

National Supercomputing Mission Workshop on Computational Design of Electrocatalyst (CDE-2024)

**Module 2: ORR Free energy and Predictive Model Equation
(19th February 2024)**

Tutor: Prof. Ranjit Thapa

Contact: ranjit.t@srmmap.edu.in, sourav_ghosh@srmmap.edu.in

Exercise 1: Free energy calculations and plotting of Oxygen Reduction Reaction (ORR).

Exercise 2: Obtaining Electronic descriptors from density of states (DOS) for sp_2 carbon catalyst.

Exercise 3: Construction of predictive model equation

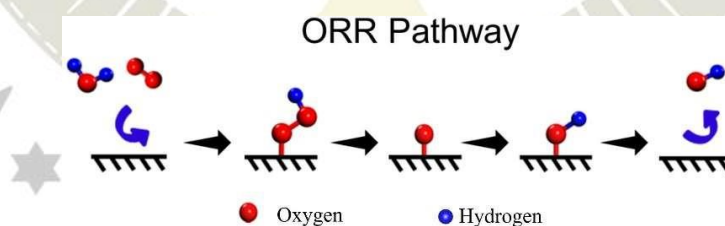
Exercise 1:

ORR Equation:

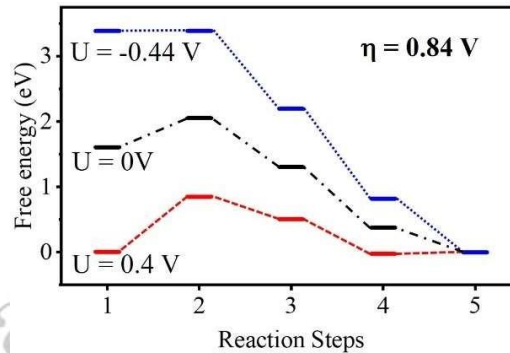
The reaction steps in alkaline medium are given by,



* Represents active site on the catalyst. Key reaction intermediates = OOH, O and OH.



Schematic of the ORR reaction steps.



Typical free energy plot for ORR reaction under different potentials.

Free energy profile:

The Gibbs free energy ‘G’ for a reaction is calculated using the formula,

$$G = E + \text{ZPE} - TS - neU + G_{\text{pH}} + G_{\text{field}}$$

Effect of applied bias: $-eU$ (Electrode potential), Effect of pH: $G_{\text{pH}} = k_B T \ln 10 \times \text{pH}$ and effect of G_{field} is small and negligible.

Here ‘E’ is the total energy obtained from DFT calculations (Enthalpy).

‘ZPE’ is the zero point energy contribution.

‘S’ is the entropic contribution. ‘T’ is the temperature.

(Both ZPE and TS can be calculated from the vibrational frequencies obtained from DFT calculations)

Note: ZPE and TS of small adsorbed molecules/atoms and surface are small and thus negligible.

To calculate the free energy profile for ORR reaction, four calculations are to be done.

i) Surface **ii)** OOH adsorption on active site (OOH*) **iii)** O adsorption on active site (O*) and **iv)** OH adsorption on active site (OH*).

1. With the provided user id, login to the server following the procedure given under “**How to access the server:**” from Day-1 and copy the folder “**day2**” to your respective folder using ‘cp -dr’ command.

Note: user_ID will be the ID which you used for Day-1 hands on session.

2. Go to the copied folder and run the calculation for the surface using the command

```
mpirun -np 4 pw.x -i surrelax.in | tee surrelax.out &
```

3. Likewise, run the calculations for OOH*, O* and OH* one by one.

```
mpirun -np 4 pw.x -i oohrelax.in | tee oohrelax.out &
```

```
mpirun -np 4 pw.x -i orelax.in | tee orelax.out &
```

```
mpirun -np 4 pw.x -i ohrelax.in | tee ohrelax.out &
```

4. Get the total energy of the four calculations from the output file using **vi** command.

Now we have four DFT total energies from which the Free energy profile can be constructed.

i) E_{SUR} , ii) E_{OOH} , iii) E_O and iv) E_{OH}

The free energies of the free molecules i.e. H_2O , O_2 and OH are calculated from the following relations. The reference molecules from which other energies calculated are H_2O and H_2 .

$$G_{H_2O(l)} = G_{H_2O(l)} + RT \ln\left(\frac{p}{p_0}\right) \quad T = 298.15 \text{ K}$$

$$G_{O_2(g)} = 2G_{H_2O(l)} - 2G_{H_2} + 4.92 \text{ eV} \quad p = 0.035 \text{ bar}$$

$$G_{OH^-} = G_{H_2O(l)} - 2G_{H^-} \quad p_0 = 1 \text{ bar}$$

$$G_{H^-} = \frac{1}{2} G_{H_2} - k_B T \ln 10 \times \text{pH}$$

The values are given below in the table

G_{H_2O}	-14.393 eV
G_{OH}	-10.114 eV
G_{O_2}	-10.066 eV

O_2 free energy is derived from free energy of $H_2O(l)$ and H_2 , and corrected for the standard potential.

5. Use the DFT calculated total energies (catalyst and adsorbed intermediates) and free energies of the free molecules (G_{H_2O} , G_{O_2} and G_{OH}) in equation 1 to 5 to get the free energies of each step.

Use the following energies $E_{SUR} = -459.534 \text{ eV}$; $E_{OOH^*} = -473.128 \text{ eV}$; $E_{O^*} = -465.879 \text{ eV}$;
 $E_{OH^*} = -469.706 \text{ eV}$

$$G_1 = E_{SUR} + O_2 + 2H_2O = -459.534 + (-10.066) + 2(-14.393) = -498.38 \text{ eV}$$

$$G_2 = OOH^* + OH^- + H_2O = -473.128 + (-10.114) + (-14.393) = -497.63 \text{ eV}$$

$$G_3 = O^* + H_2O + 2OH^- = -465.879 + (-14.393) + 2(-10.114) = -500.50 \text{ eV}$$

$$G_4 = OH^* + 3OH^- = -469.706 + 3(-10.114) = -500.04 \text{ eV}$$

$$G_5 = E_{SUR} + 4OH^- = -459.534 + 4(-10.114) = -499.99 \text{ eV}$$

6. Now calculate ΔG_1 , ΔG_2 , ΔG_3 , ΔG_4 , ΔG_5 under zero applied potential i.e. $U = 0V$.

Change in Gibbs free energy is given by $\Delta G = \Delta E + \Delta ZPE - T\Delta S - neU$

$$\Delta G_1 = G_1 - G_5 = 1.60 \text{ eV}$$

$$\Delta G_2 = G_2 - G_5 = 2.35 \text{ eV}$$

$$\Delta G_3 = G_3 - G_5 = -0.51 \text{ eV}$$

$$\Delta G_4 = G_4 - G_5 = -0.05 \text{ eV}$$

$$\Delta G_5 = G_5 - G_5 = 0 \text{ eV}$$

Note: Reference is G_5 because it is not affected by the applied bias as there is no electron involved at that step.

7. Calculate ΔG_1 , ΔG_2 , ΔG_3 , ΔG_4 , ΔG_5 at $U = 0.4$ V (equilibrium potential for ORR in alkaline medium).

$$\Delta G_1 = (G_1 - G_5) - 4(0.4) = 0.00 \text{ eV}$$

$$\Delta G_2 = (G_2 - G_5) - 3(0.4) = 1.15 \text{ eV}$$

$$\Delta G_3 = (G_3 - G_5) - 2(0.4) = -1.31 \text{ eV}$$

$$\Delta G_4 = (G_4 - G_5) - 1(0.4) = -0.45 \text{ eV}$$

$$\Delta G_5 = (G_5 - G_5) = 0.00 \text{ eV}$$

The step having the highest positive energy difference is the potential determining step (PDS) and the overpotential (η) is calculated from this step. Overpotential = $\Delta G_{\text{max}}/e = 1.15 \text{ eV}/e = \mathbf{1.15 \text{ V}}$

8. Calculate ΔG_1 , ΔG_2 , ΔG_3 , ΔG_4 , ΔG_5 at $U =$ onset potential, where onset potential is given by this equation.

At, $U = -0.75$ V (onset potential = Equilibrium potential - Overpotential)

$$\Delta G_1 = (G_1 - G_5) - 4(-0.75) = 4.62 \text{ eV}$$

$$\Delta G_2 = (G_2 - G_5) - 3(-0.75) = 4.62 \text{ eV}$$

$$\Delta G_3 = (G_3 - G_5) - 2(-0.75) = 1.00 \text{ eV}$$

$$\Delta G_4 = (G_4 - G_5) - 1(-0.75) = 0.69 \text{ eV}$$

$$\Delta G_5 = (G_5 - G_5) = 0.00 \text{ eV}$$

9. This procedure can be done in various tools such as excel, python, origin etc. Now we will carry out in the excel sheet provided in the “workshop-CDE2024” folder in the desktop “**ORR Free energy**”

Paste the E_{SUR} , E_{OOH} , E_{O} and E_{OH} values in the corresponding cell in the sheet.

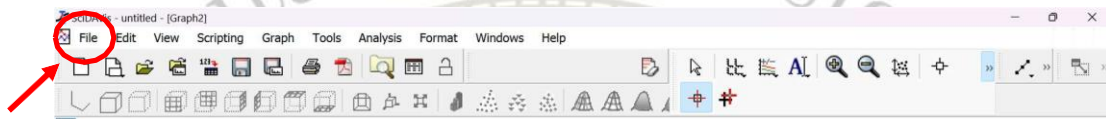
E_{SUR}	
E_{OOH}	
E_{O}	
E_{OH}	

Exercise 2:

How to Plot Density of States (DOS) and find descriptors:

1. Open folder “workshop-CDE2024” in desktop and then open “Day-2” folder. It will have DOS19.dat file. This is the atom projected density of states (PDOS) of the active site.
2. Open SciDAVis in the taskbar.

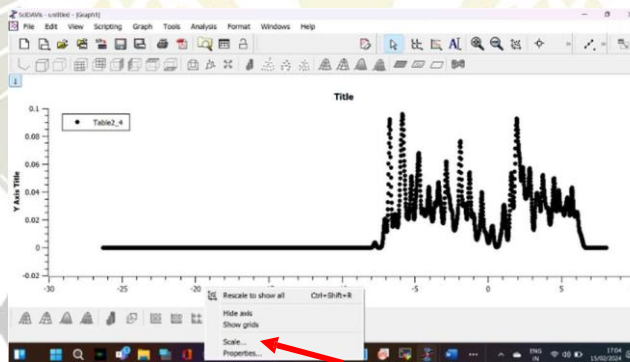
3. Then import DOS19.dat file by clicking on “File” on top Left corner and then click on “Import ASCII” and select the DOS.dat file to open “From files”.



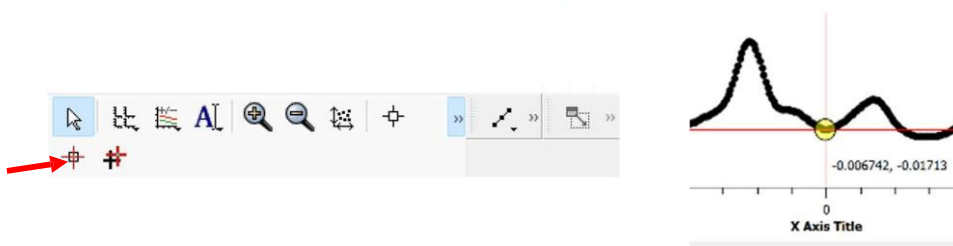
4. You can see the columns like as follows. Now select data from column having ‘ π -orbital’ states (Column number 4).

	-26.321[eV]	0[eV]	1[eV]	2[eV]	3[eV]	4[eV]	5[eV]	6[eV]
1	-26.309000000000000	0	0	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000
2	-26.298000000000000	0	0	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000
3	-26.286000000000000	0	0	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000
4	-26.275000000000000	0	0	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000
5	-26.263000000000000	0	0	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000
6	-26.252000000000000	0	0	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000
7	-26.240000000000000	0	0	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000
8	-26.229000000000000	0	0	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000
9	-26.217000000000000	0	0	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000
10	-26.206000000000000	0	0	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000
11	-26.195000000000000	0	0	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000
12	-26.183000000000000	0	0	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000
13	-26.172000000000000	0	0	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000
14	-26.160000000000000	0	0	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000
15	-26.149000000000000	0	0	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000	0.000000000000000

5. Then right click > Plot > select ‘Line’ to plot DOS plot.
6. Now right click on the scale to see “Scale” option to rescale x-axis it to -3 to +3.



7. On the top right corner select “Data reader” and note the y value of the DOS at x = 0 (Fermi level) This is $D_{\pi}(E_F)$.



8. Next, to find the occupancy, integrate the DOS with limit from $x = -\infty$ to E_F (Occupied states). Click 'Analysis' from the menu and select "**Integrate**". Change Upper limit value to '-0'. The area is occupancy of π -orbital (O_π)
9. Now for relative occupancy we need to calculate O_π of carbon atom in the pristine system. Repeat steps 3 to 8 for new file 'DOS61.dat'. (*Ignore step 7 as $D_\pi(E_F)$ is not required*).
10. Then take the difference using this formula to get Relative Occupancy ($R-O_\pi$).

$$R-O_\pi = \left[\int_{-\infty}^0 \rho_\pi dE \right]_{\text{active site}} - \left[\int_{-\infty}^0 \rho_\pi dE \right]_{\text{carbon atom in pristine system}}$$



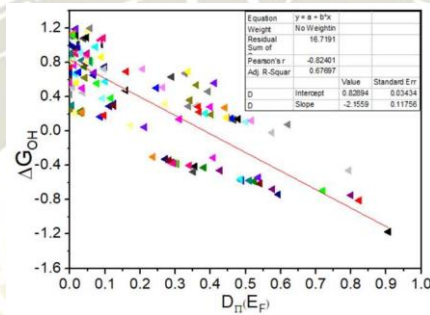
Exercise 3:

Predictive model equation:

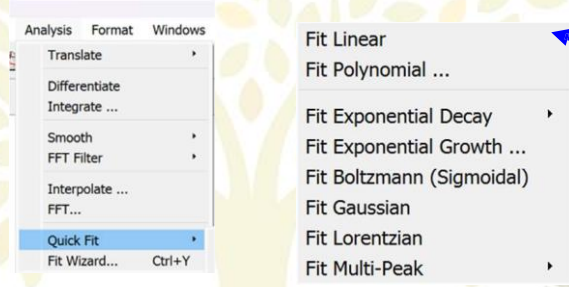
1. Open the Excel file ‘Descriptors’ provided in the ‘CDE2024’ > ‘Day-2’ folder. The data are electronic parameters $D_{\pi}(E_F)$, $R-O_{\pi}$ and ΔG_{OH} .
2. Open SciDAVis in your taskbar to plot.



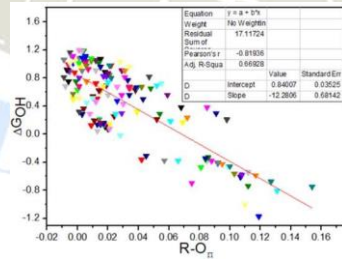
3. Create a new table from File > New > New Table.
4. Copy $D_{\pi}(E_F)$ and ΔG_{OH} from excel sheet and paste in the newly created table. Plot $D_{\pi}(E_F)$ vs ΔG_{OH} by selecting ΔG_{OH} column. (Select the column > Plot > Scatter).



5. Go to Analysis on the top and click on “Quick fit” and click “Linear fit”.



6. As the fit is linear, intercept and slope is obtained which is of the form “ $y = mx + c$ ”
 $\Delta G_{OH} = -2.15 * D_{\pi}(E_F) + 0.83$
7. Repeat steps 3 to 6 and plot $R-O_{\pi}$ vs ΔG_{OH}
8. Find the linear equation from steps 5 and 6 to obtain the equation
 $\Delta G_{OH} = -12.28 * (R-O_{\pi}) + 0.84$



9. After equating these two equations, we will get a relationship between $D_{\pi}(E_F)$ and relative occupancy.

$$D_{\pi}(E_F) = 5.71 * (R-O_{\pi})$$

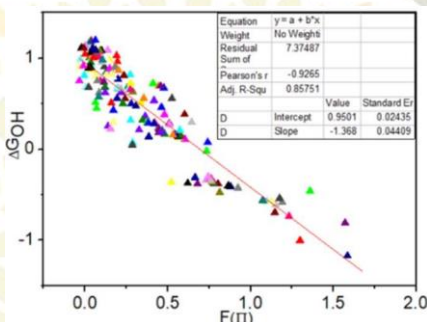
10. From this relationship we can define a function $F(\pi)$ which is a linear combination of these two parameters.

$$F(\pi) = 5.71(R-O_{\pi}) + D_{\pi}(E_F)$$

11. In the excel sheet create a new column with the formula in the previous step. Then click the corner of the cell and drag till last row.

B	C	D	E
Dπ(EF)	R-Oπ	ΔGOH	
0.355	0.092	-0.411	=B2 + 5.71*C2
0.303	0.066	-0.379	
0.301	0.088	-0.38	
0.086	0.069	0.168	

12. Again, create a new table in SciDAVis, then copy paste $F(\pi)$ and ΔG_{OH} . Plot Scatter plot $F(\pi)$ vs ΔG_{OH} .

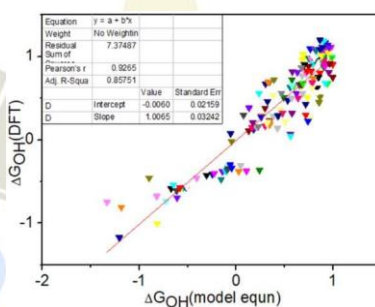


13. After linear fitting we will get an equation to estimate ΔG_{OH} .

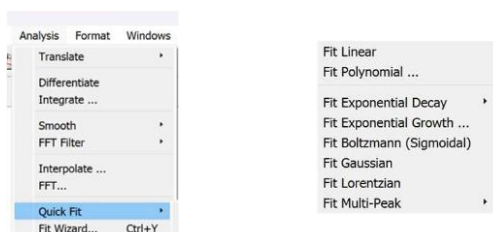
Predictive model equation: $\Delta G_{OH} = -1.36 * F(\pi) + 0.95$

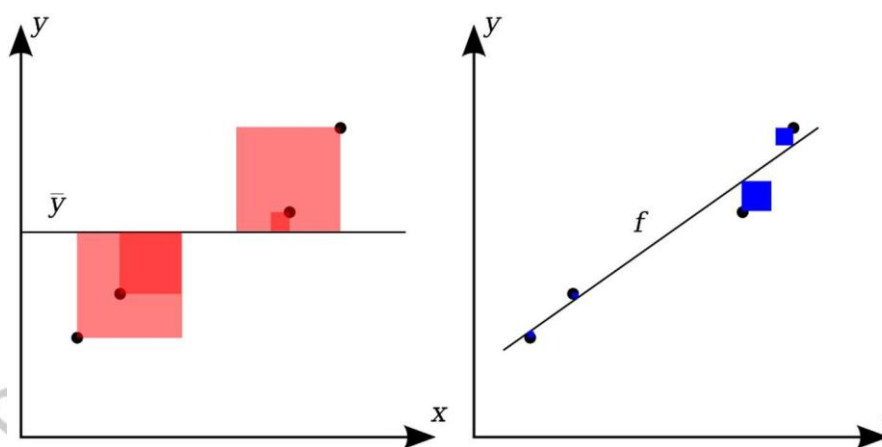
14. Now using this predictive model equation, in the Excel sheet calculate ΔG_{OH} .

15. Copy and paste ΔG_{OH} from DFT calculation and ΔG_{OH} from predictive model from excel to SciDAVis and Plot Scatter.



16. Go to Analysis on the top and click on “Quick fit” and click “Linear fit”.





17. The R^2 greater than 0.9 validates the predictive power of the predictive model equation. In other words, using this equation one can get the ΔG_{OH^*} values for any sp² carbon based system without having to perform the DFT calculation. This reduces the computational cost to a greater extent and shows how a good descriptor can help in not just explaining the reaction but also predicting it.

The Key points of the “ π electron” descriptor are

- Applicable to any sp² carbon based system
- Applicable to any electrocatalytic reaction
- Can predict in addition to explain the catalytic activity

Note: The instructions given in this manual may change slightly depending on the software(s) and platform used. However the procedure and the flow is general.

References:

- (1) Man, I. C.; Su, H.; Calle-vallejo, F.; Hansen, H. A.; Martínez, J. I.; Inoglu, N. G.; Kitchin, J.; Jaramillo, T. F.; Nørskov, J. K.; Rossmeisl, J. Universality in Oxygen Evolution Electrocatalysis on Oxide Surfaces. *2011*, 1159–1165. <https://doi.org/10.1002/cctc.201000397>.
- (2) Rossmeisl, J.; Logadottir, A.; Nørskov, J. K. Electrolysis of Water on (Oxidized) Metal Surfaces. *Chem. Phys.* **2005**, *319* (1–3), 178–184. <https://doi.org/10.1016/j.chemphys.2005.05.038>.
- (3) Rossmeisl, J.; Qu, Z. W.; Zhu, H.; Kroes, G. J.; Nørskov, J. K. Electrolysis of Water on Oxide Surfaces. *J. Electroanal. Chem.* **2007**, *607* (1–2), 83–89. <https://doi.org/10.1016/j.jelechem.2006.11.008>.
- (4) Nørskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jónsson, H. Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode. *J. Phys. Chem. B* **2004**, *108* (46), 17886–17892. <https://doi.org/10.1021/jp047349j>.
- (5) Kapse, S.; Barman, N.; Thapa, R. Identification of ORR Activity of Random Graphene-Based Systems Using the General Descriptor and Predictive Model Equation. *Carbon N. Y.* **2023**, *201*, 703–711. <https://doi.org/https://doi.org/10.1016/j.carbon.2022.09.059>.