OER, ORR, HER calculations

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This ppt describes how to calculate the oxygen evolution reaction (OER) (water splitting) oxygen reduction reaction (ORR) (fuel cell) hydrogen evolution reaction (HER) (water splitting)

References:

(1)A.L. J.R. J. K. Nørskov, L. Lindqvist, Origin of the overpotential for oxygen reduction at a fuel-cell cathode, J. Phys. Chem. B 108 (2004) 17886-17892.

The water splitting process: OER at anode

At the anode side, 4 holes are used, either to convert 4 OH^- into 2 H_2O and one O_2 (for the alkaline condition):

$$4h^+ + 4OH^- \rightarrow 2H_2O(l) + O_2(g)$$

Here (l) means liquid phase, (g) means gas phase.

Or 4 holes are used to convert 2 water molecules into four H^+ and one O^2 (for the acid condition):

$$4h^+ + 2H_2O \rightarrow 4H^+ + O_2(g)$$

In either case, this is a four step process, and we have four intermediate states (species).

The four intermediate states

(1) *(the bare surface site); (2) HO* (the surface site with one HO absorption)
(3) O* (the surface site with one O absorption); (4) HOO* (the surface site with one HOO absorption)

To make the catalytic cycle complete, we can also define a state: (5) $*+O_2$, the original state plus one released gas phase O_2.

If we set the reference energy at * (its Gibbs free energy is zero), then our task is to calculate the free energies of the other intermediate states at different electrode potential and pH value.

In order to calculate them, let's follow the reactions from one state to a subsequent state (note, although we have used acid condition reactions, the calculated overpotentials will be the same as using the alkaline condition reactions):

$$H_2O\ (l) + * \rightarrow HO* + H^+ + e\text{-} \qquad (1a)$$

$$HO* \rightarrow O* + H^+ + e\text{-} \qquad (1b)$$

$$O* + H_2O\ (l) \rightarrow HOO* + H^+ + e\text{-} \qquad (1c)$$

$$HOO* \rightarrow * + O_2\ (g) + H^+ + e\text{-} \qquad (1d)$$

The Gibbs free energies of the four intermediate states

Use the above Eq.(1), we can get the Gibbs free energy formula for the intermediate states (this is valid for both acid and alkaline conditions, although we derive it from the reaction in acid condition):

$$\Delta G_{*} = 0 \qquad (2a)$$

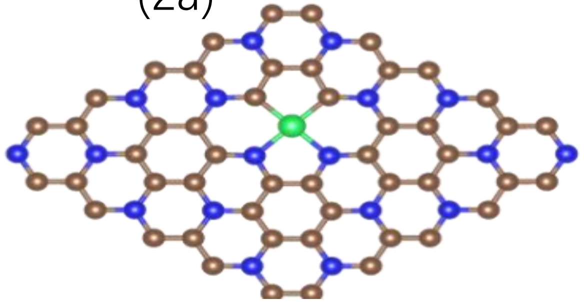
$$\Delta G_{HO*} = G_{HO*} + G_{H+} + \mu_{e-} - G_{*} - G_{H2O,l} \qquad (2b)$$

$$\Delta G_{O*} = G_{O*} + 2G_{H+} + 2\mu_{e-} - G_{*} - G_{H2O,l} \qquad (2c)$$

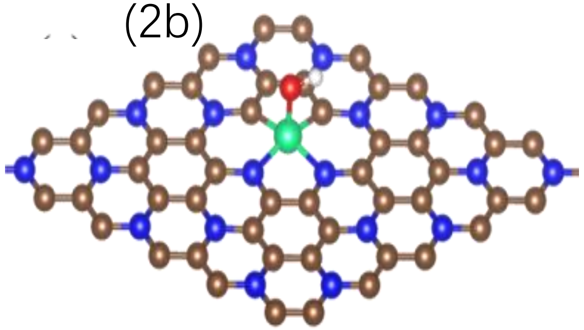
$$\Delta G_{HOO*} = G_{HOO*} + 3G_{H+} + 3\mu_{e-} - G_{*} - 2G_{H2O,l} \qquad (2d)$$

$$\Delta G_{*+O2} = G_{O2} + 4\,G_{H+} + 4\mu_{e-} - 2G_{H2O,l} \qquad (2e)$$

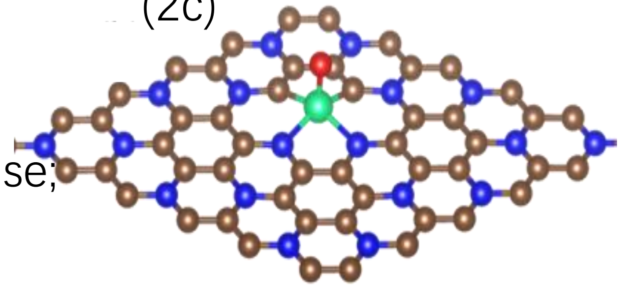
(2a)



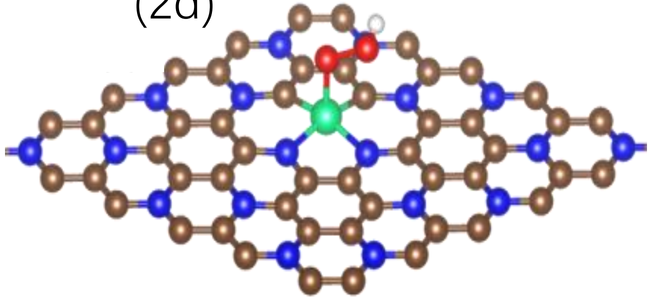
(2b)



(2c)



(2d)



Here “l” means the liquid phase; O_2 is in gas phase;

μ_e is the electron Gibbs free energy,
it equals the electrode potential;
G_{H+} is the Gibbs free energy of H+ in water,
it depends on pH value.

The Gibbs free energies of the four intermediate states

Since G_{H+} + μ_e(SHE) = 0.5H_2(g) at pH=0 (the equilibrium to generate H_2 gas),

here μ_e(SHE) is the voltage for standard hydrogen electrode (the above equation is its definition!).

So, if we define: $\mu_e = \mu_e(SHE) - U$, in Eq.(2), i.e, using SHE as the reference for the voltage, we have:

$$\Delta G_* = 0 \quad (3a)$$

$$\Delta G_{HO*} = G_{HO*} + 0.5G_{H2,g} - U - G_* - G_{H2O,l} \quad (3b)$$

$$\Delta G_{O*} = G_{O*} + G_{H2,g} - 2U - G_* - G_{H2O,l} \quad (3c)$$

$$\Delta G_{HOO*} = G_{HOO*} + 1.5G_{H2,g} - 3U - G_* - 2G_{H2O,l} \quad (3d)$$

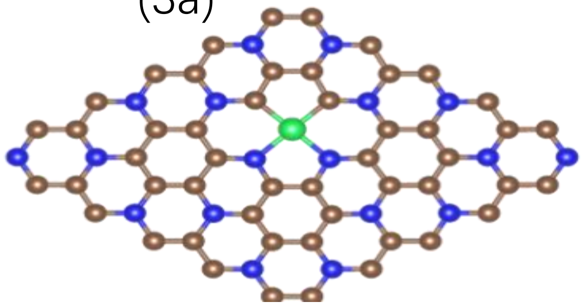
$$\Delta G_{*+O2} = 4*1.23\text{ eV} - 4U \quad (3e)$$

Here we have used:

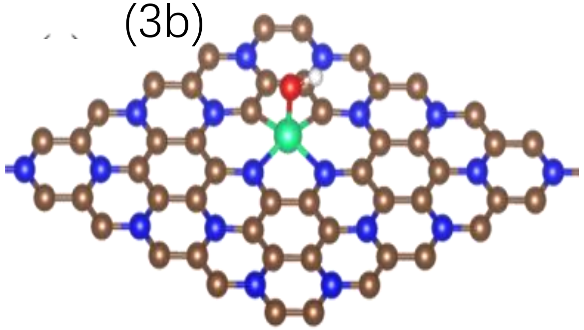
$G_{O2} + 2G_{H2} - 2G_{H2O,l} = 4*1.23$ eV

This is the theoretical energy needed to splitting the water.

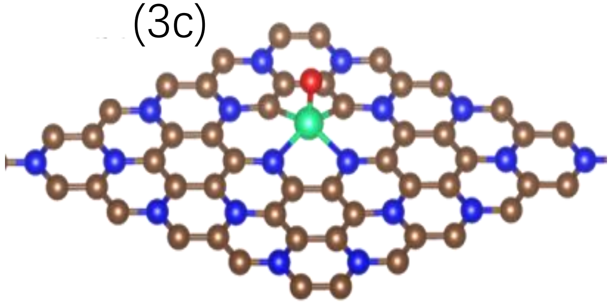
(3a)



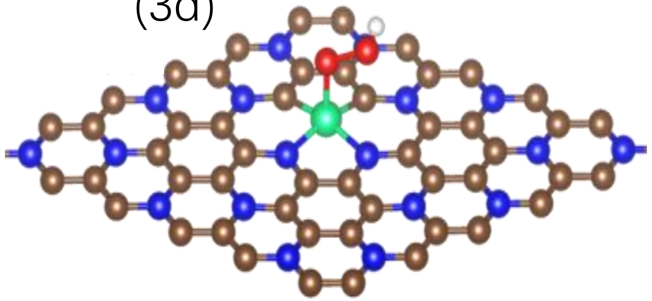
(3b)



(3c)

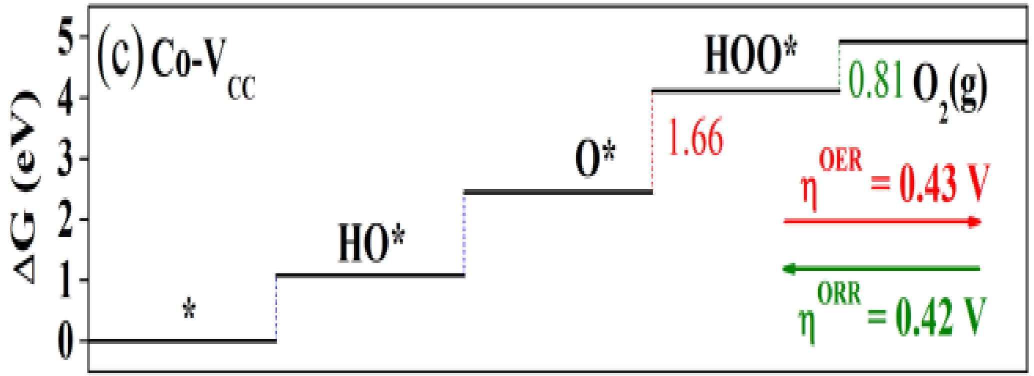


(3d)



The Gibbs free energies of the four intermediate states

The calculated ΔG_{*}, ΔG_{HO*}, ΔG_{O*}, ΔG_{HOO*} ΔG_{*+O2} can be plotted as following (under condition U=0):



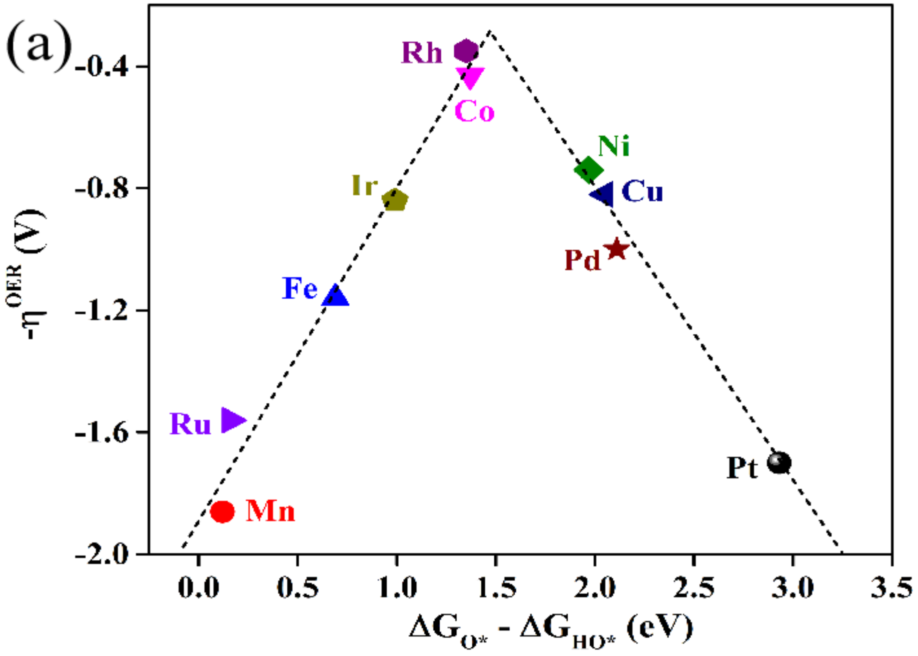
Now, the above graph is for U=0. In order for the OER to be successful, U must be used to make the reaction (a)-(e) always go down hill. This minimum U is determined by the maximum gap between the four intermediate states (for this case, it is the O* to HOO* step). The OER over potential (the potential larger than the ideal 1.23 eV) equals this maximum gap (1.66 eV) minus 1.23 eV (e.g., potential is 0.43 eV).
When the four energies are equally distributed, it is the ideal case, and the over potential is 0.

For ORR (fuel cell, where the reaction goes backword), the minimum voltage we get throughout these four steps determine the battery voltage. So, the minimum gap between the four intermediate states is the bottleneck (here, from O2(g) to HOO* and the gap is 0.81 eV). The ORR over potential equals the ideal 1.23 eV minus this minimum gap, thus equals 0.42 eV.

Note: in the above, we have ignored any possible additional transition barriers from one state to another. Such barrier can further increase the over potential. What we consider here is a simple model.

Volcano plot

Sometime, we can plot some trend crossing different catalysis, using one descriptor of the reaction. For example, it is found that, crossing different catalysis, the G_{HOO*}-G_{HO*} are almost the same, and the OER bottleneck happens either in HO* to O* step, or in O* to HOO*. As a result, the over potential is a single curve of ΔG_{O*}-ΔG_{HO*} (the gap from HO* to O*) and it has a absolute value linear function as the following (volcano plot):



Such trend can be used to optimize the catalyst.

Calculating the intermediate state free energies

So, what we need to do now, is to calculate ΔG_{*}, ΔG_{HO*}, ΔG_{O*}, ΔG_{HOO*} according Eq.(3).

The advantages of Eq.(3) is that, it does not have H+ (which we don't know how to calculate), only has $H_2(g)$, $H_2O(l)$, and the neutral intermediate systems X*. In calculating these quantities, we have the following comments:

- G_X*: $G_{X*}=E_{X*}+ZPE_{X*}-TS_{X*}$. Here Ex* is the DFT calculated ground state energy plus the phonon thermal energy (which usually can be ignored), ZPEx* is the zero point energy of the phonon modes, and TSx is the phonon entropy term (can be ignored except for the gas H2O and H2). $ZPE = 0.5\sum_i \hbar\omega_i$

- E_X*: it is one's own responsibility to find out the reaction site, and configurations. Then one should relax the structure, and calculate the total energy with solvent model (the best is to relax the structure with solvent model, or one can relax in vacuum, then have one shot SCF calculation with solvent model).

- G_H2O(l): $G_{H2O,l}=E_{H2O}+ZPE_{H2O}-TS_{H2O}$, and $TS_{H2O}=0.67$ eV is the entropy term of the gas phase which is in equilibrium with the liquid water. E_{H2O} is the DFT calculated isolated H2O molecule energy, and ZPE_{H2O} is the isolated molecule ZPE. [1]

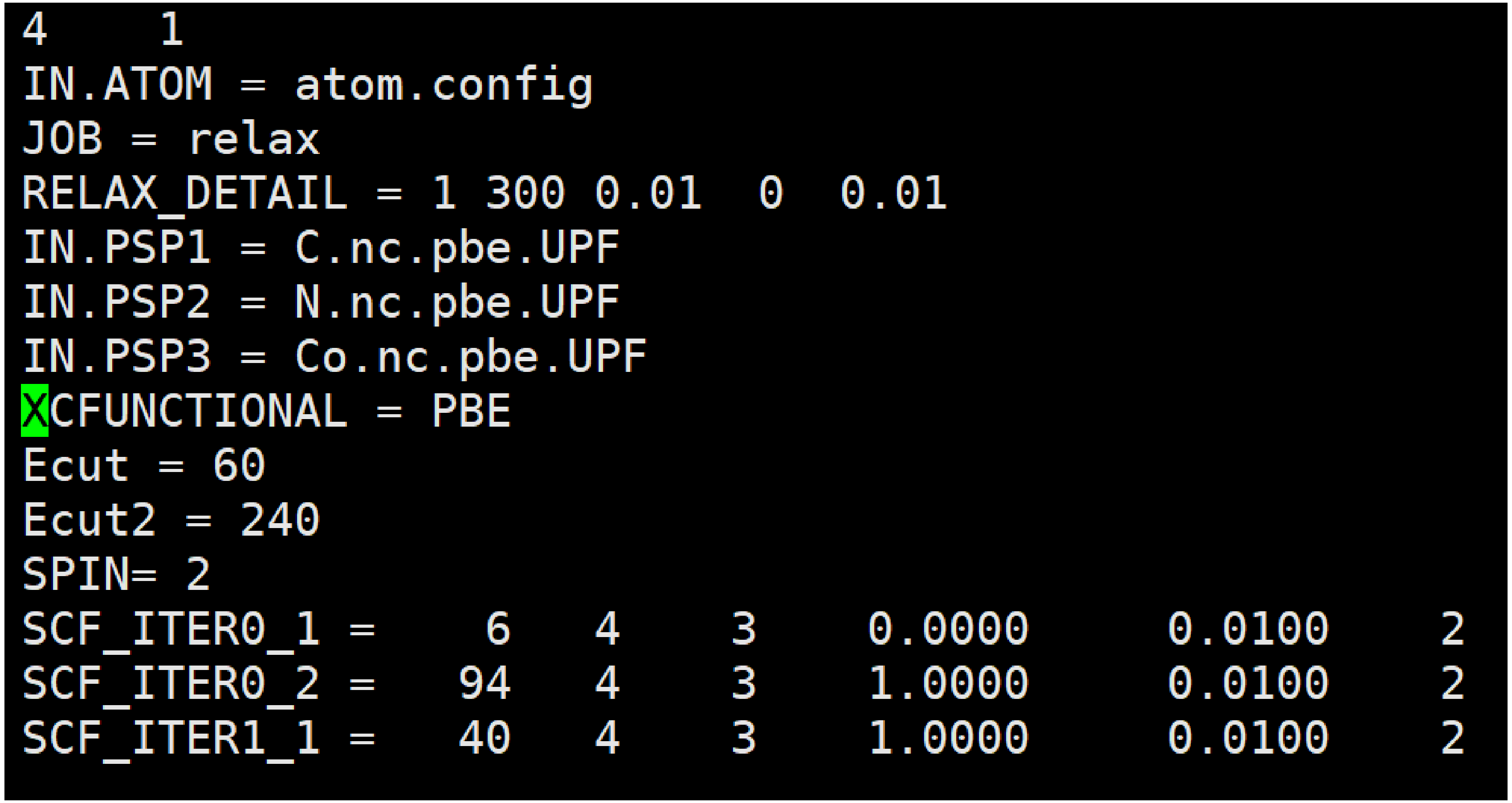
- G_H2(g): $G_{H2(g)}=E_{H2}+ZPE_{H2}-TS_{H2}$, and $TS_{H2}=0.41$ eV. [1] (Note we have avoided the direct calculation of O_2, which usu can have a big DFT error).

[1] J.D.P. P. Atkins, Atkins-physical-chemistry, (2014).

So, what we need to do now, is to calculate Ex* and ZPEx*

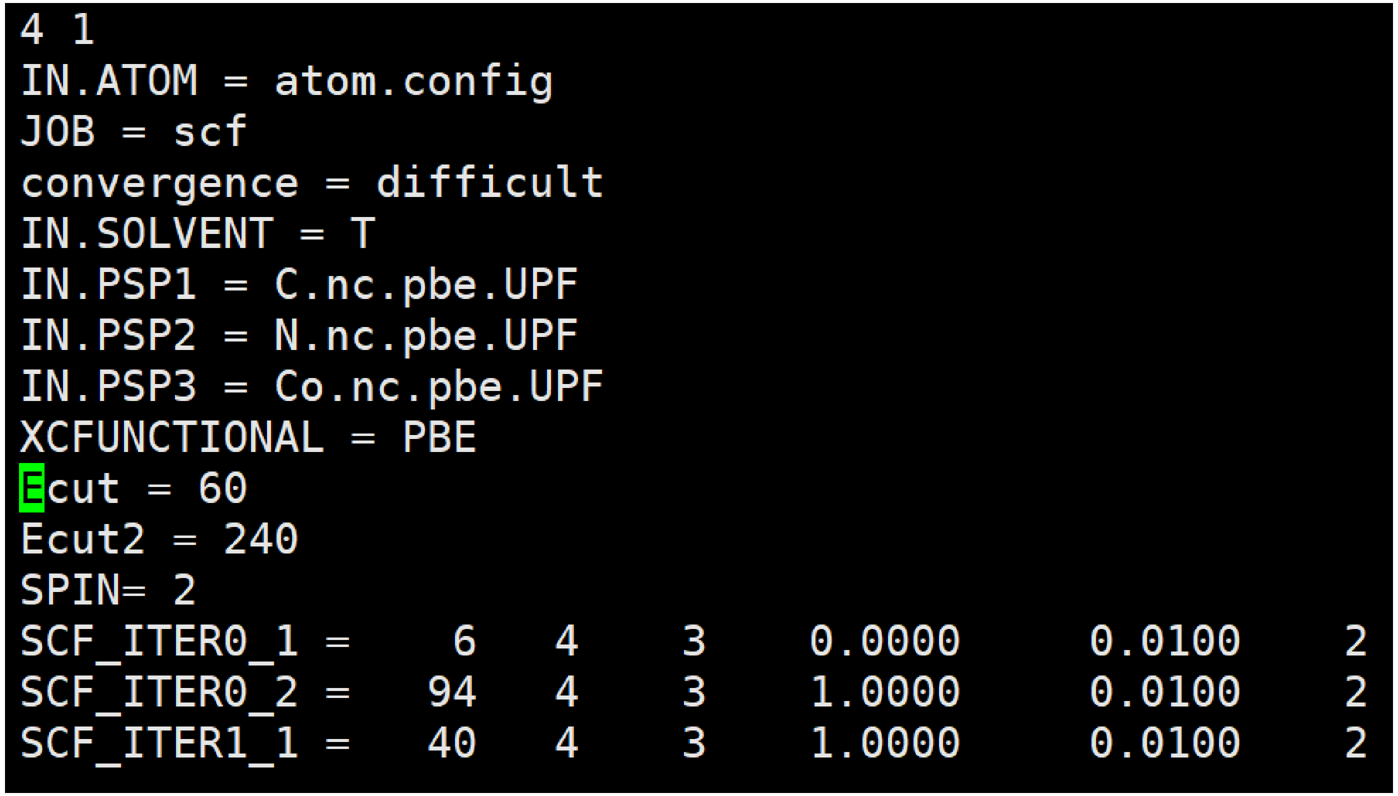
For Ex* , first relax the structure, then do SCF calculation with solvent model

◆ Prepare etot.input for relax



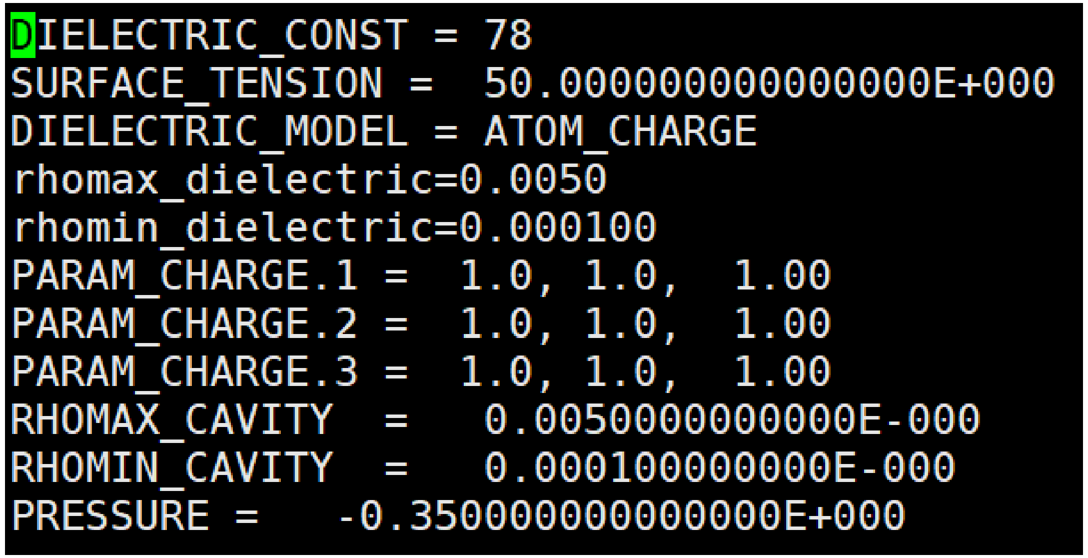
```
4    1
IN.ATOM = atom.config
JOB = relax
RELAX_DETAIL = 1 300 0.01  0  0.01
IN.PSP1 = C.nc.pbe.UPF
IN.PSP2 = N.nc.pbe.UPF
IN.PSP3 = Co.nc.pbe.UPF
XCFUNCTIONAL = PBE
Ecut = 60
Ecut2 = 240
SPIN= 2
SCF_ITER0_1 =    6   4    3    0.0000     0.0100    2
SCF_ITER0_2 =   94   4    3    1.0000     0.0100    2
SCF_ITER1_1 =   40   4    3    1.0000     0.0100    2
```

- Copy final.config to atom.config
  Prepare etot.input for solvent scf



```
4 1
IN.ATOM = atom.config
JOB = scf
convergence = difficult
IN.SOLVENT = T
IN.PSP1 = C.nc.pbe.UPF
IN.PSP2 = N.nc.pbe.UPF
IN.PSP3 = Co.nc.pbe.UPF
XCFUNCTIONAL = PBE
Ecut = 60
Ecut2 = 240
SPIN= 2
SCF_ITER0_1 =    6    4    3    0.0000     0.0100    2
SCF_ITER0_2 =   94    4    3    1.0000     0.0100    2
SCF_ITER1_1 =   40    4    3    1.0000     0.0100    2
```

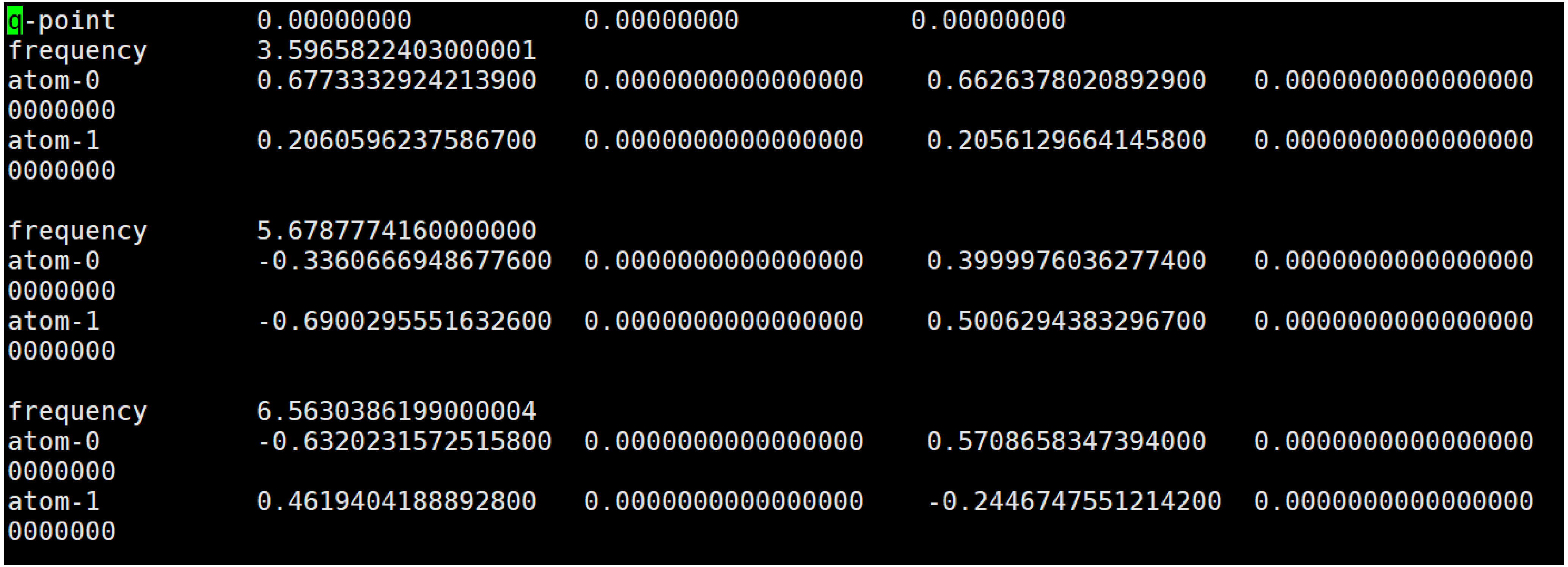
- For solvent module, IN.SOLVENT is needed,
  here is a simple example, for more details, please
  refer to the manual (chapter 2.1.55 IN.SOLVENT)



```
DIELECTRIC_CONST = 78
SURFACE_TENSION =  50.000000000000000E+000
DIELECTRIC_MODEL = ATOM_CHARGE
rhomax_dielectric=0.0050
rhomin_dielectric=0.000100
PARAM_CHARGE.1 =  1.0, 1.0,  1.00
PARAM_CHARGE.2 =  1.0, 1.0,  1.00
PARAM_CHARGE.3 =  1.0, 1.0,  1.00
RHOMAX_CAVITY  =   0.0050000000000E-000
RHOMIN_CAVITY  =   0.000100000000E-000
PRESSURE =   -0.350000000000000E+000
```

For ZPE* , only phonon frequency at Gamma point for -O, -OH, -OOH atoms are needed, please follow the “pypwmat” module on the website, to calculate the subsystem phonon

Get the file: mesh.yaml.dat

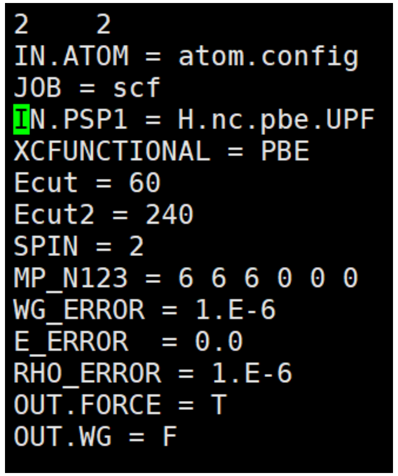


```
q-point         0.00000000           0.00000000           0.00000000
frequency       3.5965822403000001
atom-0          0.6773332924213900   0.0000000000000000    0.6626378020892900   0.0000000000000000
0000000
atom-1          0.2060596237586700   0.0000000000000000    0.2056129664145800   0.0000000000000000
0000000

frequency       5.6787774160000000
atom-0          -0.3360666948677600  0.0000000000000000    0.3999976036277400   0.0000000000000000
0000000
atom-1          -0.6900295551632600  0.0000000000000000    0.5006294383296700   0.0000000000000000
0000000

frequency       6.5630386199000004
atom-0          -0.6320231572515800  0.0000000000000000    0.5708658347394000   0.0000000000000000
0000000
atom-1          0.4619404188892800   0.0000000000000000    -0.2446747551214200  0.0000000000000000
0000000
```

Here the default unit for phonon Frequency is THz , for ZPE calculation: 1THz = 0.004135 eV

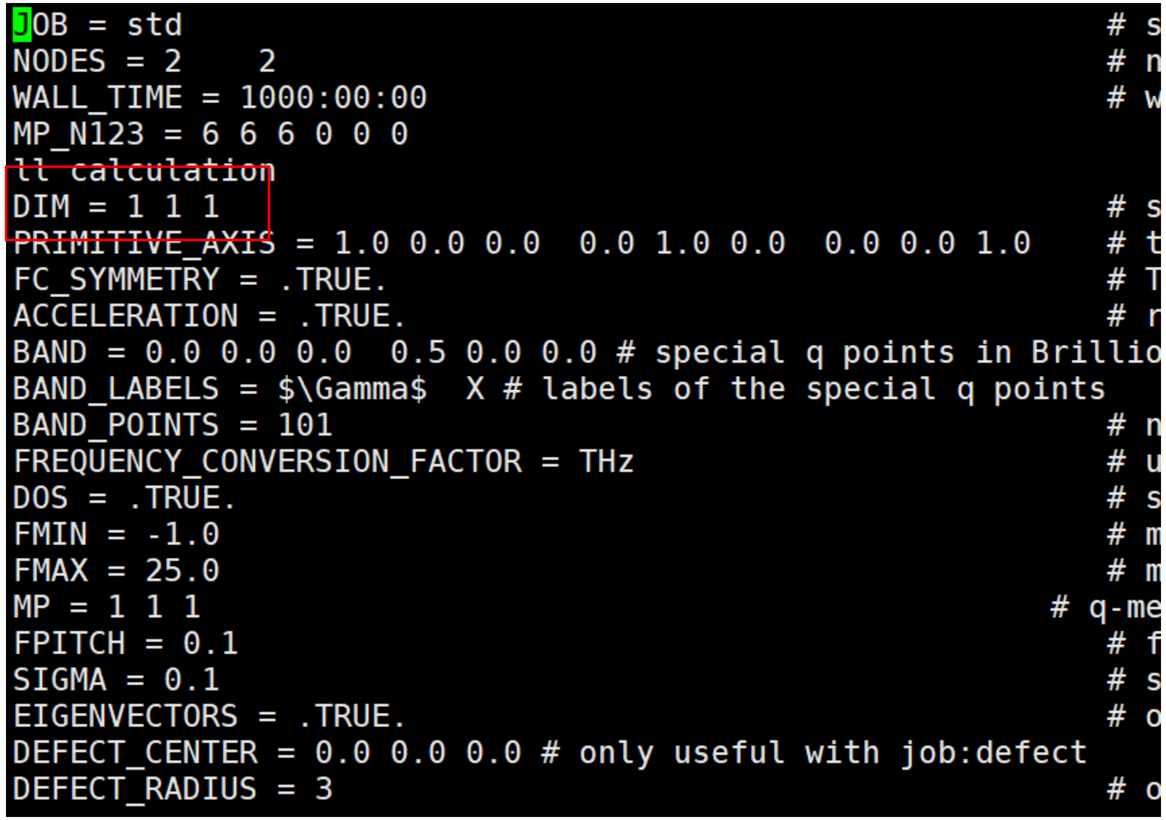
For H2 and H2O, ZPE* can be calculated use the std phonon in “pypwmat” module

Step 1: Put H2 and H2O in a vacuum box, then relax and get the Etot
Step 2: prepare a new directory, copy the relaxed structure and psp to the new dir, prepare etot.input



```
2    2
IN.ATOM = atom.config
JOB = scf
IN.PSP1 = H.nc.pbe.UPF
XCFUNCTIONAL = PBE
Ecut = 60
Ecut2 = 240
SPIN = 2
MP_N123 = 6 6 6 0 0 0
WG_ERROR = 1.E-6
E_ERROR  = 0.0
RHO_ERROR = 1.E-6
OUT.FORCE = T
OUT.WG = F
```

Step 3: type PWmatPhonon.py, it will generate a
file “PWphonon.in”
Edit PWphonon.in, DIM = 1 1 1 for vacuum system
MP = 1 1 1,for gamma point
For more detail, please refer to the pypwmat module
Step 4: type PWmatPhonon.py again, then it will start Phonon calculation. After calculation finished,
Cd phonon_std dir and type ./extract_phonon_data.sh
It will generate the mesh.yaml.dat file



```
JOB = std                                                          # s
NODES = 2    2                                                     # n
WALL_TIME = 1000:00:00                                             # w
MP_N123 = 6 6 6 0 0 0
ll calculation
DIM = 1 1 1                                                        # s
PRIMITIVE_AXIS = 1.0 0.0 0.0  0.0 1.0 0.0  0.0 0.0 1.0             # t
FC_SYMMETRY = .TRUE.                                               # T
ACCELERATION = .TRUE.                                              # r
BAND = 0.0 0.0 0.0  0.5 0.0 0.0 # special q points in Brillio
BAND_LABELS = $\Gamma$  X # labels of the special q points
BAND_POINTS = 101                                                  # n
FREQUENCY_CONVERSION_FACTOR = THz                                  # u
DOS = .TRUE.                                                       # s
FMIN = -1.0                                                        # m
FMAX = 25.0                                                        # m
MP = 1 1 1                                                      # q-me
FPITCH = 0.1                                                       # f
SIGMA = 0.1                                                        # s
EIGENVECTORS = .TRUE.                                              # o
DEFECT_CENTER = 0.0 0.0 0.0 # only useful with job:defect
DEFECT_RADIUS = 3                                                  # o
```

All the data we need list here:

structure	3N-C-CO	3N-C-CO-OH	3N-C-CO-O	3N-C-CO-OOH	H2	H20
E* (eV)	-16601.6905	-17051.9418	-17034.2265	-17483.7925	-31.7312	-466.6826

structure	frequency	ZPE
3N-C-CO		0
3N-C-CO-OH	3.59; 5.68; 6.56; 13.77; 25.48; 110.50	0.34
3N-C-CO-O	3.78; 4.95; 20.19	0.06
3N-C-CO-OOH	2.11; 3.71; 4.70; 6.04; 9.52; 14.01; 24.09; 38.26; 107.53	0.43
H2	-2.34; -2.34; 0; 0; 0; 129.53	0.26
H2O	-6.57; 0; 0; 0; 0.72; 1.91; 48.33; 110.93; 114.27	0.56

From eq (3): $\Delta G_{HO*} = G_{HO*} + 0.5G_{H2,g} - U - G_{*} - G_{H2O,l}$

and silde 9 : G_X*: $G_{X*} = E_{X*} + ZPE_{X*} - TS_{X*}$.

$\Delta G_{HO*} = (E_{HO*} + ZPE_{HO*} - TS_{HO*}) + 0.5G_{H2,g} - U - (E_{*} + ZPE_{*} - TS_{*}) - G_{H2O,l} = 0.94$ eV

Here, $U=0$, $ZPE_{*}=0$, $TS_{HO*}=0$; $TS_{*}=0$

G_H2O(l): $G_{H2O,l} = E_{H2O} + ZPE_{H2O} - TS_{H2O}$, and $TS_{H2O} = 0.67$ eV

G_H2(g): $G_{H2(g)} = E_{H2} + ZPE_{H2} - TS_{H2,}$ and $TS_{H2} = 0.41$ eV

ΔG_{O*} ΔG_{HOO*} ΔG_{*+O2} can be calculated the same way

$\Delta G_{O*} = G_{O*} + G_{H2,g} - 2U - G_{*} - G_{H2O,l} = 2.46$ eV

$\Delta G_{HOO*} = G_{HOO*} + 1.5G_{H2,g} - 3U - G_{*} - 2G_{H2O,l} = 4.09$ eV

$\Delta G_{*+O2} = 4*1.23$ eV$- 4U = 4.92$ eV

The calculated ΔG_{*}, ΔG_{HO*}, ΔG_{O*}, ΔG_{HOO*} ΔG_{*+O2} can be plotted as following :