

Exercise Session 2

IESM Fall 2024-2025

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Notebook Reminders

- If you're on our [exercise website](https://exercise.epfl.ch) click the rocket button on the top right, choose JupyterHub (noto.epfl.ch)



- Make sure to always activate (top right) the Computational Chemistry kernel



Notebook Reminders

- .iynb files organized in cells
 - Markdown (text)
 - Code
- You can edit the cells directly
- Run a code cell by pressing Play button (or Ctrl+Enter or Shift+Enter)



Text cell

```
[1]: x = 1  
     y = 2
```

```
[ ]: print(x+y)
```

Psi4 Introduction

- Psi4 Manual
- Open-Source ab initio electronic structure software package
- Allows for calculations such as: HF, CI, DFT, molecular energies/structures, reaction mechanisms, transition state search, vibrational frequencies, molecular orbitals/densities, geometry optimization, atomic charges, electrostatic potentials, NMR properties, and more
- Other electronic structure software you may know: Gaussian, CP2K, CPMD, Quantum Espresso, ORCA, NWChem



Psi4 with Python

- We can use Psi4 as a python module with PsiAPI directly in Jupyter Notebooks
- We import Psi4 and use the psi4 directive to ask Psi4 to perform an action

```
[1]: import psi4
import pandas as pd
import numpy as np
import matplotlib.pyplot as plt

plt.style.use(['seaborn-poster', 'seaborn-ticks'])
```

```
[2]: psi4.set_memory('2 GB')
psi4.set_num_threads(2)
```

Memory set to 1.863 GiB by Python driver.
Threads set to 2 by Python driver.

```
[3]: h = psi4.geometry("""
0 2
H 0.0 0.0 0.0
""")
```

Viewing Output

- We often set an output file (usually a .log file) to store information from a calculation
- You can find them in the lefthand navigation directory

The screenshot shows a JupyterLab environment. On the left is a file browser for the 'Ex2' directory, listing files like '6-311G-output.log', '6-31G-output.log', 'data_and_plots.ipynb', 'Energy.dat', 'eq_RHF-output.log', 'eq_UHF-output.log', 'Ex2.ipynb', 'IESM_Ex2__20220...', 'IESM_Ex2.ipynb', 'large_RHF-output.log', 'large_UHF-output.log', 'STO-3G-output.log', and 'timer.dat'. The file '6-311G-output.log' is selected. On the right, the 'Ex2.ipynb' notebook is open, showing the output of a Gaussian calculation. The output includes the start of a calculation, basis set loading, SCF convergence, and geometry optimization results.

```

6 *** tstart() called on noto.epfl.ch
7 *** at Wed Jan 26 17:15:38 2022
8
9 => Loading Basis Set <=
10
11 Name: 6-311G
12 Role: ORBITAL
13 Keyword: BASIS
14 atoms 1 entry H line 21 file /opt/psi4conda/psi4conda-1.4rc3/share/psi4/basis/6-311g.gbs
15
16 -----
17
18 SCF
19 by Justin Turney, Rob Parrish, Andy Simmonett
20 and Daniel G. A. Smith
21 UHF Reference
22 2 Threads, 1907 MiB Core
23 -----
24
25 ==> Geometry <==
26
27 Molecular point group: d2h
28 Geometry (in Angstrom), charge = 0, multiplicity = 2:
29
30 Center X Y Z Mass
31 -----
32 H 0.000000000000 0.000000000000 0.000000000000 1.007825032230
33
34 Running in d2h symmetry.
35
36 Rotational constants: A = ***** B = ***** C = ***** [cm^-1]
37 Rotational constants: A = ***** B = ***** C = ***** [MHz]
38 Nuclear repulsion = 0.000000000000
39
40 Charge = 0
  
```

Linux & Terminal

- Linux bash commands in notebooks (cell starts with !)

```
!grep 'iter' large_RHF-output.log
```

```
@DF-RHF iter 1: -0.73775656591694 -7.37757e-01 2.26180e-02 DIIS
@DF-RHF iter 2: -0.74503745659583 -7.28089e-03 2.27444e-03 DIIS
@DF-RHF iter 3: -0.74511202947724 -7.45729e-05 5.15094e-06 DIIS
@DF-RHF iter 4: -0.74511202986000 -3.82762e-10 6.49170e-09 DIIS
```

- Linux commands (even Psi4 calculations) directly via a terminal view of your notebooks



Jupyter Servers

- “Noto can run up to 15 parallel Jupyter backend servers to provide a total of up to 240 GB of RAM and 240 CPU, shared between all users. Our current policy is to allocate up to a maximum of 2 GB of RAM and 2 CPUs per user.”

Node > Socket > Core (independent processing unit)



Intel Sandybridge socket with eight cores
Stampede node with two sockets and a co-processor
Server room

(Images from *TACC HPC textbook*)

Exercise 2 - Basis Sets & Psi4

First steps in Psi4 - [Exercise page](#)

- Understand what are basis functions
- Get familiar with basis function notation
- Basics of Psi4
- Get familiar with molecular geometries

Learning goals

Understand what are basis functions

Get familiar with basis function notation

Basics of **Psi4**

Get familiar with molecular geometries

Chapter in script

Chapter 3 - Basis functions in quantum chemistry

Resources

Jensen, F. (2017). Introduction to computational chemistry. John Wiley & sons.

- Chapter 5 - Basis Sets

Exercise 2 - Tips

Tips!

- Please focus on understanding basis sets well first and then getting familiar with Psi4 :)
- Practice single-point calculations for an H-atom and water molecule with `psi4.energy()` commands
 - Requires input geometry (Z-matrix or Cartesian coordinates)
 - Psi4 finds lowest energy combination of wavefunction coefficients for the given geometry
 - By comparing energy values with different basis sets we can discuss the effect of basis set selections on accuracy and cost (Additional note: is the total energy always meaningful? – think about that especially in the H₂O exercise)
 - We will compute the energy of the system with the selected basis set **and** a method of choice. In this exercise we will always be UHF (unrestricted Hartree Fock), but don't worry too much about it for now: you will get familiar with this and other methods in the next lectures/exercises!