

# Exercise Session 3

## IESM Fall 2025-2026

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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

# Exercise 3

## 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  Geometry optimization procedure  Basics of HF theory: RHF vs UHF	Chapter 3 - Basis functions in quantum chemistry  Chapter 4 - An introduction to Hartree Fock theory	Jensen, F. (2017). Introduction to computational chemistry. John Wiley & sons.  • Chapter 5 - Basis Sets  Introduction to Hartree-Fock Molecular Orbital Theory by the Sherrill group: <a href="#">slides</a> and videos ( <a href="#">part 1</a> , <a href="#">part 2</a> )  Geometry Optimization by the Sherrill group: <a href="#">slides</a> and <a href="#">video</a>

## Influence of basis set

- System under study:  $\text{H}_2$  molecule at equilibrium bondlength (H–H distance 0.7414 Å)



- 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)

## Introduction to HF Theory

- 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**

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

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

## SCF method

HF equations (will be derived in detail during Lectures)

$$E_{HF} = \sum_i \left\langle \phi_i \left| \hat{h} \right| \phi_i \right\rangle + \frac{1}{2} \sum_{i,j} ([\phi_i \phi_i | \phi_j \phi_j] - [\phi_i \phi_j | \phi_j \phi_i]) \quad \forall \phi_i$$

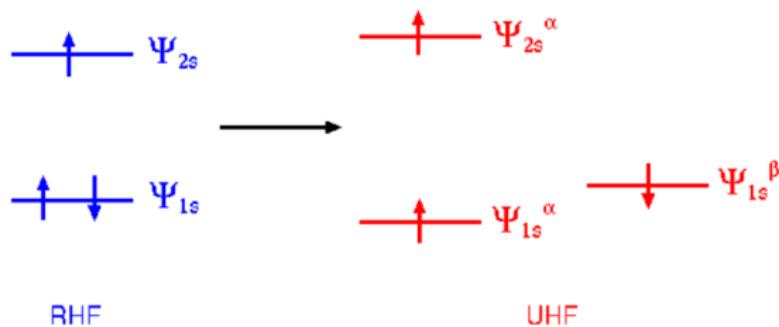
where  $[\dots|\dots]$  integrals contain Coulomb and Exchange operators, whose action on orbital  $\phi_i$  depends on all the other one-electron orbitals  $\phi_j$ . Hence, HF equations have to be solved iteratively until self-consistency (**selfconsistent field SCF method**)

	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 ( $\alpha$  or  $\beta$ , 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  $\alpha$  spin and the other by the  $\beta$  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  $\alpha$  and  $\beta$  spins. This allow to describe **open-shell systems** (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).

## RHF vs UHF



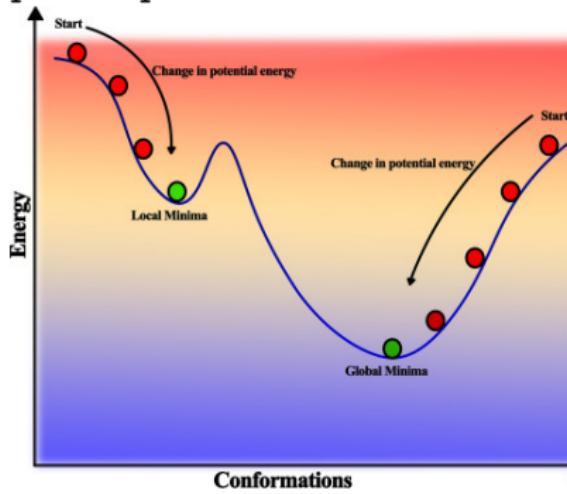
[Image source] Note that here  $\Psi$  is a MO!

- 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)!