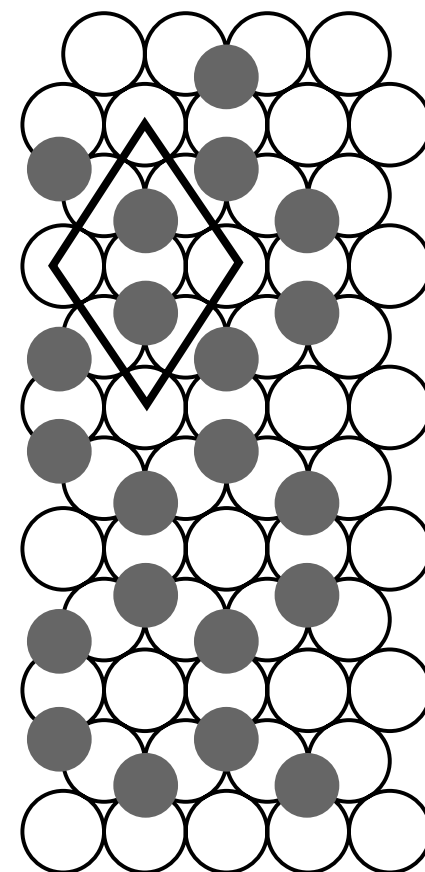


## *Electronic Structure Methods for Materials Modelling*

# A very quick glance at **Surface Calculations**

- Learning Outcomes
  - *A whole different playground*
  - *A number of possibilities*

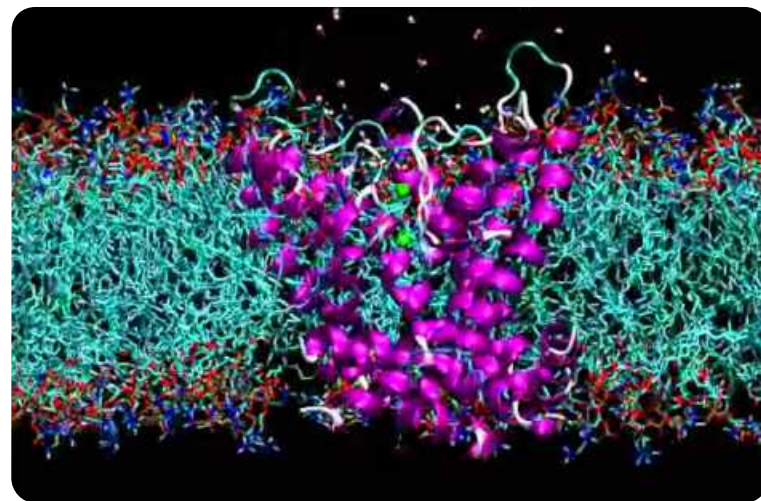
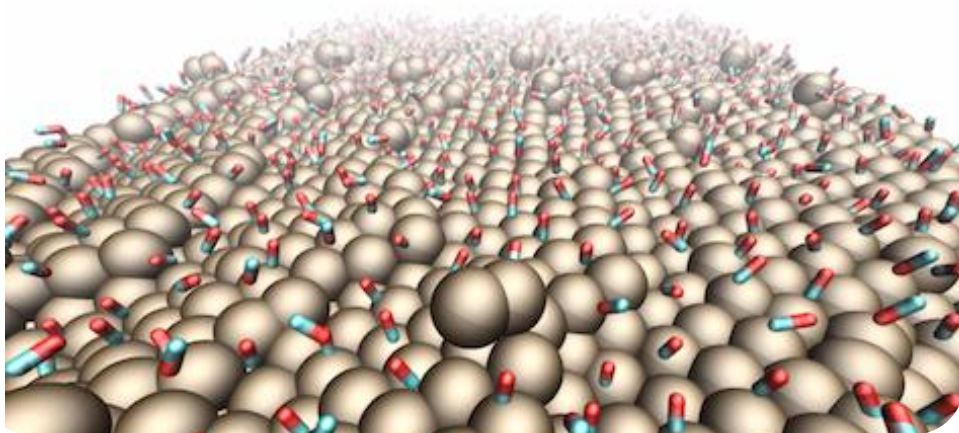
- Out there: surfaces (& interfaces)
- The technicalities
  - Slab models, K-points sampling, Vacuum convergence, Surface dipole
- Surface relaxation:
  - Polar vs non-polar surface (the case of CdSe)
- Surface reconstruction:
  - The going gets tough (the case of Si(001)-(2x1))
- Adsorbates
  - Physi- and Chemi- sorption
  - Binding energies (asymmetric growth of CdSe clusters)
  - Electronic structure of the adsorbate + surface system
- STM & DFT
- Complex interfaces
  - The rise of ab initio MD
- Next: Disordered Systems



First principles calculations do a pretty good jobs in describing many properties of bulk phases

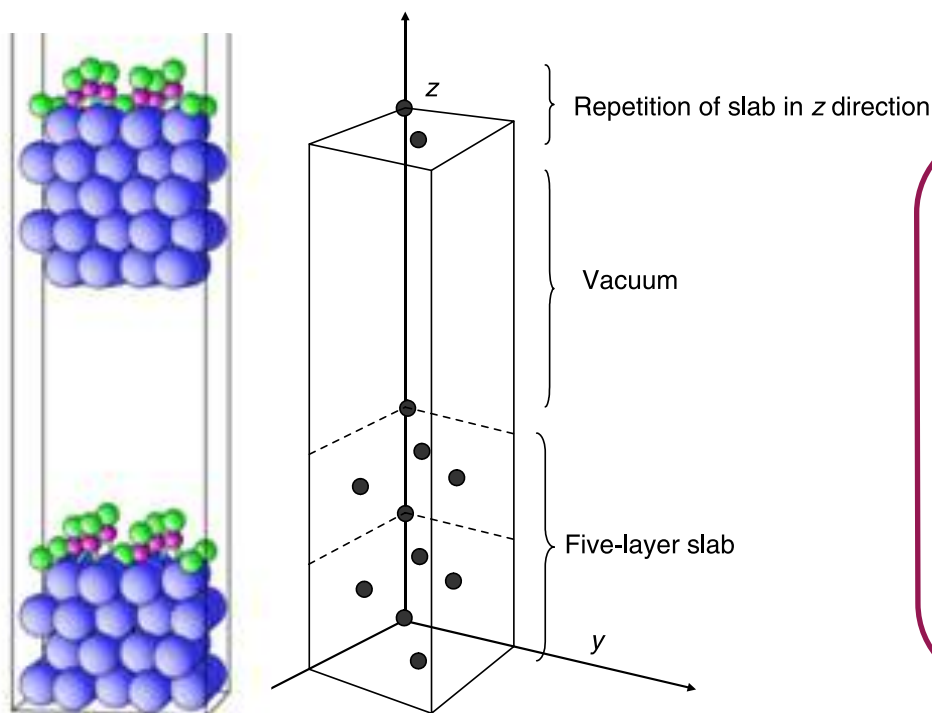


Most of the interesting stuff (chemical reactions, catalysis, corrosion... everything really) happens at surfaces and even more at interfaces between different materials and different phases



Is DFT able to deal with those as well?  
Yes - with some limitations

When modelling a bulk phase, 3D periodic boundary conditions are usually applied



At a surface/interface, periodicity and translational symmetry of a bulk crystal are destroyed

To model a surface (or an interface) people usually build slabs- 2D slices of the system

Most of the times, you keep 3D PBC, introducing some vacuum between the slabs

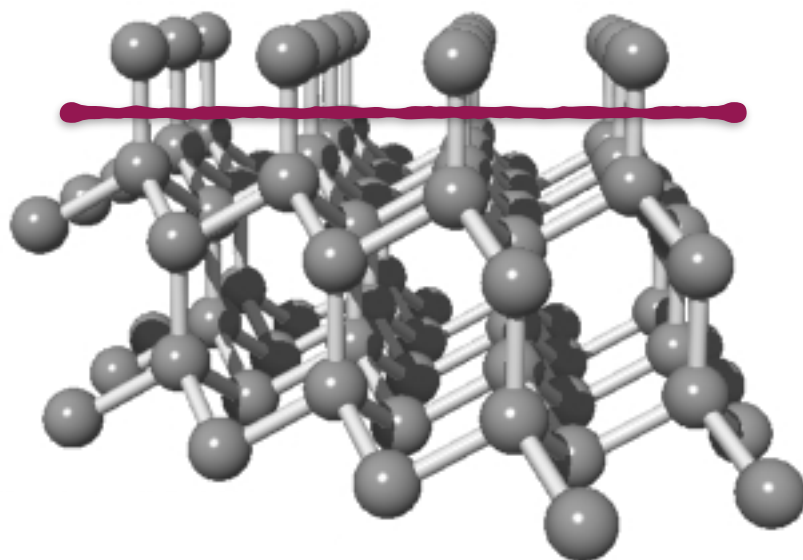
As a consequence:

- If you are sampling the Brillouin zone of a crystalline system, you need **different  $k$ -points meshes** with respect to the bulk
- You need to be sure that the **vacuum region** is large enough so that the electron density tails off to zero within it
- If you have an asymmetric slab (multicomponent systems, adsorbates, interfaces between different materials) you have to deal with a **surface dipole**



# Surfaces

## *A different chemistry*



Atoms at surface & interfaces

Broken bonds ( or different coordination number) as compared to their bulk counterparts.

The structure of the system at the surfaces can be different (it usually is) with respect to the bulk

***Surface relaxation***

Mild deformation of the structure close to the surface (e.g. different interlayer spacing in a crystalline lattice)

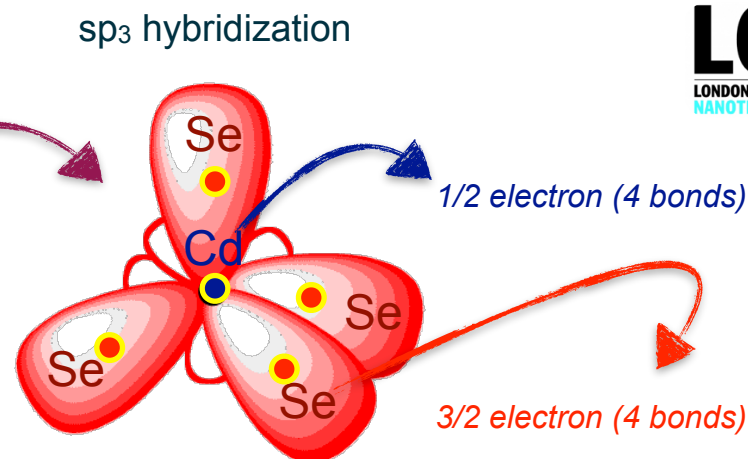
***Surface reconstruction***

Actual rearrangements (new symmetry, new bonds) of the surface atoms in e.g. different patterns

# Surface relaxation

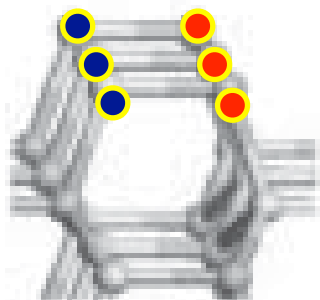
## The case of CdSe

Electronic structure:  
Cd: [Kr] 4d<sup>10</sup>5s<sup>2</sup> (nominal valence = 2)  
Se: [Ar] 3d<sup>10</sup>4s<sup>2</sup>4p<sup>4</sup> (nominal valence = 6)



Non polar surfaces  
(stoichiometric)

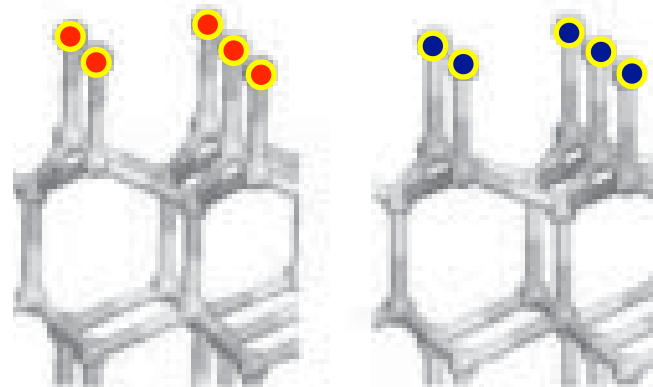
(01 $\bar{1}$ 0)



Zero net dipole moment

Polar surfaces  
(Se-only or Cd-only terminated)

(0001)Se (000 $\bar{1}$ )Cd



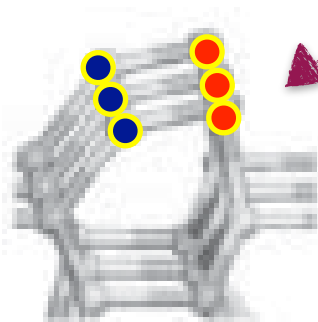
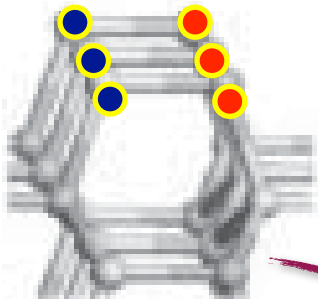
Non-zero net dipole moment

# Surface relaxation

## The case of CdSe

$(01\bar{1}0)$

Non polar



*Significant relaxation*

### ***At the surface:***

- Under coordinated atoms
- Unshared electrons

Every surface tries to minimise its energy

- Finding an optimal (minimal stress) geometry
- Sharing the unshared electrons

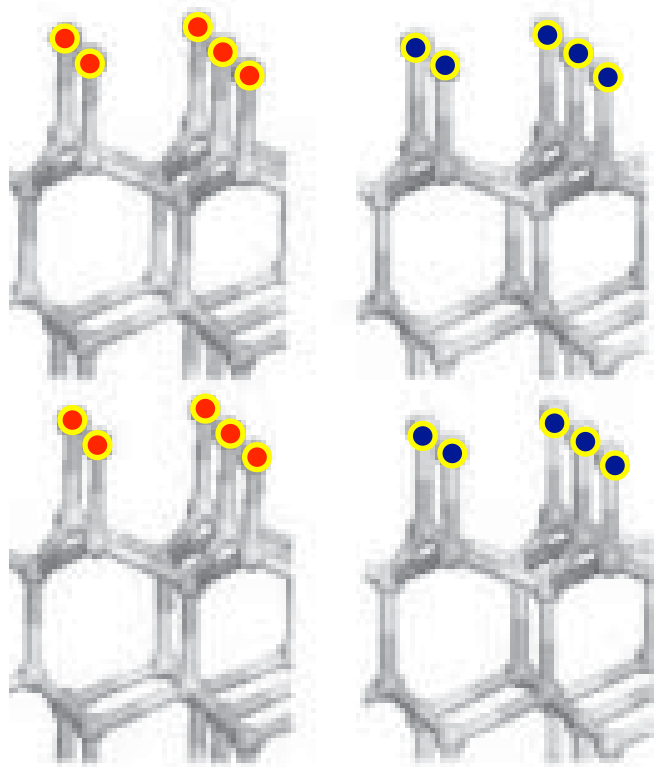
Cd donates its unshared electrons to (the more electronegative ) Se

Se atoms at the surface have two - doubly filled - dangling bonds  
Enhanced reactivity with respect to electronegative species

# Surface relaxation

## The case of CdSe

$(0001)\text{Se}$      $(000\bar{1})\text{Cd}$



Polar (Cd-only or Se-only terminated) surfaces

- Only one atomic type at the surface
- Transfer of electrons from the dangling bonds is not possible

*Negligible relaxation*

Does that mean that polar surfaces are always basically identical to the bulk structure?

No! Other mechanisms can kick in...

How good is DFT with surface relaxation?

Usually very good  
(Classical forcefield are usually very bad [no explicit electrons, which matter a lot in here])

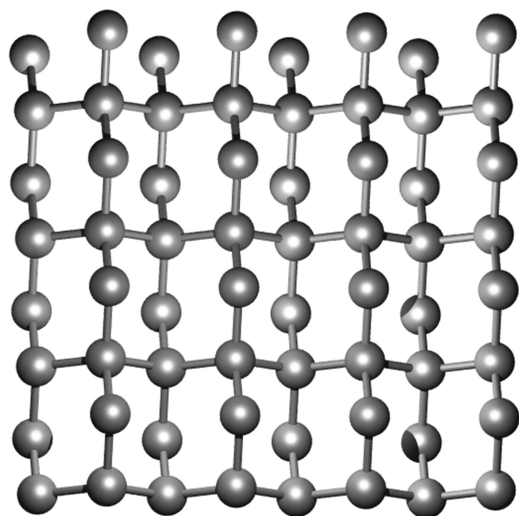
# Surface reconstruction

## *The going gets tough*

### **Surface reconstruction:**

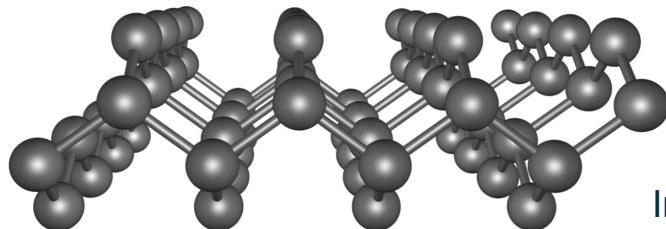
- Not a simple relaxation: atoms at the surface form new bonds
- Different symmetry of surface atoms with respect to the bulk structure

A classical example: Si (001)



2-fold coordination at the surface (it's 4 in the bulk)

DFT is happy with this structure  
(not very different from the bulk)

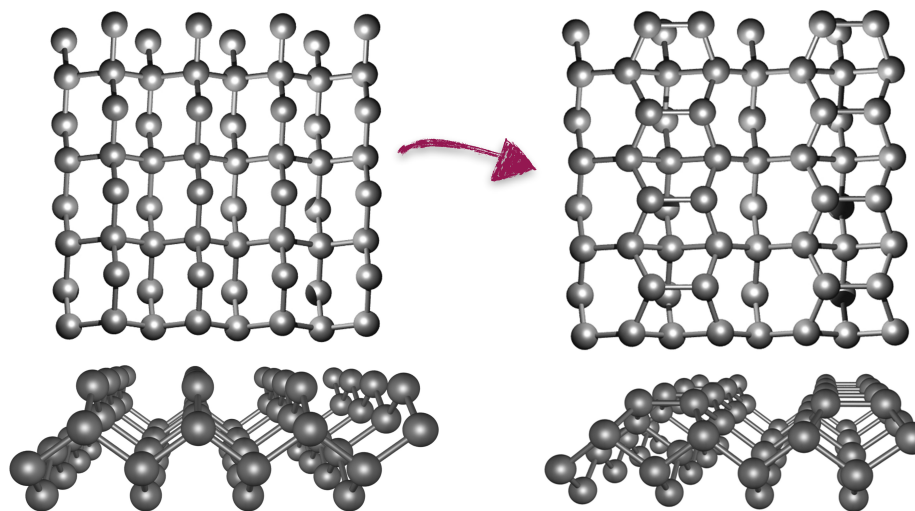


In terms of the electronic structure, you have two dangling bonds  
(one unpaired electron each) for each surface Si atom...

# Surface reconstruction

## *The going gets tough*

In this case (and many other) the system prefers to pair the unpaired electrons by forming new bonds  
Even if in doing so you create a sizeable strain on the existing bonds



A standard DFT calculation will tell you that the reconstructed surface has in this case  $\sim 0.7$  eV/ surface atom more stable than the unreconstructed one... that's quite a difference!



The reconstructed surface (global minimum) won't emerge spontaneously within a DFT calculation of the unrelaxed one (local minimum)!



The interesting stuff at surfaces happens when you have something on top of them!  
(Mainly) two scenarios:

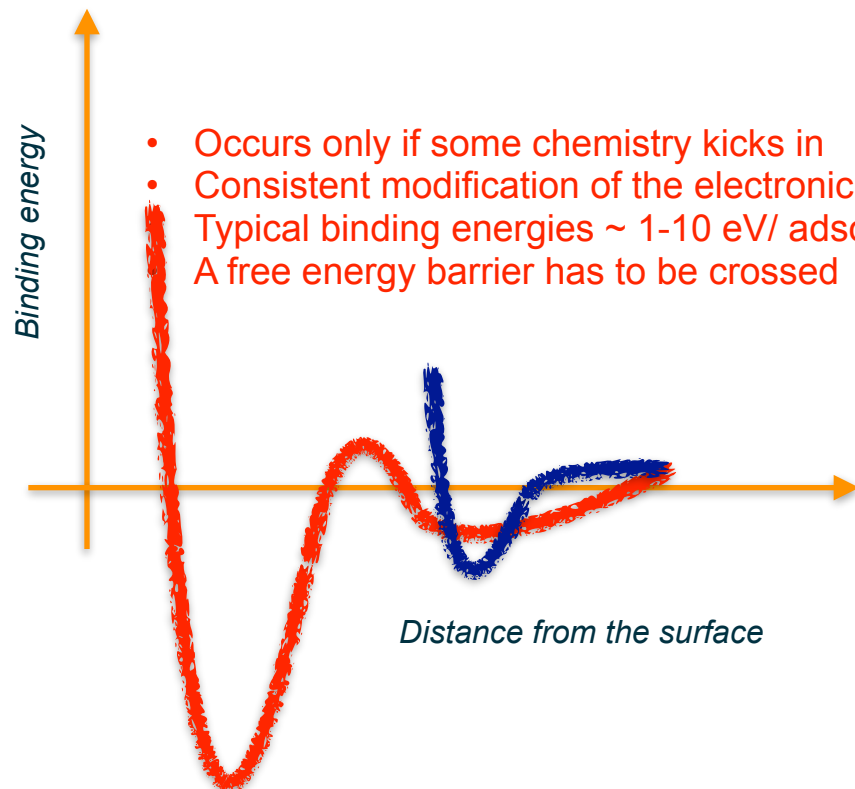
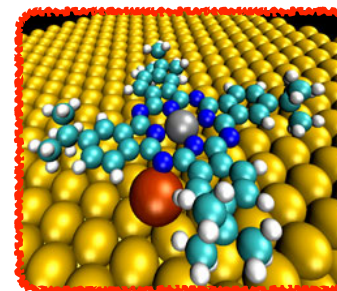
### Physisorption

- Occurs every time you have something close to something else (to a certain extent)
- No sizeable change of the electronic structure of the systems involved
- Typical binding energies  $\sim 10\text{-}100\text{ meV}$  / adsorbed species
- No activation energy



### Chemisorption

- Occurs only if some chemistry kicks in
  - Consistent modification of the electronic structure of the systems involved upon adsorption
- Typical binding energies  $\sim 1\text{-}10\text{ eV}$  / adsorbed species  
A free energy barrier has to be crossed



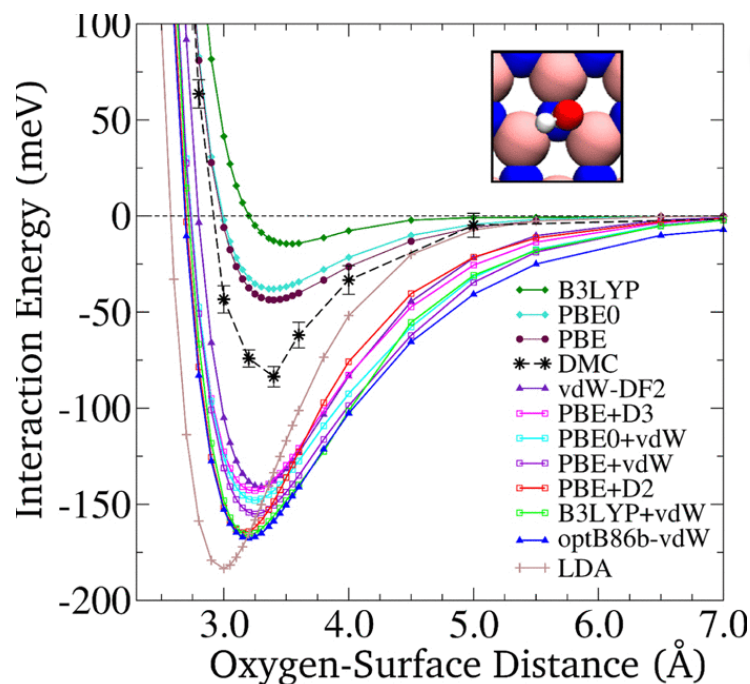
Sounds easy?

Binding energies are usually very easy to obtain via DFT calculations



In many cases, results are exceedingly dependent on the choice of the XC functional

*e.g. water on boron nitride*



Especially in the case of physisorption...

Why?

Including long range dispersion forces (Van der Waals interactions) is not trivial within DFT

Most XC functionals are based on local approximation of the electronic densities (and that includes GGA functionals!)

*More on that in Prof. Michaelides' Lecture*

### *Surfaces modify adsorbed species*

- Bond breakage
- Charge transfer
- Reactivity
- Long-range ordering

### *Adsorbed species modify surfaces*

- Surface relaxation
- Surface reconstruction
- Reactivity
- Crystal growth

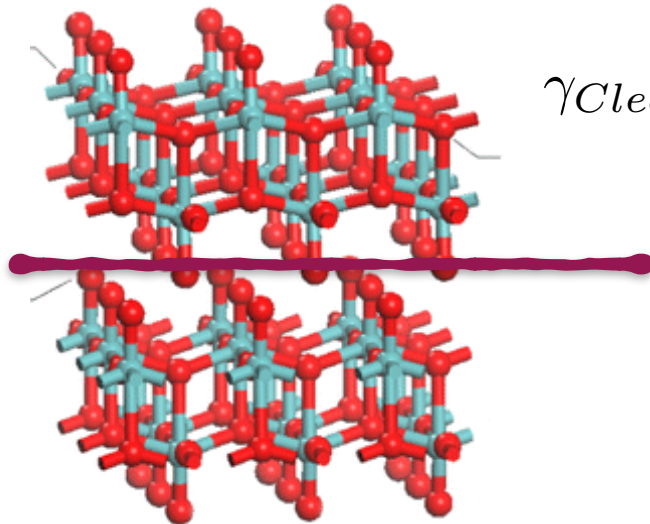


An example:  
*Controlling the equilibrium shape of a crystalline system*

**CdSe again!**

Let's start by defining the energy cost to be paid for creating a surface out of the bulk system as the surface energy  $\gamma_{\text{Clean}}$ :

$$\gamma_{\text{Clean}} = \frac{1}{A} \cdot (E_{\text{Slab}} - N E_{\text{Bulk}})$$



Total surface area of the slab

Total energy of the slab

N. of atoms

Total energy of the bulk

# Adsorbates

## Surfaces & Adsorbates

And the energy gain  $E_b$  for an adsorbate to sit on top of the surface

$$E_b = \frac{1}{N_{Ad}} \cdot (E_{Slab,Ad} - E_{Slab} - N_{Ad} \cdot \mu_{Ad,gas})$$

Number of adsorbates

Total energy of the slab with  
the adsorbate(s) on top

Chemical potential of the adsorbate in the gas phase

So that we can write the surface energy of e.g. a surface with some adatoms on top as:

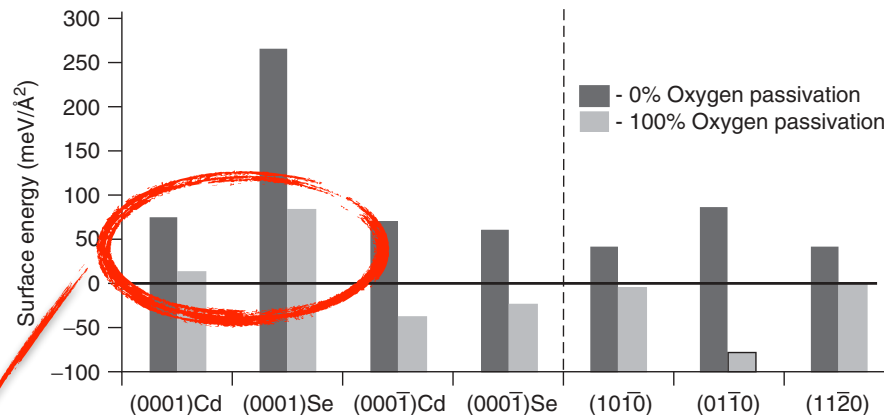
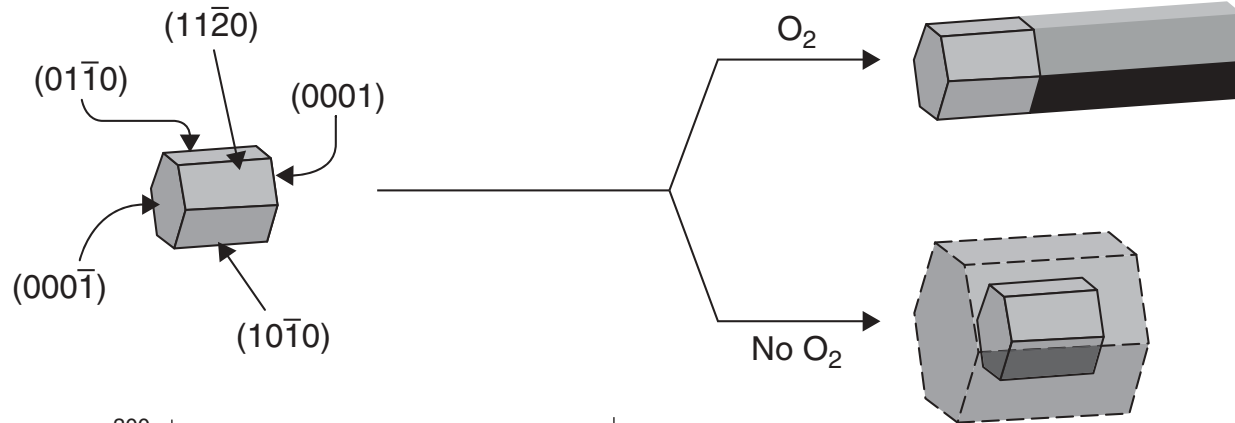
$$\gamma_{Slab,Ad} = \gamma_{Clean} + N_{Ad} \frac{E_b}{A}$$

This expression depends on the binding energy, which in turn, being a function for the chemical potential, is a function of temperature, pressure, chemical environment and surface coverage.

Playing with this variables rules which passivated surfaces (i.e. with adatoms on top) are the most stable ones

Ultimately determines the equilibrium shape and the morphology of the growing crystal  
(And all of this can be obtained via not-so-complicated DFT calculations!)

A practical example:  
the anisotropic, asymmetric growth of CdSe nano crystals in the presence of oxygen



*Piling up Cd-only and Se-only terminated surfaces along the (0001) - higher surface energy if passivated with O<sub>2</sub>*

In general, you would expect a modification of both the electronic structure of the adsorbate and the surface, to an extent proportional to the strength of their interaction

A “simple” framework: the Newns-Anderson model

$$\hat{\mathcal{H}} = E_{Ad} \cdot \hat{n}_{Ad} + \sum_k E_k \cdot \hat{n}_k \sum_k (V_{Ad,k} \cdot \hat{b}_{Ad}^\dagger \hat{b}_k + V_{k,Ad} \cdot \hat{b}_k^\dagger \hat{b}_{Ad})$$

$E_{Ad}$  Energy level (a single valence state) of the unperturbed adsorbate

$E_k$  (Bloch) one electron energy levels of the surface

$V_{Ad,k}$  Hopping matrix element - perturbation caused by the adsorbate  
(**quantifies the surface-adsorbate interaction**)

$\hat{n}_\alpha = \hat{b}_\alpha^\dagger \hat{b}_\alpha, \quad \alpha = Ad, k$  Number operator expressed as a function of creation/annihilation operators (counts the number of states)



Applying Hartree-Fock approximation and the  
Green's functions formalism...



The adsorbate (projected) density of states can be written as:

$$\rho_{Ad}(E) = \frac{1}{\pi} \frac{\Delta E}{(E - E_{Ad} - \Lambda E)^2 + \Delta^2 E}$$

$$\Lambda E \propto \sum_k \frac{|V_{Ad,k}|^2}{E - E_k} \quad \bullet \rightarrow \text{Shift function}$$

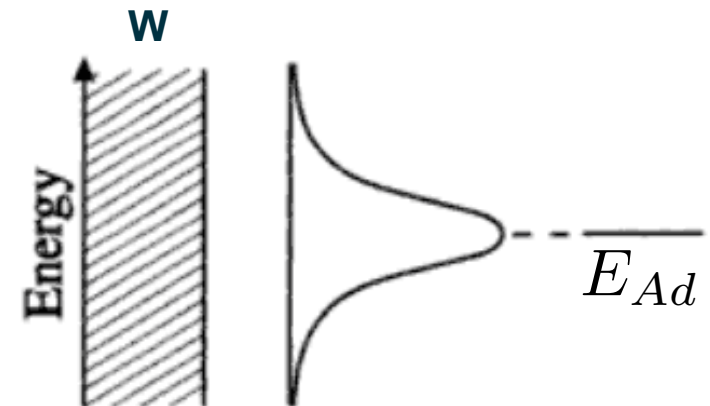
$$\Delta E = \pi \sum_k |V_{Ad,k}|^2 \delta(E - E_k) \quad \bullet \rightarrow \text{Chemisorption function}$$

*A local projection of the substrate density of states around the adsorbate*

Two limiting cases for the chemisorption function

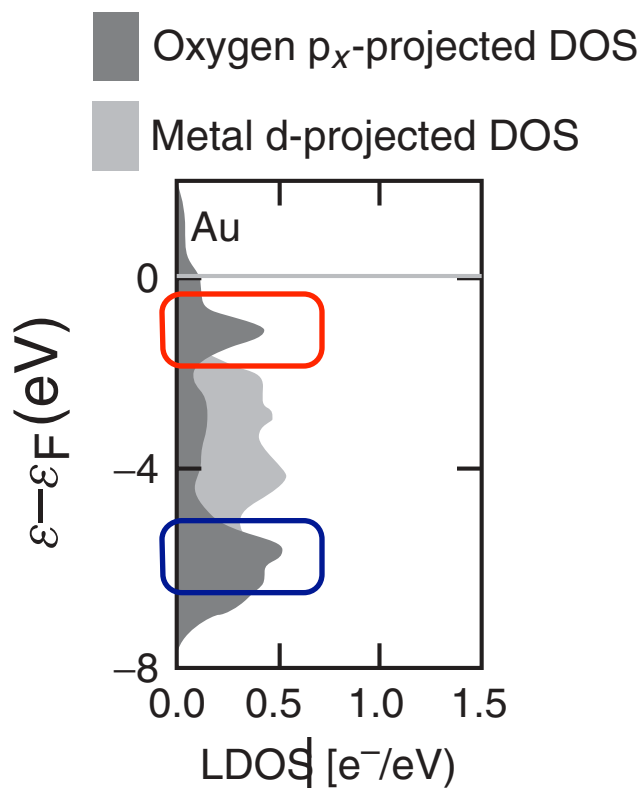
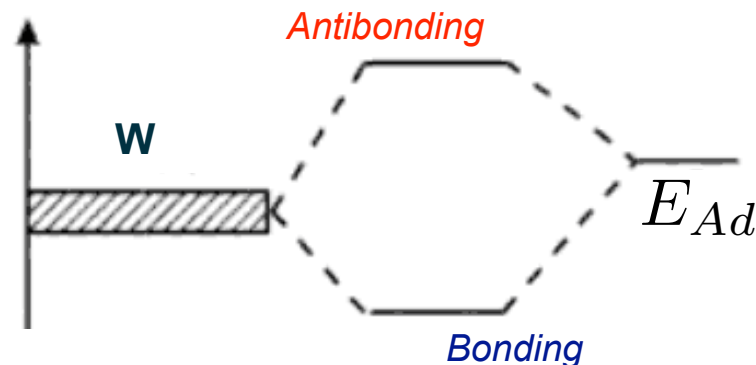
### Weak chemisorption

- The electronic bandwidth of the surface (**W**) is much larger than the adsorbate-surface interaction (**V<sub>Ad,k</sub>**)
- The chemisorption function does not depend on the energy anymore and the density of states for the adsorbate is basically a Lorentzian function
- Typically so-band of a simple metal



### Strong chemisorption

- The electronic bandwidth of the surface ( $W$ ) is small
- The surface-adsorbate interaction ( $V_{Ad,k}$ ) gives rise to bonding and anti bonding states
- Typically metallic surfaces with narrow d-bands



e.g. oxygen adatom on top of gold

A lot of information about the surface-adsorbates system can be obtained by just static DFT calculations

However, things are not always as easy as a single adatom on a pristine metallic surface...

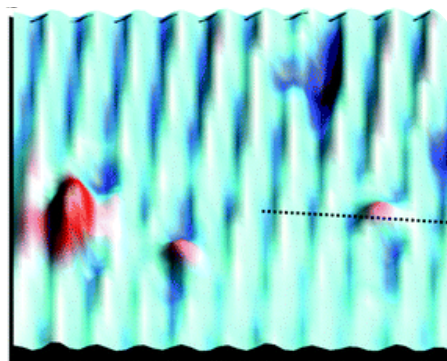
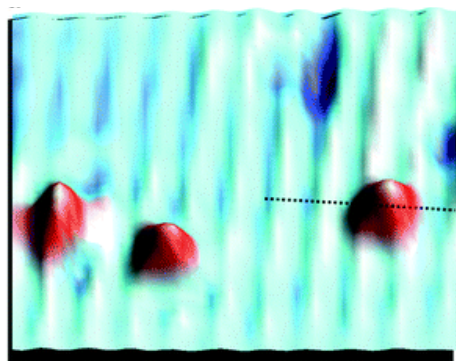
# *(Accurate) DFT meets (clean) experiments*

The electronic density of states is a very useful quantity  
It can be used to complement experiments in a number of ways...

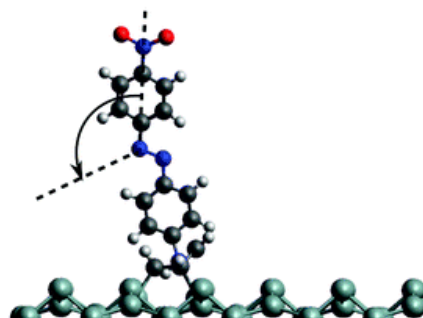
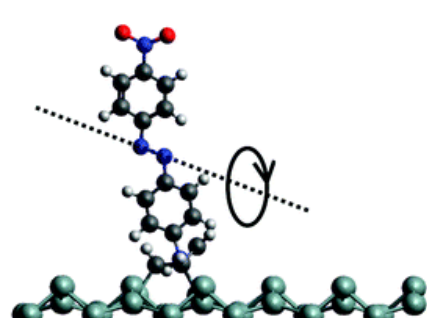


Scanning Tunneling Microscope (STM) measurements  
(1986 Nobel prize - Binnig & Rohrer)

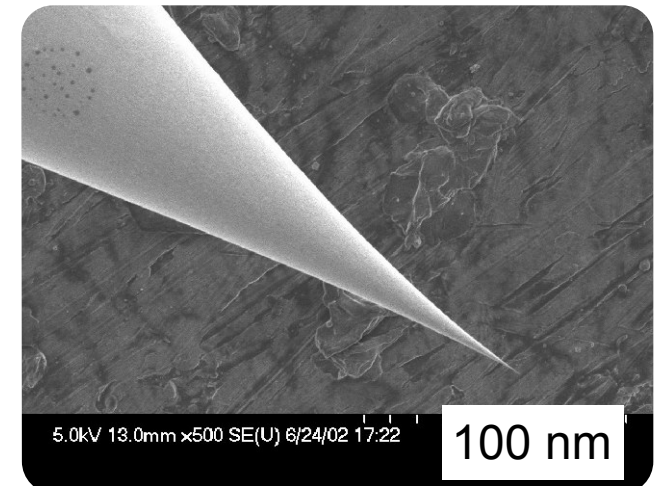
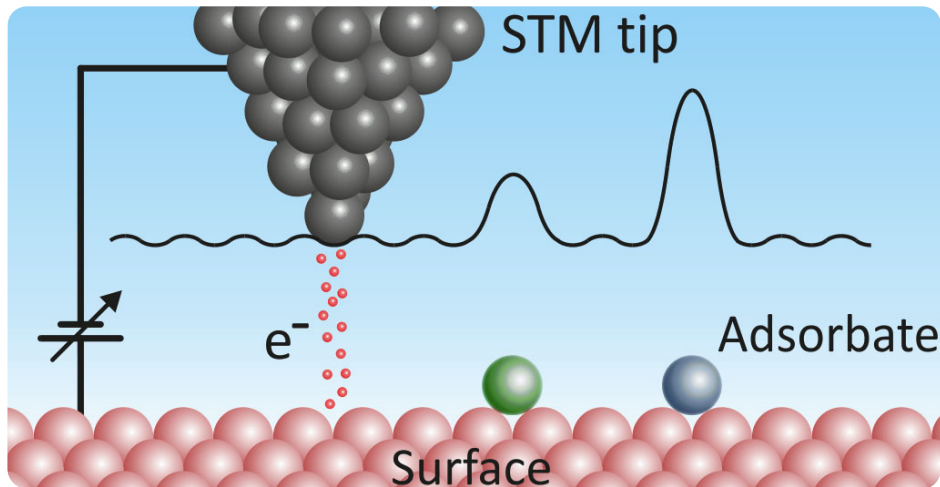
Gives spatially resolved (often at the atomic level) information about a conducting  
(metallic, semiconducting...) surface, with or without adsorbates on top



Useful comparison between (accurate) DFT  
calculations and (clean) experimental data  
In some cases, DFT can help in interpret (not  
over interpret) the experiments



STM data are a non trivial convolution of the atomic heights at the surface and the electronic structure of the latter



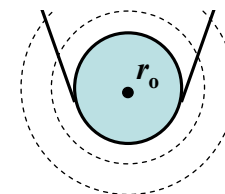
*The final result is a function of:*

- The density of states at the surface
- The structure of the surface
- The density of states of the tip
- The structure of the tip

Note that you don't image the surface directly,  
rather you monitor the current flowing through tip and surface (tunneling current)

# Tersoff-Hamann approximation

The simplest formulation of the STM current  $I_{STM}$  can be obtained by modelling the tip as a locally spherical potential centered at  $\mathbf{r}_{Tip}$



## Tersoff-Hamann approximation

$$I_{STM} \propto \sum_{i=1}^{N_{Surf}} |\psi(\mathbf{r}_{Tip})|^2 \delta(E_{Tip} - E_i) = \rho(\mathbf{r}_{Tip}, E_f)$$

The tunnelling current is proportional to the LDOS of the surface evaluated at the position of the tip (that is, through the vacuum region)



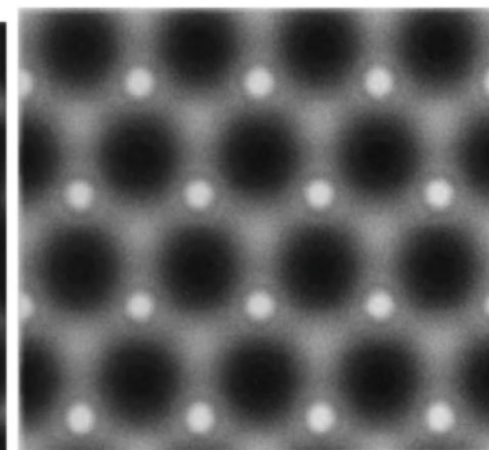
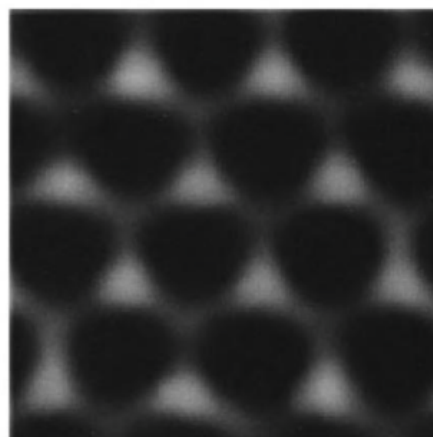
Sum of the (broadened) KS states

Very straightforward implementation  
(you just need the LDOS)



The tip is not taken into account *at all*

Ok for semiconductors, not so good for  
metallic surfaces...



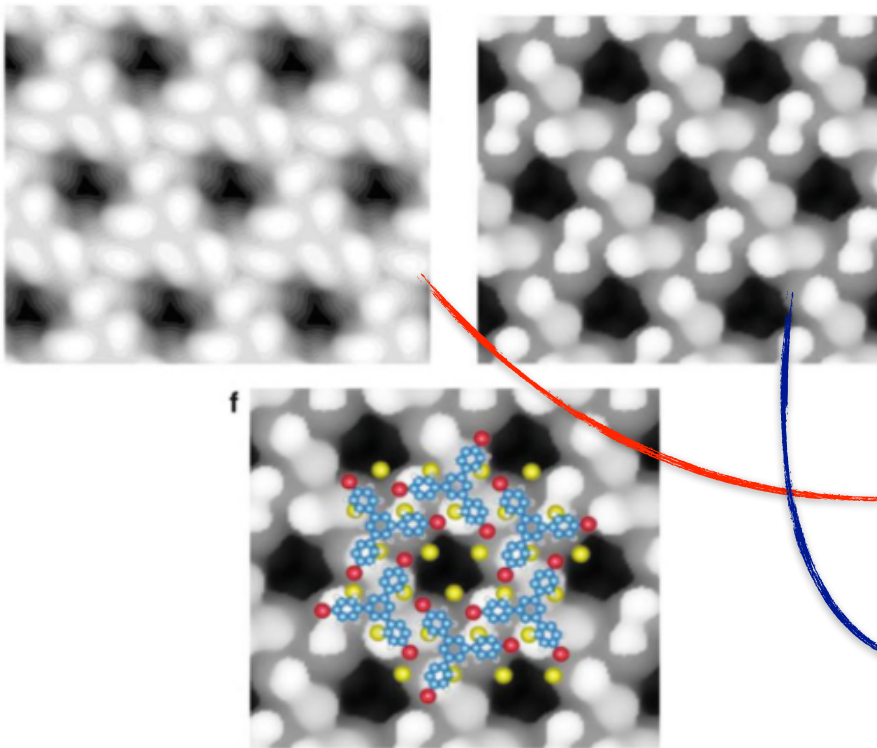
**Fig. 4.21.** Comparison of measured (*left panel*) and simulated (*right panel*) STM image of highly oriented pyrolytic graphite(0001) (courtesy of W. Heckl and T.

# Bardeen approximation

Beyond the Tersoff-Hamann approximation:  
**The Bardeen approach**

$$I_{STM} \propto \sum_{i=1}^{N_{Surf}} \sum_{j=1}^{N_{Tip}} \left| \left( \int_{S_{Div}} \psi_j^* \nabla \psi_i - \psi_i \nabla \psi_j^* \right) ds \right|^2 \delta(E_j - E_i - eV)$$

Integral over all the surfaces lying within the vacuum region between the surface and the tip
Applied voltage



- The interaction between the tip and the surface is taken into account (it's a perturbative approach)
- Requires a model (in fact, several models) for the tip structure and the tip LDOS as well

*Tersoff-Hamann*

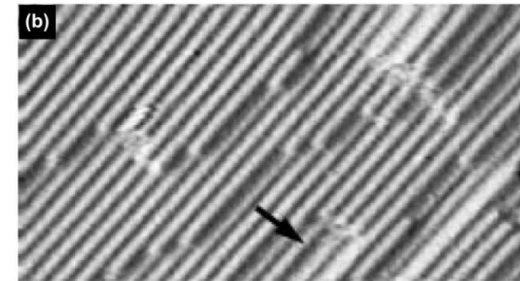
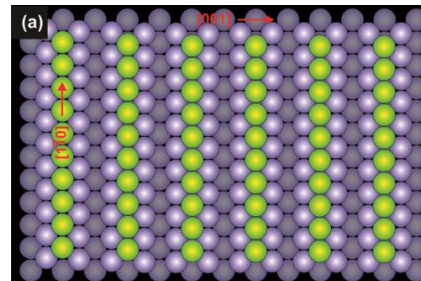
*Bardeen*



# Complex interfaces

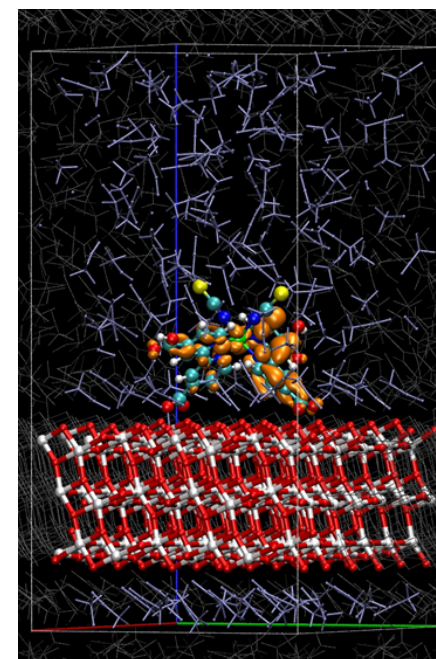
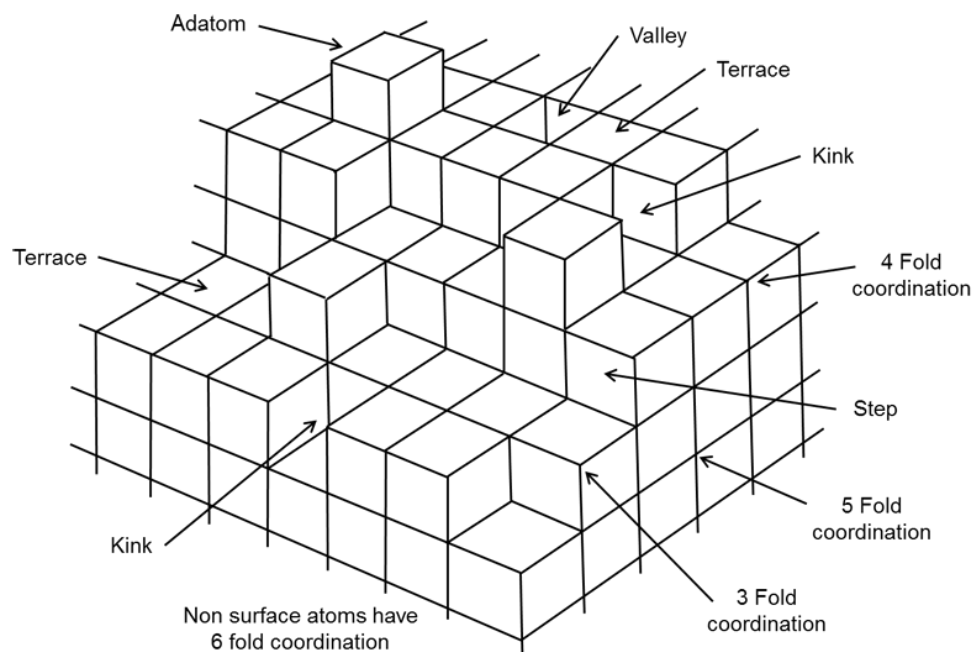
## "Real" systems

Surfaces are very rarely flat, defects-free objects...  
(In very few cases can be characterised by State of the art techniques such as STM @ Ultra-high vacuum conditions)



**Fig. 7.** (a) A model of (1x2) missing row reconstruction of Au(110). Green colored atoms are the top rows. (b) An STM image of Au(110) reconstruction [98M]. The image shows several terraces with atomic rows along the [110] direction separated by 0.8 nm. At the lower part of the image, two lines are observed with a longer separation of 1.2 nm [indicated with an arrow].

However, as a rule of thumb...



# Complex interfaces

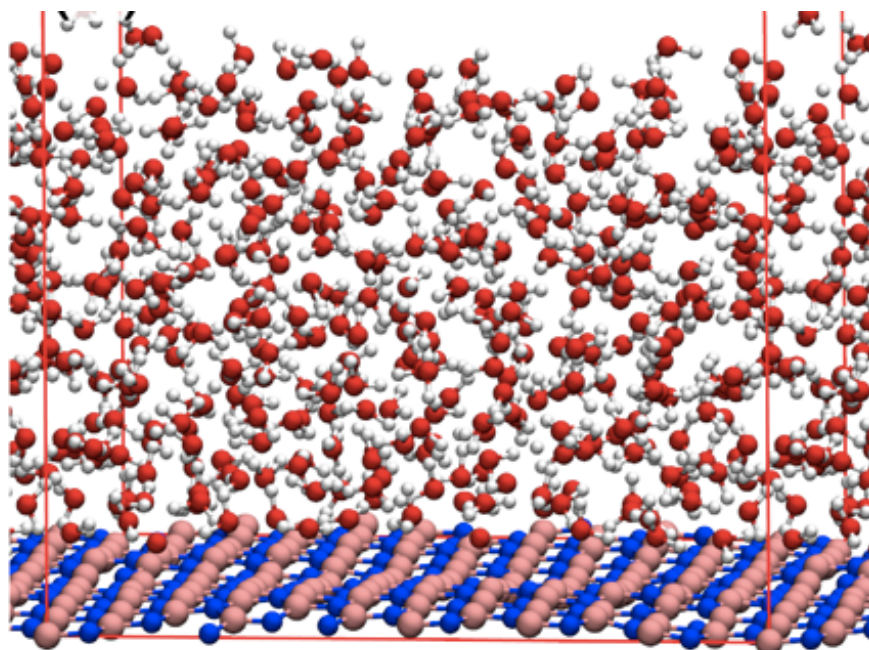
## *Ab initio MD*

On top of the complexity of surface and interfaces...



Dynamical properties at interfaces:  
*Ab initio MD* is (slowly) emerging as a possibility

An example: friction of liquid water on boron nitride



How do we get dynamical properties in the first place?

A quick introduction in the next Lecture...

We **need** DFT simulations of surfaces & interfaces  
Classical force field are very rarely accurate enough!

# End of lesson

*Next: Disordered Systems*

- Learning Outcomes
  - *A whole different playground*
  - *A number of possibilities*