DFT Project: Water Splitting Reaction Free Energy
Project Description

Computational Electrocatalysis – RWTH Aachen University

Prerequisite: Basic Python programming skills (variables, loops, and simple plotting) are required.

If the upcoming pages look dense at first sight, don't worry: a step-by-step workflow is outlined in Section 1 to guide you through the entire project. For the project basic knowledge of the programming language Python is required.

Project Description

This project takes you through a step-by-step computational study of the water splitting reaction:

$$2H_2O \; \rightleftharpoons \; 2H_2 + O_2 \tag{1}$$

moving systematically from pure electronic energies to room-temperature Gibbs free energies.
You will learn:

1. Constructing Molecules

Define each molecule by listing atomic symbols and their Cartesian coordinates (x, y, z in Å). Using PySCF: You will code these coordinates into Python and build a molecule.

2. Geometry Optimisation

Relax each molecule to its lowest-energy arrangement using a basic method (Hartree–Fock with the STO-3G basis-set):

- Run an optimisation routine that adjusts atomic positions until energy changes are minimal.

- Measure the final bond lengths (H–H in H_2, O–O in O_2, both O–H bonds in H_2O) and compare with known experimental values.

- For the H_2O molecule you additionally measure the bond angle between the H-O-H bonds. Compare this also with literature values.

You will see how theory predicts realistic geometries and learn about basis sets.

3. Reaction Energy

Calculate the reaction energy of the water splitting reaction (Eq. 1) (report the electronic energy of the optimised structure first, then the reaction energy).

4. Basis-set Convergence

Investigate how the size of the basis-set affects the calculated reaction energy:

Reaction energy

$$\Delta E_{\mathrm{r}}(\text{basis}) = (2E_{\mathrm{H}_2} + E_{\mathrm{O}_2}) - 2E_{\mathrm{H}_2\mathrm{O}} \quad (\text{products} - \text{reactants}).$$

– Evaluate the reaction energy ΔE_{r} with the following basis sets: STO-3G, 3-21G, 6-31G, cc-pVDZ, cc-pVTZ, cc-pVQZ, cc-pV5Z.

– Plot ΔE_{r} versus basis set to observe when the energy stops changing significantly.

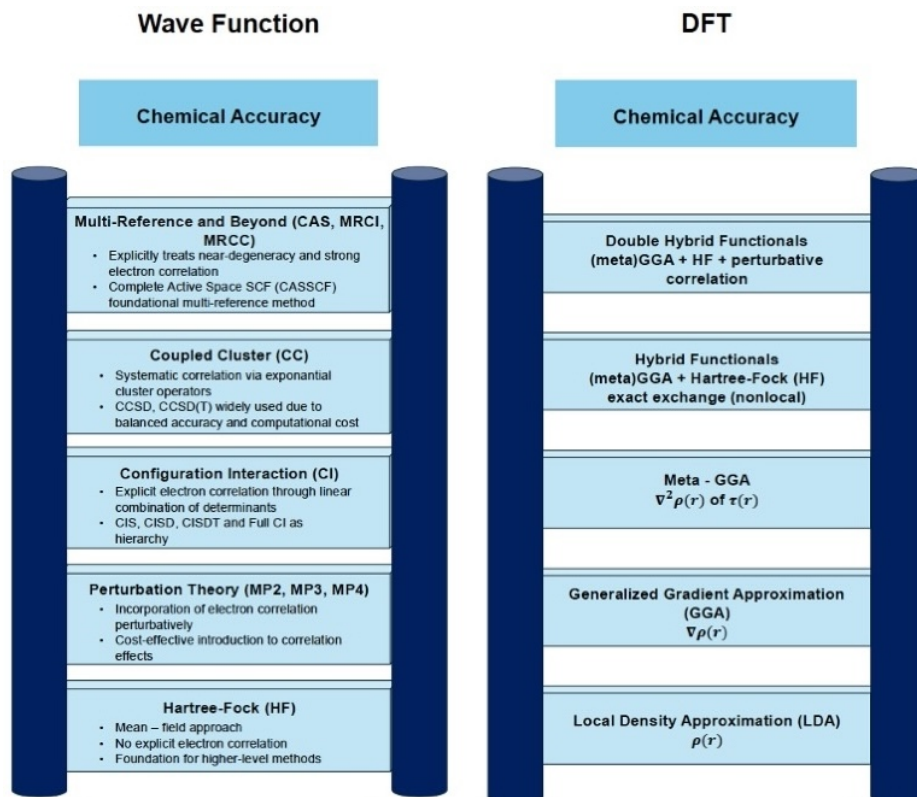## 5. Method Hierarchy (Jacob's Ladder)

Figure 1: Schematic illustration of Jacob's Ladder for Wave-function (left) and DFT (right) methods. Each rung adds more information from the electronic structure, improving accuracy.

Fig. 1 presents Jacob's Ladder as a conceptual framework for the hierarchy of approximations for wave-function and DFT methods, climbing from the simplest to the most accurate methods toward chemical accuracy. Improve upon Hartree–Fock by adding electronic correlation. You will:

– Calculate the reaction energy using HF, MP2, and CCSD for the water splitting reaction.

– In parallel, perform density functional theory (DFT) calculations: begin with the Perdew-Burke-Ernzerhof (PBE) approximation, which treats electron exchange with the Generalized Gradient Approximation (GGA). Proceed to a hybrid functional (e.g., PBE0), and discuss double-hybrid options.

6. Thermodynamic Corrections

When we compute the energy of a chemical system using DFT or a high-level wave-function method, we obtain the electronic energy at $0\,\mathrm{K}$, without accounting for the motions of nuclei or the effects of temperature. To connect these raw energies to experiments carried out at room temperature ($298.15\,\mathrm{K}$), we must

add thermodynamic corrections that convert electronic energies into Gibbs free energies (G).

The main corrections are:

- **Zero-Point Energy (ZPE)**: Even at $0\,\mathrm{K}$, each vibrational mode has a residual energy ($\frac{1}{2}\hbar\omega$). Adding ZPE accounts for the quantum mechanical ground state vibrations of bounds (for examples, the O-H bond stretches in water).

- **Thermal Enthalpy Correction (ΔH)**: At finite temperature, vibrations, rotations, and translations contribute extra thermal energy. Usually, ΔH is computed from statistical mechanics formulas for each degree of freedom. In this project we will use literature values for ΔH. This raises the enthalpy from its $0\,\mathrm{K}$ value to the value at 298.15 K.

- **Entropy Correction ($-$TΔS)**: Molecules gain entropy through increased vibrational, rotational and translational disorder at room temperature. Multiplying the computed entropy change ΔS by $-$T gives the entropic contribution to the free energy.

Putting these together,

$$\mathrm{G}(298.15\,\mathrm{K}) = E_{DFT} + ZPE + \Delta\mathrm{H} - T\cdot\Delta\mathrm{S}, \tag{2}$$

where E_{DFT} is the electronic energy from your quantum-chemistry calculation.

- Look up experimental ZPE, ΔH, and ΔS values in the NIST database[1] and add them to your calculated electronic energies.

- (Optional) Compute vibrational frequencies in PySCF to estimate the ZPE, ΔH, and ΔS yourself.

G of the respective molecule of interest (molecule H_2O, molecule H_2, and molecule O_2) can be used to compute the reaction free energy of the water splitting reaction (Eq. 1):

To compute the reaction energies G is computed for the systems of interest. If you haven't calculated the vibrational frequencies by yourself, the literature value has to be adopted for ΔS, and ΔH. The literature values can be obtained from the NIST database. G at 298.15 K for a gas-phase molecule like H_2 or O_2 is therefore computed according to Eq. 2.

An exception in the computation of ΔG for molecules relevant to water splitting is the water molecule. Since water exists as a liquid at 298.15 K, its G is determined using the following expression:

$$G^{298.15\,\mathrm{K}}_{H_2O(l)} = \left(\Delta\mathrm{H}_{H_2O(l)} - \Delta\mathrm{H}_{H_2O(g)}\right) - T\cdot\left(S^{298.15\,\mathrm{K}}_{H_2O(l)} - S^{298.15\,\mathrm{K}}_{H_2O(g)}\right) + G^{298.15\,\mathrm{K}}_{H_2O(g)} \tag{3}$$

Now the reaction free energy ΔG_r can be calculated as:

$$\Delta G_{\mathrm{r}} = G_{\mathrm{prod}} - G_{\mathrm{reac}}, \tag{4}$$

where G_{prod} and G_{reac} denote the Gibbs free energies of the reaction products and reactants, respectively.


[1] https://cccbdb.nist.gov/

7. Accuracy Analysis

Assess for common approximations:

- Re-relax molecular geometries at higher levels (e.g., MP2, CCSD) to include structural changes.

- Create a final accuracy analysis table summarising contributions from basis, method, and thermodynamics corrections.

- The obtained results should be compared with literature values.

1 Project Workflow

This section provides the recommended workflow. *Please use it as the structural template when preparing your report☺.*

1. Define Cartesian coordinates for the molecules H_2, O_2 and H_2O respectively (see Sec. 2).

2. Relax each molecule with a single, inexpensive reference method/basis (e.g. HF/STO–3G) to obtain an initial geometry.

3. Converge the reaction energy of each relaxed structure w. r. t. the basis-set.

4. Compute reaction energies

$$2\,H_2O \;\rightleftharpoons\; 2\,H_2 + O_2$$
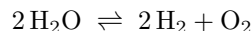
with an ascending hierarchy of electronic structure methods. When you compute the reaction energies, remember to add thermodynamic corrections. Discuss the remaining deviation from experiment.

2 Getting Started

In this project you will use the open-source quantum chemistry package **PySCF**[2]. Make sure it is installed in your Python environment (`pip install pyscf` or `conda install -c conda-forge pyscf`). You can find the installation guide here `https://pyscf.org/install.html`.

2.1 Minimal `PySCF` workflow

Pseudocode 1 Building and initialising a molecule

Require: Atom labels $\{\text{symbol}_i\}$ and coordinates $\{\mathbf{r}_i\}$ in Å
 1: **mol** $\leftarrow$ gto.Mole()
 2: **for all** i **do**
 3:     Append string "`<symbol> x y z`" to **mol.atom**
 4: **end for**
 5: Assign a basis
 6: **mol.unit** $\leftarrow$ "Angstrom"
 7: MOL(build)

Assigning basis sets per atom

In `PySCF` you can pass a **dict** such as

`mol.basis = {'H': 'cc-pVQZ', 'O': 'cc-pVTZ'}`

to use different basis sets for different elements.

`PySCF` helpful abbreviations

Listing 1: PySCF helpful abbreviations

```
1  from pyscf import gto, scf, mp, cc, fci
2
3  # 1. Molecule container
4  mol = gto.Mole()                            # empty Mole object
5  mol_H2 = gto.M(atom="H 0 0 0; H 0 0 0.74",  # example molecule
```

```
6                   basis="sto-3g")
7
8  # 2. Mean-field calculation
9  mf = scf.UHF(mol).run()          # unrestricted  H a r t r e e Fock
10 print(mf.e_tot)                  # total energy (Eh)
11
12 # handy attributes
13 - mf.mo_coeff                     # molecular-orbital coefficients
14 - mf.converged                   # SCF convergence flag (true/false)
15
16 # 3. Post-HF
17 e_mp2  = mp.MP2(mf).run().e_tot              # MP2
18 e_ccsd = cc.CCSD(mf).run().e_tot            # CCSD
19 e_fci  = fci.FCI(mol, mf.mo_coeff).kernel()[0]   # FCI
20
21 # 4. Unit conversion
22 HARTREE2EV = 27.2114  # 1 Hartree     27.2114 eV
23 # precise value:
24 # from scipy.constants.physical_constants['Hartree energy in eV'][0]
```

Geometry optimiser in `PySCF`

`PySCF` calls an extra library to relax structures. The most widely used is `berny`. In case of installation issues, the code below switches to `geomeTRIC`.

Listing 2: Geometry-optimiser

```
1  from pyscf import scf
2
3  try:
4      from pyscf.geomopt import berny_solver          # most common optimiser
5      optimise = berny_solver.optimize
6      opt_name = "Berny"
7  except ModuleNotFoundError:
8      from pyscf.geomopt import geometric_solver       # another optimiser in case first didn't
              work
9      optimise = geometric_solver.optimize
10     opt_name = "geomeTRIC"
```

3   Tasks (to be completed & reported)

T1 Coordinates. Enter experimental geometries for the three molecules. Cite your source.

T2 Geometry relaxation. Optimise the geometries using Hartree-Fock with the STO-3G basis-set as described in 2. Geometry Optimisation

T3 Reaction energy. Calculate the reaction energy of the water splitting reaction using the optimised structure.

T4 SCF total energy. Record the converged Hartree-Fock energy for each molecule before starting the basis set study.

T5 Basis-set convergence. Using the pseudocode in Alg. 2, generate a plot of reaction energy vs. different basis sets ($n = STO - 3G, 3 - 21G, 6 - 31G, D, T, Q, 5$).

T6 Single-molecule vs. reaction-energy convergence. For the water molecule, plot the convergence of the basis sets of its total SCF energy along with the convergence of the total reaction energy
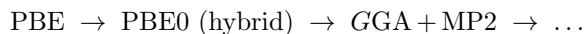
$$2\,H_2O \;\rightleftharpoons\; 2\,H_2 + O_2$$
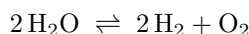
Discuss possible reasons why the reaction energy appears to converge faster than the total energy of the isolated molecule.

T7 Method ladder. With the basis that converged and you decided to use, compute the reaction energy with the following methods:

$$HF \rightarrow MP2 \rightarrow CCSD$$

and, in parallel,

$$PBE \rightarrow PBE0 \text{ (hybrid)} \rightarrow GGA + MP2 \rightarrow \ldots$$

T8 Zero-point energy. Look up experimental ZPE values in the NIST database[3] and add them to your best electronic energies. Optionally, compute harmonic vibrational frequencies with `PySCF` and compare.

T9 Corrections and discussion.

- Examine how your reaction energy changes when you include (i) geometry relaxation at every new level of theory, and (ii) the thermodynamic correction terms.

- Create a bar chart that displays for each electronic structure method the deviation of its thermodynamically corrected reaction energy from the literature value. And add a brief discussion that compares the methods and explains the sources of the observed errors.

- Use the literature value for the reaction free energy [4]

$$\Delta G_r^{298\,\text{K}} \approx 4.92 \text{ eV} \quad \text{for the water-splitting reaction}$$

Pseudocode 2 Basis–set convergence of the $2\,H_2 + O_2 \rightarrow 2\,H_2O$ reaction energy

---

1: **for** basis $\in$ {STO-3G, 3-21G, 6-31G, cc-pVDZ, cc-pVTZ, cc-pVQZ, cc-pV5Z} **do** $\triangleright$ — build the three molecules in this basis —
2:     set_basis(H_2, basis)
3:     set_basis(O_2, basis)
4:     set_basis(H_2O, basis) $\triangleright$ — SCF energies (Hartree) —
5:     $E_{H_2} \leftarrow$ run_scf(H_2, method)
6:     $E_{O_2} \leftarrow$ run_scf(O_2, method
7:     $E_{H_2O} \leftarrow$ run_scf(H_2O, method)
8:     $\Delta E_r \leftarrow 2E_{H_2O} - (2E_{H_2} + E_{O_2})$ $\triangleright$ — reaction energy (Hartree) —
9:     $\Delta E_{eV} \leftarrow \Delta E_{rxn} \times 27.211386$ $\triangleright$ — convert to eV if desired —
10:     Append $(n(\text{basis}), \Delta E_{eV})$ to list
11: **end for**

Report Guidelines

- Keep the final report approximately around 10 pages.

- Discuss your numerical results and interpret what they mean in the context of electrocatalytic water splitting.

- Include snippets of your code wherever it supports your results.

---

[3] https://cccbdb.nist.gov/

[4] Derived from the reverse of the Gibbs free energy of formation of liquid water, $\Delta G_f^\circ[H_2O(l)] = -237.18$ kJ mol^{-1} (NIST-JANAF Thermochemical Tables, 4th ed., 1998); https://janaf.nist.gov). Two moles of H_2O give $+474.36$ kJ mol^{-1}, which converts to $474.36/96.485 \approx +4.92$ eV, using 1 eV $= 96.485$ kJ mol^{-1}.