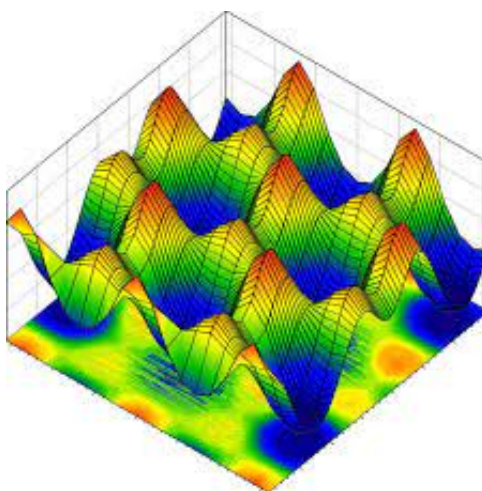


THE UNIVERSITY OF FRANCHE-COMTÉ

MASTER COMPUPHYS - FORTRAN PRACTICAL POOL

Building of a multidimensional potential energy surface applied to the gas/surface reactivity



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1 Introduction

The catalysis processes are use in many fields to improve the rapidity or to change the natural order of a chemical reaction, to study the effect of this process we need to use molecular dynamics method and simulation. The molecular dynamics methods are based on the forces present in a system, theses forces can be deduced by take the minus derivative of the potential energy of a system. Our system is the reaction between nitrogen molecule N_2 and the tungsten surface $W(1, 0, 0)$, to study this catalysis processes we need to compute the potential energy surface of the tungsten surface. We will compute it with the LEPS potential and compare it to the CRP potential. Three level step are involved in this subject :

- Alpha version : N/W(100) interaction with the LEPS atom/surface potential based on the Morse potential
- Beta version : N/W(100) interaction with the LEPS atom/surface potential based on the Modified-Morse potential
- Golden version : N_2 /W(100) interaction with the LEPS molecule/surface potential

2 Alpha Version :

In this first part we have to fit the potential for 3 sites of high symmetry sites (bridge, top and hollow) by building the 3D-PES script. The first step is to deduce the three parameter α , D , r_{eq} with a non linear-fit for the three high symmetry sites.

The next step is to expressed the parameter by the Fourier expansion at the third order in order to define the all surface of a unit cell of tungsten. The last step will use these Fourier expansion to plot the 1D cuts for all the symmetry sites.

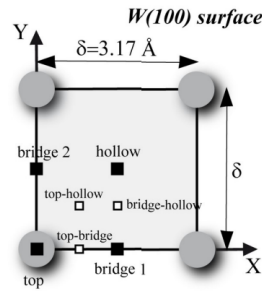


Figure 1: The (100) surface of the tungsten (atom in gray circle) with black squares the high symmetry sites and the gray squares the lower symmetry sites.

2.1 Theory

The potential use in this part is :

$$V^{3D}(\mathbf{r}_{at}) = D [\exp(-2\alpha(Z_{at} - r^{eq})) - 2 \exp(-\alpha(Z_{at} - r^{eq}))]$$

With :

- D the potential energy depth
- α the range of the potential
- r_{eq} the equilibrium distance between the atom and the surface

In the second part we have to find the Fourier coefficient of the Fourier expansion for the three high symmetry sites for the all coefficients :

$$Four(X_{at}, Y_{at}) = P_0 + P_1 \left(\cos \frac{2\pi X_{at}}{\delta} + \cos \frac{2\pi Y_{at}}{\delta} \right) + P_2 \left(\cos \frac{2\pi(X_{at} + Y_{at})}{\delta} + \cos \frac{2\pi(X_{at} - Y_{at})}{\delta} \right)$$

for the all sites we can put this under matrix form :

$$\begin{pmatrix} \lambda_h \\ \lambda_b \\ \lambda_t \end{pmatrix} = \underbrace{\begin{pmatrix} 1 & \cos \frac{2\pi X_h}{\delta} + \cos \frac{2\pi Y_h}{\delta} & \cos \frac{2\pi(X_h+Y_h)}{\delta} + \cos \frac{2\pi(X_h-Y_h)}{\delta} \\ 1 & \cos \frac{2\pi X_b}{\delta} + \cos \frac{2\pi Y_b}{\delta} & \cos \frac{2\pi(X_b+Y_b)}{\delta} + \cos \frac{2\pi(X_b-Y_b)}{\delta} \\ 1 & \cos \frac{2\pi X_t}{\delta} + \cos \frac{2\pi Y_t}{\delta} & \cos \frac{2\pi(X_t+Y_t)}{\delta} + \cos \frac{2\pi(X_t-Y_t)}{\delta} \end{pmatrix}}_M \times \begin{pmatrix} P_0 \\ P_1 \\ P_2 \end{pmatrix}$$

with :

- $\lambda_{h,b,t}$ a coefficient between D, α, r_{eq} .
- h, b, t the site name, respectively hollow, bridge and top.
- $X_{h,b,t}$ the coordinates on x for the previous site.
- $Y_{h,b,t}$ the coordinates on y for the previous site.

We can write the matrix M because the coordinates are expressed in unit cell like $X_{hollow} = 0.5 * \delta$:

$$\begin{pmatrix} 1 & -2 & 2 \\ 1 & 0 & -2 \\ 1 & 2 & 2 \end{pmatrix}$$

We can compute the coefficients with the Cramer's rule :

$$P_i = \frac{\det(M_k)}{M}$$

$$M_k = (m_{i,j,k}) \text{ with } m(i, j, k) = \begin{cases} m_{i,j} & \text{if } j \neq k \\ \lambda_{h,b,t} & \text{if } j = k \end{cases}$$

With those coefficient we have an expression for all the coefficient for all point X,Y of the 2D space and we can make the 1D cuts for all the symmetry sites.

2.2 Program

Now we have see the theory part for the alpha we can build the program to perform 1D cuts. All the programs are commented to explain how its works but I drew a diagram to explain how the programs communicate in the folder Alpha :

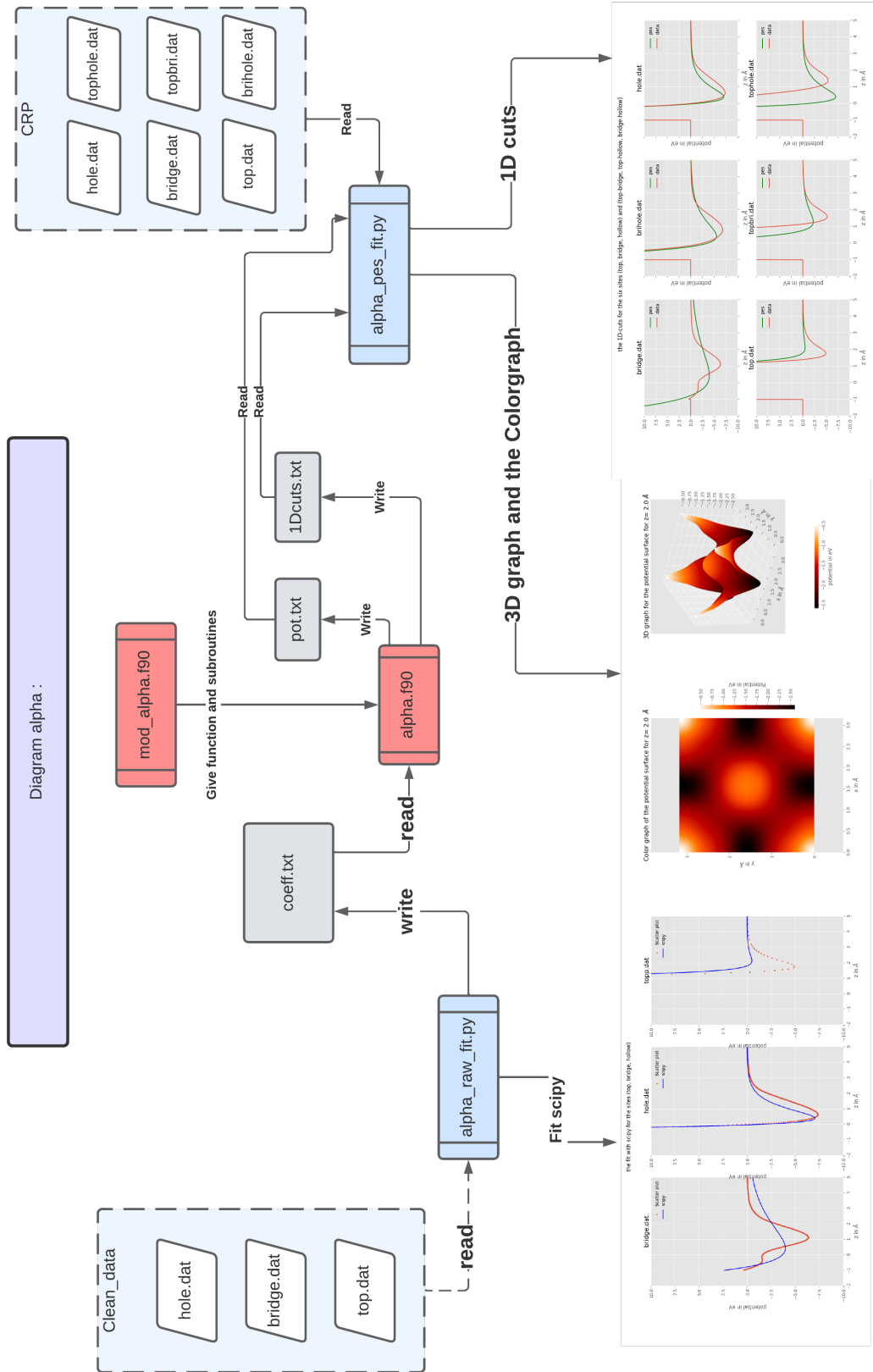


Figure 2: schema summarizing the alpha program

On this schema we can see the program plot what we want with 4 program files :

The first is in python named "alpha_raw_fit.py" read the folder "Clean_data", in this folder i took the data files given in the CRP-NW100. This data are the potential on symmetry site along this Z axis I have called this clean data because the CRP need other values that are given at the beginning and the end of these files, so in this files i have clean them by

delete this values.

After the python program use `scipy.curve fit` function to perform a non-linear fit on these sites and guess the parameter D, α, r_{eq} and write them in the file "coeff.txt" for all the high symmetry files.

The program "alpha.f90" read this file, put it under a matrix form, solve it by finding the coefficients P_i with the function and subroutines write in the file "mod alpha.f90" and finally compute the three parameter that governed the Morse potential.

With these coefficient P_i for each parameter we can evaluate each for the all unit cell, and with the value of these coefficient for the all unit cell we can evaluate the potential for each point $V(X, Y, Z)$.

Finally the program "alpha.f90" write the values of the potential for a whole unit cell and a given Z in file "pot.txt" and the values of the potential for all the symmetry site along Z in "1D cuts.txt".

The last step use the "alpha_pes_fit.py" to plot the CRP 1D cuts from the folder CRP and the PES 1D cuts from the file "1Dcuts.txt" and for a unit cell and a given Z the 3D graph and the color graph.

One of the goals of this project is to code in Fortran, the most important part of computation is in the file "alpha.f90" and his mod "mod_alpha.f90" :

First the file "alpha.f90" read in line the file coeff.txt that contains the coefficients arranged in line D, α, r_{eq} for each high symmetry sites and he put them in an array called Coef.

After he build the x-axis and the y-axis between 0 and 3.17 (there are the same) for an unit cell in a vector l.

The following computation build the matrix M by affecting the subroutine "fourier_dev" in the mod file, this function give the Fourier development for given coordinates and a vector of coefficients (normally its P_i ,but if we put our system under matrix form, the matrix M is without them so in the program we will replace them by a vector K with all components equal to one.

To solve this system in order to find the Cramer's components we do a loop, for each iteration we call the subroutine "cramer" in the mod file. This function compute the Cramer's rule like seen in the theory part to compute the coefficients P_i . It take the same λ coefficient for all the symmetry site by taking a columns in the matrix Coef, the matrix M and an empty vector P to store the value of Cramer's components. After the call the vector P we will be store in the matrix mP, like that after all the iterations we will have an array of Cramer's coefficients with each line for a parameter.

With this matrix we can call our subroutine "Fourier" that compute the Fourier expansion for each parameter of our potential. This subroutine take the matrices D, al, req that represent the values of them for a given coordinates X_{at}, Y_{at} . It compute that in two loops one on the x-axis and one on the y-axis for each iteration we compute the Fourier expansion by taking the sum all the subroutines "fourier_dev" with the good P_i coefficients.

Finally with the matrices associated to each parameter we can compute the potential by call the function "pot" that compute the potential for given coordinates X_{at}, Y_{at}, Z_{at} . We compute the potential for a whole unit cell and a given Z and also the 1D cuts (with the good coordinates X_{at}, Y_{at} for each cuts).

2.3 Result

To obtains the result you have to run those program in this order :

- "alpha_raw_fit.py"
- "alpha.f90" by write in the terminal "gfortran mod_alpha.f90 alpha.f90"
- "alpha_pes_fit.py"

At the beginning we have to perform a non linear fit on the data from "CRP-NW100", I have perform this with the function "curve fit" of scipy to obtains the parameter D, α, r_{eq} :

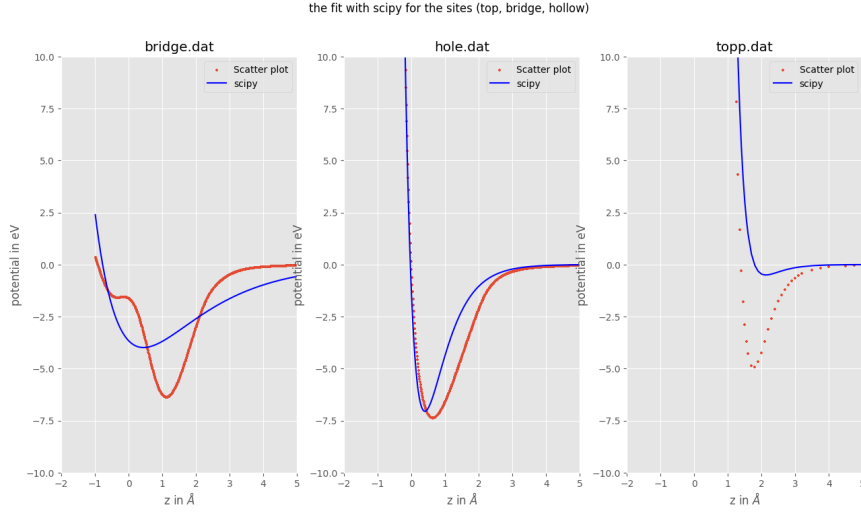


Figure 3: Subplot of the non linear fit of data from CRP-NW100

I have reduced the region of the plot between $-10; 10$ for the y-axis and $-2; 5$ for the x-axis to see the most interesting part of our potential.

On this graph we can see the equation doesn't match clearly with the data but we can propagate it to a whole unit cell.

By running the first python file we have created the file "coeff.txt" that contains the parameter D, α, r_{eq} for the three high symmetry site, now we can running the file "alpha.f90" that will compute the potential and the file "alpha pes fit.py" to plot all the data :

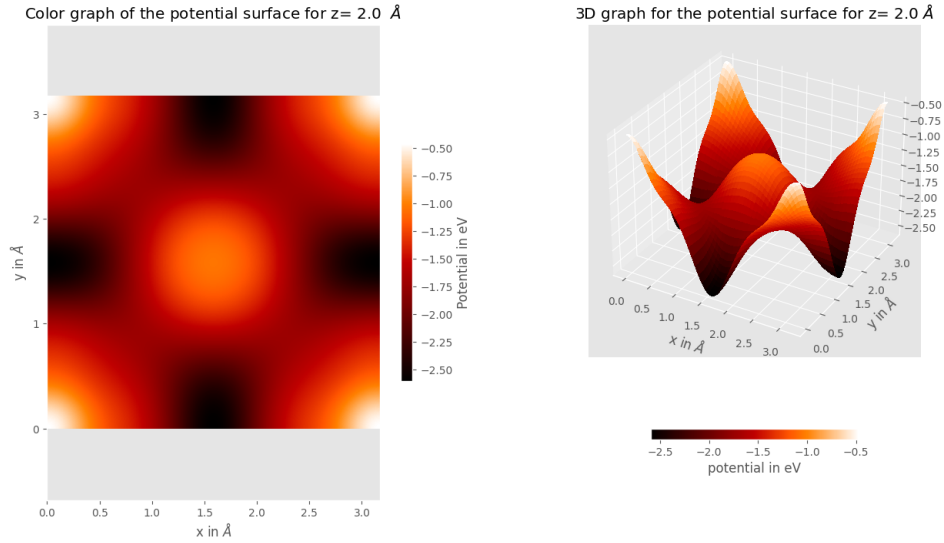


Figure 4: Subplot of color graph and 3D graph for a unit cell at $z = 2\text{Å}$

On these graph we can see a unit cell for an arbitrary $z = 2\text{Å}$, the potential is higher in the corner this is logical because we approach of the atoms in the corner and in the middle of the unit cell we have a high potential but not like of atoms in the corner because we a bcc crystal so we have an atoms in the middle more deep than the other like we can see on the 3D graph.

Now we can plot the 1D cuts to compare them to the CRP-NW100 script with 1000 points between $z = -2; 5$:

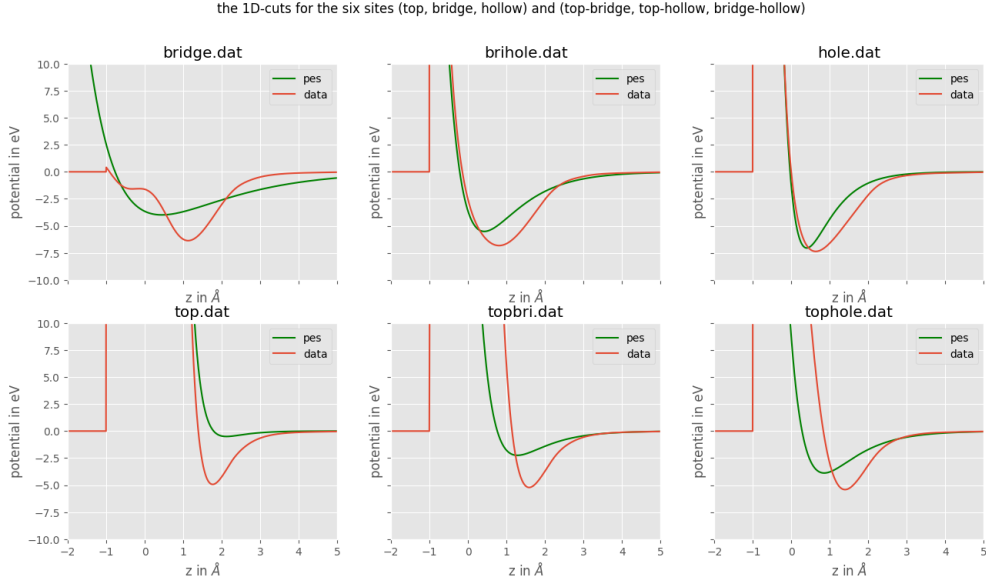


Figure 5: Subplot of the comparison between data from CRP script for atom/surface and our PES-fit

We can see on these graph we don't fit the curves with a good accuracy and this make sense because all of our method take the coefficients from the scipy fit so we can't be more accurate than it.

For the high symmetry sites I expected a better fit than the lower because we take the coefficient form them, the most accurate is the hole site.

For the lower symmetry sites just for brihole site our fit have a correct behavior we the other we are like shift from the data.

3 Beta Version :

In the beta version we have to improve our previous 3D-pes script by taking a modified version of the Morse potential :

$$V^{3D}(\mathbf{r}_{at}) = D [\exp(-2\alpha(Z_{at} - r^{eq})) - 2 \exp(-\alpha(Z_{at} - r^{eq}))]$$

But now the parameter α will depend of Z_{at} , D, r_{eq} are not changed :

$$\alpha(Z_{at}) = (1 - f_{\alpha}(Z_{at}))(\alpha_{rep}^0 + \alpha_{rep}^1 \times Z_{at}) + (f_{\alpha}(Z_{at}))(\alpha_{att}^0 + \alpha_{att}^1 \times Z_{at})$$

With $f_{\alpha}(Z_{at})$:

$$f_{\alpha}(Z_{at}) = \frac{1}{2} (1 + \tanh(a \times Z_{at} + b))$$

3.1 Theory

With this modification our potential depends on $Z, D, r_{eq}, \alpha_{rep}^0, \alpha_{rep}^1, \alpha_{att}^0, \alpha_{att}^1, a, b$.

In order to compute the potential in a unit cell or several we have to compute the Fourier expansion of our parameter for every sites at the fifth order :

$$\begin{aligned} \text{Four}(X_{at}, Y_{at}) = & P_0 + P_1 \left(\cos \frac{2\pi X_{at}}{\delta} + \cos \frac{2\pi Y_{at}}{\delta} \right) + P_2 \left(\cos \frac{2\pi(X_{at}+Y_{at})}{\delta} + \cos \frac{2\pi(X_{at}-Y_{at})}{\delta} \right) \\ & + P_3 \left(\cos \frac{4\pi X_{at}}{\delta} + \cos \frac{4\pi Y_{at}}{\delta} \right) \\ & + P_4 \left(\cos \frac{2\pi(2X_{at}+Y_{at})}{\delta} + \cos \frac{2\pi(X_{at}+2Y_{at})}{\delta} + \cos \frac{2\pi(2X_{at}-Y_{at})}{\delta} + \cos \frac{2\pi(X_{at}-2Y_{at})}{\delta} \right) \\ & + P_5 \left(\cos \frac{4\pi(X_{at}+Y_{at})}{\delta} + \cos \frac{4\pi(X_{at}-Y_{at})}{\delta} \right) \end{aligned}$$

We can put under matrix form this equation for all the coefficients for each symmetry sites:

$$\begin{pmatrix} \lambda_b \\ \lambda_{bh} \\ \lambda_h \\ \lambda_t \\ \lambda_{tb} \\ \lambda_{th} \end{pmatrix} = \underbrace{\begin{pmatrix} 1 & 0 & -2 & 2 & 0 & 2 \\ 1 & -1 & 0 & 0 & 2 & -2 \\ 1 & -2 & 2 & 2 & -4 & 2 \\ 1 & 2 & 2 & 2 & 4 & 2 \\ 1 & 1 & 0 & 0 & -2 & -2 \\ 1 & 0 & 0 & -2 & 0 & 2 \end{pmatrix}}_M \times \begin{pmatrix} P_0 \\ P_1 \\ P_2 \\ P_3 \\ P_4 \\ P_5 \end{pmatrix}$$

- $\lambda_{h,b,t,tb,bh,th}$ a coefficient between $D, r_{eq}, \alpha_{rep}^0, \alpha_{rep}^1, \alpha_{att}^0, \alpha_{att}^1, a, b$
- h, b, t, tb, bh, th the site name, respectively hollow, bridge, top bridge, top hollow and bridge hollow
- $P_{1,2,3}$ the Fourier's coefficient

The matrix M is like in the alpha version, each element are a term of the Fourier expansion at the coordinates of the same line that $\lambda_{h,b,t,tb,bh,th}$. That mean for the first line we have the coordinates of λ_b . We can compute the coefficient P_i with the Cramer's rules :

$$P_i = \frac{\det(M_k)}{M}$$

$$M_k = (m_{i,j,k}) \text{ with } m(i,j,k) = \begin{cases} m_{i,j} & \text{if } j \neq k \\ \lambda_{h,b,t,tb,bh,th} & \text{if } j = k \end{cases}$$

With these coefficients we can compute the potential for any point therefore plot the color graph, the 3D graph and the 1D cuts for each symmetry sites.

3.2 Program

Like in the alpha version all of those program are already commented but I drew a diagram to explain how those program in the Beta folder works :

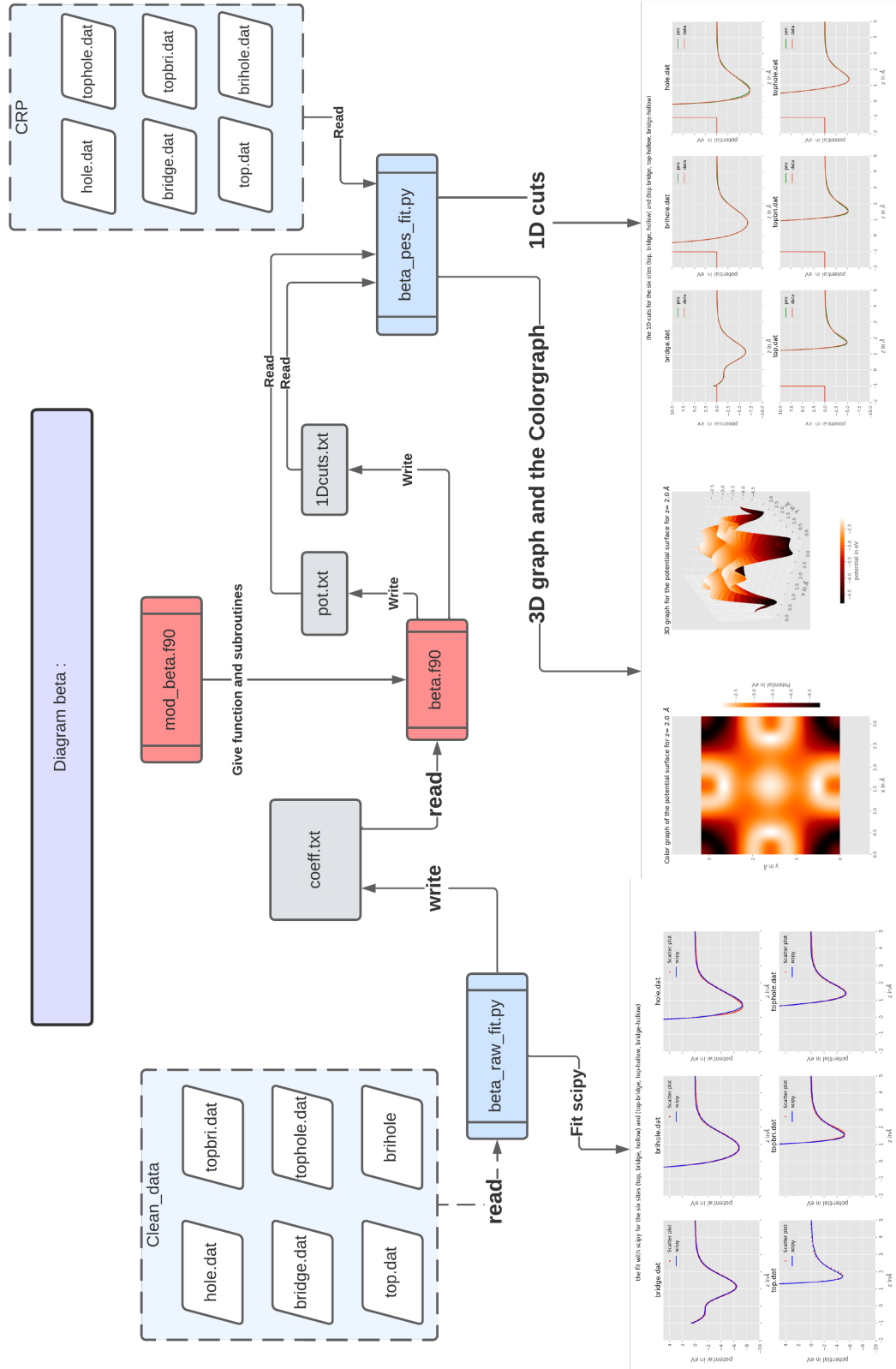


Figure 6: schema summarizing the alpha program

Those program in this folder works like in the alpha , so I will not explain it like in the alpha because the only difference is in the folder "Clean data" we have the raw data from all the symmetry sites.

The program "beta.f90" don't need to be explained because it perform the same calculations than the file "alpha.f90", the main difference his the dimensions of the array use to manipulate the computation because we have 8 parameter coming from the modified Morse potential.

3.3 Result

To obtains the result you have to run those program in this order :

- "beta_raw_fit.py"
- "beta.f90" by write in the terminal "gfortran mod_beta.f90 beta.f90"
- "beta_pes_fit.py"

The raw fit was more complicated than in the alpha version because the potential is more complicated, so to obtains good fit i have specify an initial value of parameter. These values are the average of the values find by curves_fit without specifiy any initial parameter. For a and b after a study of the function I sew how the potential equation work, $f_{\alpha}(Z_{at})$ is like a commutator depend on Z , he has to be equal to one in the attractive part and zero in the repulsive part, to do that b has to be close to $-r_{eq}$ and $a = 1$. In the initial value I put the respectively good initial value for b for each sites.

I obtains for the raw fit :

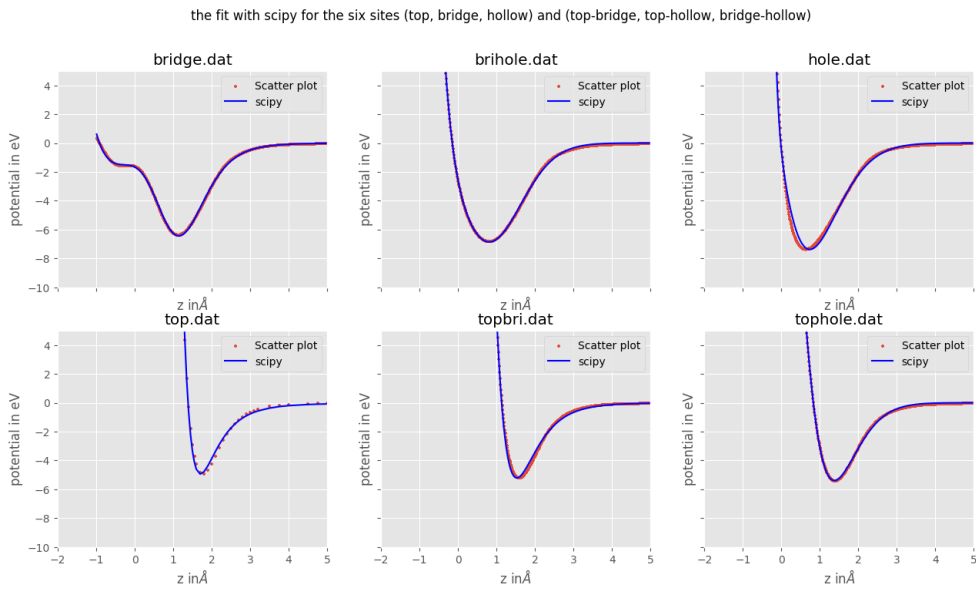


Figure 7: Subplot of the non linear fit of data from CRP script for atom/surface

We can see that beta is much better than the alpha fit, all the fit sites are very close to the data. Now we can plot the 3D and the color graph :

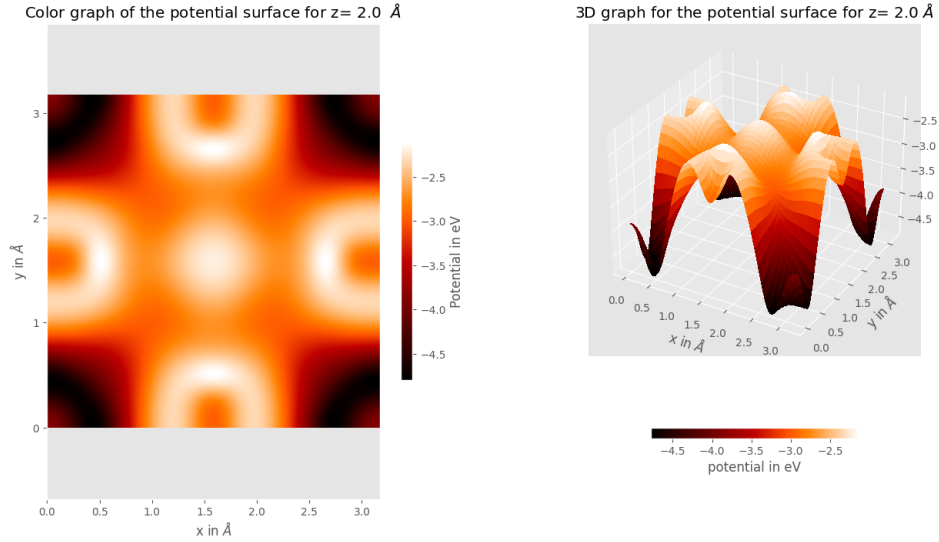


Figure 8: Subplot of the comparison between data from CRP script for atom/surface and our PES-fit

We can see the 3D graph aren't make sense, in the corner we don't have the higher potential like in the beta version, I think this part of my program is wrong but i don't understand why because we will see that the 1D cuts are good the only reasons that I have this error is I think the choice of b and a because they are specific for each sites so maybe this is not a good approximation for each coordinates in the whole unit cell.

Now we can look the 1D cuts and compare them to the CRP curves from "CRP-NW100" :

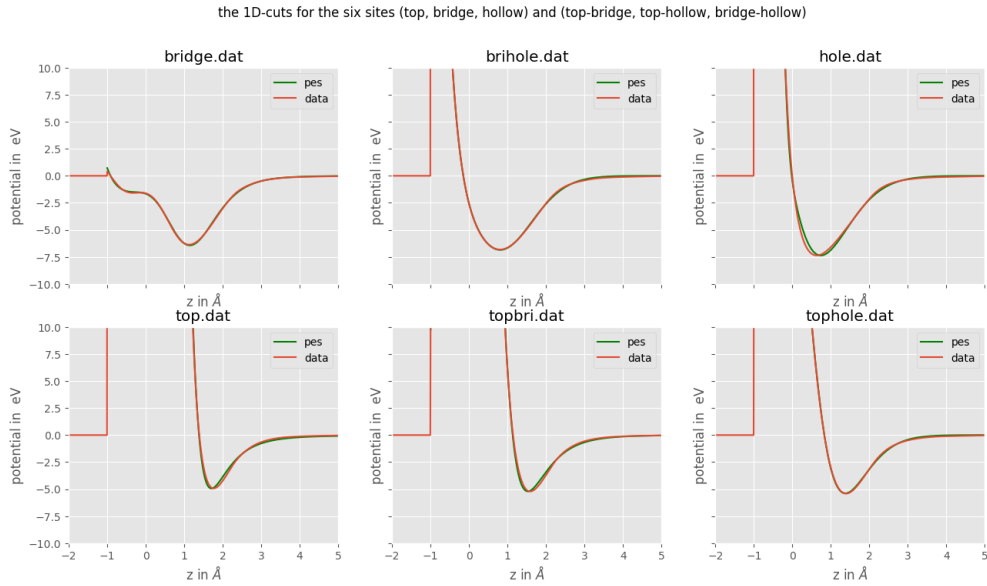


Figure 9: Subplot of the comparison between data from CRP script for atom/surface and our PES-fit

We can see the 1D cuts have very good behavior and fit very close to the CRP curves in the folder "CRP-NW100", even for the whole curve because we look a specific region (the most interesting I suppose).

4 Conclusion

In this project I have study the catalysis process that require molecular dynamics, we can obtains the force by taking the derivative of the potential. The study focus on the interactions between N2 and surface of tungsten W100. I have

perform this for two level of analysis :

-Alpha version : on the analysis I conclude on the wrong behavior of this model for all the symmetry sites, I expected the good behavior of this model for the high symmetry sites but even for those graph the model is not close to the data.

-Beta version : on the analysis I conclude on the very good behavior of this for all the sites by taking a modified version of the Morse potential, the parameter alpha depend on z that allows set the good curving of the potential for the repulsive and attractive part.

-Golden version : I didn't perform the golden version because this take me to long to have CRP curves for molecules/-surface, I only success to running the script to obtains the value of potential of a given couple of coordinates.

This project was very interesting, he made me want to learn more about the subject, especially about going further by studying molecular dynamics.