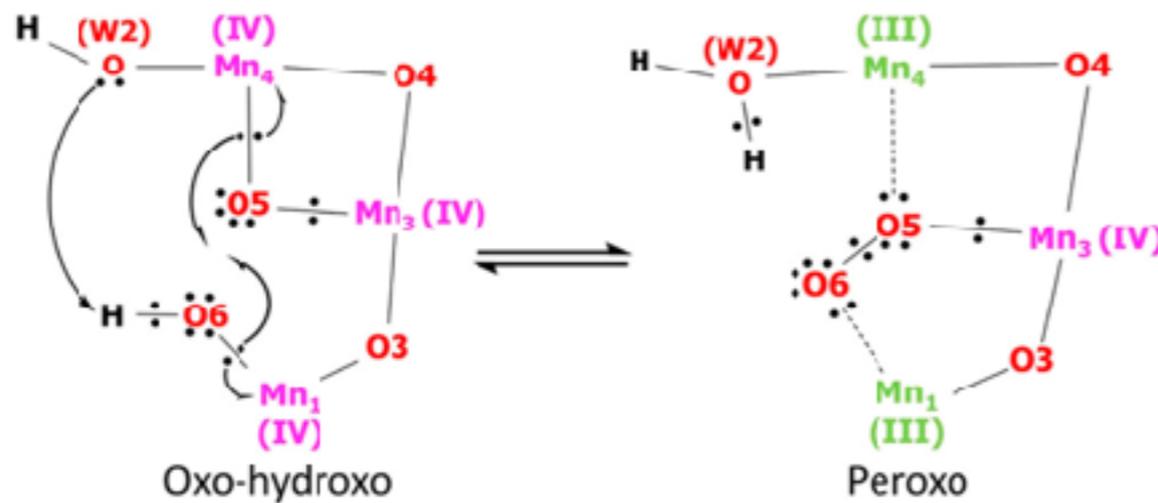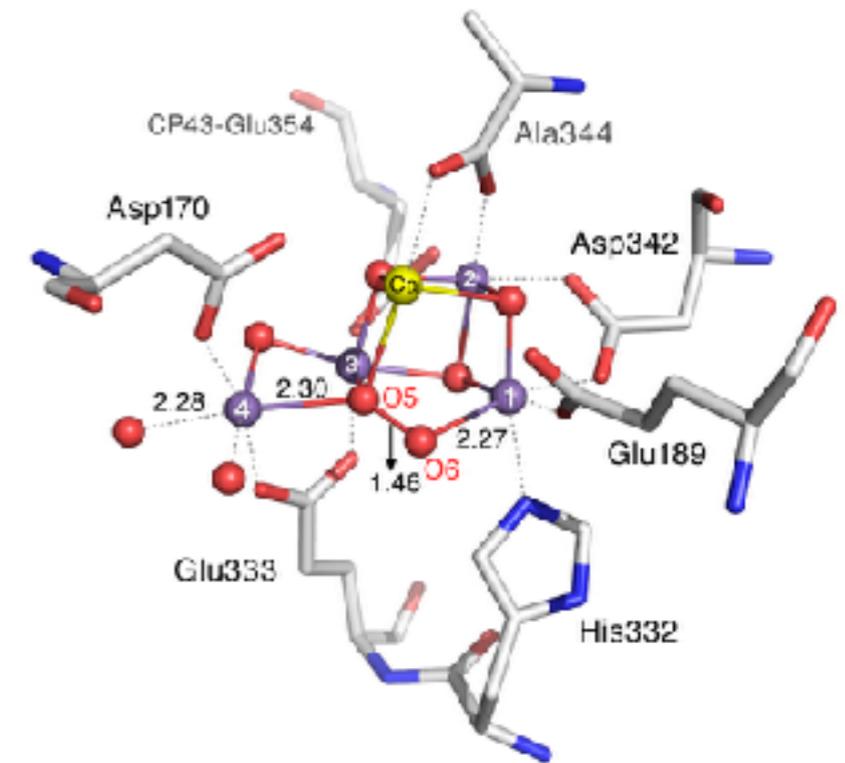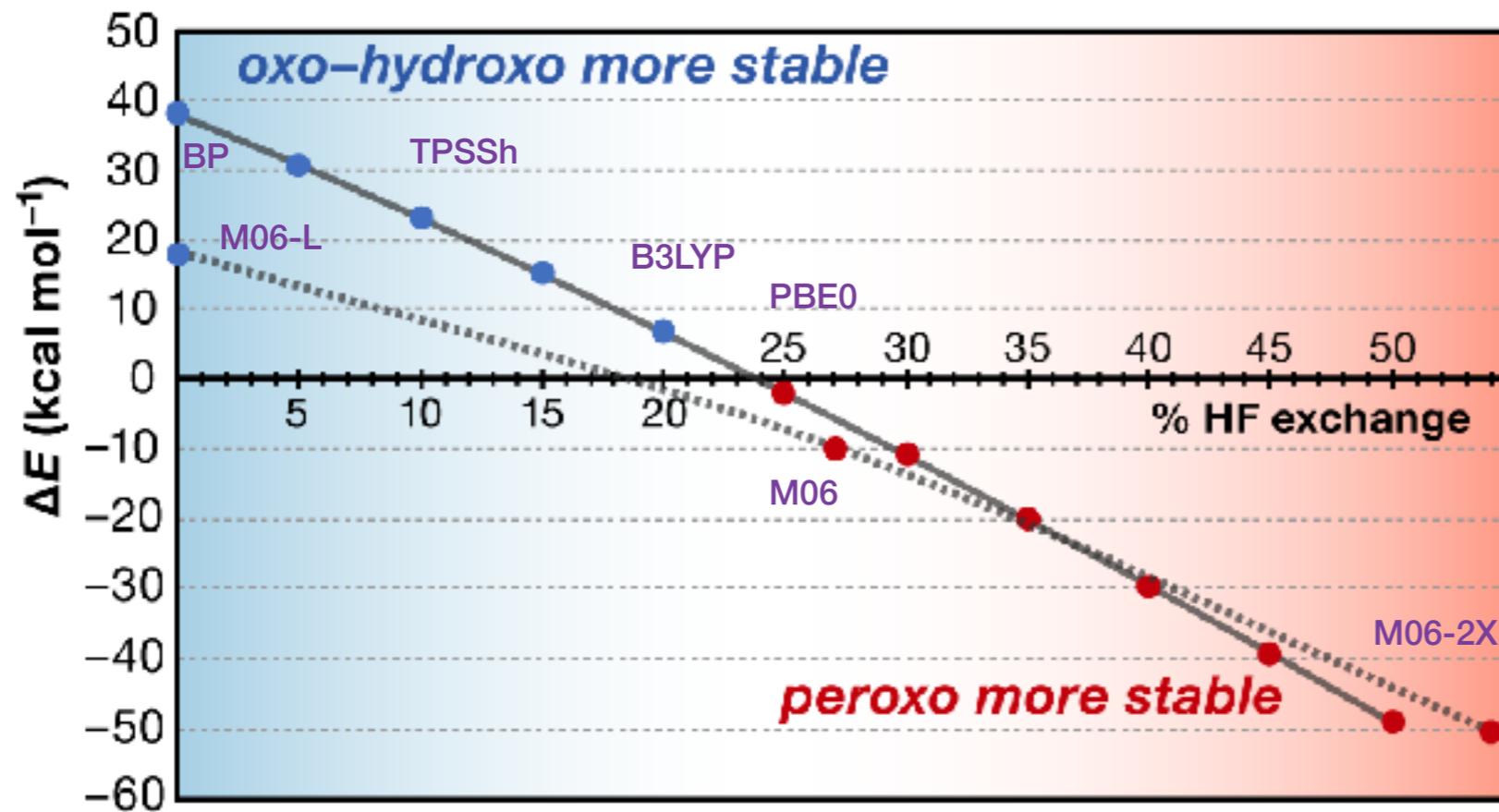
How can we decide?

Double-Hybrid functionals

They mix standard DFT exchange and correlation with HF exchange and an additional second-order perturbation theory contribution.

$$E_{XC}^{DHDF} = (1 - \alpha_X)E_X^{DFT} + \alpha_X E_X^{HF} + (1 - \alpha_C)E_C^{DFT} + \alpha_C E_C^{PT2}$$

The PT2 contribution is obtained through a Møller–Plesset perturbational term (MP2) based on Kohn–Sham orbitals that were self-consistently optimized with respect to the first three terms.

$$E_C^{PT2} = \frac{1}{4}\sum_{ia}\sum_{jb}\frac{\left[(ia|jb) - (ib|ja)\right]^2}{e_i + e_j - e_a - e_b}$$

Archetypal example: **B2PLYP**. Current "best": **PWPB95**

Victims of even more refitting and purpose-focused optimization (SCS-MP2, SOS-MP2) …
for kinetics, for thermochemistry, for …

$$E_{XC}^{DSD} = (1 - \alpha_X)E_X^{DFT} + \alpha_X E_X^{HF} + c_C E_C^{DFT} + c_O E_C^{OS-PT2} + c_S E_C^{SS-PT2} + E_{disp}$$

Considered among the best functionals available ("top-rung")

BUT not without important exceptions and unexpected failures

Mid-range correlation and dispersion in DFT

Octane vs. iso-octane:
DFT underestimates the stability of branched
hydrocarbon isomers
e.g. B3LYP -9 kcal/mol vs exp. +2 kcal/mol
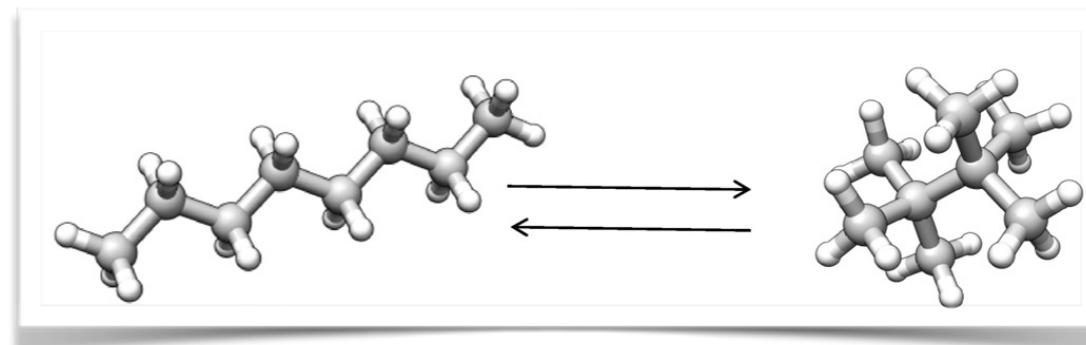
Origin: deficiency in medium-range correlation - DFT is too "short-sighted"

Similar deficiency in any systems where **dispersion** is important.

Semi-empirical fix in the form of an add-on term: **D3BJ**, **D4** (Grimme).

$$E_{\text{DFT-D3}} = E_{\text{KS-DFT}} + E_{\text{disp}}$$

$$E_{\text{disp}} = -\sum_{A<B}\sum_{n=6,8} s_n \frac{C_n^{AB}}{r_{AB}^n}$$

Beneficial in the vast majority of cases, but always be careful…

A more important question:
relative energies are wrong - are spectroscopic properties also "wrong"?

Functionals in ORCA

Table 6.2: Density functionals available in ORCA.

Local and gradient corrected functionals	
HFS	Hartree–Fock–Slater Exchange only functional
LDA or LSD	Local density approximation (defaults to VWN5)
VWN or VWN5	Vosko–Wilk–Nusair local density approx. parameter set "V"
VWN3	Vosko–Wilk–Nusair local density approx. parameter set "III"
PWLDA	Perdew-Wang parameterization of LDA
BP86 or BP	Becke '88 exchange and Perdew '86 correlation
BLYP	Becke '88 exchange and Lee-Yang-Parr correlation
OLYP	Handy's "optimal" exchange and Lee-Yang-Parr correlation
GLYP	Gill's '96 exchange and Lee-Yang-Parr correlation
XLYP	The Xu and Goddard exchange and Lee-Yang-Parr correlation
PW91	Perdew-Wang '91 GGA functional

mPWPW	Modified PW exchange and PW correlation
mPWLYP	Modified PW exchange and LYP correlation
PBE	Perdew-Burke-Erzerhoff GGA functional
RPBE	"Modified" PBE
REVPBE	"Revised" PBE
PWP	Perdew-Wang '91 exchange and Perdew '86 correlation

Hybrid functionals	
B1LYP	The one-parameter hybrid functional with Becke '88 exchange and Lee-Yang-Parr correlation (25% HF exchange)
B3LYP and B3LYP/G	The popular B3LYP functional (20% HF exchange) as defined in the TurboMole program system and the Gaussian program system, respectively
O3LYP	The Handy hybrid functional
X3LYP	The Xu and Goddard hybrid functional
B1P	The one-parameter hybrid version of BP86
B3P	The three-parameter hybrid version of BP86
B3PW	The three-parameter hybrid version of PW91
PW1PW	One-parameter hybrid version of PW91
mPW1PW	One-parameter hybrid version of mPWPW
mPW1LYP	One-parameter hybrid version of mPWLYP
PBE0	One-parameter hybrid version of PBE
PW6B95	Hybrid functional by Truhlar
BHANDHLYP	Half-and-half hybrid functional by Becke

Meta-GGA and hybrid meta-GGA functionals	
TPSS	The TPSS meta-GGA functional
TPSSh	The hybrid version of TPSS (10% HF exchange)
TPSS0	A 25% exchange version of TPSSh that yields improved energetics compared to TPSSh but is otherwise not well tested
M06L	The Minnesota M06-L meta-GGA functional
M06	The M06 hybrid meta-GGA (27% HF exchange)
M062X	The M06-2X version with 54% HF exchange
B97M-V	Head-Gordon's DF B97M-V with nonlocal correlation
B97M-D3BJ	Modified version of B97M-V with D3BJ correction by Najibi and Goerigk
SCANfunc	Perdew's SCAN functional

Range-separated hybrid functionals	
ωB97	Head-Gordon's fully variable DF ωB97
ωB97X	Head-Gordon's DF ωB97X with minimal Fock exchange
ωB97X-D3	Chai's refit incl. D3 in its zero-damping version
ωB97X-V	Head-Gordon's DF ωB97X-V with nonlocal correlation
ωB97X-D3BJ	Modified version of ωB97X-V with D3BJ correction by Najibi and Goerigk
ωB97M-V	Head-Gordon's DF ωB97M-V with nonlocal correlation
ωB97M-D3BJ	Modified version of ωB97M-V with D3BJ correction by Najibi and Goerigk
CAM-B3LYP	Handy's fit

LC-BLYP	Hirao's original application

Perturbatively corrected double-hybrid functionals (add the prefix RI- or DLPNO- to use the respective approximation for the MP2 part)	
B2PLYP	Grimme's mixture of B88, LYP, and MP2
B2PLYP-D	B2PLYP with Grimme's empirical dispersion correction from 2006 (D2) [1]
B2PLYP-D3	B2PLYP with Grimme's atom-pairwise dispersion correction from 2010 [2] and Becke-Johnson damping (D3BJ)
mPW2PLYP	mPW exchange instead of B88, which is supposed to improve on weak interactions.
mPW2PLYP-D	mPW2PLYP with Grimme's empirical dispersion correction from 2006 (D2)
B2GP-PLYP	Gershom Martin's "general purpose" reparameterization
B2K-PLYP	Gershom Martin's "kinetic" reparameterization
B2T-PLYP	Gershom Martin's "thermochemistry" reparameterization
PWPB95	Goerigk and Grimme's mixture of modified PW91, modified B95, and SOS-MP2
DSD-BLYP	Gershom Martin's "general purpose" double-hybrid with B88 exchange, LYP correlation and SCS-MP2 mixing, i.e. not incl. D3BJ correction
DSD-PBEP86	Gershom Martin's "general purpose" double-hybrid with PBE exchange, P86 correlation and SCS-MP2 mixing, i.e. not incl. D3BJ correction
DSD-PBEB95	Gershom Martin's "general purpose" double-hybrid with PBE exchange, B95 correlation and SCS-MP2 mixing, i.e. not incl. D3BJ correction

Range-separated double-hybrid functionals (add the prefix RI- or DLPNO- to use the respective approximation for the MP2 part)	
ωB2PLYP	Goerigk and Casanova-Páez's range-separated DHDF, with the correlation contributions based on B2PLYP, optimized for excitation energies
ωB2GP-PLYP	Goerigk and Casanova-Páez's range-separated DHDF, with the correlation contributions based on B2GP-PLYP, optimized for excitation energies

Dispersion corrections (see 8.1.4.6 and 9.3.2.11 for details)	
D4	density dependent atom-pairwise dispersion correction with Becke-Johnson damping and ATM
D3BJ	Atom-pairwise dispersion correction to the DFT energy with Becke-Johnson damping
D3ZERO	Atom-pairwise dispersion correction with zero damping
D2	Empirical dispersion correction from 2006 (not recommended)

Functionals in ORCA

```
! B3LYP D3BJ RIJCOSX def2-TZVP def2/J Grid5 GridX7
```

```
%method
    functional B3LYP
    ScalHFX 0.15
end
```

$$E_{\mathrm{XC}} = aE_{\mathrm{HF}}^{\mathrm{X}} + (1-a)\,E_{\mathrm{LSD}}^{\mathrm{X}} + bE_{\mathrm{GGA}}^{\mathrm{X}} + E_{\mathrm{LSD}}^{\mathrm{C}} + cE_{\mathrm{GGA}}^{\mathrm{C}}$$

```
%method
    Exchange X_B88
    Correlation C_LYP
    ACM a, b, c
end
```

$$E_{XC} = aE_X^{HF} + (1-a)\,E_X^{DFT} + (1-c)\,E_C^{DFT} + cE_C^{MP2}$$

```
%method
    ScalHFX  = a
    ScalDFX  = 1-a
    ScalGGAC = 1-c
    ScalLDAC = 1-c
    ScalMP2C = c
end
```

$$r_{12}^{-1} = \underbrace{\frac{1 - [\alpha + \beta \cdot \mathrm{erf}(\mu \cdot r_{12})]}{r_{12}}}_{\mathrm{SR}} + \underbrace{\frac{\alpha + \beta \cdot \mathrm{erf}(\mu \cdot r_{12})}{r_{12}}}_{\mathrm{LR}}$$
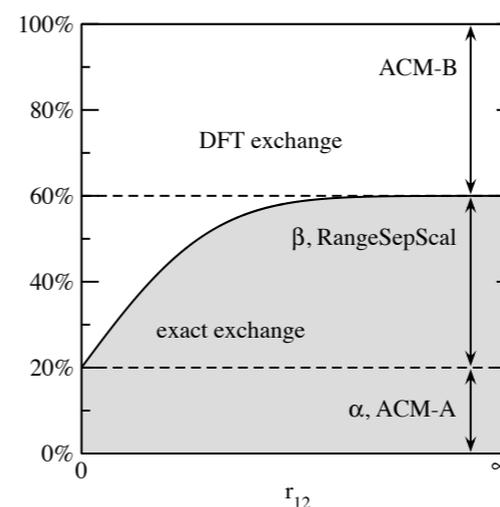

```
%method
    RangeSepEXX true
    RangeSepMu 0.25
    RangeSepScal 0.7
    ACM 0.2, 0.1, 1.0
end
```

Which functional should I use?

What can I calculate with DFT? What functional should I choose?

(m)GGA – Hybrid – Double Hybrid
sequence generally true
but depends on system and property
Main problem: inconsistency, unpredictability.

Literature is crucial.
Benchmarking is important. But:
How to use it? How to do it?
How not to get lost in it?

Many types of system or properties are absent or under-represented in standard benchmark sets. E.g. most evaluation studies cannot sufficiently address the enormous chemical space of transition metal systems, heavier elements, …

You cannot get an easy answer for the "best" functional. Too many parameters! It is essential to understand how they interrelate in your case.

System – Property – Method

How to choose a method without relying on intentional bias & error cancellation?

Which functional should I use?

Geometries GGA functionals adequate, sometimes better than hybrids.
BP86 a decent choice, perhaps TPSS. Include dispersion corrections.
Use with RI approximation (fast!)

Energies: **(m)GGA – Hybrid – Double Hybrid** sequence generally true for
thermodynamics, reaction barriers. Also true for redox potentials, but the
situation is less clear for spin-state energetics.
* Double hybrids discouraged for *exchange coupling interactions*!

"How accurate is DFT?" - Distinct physical origin of energy differences

Spectroscopy: **(m)GGA – Hybrid – Double Hybrid** sequence generally true, but quality
of results very system-dependent.

Frequencies: often GGA sufficient

Optical: TD-DFT…

EPR: advantage of hybrid functionals for g, **ZFS**, hyperfines;
TPSSh a favorite in many studies, but no general recipes

NMR: less sensitive, but go with a hybrid

Mössbauer: choose a hybrid, strong support for double-hybrids

Basis Sets

Linear Combination of Atomic Orbitals (LCAO)

The SCF procedure involves solving single-electron equations for **molecular orbitals**.

Can we think of a general, transferable, computer-friendly approach?

We need a standard set of building blocks, so that we don't have to guess or search for possible mathematical forms of MOs.

Is there a way to standardize this task and make it transferable?

We will express the molecular orbitals as linear combinations of atomic orbitals.

$$\psi_i(\mathbf{x}) = \sum_\mu c_{\mu i} \varphi_\mu(\mathbf{x})$$

Each atom comes with its set of AOs. We can construct any molecule we want and express any MO of this molecule in terms of the standard AOs of its constituent atoms.

$$F\psi_i = \varepsilon_i \psi_i \qquad\qquad \sum_\nu F_{\mu\nu}(\mathbf{c})c_{\mu i} = \varepsilon_i \sum c_{\nu i} S_{\mu\nu} \quad (all\ \mu, i)$$
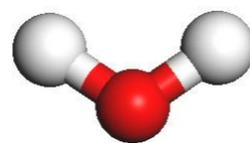
Basis functions

Let's generalize this:

Use more than one function for an "atomic orbital"
(more flexible representation of MOs)

Use mathematical forms that are convenient for calculations
(if they are not all that good, compensate by higher number)

We call these more "general atomic orbitals" **basis functions**

We assign a set of fixed functions (a **basis set**) to each atom. Then the task of finding the MOs is reduced to optimizing the MO expansion coefficients in terms of these fixed basis functions.

$$\psi_i(\mathbf{x}) = \sum_{\mu} c_{\mu i} \varphi_{\mu}(\mathbf{x})$$

Slater vs Gaussian type functions (STF / GTF)

Slater-type functions (exponent contains *-r*) are great because they best resemble hydrogen AOs and have the right shape close to the nucleus (cusp) and far from the nucleus (rate of decay)

Slater function
$$s_\nu(\mathbf{r}) = e^{-\zeta_\nu |\mathbf{r}|} = e^{-\zeta_\nu \sqrt{(x^2+y^2+z^2)}}$$

Gaussian function
$$g_\nu(\mathbf{r}) = e^{-\zeta_\nu \mathbf{r}^2} = e^{-\zeta_\nu (x^2+y^2+z^2)}$$

But it is computationally simpler to use Gaussian-type functions (exponent $-r^2$).

$$e^{-0.27\mathbf{r}^2}$$

$$0.68e^{-0.15\mathbf{r}^2} + 0.43e^{-0.86\mathbf{r}^2}$$

$$0.44e^{-0.11\mathbf{r}^2} + 0.53e^{-0.41\mathbf{r}^2} + 0.15e^{-2.23\mathbf{r}^2}$$
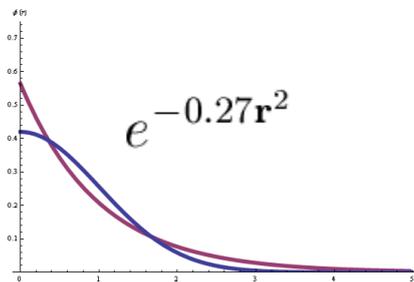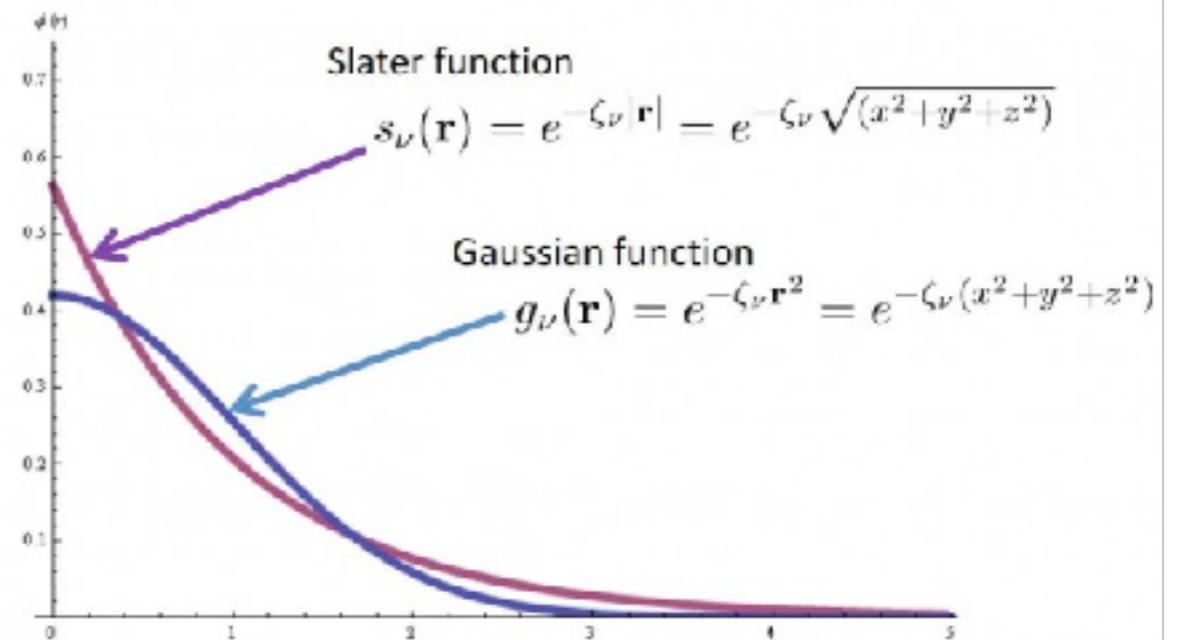
To compensate for their worse shape, we use several GTFs at the same time.

A single GTF is called a **primitive**.

The **_exponent_** (ζ) determines how diffuse the function is.

Several primitives can be combined into a linear combination to form a **contracted GTF**, with fixed **_contraction coefficients_**.
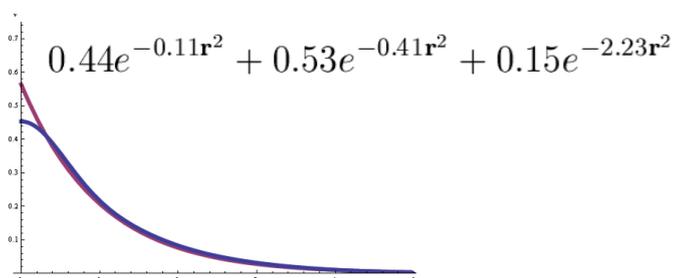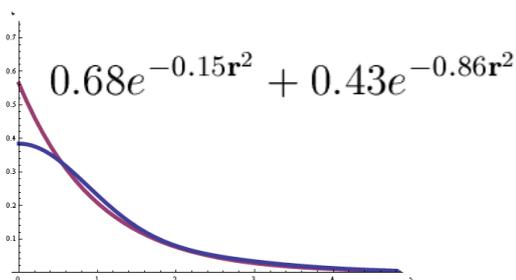
Left: example of **STO-*n*G** progression

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Minimal vs. expanded basis sets

**STO-nG**: one CGTF per atomic orbital. Not flexible enough.

Double-zeta (**DZ**): two GTFs (contracted or not) per AO.
Similarly: triple-zeta (**TZ**), quadruple-zeta (**QZ**) etc

In practice: use multiple (c)GTFs only for the valence space.

More flexibility:
- **polarization** functions = higher angular momentum than the valence occupied orbitals (can also be viewed as correlation functions)
- **diffuse** functions = functions with same angular momentum but smaller exponent (important for weak interactions, anions)

Families of basis sets:

Pople-type: 3-21G, 6-31G, 6-31G*, 6-31+G, 6-311G, …
Ahlrichs–Weigend: def2-SVP, def2-TZVP, …
Correlation consistent basis sets: cc-pVDZ, cc-pVTZ, aug-cc-pVT, cc-pVQZ, …
Property-optimized basis sets: EPR-II, EPR-III, CP(PPP), aug-cc-pVTZ-J, …
Relativistic basis sets: cc-pVTZ-DK, ZORA/DKH-SARC-TZVP, …

How does it look like?

```
#  Basis set for element : C
 NewGTO C
 S 5
    1      4232.6100000000          0.0023413403
    2       634.8820000000          0.0179264279
    3       146.0970000000          0.0870196239
    4        42.4974000000          0.2967017109
    5        14.1892000000          0.6883875263
 S 1
    1         1.9666000000          1.0000000000
 S 1
    1         5.1477000000          1.0000000000
 S 1
    1         0.4962000000          1.0000000000
 S 1
    1         0.1533000000          1.0000000000
 S 1
    1         0.0479000000          1.0000000000
 P 4
    1        18.1557000000          0.0185340026
    2         3.9864000000          0.1154420160
    3         1.1429000000          0.3862060535
    4         0.3594000000          0.6400890887
 P 1
    1         0.1146000000          1.0000000000
 D 1
    1         0.5500000000          1.0000000000
```

contracted GTF

primitive GTFs

contracted GTF

exponents   coefficients

Effective core potentials

Replace the inner functions by a single potential.

One way to include relativistic effects.

Not to be used when properties that depend on the density near the core are studied.

Examples: SDD, LANL2DZ, …

Our suggestion: better to use an approximate relativistic Hamiltonian (e.g. DKH2, ZORA) with appropriate all-electron basis sets (e.g. SARC-TZVP)

Auxiliary basis sets

Used in the approximate solution of certain integrals (RI approximations)

e.g. Coulomb (J), exchange (K)

Fit the density or actual products of basis functions

- def2/J, def2/JK, xxx/C, …

Relativistic Hamiltonians and Basis Sets

Douglas–Kroll–Hess (**DKH**) or Zero-order regular approximation (**ZORA**)

They have different behavior close to the nucleus.

Require tailor-made basis sets, e.g.: `cc-pVTZ-DK`, `SARC-ZORA-TZVP`.

(*ORCA might complain if an adapted basis set is not detected*)
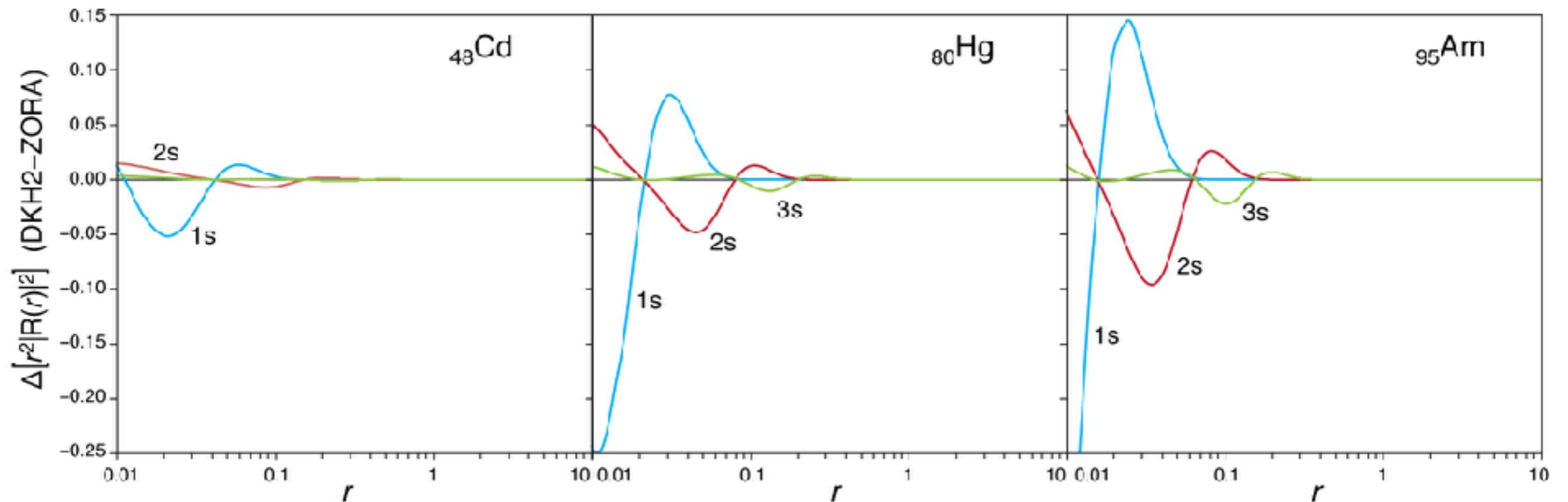
Relativistic Hamiltonians and Basis Sets

cc-pVDZ

```
IRON
S   20
1          4.316265E+06          8.048803E-06
2          6.463424E+05          6.258306E-05
3          1.470897E+05          3.290239E-04
4          4.166152E+04          1.387355E-03
5          1.359077E+04          5.023256E-03
6          4.905750E+03          1.610140E-02
7          1.912746E+03          4.590034E-02
8          7.926043E+02          1.136154E-01
9          3.448065E+02          2.283869E-01
10         1.558999E+02          3.221159E-01
11         7.223091E+01          2.383661E-01
12         3.272506E+01          7.404667E-02
13         1.566762E+01          9.214197E-02
14         7.503483E+00          9.339790E-02
15         3.312223E+00          1.573965E-02
16         1.558471E+00         -4.186682E-04
17         6.839140E-01          5.376318E-05
18         1.467570E-01         -3.816654E-05
19         7.058300E-02          4.319603E-05
20         3.144900E-02         -3.401019E-06
```

cc-pVDZ-DK

```
IRON
S   20
1          4.316265E+06          1.400000E-04
2          6.463424E+05          4.050000E-04
3          1.470897E+05          1.119000E-03
4          4.166152E+04          2.907000E-03
5          1.359077E+04          7.571000E-03
6          4.905750E+03          1.981800E-02
7          1.912746E+03          5.073400E-02
8          7.926043E+02          1.187290E-01
9          3.448065E+02          2.311640E-01
10         1.558999E+02          3.193220E-01
11         7.223091E+01          2.336480E-01
12         3.272506E+01          7.402200E-02
13         1.566762E+01          9.095200E-02
14         7.503483E+00          8.889800E-02
15         3.312223E+00          1.430200E-02
16         1.558471E+00         -3.870000E-04
17         6.839140E-01          8.000000E-06
18         1.467570E-01         -2.500000E-05
19         7.058300E-02          3.200000E-05
20         3.144900E-02         -1.000000E-06
```

Similar modifications for other relativistic versions and property-optimized basis sets.

Most common: s-decontraction, tight primitives (also for Finite Nucleus calculations)

Combination of Methods and Basis Sets

Method	Approximation	basis set (and auxiliaries)
CASSCF/NEVPT2		\<basis\>
CASSCF/NEVPT2	RI-JK	\<basis\>+ \<basis\>/JK
CASSCF/NEVPT2	RIJCOSX	\<basis\>+ \<basis\>/J + \<basis\>/C
CASSCF/NEVPT2	TrafoStep RI	\<basis\>+ \<basis\>/JK or \<basis\>/C
NEVPT2-F12	TrafoStep RI	\<basis\>-F12 + \<basis\>-F12/CABS + \<basis\>/JK or \<basis\>/C
TDDFT		\<basis\>
TDDFT	Mode RIInts	\<basis\>+ \<basis\>/C
MP2		\<basis\>
F12-MP2		\<basis\>-F12 + \<basis\>-F12/CABS
RI-MP2		\<basis\>+ \<basis\>/C
HF+RI-MP2	RIJCOSX	\<basis\>+ \<basis\>/C + \<basis\>/J
F12-RI-MP2		\<basis\>-F12 + \<basis\>-F12/CABS + \<basis\>/C
DLPNO-MP2		\<basis\>+ \<basis\>/C
HF+DLPNO-MP2	RI-JK	\<basis\>+ \<basis\>/C + \<basis\>/JK
F12-DLPNO-MP2		\<basis\>-F12 + \<basis\>-F12/CABS + \<basis\>/C
CCSD		\<basis\>
RI-CCSD		\<basis\>+ \<basis\>/C
(D)LPNO-CCSD		\<basis\>+ \<basis\>/C
HF+(D)LPNO-CCSD	RIJCOSX	\<basis\>+ \<basis\>/C + \<basis\>/J
F12-CCSD		\<basis\>-F12 + \<basis\>-F12/CABS
F12-RI-CCSD		\<basis\>-F12 + \<basis\>-F12/CABS + \<basis\>/C
HF+F12-RI-CCSD	RI-JK	\<basis\>-F12 + \<basis\>-F12/CABS + \<basis\>/C + \<basis\>/JK

Many choices in ORCA, additional choices online

6-311G(2d)	H–Br	cc-pCVTZ-PP[2]	Ca, Sr, Ba, Ra
6-311G(2d,p)	H–Br	cc-pCVQZ-PP[2]	Ca, Sr, Ba, Ra
6-311G(2d,2p)	H–Br	cc-pCV5Z-PP[2]	Ca, Sr, Ba, Ra
6-311G(2df)	H–Br	aug-cc-pCVDZ-PP[2]	Ca, Sr, Ba, Ra
6-311G(2df,2p)	H–Br	aug-cc-pCVTZ-PP[2]	Ca, Sr, Ba, Ra
6-311G(2df,2pd)	H–Br	aug-cc-pCVQZ-PP[2]	Ca, Sr, Ba, Ra
6-311G(3df)	H–Br	aug-cc-pCV5Z-PP[2]	Ca, Sr, Ba, Ra
6-311G(3df,3pd)	H–Br	cc-pwCVDZ-PP[2]	Ca, Cu–Kr, Sr–Xe, Ba, Hf–Rn, Ra
6-311+G*	H–Br	cc-pwCVTZ-PP[2]	Ca, Cu–Kr, Sr–Xe, Ba, Hf–Rn, Ra
6-311+G**	H–Br	cc-pwCVQZ-PP[2]	Ca, Cu–Kr, Sr–Xe, Ba, Hf–Rn, Ra
6-311+G(d)	H–Br	cc-pwCV5Z-PP[2]	Ca, Cu–Kr, Sr–Xe, Ba, Hf–Rn, Ra
6-311+G(d,p)	H–Br	aug-cc-pwCVDZ-PP[2]	Ca, Cu–Kr, Sr–Xe, Ba, Hf–Rn, Ra
6-311+G(2d)	H–Br	aug-cc-pwCVTZ-PP[2]	Ca, Cu–Kr, Sr–Xe, Ba, Hf–Rn, Ra
6-311+G(2d,p)	H–Br	aug-cc-pwCVQZ-PP[2]	Ca, Cu–Kr, Sr–Xe, Ba, Hf–Rn, Ra
6-311+G(2d,2p)	H–Br	aug-cc-pwCV5Z-PP[2]	Ca, Cu–Kr, Sr–Xe, Ba, Hf–Rn, Ra
6-311+G(2df)	H–Br	cc-pVDZ-DK	H–Ar, Sc–Kr
6-311+G(2df,2p)	H–Br	cc-pVTZ-DK	H–Ar, Sc–Kr, Y–Xe, Hf–Rn
6-311+G(2df,2pd)	H–Br	cc-pVQZ-DK	H–Ar, Sc–Kr, In–Xe, Tl–Rn
6-311+G(3df)	H–Br	cc-pV5Z-DK	H–Ar, Sc–Kr
6-311+G(3df,3pd)	H–Br	aug-cc-pVDZ-DK	H–Ar, Sc–Kr
6-311++G**	H–Br	aug-cc-pVTZ-DK	H–Ar, Sc–Kr, Y–Xe, Hf–Rn
6-311++G(d,p)	H–Br	aug-cc-pVQZ-DK	H–Ar, Sc–Kr, In–Xe, Tl–Rn
6-311++G(2d,p)	H–Br	aug-cc-pV5Z-DK	H–Ar, Sc–Kr
6-311++G(2d,2p)	H–Br	cc-pwCVDZ-DK	Li–Be, Na–Mg, Ca–Zn
6-311++G(2df,2p)	H–Br	cc-pwCVTZ-DK	Li–Be, Na–Mg, Ca–Zn, Y–Xe, Hf–Rn
6-311++G(2df,2pd)	H–Br	cc-pwCVQZ-DK	Li–Be, Na–Mg, Ca–Zn, In–Xe, Tl–Rn
6-311++G(3df,3pd)	H–Br	cc-pwCV5Z-DK	Li–Be, Na–Mg, Ca–Zn
SV	H–Kr	aug-cc-pwCVDZ-DK	Li–Be, Na–Mg, Sc–Zn
SV(P)	H–Kr	aug-cc-pwCVTZ-DK	Li–Be, Na–Mg, Sc–Zn, Y–Xe, Hf–Rn
SVP	H–Kr	aug-cc-pwCVQZ-DK	Li–Be, Na–Mg, Sc–Zn, In–Xe, Tl–Rn
TZV	H–Kr	aug-cc-pwCV5Z-DK	Li–Be, Na–Mg, Sc–Zn
TZV(P)	H–Kr	Partridge-1	H, Li–Sr
TZVP	H–Kr	Partridge-2	H, Li–Kr
TZVPP	H–Kr	Partridge-3	H, Li–Zn
QZVP	H–Kr	Partridge-4	Sc–Zn
QZVPP	H–Kr	ANO-SZ	H–Ar, Sc–Zn
DKH-SV(P)	H–Kr	LANL08[3]	Na–La, Hf–Bi
DKH-SVP	H–Kr	LANL08(f)[3]	Sc–Cu, Y–Ag, La, Hf–Au
DKH-TZV(P)	H–Kr	LANL2DZ[3]	H, Li–La, Hf–Bi, U–Pu
DKH-TZVP	H–Kr	LANL2TZ[3]	Sc–Zn, Y–Cd, La, Hf–Hg
DKH-TZVPP	H–Kr	LANL2TZ(f)[3]	Sc–Cu, Y–Ag, La, Hf–Au
DKH-QZVP	H–Kr	Sapporo-DZP-2012	H–Xe
DKH-QZVPP	H–Kr	Sapporo-TZP-2012	H–Xe
ZORA-SV(P)	H–Kr	Sapporo-QZP-2012	H–Xe
ZORA-SVP	H–Kr	Sapporo-DKH3-DZP-2012	K–Rn
ZORA-TZV(P)	H–Kr	Sapporo-DKH3-TZP-2012	K–Rn
ZORA-TZVP	H–Kr	Sapporo-DKH3-QZP-2012	K–Rn
ZORA-TZVPP	H–Kr	SARC-DKH-SVP	Hf–Hg
ZORA-QZVP	H–Kr	SARC-DKH-TZVP	Xe–Rn, Ac–Lr
ZORA-QZVPP	H–Kr	SARC-DKH-TZVPP	Xe–Rn, Ac–Lr
def2-mSVP[1]	H–Rn	SARC-ZORA-SVP	Hf–Hg
def2-mTZVP[1]	H–Rn	SARC-ZORA-TZVP	Xe–Rn, Ac–Lr
def2-SV(P)[1]	H–Rn	SARC-ZORA-TZVPP	Xe–Rn, Ac–Lr
def2-SVP[1]	H–Rn	SARC2-DKH-QZV	La–Lu
def2-TZVP(-f)[1]	H–Rn	SARC2-DKH-QZVP	La–Lu
def2-TZVP[1]	H–Rn	SARC2-ZORA-QZV	La–Lu
def2-TZVPP[1]	H–Rn	SARC2-ZORA-QZVP	La–Lu
def2-QZVP[1]	H–Rn	D95	H, Li–Li, B–Ne, Al–Cl

def2-QZVPP[1]	H–Rn	D95p	H, Li–Li, B–Ne, Al–Cl
def2-SVPD[1]	H–La, Hf–Rn	EPR-II	H, B–F
def2-TZVPD[1]	H–La, Hf–Rn	EPR-III	H, B–F
def2-TZVPPD[1]	H–La, Hf–Rn	IGLO-II	H, B–F, Al–Cl
def2-QZVPD[1]	H–La, Hf–Rn	IGLO-III	H, B–F, Al–Cl
def2-QZVPPD[1]	H–La, Hf–Rn	UGBS	H–Th, Pu–Am, Cf–Lr
DKH-def2-SV(P)	H–Kr	CP	Sc–Zn
DKH-def2-SVP	H–Kr	CP(PPP)	Sc–Zn
DKH-def2-TZVP(-f)	H–Kr	Wachters+f	Sc–Cu
DKH-def2-TZVP	H–Kr	cc-pVDZ-F12	H–Ar
DKH-def2-TZVPP	H–Kr	cc-pVTZ-F12	H–Ar
DKH-def2-QZVPP	H–Kr	cc-pVQZ-F12	H–Ar
ZORA-def2-SV(P)	H–Kr	cc-pVDZ-PP-F12[2]	Ga–Kr, In–Xe, Tl–Rn
ZORA-def2-SVP	H–Kr	cc-pVTZ-PP-F12[2]	Ga–Kr, In–Xe, Tl–Rn
ZORA-def2-TZVP(-f)	H–Kr	cc-pVQZ-PP-F12[2]	Ga–Kr, In–Xe, Tl–Rn
ZORA-def2-TZVP	H–Kr	cc-pCVDZ-F12	Li–Ar
ZORA-def2-TZVPP	H–Kr	cc-pCVTZ-F12	Li–Ar
ZORA-def2-QZVPP	H–Kr	cc-pCVQZ-F12	Li–Ar
ma-def2-mSVP[1]	H–Rn	**Coulomb-fitting auxiliary basis sets (AuxJ)**	
ma-def2-SV(P)[1]	H–Rn	def2/J	H–Rn
ma-def2-SVP[1]	H–Rn	def2-mTZVP/J	H–Rn
ma-def2-TZVP(-f)[1]	H–Rn	SARC/J	H–Rn, Ac–No
ma-def2-TZVP[1]	H–Rn	**Coulomb and exchange-fitting auxiliary basis sets (AuxJK)**	
ma-def2-TZVPP[1]	H–Rn	def2/JK	H–Ba, Hf–Rn
ma-def2-QZVP[1]	H–Rn	def2/JKsmall	H–Ra, Th–Lr
ma-def2-QZVPP[1]	H–Rn	cc-pVTZ/JK	H, B–F, Al–Cl, Ga–Br
ma-DKH-def2-SV(P)	H–Kr	cc-pVQZ/JK	H, B–F, Al–Cl, Ga–Br
ma-DKH-def2-SVP	H–Kr	cc-pV5Z/JK	H, B–F, Al–Cl, Ga–Br
ma-DKH-def2-TZVP(-f)	H–Kr	aug-cc-pVTZ/JK	H, B–F, Al–Cl, Ga–Br
ma-DKH-def2-TZVP	H–Kr	aug-cc-pVQZ/JK	H, B–F, Al–Cl, Ga–Br
ma-DKH-def2-TZVPP	H–Kr	aug-cc-pV5Z/JK	H, B–F, Al–Cl, Ga–Br
ma-DKH-def2-QZVPP	H–Kr	SARC2-DKH-QZV/JK	La–Lu
ma-ZORA-def2-SV(P)	H–Kr	SARC2-DKH-QZVP/JK	La–Lu
ma-ZORA-def2-SVP	H–Kr	SARC2-ZORA-QZV/JK	La–Lu
ma-ZORA-def2-TZVP(-f)	H–Kr	SARC2-ZORA-QZVP/JK	La–Lu
ma-ZORA-def2-TZVP	H–Kr	**Auxiliary basis sets for correlated methods (AuxC)**	
ma-ZORA-def2-TZVPP	H–Kr	def2-SVP/C	H–La, Hf–Rn
ma-ZORA-def2-QZVPP	H–Kr	def2-TZVP/C	H–La, Hf–Rn
old-SV	H–I	def2-TZVPD/C	H–La, Hf–Rn
old-SV(P)	H–I	def2-TZVPP/C	H–La, Hf–Rn
old-SVP	H–I	def2-TZVPPD/C	H–La, Hf–Rn
old-TZV	H–I	def2-QZVPP/C	H–La, Hf–Rn
old-TZV(P)	H–I	def2-QZVPPD/C	H–La, Hf–Rn
old-TZVP	H–I	cc-pVDZ/C	H–Ar, Ga–Kr
old-TZVPP	H–I	cc-pVTZ/C	H–Ar, Sc–Kr
old-DKH-SV(P)	H–I	cc-pVQZ/C	H–Ar, Sc–Kr
old-DKH-SVP	H–I	cc-pV5Z/C	H–Ar, Ga–Kr
old-DKH-TZV(P)	H–I	cc-pV6Z/C	H–He, B–Ne, Al–Ar
old-DKH-TZVP	H–I	aug-cc-pVDZ/C	H–He, Be–Ne, Mg–Ar, Ga–Kr
old-DKH-TZVPP	H–I	aug-cc-pVTZ/C	H–He, Be–Ne, Mg–Ar, Sc–Kr
old-ZORA-SV(P)	H–I	aug-cc-pVQZ/C	H–He, Be–Ne, Mg–Ar, Sc–Kr
old-ZORA-SVP	H–I	aug-cc-pV5Z/C	H–Ne, Al–Ar, Ga–Kr
old-ZORA-TZV(P)	H–I	aug-cc-pV6Z/C	H–He, B–Ne, Al–Ar
old-ZORA-TZVP	H–I	cc-pwCVDZ/C	B–Ne, Al–Ar, Ga–Kr
old-ZORA-TZVPP	H–I	cc-pwCVTZ/C	B–Ne, Al–Ar, Sc–Kr
ANO-pVDZ	H–Ar, Sc–Zn	cc-pwCVQZ/C	B–Ne, Al–Ar, Ga–Kr
ANO-pVTZ	H–Ar, Sc–Zn	cc-pwCV5Z/C	Li–Ne, Al–Ar
ANO-pVQZ	H–Ar, Sc–Zn	aug-cc-pwCVDZ/C	B–Ne, Al–Ar, Ga–Kr

External sources of basis sets

https://bse.pnl.gov/bse/portal

External sources of basis sets

http://www.cosmologic-services.de/basis-sets/basissets.php

External sources of basis sets

http://www.grant-hill.group.shef.ac.uk/ccrepo/index.html

Definition of basis sets in ORCA

```
! B3LYP def2-TZVP def2/J Decontract DecontractAux
```

```
%basis
    basis "def2-TZVP"
    aux   "def2/J"
    auxJK "def2/JK"
    auxC  "def2-TZVP/C"
    CABS  "cc-pVDZ-F12-OptRI"
end
```

```
%basis
    basis "def2-TZVP"
    NewGTO C  "def2-QZVPP" end
    NewGTO Fe "CP(PPP)" end
end
```

```
%basis
    NewGTO Pt "SARC-ZORA-TZVP"
end

%method IntAcc 6.0 end
```

```
%basis
    NewGTO H
    S 3
    1      144.0976000000      0.0870196239
    2       32.7787000000      0.2967017109
    3        6.1862000000      0.6883875263
    S 1
    1        0.8000000000      1.0000000000
    end
    AddGTO O
    D 1
    1 0.500  1.000
    end
    auxJ "AutoAux"
end                          # Lots of customization!
```

```
%basis
    GTOname "newbasis.bas"
end
```

Dimitrios A. Pantazis

Which basis set should I use?

The basis set is only one ingredient…

System – Property – Method

Examples:

Au complex → relativity! → ECPs? or scalar relativistic Hamiltonian e.g. DKH2?
⇒ need DKH-adapted basis sets, e.g. SARC

Anionic system or specific properties may require diffuse functions

Coupled-cluster calculation → requires careful convergence to basis set limit
⇒ cc-pVnZ family of basis sets plus extrapolation. Or F12?

case study on redox potentials: CCSD(T) vs DFT with basis set size
M. Isegawa, F. Neese, D. A. Pantazis, *J. Chem. Theory Comput.* **2016**, *12*, 2272-2284

Spectroscopic properties (e.g. Mössbauer shifts, hyperfine coupling constants) ⇒ need

appropriately optimized basis sets, e.g. CP(PPP), EPR-III
(here bigger is not better!)

Hierarchy of post-Hartree–Fock methods

▸ HF theory - fundamental issues: Coulomb and Fermi hole

post-HF methods:

▸ Use the "unoccupied orbitals"

▸ Perturbation theory (MP2)

▸ Single-reference methods: Coupled-Cluster

▸ Increase flexibility in Ψ: more than one determinant - multi-reference methods

▸ Configuration interaction - Complete Active Space CI - CAS-SCF, …

▸ Other approaches - MRCI, DDCI, SORCI, …
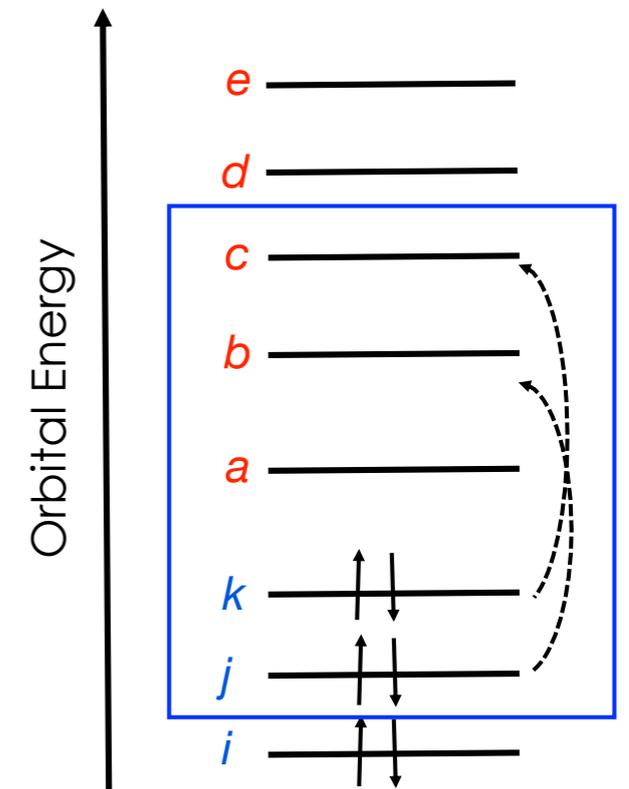
Well-defined hierarchy of methods - but also with increasing cost and complexity.

CCSD(T) is a highly successful and robust approach.

Multi-reference methods are demanding in their application, but allow access to properties or levels of accuracy otherwise unattainable!

Example
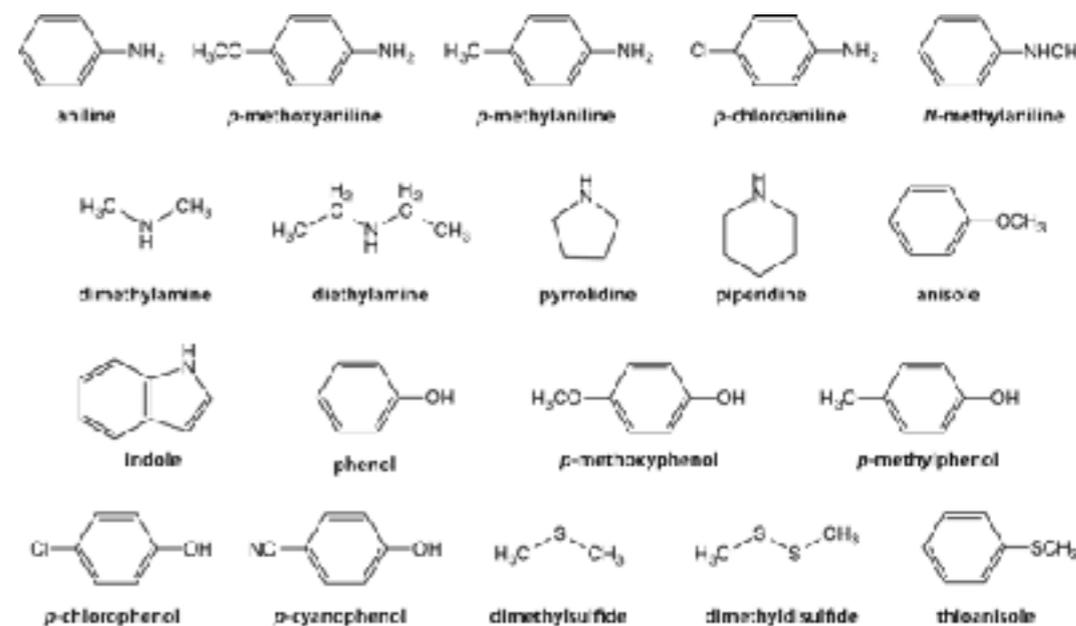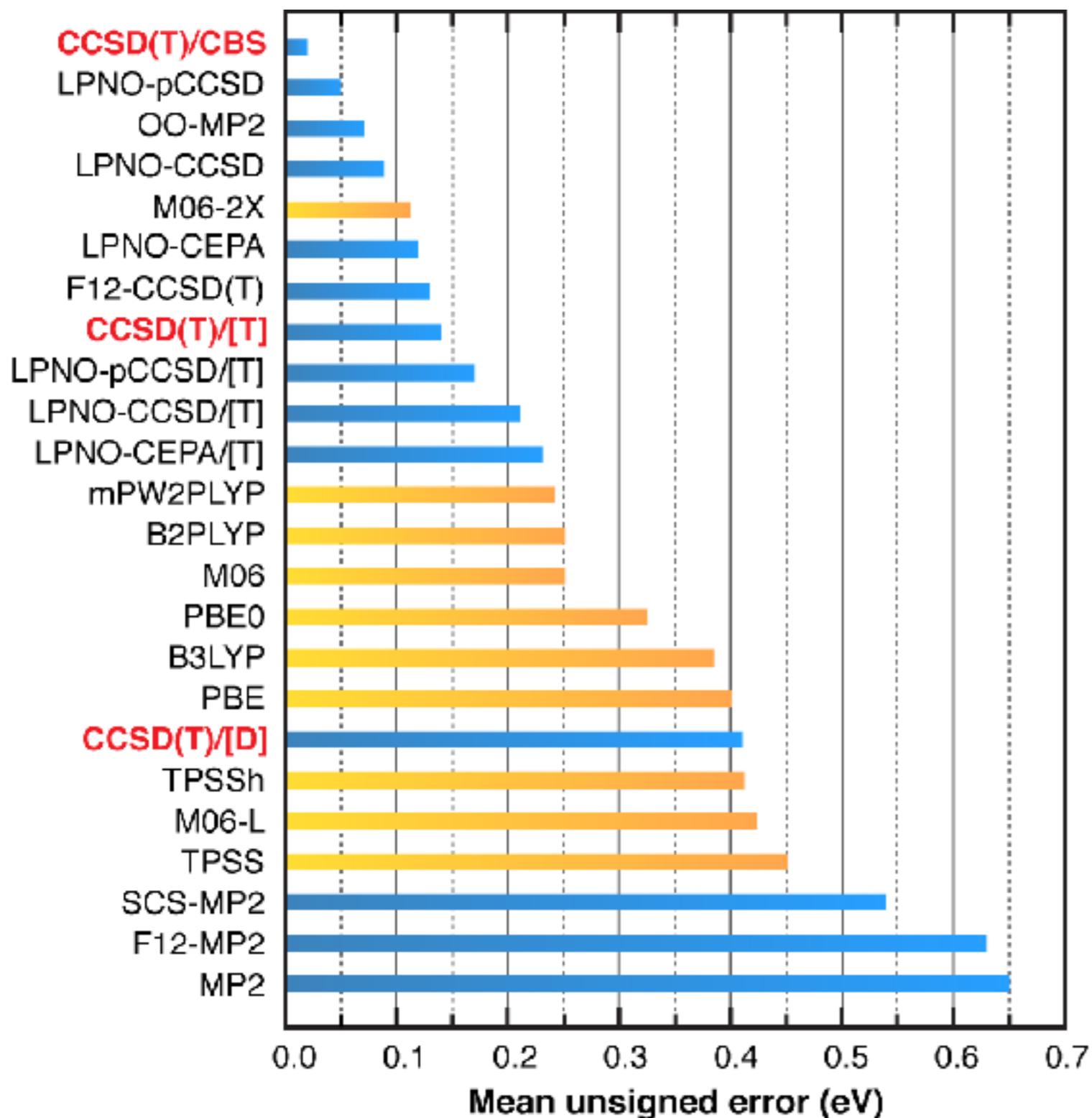
What if the computed numbers with the smaller basis set are better than with the larger?

M. Isegawa, F. Neese, D. A. Pantazis, *J. Chem. Theory Comput.* **2016**, *12*, 2272-2284

Basis set Extrapolation

$$E_{\text{corr}}^{(\infty)} = \frac{X^\beta E_{\text{corr}}^{(X)} - Y^\beta E_{\text{corr}}^{(Y)}}{X^\beta - Y^\beta}$$

```
! CCSD(T) Extrapolate(2/3)
```

= cc-pVDZ, cc-pVTZ

Extrapolate(*X/Y, basis*)
basis: cc, aug-cc, cc-core, ano, def2

Extrapolate(*n, basis*), e.g. Extrapolate(3, cc)

```
Alpha(2/3)        :   4.420 (SCF Extrapolation)
Beta(2/3)         :   2.460 (correlation extrapolation)


SCF energy with basis cc-pVDZ:                        -76.026430944
SCF energy with basis cc-pVTZ:                        -76.056728252
Extrapolated CBS SCF energy (2/3) :                   -76.066581429 (-0.009853177)


MDCI energy with basis cc-pVDZ:                        -0.214591061
MDCI energy with basis cc-pVTZ:                        -0.275383015
Extrapolated CBS correlation energy (2/3) :            -0.310905962 (-0.035522947)


Estimated CBS total energy (2/3) :                    -76.377487391
```