Script for the Experiment:

Introduction — Density Functional Theory (DFT) Calculations of Water Splitting on Gold

1 Introduction

This *in-silico* experiment uses density functional theory (DFT) to model the oxygen evolution (OER) and hydrogen evolution (HER) reactions on a gold surface. You will simulate the elementary reaction steps of both electrocatalytic processes on a slab model of gold (finite-thickness slice of a gold crystal), compute free energies for reaction intermediates, and determine activity descriptors to describe the catalytic activity in relation to catalyst performance. The focus of this laboratory experiment is on learning how to create physically meaningful surface models, correctly collect the numerical data, and interpret what these numbers tell us about catalytic behavior.

1.1 Why this experiment matters

1. Scientific and technological relevance

Water splitting $2H_2O \longrightarrow 2H_2 + O_2$ is central to sustainable energy technologies because it converts electrical energy into chemical fuel (hydrogen) that can be stored and transported. Improving the efficiency of water splitting devices (electrolyzers) depends on developing catalysts that lower the energetic barriers for both half-reactions (OER and HER) while remaining stable under operating conditions. Computational methods such as DFT give atomistic insight into how reaction intermediates bind and transform on surfaces. Calculating free energies for reaction intermediates on model surfaces is often used to rationalize experimental trends and guide the development of better catalysts. You will apply this approach in this laboratory experiment by modeling the OER and HER on the Au(111) surface to learn the application of descriptor-based analysis.

> ⓘ NOTE
>
> You may also model a different surface if this is agreed upon with the supervisors before the start of the experiment.

The OER is the oxidation process that happens at the anode of an electrolyzer:

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \tag{1}$$

The other half reaction, HER, corresponds to the reduction of protons to hydrogen:

$$2H^+ + 2e^- \longrightarrow H_2 \tag{2}$$

In electrolyzers, a major bottleneck is caused by the sluggish kinetics of the four-electron transfer OER. In practical applications, this implies that a higher overpotential must be applied for the OER than for the HER.

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2. Why gold is a useful model system

Gold (Au) is an excellent model catalyst for this model experiment using DFT:

- Well-characterized surfaces: Au(111), Au(100), and Au(110) are among the most studied surface facets. Therefore, literature values and experimental data exist for comparison, which helps validate computational choices in a lab course. Here you can compare the computational results with the experimental results of the E2 experiment (if your group did not study Au in this experiment, the data of a previous group will be provided). See Section 5 Evaluation of this Experiment for instructions on how to compare the results of the two experiments.

3. How the computational results connect to experiments

While DFT provides electronic energies and derived thermochemical quantities, the results can be mapped to experimentally measurable trends:

- Activity descriptor estimates from free-energy diagrams provide qualitative predictions of activity (this will be explained in the Section 7.0.1 From Free-Energy Changes to G_{max} the Activity Descriptor.

- Relative trends across adsorption sites or facets can explain facet-dependent activity, which are experimentally accessible using electrodes at the single-crystal level.

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2 Pre-Calculation preparation

1. Get the Repository

You can either: `git clone` or manually download and unpack this repository. Afterward, open the Windows Powershell, Command Prompt or VS Code and navigate to the repository directory. Create five empty folders (the names of these folders should contain no whitespace).

> ⓘ CAUTION
>
> If the repository is cloned to a sciebo folder, any files created during the calculation will be automatically synced to the students sciebo account.

2. Create a Python Environment

This experiment uses uv as the Python package and environment manager. To create and sync the virtual environment, run:

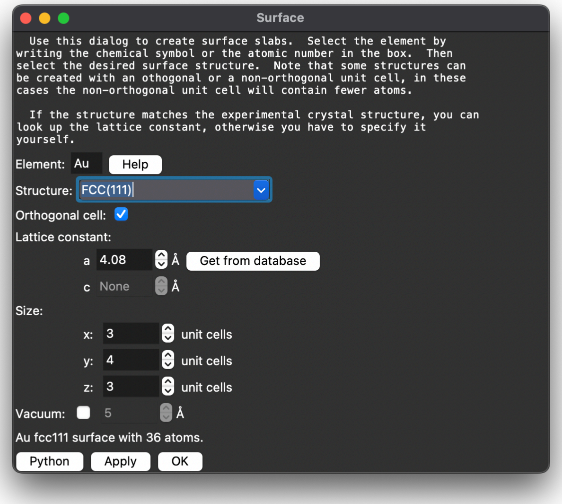
```bash
uv sync
```

3. Generate the atomic structure files

The Atomic Simulation Environment (ASE) is used for generating the structure files. In order to use the graphical user interface simply execute:

```bash
uv run ase gui
```

Navigate to the setup option and open the `Surface slab` window. Unless otherwise instructed, create a Au(111) surface slab with three atoms in the x direction, four in the y direction, and three in the z direction. Set no vacuum. The `Surface slab` window should now look similar to this:



Surface

  Use this dialog to create surface slabs. Select the element by writing the chemical symbol or the atomic number in the box. Then select the desired surface structure. Note that some structures can be created with an othogonal or a non-orthogonal unit cell, in these cases the non-orthogonal unit cell will contain fewer atoms.

  If the structure matches the experimental crystal structure, you can look up the lattice constant, otherwise you have to specify it yourself.

Element: Au

Structure: FCC(111)

Orthogonal cell: ☑

Lattice constant:

a 4.08 Å

c None Å

Size:

x: 3 unit cells

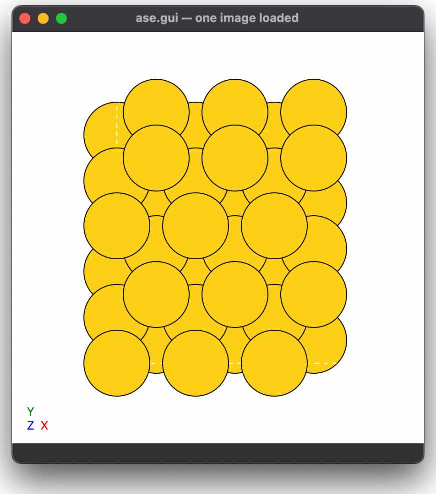
y: 4 unit cells

z: 3 unit cells

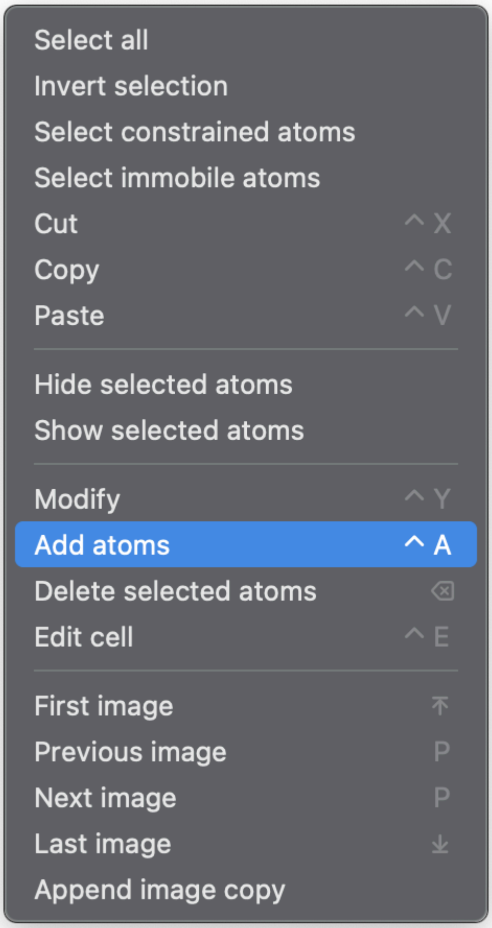
Vacuum: ☐ 5 Å

Au fcc111 surface with 36 atoms.

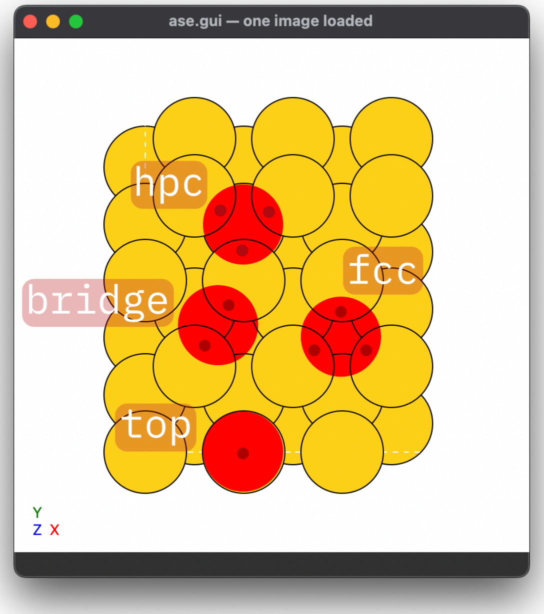
Once you have pressed ok, you should see the following gold slab:



Save this structure in one of the empty folders (the name should contain no whitespace and the file extension should be `.xyz`). Now model the different intermediates by adding the atoms to the cell via the `Add atoms` option.

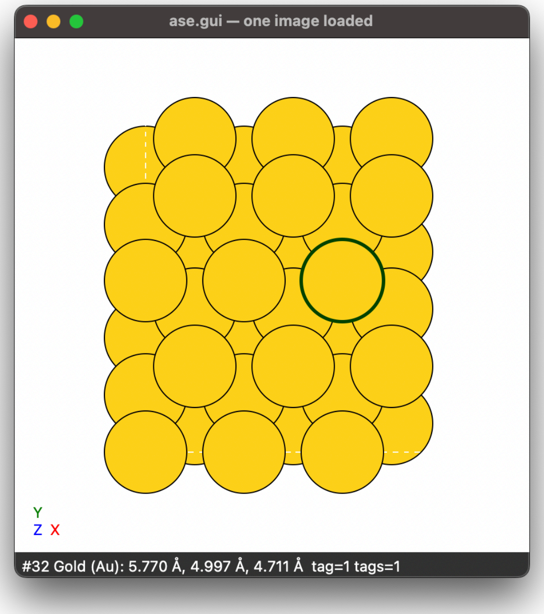


The Au(111) surface has four different adsorption sites. These are the top, hpc, bridge and fcc adsorption sites:



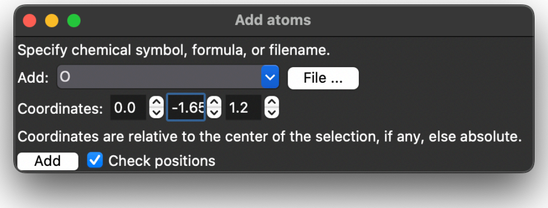
All atoms will be placed on the fcc adsorption site for this experiment.

You can select an atom in the cell by simply left-clicking on it. If you have selected an atom in the cell the window should look similar to this:



#32 Gold (Au): 5.770 Å, 4.997 Å, 4.711 Å tag=1 tags=1

If you now press the `Add atoms` option the following window should appear:



Specify chemical symbol, formula, or filename.

Add: O

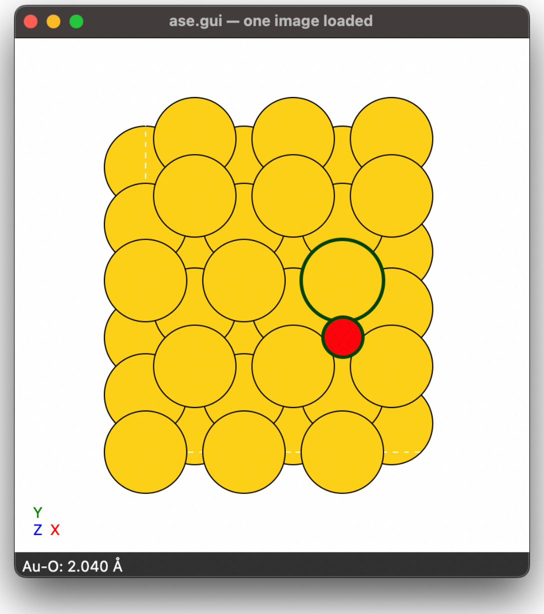
Coordinates: 0.0 -1.6 1.2

Coordinates are relative to the center of the selection, if any, else absolute.

☑ Check positions

Here you input which atom type to add and it's position. The position here is either absolute in the cell dimensions or relative to a selected atom in the cell. In order to place the adsorbates at the correct position select the upper Au atom of the fcc adsorption site. Here you add the first adsorbate shifted by −1.65 Å in the y-direction and 1.2 Å in the z-direction.

If you add an oxygen the cell should change to:



Au-O: 2.040 Å

Now you have a structure file for the gold slab with an oxygen adsorbate. In this experiment you will run the calculations for the mononuclear mechanism of the OER. This mechanism is given by the following elementary steps:

$$\begin{aligned} M + H_2O &\longrightarrow M - OH + (H^+ + e^-), \quad \Delta G_1 \\ M - OH &\longrightarrow M - O + (H^+ + e^-), \quad \Delta G_2 \\ M - O + H_2O &\longrightarrow M - OOH + (H^+ + e^-), \Delta G_3 \\ M - OOH &\longrightarrow M + O_2 + (H^+ + e^-), \quad \Delta G_4 \end{aligned} \tag{3}$$

The mechanism for the HER is given by the following elementary steps:

$$\begin{aligned} M + (H^+ + e^-) &\longrightarrow M - H, \ \Delta G_5 \\ M - H + (H^+ + e^-) &\longrightarrow M + H_2, \Delta G_6 \end{aligned} \tag{4}$$

In these equations, M stands for the active metal site (in our case the fcc position of a Au surface atom). In order to investigate the elementary reaction steps of these mechanisms, the free-energy changes of the different elementary steps must be calculated (as will be outlined in Section 7.0.1 From Free-Energy Changes to G_{max} the Activity Descriptor). As such, the free energies of the different adsorbates in the OER and HER have to be calculated. To be more precise, five different structures (the gold slab, gold slab + adsorbed H, gold slab + adsorbed OH, gold slab + adsorbed O and gold slab + adsorbed OOH) must be created. It was already shown how to prepare the gold slab and the gold slab + adsorbed O structure. For the respective bond lengths of all structures, you can make use of the following table:

Bond	length [Å]
Au-O	~2.1-2.3
Au-H	~1.8-1.9
O-O	~1.4-1.5
O-H	~0.95-1.0

(in case a different slab then the Au(111) is modeled, you can look up the approximate bond lengths of some metal adsorbates in this publication)

☞ HINT

The Au-OH and Au-OOH intermediates are angled.

Prepare the files for each of the required structures and save them in the five folders (in the end, each folder should contain exactly one `.xyz` file).

3 Running the Calculations

The calculations will be carried out inside Podman containers. All necessary software is installed. Follow the steps below carefully to set up your environment and run the simulation.

1. Set up Podman

First, initialize a Podman machine:

```bash
podman machine init
```

Because of the network configuration, an additional step must be completed **BEFORE** starting the machine:

```bash
podman machine set --user-mode-networking
```

Now you can start the machine:

```bash
podman machine start
```

2. Run the Calculation Script

Once the structure files are ready, execute the main script:

```bash
uv run execute-containers.py
```

4 Interpreting a CP2K run — concise guide

Below are short, practical steps to extract the DFT result from a CP2K output to calculate the Gibbs free-energy change ΔG of an elementary reaction step. CP2K is a quantum chemistry and solid-state physics software package.

4.1 Where to look in the output

1. **Top of the file:** run metadata (build, global input parameters).

```txt
DBCSR| CPU Multiplication driver                                           XSMM (U)
DBCSR| Multrec recursion limit                                              512 (U)
DBCSR| Multiplication stack size                                           1000 (D)
DBCSR| Maximum elements for images                                    UNLIMITED (U)
```

```
DBCSR| Multiplicative factor virtual images                                   1 (U)
DBCSR| Use multiplication densification                                       T (D)
DBCSR| Multiplication size stacks                                             3 (U)
DBCSR| Use memory pool for CPU allocation                                     F (U)
DBCSR| Number of 3D layers                                               SINGLE (U)
DBCSR| Use MPI memory allocation                                              F (U)
DBCSR| Use RMA algorithm                                                      F (U)
DBCSR| Use Communication thread                                               T (U)
DBCSR| Communication thread load                                             87 (D)
DBCSR| MPI: My process id                                                     0
DBCSR| MPI: Number of processes                                             400
DBCSR| OMP: Current number of threads                                         1
DBCSR| OMP: Max number of threads                                             1
DBCSR| Split modifier for TAS multiplication algorithm                  1.0E+00 (U)


 **** **** ******  **  PROGRAM STARTED AT               2024-11-08 16:12:57.134
***** ** ***  *** **   PROGRAM STARTED ON                              ndstd067
**    ****   ******    PROGRAM STARTED BY                               cbi587k
***** **    ** ** **   PROGRAM PROCESS ID                                 71329
 **** **  *******  **  PROGRAM STARTED IN /lustre/hpc_home/cbi587k/Project/Gold
                                          /CDFT/Relax/OH

CP2K| version string:                                       CP2K version 2024.1
```

```txt
CP2K| Input file name                                                    Au.inp

GLOBAL| Force Environment number                                              1
GLOBAL| Basis set file name                                        BASIS_MOLOPT
GLOBAL| Potential file name                                      GTH_POTENTIALS
GLOBAL| MM Potential file name                                     MM_POTENTIAL
GLOBAL| Coordinate file name                                   ./Coordinate.xyz
GLOBAL| Method name                                                        CP2K
GLOBAL| Project name                                       GeometryOptimization
GLOBAL| Run type                                                        GEO_OPT
GLOBAL| FFT library                                                       FFTW3
GLOBAL| Diagonalization library                                            ELPA
GLOBAL| DGEMM library                                                      BLAS
GLOBAL| Minimum number of eigenvectors for ELPA usage                        16
GLOBAL| Orthonormality check for eigenvectors                          DISABLED
GLOBAL| Matrix multiplication library                                     COSMA
GLOBAL| All-to-all communication in single precision                          F
GLOBAL| FFTs using library dependent lengths                                  F
GLOBAL| Grid backend                                                       AUTO
GLOBAL| Global print level                                               MEDIUM
GLOBAL| MPI I/O enabled                                                       T
GLOBAL| Total number of message passing processes                           400
GLOBAL| Number of threads for this process                                    1
GLOBAL| This output is from process                                           0
GLOBAL| Stack size for threads created by OpenMP (OMP_STACKSIZE)        default
GLOBAL| CPU model name                         Intel(R) Xeon(R) Platinum 8480+
GLOBAL| CPUID                                                              1003
```

2. **Input sections:** CP2K prints each input section under headings (e.g. `QUICKSTEP` for DFT) and derived quantities (number of basis functions, grids, etc.).

```
*******************************************************************************
*******************************************************************************
**                                                                           **
**     #####                         ##              ##                      **
**    ##   ##            ##          ##              ##                      **
**   ##     ##                       ##            ######                    **
**   ##     ##  ##   ##  ##   #####  ##  ##   ####   ##    #####    #####    **
**   ##     ##  ##   ##  ##  ##      ## ##   ##      ##   ##   ##  ##   ##   **
**   ##  ## ##  ##   ##  ##  ##      ####     ###    ##   ######   ######    **
**    ##  ###   ##   ##  ##  ##      ## ##      ##   ##   ##       ##        **
**     #######   #####   ##   #####  ##  ##  ####    ##    #####   ##        **
**           ##                                                    ##        **
**                                                                           **
**                                                ... make the atoms dance   **
**                                                                           **
**            Copyright (C) by CP2K developers group (2000-2024)             **
**                      J. Chem. Phys. 152, 194103 (2020)                    **
**                                                                           **
*******************************************************************************

DFT| Spin restricted Kohn-Sham (RKS) calculation                            RKS
DFT| Multiplicity                                                             1
DFT| Number of spin states                                                    1
DFT| Charge                                                                   0
DFT| Self-interaction correction (SIC)                                       NO
DFT| Cutoffs: density                                              1.000000E-10
DFT|          gradient                                             1.000000E-10
DFT|          tau                                                  1.000000E-10
DFT|          cutoff_smoothing_range                               0.000000E+00
DFT| XC density smoothing                                                  NONE
DFT| XC derivatives                                                          PW

FUNCTIONAL| PBE:
FUNCTIONAL| J.P.Perdew, K.Burke, M.Ernzerhof, Phys. Rev. Letter, vol. 77, n 18,
FUNCTIONAL|  pp. 3865-3868, (1996) {spin unpolarized}

vdW POTENTIAL|                                                   Pair Potential
vdW POTENTIAL|          DFT-D3 (Version 3.1)
vdW POTENTIAL|          Potential Form: S. Grimme et al, JCP 132: 154104 (2010)
vdW POTENTIAL|          Zero Damping
vdW POTENTIAL|          Cutoff Radius [Bohr]:                              20.00
vdW POTENTIAL|          s6 Scaling Factor:                                1.0000
vdW POTENTIAL|          sr6 Scaling Factor:                               1.2170
vdW POTENTIAL|          s8 Scaling Factor:                                0.7220
vdW POTENTIAL|          Cutoff for CN calculation:                    0.1000E-05
```

3. **SCF report:** the self-consistent Kohn-Sham loop appears later — it contains the convergence history and final electronic densities/energies.

```txt
*******************************************************************************
***                    GEOMETRY OPTIMIZATION COMPLETED                      ***
*******************************************************************************

                   Reevaluating energy at the minimum

Number of electrons:                                                       1987
Number of occupied orbitals:                                               1011
Number of molecular orbitals:                                              1294

Number of orbital functions:                                               6143
Number of independent orbital functions:                                   6143

Extrapolation method: PS Nth order
Extrapolation order:  3
```

```txt
SCF WAVEFUNCTION OPTIMIZATION

Step     Update method      Time    Convergence         Total energy    Change
------------------------------------------------------------------------------
   1 Broy./Diag. 0.10E+00    1.4     0.00053928     -6004.5947720300 -6.00E+03
   2 Broy./Diag. 0.10E+00    1.6     0.00000754     -6004.5947200750  5.20E-05
   3 Broy./Diag. 0.10E+00    1.6     0.00005164     -6004.5948335964 -1.14E-04
   4 Broy./Diag. 0.10E+00    1.7     0.00000476     -6004.5942215820  6.12E-04
   5 Broy./Diag. 0.10E+00    1.7     0.00001093     -6004.5945176155 -2.96E-04
   6 Broy./Diag. 0.10E+00    1.6     0.00000418     -6004.5949457514 -4.28E-04
   7 Broy./Diag. 0.10E+00    1.7     0.00000643     -6004.5950120544 -6.63E-05
   8 Broy./Diag. 0.10E+00    1.7     0.00000855     -6004.5949311804  8.09E-05
   9 Broy./Diag. 0.10E+00    1.6     0.00000235     -6004.5948145219  1.17E-04
  10 Broy./Diag. 0.10E+00    1.6     0.00000365     -6004.5947540640  6.05E-05
  11 Broy./Diag. 0.10E+00    1.7     0.00000129     -6004.5947248587  2.92E-05
  12 Broy./Diag. 0.10E+00    1.6     0.00000259     -6004.5947550763 -3.02E-05
  13 Broy./Diag. 0.10E+00    1.6     0.00000056     -6004.5947928891 -3.78E-05

*** SCF run converged in    13 steps ***


Electronic density on regular grids:      -1986.9999999999        0.0000000001
Core density on regular grids:             1986.9999999967       -0.0000000033
Total charge density on r-space grids:       -0.0000000032
Total charge density g-space grids:          -0.0000000032

Overlap energy of the core charge distribution:               0.00000073164326
Self energy of the core charge distribution:             -10456.53763838543819
Core Hamiltonian energy:                                   3333.54401951931413
Hartree energy:                                            2069.37810653878751
Exchange-correlation energy:                               -947.58622348190420
Dispersion energy:                                           -3.38395793185860
Electronic entropic energy:                                  -0.00909986553722
Fermi energy:                                                -0.02069230352853

Total energy:                                             -6004.59479288911461
```

All this data was taken from the `example_output.out` file.

4.2 How to recognize SCF convergence

- CP2K prints a message that the self-consistent field (SCF) has converged. After that you will see the final energy.

4.3 Where to find the DFT energy

- Search for the last line containing:

```
Total energy:
```

- The numeric value after **Total energy:** is the final DFT electronic energy for the structure (units: **eV** if you did not change the script). In the `example_output.out` file, the total energy is `-6004.59479288911461`.

4.4 Approximating Gibbs free energy

- For this experiment, we approximate the Gibbs free energy by using the DFT energy:

$$G \approx E^{\mathrm{DFT}} \tag{5}$$

To be more precise, this approximation neglects zero-point energy and entropy corrections, which formally need to be considered when deriving Gibbs free energies.

To determine the Gibbs free-energy changes (ΔG), we set up reaction equations of the elementary steps and reference those with respect to the free energies of H_2O and H_2, which serve as reference species in the reaction equations. This is further explained in Section 7.0.1 From Free-Energy Changes to G_{max} the Activity Descriptor. Please use the provided reference values for the two molecules:

$$\begin{aligned} G(H_2O) &= -14\ \mathrm{eV} \\ G(H_2) &= -7\ \mathrm{eV} \end{aligned} \tag{6}$$

5 Evaluation of this Experiment

In order to ensure that the lab report is comprehensible , it is essential to include the most significant details of the computational setup. These are the software you used, the functional you used for the calculation and whether or not all structured were geometrically optimized.

For this experiment you will first determine the free-energy changes of all the elementary steps for both the OER and the HER, as will be outlined below. Next you must determine for which applied electrode potential you want to analyze your data. The electrode potential you need to investigate are determined by the experimental setup you employed in the E2 experiment (or the setup outlined in the report that will be issued if you did not investigate Au in that experiment). First determine the potential window in which you measured the cyclic voltammogram. You will evaluate this experiment using the highest and lowest electrode potentials you used in the Au voltammogram (the highest potential refers to the OER, while the lowest on is for the HER) and for the equilibrium potential of both reactions. For both applied electrode potentials determine the G_{max} value and plot the free-energy diagram for the electrode potentials corresponding to the experimental setup. Keep in mind that G_{max} represents the thermodynamic part of the activation barrier using an energetic span model: a smaller G_{max} corresponds to a higher electrocatalytic activity of the catalyst. First, compare the results of the two different electrode potentials. At which electrode potential is Au more active, what are the limiting spans in the G_{max} approach, and can you explain these results? Make a qualitative comparison with the experimental observations by answering the following questions: Did you see oxygen/hydrogen production at the equilibrium potentials on the Au electrode, do the calculations predict high activity at these electrode potentials, and what about the other electrode potentials used in the cyclic voltammetry? (In this context, you may assume that $G_{\mathrm{max}}(U) \geq 0.4$ eV serves as the activity cutoff; i.e. any value above 0.4 eV corresponds to an inactive catalyst)

6 Introduction to DFT

DFT is a quantum-mechanical framework widely used in physics and chemistry to compute the properties of atoms, molecules, and materials. In principle, one would solve the many-electron Schrödinger equation ($\hat{H}\Psi = E\Psi$) for the electron wavefunction Ψ, but this is intractable for more than a few electrons. DFT offers an alternative: using the Hohenberg-Kohn theory, the ground-state energy and properties of a system are uniquely determined by the electron density $\rho(r)$ - a function of only 3 spatial coordinates - rather than the full many-body wavefunction. Here r is the position vector (x, y, z) specifying a point in real space. This density-based approach drastically reduces the complexity (wavefunctions depend on 3 N variables with N indicating the total number of electrons in the system, whereas the density depends on only 3 variables), making first-principles calculations of real materials feasible on modern computers.

The core idea: *All properties of a quantum system can be determined from its electron density, $n(\mathbf{r})$.*

6.1 Energy Functionals and the Hohenberg-Kohn Theorems

A **functional** is a “function of a function”. In DFT the key object is the energy functional $E[n]$, which assigns a number (the total energy) to each electron density $\rho(r)$. The Hohenberg-Kohn theorems guarantee that the true ground-state density ρ_0 minimizes this energy functional and that $E\left[n_0\right]$ gives the exact ground-state energy. In practice, the total energy is expressed by the respective contributions of the different elementary particles:

$$E[n] = T_s[n] + E_{\text{nuc-el}}[n] + E_H[n] + E_{\text{XC}}[n] \tag{7}$$

Here, T_s is the kinetic energy of a fictitious non-interacting system of electrons, $E_{\text{nuc-el}}$ is the (known) electron-nuclear attraction, E_H is the classical Hartree (electron-electron repulsion) energy, and E_{XC} is the **exchange-correlation** functional. In other words, DFT replaces the complicated many-electron interactions by an effective problem of non-interacting electrons (the Kohn-Sham scheme), plus a single functional $E_{\text{XC}}[n]$ that captures all the remaining quantum exchange and correlation effects. In Kohn-Sham DFT, one solves a set of one-electron “orbitals” self-consistently until the resulting density $\rho(r)$ reproduces the true interacting density.

However, the unknown part of DFT is the form of the exchange-correlation functional $E_{\text{XC}[n]}$. The DFT result is highly sensitive to the choice of the exchange-correlation functional due to the intrinsic errors associated with the Kohn-Sham equation. Many approximations exist. The simplest is the Local Density Approximation (LDA), but most modern applications use **Generalized Gradient Approximations (GGA)**, which include the gradient of $\rho(r)$. One of the most common GGA functionals is **PBE** (Perdew-Burke-Ernzerhof). PBE uses no empirical fitting (it obeys known physical constraints) and works reasonably well for a wide range of systems. In practice, PBE often gives a good balance of accuracy and speed the investigation of chemical processes and materials.

6.2 Dispersion Corrections: DFT-D3

One limitation of standard DFT functionals (even PBE) is that they often neglect **long-range van der Waals (dispersion)** forces - the weak attractive interactions (London forces) between well-separated electrons. Semi-local DFT functionals do not include these naturally. To fix this, an empirical dispersion term is added to the DFT calculations. A popular scheme is Grimme’s **DFT-D3** correction. In DFT-D3, one adds a pairwise potential

$$E_{\mathrm{disp}} = -\sum_{i<j}\left(\frac{C_{6,ij}}{r_{ij}^{6}} + \frac{C_{8,ij}}{r_{ij}^{8}} + \dots\right) f_{\mathrm{damp}}\left(r_{ij}\right) \tag{8}$$

where r_{ij} is the distance between atoms i and j, $C_{6,ij}$ and $C_{8,ij}$ are dispersion coefficients (fitted for each atom pair), and f_{damp} is a damping function. The $-\frac{C_6}{r^6}$ and $-\frac{C_8}{r^8}$ forms captures the missing attraction at long range. Unlike other corrections, Grimme's D3 approach can even include a **three-body** term (the Axilrod-Teller-Muto contribution) to account for cooperative dispersion among triples of atoms. The result is a corrected energy $E_{\mathrm{DFT\text{-}D3}} = E_{\mathrm{KS\text{-}DFT}} + E_{\mathrm{disp}}$, which greatly improves accuracy for molecules and materials where dispersion is important (e.g., stacked organic molecules, biomolecules, or layered materials).

6.3 Why DFT is Useful

DFT has become a workhorse of computational science because it strikes a good balance between accuracy and cost. More accurate wavefunction methods (coupled-cluster, MP2, etc.) are often too slow for large systems, whereas simpler molecular mechanics lack quantum details and thus accuracy. DFT provides a true quantum-mechanical treatment of electrons at costs that scales reasonably with system size. In catalysis research, DFT calculations allows a wide range of features and properties to be tackled, such as the estimation of adsorption free energies, activation energy barriers, and information on the electronic structure. In other words, DFT can predict how strongly a reactant binds to a surface, or what the energy barrier of a reaction step is - information critical for designing better catalysts.

6.4 Limitations of DFT

DFT often struggles with systems where electrons are strongly correlated (such as certain transition-metal compounds or bond-breaking situations). It is also inherently a ground-state method, so the determination of excited electronic states would require advanced approaches that go beyond the introduction in this experiment. As a result, more expensive wavefunction-based methods (like coupled-cluster) are used for very accurate results in these challenging cases. In short, DFT trades some accuracy for efficiency by using density-based approximations, although students should recap its limitations in difficult systems.

Further reading:

- https://www.numberanalytics.com/blog/density-functional-theory-electrochemistry-guide

7 From Free-Energy Changes to $G_{\max}$ the Activity Descriptor

7.0.1 Free-energy change of an elementary reaction step

Considering stoichiometry (products positive, reactants negative), the Gibbs free-energy change of chemical reaction is given by the following relation:

$$\Delta G = \sum_{\text{products}} v_i G_i - \sum_{\text{reactants}} v_j G_j \tag{9}$$

If the reactant stoichiometric coefficients *v* are taken as negative values, this expression simplifies to:

$$\Delta G = \sum_i v_i G_i. \tag{10}$$

For example, the free-energy change for $A + B \longrightarrow C + D$ is:

$$\Delta G = G_C + G_D - G_A - G_B. \tag{11}$$

CHE approximation for proton-electron transfers. In the computational hydrogen electrode (CHE) framework a proton-electron pair is referenced to molecular hydrogen:

$$G(H^+) + G(e^-) \approx G\left(\frac{1}{2}H_2\right) \tag{12}$$

and each proton-electron transfer shifts the energy by eU (sign convention used here: + for cathodic transfers, − for anodic transfers). This means that for electrochemical reactions containing a proton electron pair, the energy can be approximated by using the free-energy of gaseous hydrogen. Taking for example the following elementary steps:

$$\mathrm{M + H_2O \longrightarrow M - OH + H^+ + e^-} \tag{13}$$

and using the CHE approach:

$$\mathrm{M + H_2O \longrightarrow M - OH + \frac{1}{2}H_2} \tag{14}$$

, the free-energy change ΔG_1^0 of this elementary step reads:

$$\Delta G_1^0 = G_{\mathrm{M-OH}} + \frac{1}{2}G_{\mathrm{H_2}} - G_{\mathrm{M}} - G_{\mathrm{H_2O}} \tag{15}$$

Since this elementary step is the first of the OER mechanism (see below), the corresponding free-energy change is typically referred to as ΔG_1. Currently this free-energy change is potential independent (or more accurately, it is the free-energy change for zero applied electrode potential). In order to incorporate the potential dependence in the free-energy change, we must first determine if the reaction is anodic or cathodic. As this is an oxidation reaction, it is an anodic process. Next we must determine the number of electrons transferred in this step, which is 1. Therefore, the potential-dependent $\Delta G_1(U)$ value reads:

$$\Delta G_1(U) = \Delta G_1^0 - 1 \cdot eU \tag{16}$$

In this equation, the minus sign stems from the fact that the reaction in Equation 13 corresponds to an anodic process. U is the applied potential on the reversible hydrogen electrode (RHE) scale, and e denotes the elementary charge (this constant simply converts volt to electronvolt in a 1:1 ratio).

While we have explained the determination of the $\Delta G_1(U)$ value, all other free-energy changes of the mononuclear OER mechanism are determined using the same approach. This knowledge is important to estimate the electrocatalytic activity through thermodynamic considerations, as explained below.

7.1 Free-Energy Spans and the G_{max} descriptor

DFT calculations can be used to predict the activity trends of catalysts, which is achieved through a so-called descriptor-based analysis. One of the descriptors used in the determination of trends for electrocatalytic systems is the $G_{\mathrm{max}}(U)$ descriptor, which is based on the application of a free-energy span model in dependence of the applied electrode potential, U, which is the driving force for the catalytic process. This approach generalizes the energetic span model of homogeneous catalysis to electrochemical reactions. In practice, one computes the free-energy changes of all elementary reaction steps as a function of applied electrode potential (see above). This knowledge enables expressing the potential-dependent free-energies of all reaction intermediates (RIs), based on which the largest free-energy span between any two intermediate states – $G_{\mathrm{max}}(U)$ – is extracted. We show this transformation here for the intermediate states in the OER:

$$\begin{gathered}
\Delta G_{\mathrm{M}}(U) = O \\
\Delta G_{\mathrm{M-\,OH}}(U) = \Delta G_1^0 - 1eU \\
\Delta G_{\mathrm{M-O}}(U) = \Delta G_1^0 + \Delta G_2^0 - 2eU \\
\Delta G_{\mathrm{M-\,OOH}}(U) = \Delta G_1^0 + \Delta G_2^0 + \Delta G_3^0 - 3eU \\
\Delta G_{\mathrm{M+O_2}}(U) = 4.92 - 4eU
\end{gathered} \tag{17}$$

In order to calculate the $G_{\mathrm{max}}(U)$ descriptor, we have to identify the largest free-energy span in the catalytic cycle. Given that the OER consists of four steps, there are ten spans in total. $G_{\mathrm{max}}(U)$ can be calculated as follows:

$$
\begin{gathered}
G_{\mathrm{max}} = \max\Big(\Delta G_{\mathrm{M-OH}}(U) - \Delta G_{\mathrm{M}}(U), \\
\Delta G_{\mathrm{M-O}}(U) - \Delta G_{\mathrm{M}}(U), \\
\Delta G_{\mathrm{M-OOH}}(U) - \Delta G_{\mathrm{M}}(U), \\
\Delta G_{\mathrm{M+O_2}}(U) - \Delta G_{\mathrm{M}}(U), \\
\Delta G_{\mathrm{M-O}}(U) - \Delta G_{\mathrm{M-OH}}(U), \\
\Delta G_{\mathrm{M-OOH}}(U) - \Delta G_{\mathrm{M-OH}}(U), \\
\Delta G_{\mathrm{M+O_2}}(U) - \Delta G_{\mathrm{M-OH}}(U), \\
\Delta G_{\mathrm{M-OOH}}(U) - \Delta G_{\mathrm{M-O}}(U), \\
\Delta G_{\mathrm{M+O_2}}(U) - \Delta G_{\mathrm{M-O}}(U), \\
\Delta G_{\mathrm{M+O_2}}(U) - \Delta G_{\mathrm{M-OOH}}(U)\Big)
\end{gathered}
\tag{18}
$$

$G_{\mathrm{max}}(U)$ thereby approximates the rate-determining transition state under applied bias by relying on thermodynamics considerations. In other words, $G_{\mathrm{max}}(U)$ quantifies the most energetically demanding segment of a catalytic cycle under electrochemical conditions.

One example of the G_{max} descriptor together with the corresponding free free-energy span can be seen in the following figure. Note that the energetics of the transition states is arbitrarily chosen.

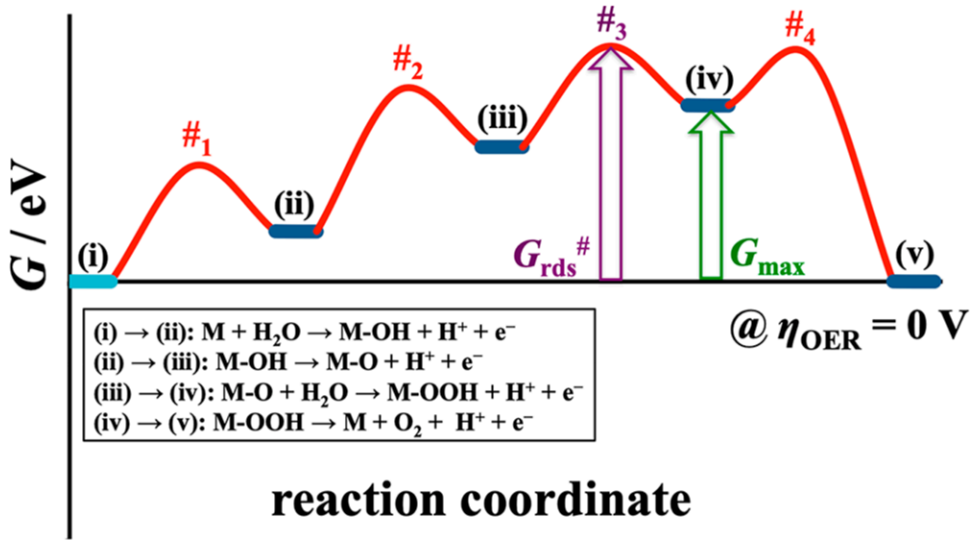


Figure 1: The free energy span with the computed G_{max} descriptor. The $\#_i$ stand for the various transition states. $G^{\#}_{\mathrm{rds}}$ is the free energy change of the rate-determining transition state. Figure adopted from reference Exner.

7.2 Examples

7.2.1 Example 1: OER (4-electron cycle)

Consider OER on an active metal site (M) such as the fcc position on Au(111):

$$
\begin{aligned}
\mathrm{M} + \mathrm{H_2O} &\longrightarrow \mathrm{M-OH} + (\mathrm{H^+} + \mathrm{e^-}), \quad \Delta G_1 \\
\mathrm{M-OH} &\longrightarrow \mathrm{M-O} + (\mathrm{H^+} + \mathrm{e^-}), \quad \Delta G_2 \\
\mathrm{M-O} + \mathrm{H_2O} &\longrightarrow \mathrm{M-OOH} + (\mathrm{H^+} + \mathrm{e^-}), \Delta G_3 \\
\mathrm{M-OOH} &\longrightarrow \mathrm{M} + \mathrm{O_2} + (\mathrm{H^+} + \mathrm{e^-}), \quad \Delta G_4
\end{aligned}
\tag{19}
$$

with arbitrarily chosen free-energy changes:

- $\Delta G_1 = 1.40$ eV (calculated with: $G_{\mathrm{M-OH}} + \frac{1}{2}G_{\mathrm{H_2}} - G_{\mathrm{M}} - G_{\mathrm{H_2O}}$)
- $\Delta G_2 = 1.60$ eV (calculated with: $G_{\mathrm{M-O}} + \frac{1}{2}G_{\mathrm{H_2}} - G_{\mathrm{M-OH}}$)
- $\Delta G_3 = 1.20$ eV (calculated with: $G_{\mathrm{M-OOH}} + \frac{1}{2}G_{\mathrm{H_2}} - G_{\mathrm{M-O}} - G_{\mathrm{H_2O}}$)
- $\Delta G_4 = 4.92 - \left(\Delta G_1 + \Delta G_2 + \Delta G_3\right) = 0.72$ eV

The free-energies of the different intermediates at zero applied electrode potential are:

- $\Delta G_{\mathrm{M}} = 0$ eV
- $\Delta G_{\mathrm{M-OH}} = \Delta G_1 = 1.40$ eV
- $\Delta G_{\mathrm{M-O}} = \Delta G_1 + \Delta G_2 = 3.00$ eV
- $\Delta G_{\mathrm{M-OOH}} = \Delta G_1 + \Delta G_2 + \Delta G_3 = 4.20$ eV
- $\Delta G_{\mathrm{M+O_2}} = \Delta G_1 + \Delta G_2 + \Delta G_3 + \Delta G_4 = 4.92$ eV

By applying an overpotential of η=0.3 V with respect to the OER equilibrium potential (i.e., $U = 1.53$ V vs RHE), the free-energy of each $\mathrm{H^+/e^-}$ step is reduced by -1.53 eV. Therefore, we obtain:

- $\Delta G_{\mathrm{M+H_2O}}(U) = 0$ eV (reference)
- $\Delta G_{\mathrm{M-OH}}(U) = 1.4 - 1.53 = -0.13$ eV
- $\Delta G_{\mathrm{M-O}}(U) = 3.0 - 2 \cdot 1.53 = -0.06$ eV (two electrons transferred to reach *OH)
- $\Delta G_{\mathrm{M-OOH}}(U) = 4.2 - 3 \cdot 1.53 = -0.39$ eV (three electrons transferred to reach *O)
- $\Delta G_{\mathrm{M+O_2}}(U) = 4.92 - 4 \cdot 1.53 = -1.2$ eV (four electrons transferred to reach *OOH)

Identify the largest upwards span (cf. Figure 2 for visualization): here, the M-OH to M-O transition is the only positive span when evaluating the energetics based on equation (18):

- M-OH → M-O: 0.07 eV

Therefore $G_{\mathrm{max}}(U = 1.53V)$ amounts to 0.07 eV. This span corresponds to the formation of $\mathrm{M-O}$ based on $\mathrm{M-OH}$. While the $G_{\mathrm{max}}(U)$ descriptor identifies the largest thermodynamic free-energy span, it has shown to scale with the kinetics, and thus one could approximate that the rate-determining step (RDS) might be given by $\mathrm{M-OH} \longrightarrow \mathrm{M-O}$ as well.

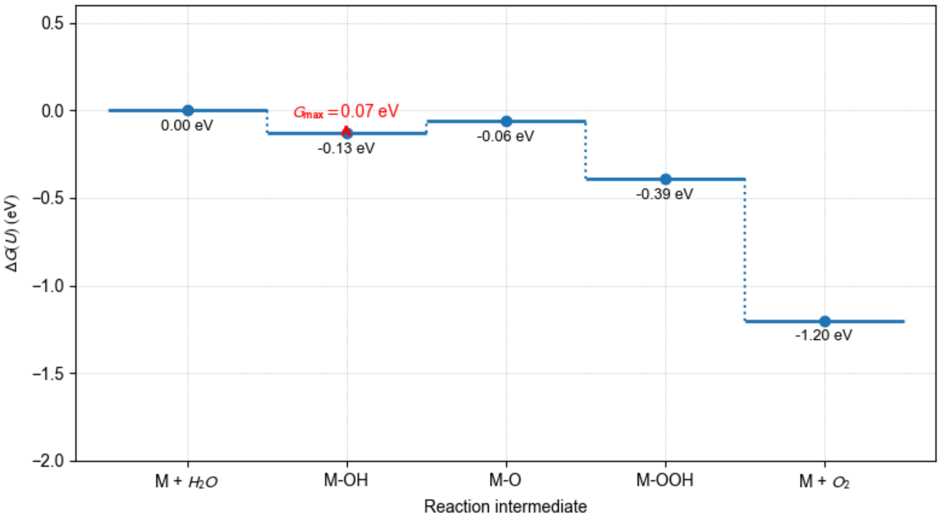


Figure 2: The OER free energy span with the computed G_{max} descriptor at U = 1.53 V vs RHE.

7.2.2 Example 2: HER (2-electron cycle)

For the hydrogen evolution reaction, consider a simple two-step Volmer-Heyrovsky mechanism on a metal (M) surface:

$$\begin{aligned} \mathrm{M} + (\mathrm{H}^+ + \mathrm{e}^-) &\longrightarrow \mathrm{M-H},\ \Delta G_5 \\ \mathrm{M-H} + (\mathrm{H}^+ + \mathrm{e}^-) &\longrightarrow \mathrm{M} + \mathrm{H}_2, \Delta G_6 \end{aligned} \tag{20}$$

with:

- $\Delta G_5 = 0.4$ eV (bare surface)
- $\Delta G_6 = 0 - \Delta G_5 = -0.4$ eV (surface with one H)

At equilibrium (0 V vs RHE) the spans are:

- $\mathrm{M} \longrightarrow \mathrm{M-H}$: +0.4 eV
- $\mathrm{M-H} \longrightarrow \mathrm{M} + \mathrm{H}_2$: −0.4 eV (not uphill)
- $\mathrm{M} \longrightarrow \mathrm{M} + \mathrm{H}_2$: 0 eV

The largest uphill span is +0.4 eV (M→M-H). Thus $G_{\mathrm{max}}(U = 0V) = 0.4$ eV. In this case, the span corresponds to the binding free energy of hydrogen.

Further reading:

- Exner

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8 Pre-Experiment Test

Here are some points relevant for the pre-experiment test

- Density functional theory (DFT) and dispersion correction
- Computational hydrogen electrode (CHE)
- Slab model and periodic boundary conditions
- How to read a free-energy diagram
- Mononuclear OER mechanism
- HER mechanism (Volmer, Heyrovsky steps)
- Bond distances between Au, O, H and any combination thereof
- Adsorption sites on Au(111)
- Electrolyzer