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Qunatum Methods for Plasma-Facing Materials

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Quantum methods for plasma-facing materials

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Marseille, FRANCE

When ab initio calculations ?

Physical sputtering, high energy particles impinging ➡ **no use**

Molecular dynamics ➡ the systems DFT (*ab initio MD*) can investigate are several orders of magnitude smaller than classical MD

Quantum theory ➡ ➡ ➡ ***when chemistry*** is concerned because chemistry is essentially a problem of electrons (exchange of electrons, sharing electrons..)

♳ Fundamental mechanisms of hydrogen atoms retention and release

♴ Barrier of activation and Transition states (diffusion, trapping,..), QT gives the barrier to overcome, the problem of ***HOW*** is dynamics

♵ Structure of materials and alloys (C/Be/W)

♶ Electronic structure: DOS, spectroscopy .....

Quantum method

The time-independent Schrödinger equation $H\Psi = E\Psi$

For a many-body system where *H* is an **operator**

$$H = \sum_{i=1}^{n}\left(-\frac{1}{2}\Delta_i + V_{N_i}\right) + \sum_{i=1}^{n}\sum_{j<i}\frac{1}{r_{ij}}$$

The SE can be solved exactly for very few systems, for atoms and molecules the variational method allows to develop the approximate wave function Ψ in an orbital basis set φ (most often gaussian-type orbitals).

Hartree-Fock

The Hartree-Fock method makes four major simplifications:

* The Born-Oppenheimer approximation is inherently assumed. The full molecular wavefunction is actually a function of the coordinates of each of the nuclei, in addition to those of the electrons.

* Typically, relativistic effects are completely neglected. The momentum operator is assumed to be completely non-relativistic.

* The variational solution is assumed to be a linear combination of a finite number of basis functions. The finite basis set is assumed to be approximately complete.

* Each energy eigenfunction is assumed to be describable by a single Slater determinant, an antisymmetrized product of one-electron wavefunctions (i.e. orbitals).

Molecular orbital

$$\phi_i = c_{1i}\chi_1 + c_{2i}\chi_2 + c_{3i}\chi_3 + \cdots + c_{ni}\chi_n$$

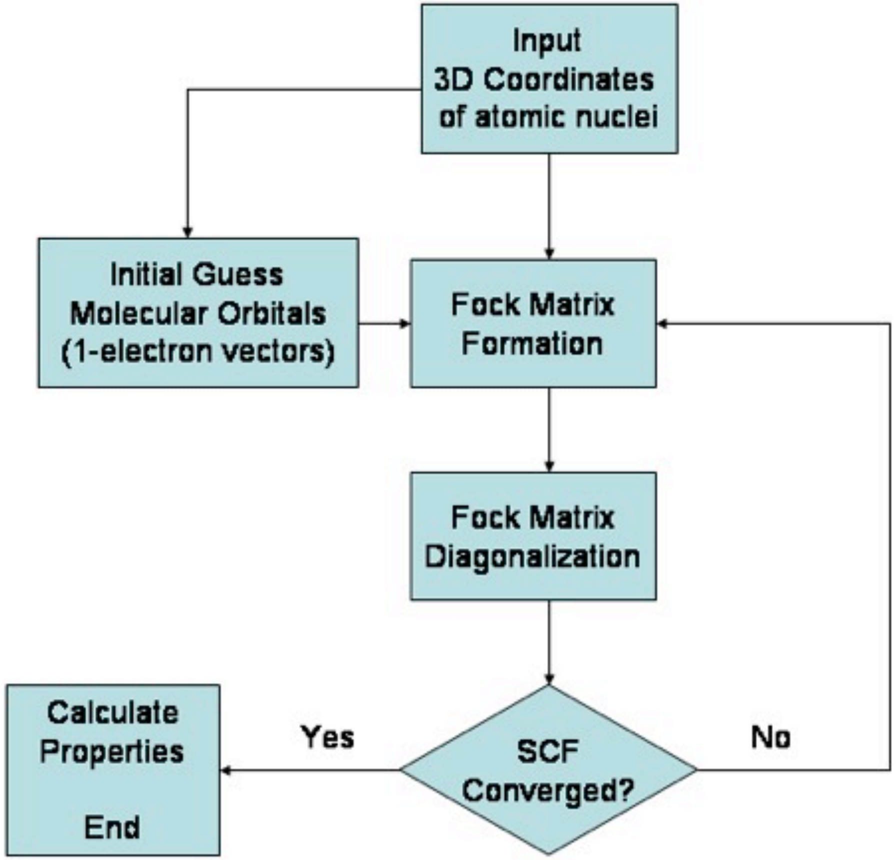
The ***Fock*** operator:

$$\hat{F}[\{\phi_j\}](1) = \hat{H}^{\text{core}}(1) + \sum_{j=1}^{n/2}[2\hat{J}_j(1) - \hat{K}_j(1)]$$

J: Coulomb (classical)
K: Exchange (quantum)

Correlation energy

$$\Delta E_{correl} = E_{exact} - \lim(E_{HF})_{basis}$$



Input
3D Coordinates
of atomic nuclei

Initial Guess
Molecular Orbitals
(1-electron vectors)

Fock Matrix
Formation

Fock Matrix
Diagonalization

SCF
Converged?

Yes

No

Calculate
Properties

End

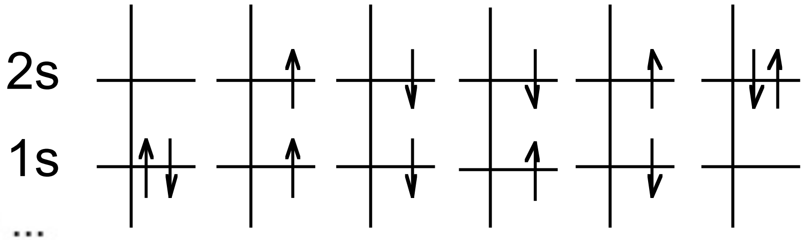
Calculating the correlation energy: Interaction of Configurations

Configuration interaction (CI) is a post Hartree-Fock method for solving the non-relativistic Schrödinger equation within the Born-Oppenheimer approximation for a quantum chemical multi-electron system. Mathematically, configuration simply describes the linear combination of Slater determinants used for the wave function. In terms of a specification of orbital occupation interaction means the mixing (interaction) of different electronic configurations

He ground state ($1s^2$)

He excited states:

$$\Psi = \sum_{I=0} c_I \Phi_I^{SO} = c_0 \Phi_0^{SO} + c_1 \Phi_1^{SO} + \ldots$$



The solution can be perturbation (Møller-Plesset, MP2) or variational (Full CI, CCSD, CCSD(T),..)

Problem: cutting the series?

Density functional theory

In DFT the key variable is the particle density , which for a normalized Ψ is given by

$$n(\vec{r}) = N \int \mathrm{d}^3 r_2 \int \mathrm{d}^3 r_3 \cdots \int \mathrm{d}^3 r_N \, \Psi^*(\vec{r}, \vec{r}_2, \dots, \vec{r}_N) \Psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N)$$

for a given ground-state electron density it is possible, in principle, to calculate the corresponding ground-state wave-function ➨ Ψ_0 is a unique functional of n(0). Every quantity O is a functional of n(0)

$$O[n_0] = \left\langle \Psi[n_0] \middle| \hat{O} \middle| \Psi[n_0] \right\rangle$$

In the Schrödinger equation

$$\hat{H}\Psi = \left[\hat{T} + \hat{V} + \hat{U}\right]\Psi = \left[\sum_i^N -\frac{\hbar^2}{2m}\nabla_i^2 + \sum_i^N V(\vec{r}_i) + \sum_{i<j}^N U(\vec{r}_i, \vec{r}_j)\right]\Psi = E\Psi$$

$$E[n] = T[n] + U[n] + \int V(\vec{r}) n(\vec{r}) \mathrm{d}^3 r$$

T(n) and *U*(n) are called ***universal functionals***, *V*(n) is called a non-universal functional, as it depends on the system under study

First, one considers an energy functional that doesn't explicitly have an electron-electron interaction energy term

$$E_s[n] = \left\langle \Psi_s[n] \middle| \hat{T}_s + \hat{V}_s \middle| \Psi_s[n] \right\rangle \qquad \hat{V}_s = \hat{V} + \hat{U} + \left(\hat{T} - \hat{T}_s\right)$$

Thus, one can solve the so-called Kohn-Sham equations of this auxiliary non-interacting system

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_s(\vec{r})\right]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r})$$

which yields the orbitals that reproduce the density of the original many-body system.

The effective single-particle potential can be written in more detail as:

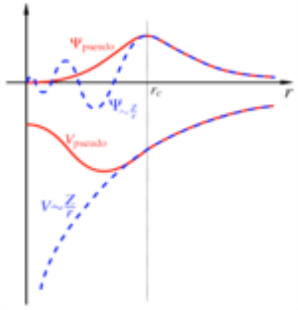
$$V_s(\vec{r}) = V(\vec{r}) + \int \frac{e^2 n_s(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} \mathrm{d}^3 r' + V_{\mathrm{XC}}[n_s(\vec{r})]$$

where the second term denotes the so-called Hartree term describing the electron-electron Coulomb repulsion, while the last term is called the exchange-correlation potential

The major problem with DFT is that the exact functionals for exchange and correlation are not known except for the free electron gas, therefore approximations must be found

Solid state DFT applications

Computational details



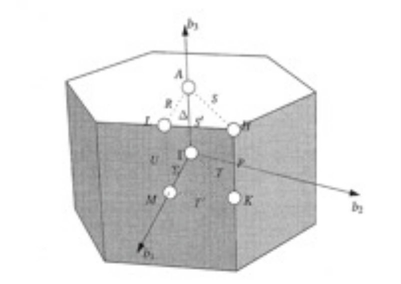
- *PBE* GGA functional + ultrasoft pseudopotentials and plane wave Bloch functions

- Systems ~ 100 atoms

- Energy profiles (PES): each configuration is fully optimized (BFGS gradient optimization) excepted the selected reaction coordinates.

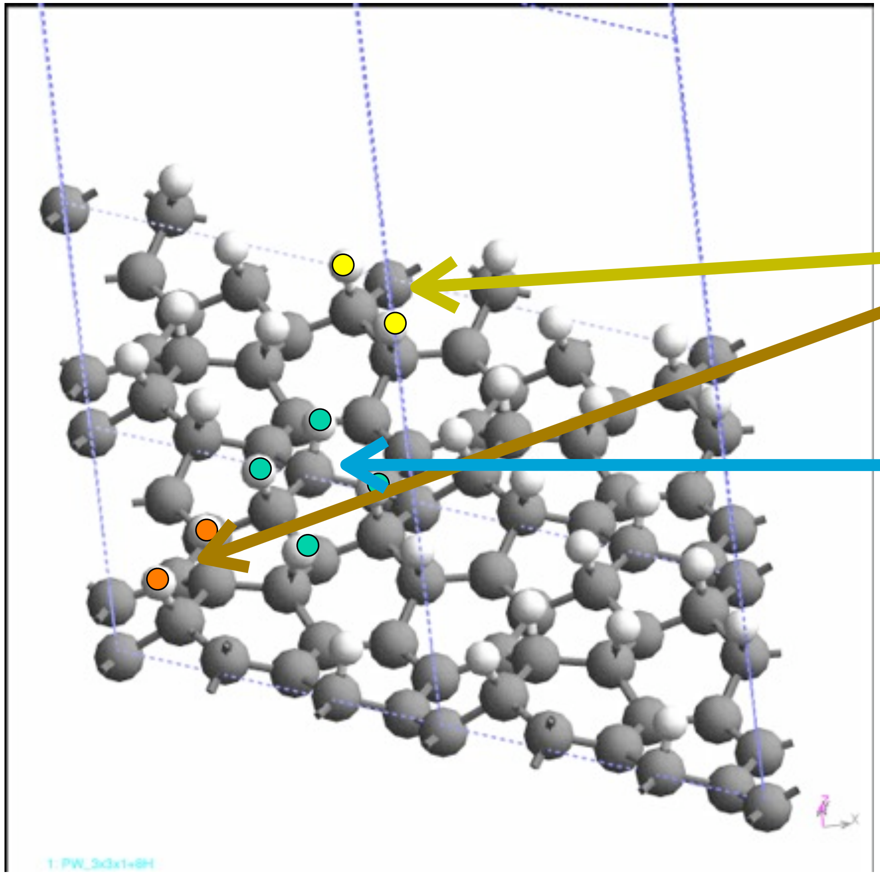
- The barriers of activation are calculated using the Nudged Elastic Band theory

- BZ sampling 6x6x1 (surface) 6x6x6 (bulk)



Graphite

Multiple adsorption



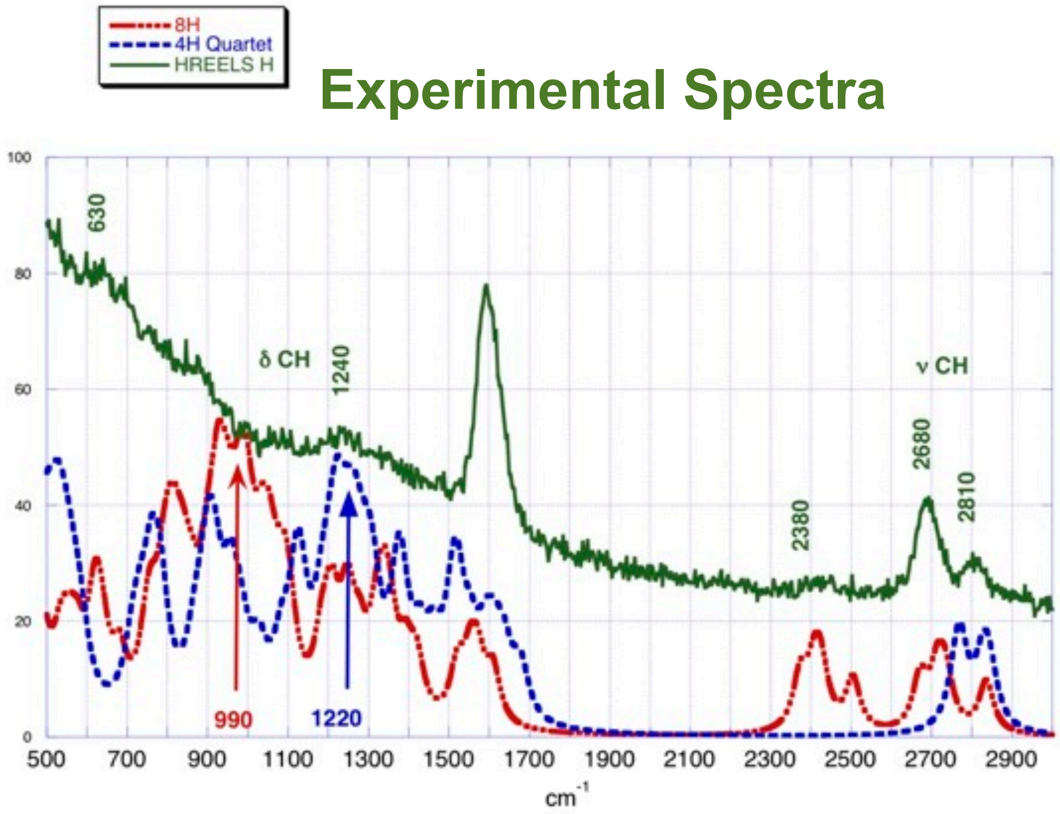
Two patterns :

2 weakly bonded doublets

1 Strongly bonded quartet

<u>No single adsorption</u>

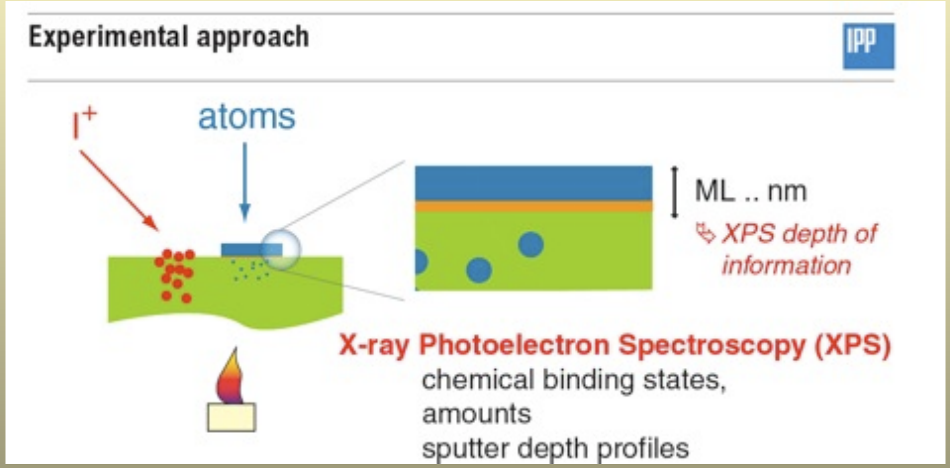
Phonons calculation vs. HREELS



Phonon at Γ point

Beryllium - tungsten mixed material

The goal: giving a quantum description of the first steps of Be/W alloying starting from surface reactions



Experimental approach

X-ray Photoelectron Spectroscopy (XPS)

chemical binding states,
amounts
sputter depth profiles

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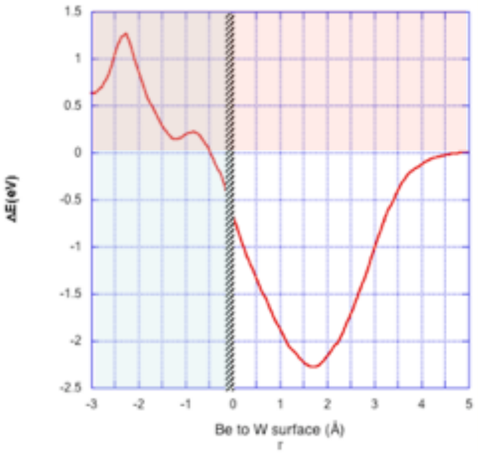
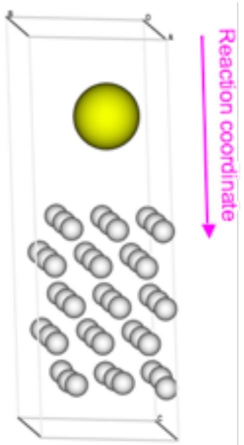
W on Be → alloy formation

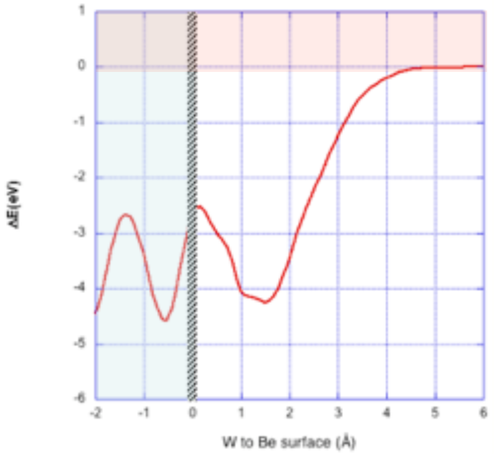
Be on W → no stable alloy

Energy profiles

Be on/in W(100)







W on/in Be(0001)

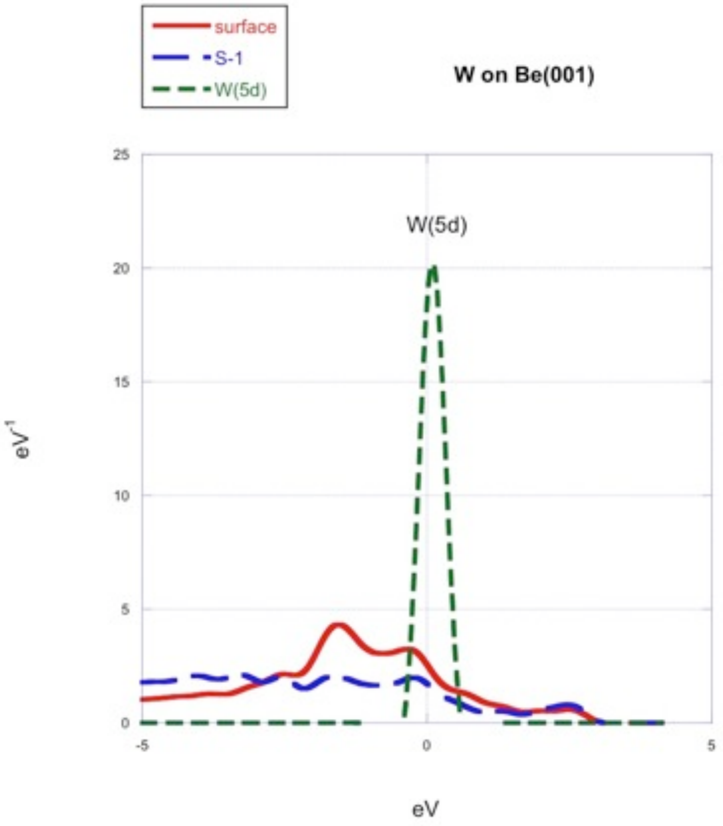
Adsorption energy -2.3 eV

Trapping energy: endothermic

Adsorption energy -4.2 eV

Trapping energy -4.8 eV

Be(0001) surface + W atom DOS



1/ The Fermi energy falls in the middle of the partly filled W(5d) and Be(2s2p) bands

2/ Negligible Be(0001) surface reconstruction ➡

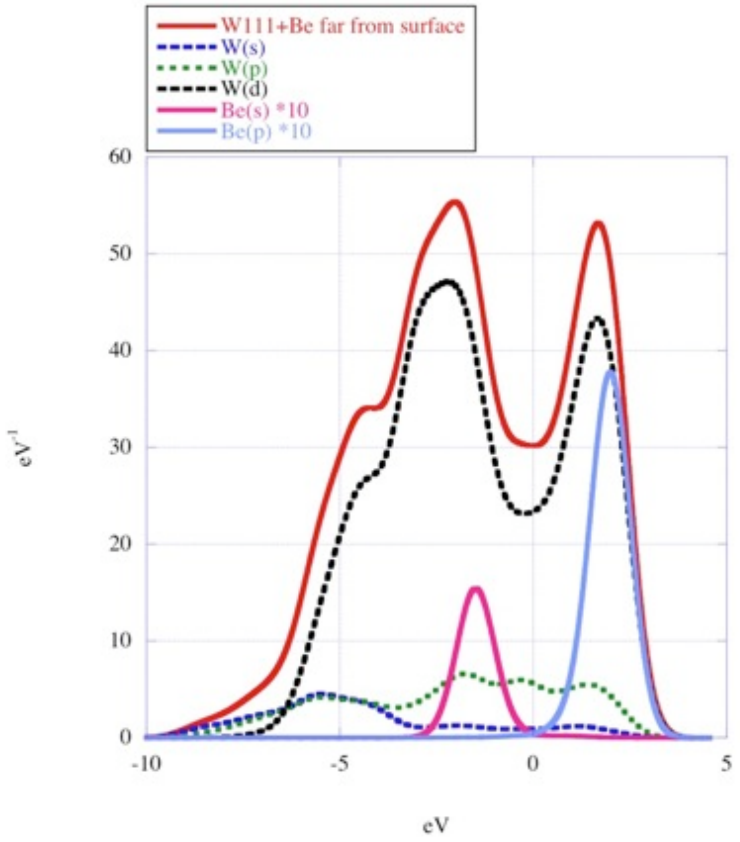
3/ The surface and sub-surface DOSs are not very different

⬇

Exothermic W adsorption & trapping
⇛ Stable alloy formation

W(100) surface + Be atom DOS

Non-interacting system



- *Atomic Be $(2s)^2(2p)^0$*
  ☞ the Be(2p) band is empty
- W(5d) band is half filled

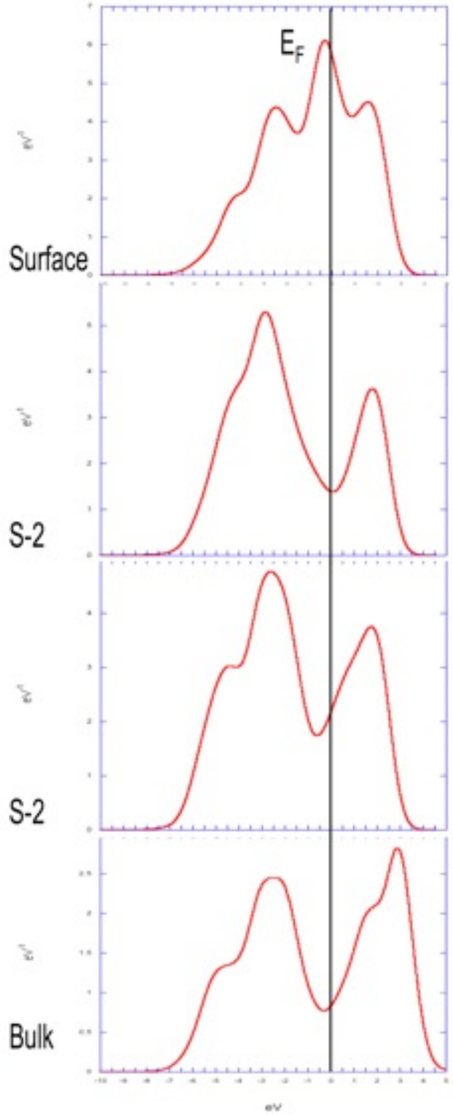
Binding Be - W(100) needs:
① electron transfer Be(2s) ⇒ Be(2p) then

sp^2 hybrid orbitals whose projected DOS will extend on both sides of E_F

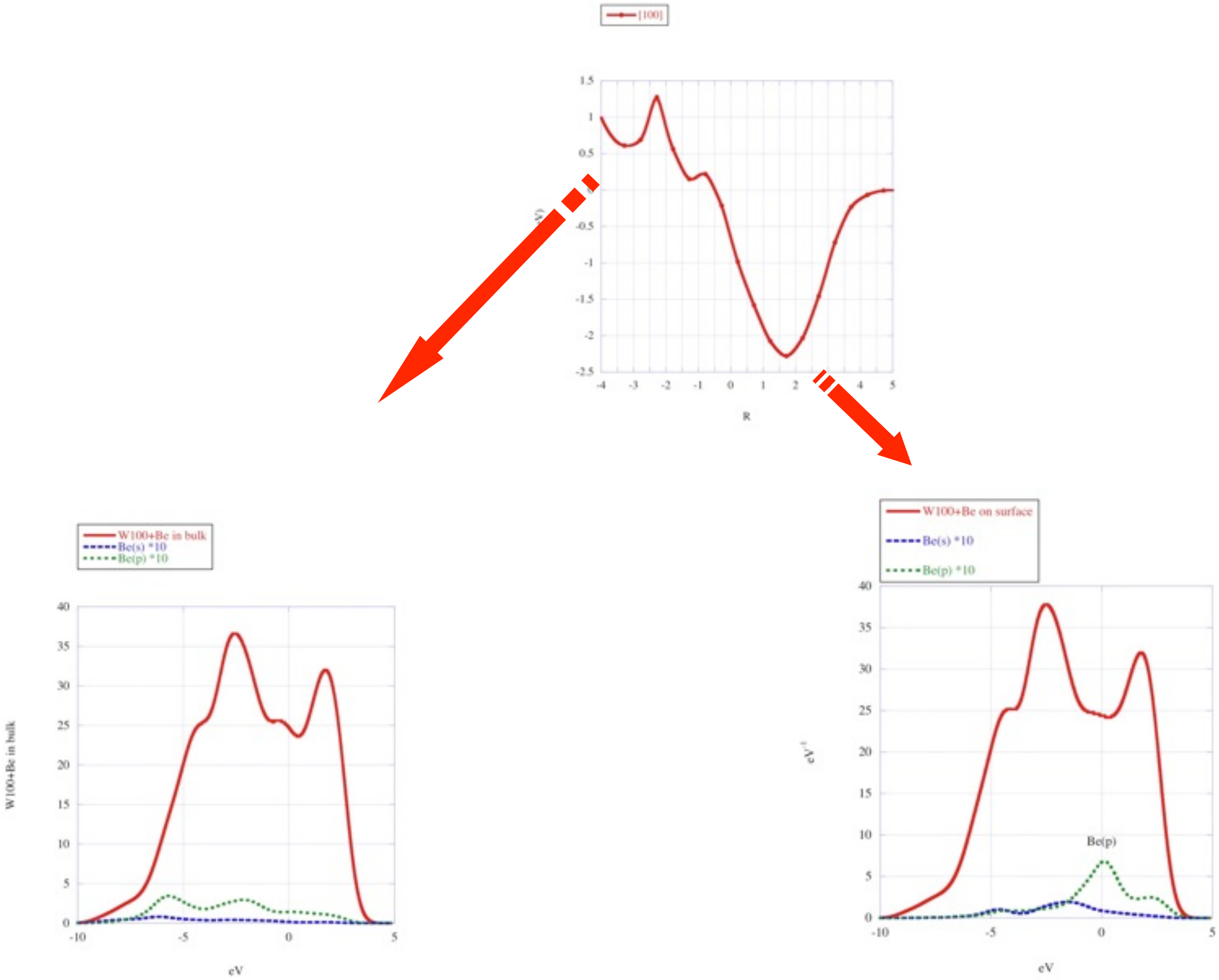
② combination Be(sp^2) - W(5d)

W(5d) DOS

Because of surface reconstruction, the surface DOS is very different from those of inner layers

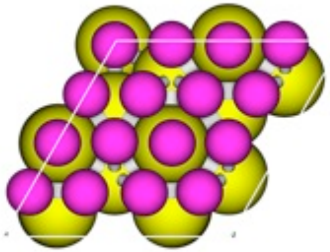


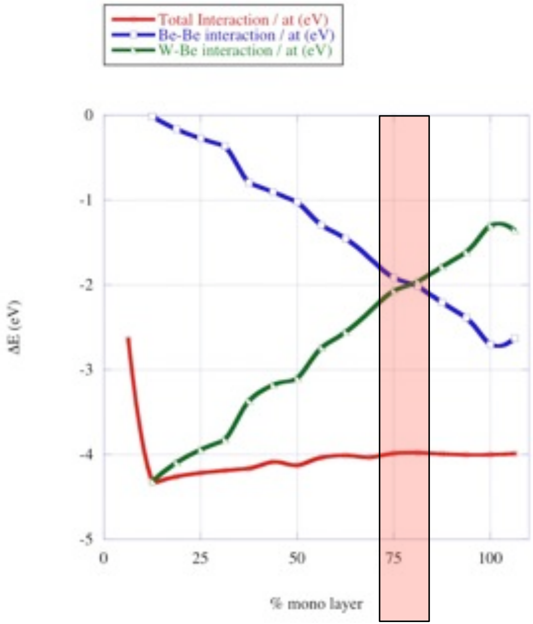
The shortest is the distance between the maximum of W(d) band to the Fermi energy, the most efficient the interaction is

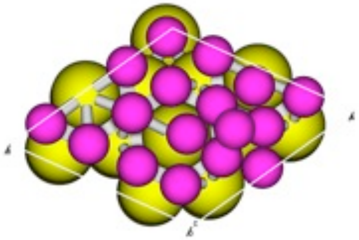

[100]
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
-4
-3
-2
-1
0
1
2
3
4
5
R
W100+Be in bulk
Be(s) *10
Be(p) *10
W100+Be in bulk
40
35
30
25
20
15
10
5
0
-10
-5
0
5
eV
W100+Be on surface
Be(s) *10
Be(p) *10
eV⁻¹
Be(p)
40
35
30
25
20
15
10
5
0
-10
-5
0
5
eV

With coverage:

Vertical interaction
Lateral interaction



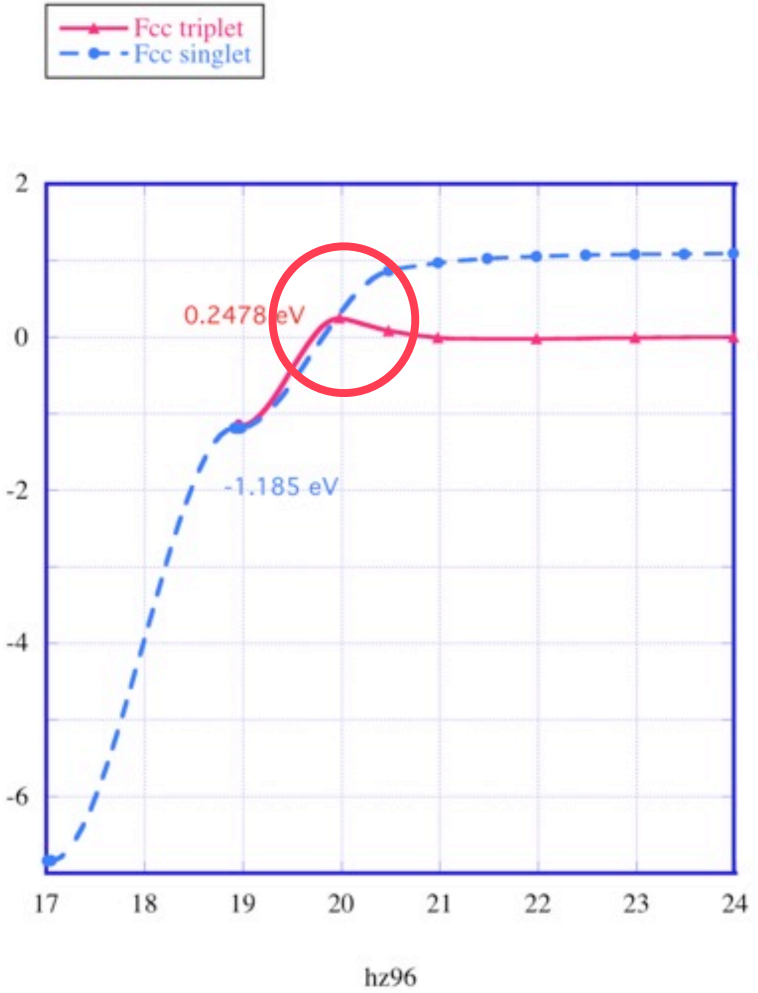


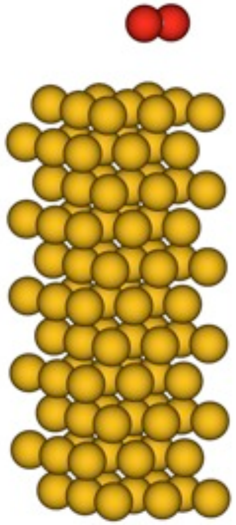


Vertical interaction is predominant

Be clusterization

Be(0001) oxidation

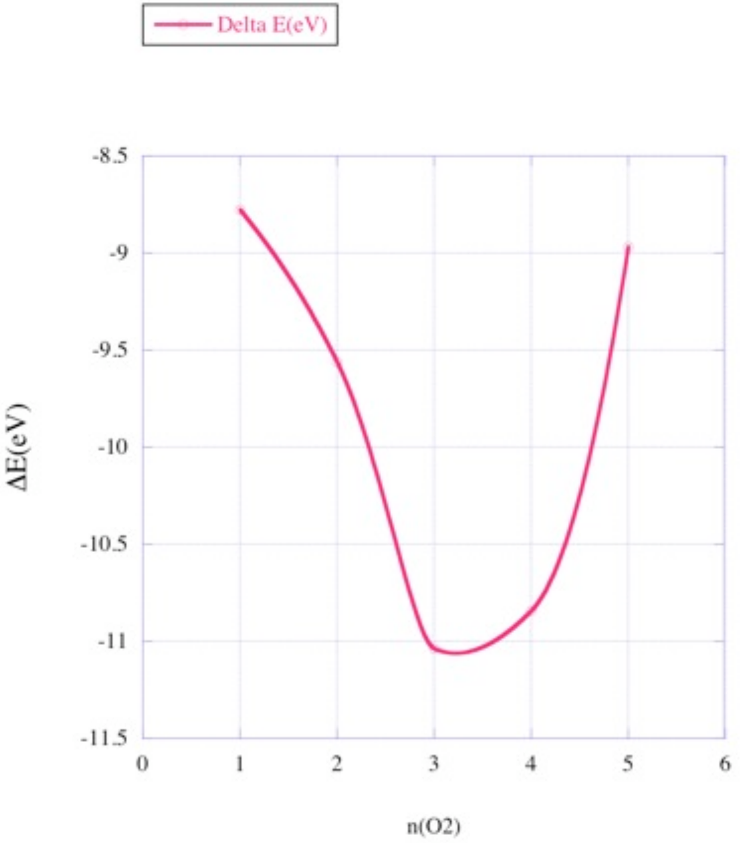




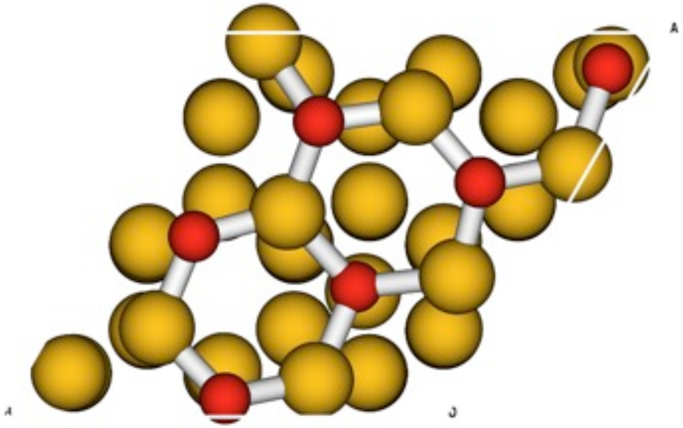
Molecular oxygen ground state is a spin-triplet state (~ bi-radical).

Its dissociation could be activated[1]. The barrier is due to T~S conical intersection

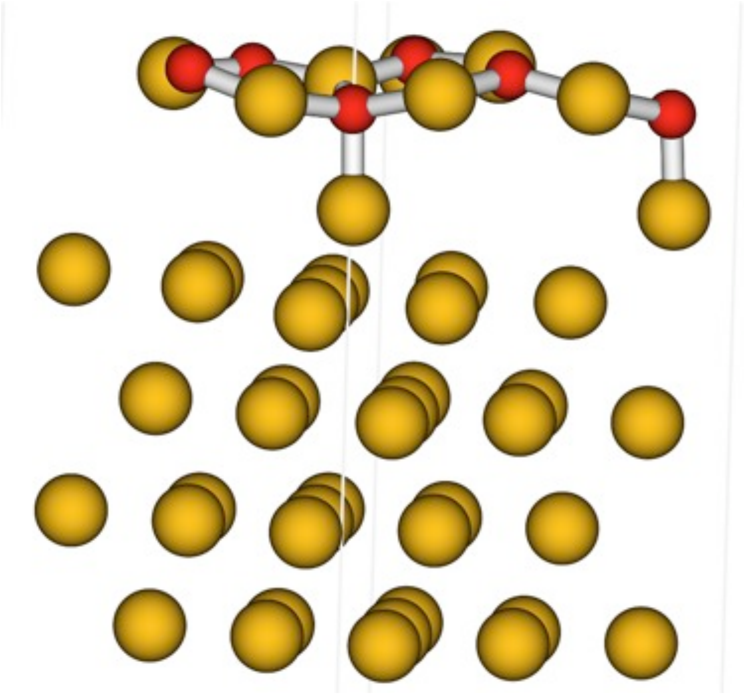
Multiple dissociative adsorption



The minimum is reached for 3 molecules

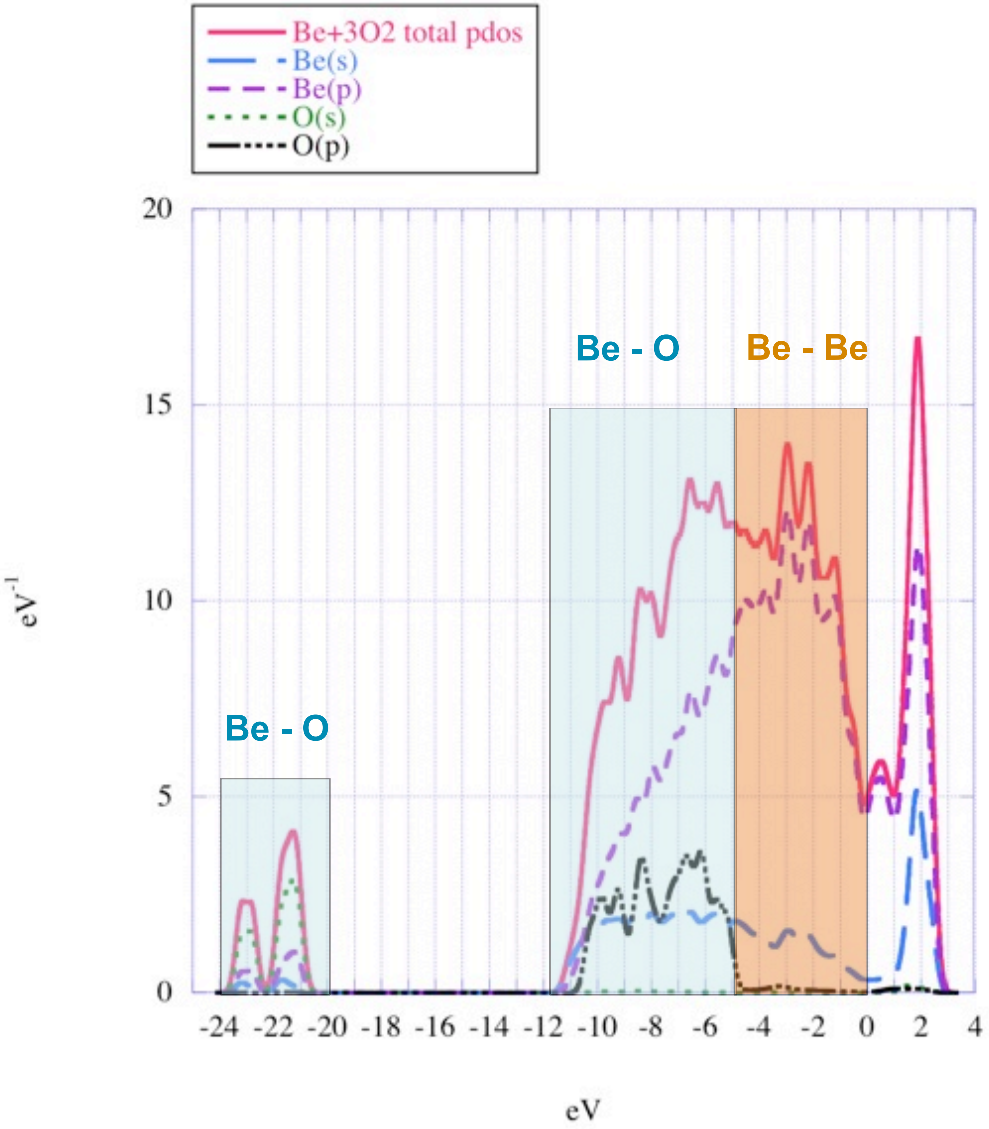


Hexagonal superstructure



The oxidized layer tends to dissociate from the crystal

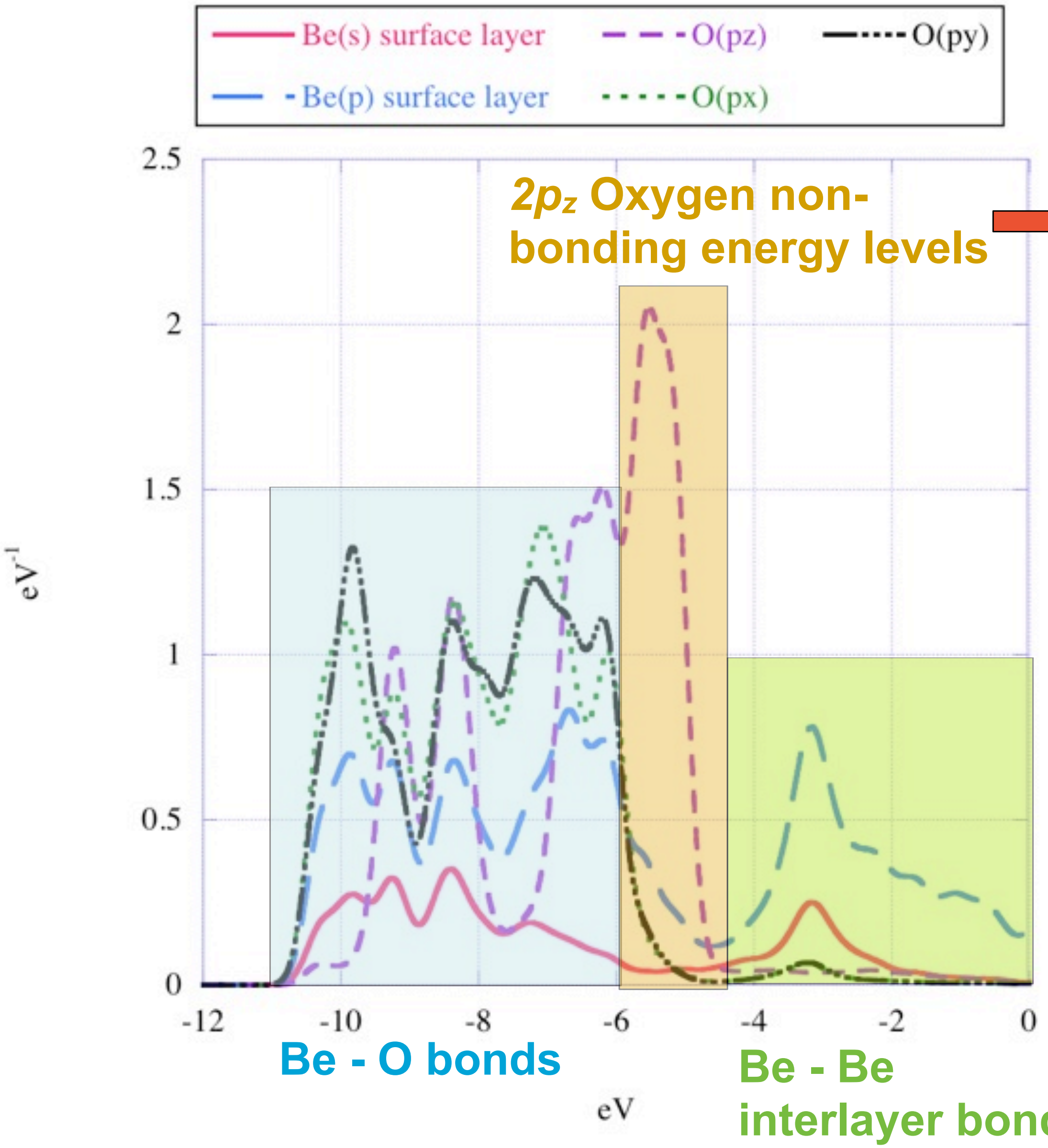
The DOS interpretation



In average, each oxygen atom gains 0.2 electrons from the surrounding beryllium atoms included in the layer.

On the total each O(*2p*) shell now bears nearly 5 electrons

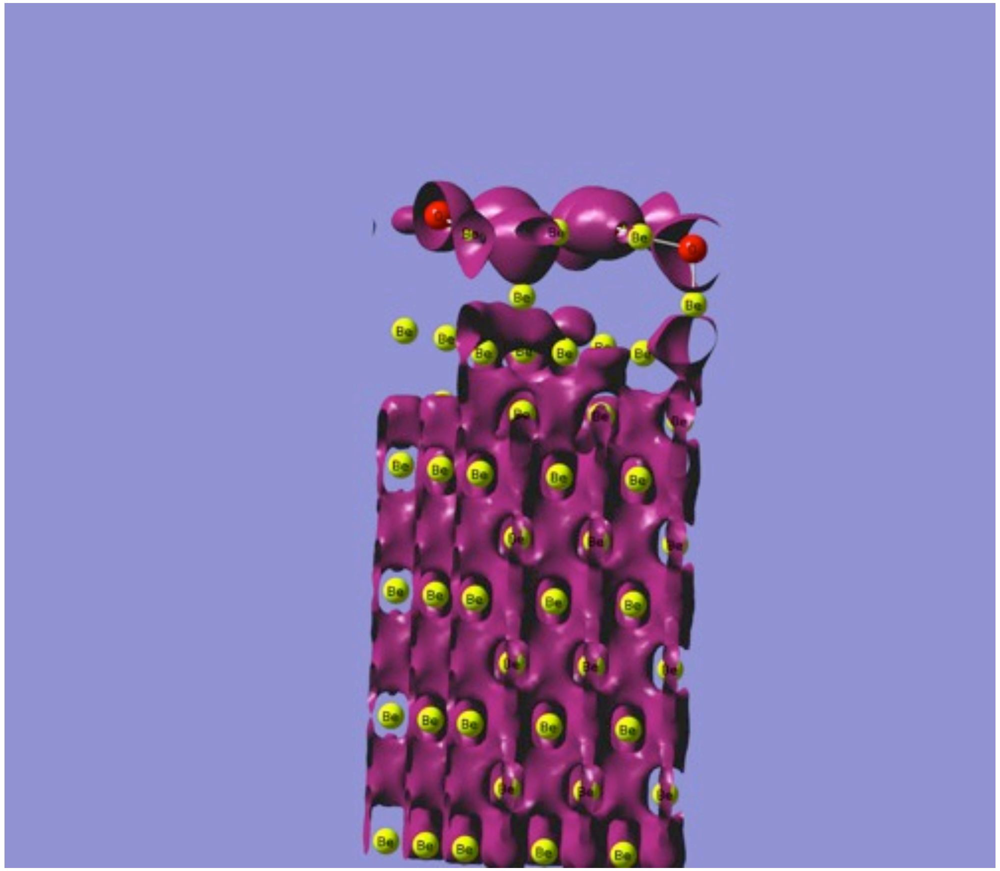
Zoom on the surface layer



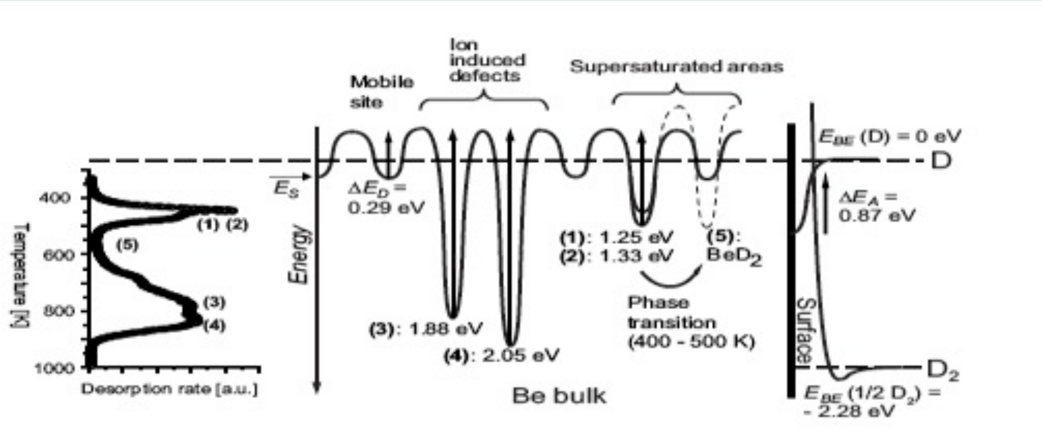
2p_z Oxygen non-bonding energy levels → *localized above and below the surface* → *Pauli repulsion*

Be - O bonds

Be - Be interlayer bonds

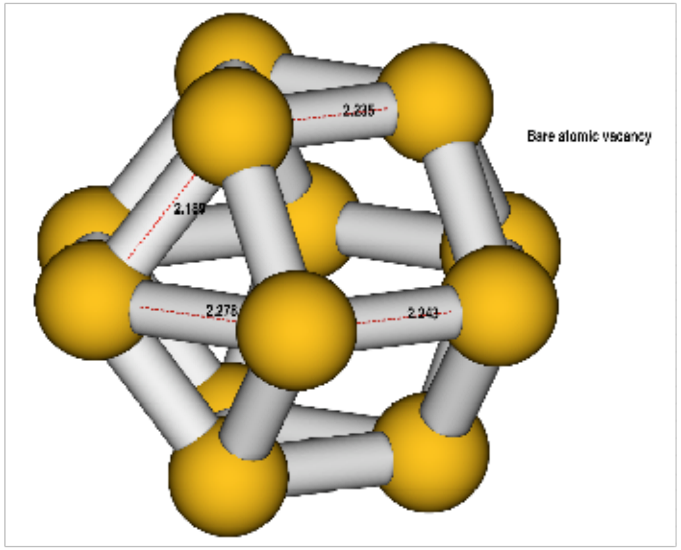

Be
O

Diffusion processes in beryllium: contribution to H/D desorption mechanisms



M. Reinelt & Ch. Linsmeier 1 keV D^+ ions implantation

with Ch.Linsmeier's permission

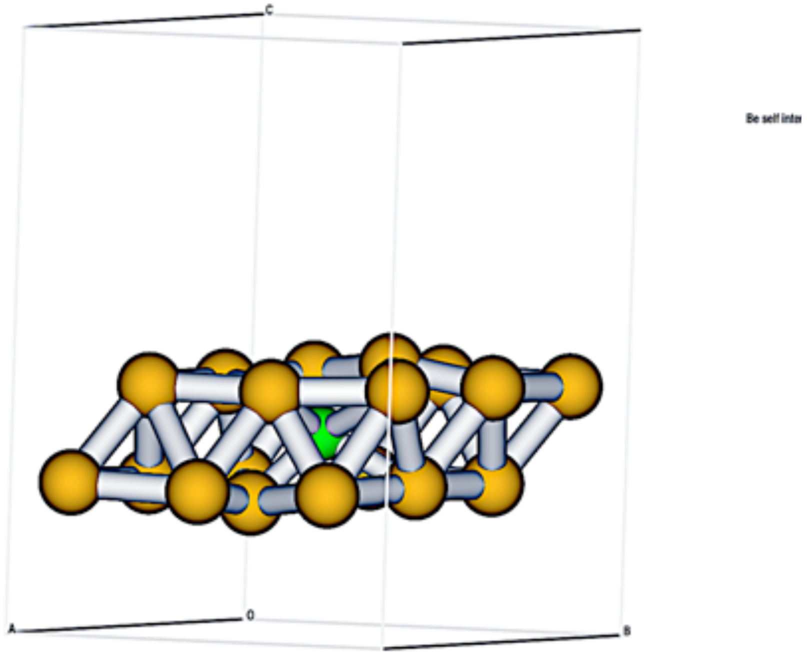


Mono-vacancy in Be

Formation energy: 0.96 eV
Activation barrier to vacancy diffusion:
TS = 0.72 eV isotropic

Be diffusion in beryllium crystal

Self interstitial formation energy 4.18 eV

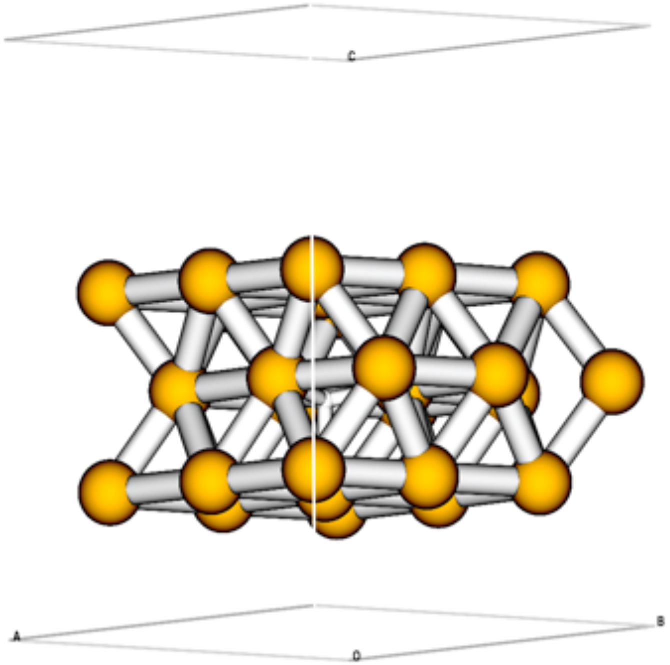


Low barriers to diffusion

100	0.007 eV
010	0.004 eV
110	0.039 eV
001	0.216 eV

Anisotropy of the Be crystal

H interstitial

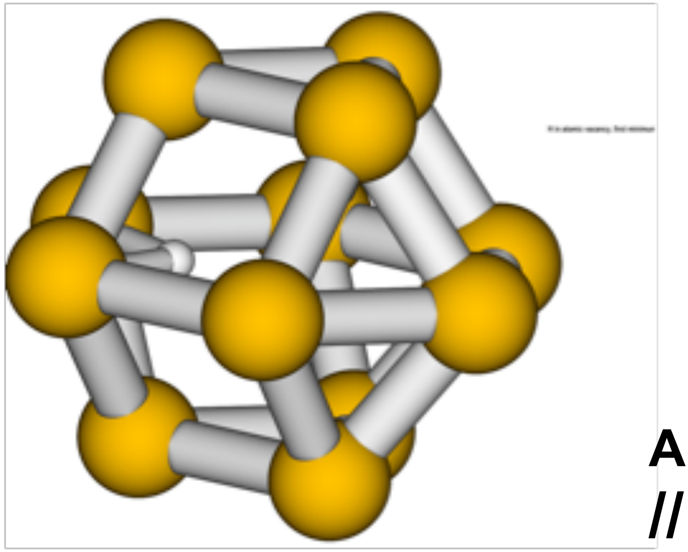


H interstitial

Formation energy 1.82 eV

Diffusion // to the hexagonal plane: TS 0.41 eV
Normal to the plane: TS 0.74 eV

H in vacancy



Activation energies

// → 1.70 eV

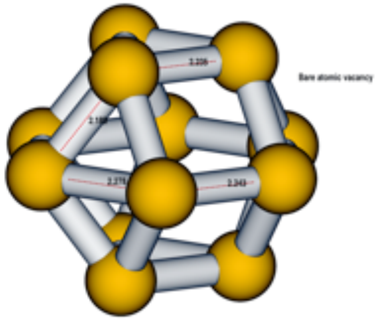
← 0.85 eV (Interstitial diffusion energy from 0.41 eV to 0.74 eV)

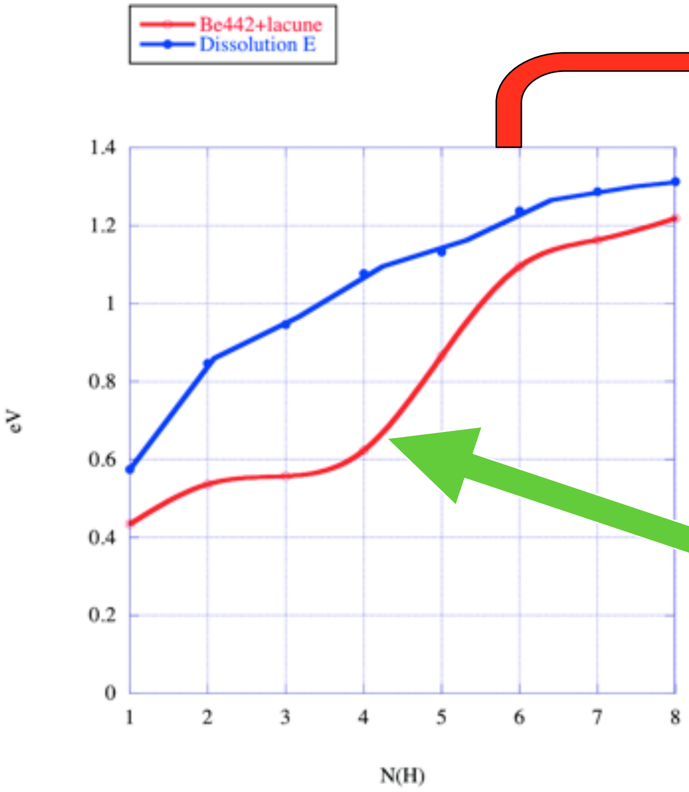
⊥ → 1.60 eV

← 0.63 eV

Hydrogen trapping in beryllium atomic vacancy

n H	Detrapping TS → (eV)	Trapping TS ← (eV)	H-H Å	Vacancy radius (Å)
0H				2.26
1H	1.32	0.36	-	2.70
2H	1.32	0.40	-	2.72
3H	1.33	0.40	-	2.72
4H	1.32	0.40	-	2.76
5H	1.37	0.42	-	2.80
6H	0.98	1.37	0.85	2.82





H_2 isolated in a vacancy is not stable.

Solution energy in Vc < in bulk

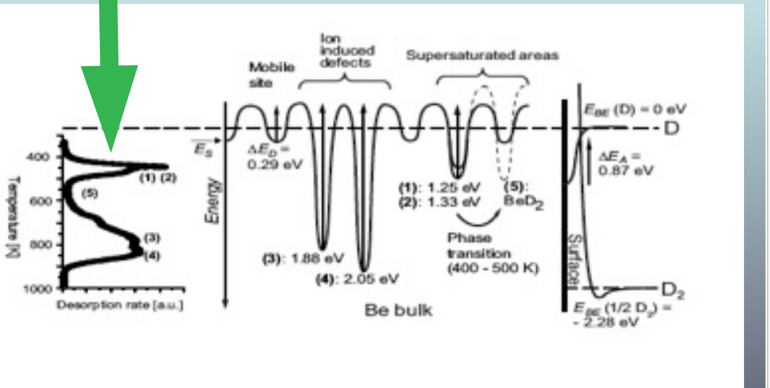
Relations H - vacancy

Formation energy of a vacancy:

- **in the bulk:** 0.96 eV
- **close to an interstitial H** 0.27 - 0.58 eV

It is also well known that vacancies can be created at the surface during H desorption

Model for H/D desorption



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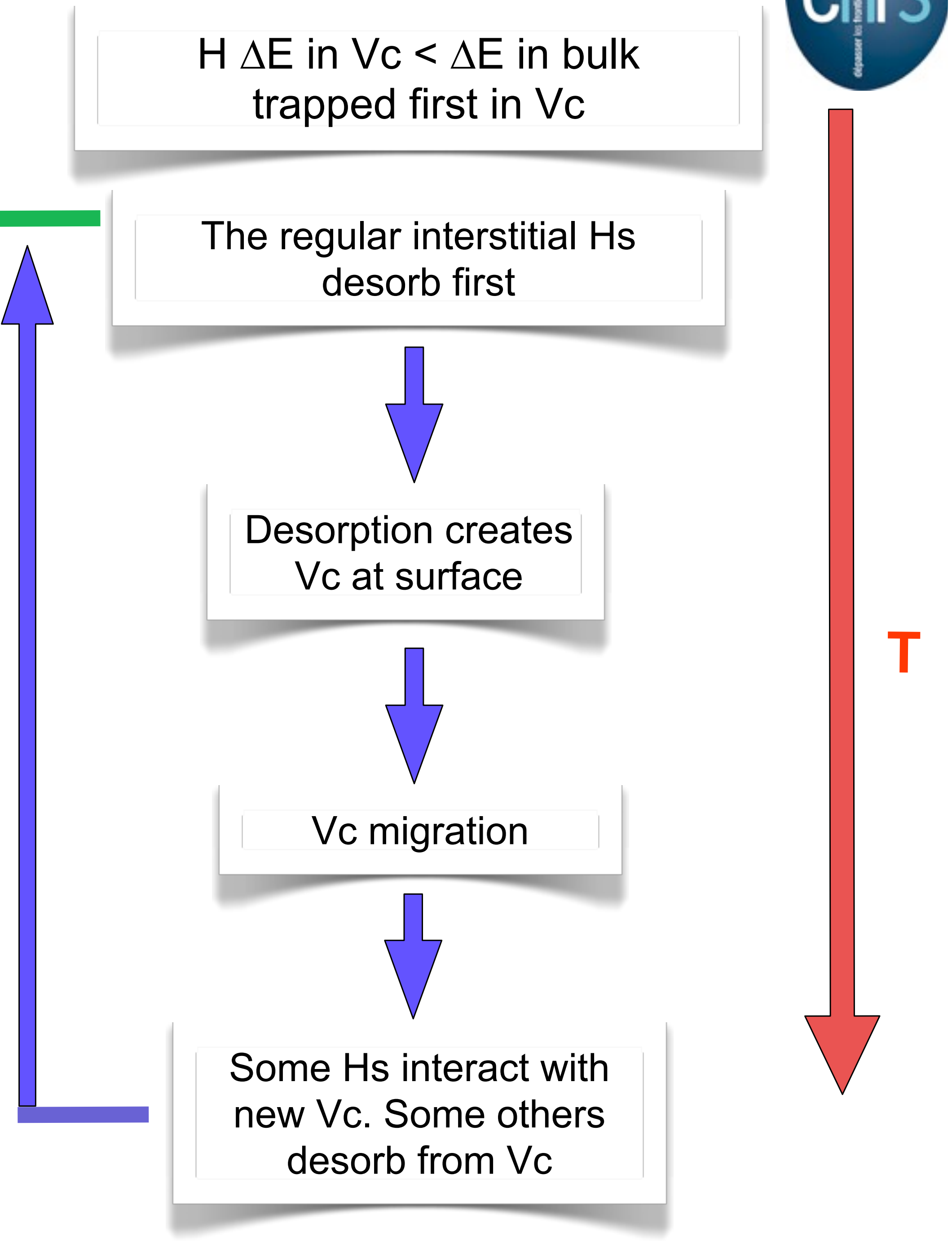

H ΔE in Vc < ΔE in bulk
trapped first in Vc

The regular interstitial Hs
desorb first

Desorption creates
Vc at surface

Vc migration

Some Hs interact with
new Vc. Some others
desorb from Vc

A ALLOUCHE, M OBERKOFLER, M REINELT AND CH LINSMEIER
J. Phys.Chem. C 114, 3588 (2010)

M OBERKOFLER, M REINELT, A ALLOUCHE, S LINDIG AND CH LINSMEIER
Phys.Scr. T 138, 014036 (2009)