# Problem with Kohn-Sham equations

(So much time consuming)

$$H_s \Psi = E_{el} \Psi$$

$$(T_s + V_{e-e}[n] + V_{ext}[n] + V_{XC}[n])\varphi_i = E\varphi_i \quad i = 1, 2, .., N$$

$$n(r) = \sum_{i=1}^{N} |\varphi_i|^2$$

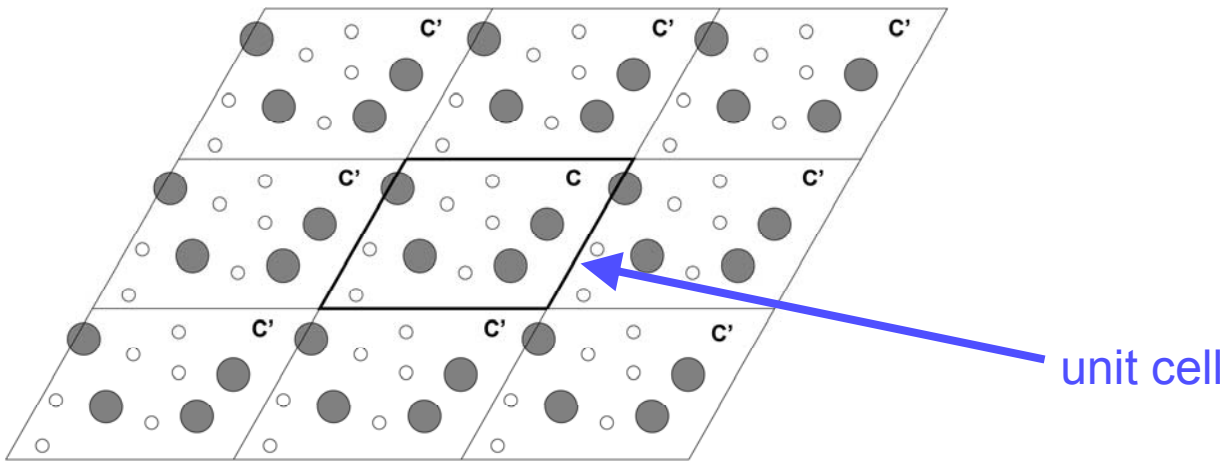
- The one-particle Kohn-Sham equations can be solved for an system with maximum few hundred number of atoms.
- In a crystal or a slab however we have a order of $10^{23}$ number of atoms. Simulating such an amount of particles is impossible due to the huge computer time consuming.
- If the system is fully periodic a appropriate choice would be to use periodic boundary conditions.

# *Periodic boundary conditions*

***Crystal:*** is an infinite array of discrete points with an arrangement and orientation that appears exactly the same on all

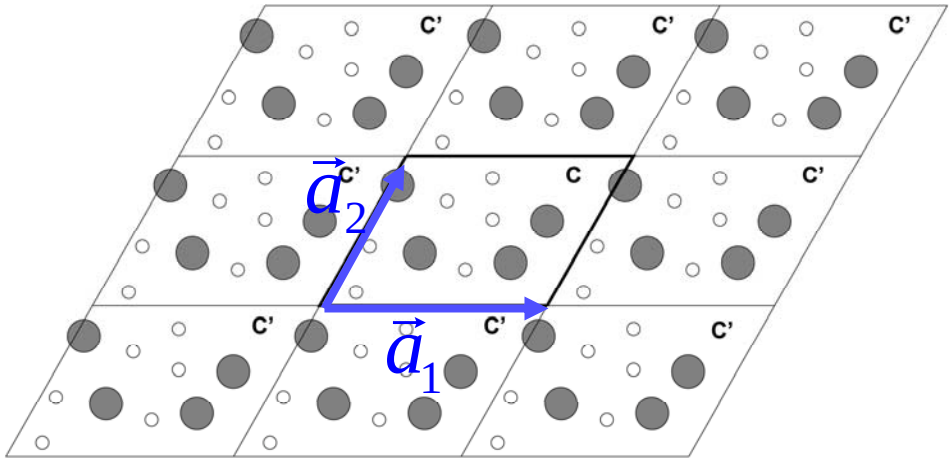
***Unit cell:*** It is a part of the lattice which is repeated in all directions

Example:




In this example the unit cell was repeated twice in x,y,xy and –xy directions

- Every unit cell consist of 3 lattice vectors $a_1, a_2, a_3$
- The lattice vectors can not be all in the same plane




- In order to specify the position of the atoms in whole crystal. It is just enough to specify the position of the atoms in the unit cell

- If the position of one atom in the unit cell is $r_1$ the position of this atom in the next unit cells is given by:

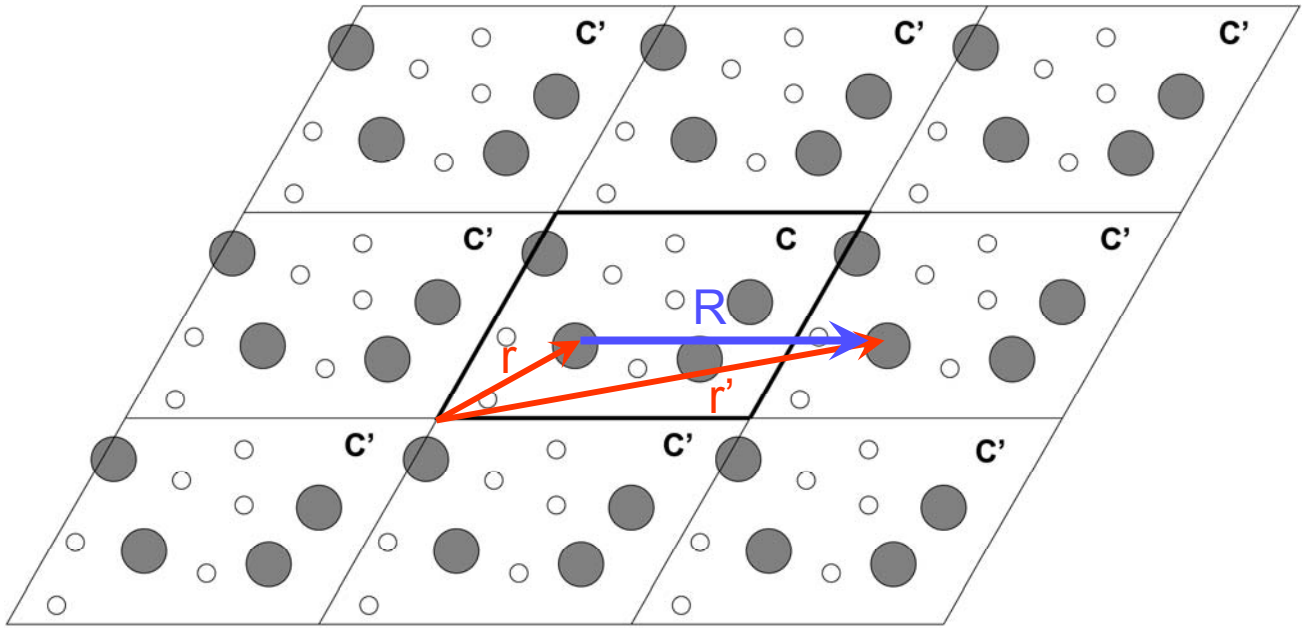
$$\vec{r}' = \vec{r}_1 + \vec{R}$$

where:

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

and $n_1, n_2, n_3$ are integer numbers

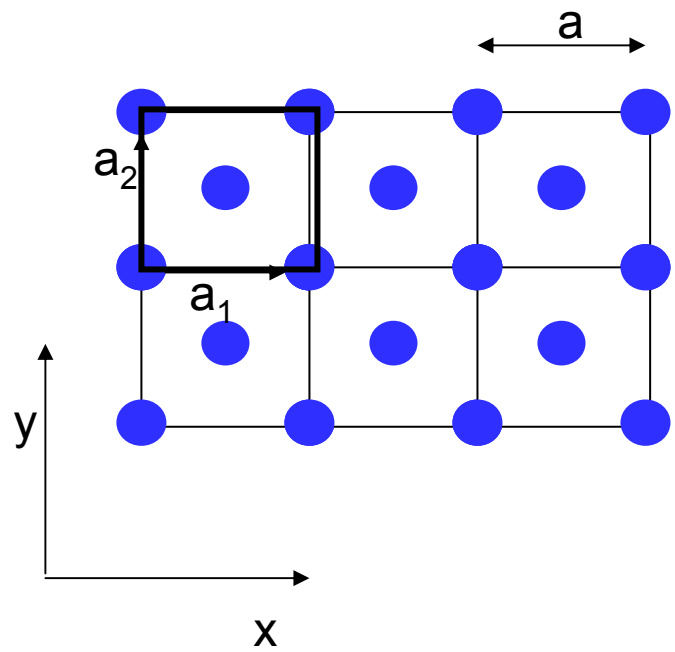
Example:




$R$: $n_1 = 1, \quad n_2 = 0, \quad n_3 = 0$

The calculation saving comes since only the atoms and electrons inside the unit cell of the calculation sometimes also called super-cell needs to be explicitly considered.

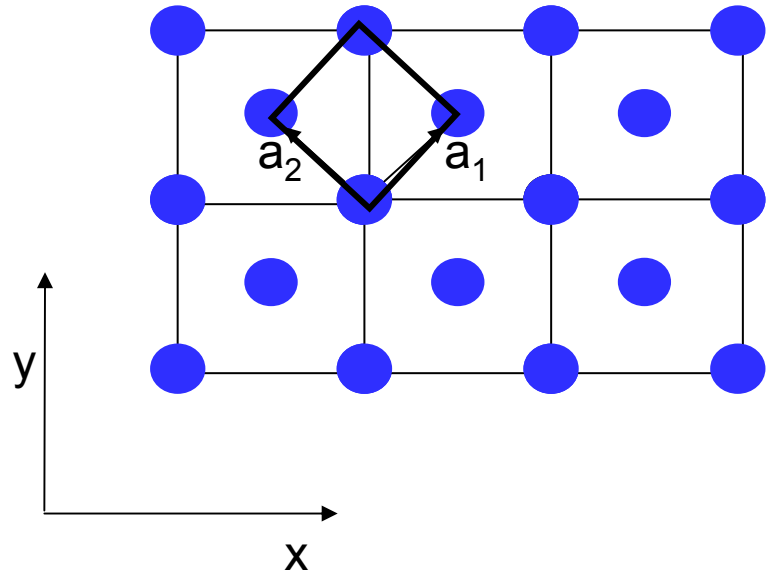
Example 2: Find the lattice vectors.




$\mathbf{a_1} = a\,\mathbf{i} = (1\ 0\ 0)\ a$
$\mathbf{a_2} = a\,\mathbf{j} = (0\ 1\ 0)\ a$

There are two atoms in the super cell. The position of these two atoms are (000) and (½ ½ 0). Note that we consider a two dimension Bravais lattice therefore the position of atoms along z-direction are zero.

***Primitive unit cell:*** is a super cell in which contains only one atom. The Bravais lattice of a primitive super cell is given by:




$$\vec{a}_1 = a.\cos\left(45^\circ\right)\hat{i} + a.\sin\left(45^\circ\right)\hat{j} = a\left(\frac{\sqrt{2}}{2}\hat{i} + \frac{\sqrt{2}}{2}\hat{j}\right)$$

$$\vec{a}_1 = -a.\cos\left(45^\circ\right)\hat{i} + a.\sin\left(45^\circ\right)\hat{j} = a\left(\frac{-\sqrt{2}}{2}\hat{i} + \frac{\sqrt{2}}{2}\hat{j}\right)$$

What is the position of the atom in the unit cell?

# Bravais lattice in three dimensions

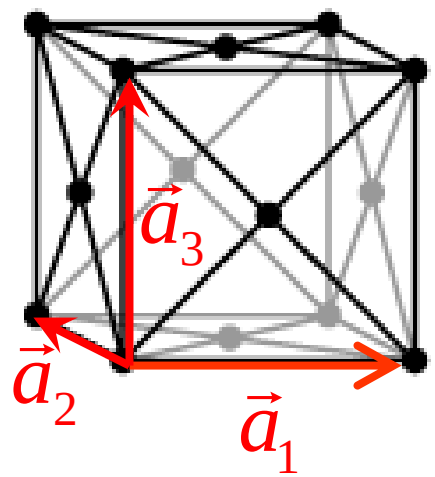
- Depending on the angles between lattice vectors and the ratio of the length of lattice vectors, there are 14 type of unit cell or Bravais lattice. One of the most important one in electrochemistry is cubic Bravais lattice.

$$|\vec{a}_1| = |\vec{a}_2| = |\vec{a}_3|, \quad \alpha = \beta = \gamma = 90^\circ$$

- Face Center Cubic or FCC is a cubic lattice

Lattice vectors

$$\vec{a}_1 = a.\hat{i}$$
$$\vec{a}_2 = a.\hat{j}$$
$$\vec{a}_3 = a.\hat{k}$$




Atom positions

$$\vec{r}_1 = (0,0,0)$$
$$\vec{r}_2 = \left(\frac{1}{2},\frac{1}{2},0\right)$$
$$\vec{r}_3 = \left(\frac{1}{2},0,\frac{1}{2}\right)$$
$$\vec{r}_4 = \left(0,\frac{1}{2},\frac{1}{2}\right)$$

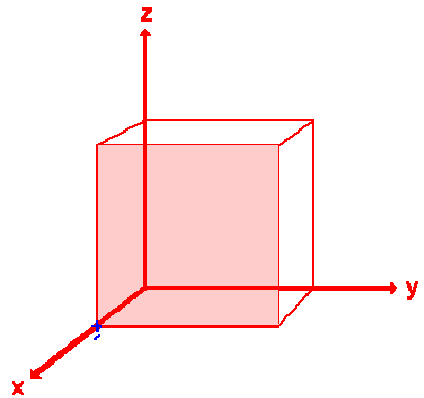
Practice: What is the primitive unit cell of this Bravais lattice?

# Surface science

***Miller index***: a set of numbers which quantify the intercepts and thus is used to uniquely identify the plane or surface.

- First the interception of the surface with x, y and z is calculated.
- Then it is devided to lattice constant (a)
- The inverse of those numbers is the miller index of that surface.

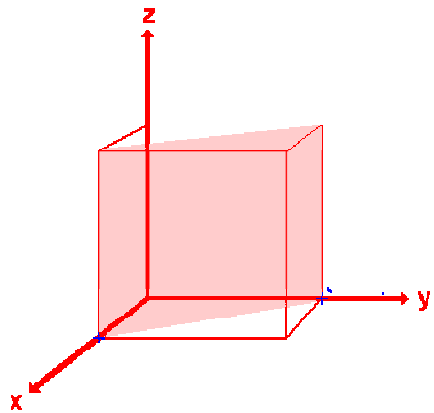
Example:




Interception: x=a, y=∞, z= ∞

Miller index: (a/a, 1/ ∞, 1/ ∞)= (100)

**surface (100)**



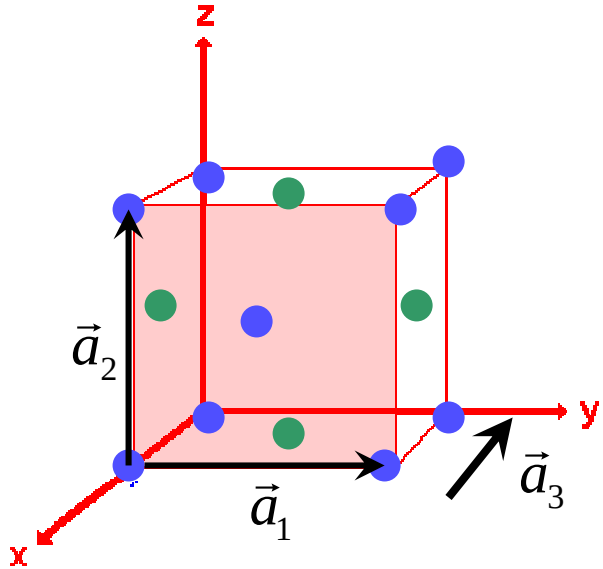

Interception: x=a, y=a, z= ∞

Miller index: (a/a, a/ a, 1/ ∞)= (110)

**surface (110)**

# Surface (100)

- We consider a FCC Bravais lattice
- The lattice vectors are chosen in a way that $\vec{a}_3$ is perpendicular to the surface

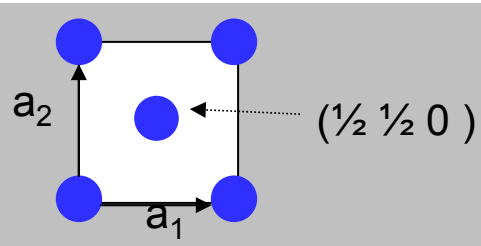



atom positions

$\vec{r}_1 = (0,0,0)$

$\vec{r}_2 = \left(\frac{1}{2},\frac{1}{2},0\right)$

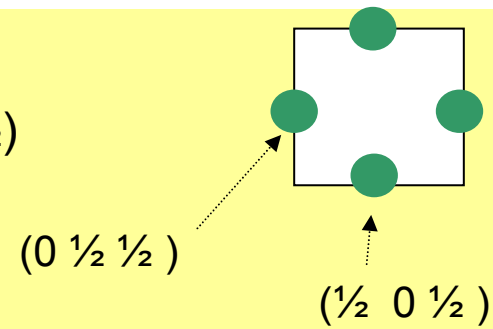
First layer ($a_3$=0)




$\vec{r}_3 = \left(\frac{1}{2},0,\frac{1}{2}\right)$

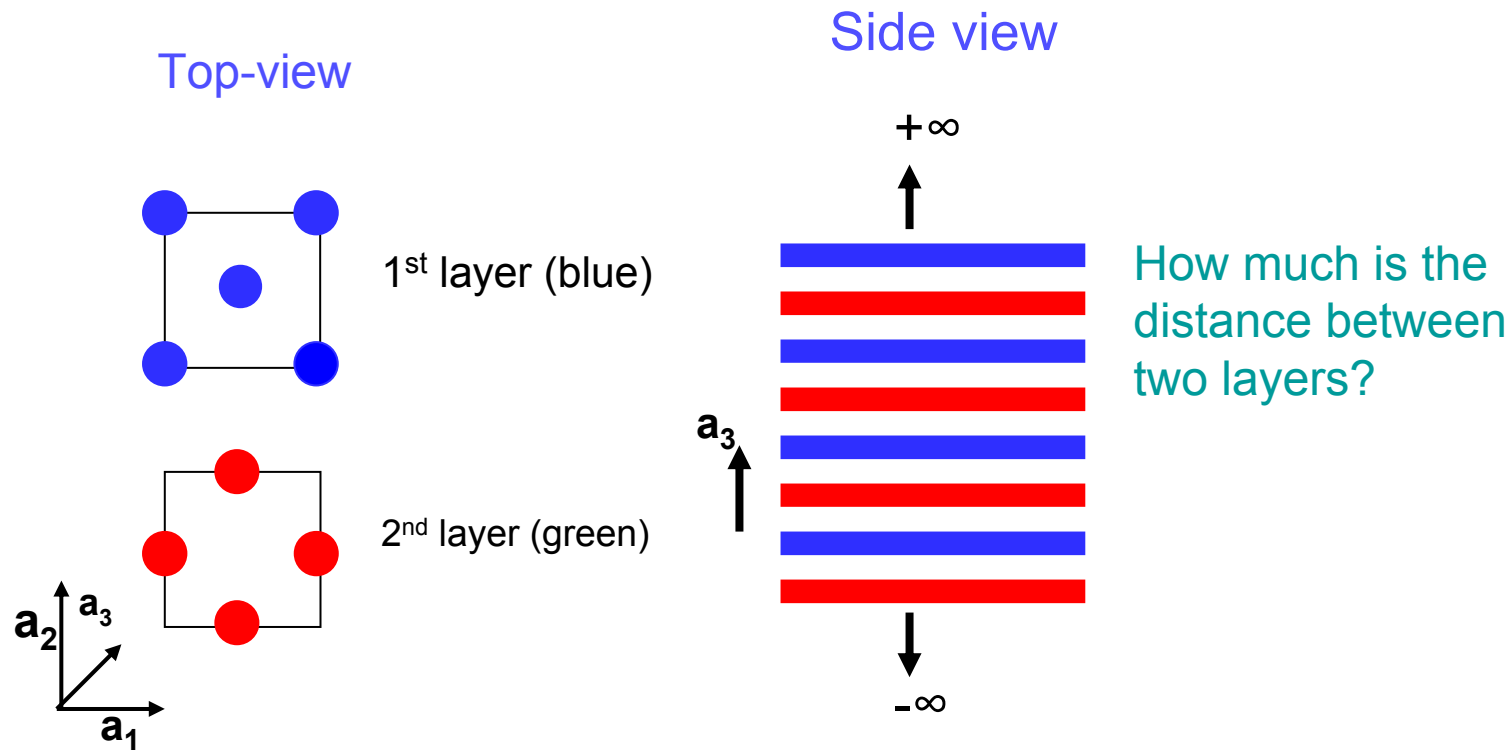
$\vec{r}_4 = \left(0,\frac{1}{2},\frac{1}{2}\right)$

Second layer ($a_3$= ½)



# How do we create a surface

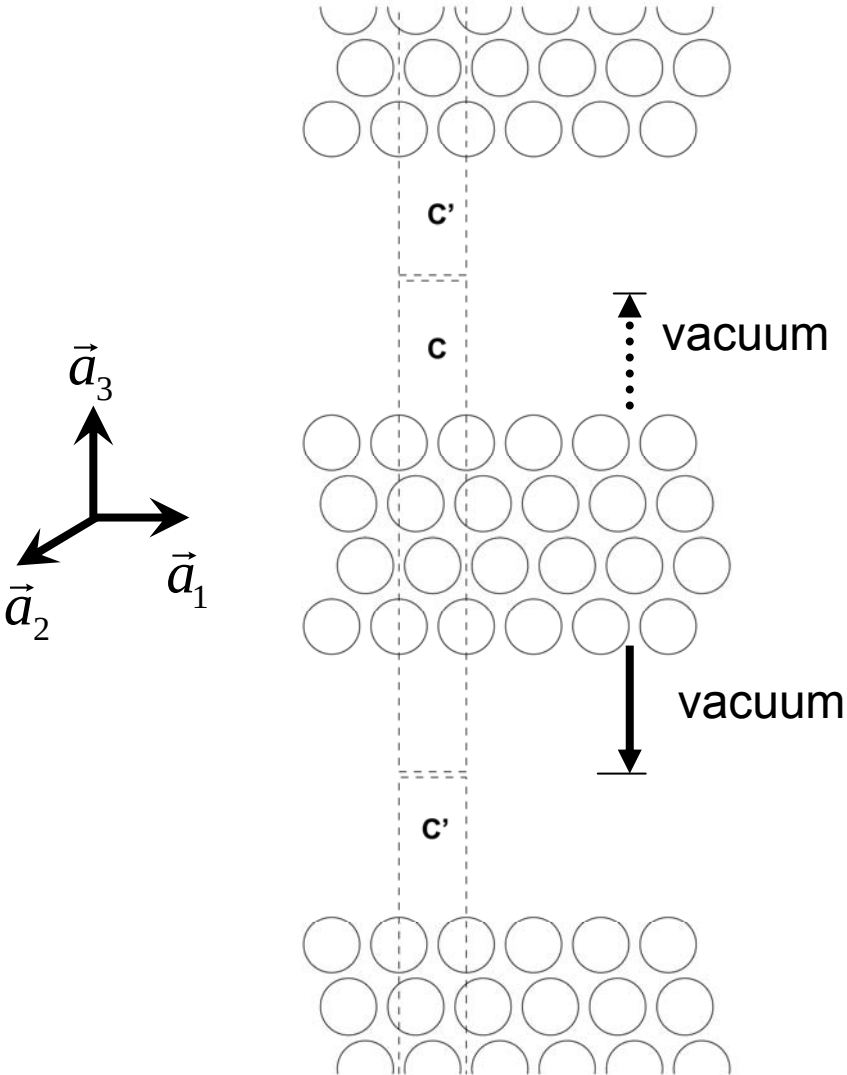
- Surface is defined as a symmetry breaking along z direction




The problem is that the unit cell will be repeated infinite times along x,y and z direction

# Large super cell along the vector perpendicular to the surface ($a_3$)

One approach to make an artificial surface is to consider a large super-cell along $a_3$ direction.




Note: The periodic boundary conditions are still preserved but the super-cell is chosen to be so large that the slabs do not interact. Usually a distance of 12Å is sufficient.

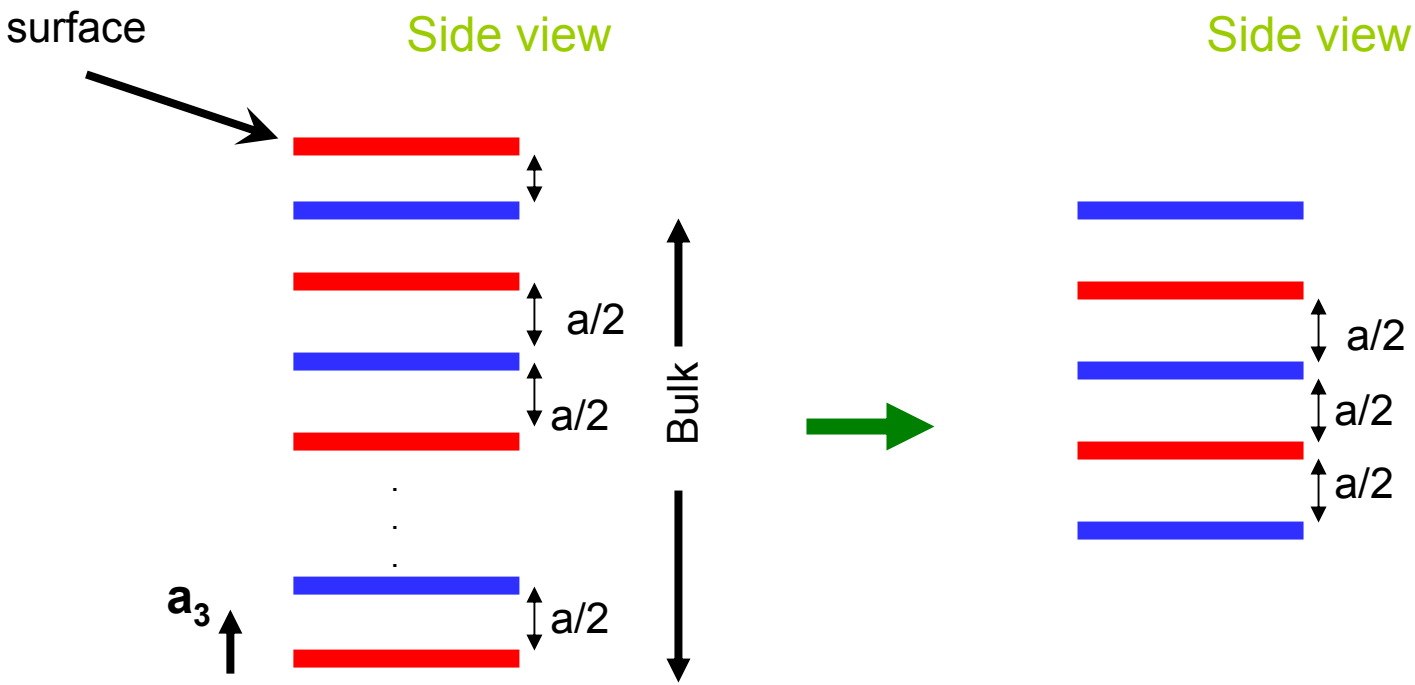
Question: What is the distance between two layers in surface(100)? If the Pd lattice constant $a_{Pd}$=3.96Å how many vacuum layers we need for surface(100) in order to have no interaction between two slabs?

Question: How can we perform a simulation of CO molecule in gas phase (a isolated CO molecule)?

# *Number of layers*

***In reality:***
*infinite number of layers*

***In simulation:***
*Only 4 to 5 number of layers*



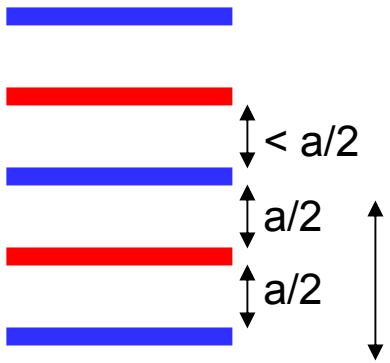

We consider only 4 to 5 layers

The more packed a layer is the less number of layers are needed.

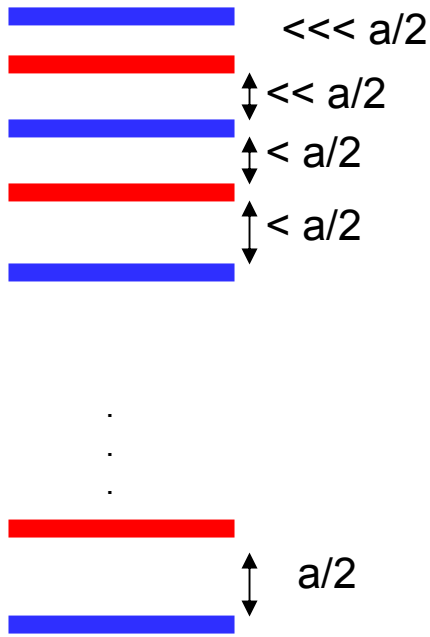
How do we realize how many layers is sufficient?

# Geometry optimizations along Z direction

Before optimize geometry




after optimize geometry

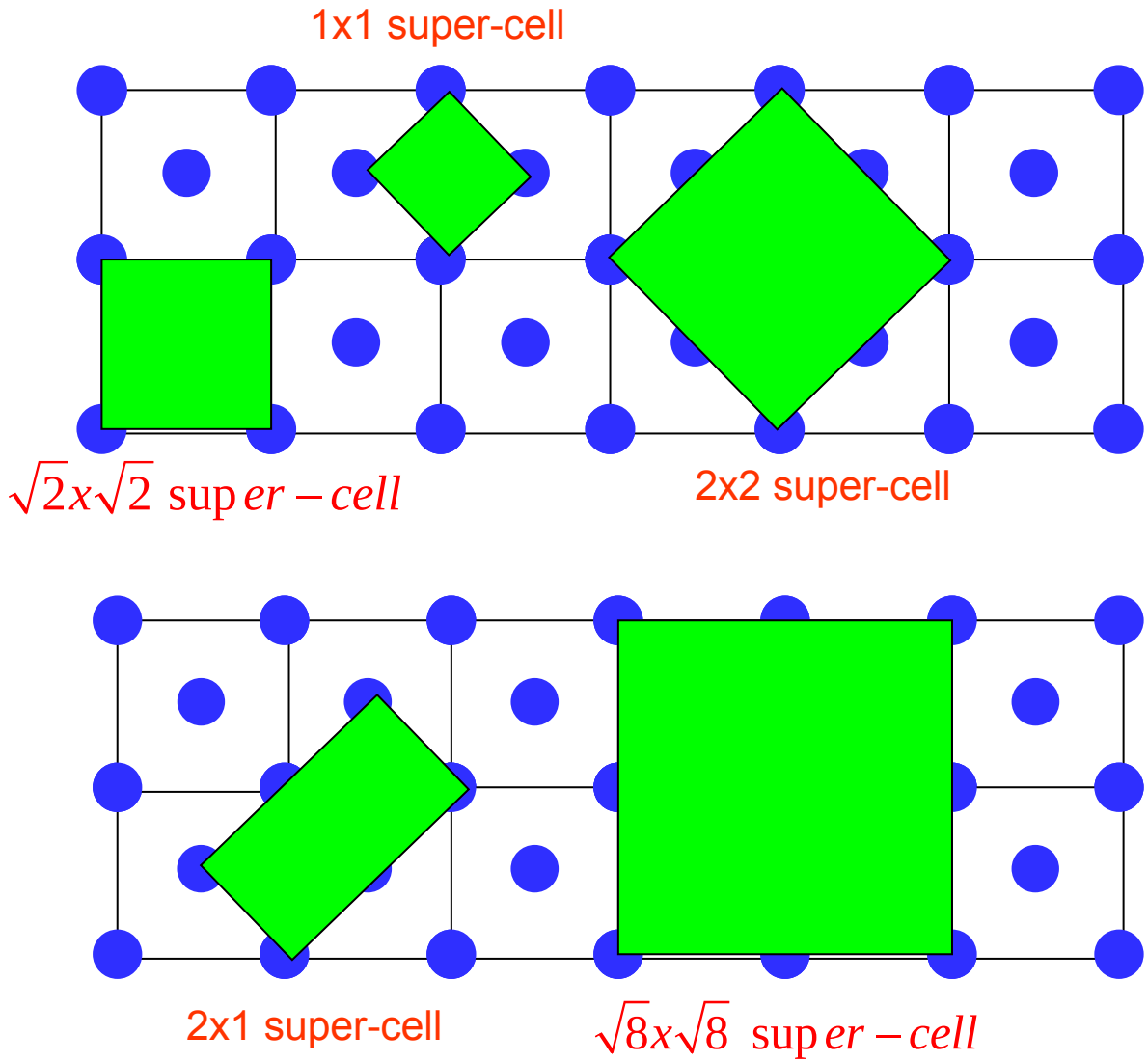


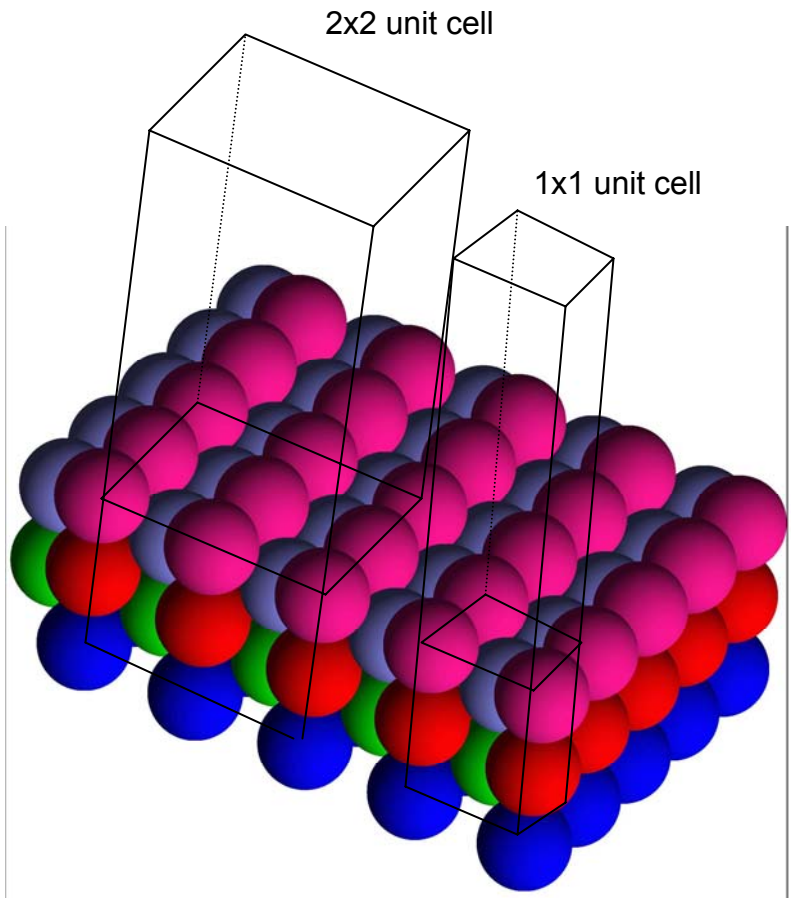

The sufficient number of layers is obtained by increasing the number of layer step by step until the separation at the first layers = a/2, Problem: Then we need a large number of layer

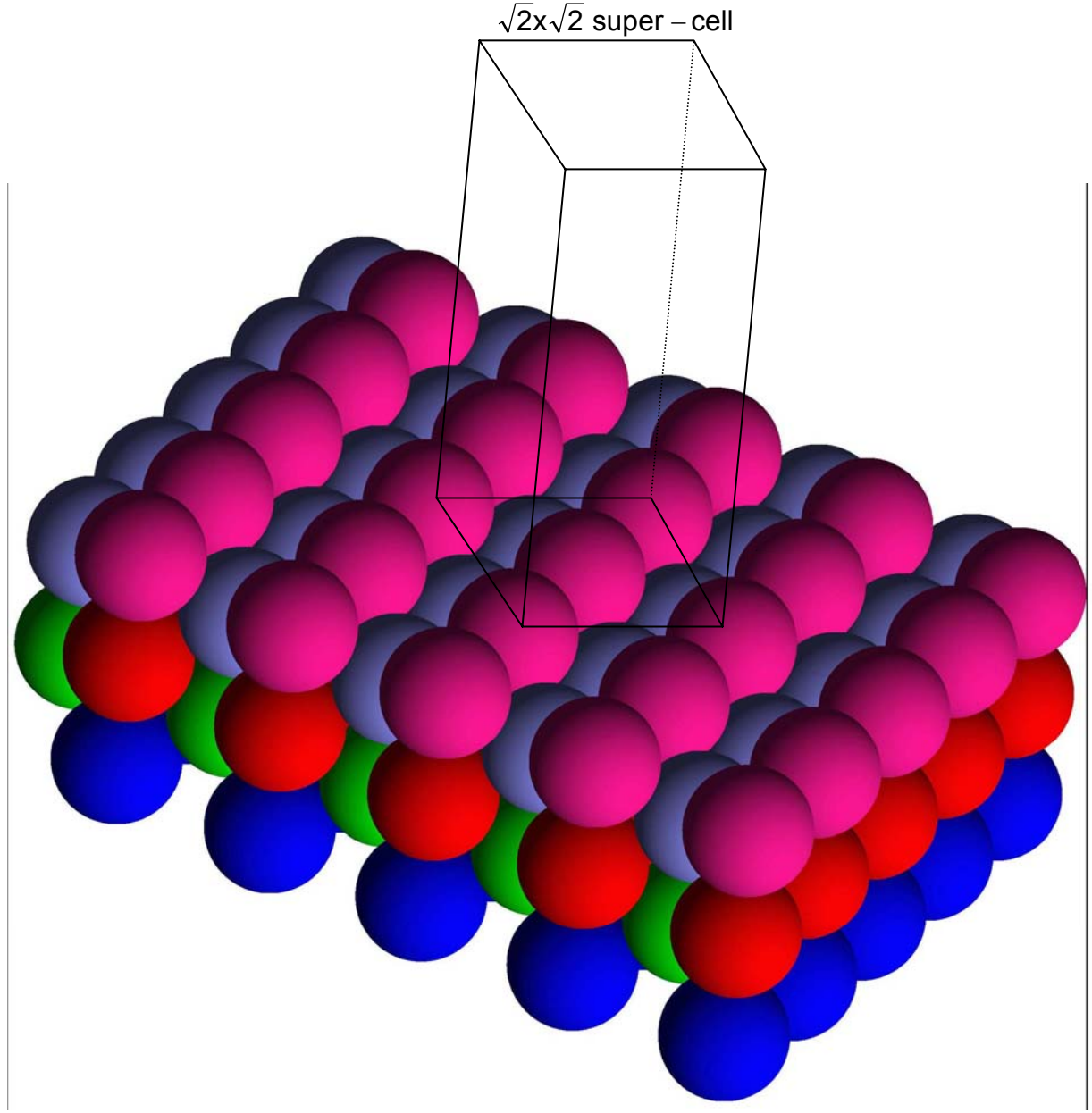
Approximation: We consider 4 layers for (111) and 5 layers for (100) and (110) but we do not allow the first few layers to move

## The size of the super-cell along $\vec{a}_1$ and $\vec{a}_2$

Usually in surface science the size of the super-cell is indicated by the number of atoms inside a super-cell.




2x2 unit cell
1x1 unit cell


√2x√2 super – cell

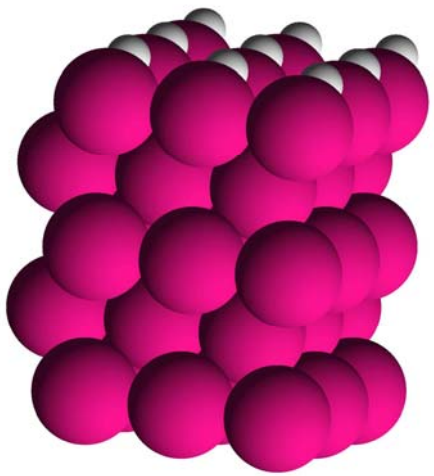
# Coverage (θ)

The coverage (θ) is define as:

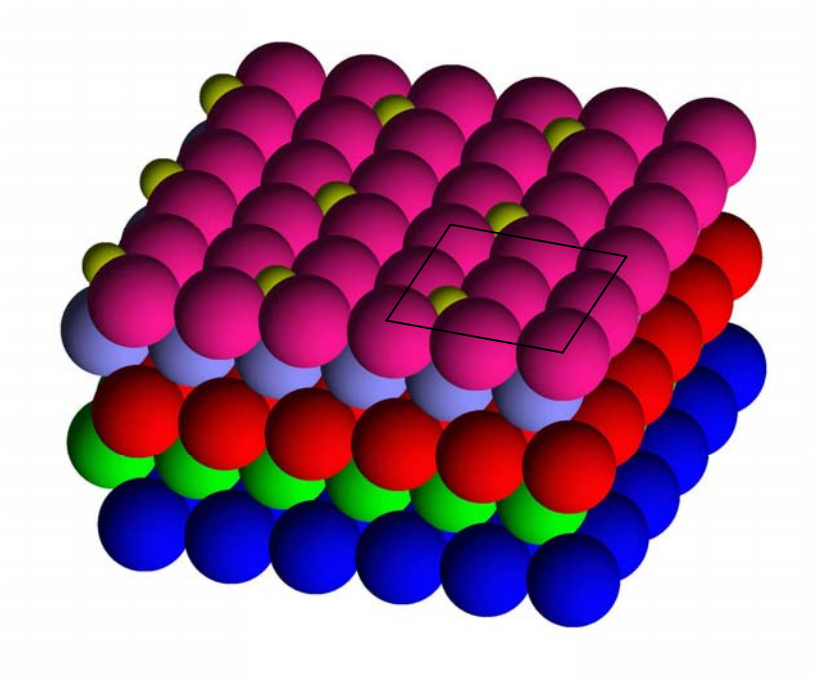
$$\theta = \frac{number\ of\ \ adsorbates}{number\ of\ \ surface\ atoms\ in\ the\ \ unit-cell}$$

Examples:

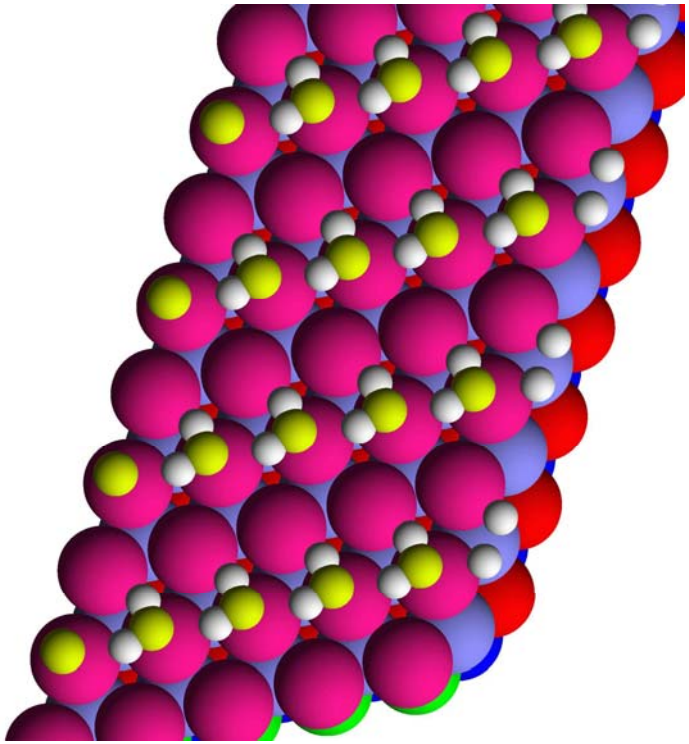
θ = 1ML



θ = ¼ = 0.25ML



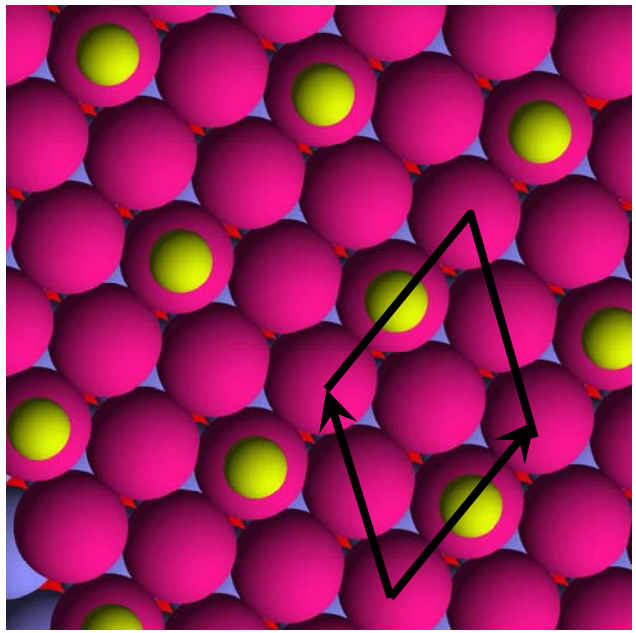
top view



2x1 super-cell

θ = ½ = 0.5ML

top view



2x2 super-cell

θ = 0.25

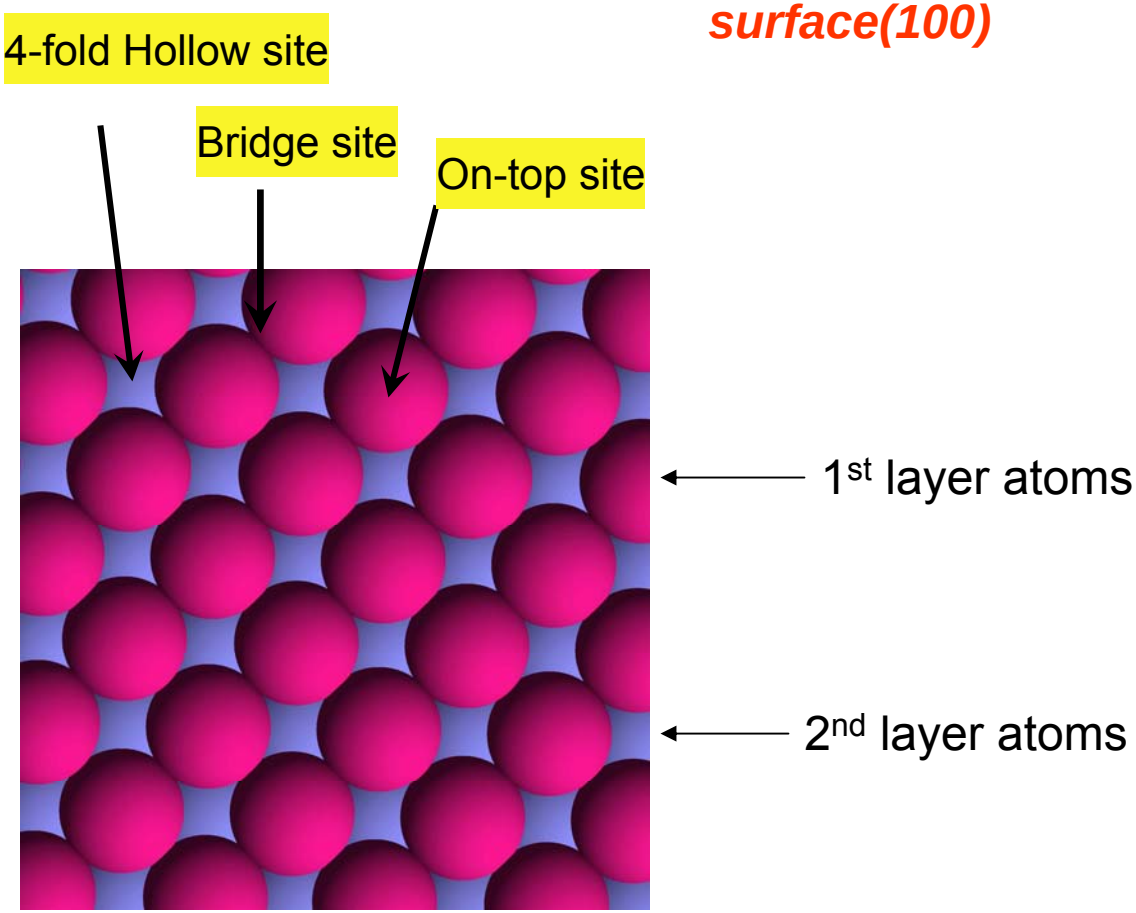
# High symmetry sites

We would like to know the most possible places (sites) for an adsobate on the surface

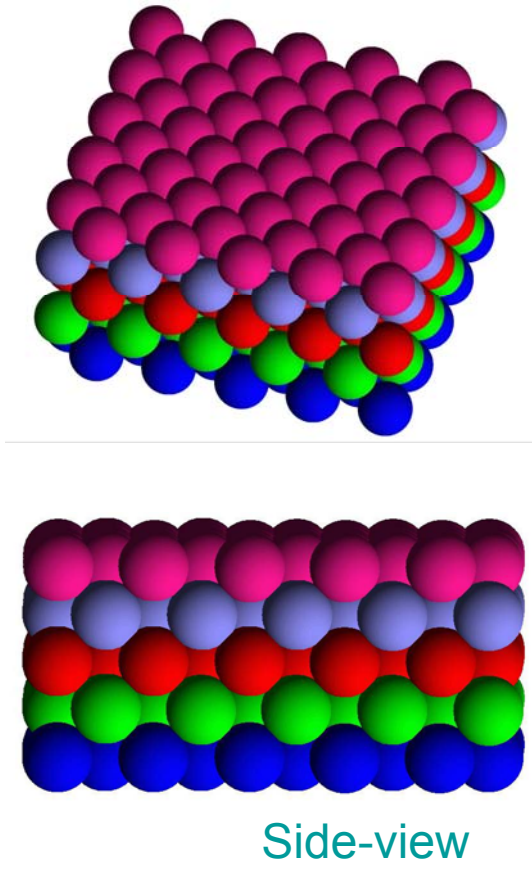
This depends on the symmetry of the surface.

***Example:***

***surface(100)***



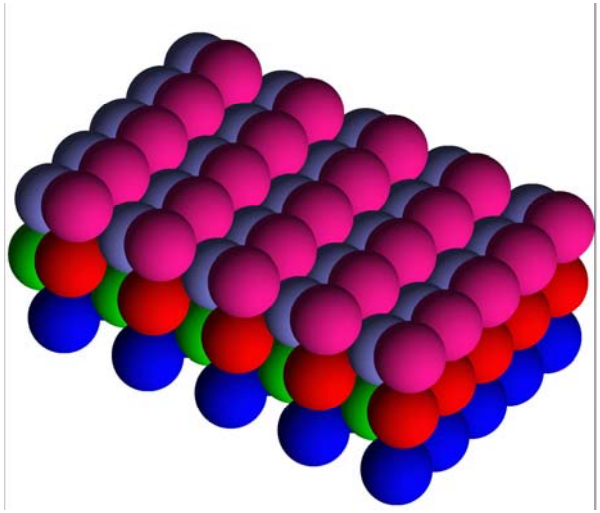

Top-view

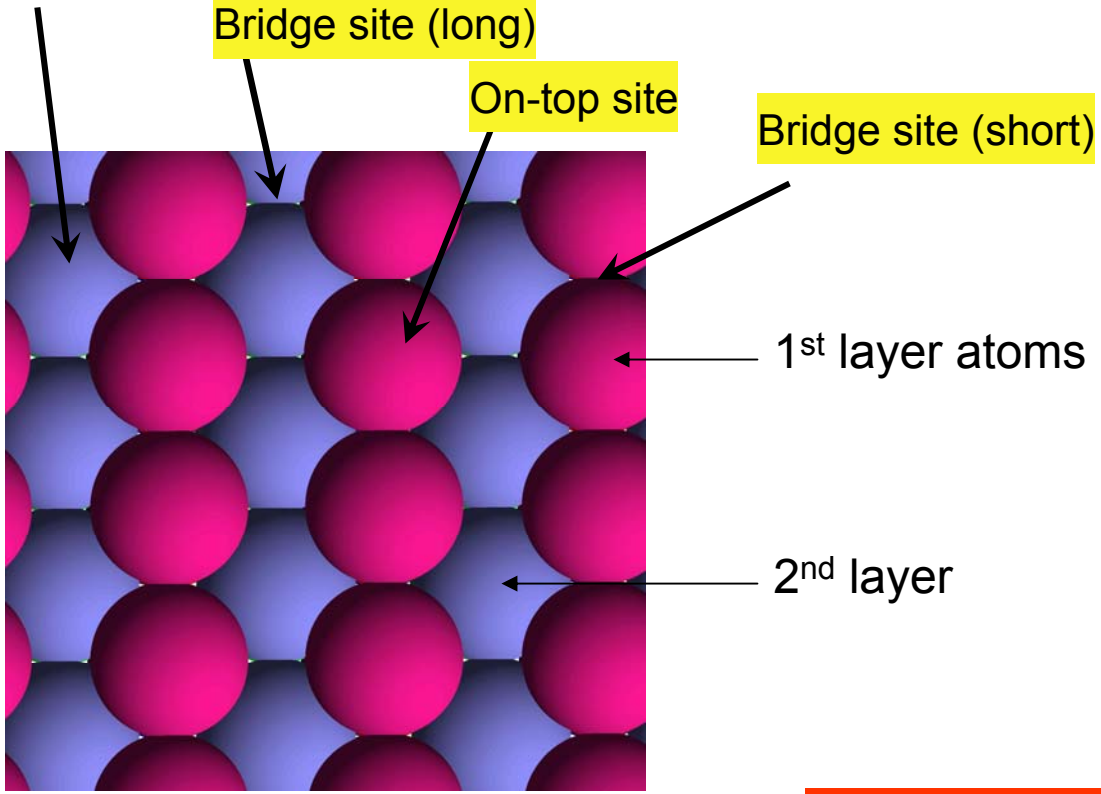


Side-view

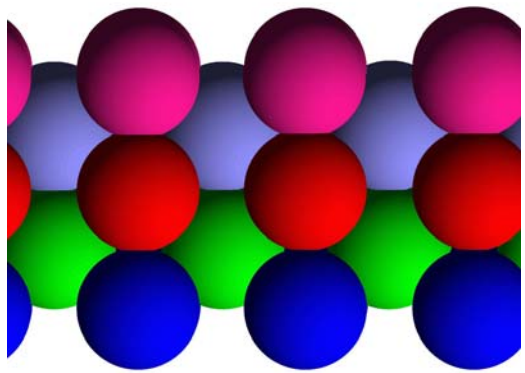
**For surface (100) there are 3 high symmetry sites**

## *surface(110)*






Top-view

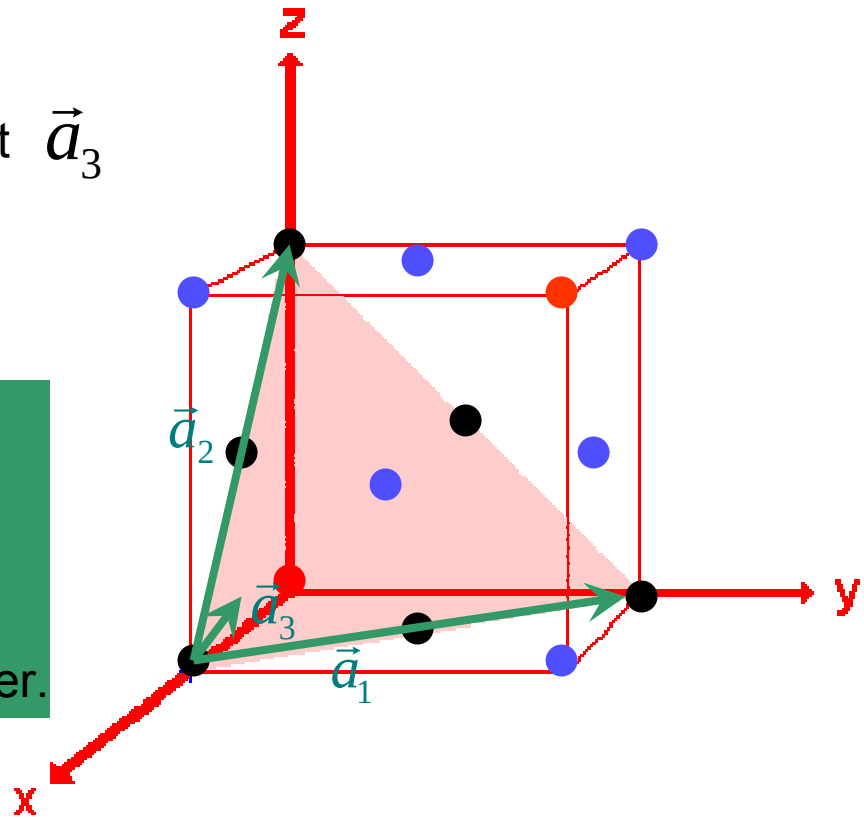


Side-view

**For surface (110) there are 4 high symmetry sites**

# Surface (111)

- We consider a FCC Bravais lattice
- The lattice vectors are chosen in a way that $\vec{a}_3$ is perpendicular to the surface




The black atoms stay at the first layer

The blue atoms stay at the second layer

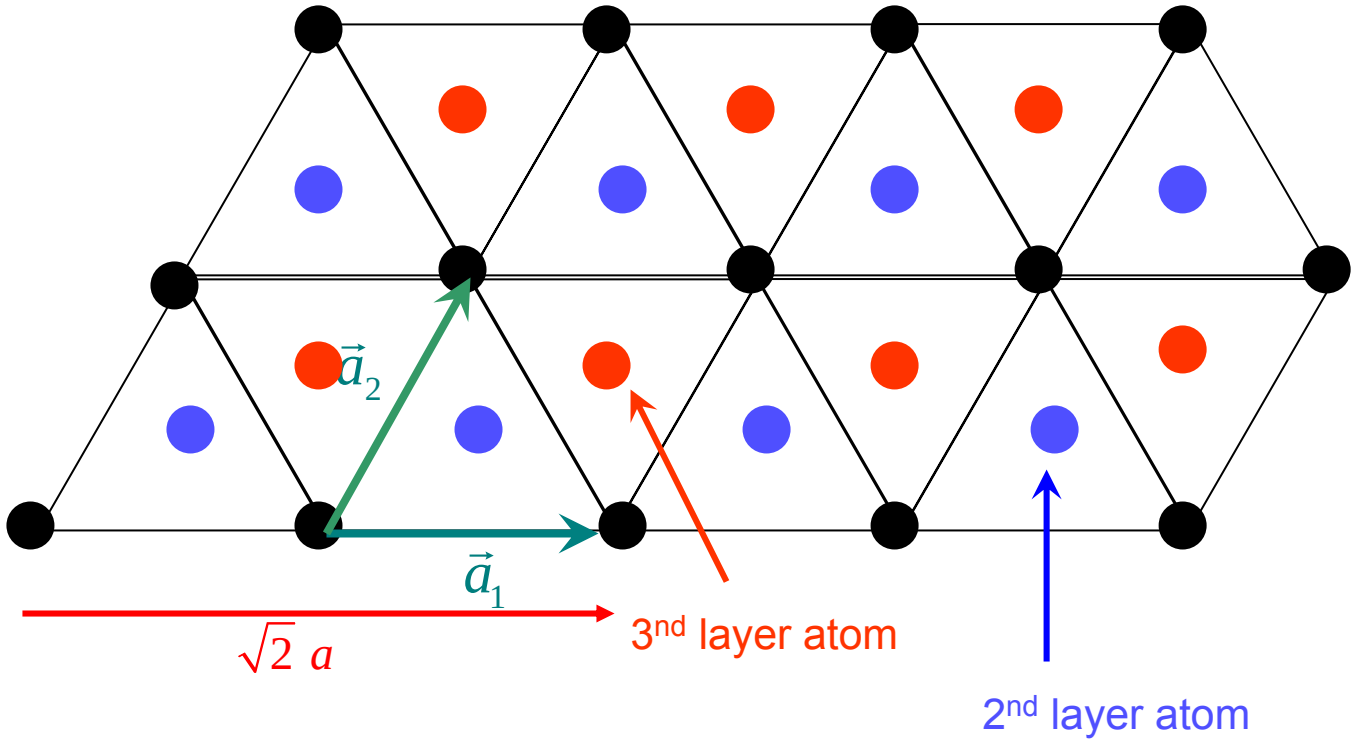
The red atoms stay at the third layer

The fourth layer is the same as the first layer.

The (111) surface contains 3 different layers. They stay on top of each other, i.e.

ABCABCABCABC

Note: $|\vec{a}_1| = \sqrt{2}a, \quad |\vec{a}_2| = \sqrt{2}a, \quad |\vec{a}_3| = \sqrt{3}a$



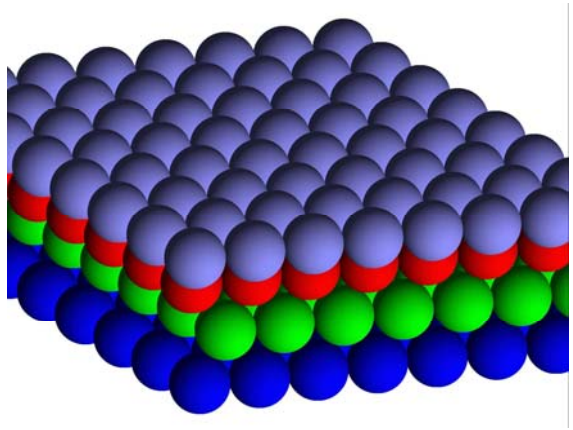

Atom positions:

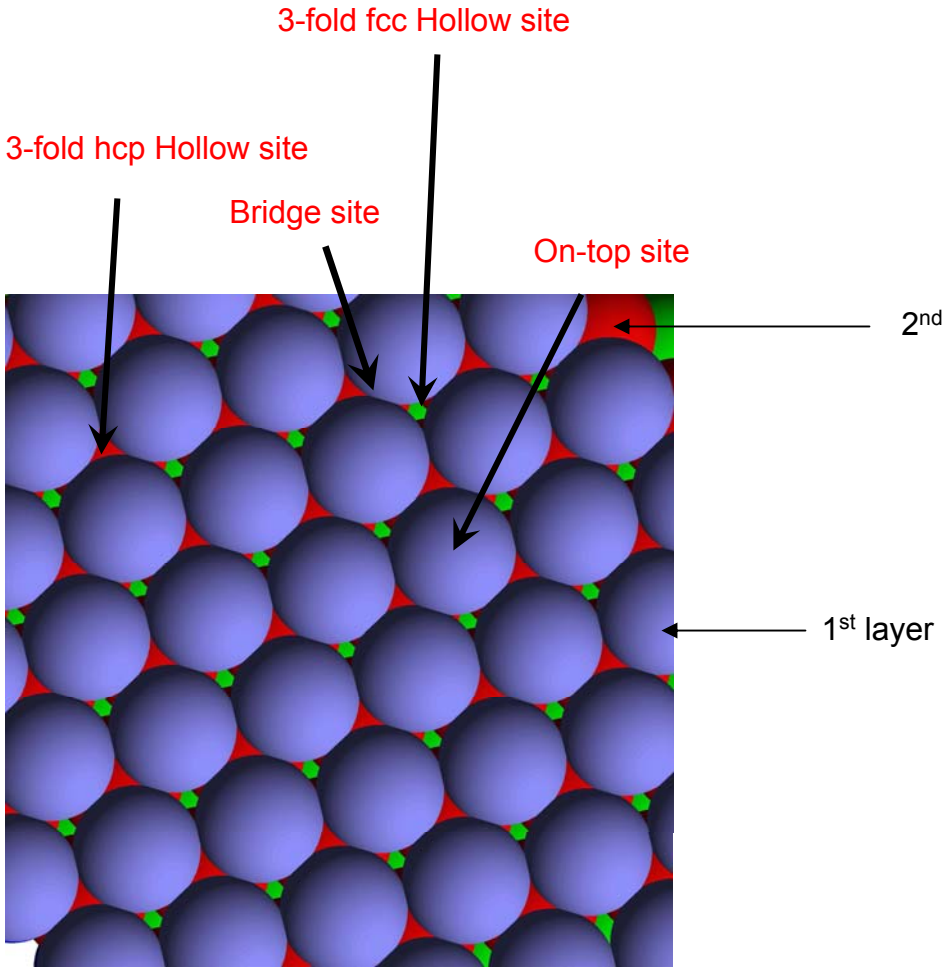
1st layer atom position: (0 0 0)

2nd layer atom position: $\left(\frac{\sqrt{2}}{4}\ \frac{\sqrt{6}}{12}\ \frac{\sqrt{3}}{3}\right)$

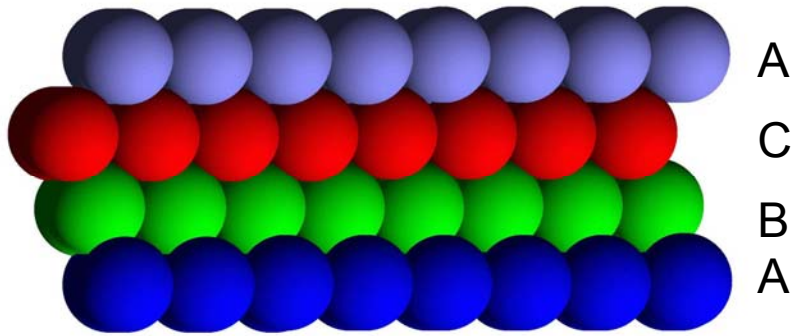
3rd layer atom position: $\left(0\ \frac{\sqrt{6}}{6}\ \frac{2\sqrt{3}}{3}\right)$

***1. High symmetry sites for surface (111)***






Top-view

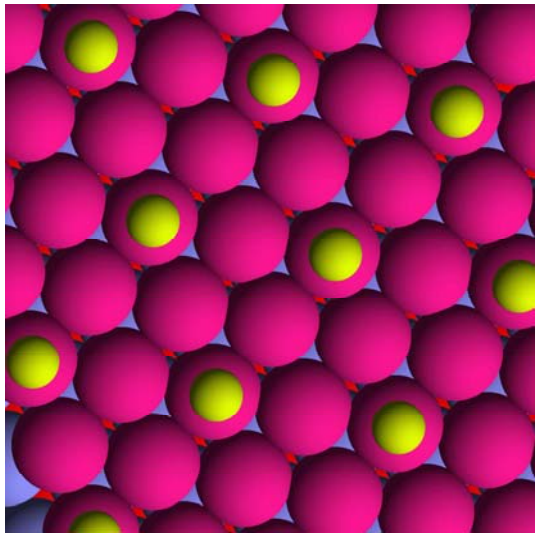



Side-view

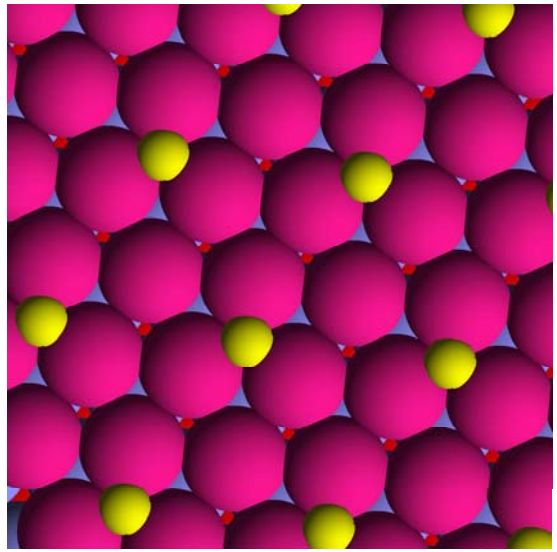
**For surface (111) there are 4 high symmetry sites**

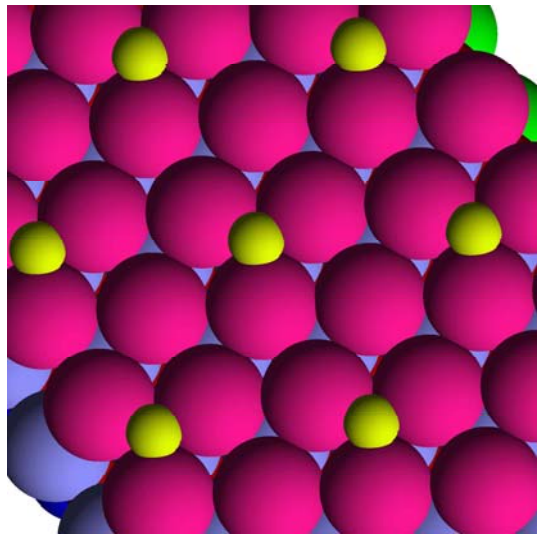
# Some examples

Hydrogen adsorption on-top site, θ=0.25



Hydrogen adsorption on fcc site, θ=0.25





Hydrogen adsorption
hcp site, θ=0.25