Density Functional Theory
Introductory notes

\[ |\Psi(x_1, x_2, \ldots x_N)|^2 dx_1 dx_2 \ldots dx_N \]

- Probability of finding electron 1 in \( dx_1 \), electron 2 in \( dx_2 \) etc.

- Integrate over spin-space coordinates of electrons 2–\( N \) and spin of 1:

\[ \left( \int \cdots \int |\Psi(x_1, x_2, \ldots x_N)|^2 ds_1 dx_2 \cdots dx_N \right) dr_1 \]

- Probability of finding electron 1 in volume element \( dr_1 \) (other electrons can be anywhere).

\[ \left( N \int \cdots \int |\Psi(x_1, x_2, \ldots x_N)|^2 ds_1 dx_2 \cdots dx_N \right) dr_1 = \rho(r_1) dr_1 \]

- Probability of finding any electron in \( dr_1 \).

\[ \rho(r_1) = N \int \cdots \int |\Psi(x_1, x_2, \ldots x_N)|^2 ds_1 dx_2 \cdots dx_N \]

- \( \rho(r) \) is the electron density.
Density

- Wave function: a complicated function of $4 \times N_{\text{el}}$ 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 $Z$.

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

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

$$N_{el} = \int \rho(r) \, dr$$

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

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 \( \rho(r) \) to the energy \( E \),
i.e. we need to express the energy as a functional of the density, \( E[\rho] \)

Hamiltonian

\[
\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{en} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_{i}^2 + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{i} v(r_{i})
\]

External potential

\[
v(r_{i}) = -\sum_{A} \frac{Z_{A}}{r_{Ai}}
\]

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)

⇒ the electronic energy can be expressed completely as a functional of the density

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

**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

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

⇒ One can already use all of the above to do calculations!

Minimize the energy with respect to var. density by constraining

\[ \int \rho(\mathbf{r})d\mathbf{r} = N_{el} \]
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!

$$\hat{H} = -\sum_{i}^{N} \frac{1}{2} \nabla_{i}^{2} + \sum_{i}^{N} v_{\text{eff}}(\mathbf{r}_{i}) \quad \left( -\frac{1}{2} \nabla^{2} + v_{\text{eff}}(\mathbf{r}) \right) \varphi_{i}(\mathbf{r}) = \epsilon_{i} \varphi_{i}(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_{i}^{N} \varphi_{i}^{2}(\mathbf{r}) \quad T_{s}[\rho] = \sum_{i}^{N} \langle \varphi_{i} | -\frac{1}{2} \nabla^{2} | \varphi_{i} \rangle$$

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


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

$\Rightarrow$ guess $E_{\text{XC}}$ 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 $\rho(r)$ is constant. The kinetic energy of the electrons in this system is proportional to $\rho(r)^{5/3}V$. 
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.

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

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)

\[ E_{XC}[\rho] = \int F(\rho, \nabla \rho) dr \]

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

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

\[ E_{\text{XC}} = \int F(\rho, \nabla \rho, \nabla^2 \rho) d\mathbf{r} \]

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

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-O₂ 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.

Archetypal example: **B2PLYP**. Current “best”: **PWBP95**

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).

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

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

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

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

Dimitrios A. Pantazis
Thus, you are well advised to provide a number that is significantly less than your physical memory. Note input. Further functionals are available via the feature. Since any of these keywords will select a DFT method, the keyword "DFT" is not needed in the run on a really small memory computer or you are running a gigantic job. It needs and if it runs out of physical memory you are out of luck. This, however, rarely happens unless you simultaneously we provide a global variable to control the size of these dominant scratch arrays. However, since these modules are never running based correlation calculations) require large scratch arrays. Each module has an independent variable sets 4000 MB (= 4 GB) as the limit for these scratch arrays.

Global memory use.

### 6.2 Keyword Lines

<table>
<thead>
<tr>
<th>Local and gradient corrected functionals</th>
<th>Co EF</th>
<th>M06</th>
<th>M06-2X</th>
<th>M06-L</th>
<th>M06h</th>
<th>M06h2X</th>
<th>B97-MV</th>
<th>B97-MV-3DJH</th>
<th>SCAN/None</th>
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<tr>
<td>HF</td>
<td>Hartree–Fock-Slater Exchange only functional</td>
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<td>LDA or LSD</td>
<td>Local density approximation (defaults to VWN5)</td>
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<td>B96 or BP</td>
<td>Becke ’88 exchange and Perdew ’86 correlation</td>
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<td>BLYP</td>
<td>Becke ’88 exchange and Lee-Yang-Parr correlation</td>
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<td>GLYP</td>
<td>Gill’s ’96 exchange and Lee-Yang-Parr correlation</td>
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<td>XLYP</td>
<td>The Xu and Goddard exchange and Lee-Yang-Parr correlation</td>
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<td>PW91</td>
<td>Perdew-Wang ’91 GGA functional</td>
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### Hybrid functionals

| mPW | Modified PW exchange and PW correlation |
| mPW1PW | One-parameter hybrid version of mPW |
| mPW1LYP | One-parameter hybrid version of mPWLYP |
| PHE9 | One-parameter hybrid version of PBE |
| PW89h95 | Hybrid functional by Truhlar |

### Meta-GGA and hybrid meta-GGA functionals

| TPSSh | The hybrid version of TPSS (10% HF exchange) |
| TPSSh | The hybrid 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) |
| M06h2X | The M06-2X version with 54% HF exchange |
| B97-MV | Head-Gordon’s DF B97-MV with no functional correlation |
| B97-MV-3DJH | Modified version of B97-MV with 3DJ correction by Nazhi and Goerigk |
| SCAN/None | Perdew’s SCAN functional |

### Range-separated hybrid functionals

| wi97 | Head-Gordon’s fully variable DF wi97 |
| wi97X | Head-Gordon’s DF wi97X with minimal Fock exchange |
| wi97X-D3 | Chai’s refit incl. D3 in its zero-damping version |
| wi97X-V | Head-Gordon’s DF wi97X-V with no correlation |
| wi97X-3DJH | Modified version of wi97X-V with 3DJ correction by Nazhi and Goerigk |
| wi97M-V | Head-Gordon’s DF wi97M-V with no correlation |
| wi97M-3DJH | Modified version of wi97M-V with 3DJ correction by Nazhi and Goerigk |
| CAM-BLYP | Handy’s fit |

### Meta-GGA and hybrid meta-GGA functionals

| LC-BLYP | Hira’s original application |

### Perturbatively corrected double-hybrid functionals

| B2PLYP | Grimme’s mixture of B88, LYP, and MP2 |
| B2PLYP-D | B2PLYP with Grimme’s empirical dispersion correction from 2010 (D2) |
| B2PLYP-D3 | B2PLYP with Grimme’s atom-pairwise dispersion correction |
| 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) |
| RGP-FLYP | Gerdsh Marin’s “general purpose” reparameterization |
| RIK-FLYP | Gerdsh Marin’s “kinetic” reparameterization |
| BGT-FLYP | Gerdsh Marin’s “thermochemistry” reparameterization |
| PW91h5 | Georghi and Grimme’s mixture of modified PW91, modified B95, and SOS-MP2 |
| DSD-BLYP | Gerdsh Marin’s “general purpose” double-hybrid with B88 exchange, LYP correlation and SCS-MP2 mixing, i.e. not incl. DSHJ correction |
| DSD-FBE98 | Gerdsh Marin’s “general purpose” double-hybrid with PRE exchange, F86 correlation and SCS-MP2 mixing, i.e. not incl. DSHJ correction |
| DSD-FBE95 | Gerdsh Marin’s “general purpose” double-hybrid with PRE exchange, B95 correlation and SCS-MP2 mixing, i.e. not incl. DSHJ correction |

### Range-separated double-hybrid functionals

| wRGPFLYP | Georghi and Casanova-Pace’s range-separated DHDF, with the correlation contributions based on B2PLYP, optimized for excitation energies |
| wRGPFLYP | Georghi and Casanova-Pace’s range-separated DHDF, with the correlation contributions based on RGPFLYP, optimized for excitation energies |

### Dispersion corrections

| D1 | density-dependent atom-pairwise dispersion correction with Becke-Johnson damping and ATM |
| DSHJ | Atom-pairwise dispersion correction to the DFT energy with Becke-Johnson damping |
| DZERO | 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

* Grids important in DFT

%method
  functional B3LYP
  ScalHFX 0.15
end

\[ E_{XC} = a E_{HF}^X + (1 - a) E_{DFT}^X + (1 - c) E_{C}^{DFT} + c E_{MP2}^{C} \]

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

* Additionally: Libxc functionals

* Several dispersion corrections

\[ r_{12}^{-1} = \left( 1 - \frac{[\alpha + \beta \cdot \text{erf}(\mu \cdot r_{12})]}{r_{12}} \right) \cdot \frac{r_{12}}{\text{SR}} + \frac{\alpha + \beta \cdot \text{erf}(\mu \cdot r_{12})}{r_{12}} \cdot \frac{r_{12}}{\text{LR}} \]

%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?

<table>
<thead>
<tr>
<th>Geometries</th>
<th>GGA functionals adequate, sometimes better than hybrids. BP86 a decent choice, perhaps TPSS. Include dispersion corrections. Use with RI approximation (fast!)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Energies:</strong></td>
<td><strong>(m)GGA – Hybrid – Double Hybrid</strong> 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 <em>exchange coupling interactions</em>!</td>
</tr>
</tbody>
</table>
| 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.**

\[ \psi_i(x) = \sum_{\mu} c_{\mu i} \phi_{\mu}(x) \]

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.
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.

\[ \psi_i(x) = \sum_{\mu} c_{\mu i} \phi_{\mu}(x) \]
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).

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

To compensate for their worse shape, we use several GTFs at the same time. A single GTF is called a **primitive**.

The **exponent** (\(\zeta\)) 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
Minimal vs. expanded basis sets

**STO-\(n\)G**: 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**, …
# Basis set for element : C

<table>
<thead>
<tr>
<th>NewGTO</th>
<th>C</th>
</tr>
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<tr>
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- **contracted GTF**
- **primitive GTFs**

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

<table>
<thead>
<tr>
<th>IRON</th>
<th>cc-pVDZ</th>
<th>cc-pVDZ-DK</th>
</tr>
</thead>
<tbody>
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</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Method</th>
<th>Approximation</th>
<th>Basis set (and auxiliaries)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CASSCF/NEVPT2</td>
<td>RI-JK</td>
<td>&lt;basis&gt;</td>
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<tr>
<td>CASSCF/NEVPT2</td>
<td>RIJCOSX</td>
<td>&lt;basis&gt; + &lt;basis&gt;/J + &lt;basis&gt;/C</td>
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<tr>
<td>CASSCF/NEVPT2</td>
<td>TrafoStep RI</td>
<td>&lt;basis&gt; + &lt;basis&gt;/JK or &lt;basis&gt;/C</td>
</tr>
<tr>
<td>NEVPT2-F12</td>
<td>TrafoStep RI</td>
<td>&lt;basis&gt;-F12 + &lt;basis&gt;-F12/CABS + &lt;basis&gt;/JK or &lt;basis&gt;/C</td>
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<tr>
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<td>Mode RIInts</td>
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<tr>
<td>RI-MP2</td>
<td></td>
<td>&lt;basis&gt; + &lt;basis&gt;/C</td>
</tr>
<tr>
<td>HF+RI-MP2</td>
<td>RIJCOSX</td>
<td>&lt;basis&gt; + &lt;basis&gt;/C + &lt;basis&gt;/J</td>
</tr>
<tr>
<td>F12-RI-MP2</td>
<td></td>
<td>&lt;basis&gt;-F12 + &lt;basis&gt;-F12/CABS + &lt;basis&gt;/C</td>
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<tr>
<td>DLPNO-MP2</td>
<td></td>
<td>&lt;basis&gt; + &lt;basis&gt;/C</td>
</tr>
<tr>
<td>HF+DLPNO-MP2</td>
<td>RI-JK</td>
<td>&lt;basis&gt; + &lt;basis&gt;/C + &lt;basis&gt;/JK</td>
</tr>
<tr>
<td>F12-DLPNO-MP2</td>
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<tr>
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<tr>
<td>RI-CCSD</td>
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<td>&lt;basis&gt; + &lt;basis&gt;/C</td>
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<tr>
<td>(D)LPNO-CCSD</td>
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<td>&lt;basis&gt; + &lt;basis&gt;/C</td>
</tr>
<tr>
<td>HF+(D)LPNO-CCSD</td>
<td>RIJCOSX</td>
<td>&lt;basis&gt; + &lt;basis&gt;/C + &lt;basis&gt;/J</td>
</tr>
<tr>
<td>F12-CCSD</td>
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<td>&lt;basis&gt;-F12 + &lt;basis&gt;-F12/CABS</td>
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<tr>
<td>F12-RI-CCSD</td>
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<td>&lt;basis&gt;-F12 + &lt;basis&gt;-F12/CABS + &lt;basis&gt;/C</td>
</tr>
<tr>
<td>HF+F12-RI-CCSD</td>
<td>RI-JK</td>
<td>&lt;basis&gt;-F12 + &lt;basis&gt;-F12/CABS + &lt;basis&gt;/C + &lt;basis&gt;/JK</td>
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### Choice of Basis Set

<table>
<thead>
<tr>
<th>Method</th>
<th>Elements</th>
<th>Notes</th>
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<tbody>
<tr>
<td>def2-QZVPP</td>
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<tr>
<td>def2-TZVPP</td>
<td>H–La, H–Rn</td>
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<td>def2-TZVPPD</td>
<td>H–La, H–Rn</td>
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<tr>
<td>def2-TZVPD</td>
<td>H–La, H–Rn</td>
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</tr>
<tr>
<td>def2-QZVPD</td>
<td>H–La, H–Rn</td>
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<tr>
<td>DKH-def2-TZPP</td>
<td>H–Kr</td>
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<td>DKH-def2-TZVPP</td>
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<tr>
<td>D95</td>
<td>H, Li, Be, B–Ne, Al–Cl</td>
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</table>

### Detailed Documentation

<table>
<thead>
<tr>
<th>Method</th>
<th>Elements</th>
<th>Notes</th>
</tr>
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<tbody>
<tr>
<td>def2-ZVPP</td>
<td>H–Rn</td>
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<tr>
<td>def2-QZVPP</td>
<td>H–Rn</td>
<td></td>
</tr>
<tr>
<td>def2-TZVPP</td>
<td>H–La, H–Rn</td>
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<tr>
<td>def2-TZVPD</td>
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<td>def2-TZVPPD</td>
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<tr>
<td>D95</td>
<td>H, Li, Be, B–Ne, Al–Cl</td>
<td></td>
</tr>
</tbody>
</table>

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### Additional Choices Online

- Many choices in ORCA
- Def2-TZVPP
- Def2-TZVPD
- Def2-QZVPD
- D95

---

- DKH-def2-TZPP
- DKH-def2-TZVPP
- D95
- D95p
- EPR-II
- EPR-III
- IGLO-II
- IGLO-III
- UGISS
- CP
- S(VP)
- C(P(VP))
- C(VP)

---

- D95
- D95p
- EPR-II
- EPR-III
- IGLO-II
- IGLO-III
- UGISS
- CP
- S(VP)
- C(P(VP))
- C(VP)

---

- D95
- D95p
- EPR-II
- EPR-III
- IGLO-II
- IGLO-III
- UGISS
- CP
- S(VP)
- C(P(VP))
- C(VP)
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

ccRepo
A correlation consistent basis sets repository
The correlation consistent family of basis sets have been developed over a number of years by the groups of Dunning, Peterson, Hill and others. This website provides some details about this family of basis sets and allows for their download in a number of formats. A bibliography and information on the philosophy behind correlation consistent basis sets is also provided.

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

%method
  IntAcc 6.0
end

# Lots of customization!

%basis
  GTOname "newbasis.bas"
end

%basis
  auxJ "AutoAux"
end

%method
  IntAcc 6.0
end
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

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 $\Psi$: 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!
What if the computed numbers with the smaller basis set are better than with the larger?
Basis set Extrapolation

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

Extrapolate\((X/Y, \text{basis})\)

\text{basis}: \text{cc, aug-cc, cc-core, ano, def2}

Extrapolate\((n, \text{basis})\), e.g. Extrapolate\((3, \text{cc})\)

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

\[ \text{Extrapolate}(n, \text{basis}) \rightarrow \text{Extrapolate}(3, \text{cc}) \]

\(= \text{cc-pVDZ, cc-pVTZ} \)