

Computational Chemistry 2 – Chapter 5

Molecules adsorption on surface

There is (almost) always molecules on the surface. Already at very low pressures the molecules collide to the surface. The collision number is

$$Z_c = \frac{1}{A} \frac{dN_c}{dt} = \frac{\rho v_{ave}}{4} = \frac{p v_{ave}}{4kT} = \frac{p}{(2\pi mkT)^{1/2}} = \frac{p N_A}{(2\pi MRT)^{1/2}}$$

Where p is the gas pressure, m is the mass of the molecule and T is temperature. The collision number is usually very large

For Ar ($m=39.95$ amu= 39.95 g/mol), $p=1.01325 \cdot 10^5$ Pa

$$Z_c = 2.45 \cdot 10^{27} \text{ m}^{-2} \text{ s}^{-1}$$

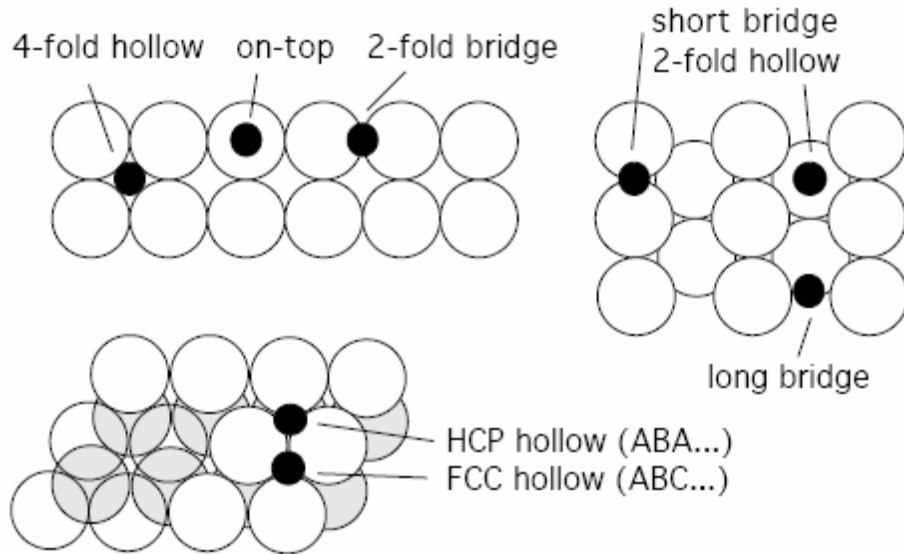
If the area is 1 nm^2 then there will be $Z_c \cdot A$ collisions,

$$2.45 \cdot 10^{27} \text{ m}^{-2} \text{ s}^{-1} \cdot 10^{-18} \text{ m}^2 = 2.45 \cdot 10^9 \text{ s}^{-1}$$

This means one collision at every $4.1 \cdot 10^{-10}$ s. In metal one atom area is ca. 0.1 nm^2 , so for each atom there will be ca. $2 \cdot 10^8$ collisions per sec. If we assume that the atom/molecule will attach to the surface with probability of 0.1 so the surface will be covered in 10^{-7} s ! If we want to study clean surface the experiments need to be done at very low pressure. The UHV (Ultra High Vacuum) pressure is lower than 10^{-7} Pa (or 10^{-12} atm.) In these conditions the surface can be "clean" for hours (assuming sticking probability of 1.0).

Adsorption sites

So where on the surface the molecules will adsorb? There are several sites on the surface. In the flat surface there are top, bridge and hollow sites. Near steps there are several different sites.



Note that the top/bridge/hollow sites can be very different and some times the naming can be a bit confusing. Experimentally it is not easy to determine where the molecules will bind. (Computationally it is rather easy.)

Naturally there can be several molecules on the surface. The coverage is computed with respect to the ideal surface unit cell and it is marked with θ . $\theta=0$ means that the surface is empty and $\theta=1$ means that every (ideal) unit cell have one atom/molecule. If the molecule is "large" the surface can saturate before $\theta=1$. If the molecules can adsorb forming several layers the θ can be larger than 1.

The thermodynamics of the coverage and pressure follows the Langmuir isotherm

$$\Theta = \frac{Kp}{1 + Kp}$$

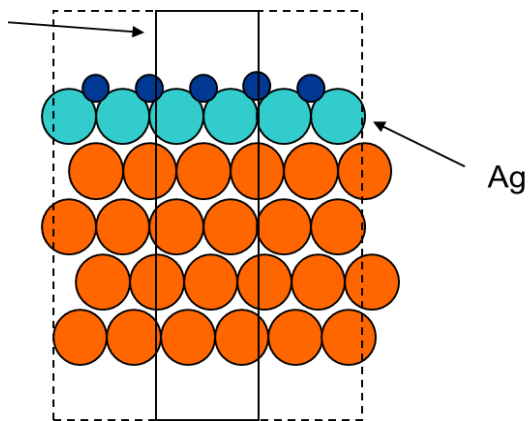
Where the K is a parameter of the model. It is the equilibrium constant between the molecule on the surface and in gas phase. If there are several gases then the isotherm is

$$\Theta_i = \frac{K_i p_i}{1 + K_1 p_1 + K_2 p_2}$$

The Langmuir isotherm is the simplest model. It does not take into account the molecular interactions but it is rather reliable at low coverages (and high temperatures).

Computational surface studies.

Computationally the surface studies are almost as easy as the bulk studies. The ASE library included to the GPAW code have several useful routines. (Try the ag tool to construct and visualize simple surfaces.) In the surface calculations one need to define the computational unit cell, the thickness of the atomic slab, the empty space and k-points.



Now the k-points are only in the xy-plane, $(2,2,1)$ or $(3,3,1)$, because the z-direction is not periodic. The calculations becomes quickly heavy since the computational cell is rather large. There should be at least 5 atomic layers, 8 Å of empty space and the surface unit cell should be at least (2×2) if molecules are adsorbed on the surface.

The surface energy is easy to compute. One need to remember that there are two surfaces in the system:

$$E_{\text{surf}} = (E_{\text{nmk}} - N E_{\text{atom,bulk}}) / 2$$

Also it is usually convenient to compute the surface energy per atom:

$$E_{\text{surf,at}} = E_{\text{surf}} / N_{\text{surf}}$$

Here N_{surf} is the number of atoms in one surface.

Usually the relaxation and simple reconstructions are easy to compute since in these cases a local atomic optimization is enough. If the reconstruction requires barrier crossing or change of the number of the surface atoms, it is very difficult to obtain the correct

structure without some experimental information. A good example is the missing row structures. In them the atom number is changing and this cannot be taken into account.

Excercise; Compute the Cu(111) surfaces relaxation using (1x1) surface cell and 5 atomic layers,

GAPW python code:

```
k = 4
cu = fcc111(symbol='Cu', size=[1, 1, 5],
            a=3.610, vacuum=8.000)

calc=(GPAW(h=0.2, nbands=-12, xc='PBE',kpts=(k, k, 1), occupations=FermiDirac(FD),
            mixer=Mixer(beta=0.10, nmaxold=4, weight=90.0),
            convergence={'eigenstates': 5.0e-6, 'density': 1.0e-4}, txt='cu111.out'))

cu.set_calculator(calc)
energy=cu.get_potential_energy()

calc.attach(calc.write,20,'Cu111-2.gpw')

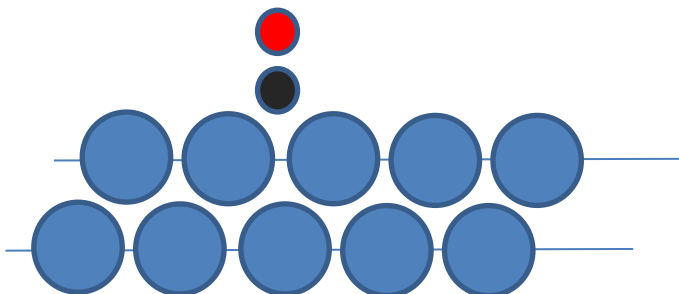
relax = QuasiNewton(cu, logfile='cu111.log')
relax.run(fmax=0.1)
```

Adsorptio computations are rather complex since we need to determine the molecules adsorption sites. The molecules adsorption energy is

$$E_{\text{bind energy}} = E(\text{surface+molec}) - E(\text{surface}) - E(\text{molec})$$

Naturally all the subsystems need to be optimized. The molecule will have several adsorption sites and it orientation can be non trivial. Also the molecule can also dissociate on the surface. Once the molecule has adsorbed to the surface a lot of information can be obtained from it. The adsorption site is interesting, the molecular vibrations can be computed and compared to experiments. The changes of intermolecular bond lengths can effect to the reactivity of the molecule.

One of the most studied molecule is CO. It internal vibrational frequency (C-O bond stretching) is very sensitive to its binding site. The CO is often used a probe molecule since its vibrations are easy to measure and they will tell quite a bit of the surface the CO is bond.



The CO vibrations on Pt(111) surface can be measured. Note that there are two stretching frequencies, one at ca. 255 and 225 meV. The higher one is associated to CO bond to single Pt atom. In the lower one surface molecule interaction is stronger and the frequency is lower. This is associated to CO that is double (or triply) bonded to the surface.

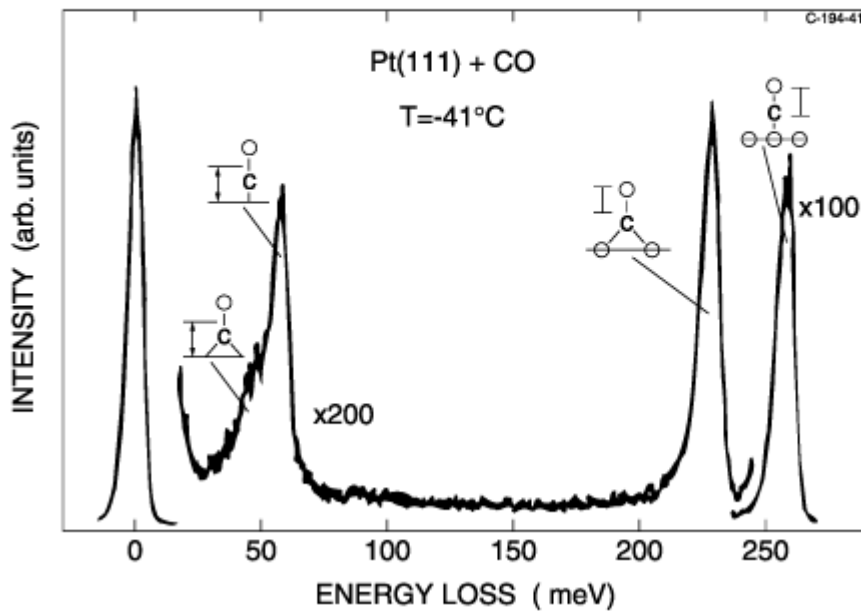


Figure: EELS spectrum of CO adsorbed on Pt(111).

Also the CO adsorption energies can be measured.

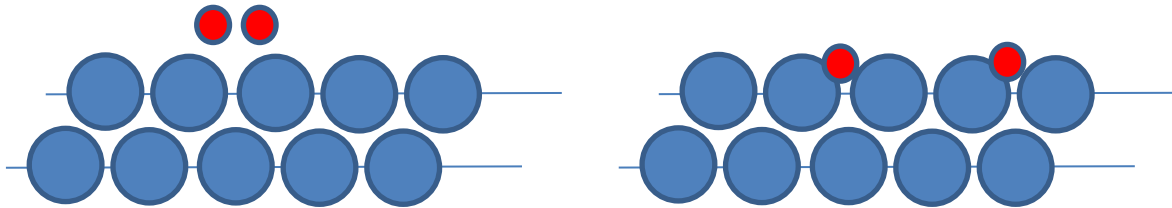
Summary of adsorption energies, E_b , of CO for different Cu adsorption sites determined from TDS. The numbers of nearest substrate neighbors of the adsorption site, NNN, is also included in the table.

Adsorption Surface	NNN	E_b (kJ/mol)
Terrace Cu(111)	9	47.3 ± 1.4
Terrace Cu(100)	8	51.1 ± 1.4
Atomic row Cu(110)	6	54.0 ± 1.4
Step edge Cu(211)	7	58.4 ± 1.4
Step edge Cu(221)	7	57.7 ± 1.4
Kink Cu(532)	6	56.8 ± 1.4
Defects Cu(100) sputtered	6-7	58.5 ± 1.4
Defects Poly-crystalline	6-7	58.2 ± 1.4

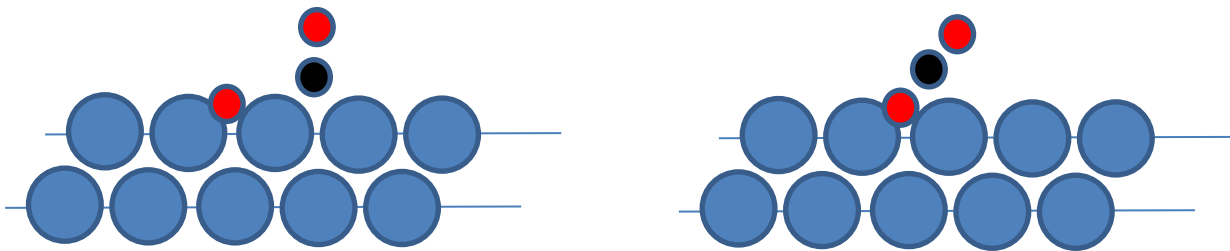
Lähde: Catalysis Letters Vol. 77, No. 1-3, 2001

Exercise 1: compute the relative adsorption probabilities.

One very important molecule that often dissociates is O₂. The dissociation depend on the surface and it is the first step to the oxidation of the surface. The atomic surface O is also important of surface oxidation reactions.



One of the simplest reactions if the CO oxidation: $O_2(g) + CO(g) \rightarrow 2O(s) + CO(s) \rightarrow O(s) + CO_2(g)$.



Computationally the adsorption energies are very sensitive to the XC-approximation. The LDA give clearly too high binding energies. The common PBE, PW91 functional gives reasonable energies which are probably a bit too high. A corrected PBE, RPBE is rather common functions in surface calculations. With RPBE the binding energies are rather good, probably a bit under bonding. The binding energy depend also on the coverage.

supercell	θ (ML)	method	XC	dBE(eV)
3x2√3	1/12	VASP, USP	PW91	0.25
2x2	¼	Dacapo, USP	PW91	0.23
2x2	¼	Dacapo, USP	PBE	0.24
2x2	¼	Dacapo, USP	RPBE	0.16
2x2	¼	Dacapo, USP	LDA	0.45
c(4x2)	¼	VASP, USP	LDA	0.41

c(4x2)	¼	Dacapo, USP	PW91	0.23
c(4x2)	¼	VASP, USP	PW91	0.18
c(4x2)	¼	VASP, PAW	PW91	0.13

TABLE: Binding Energy at *fcc*- Relative to Atop-Site for Low-Coverage CO/Pt(111), Lähde: *J. Phys. Chem. B* **2001**, *105*, 4018-4025.

Next there is some numbers of H adsorption on Pt(111) surface. Also here there is quite large variations.

H at Pt(111) surface, 4x4 unit cell, H binding energy compared to H₂ molec

supercell	nH	method	XC	BE/H(eV)
4x4	8	CP2K, Gaus, GTH pseudo	PBE	-0.413
same	12	same	PBE	-0.406
	16		PBE	-0.410
	8		PBE + vdw	-0.514
	12		PBE + vdw	-0.507
	16		PBE + vdw	-0.510
	8		RPBE	-0.235
	12		RPBE	-0.225
	16		RPBE	-0.226
	16		XPBE	-0.239

Below the CO adsorption Ni atom in NiMg₈O₉ cluster with several very different GGA, hybrid GGA and meta-GGA functionals. Due to the cluster geometry so many functional can be used. As one can see the results varies quite a bit.

Source: *J. Chem. Phys.* 132, 104701 (2010); <http://dx.doi.org/10.1063/1.3340506>

Table VII. Calculated results for gas-phase CO (values in parentheses) and for C-down adsorbed CO on top of a Ni²⁺ site on the NiMg₈O₉ model of the Ni-doped MgO(100) surface. [The $\theta(\text{Ni-C-O})$ angle is in all cases close to zero degrees.]

Method	D _e without CpC (eV)	D _e with CpC (eV)	R(Ni-C) (Å)	R(C-O) (Å)
B3LYP	0.16	0.06	2.10	1.131
M06-L	0.55	0.44	1.96	1.139
M06	0.40	0.29	2.07	1.128
M05	0.20	0.09	2.11	1.132
SOGGA	0.99	0.82	1.83	1.153
PBE	0.62	0.48	1.88	1.152
PBEsol	0.93	0.77	1.84	1.153

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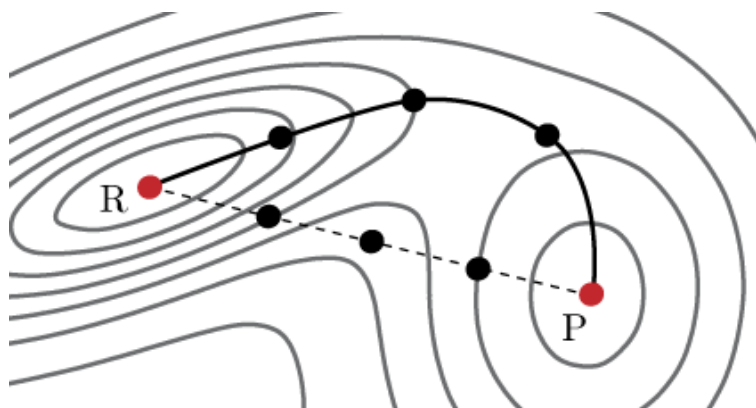
Method	D _e without CpC (eV)	D _e with CpC (eV)	R(Ni-C) (Å)	R(C-O) (Å)
revPBE	0.37	0.24	1.91	1.154
RPBE	0.35	0.23	1.92	1.155
TPSS	0.54	0.41	1.92	1.149
BP86	0.53	0.39	1.89	1.153
PBE0	0.29	0.18	2.07	1.128
TPSSh	0.39	0.27	1.99	1.139
MOHLYP	0.13	0.00	1.92	1.161
B97-2	0.17	0.07	2.09	1.129
B97-3	0.11	0.02	2.20	1.127
TPSSKCIS	0.50	0.37	1.92	1.149
MPWLYP1M	0.33	0.20	1.96	1.145
B1B95	0.26	0.14	2.10	1.126

Reaction barrier

The chemical reactivity is a very interesting topic and the surface reactions are no exception. In fact most of the industrial catalytically reactions happen on surfaces. The most common surface catalyst are the Platinum group metal (PGM), Pt, Pd, Rh, Ir etc.). There is an enormous amount of application of the surface reactions and thus they have been studied a lot. One of the new aspect of surface catalysis is to get rid of the PGMs since they are very expensive and in EU they are critical (they need to be imported and even globally the quantities are low). There are several research project that try to find replacement catalyst to PGM on various reactions. In these projects also computations are used to understand the reactions.

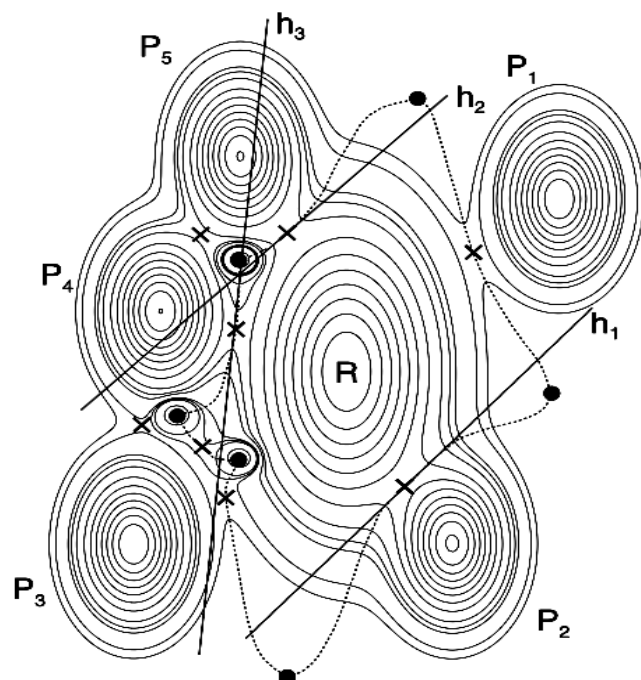
Now we need to take a quick look how the transition states can be found computationally. This has been discussed already in the Computational Chemistry I course. So we go through this rather quickly.

The transition state search algorithms are (much) more complex than minimization algorithms. There are several methods and here we concentrate to the NEB (Nudged Elastic Band) method. Here it is important to remember that points in these pictures always correspond to some real geometry of the atoms. In the NEB method a reaction path



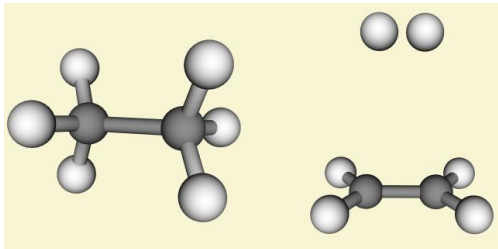
Schematic picture of a reaction path

Source: <http://www.quantumwise.com/documents/manuals/ATK-2008.10/chap.relax.html>



A picture of a more complex reaction. Here is one reactant R and several products P1...P5. The crosses are the transition states (TS). Note that there is two TS between R and P3. Also there are TS between the products. In principle the easiest path from R to P5 can go via P4.

Let us look a simple reaction: $C_2H_6 \rightarrow C_2H_4 + H_2$



Kuva: $C_2H_6 \rightarrow C_2H_4 + H_2$

We can now construct the initial reaction path as linear interpolation of the reactant and product coordinates:

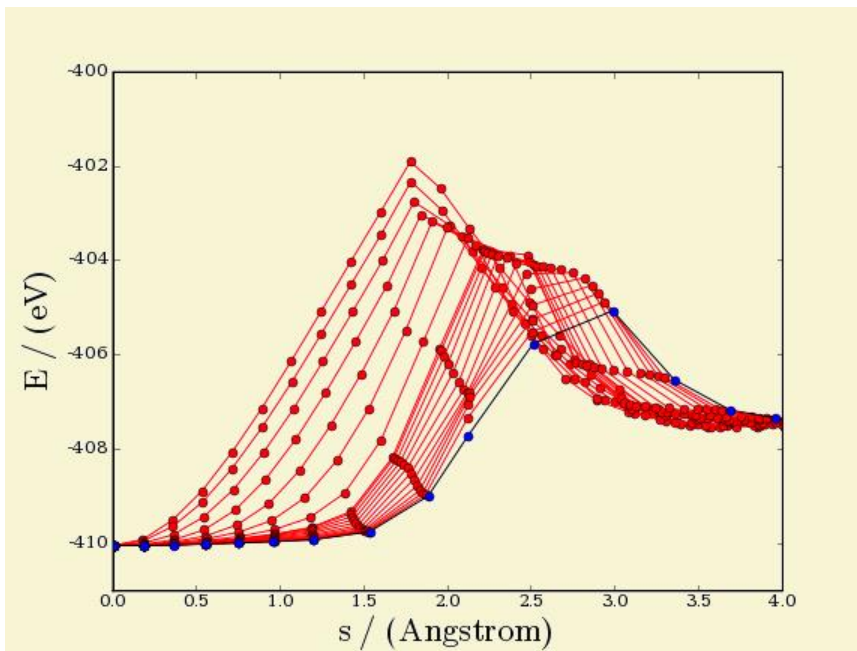
$$R_I(i) = [(N_{Neb}-i) * R_I(react) + i * R_I(prod)] / N_{Neb}$$

(The straight dotted line in the figure above). N_{Neb} is typically around 10. In the NEB methods there is a spring between the points R_I : $k(R_I - R_{I+1})^2$.

Now we need to minimize the energy of the whole path. In ideal case the original path slide to the correct path (solid line in the picture above).

Note that for stable algorithm only the perpendicular force of the energy and the parallel force of the spring are used. (The perpendicular and parallel forces are with respect of the NEB path.) See the added NEB document. (http://www.openmx-square.org/tech_notes/NEB.pdf)

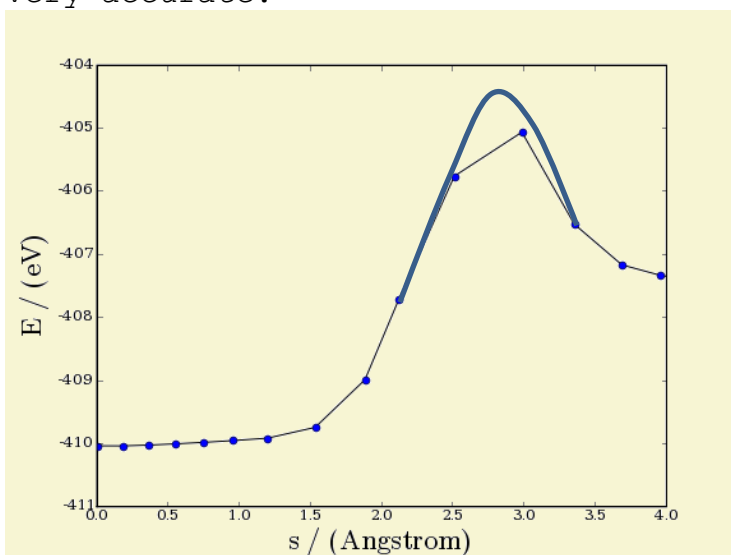
Now we can start the NEB:



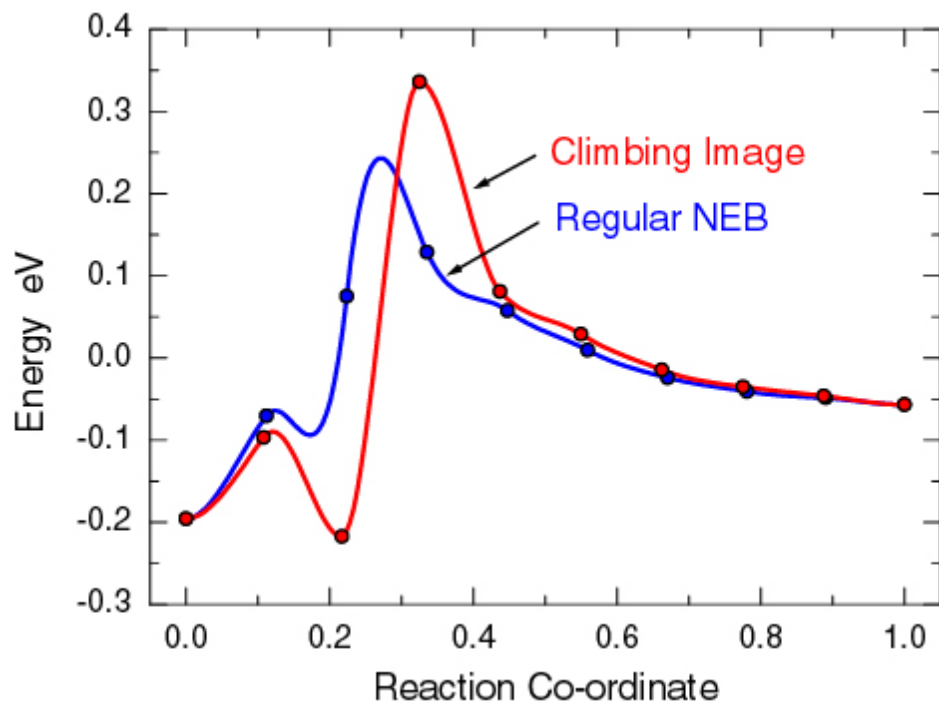
Kuva: NEB development during the iterations.

Due to the optimization nature of NEB the points tend to go towards the starting and end points. There will be only few points near the TS and it is very unlikely that the correct TS is any of the NEB points.

One can interpolate the maximum from the NEB data, but this is not very accurate.

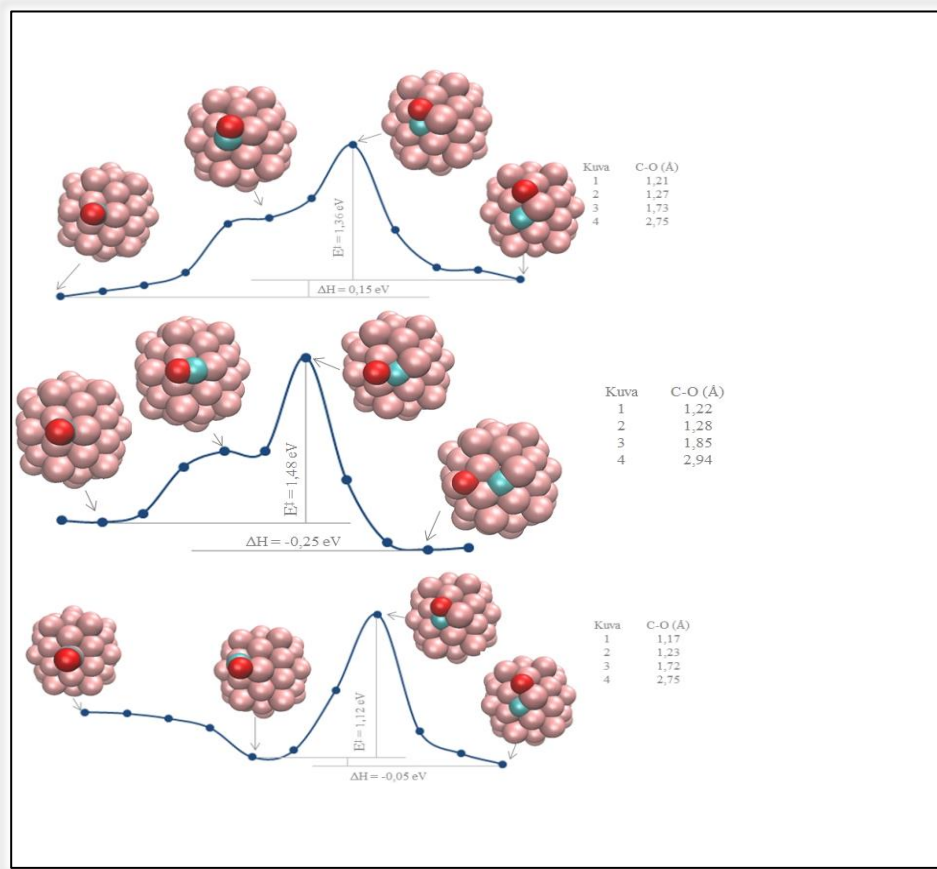


There are also several improved versions of NEB, like Climbing-Image-NEB. Also NEB can be restarted from any points near the maximum. In general it is not easy to find the transition state. Note also that the NEB will find the maxima of the atomic total energy, not the free energy, so the entropy need to be estimated separately. Also the NEB calculation are time consuming since every point in the path is a quantum mechanical calculation.



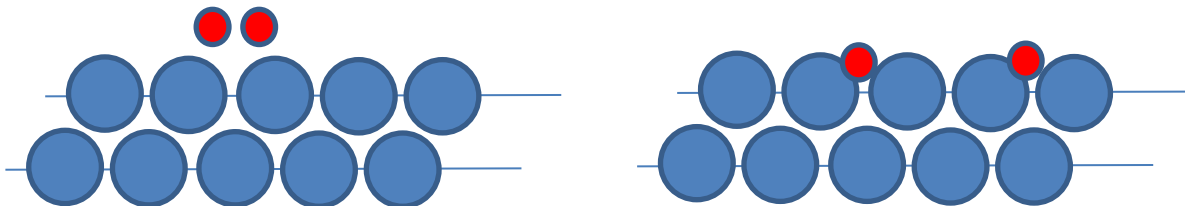
Source: <http://theochem.org/CompChem11f/NEBandQuantumHTST.pdf>

We have done a lot of NEB calculation on various systems. Below is an example of CO dissociation (CI-NEB) calculation on Fe78 cluster. Note that there are a new minima on one of the trajectories. This is fine since the starting geometry may not be the best minima for CO adsorption.



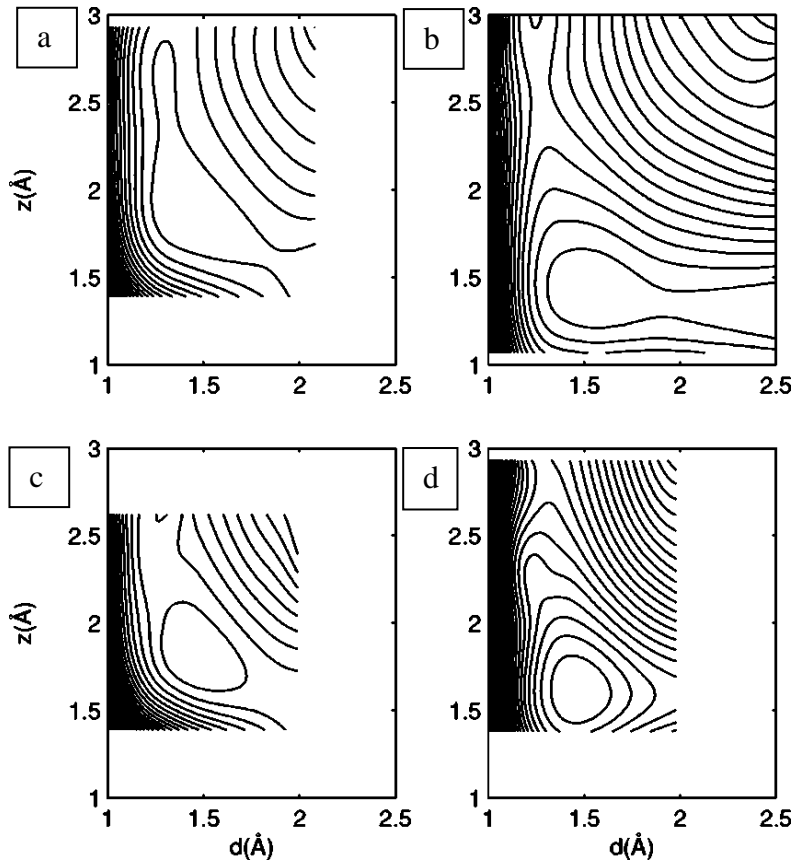
Oxygen dissociation on some metal surfaces

Oxidation and corrosion are very interesting phenomena but their investigation with ab initio methods are difficult. The reason is simple - there are so many chemical reactions that at atomic level the modelling is complex. On the other hand simpler problems like oxygen dissociation are doable. There one needs a model for the surface and an oxygen molecule.



We have studied O₂ dissociation on Al(111), Pd(111), Cu(100) and carbon nanotubes (CNT). The oxygen usually adsorbs horizontally so the dissociation can be describe with 2D elbow plot in which the height (z on the y-axis) and O-O bond length (d at the x-axis) are used as axis. The plotted value is the energy. The plot is usually presented a contour plot.

Below is an elbow plot for O₂ approaching to Cu(100) surface on different sites.



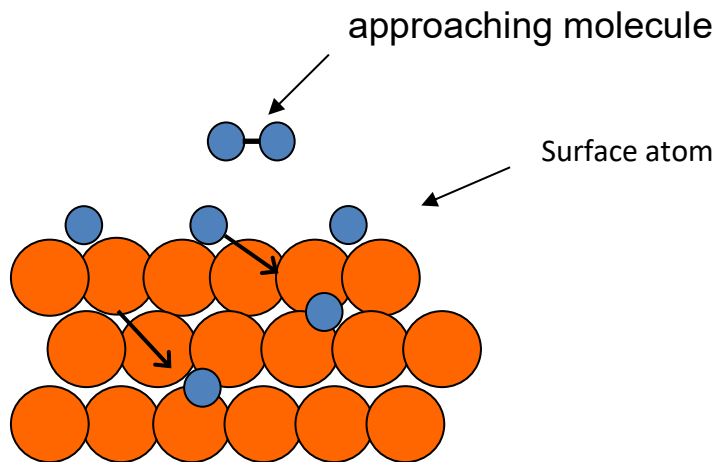
Here the two higher plot are related to dissociated molecule where there is only very small barrier. The O₂ bond length far away of the surface is ca. 1.2 Å. In picture a) the bond start elongate at height of ca. 1.8 Å and at height of 1.5 Å the bond is around 2 Å and the O₂ can be considered dissociated. In case b) the elongation happen much lower (ca. 1.4 Å). The picture c) and d) showed a stable pre-cursor state. In both the bond has elongated to ca. 1.5 Å.

The O₂ molecule can dissociate on several metal surfaces. If the O atom bond strongly to the surface the metal form

easily an oxide. This is the case in most of the metals. The noble and Pt group metals (Ag, Au, Pt, Pd) form an example. In case of some metals, like Na, K, Mg, Al etc., the reaction is explosive. It is interesting that many of the non-oxidizing metal are good (oxidation)catalysts. Naturally the not-so-strongly bound surface oxygen is very reactive and bond to other molecules. A classical example: CO oxidation on Pt or Pd.

Surface oxidation

Even most of the metals oxidizes the actual process is very complex and we can only touch some of the first steps. Naturally in the first step the molecules will dissociate to the surface. The next and more difficult step is the atoms diffusion under the surface. This usually have rather high barrier.



The study of the barriers is rather difficult, but the energies of surface and sub-surface atoms is much easier. The case of Cu is interesting: the oxygen atoms on the surface have strong repulsion so the when the coverage increases the energy become unfavorable. But is there are atoms both on and below the surface there is almost no repulsion and the coverage can increase up to 2.

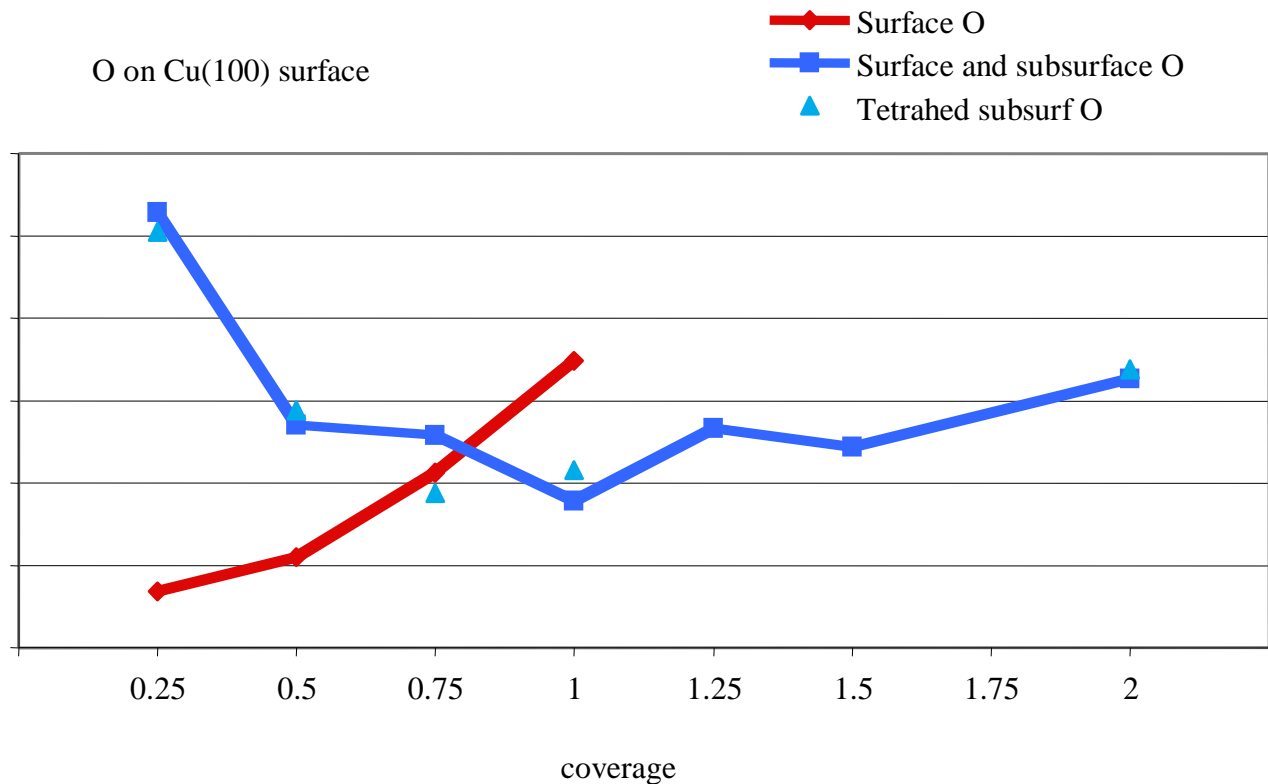
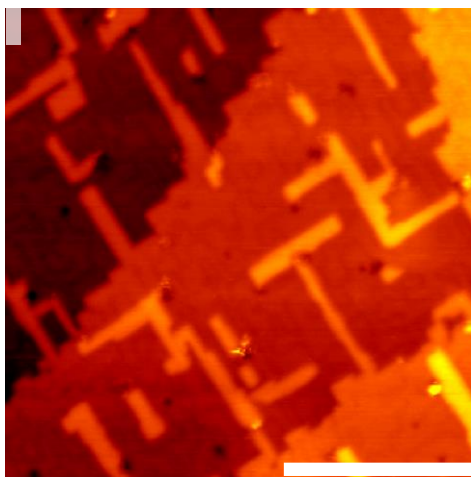


Figure: Cu(100) surface with different O coverage. At coverage 0.25 the surface is ideal but at higher coverages the surface have 'missing row' reconstruction.

Experimentally the Cu(100) surface oxidation is complex process. The Cu atoms from the 'missing row' reconstruction will form elongated islands. The experiments Mika Valden TUT.



Surface enrichment

In mixed metal systems the surface enrichment is very common phenomena. In it one of the components will enrich to the surface. Below is an example of the silver-copper mixture. Silver have somewhat larger lattice constant and in vacuum it will enrich to the surface. Because it is larger than Cu it will form a rare (9x2) structure.

The surface enrichment is rather easy to study computationally. One need to make a slab and modify the Ag positions in it and compare the energies.

θ/ML	Ag: 5% (eV)	Ag: 20 %
0.0	-0.55	-1.36
0.25	-0.31	+0.34
0.5*	+0.32	+1.41
0.75*	-	+2.46
1.0*	+1.23	-

Another interesting variant of the surface enrichment is the adsorbent induced enrichment. In vacuum the system can have one enrichment structure but with strong adsorbent like oxygen the Cu can replace the Ag. This phenomena has not been studied very much.

