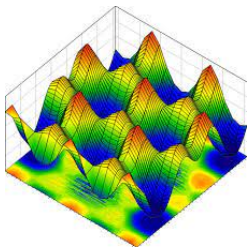
The University of Franche-Comté

Master CompuPhys - Fortran practical pool

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



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I 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 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 : N2/W(100) interaction with the LEPS molecule/surface potential

II 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.

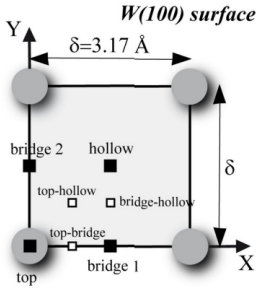

Figure 1: The (100) surface of the tungsten (atom in gray circle) with black squares the high symmetry sites and the gray squares the lower symmetry sites.

II.1 Theory

The potential use in this part is :

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

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 :

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

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

$$\begin{pmatrix}\lambda_h\\ \lambda_b\\ \lambda_t\end{pmatrix} = \underbrace{\begin{pmatrix}1 & cos\frac{2\pi 0.5}{\delta}+cos\frac{2\pi Y_h}{\delta} & cos\frac{2\pi(0.5+Y_h)}{\delta}+cos\frac{2\pi(0.5-Y_h)}{\delta}\\ 1 & cos\frac{2\pi X_b}{\delta}+cos\frac{2\pi Y_b}{\delta} & cos\frac{2\pi(X_b+Y_b)}{\delta}+cos\frac{2\pi(X_b-Y_b)}{\delta}\\ 1 & cos\frac{2\pi X_t}{\delta}+cos\frac{2\pi Y_t}{\delta} & cos\frac{2\pi(X_t+Y_t)}{\delta}+cos\frac{2\pi(X_t-Y_t)}{\delta}\end{pmatrix}}_{M} \times \begin{pmatrix}P_0\\ P_1\\ P_2\end{pmatrix}$$

with :

- $\lambda_{h,b,t}$ a coefficient between D, α, r_{eq}.
- h, b, t the site name, respectively hollow, bridge and top.
- $0.5_{h,b,t}$ 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 :

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

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

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.

II.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 have do a schema to explain how the programs communicate :

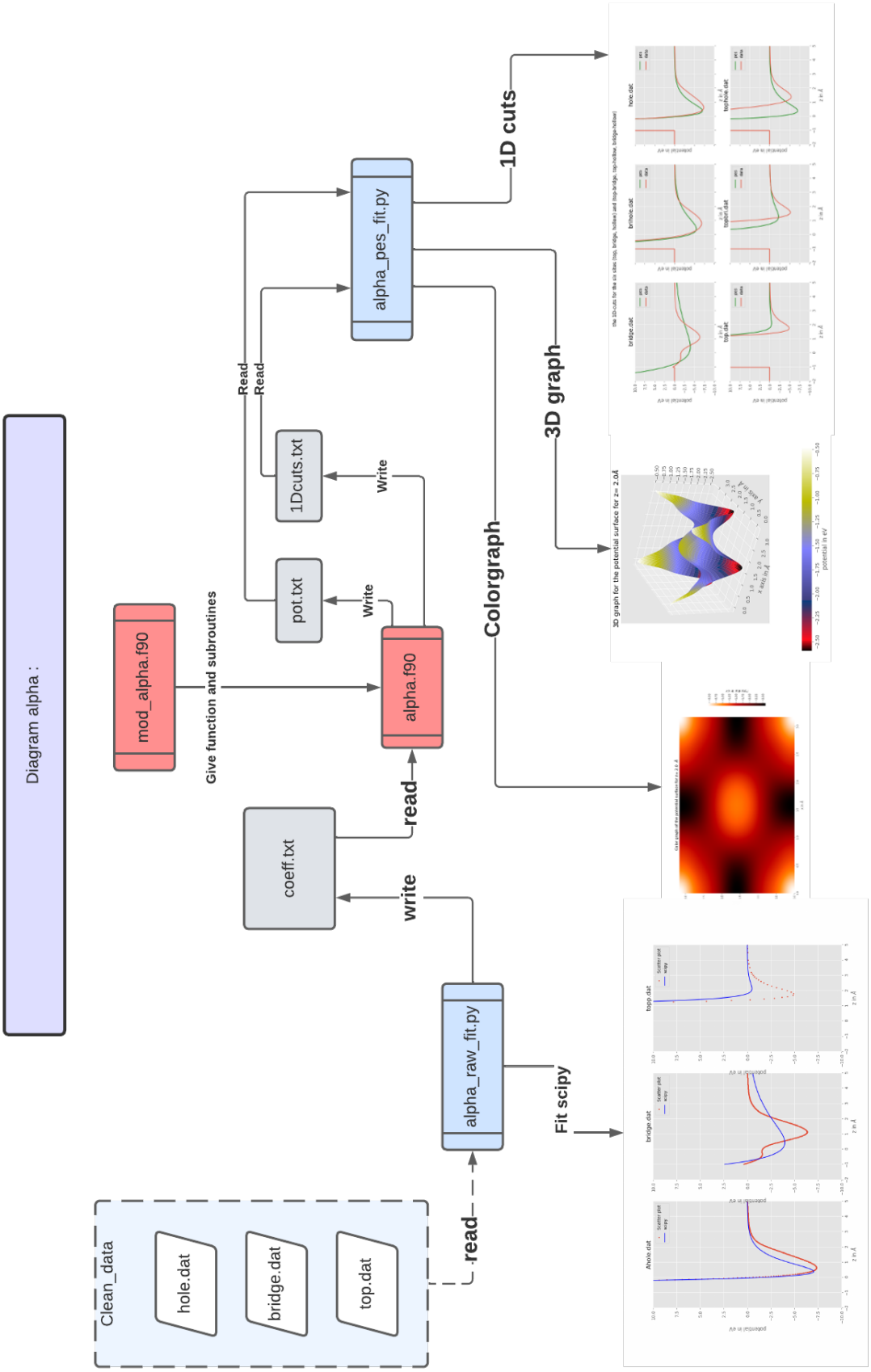

Figure 2: schema summarizing the alpha program

III Beta Version :

IV Theory

$$\begin{pmatrix} 1 & cos(2\pi 0.5) + cos(2\pi 0.5) & cos(2\pi(0.5+0.5) + cos(2\pi(0.5-0.5)) & cos(4\pi 0.5) + cos(4\pi 0.5) & cos(2\pi(2*0.5+0.5)) + cos \end{pmatrix}$$