

Numerical project

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

1 . Project description

1.1 Context

Heterogeneous catalysis is a major type of catalysis since about 90% of industrial chemical processes occur on solid catalysts. When considering heterogeneous processes between solid and gas phases, various elementary reactions have to be studied consisting of adsorption mechanisms (atomic and molecular, the latter can be dissociative or not), recombination mechanisms and desorption mechanisms (atomic and molecular). Such processes can be investigated by molecular dynamics (MD) simulations provided you know the potential energies involved. Even in the case of a simple system (e.g. atom/surface), several dimensions have to be considered to fully know the potential energies of the system also known as the potential energy surface (PES). For instance if the surface is considered as rigid, 3 dimensions must be taken into account for atom/surface system according to the positions of the atom over the surface whereas 6 dimensions are required for diatomic molecule/surface system according to the positions of the center of mass of the molecule over the surface and to the molecular internal degrees of freedom.

Knowing that gas/surface dynamics involves reactive processes, it is not possible to use non-reactive conventional PES available in classical MD software. Instead of that, numerical or analytical models have to be employed to build his own reactive multidimensional PES. The building of such PES is based on the knowledge of a sufficient number of potential energies that can be calculated by solving the electronic Schrödinger equation within the Born-Oppenheimer approximation using *ab-initio* methods.

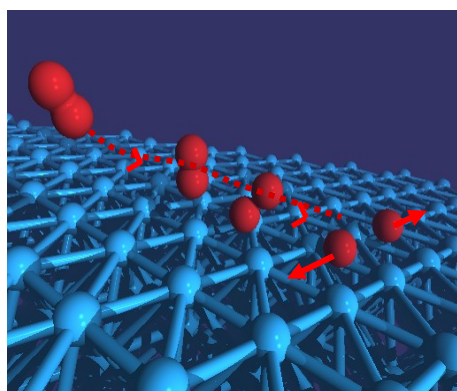


Figure 1 Illustration of a dissociative molecular process onto a solid surface

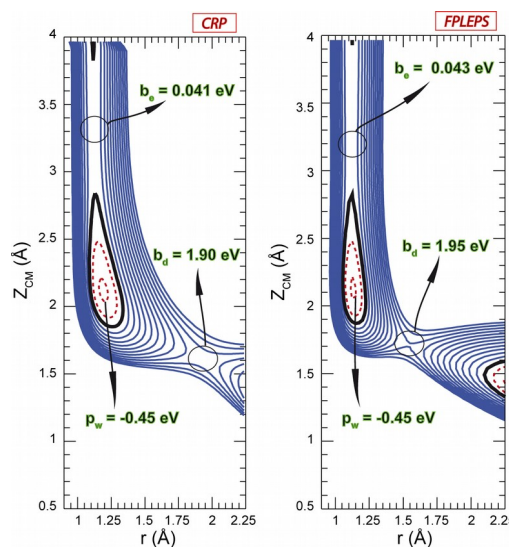


Figure 2 Contour plots of 2D-cuts obtained with two PES models (CRP and FPLEPS model) for $N_2/W(100)$ system
(from Chem. Phys. 367 (2010) 136-147)

1.2 Aim of the project

The aim of this project is to build a multidimensional potential energy surface to describe N-N₂ interacting with the tungsten surface, specifically for the crystallographic plane W(100). The PES will be based on an analytical model called the LEPS (London Eyring Polanyi Sato) model (see section 3). A numerical model (called CRP model, from *Surf. Sci.* 556 (2004) 129) is provided for the N₂/W(100) system and will be used to extract the required potential energies to fit the various parameters of the LEPS model. The CRP-PES will also be used as a reference model to compare the quality of the LEPS-PES.

The PES program will be developed in three steps corresponding to three advanced states of the PES:

- a) 3D-PES for N/W(100) atom-surface (alpha version)
- b) Improved version of the 3D atom-surface potential (beta version)
- c) 6D-PES for N₂/W(100) molecule-surface (gold version)

2 . Program specifications

2.1 Development environment

The programs defining the PES and allowing to generate the various cuts of the PES will be written in Fortran90 language. All others scripts allowing to perform the fitting procedure could be done in any coding languages (python, fortran, C...) or with any software (gnuplot, veusz, origin...).

N.B. The provided scripts for the CRP potential are written in Fortran77. No modifications should be done in those programs except for the plotting scripts that can be rewritten in Fortran90.

2.2 Deliverables description

To understand how to build the LEPS potential, please read carefully the section 3 which outlines the form of this analytical function.

➤ CRP-PES:

- Before to start the building of the LEPS potential, the very first step will consist to extract potential energies from the provided CRP-PES for various positions of N and N₂ onto W(100) surface. Please read the README file to know how to generate potential energies from the CRP-PES scripts (energies are in eV and distances are in Å). 1D-cuts or 2D-cuts could then be plotted for the following configurations:

- N/W(100) system: potential energy as a function of the N/W distance for three high-symmetry sites (cf. Figure 3), namely N atom located above the top, bridge and hollow sites.

- N₂/W(100) system: potential energy as a function of r and Z_{CM} for N₂ above the top, bridge and hollow sites with angular orientations $\theta=90^\circ$ and $\phi=0^\circ$ (cf. Figure 4 for the definition of the molecular coordinates).

- Find the global minimum on the CRP-PES for the atom/surface and molecule/surface by associating the energy barrier to reach this energy minimum.

➤ The alpha version:

In this first step, the objective is to develop a simplified 3-dimensional potential to describe the N/W(100) interactions. Here are the steps to follow:

- (a) Perform non-linear fittings on three high symmetry sites (top, bridge, hollow sites) to obtain the three parameters of the Morse potential (D , α , r^{eq}).
- (b) Deduce the 3 Fourier coefficients P_i for each Morse parameters by solving a system of linear equations (use of the Fourier expansion up to the second order).
- (c) Write the 3D-PES script.

- (d) Test your script by plotting the 1D-cuts for the three high symmetry sites (top, bridge, hollow) and for three lower symmetry sites (top-bridge, top-hollow, bridge-hollow). Find also the global minimum of the LEPS-PES.
- (e) Compare the LEPS curves with the CRP ones by representing them on the same figure. Calculate an estimation of the mean error (and eventually of the mean deviation) for every sites considered in the previous point with respect to the CRP potential energies.

➤ **The beta version:**

In this version, a modified Morse potential is used to better represent the attractive and repulsive parts of the atom/surface interactions (see section 3.2). Moreover, six surface sites will be considered in the Fourier expansion. Here are the additional steps:

- (a) Perform non-linear fittings on six sites: high symmetry sites (top, bridge, hollow) and lower symmetry sites (top-bridge, top-hollow, bridge-hollow) to obtain the eight parameters of the modified Morse potential ($D, r^{eq}, \alpha_{rep}^0, \alpha_{rep}^1, \alpha_{att}^0, \alpha_{att}^1, a, b$).
- (b) Deduce the 6 Fourier coefficients P_i for each modified Morse parameters by solving a system of linear equations (use of the Fourier expansion up to the fifth order).
- (c) Refresh the 3D-PES script.
- (d) Take up the analysis done in (d) and (e) of the previous section with the improved 3D-PES function.

➤ **The gold version:**

The final version is expected to build the 6-dimensional potential to describe the $N_2/W(100)$ interactions. The 6D-PES is based on a slightly modified LEPS model as described in section 3.3. The final requirements are:

- (a) Perform a non-linear fitting on the isolated N_2 molecule potential by taking the same modified Morse potential used for the atom/surface potential. Potential energies for N_2 molecule are given in the file "N2morse.dat". Give the binding energy and the equilibrium distance for N_2 and compare to the experimental values that can be found in literature.
- (b) Write the 6D-PES script to prepare the 2D fittings. Note that only two parameters are missing here to fully determine the 6D-PES: the Sato parameters $(\Delta_{NW}, \Delta_{N_2})$ which will be determined in the next step.
- (c) Perform new fittings on (r, Z_{CM}) 2D-cuts for N_2 above the three high symmetry sites with CRP data generated in the CRP-PES section. Two Sato parameters for each high symmetry sites should be calculated. These 2D fittings should allow to represent the potential energy barriers as best as possible.
- (d) Deduce the 3 Fourier coefficients P_i for each Sato parameters by solving a system of linear equations. Be careful here that the Fourier expansion is expressed as a function of (X_{CM}, Y_{CM}) as we are in the molecule/surface case.
- (e) Update the 6D-PES script with these new Fourier coefficients.
- (f) Plot some (r, Z_{CM}) 2D-cuts for arbitrary configurations and compare with those obtained from the CRP-PES. Discuss the quality of the multidimensional PES built during the project and give suggestions for improvements.

3 . The analytical PES model

3.1 Molecular coordinates and surface sites

The crystallographic plane (100) of the bcc (body-cubic centered) tungsten is a square as represented in figure 3. The unit cell parameter δ calculated with *ab-initio* methods (here with DFT : Density Functional Theory) is equal to 3.17 Å. The high and lower symmetry sites are also depicted. The coordinates for these sites

can be expressed in crystal units. For instance, N atom above the hollow site means that $X_N=Y_N=0.5$ for any Z_N values (the center-of-mass coordinates $X_{CM}=Y_{CM}=0.5$ should be consider for the molecular case).

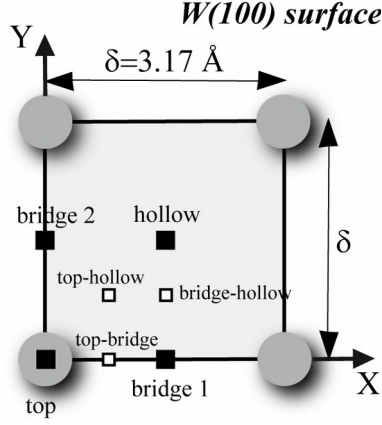


Figure 3 The (100) surface unit cell for a bcc crystal. Grey circles at the top of the square correspond to W atoms. The high symmetry sites are indicated by black squares and the white squares correspond to lower symmetry sites.

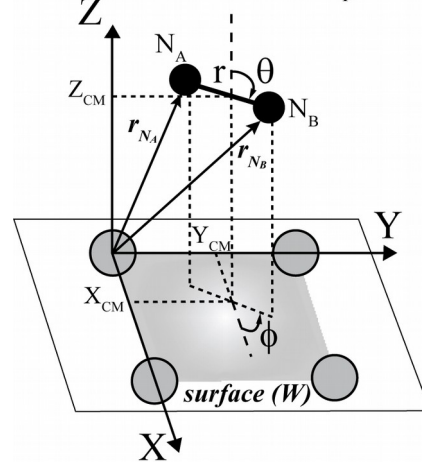


Figure 4 Molecular coordinates for the diatom-surface collision. (X_{CM}, Y_{CM}, Z_{CM}) are the center-of-mass coordinates for the AB diatom, the (r, θ, ϕ) coordinates are used to describe the rovibrational motion of the molecule.

Figure 4 shows the 6 dimensions to be considered in the molecule/surface system. (X_{CM}, Y_{CM}, Z_{CM}) are the center-of-mass coordinates of the molecule relative to the surface. (θ, ϕ) are respectively the polar and the azimuth angles defining the rotation coordinates and (r) is the interatomic distance of the diatomic molecule defining the vibration coordinate.

3.2 The atom/surface LEPS potential

In conventional LEPS potentials, the atom-surface interactions are modeled with a Morse function:

$$V^{3D}(\mathbf{r}_{at}) = D \left[\exp(-2\alpha(Z_{at} - r^{eq})) - 2 \exp(-\alpha(Z_{at} - r^{eq})) \right] \quad (1)$$

where \mathbf{r}_{at} is the position vector of the atom (N in this project) and Z_{at} is the distance of the atom with respect to the solid surface (W in this project). D , α , r^{eq} are the Morse parameters, D being the potential energy well depth, α defining the range of the potential and r^{eq} being the equilibrium distance between the atom and the solid surface.

Due to surface corrugation, the potential varies by translation of the atom along the surface. Then, a periodic dependence in (X_{at}, Y_{at}) is introduced in the three Morse parameters with a Fourier development. For the (100) symmetry of a bcc crystal, the Fourier expansion is defined to the fifth order as:

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

Each Morse parameter is described with the above Fourier expansion where P_i are the Fourier coefficients and δ is the unit cell parameter defined in figure 3. The P_i coefficients are obtained by solving a system of linear equations defined according to the values of (X_{at}, Y_{at}) coordinates of the chosen symmetry sites. For instance, in the alpha version, three high symmetry sites are chosen (top, bridge, hollow) with well-

defined (X_{at}, Y_{at}) coordinates in crystal units. In that case, we only consider the Fourier expansion to the second order, i.e. by determining the P_0, P_1, P_2 coefficients.

In the beta version, a modified Morse potential is used and defined by introducing a Z_{at} dependence for the α parameter. That modification leads to a better description of the two branches (attractive and repulsive) of the atom-surface interactions:

$$\alpha(Z_{at}) = (1 - f_\alpha(Z_{at}))(\alpha_{rep}^0 + \alpha_{rep}^1 \times Z_{at}) + (f_\alpha(Z_{at}))(\alpha_{att}^0 + \alpha_{att}^1 \times Z_{at}) \quad (3)$$

$\alpha_{rep}^0, \alpha_{rep}^1, \alpha_{att}^0, \alpha_{att}^1$ describe respectively the repulsive and attractive parts of the atom-surface potential. The switching function f_α allows the connection between the two branches at the vicinity of the potential energy minimum:

$$f_\alpha(Z_{at}) = \frac{1}{2}(1 + \tanh(a \times Z_{at} + b)) \quad (4)$$

The a and b terms are chosen to get a connection as smooth as possible. All these new parameters are also periodic function of (X_{at}, Y_{at}) according to the above procedure.

3.3 The molecule/surface LEPS potential

The LEPS potential was originally developed for gas-phase triatomic system and was then adapted to the gas-surface reactions (see *J. Chem. Phys* 63 (1975) 2340). The 6D LEPS-PES is expressed as a function of the two vectors $\mathbf{r}_{at1}(X_{at1}, Y_{at1}, Z_{at1})$ and $\mathbf{r}_{at2}(X_{at2}, Y_{at2}, Z_{at2})$ referring the position of the first and second atoms constituting the gas molecule:

$$V^{6D}(\mathbf{r}_{at1}, \mathbf{r}_{at2}) = U_{1s}(\mathbf{r}_{at1}) + U_{2s}(\mathbf{r}_{at2}) + U_{12}(\|\mathbf{r}_{at2} - \mathbf{r}_{at1}\|) - \sqrt{Q_{12}^2(\|\mathbf{r}_{at2} - \mathbf{r}_{at1}\|) + (Q_{1s}(\mathbf{r}_{at1}) + Q_{2s}(\mathbf{r}_{at2}))^2 - Q_{12}(\|\mathbf{r}_{at2} - \mathbf{r}_{at1}\|)(Q_{1s}(\mathbf{r}_{at1}) + Q_{2s}(\mathbf{r}_{at2}))} \quad (5)$$

where U_i and Q_i ($i=1s, 2s, 12$ stands for interactions between atom1/surface, atome2/surface and atom1/atom2 respectively) are the Coulomb and exchange integrals for a two-body system. Analytical expression for these integrals have been proposed:

$$U_i = \frac{D_i}{4(1 + \Delta_i)} \left[(3 + \Delta_i) \exp(-2\alpha_i(r_i - r_i^{eq})) - (2 + 6\Delta_i) \exp(-\alpha_i(r_i - r_i^{eq})) \right] \quad (6)$$

$$Q_i = \frac{D_i}{4(1 + \Delta_i)} \left[(1 + 3\Delta_i) \exp(-2\alpha_i(r_i - r_i^{eq})) - (6 + 2\Delta_i) \exp(-\alpha_i(r_i - r_i^{eq})) \right] \quad (7)$$

with $r_i = \|\mathbf{r}_{at2} - \mathbf{r}_{at1}\|$ for $i=12$ and $r_i = Z_{at}$ for $i=1s$ or $i=2s$. The D, α, r^{eq} are the Morse parameters defined previously. The Δ_i parameters are the Sato parameters introduced to describe correctly the PES in the strong interactions region between the gas molecule and the solid surface. Their values greatly affect the location and the height of the potential energy barriers along reaction pathways. In the asymptotic conditions, i.e. when one of the three-body (atom1, atom2, surface) is separated from the two others, only subsist in the V^{6D} function the U_i and Q_i terms corresponding to the interacting bodies. Let us give an example where the atom2 is far from the two others bodies, then the potential becomes:

$$V^{6D}(\mathbf{r}_{at1}, \mathbf{r}_{at2}) = U_{1s}(\mathbf{r}_{at1}) + Q_{1s}(\mathbf{r}_{at1}) = V^{3D}(\mathbf{r}_{at1}) \quad (8)$$

It is easy to check that this sum is indeed equal to the Morse potential as stated in equation 1. This feature ensures that the LEPS-PES correctly describes the various asymptotic conditions which can be encountered during a reactive process.

4 . The analytical PES model

For the main part of the project, the Fortran coding does not require specific algorithm. Nevertheless, some library available in numerical recipes (in Fortran90) can be used to solve systems of linear equations (e.g. LU decomposition). Edition of numerical recipes can be easily found on the web.