# A (very) short introduction to surfaces

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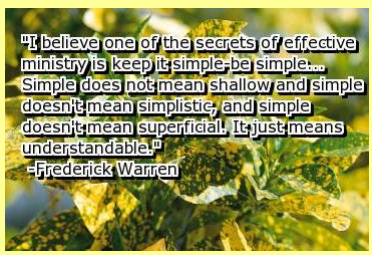



*… So, "superficial" doesn't mean "simple" ! As Wolfgang Pauli said: "God made the bulk; the surface was invented by the devil."*

## Outline

- **Do surfaces matter?**
- **Some basic definitions about surfaces**
- **Surface-sensitive techniques and numerical simulations**
- **Polar surfaces**

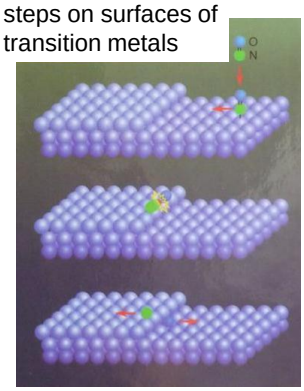
# Outline

- **Do surfaces matter?**
- Some basic definitions about surfaces
- Surface-sensitive techniques and numerical simulations
- Polar surfaces

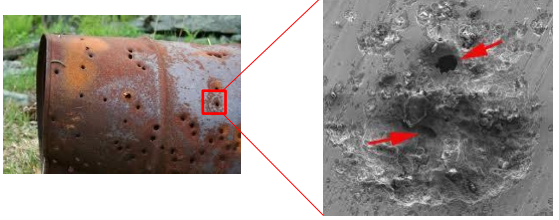
# Do surfaces really matters?

In chemistry:
most chemical reactions start or happen at surfaces

NO dissociation at steps on surfaces of transition metals




Corrosion of metals



Catalysis, chemical treatments of surfaces, coatings, lubrication, etc.

# Nanomaterials : length scales

| | |
|---|---|
| Hair | $10^{-4}$ m |
| Bacteria | $10^{-6}$ m |
| **Hemoglobin** | $10^{-8}$ m = 10 nm |
| **Benzene molecule** | $10^{-9}$ m = 1nm |
| **Atom radius** | $10^{-10}$ m = 0.1 nm |

Nano-materials: how many atoms at surfaces?

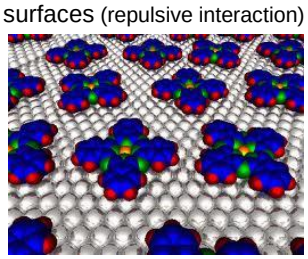
N atoms on each edge ➔ $N^3$ atoms in total
$6(N-2)^2$ on faces
12(N-2) on edges
8 on corners
➔ $6N^2$ -12N+8 at surface
➔ 49% for a 10x10x10 cube
(typical linear dimensions ~ 2 nm)

Surface contributions often determine the behaviour of nano-materials

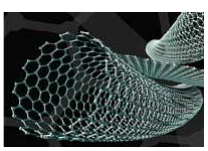
# Do surfaces really matters?

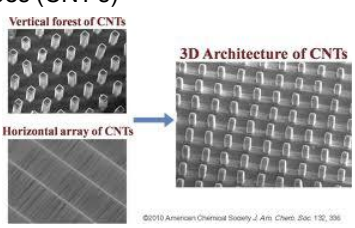
Assembled nano-materials ( 1nm = $10^{-9}$m )

Ordered structures of organo-metallic molecules on Ag surfaces (repulsive interaction)



Carbon nanotubes (CNT's)






Many technological improvements depend crucially on what we know about surface properties of materials and about their interfaces

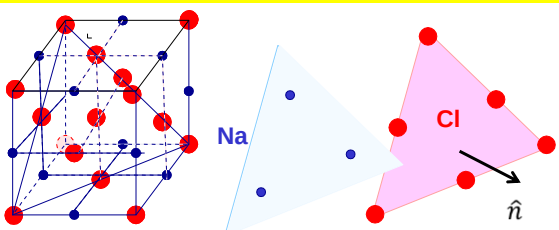
# Outline

- Do surfaces matter?
- **Some basic definitions about surfaces**
- Surface-sensitive techniques and numerical simulations
- Polar surfaces

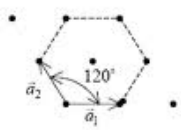
# Solid surfaces: basic definitions (1)

Ideal Surface (of a crystal)
*Termination of a periodic array of atoms, clamped in their bulk positions*

Ex: (111) Planes in NaCl

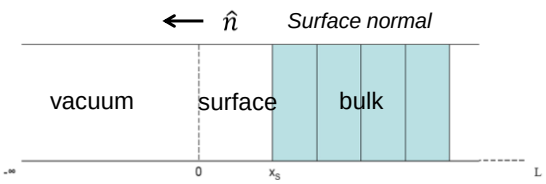



Periodic structure in 2D
*Periodic array of atoms in two dimensions, with unit vectors* $\boldsymbol{a}_1$ $\boldsymbol{a}_2$




$\hat{n} \cdot \vec{a}_1 = \hat{n} \cdot \vec{a}_2 = 0$

Surface as termination of a solid (here a crystal)
*Surface = region where properties are neither those of the bulk nor those of the vacuum*

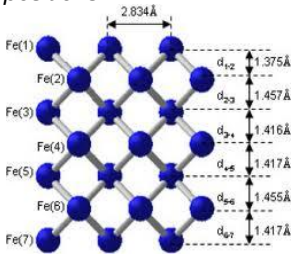


# Solid surfaces: basic definitions (2)

A surface is never ideal !

Surface relaxation

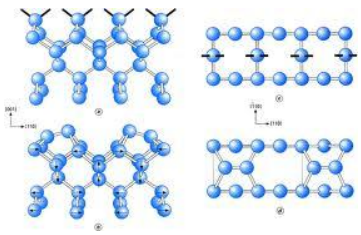
*Atoms loose some neighbors and move away from their ideal positions*




Fe(110)

Surface reconstructions

*The 2D periodicity of real surfaces may be different from the ideal one*

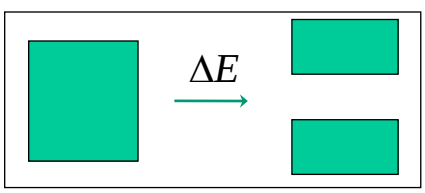


Si(001) (2x1)

# Solid surfaces: basic definitions (3)

Surface Energy $\gamma$

Energy needed to cleave the crystal in two parts at constant number of particles, per unit surface area $A$




$$\gamma = \frac{\Delta E}{2A}$$

*Useful to characterize the relative stability of different reconstructions*

However, kinetics is often more relevant than thermodynamics in obtaining the eventual surface conformation

➔ annealing, chemical or mechanical treatment of the surface, UHV, etc.

# Solid surfaces: basic definitions (4)

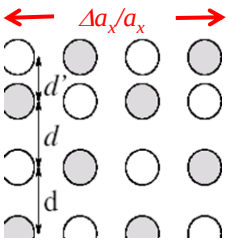
## Surface Stress

Bond lengths are increasing functions of coordination n.

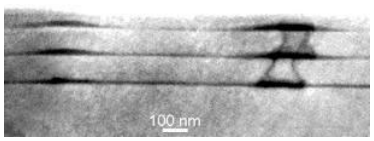
Cutting bonds at surface ➔ the remaining ones would like to contract

➔ Surface relaxation (⊥ surf.)

➔ surface stress (// surf.)

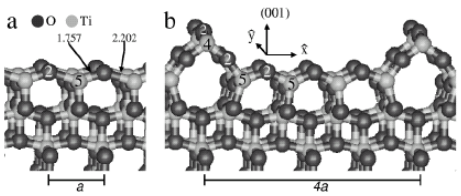



*Highly stressed surfaces reconstruct or create dislocations, domains, etc.*




Dislocations in Ge/Si(100)

*[Capellini et al, Semic.Sci.Techn. 1999]*




anatase $TiO_2$(001) (1x4) reconstruction

*[Lazzeri & Selloni PRL 2001]*

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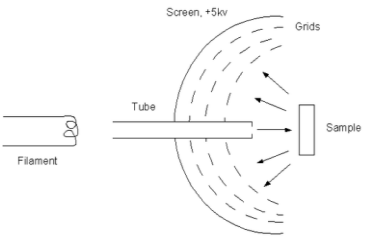
- Polar surfaces

# Surface-sensitive techniques (1)

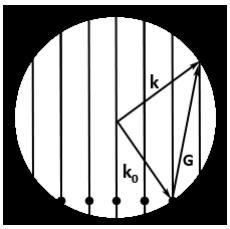
Low-Energy Electron Diffraction (LEED) ➔ 2D reciprocal lattice (wave vectors)




$$\lambda = \sqrt{\frac{h^2}{2mE}} \simeq \sqrt{\frac{1.5}{E(eV)}}\,nm$$

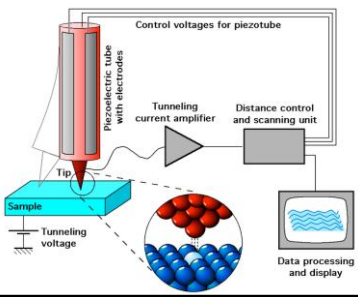
*Single elastic scattering*

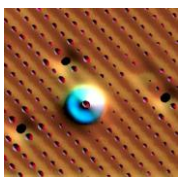
$$\vec{k} = \overrightarrow{k_0} + \vec{G}$$




Scanning Tunneling Microscope (STM) ➔ imaging the surface

*(part of the electron density)*



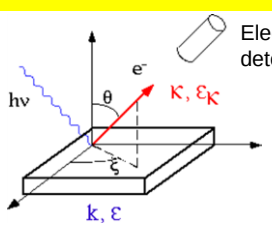



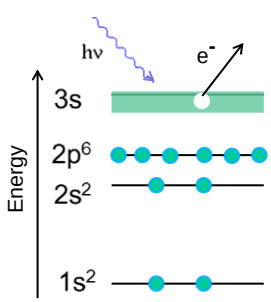
Xe/Ni(110)
www.almaden.ibm.com

# Surface-sensitive techniques (2)

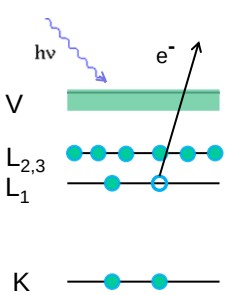
Photoemission Spectroscopy(PS)
Photon-in electron-out experiment
probing electronic energy levels

$E_{kin}$ ~ 50-200 eV ➔
electron mean free path < 1 nm

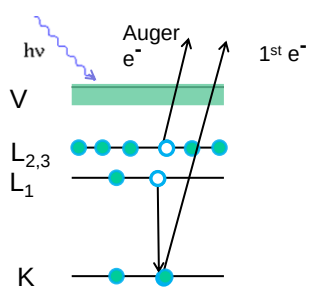



UPS:
Ultra-violet photon
$E_{kin} \sim h\nu - E_V$

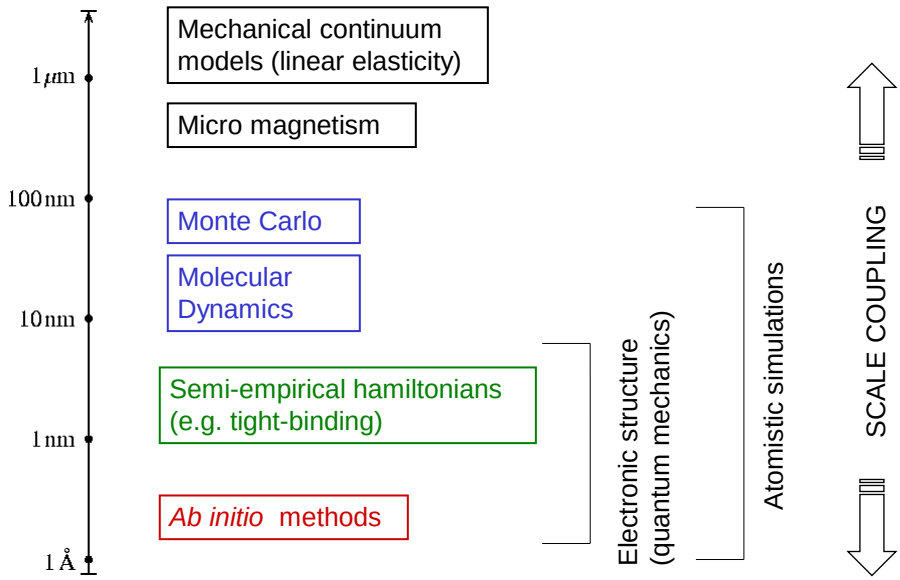



XPS:
X-ray photon
$E_{kin} \sim h\nu - E_{L1}$

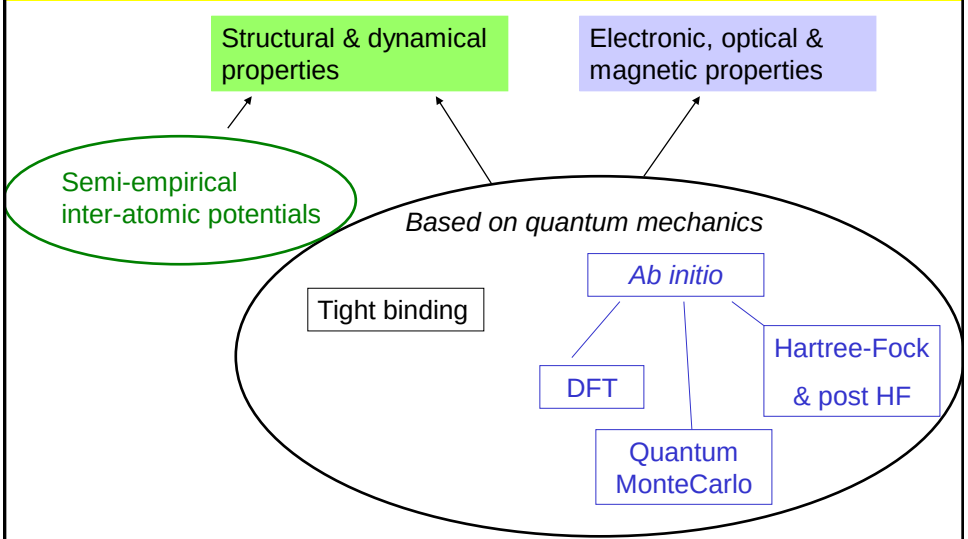



Auger PS:
X-ray photon
$E_{kin} \sim E_K - E_{L1} - E_{L2,3}$

# Computer simulations in materials science




# What does "*ab initio*" mean?




*Ab initio*: from first principles ➔ *Ab initio* theories are NOT exact, but in principle independent and complementary to experiments

# Self-consistent electron density and potential

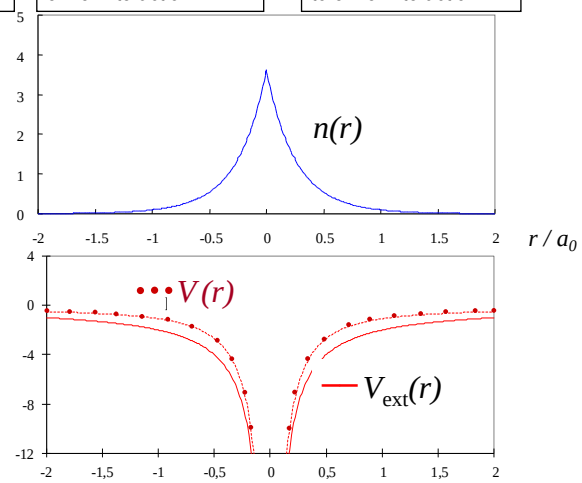
$$V(\vec{r}) = V_{ext}(\vec{r}) + \int d^3r' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + \frac{\delta E_{XC}}{\delta n(\vec{r})}$$

The "original" external potential (the nucleus)

Electrostatic (classical) $e^-$ - $e^-$ interaction

Quantum contribution to $e^-$ - $e^-$ interaction

Exact DFT ground state for the He atom
*(K. Burke et al.)*




# Density Functional Theory (DFT)

The brilliant idea from W. Kohn and L.J.Sham (1965): set up a system of $N$ one-particle Schrödinger –type equations in order to reproduce the electron density of the interacting $N$-electron system.

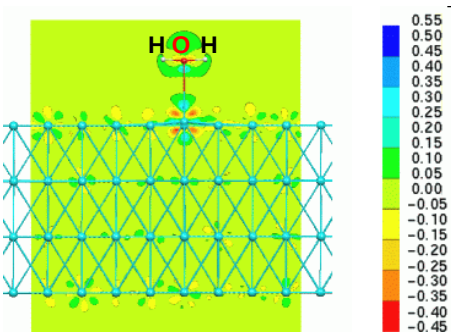
$$\begin{cases} \left( -\frac{\nabla^2}{2} + V_{ext}(\vec{r}) + \int d^3r' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + \frac{\delta E_{XC}}{\delta n(\vec{r})} \right) \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r}) \\ n(\vec{r}) = \sum_{i \in occ.} |\psi_i(\vec{r})|^2 \end{cases}$$

Exact solution if $E_{XC}$ is exact (unfortunately, $E_{XC}$ is unknown).
However, some approximations are decent and even accurate in some cases

By knowing the ground-state electron density one can compute:

- Forces on atoms → surface relaxation
- The ground-state energy → surface energy for different configurations
- The electronic structure → Simulate STM images
- The vibrational properties of the surface → compare with IR spectra
- … etc.

# Example: $H_2O$ / Ni surface

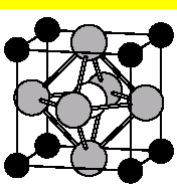



Difference of electron density between the molecule on the surface and the two separated systems

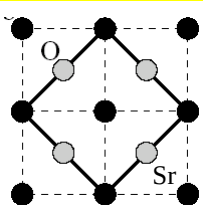
$$n(r) - n_{\text{surface}}(r) - n_{H_2O}(r)$$

➔ Information on the chemical bonding and the electron transfer

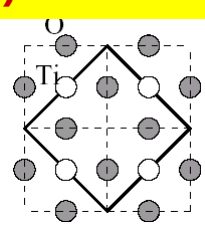
# An example: $SrTiO_3(100)$



Two distinct terminations can at least occur !




**SrO termination**



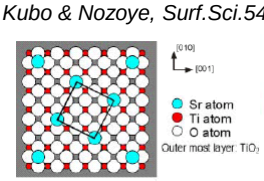

**$TiO_2$ termination**

Many reconstructions are reported, as a function of preparation conditions

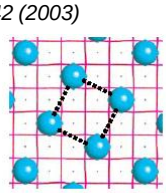
(1x1) and c(2x2) cells

**STM + DFT simulations**

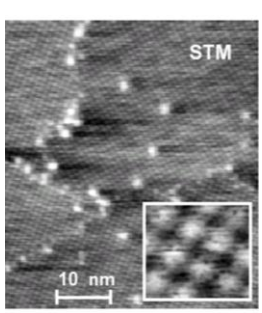
*Kubo & Nozoye, Phys.Rev.Lett. 86 (2001);*
*Kubo & Nozoye, Surf.Sci.542 (2003)*



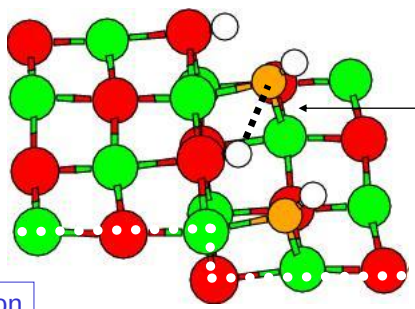

☺ **Sr adatom model**



STM spots --- Circle
Ti atoms --- Invisible



# MgO(001): spontaneous water dissociation at mono-atomic steps // [010]




Step + $H_2O_{(gas)}$

~ -0.9 eV

Molecular adsorption

Spontaneous proton transfer

~ -0.7 eV

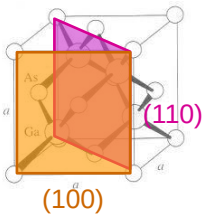
Most semi-empirical force fields are non reactive, i.e. molecules do NOT dissociate
➔ need for ab initio methods

*Costa et al, J. Chem. Phys. (2006)*

# Outline

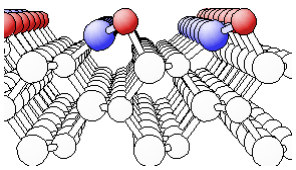
- Do surfaces matter?
- Some basic definitions about surfaces
- Surface-sensitive techniques and numerical simulations
- **Polar surfaces**

# Polar vs. not polar surfaces: GaAs(110) and GaAs(100)

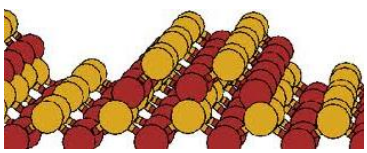



GaAs: a semiconductor with blende structure
*It is slightly ionic ($Ga^{+\delta}As^{-\delta}$)*

(110) plans are formed by both Ga and As: they are neutral
➔ GaAs(110) surface is <u>not polar</u>

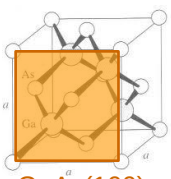


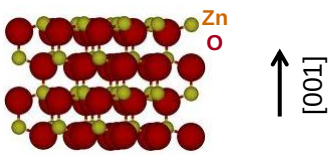

(100) plans are formed either by Ga or As: they are NOT neutral
➔ GaAs(100) surface is <u>polar</u>




# Why are polar surfaces relevant?

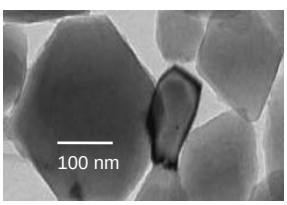
Some crystals naturally grow along polar orientations



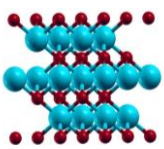




Polar surfaces are very reactive and may become stable after reaction

Hydrated MgO nano-crystals: from cubes with (100) faces to truncated octahedra with (111) faces after 7 days exposure to water

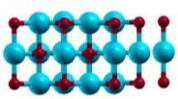



Ultra-thin polar films may be stable in other crystal phases



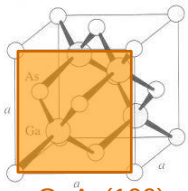
← Cubic MgO: (111) stacking

Hex-MgO (h-BN): → (0001) stacking

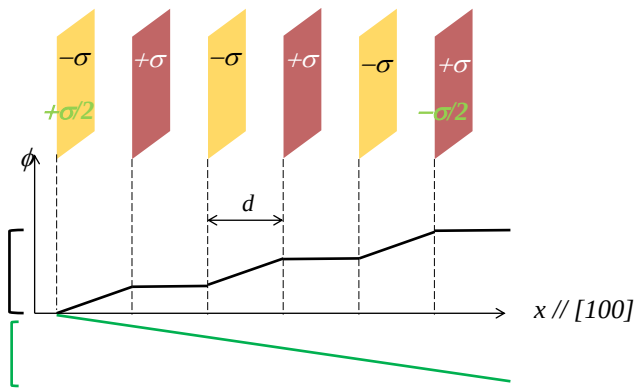


# Polar surfaces: basic electrostatics

Polar orientations: charged ideal atomic planes ➔ Model of planar capacitors




GaAs(100)




$$\Delta\phi = N\frac{\sigma\, d}{2\varepsilon_0}$$

$$\Delta\phi' = -(N-\frac{1}{2})\frac{\sigma\, d}{2\varepsilon_0}$$

$$\Delta\phi^{(1)} = \frac{\sigma\, d}{2\varepsilon_0} = \frac{q}{\varepsilon_0 a} \approx \frac{0.1}{8.9\times 5.6}\times 10^{-19+12+10} V \approx 2V$$

The potential drop of a double layer is even bigger than the fundamental gap (note $\varepsilon_r$~*10.9*)

$$\Delta\phi + \Delta\phi' = -\frac{\Delta\phi^{(1)}}{2}$$

**Electrostatic stability calls for a « compensating » surface charge $\sigma/2$**

# Polar-compensated surfaces

Drawbacks of the model:

- Electron distribution is a continuous function and charge is not just localized on atomic planes
- Insulators have a relative dielectric constant $\varepsilon_r$>1 (« screening »)
- Polar surfaces EXIST: they should be stable !

**Electrostatic stability calls for a « compensating » surface charge $\sigma/2$**

Which are the physical processes responsible for that?

I. Fill or deplete surface states
→ modification of the surface electronic structure

II. Desorption/adsorption of a macroscopic number of charged atoms
→ non-stoichiometric reconstructions, specific reactivity

But a simple surface relaxation cannot provide the compensating charges !

# Summary

- Basic processes on surfaces are relevant in many different domains (chemistry, dentistry, geo-chemistry, nano-electronics, and many others)
- Very few general rules but many different cases: there is still room for research !
- Continuous improvements of surface-sensitive techniques and numerical simulations are being achieved
- Polar surfaces: see next seminar (Friday, 20th) for more information

THANK YOU !