Exercise Session 3
IESM Fall 2025-2026

Salomé, Qihao, Thibault, Evan

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Interviews:

- You should have received a detailed feedback on Moodle for reports of Ex1
- If everything is correct, simple checkmarks are added
- Comments added when something is wrong/unclear/uncomplete
- Overall comment added to the report

Large Basis Sets, Dissociation Energy and Geometry Optimisation
(Reminder: you can download these slides from the Exercise page)

☄ **Learning goals**	📖 **Chapter in script**	🍂 **Resources**
Influence of basis sets	Chapter 3 - Basis functions in quantum chemistry	Jensen, F. (2017). Introduction to computational chemistry. John wiley & sons.
Geometry optimization procedure	Chapter 4 - An introduction to Hartree Fock theory	• Chapter 5 - Basis Sets
Basics of HF theory: RHF vs UHF		Introduction to Hartree-Fock Molecular Orbital Theory by the Sherrill group: slides and videos (part 1, part 2)
		Geometry Optimization by the Sherrill group: slides and video

Influence of basis set

- System under study: H_2 molecule at equilibrium bondlength (H–H distance 0.7414Å)

- You will compute the equilibrium energy of the molecule using different basis sets
  - 6-31G
  - 6-311G
  - aug-cc-pVTZ (Dunning's correlation-consistent basis, defined such that systematic improvement over total energies and molecular properties is possible)

- We will use HF theory (which will be treated in detail during Lectures and next Exercise session) to calculate energies
- In this exercise, you will qualitatively see the differences between RHF and UHF

HF method = approximate many-body wavefunction to a single Slater determinant

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) \approx \Psi_{HF} \equiv \frac{1}{\sqrt{N}} \left| \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \ldots \phi_n(\mathbf{r}_n) \right|$$

$\rightarrow \Psi_{HF}$ inserted into time-independent Schrödinger equation to find eigenvalue, i.e. $E = \left\langle \Psi_{HF} \middle| \hat{H}_{el} \middle| \Psi_{HF} \right\rangle$. What is found is a **variational solution**, i.e. HF energy is always above true energy.

HF equations (will be derived in detail during Lectures)

$$E_{HF} = \sum_i \left\langle \phi_i \middle| \hat{h} \middle| \phi_i \right\rangle + \frac{1}{2} \sum_{i,j} \left([\phi_i \phi_i | \phi_j \phi_j] - [\phi_i \phi_j | \phi_j \phi_i] \right) \qquad \forall \phi_i$$
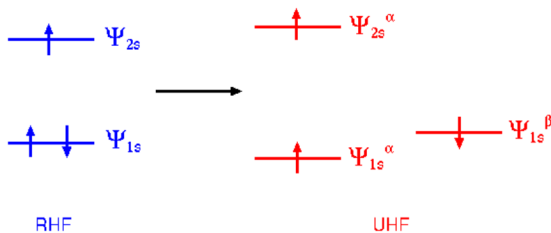
where $[\ldots|\ldots]$ integrals contain Coulomb and Exchange operators, whose action on orbital ϕ_i depends on all the other one-electron orbitals ϕ_j. Hence, HF equations have to be solved iteratively until self-consistency (**selfconsistent field SCF method**)

```
                       Total Energy        Delta E        RMS |[F,P]|

  @DF-UHF iter SAD:    -0.85212229561042   -8.52122e-01   0.00000e+00
  @DF-UHF iter   1:    -1.12493424123815   -2.72812e-01   1.62339e-02 DIIS
  @DF-UHF iter   2:    -1.12669596352817   -1.76172e-03   2.38980e-03 DIIS
  @DF-UHF iter   3:    -1.12673509439903   -3.91309e-05   3.36383e-06 DIIS
  @DF-UHF iter   4:    -1.12673509447661   -7.75795e-11   2.74379e-09 DIIS
  Energy and wave function converged.
```

RHF and UHF methods

- So far we did not discuss spin components! MO are composed of a MO spatial wavefunction ($\phi_i(\mathbf{r}_i)$) and a MO spin wavefunction (α or β, i.e. $\uparrow$ or $\downarrow$ spin)
- In practice, different HF implementations are possible:
  - **RHF** (Restricted HF): each spatial MO $\phi_i(\mathbf{r}_i)$ is used twice, once multiplied by a α spin and the other by the β spin $\Rightarrow$ same spatial component! This is reasonable for **closed-shell systems** (even number of electrons), where spatial MO is fully occupied.
  - **UHF** (Unrestricted HF): different spatial MO used for α and β spins. This allow to describe **open-shell sytems** (odd number of electrons), **but** a single Slater determinant of different orbitals for different spins is not an eigenfunction of the total spin operator $\hat{\mathbf{S}}^2$ (this produced the so-called *spin contamination*, where the ground state is *contaminated* by excited states).
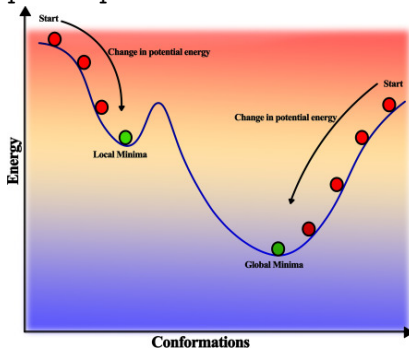
[Image source] Note that here Ψ is a MO!

- RHF suitable for closed-shell systems, UHF for open-shell
- UHF doubles the spatial orbitals, hence it is more computationally expensive

In this exercise you will record the dissociation curve for H_2 molecule - what is the effect of using RHF vs UHF?

Geometry optimization

- Until now **single-point calculations** (nuclear positions fixed)
  `psi4.energy(method/basisset, molecule)`
- **Geometry optimization**: starting from an initial
  configuration, you can follow the curvature on the PES down
  to the minimum, i.e find the equilibrium geometry
  `psi4.optimize(method/basisset, molecule)`

[Image source]

Exercise 3 - Tips

Tips!

- You'll need to edit some code cells and having a look at code in Ex2 may be helpful
- You'll use `matplotlib` to make plots, more information on it can be found here
- HF method will be treated in detail in next Lectures and Exercises, for today make sure to have understood the general idea. Psi4 manual has also a quick theory introduction on HF and is useful to get familiar with different HF methods/keywords.
- Make sure to understand the difference between a single-point calculation and a geometry optimization (you will see it in practice in Ex3.3)!