

Exercise Session 2

IESM Fall 2023-2024

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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
""")
```

- 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 pane showing a directory structure: `/ ... / Exercises / Ex2 /`. It lists several files, including `6-311G-output.log` (9 months ago), `6-31G-output.log` (9 months ago), `data_and_plots.ipynb` (a month ago), `Energy.dat` (a month ago), `eq_RHF-output.log` (9 months ago), `eq_UHF-output.log` (9 months ago), `Ex2.ipynb` (2 minutes ago), `IESM_Ex2__20220...` (2 months ago), `IESM_Ex2.ipynb` (24 days ago), `large_RHF-output.log` (9 months ago), `large_UHF-output.log` (9 months ago), `STO-3G-output.log` (9 months ago), and `timer.dat` (a year ago).

The main pane shows a Jupyter notebook with two tabs: `Ex2.ipynb` and `6-311G-output.log`. The `Ex2.ipynb` tab is active, showing a Jupyter cell with the following output:

```

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                               SCF
18   by Justin Turney, Rob Parrish, Andy Simmonett
19   and Daniel G. A. Smith
20                               UHF Reference
21                               2 Threads,   1907 MiB Core
22 -----
23
24 ==> Geometry <==
25
26 Molecular point group: d2h
27 Geometry (in Angstrom), charge = 0, multiplicity = 2:
28
29
30      Center          X              Y              Z              Mass
31 -----
32      H              0.000000000000    0.000000000000    0.000000000000    1.007825032230
33
34
35 Running in d2h symmetry.
36
37 Rotational constants: A = ***** B = ***** C = ***** [cm^-1]
38 Rotational constants: A = ***** B = ***** C = ***** [MHz]
39 Nuclear repulsion = 0.000000000000
40
41 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
```

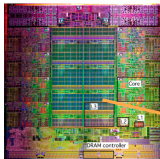
- Linux commands (even Psi4 calculations) directly via a terminal view of your notebooks



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!