

Exercise Session 3 IESM Fall 2024-2025

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Reports Feedback

Interviews:

- All of you should have recived 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)



Influence of basis set

 System under study: H₂ 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)

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

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

 $ightarrow \Psi_{HF}$ 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.

SCF method

HF equations (will be derived in detail during Lectures)

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

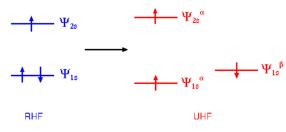
where $[\ldots | \ldots]$ integrals contain Coulomb and Exchange operators, whose action on orbital ϕ_i depends on all the other one-electron orbitals ϕ_j . Hence, HF equations have to be solved iteratively until self-consistency (selfconsistent field SCF method)

```
Delta E
                                                       RMS | [F, P] |
                        Total Energy
 @DF-UHF iter SAD:
                     -0.85212229561042
                                         -8.52122e-01
                                                       0.00000e+00
@DF-UHF iter
                     -1.12493424123815
                                         -2.72812e-01
                                                       1.62339e-02 DITS
 @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:
                                        -7.75795e-11
                                                       2.74379e-09 DIIS
                     -1.12673509447661
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 $(\alpha \text{ or } \beta, \text{ i.e. } \uparrow \text{ or } \downarrow \text{ spin})$
- 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 $\widehat{\mathbf{S}}^2$ (this produced the so-called *spin contamination*, where the ground state is *contaminated* by excited states).

RHF vs UHF



[Image source] Note that here Ψ is a MO!

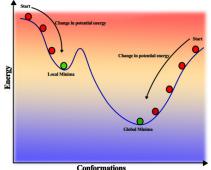
- RHF suitable for closed-shell systems, UHF for open-shell
- UHF doubles the spatial orbitals, hence it is more computationally expensive

In this exercise you will record the dissociation curve for H₂ 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)!