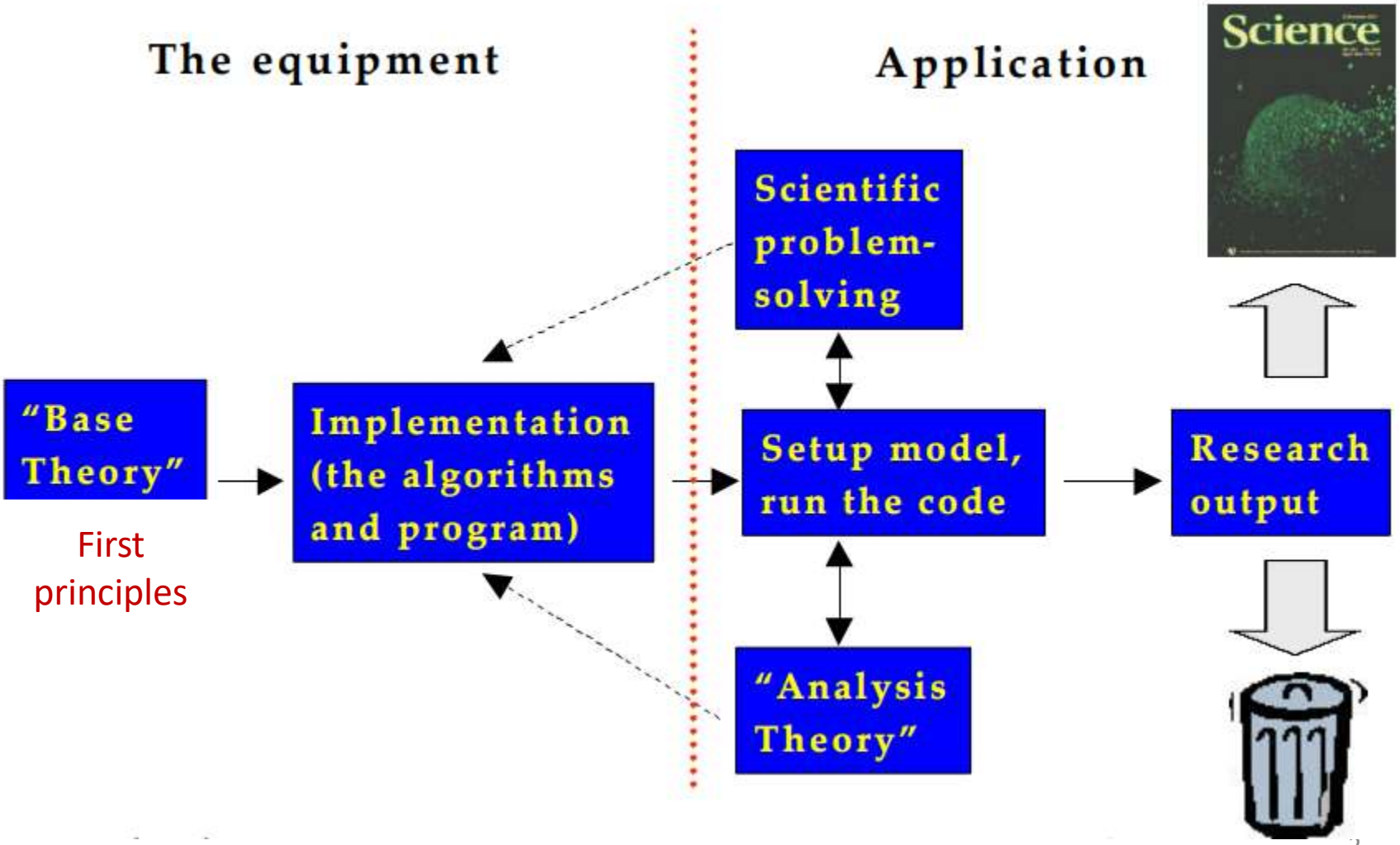
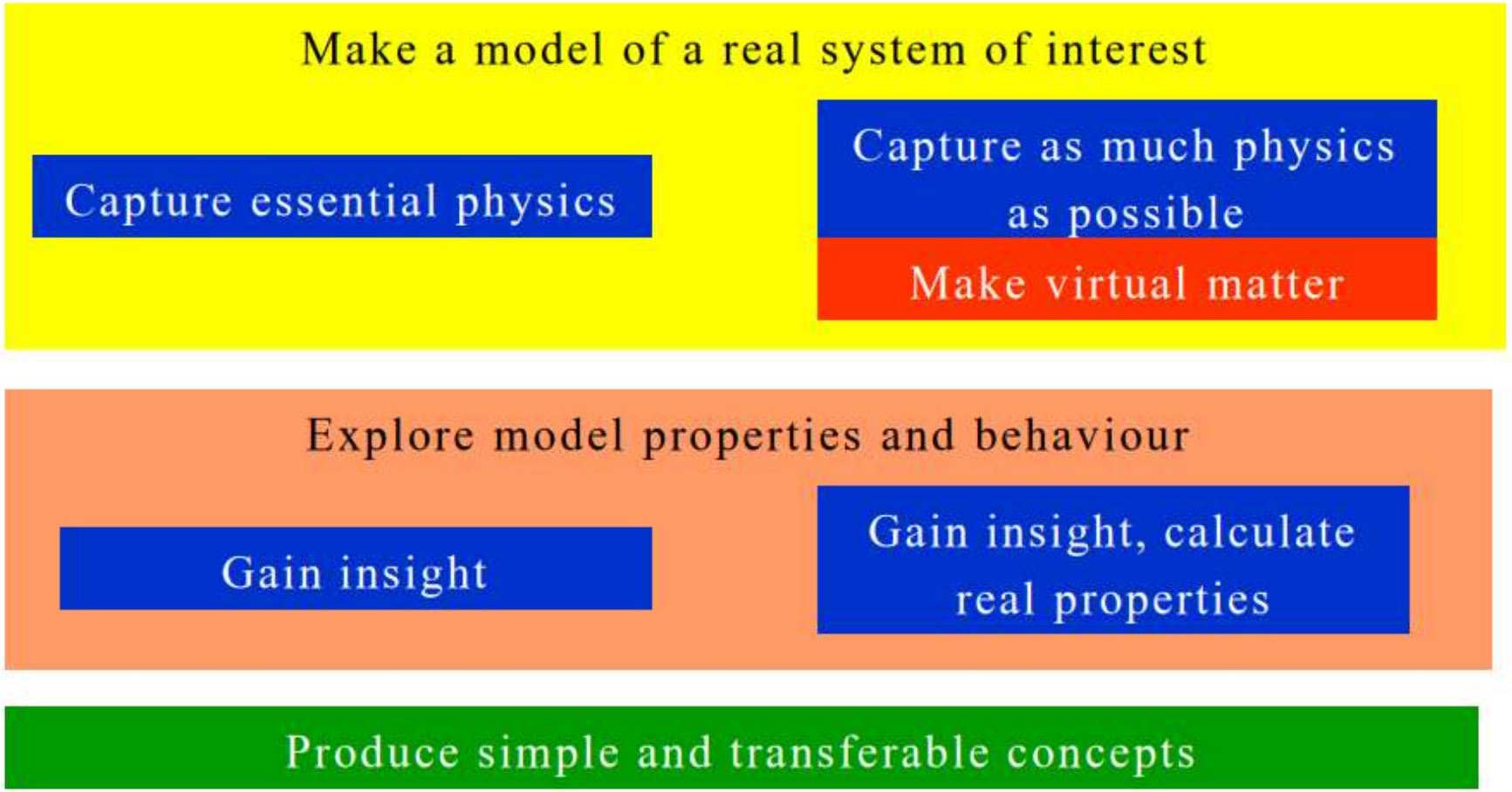
Preparation of Model

first-principles based simulation



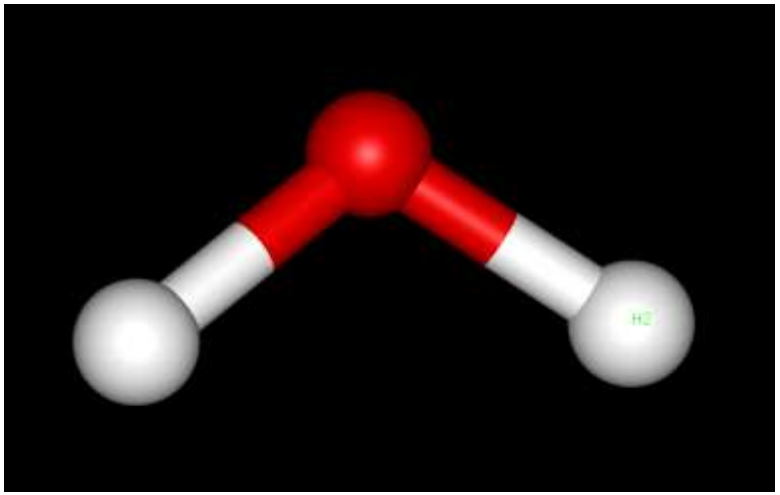
Atomistic Modelling
first-principles simulation



Simply: we start from molecule

Old fashion: write in hand or generate with code

Water example

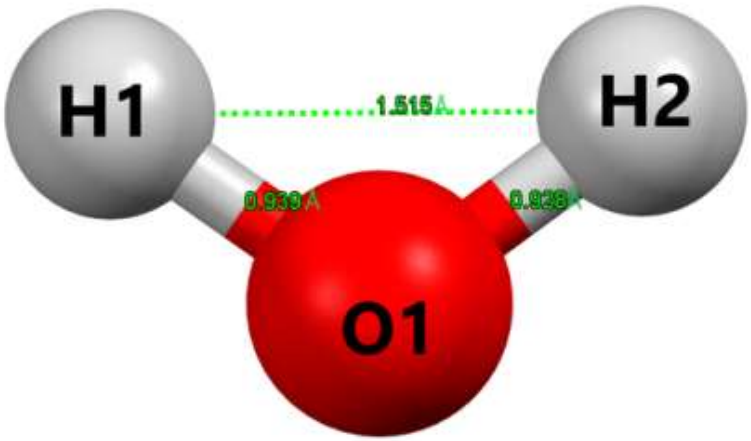


H2O.xyz

3
H2O 0.0000

O	0.000000000	0.000000000	0.000000000
H	-0.369999626	0.740000101	0.740000101
H	1.110000010	0.000000000	0.000000000

molecule



CSD: CIWKEY01

To describe the structure, we need to know the coordination of atoms in space

Cartesian coordinates

1. choose the xyz direction
2. write down the coordination

O	0.000	0.000	0.000
H	0.906	0.641	0.000
H	-0.906	0.641	0.000

3. Display the structure with software

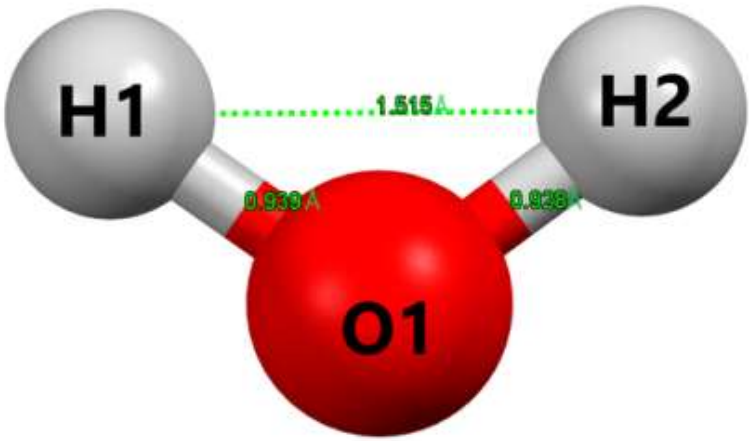
Materials Studio, Gauss View,

Z Matrix

1. traditional Z-matrix descriptions of molecular systems
2. A Z-matrix is also known as an **internal coordinate representation**.
3. a description of each atom in a molecule in terms of its atomic number, bond length, bond angle, and dihedral angle
4. The name arises because the Z-matrix assigns the second atom along the Z axis from the first atom, which is at the origin

The most-used Z-matrix format uses the following syntax:
Element-label, *atom* 1, *bond-length*, *atom* 2, *bond-angle*, *atom* 3, *dihedral-angle* [*format-code*]

molecule



CSD: CIWKEY01

To describe the structure, we need to know the coordination of atoms in space

Z-Matrix

Define the structure with distance, angle, and dihedral angle

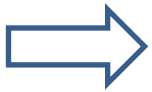
O				
H	1	0.960		
H	1	0.960	2	109.500

Cartesian vs Z-Matrix

Cartesian	direct description of molecule in space
Z-Matrix	complex, but show the internal relationship

Methane CH_4 tetrahedral symmetry

Cartesian coordinates (in Ångströms):
C 0.000000 0.000000 0.000000
H 0.000000 0.000000 1.089000
H 1.026719 0.000000 -0.363000
H -0.513360 -0.889165 -0.363000
H -0.513360 0.889165 -0.363000

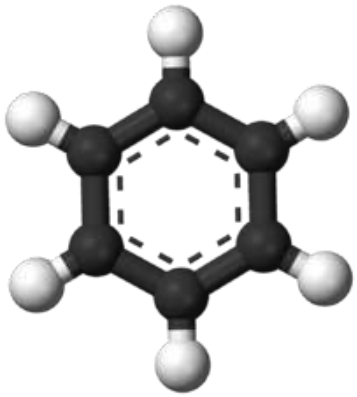


Re-orientating the molecule leads to Cartesian coordinates that make the symmetry more obvious
C 0.000000 0.000000 0.000000
H 0.628736 0.628736 0.628736
H -0.628736 -0.628736 0.628736
H -0.628736 0.628736 -0.628736
H 0.628736 -0.628736 -0.628736

The corresponding Z-matrix, which starts from the carbon atom:
C
H 1 1.089000
H 1 1.089000 2 109.4710
H 1 1.089000 2 109.4710 3 120.0000
H 1 1.089000 2 109.4710 3 -120.0000

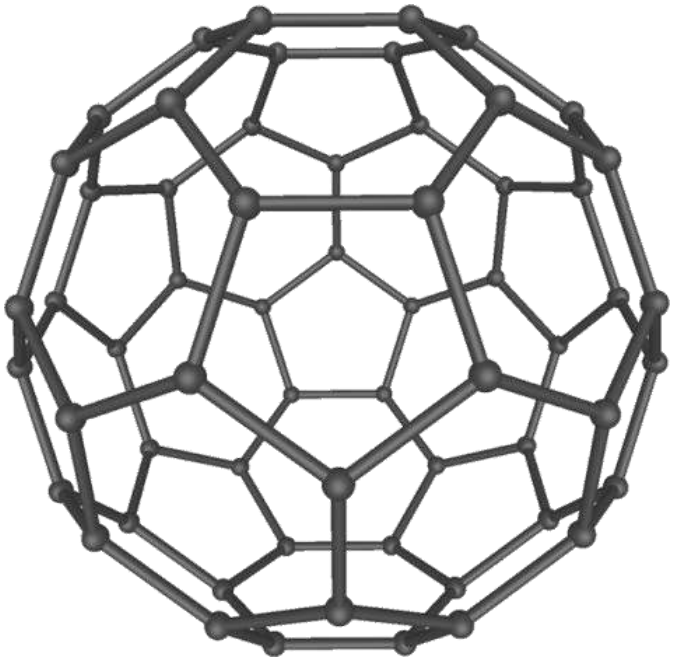
Only the 1.089000 value is not fixed by tetrahedral symmetry

molecule



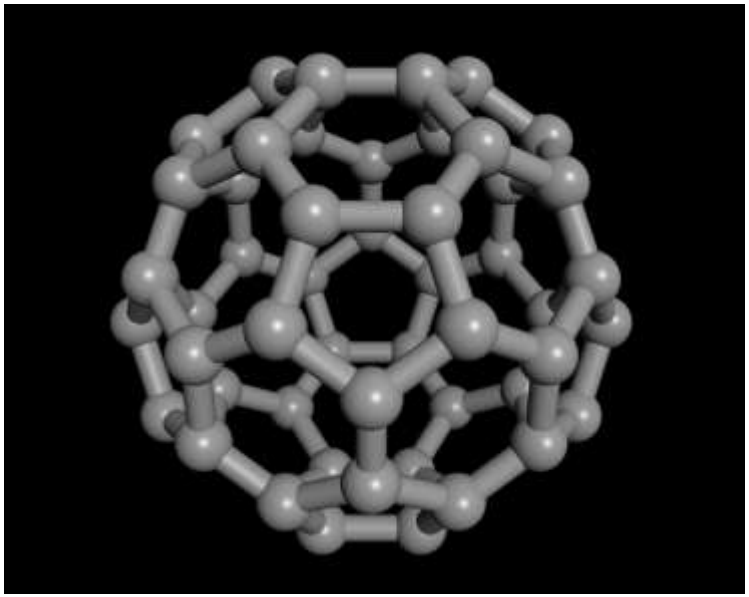
C1	-1.0035	0.4577	0.0000	C
C2	0.3916	0.4577	0.0000	C 1 1.395
C3	1.0892	1.6655	0.0000	C 2 1.395 1 120.00
C4	0.3915	2.8740	-0.0012	C 3 1.395 2 120.00 1 180.00
C5	-1.0033	2.8739	-0.0017	C 4 1.395 3 120.00 2 180.00
C6	-1.7009	1.6657	-0.0007	C 1 1.395 2 120.00 3 180.00
H7	-1.5533	-0.4946	0.0004	H 1 1.100 6 120.00 5 180.00
H8	0.9411	-0.4948	0.0013	H 2 1.100 1 120.00 6 180.00
H9	2.1889	1.6656	0.0006	H 3 1.100 2 120.00 1 180.00
H10	0.9417	3.8261	-0.0013	H 4 1.100 3 120.00 2 180.00
H11	-1.5534	3.8262	-0.0026	H 5 1.100 4 120.00 3 180.00
H12	-2.8005	1.6659	-0.0009	H 6 1.100 1 120.00 2 180.00

How about this molecule?



Old fashion: write in hand or generate with code

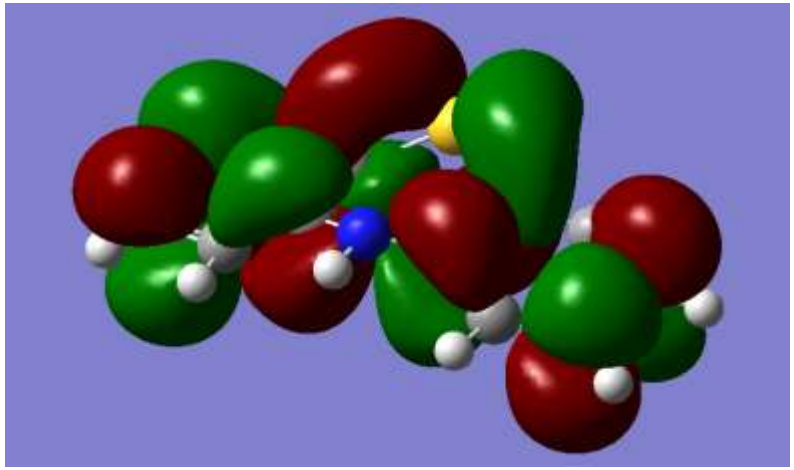
C60 example



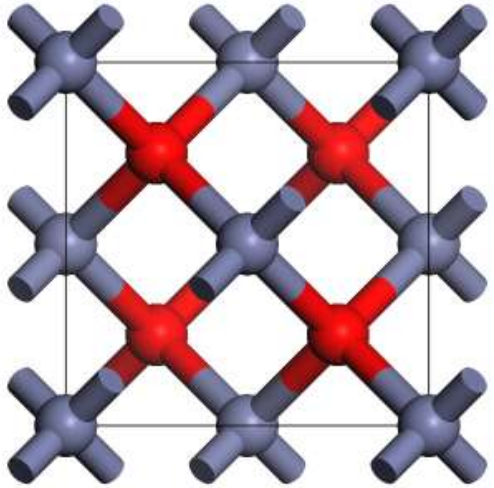
C60.xyz

```
60
C60 0.00000
C     0.000000000   0.000000000   0.000000000
C     1.463900000   0.000000000   0.000000000
C     1.916270000   1.392260000   0.000000000
C     0.731950000   2.252720000   0.000000000
C    -0.452380000   1.392260000   0.000000000
C    -1.572600000   1.756230000   0.727960000
C    -0.692330000  -0.952920000   0.727960000
C     2.156230000  -0.952920000   0.727960000
C     3.036490000   1.756230000   0.727960000
C     0.731950000   3.430590000   0.727960000
C     3.340550000  -0.568100000   1.497580000
C     3.768450000   0.748790000   1.497580000
C     3.036500000   3.001500000   1.497580000
C     1.916280000   3.815390000   1.497580000
C    -0.452370000   3.815390000   1.497580000
C    -1.572590000   3.001510000   1.497580000
C    -2.304560000   0.748790000   1.497580000
C    -1.876660000  -0.568100000   1.497580000
C     0.039620000  -1.960360000   1.497580000
C     1.424290000  -1.960360000   1.497580000
C    -0.692330000  -2.198190000   2.742850000
C    -1.876650000  -1.337730000   2.742850000
C     2.156240000  -2.198190000   2.742850000
C     3.340560000  -1.337730000   2.742850000
C     4.220810000   1.371420000   2.742860000
C     3.768450000   2.763680000   2.742860000
C     1.463910000   4.438020000   2.742860000
C    -0.000010000   4.438030000   2.742860000
C    -2.304550000   2.763680000   2.742850000
C    -2.756910000   1.371430000   2.742850000
C     0.000010000  -2.423150000   3.920720000
C     1.463910000  -2.423150000   3.920720000
C     3.768450000  -0.748790000   3.920720000
C     4.220810000   0.643460000   3.920720000
C     3.340550000   3.352620000   3.920720000
C     2.156240000   4.213080000   3.920720000
C    -1.876660000   3.352620000   3.920720000
C    -0.692340000   4.213080000   3.920720000
C    -2.304540000  -0.748790000   3.920720000
C    -2.756910000   0.643460000   3.920720000
C     1.916270000  -1.800510000   5.165990000
C     3.036500000  -0.986630000   5.165990000
C    -1.572590000  -0.986620000   5.165990000
C    -0.452360000  -1.800500000   5.165990000
C    -2.304550000   1.266100000   5.166000000
C    -1.876660000   2.582990000   5.166000000
C     0.039610000   3.975250000   5.165990000
C     1.424280000   3.975250000   5.165990000
C     3.768450000   1.266090000   5.166000000
C     3.340550000   2.582990000   5.166000000
C     0.731960000  -1.415700000   5.935610000
C    -1.572590000   0.258650000   5.935610000
C    -0.692340000   2.967800000   5.935620000
C     2.156230000   2.967790000   5.935620000
C     3.036490000   0.258650000   5.935620000
C     0.000000000   2.014880000   6.663580000
C     1.463900000   2.014880000   6.663580000
C     1.916270000   0.622630000   6.663580000
C     0.731960000  -0.237830000   6.663570000
C    -0.452370000   0.622630000   6.663570000
```

Molecule vs Solid



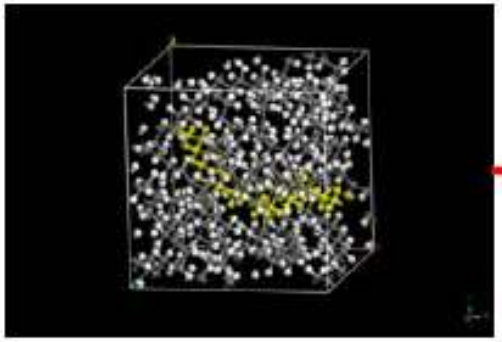
real space
Finite system



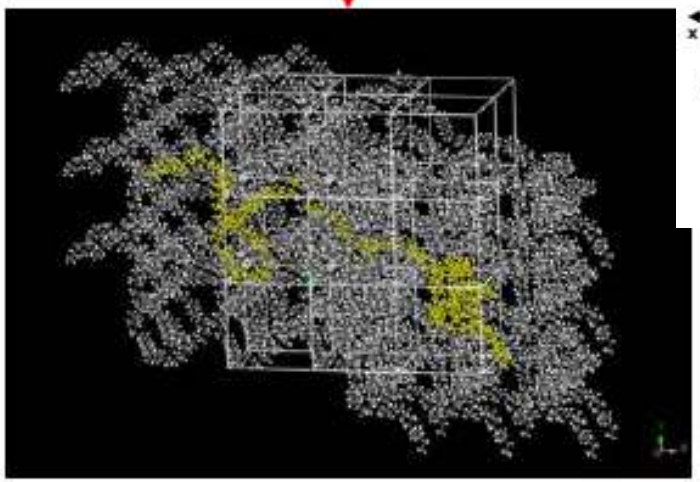
real space
infinite system

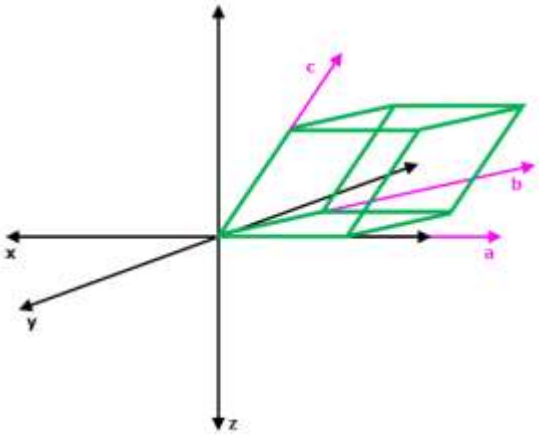
Periodic Boundary Condition (PBC)

a set of boundary conditions which are often chosen for approximating a large (infinite) system by using a small part called a *unit cell*.



The system is considered to be surrounded on all sides by replicas of itself, forming an infinite macro-lattice.

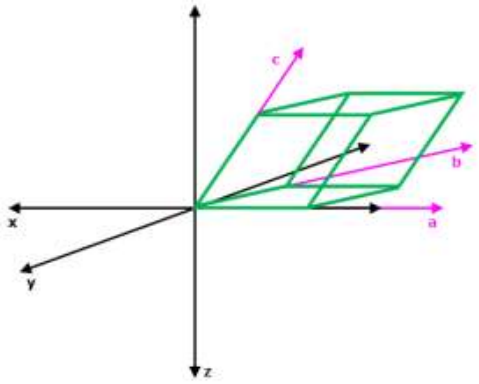




lattice constants + Atomic coordination in UnitCell

Lattice vector **a**, **b**, **c**

1. Length a, b, c, and their angles



Orthorhombic crystal

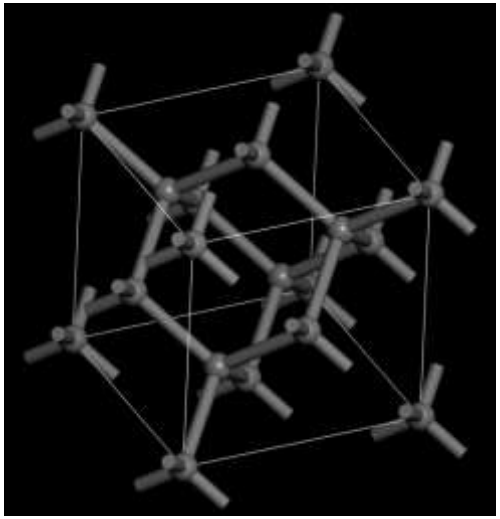
10, 10, 10, 90, 90, 90

2. Vector **a, b, c** are written in Cartesian coordination

Orthorhombic crystal

10.0 0.0 0.0
0.0 10.0 0.0
0.0 0.0 10.0

Coordination : Positions in Cartesian coordination or Fraction coordination



PBC 3.5560 3.5560 3.5560 90.0000 90.0000 90.0000

or

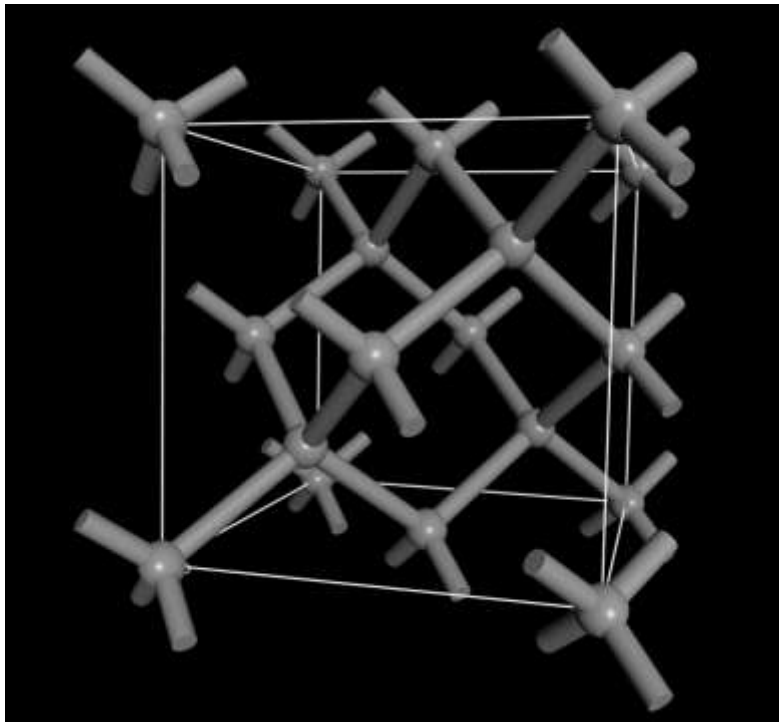
3.5560 0.0000 0.0000
0.0000 3.5560 0.0000
0.0000 0.0000 3.5560

C1	0.000000000	0.000000000	0.000000000
C2	0.000000000	1.778000000	1.778000000
C3	1.778000000	0.000000000	1.778000000
C4	1.778000000	1.778000000	0.000000000
C5	2.667000000	0.889000000	2.667000000
C6	0.889000000	0.889000000	0.889000000
C7	0.889000000	2.667000000	2.667000000
C8	2.667000000	2.667000000	0.889000000

C1	0.00000	0.00000	0.00000
C2	0.00000	0.50000	0.50000
C3	0.50000	0.00000	0.50000
C4	0.50000	0.50000	0.00000
C5	0.75000	0.25000	0.75000
C6	0.25000	0.25000	0.25000
C7	0.25000	0.75000	0.75000
C8	0.75000	0.75000	0.25000

Old fashion: write in hand or generate with code

Diamond



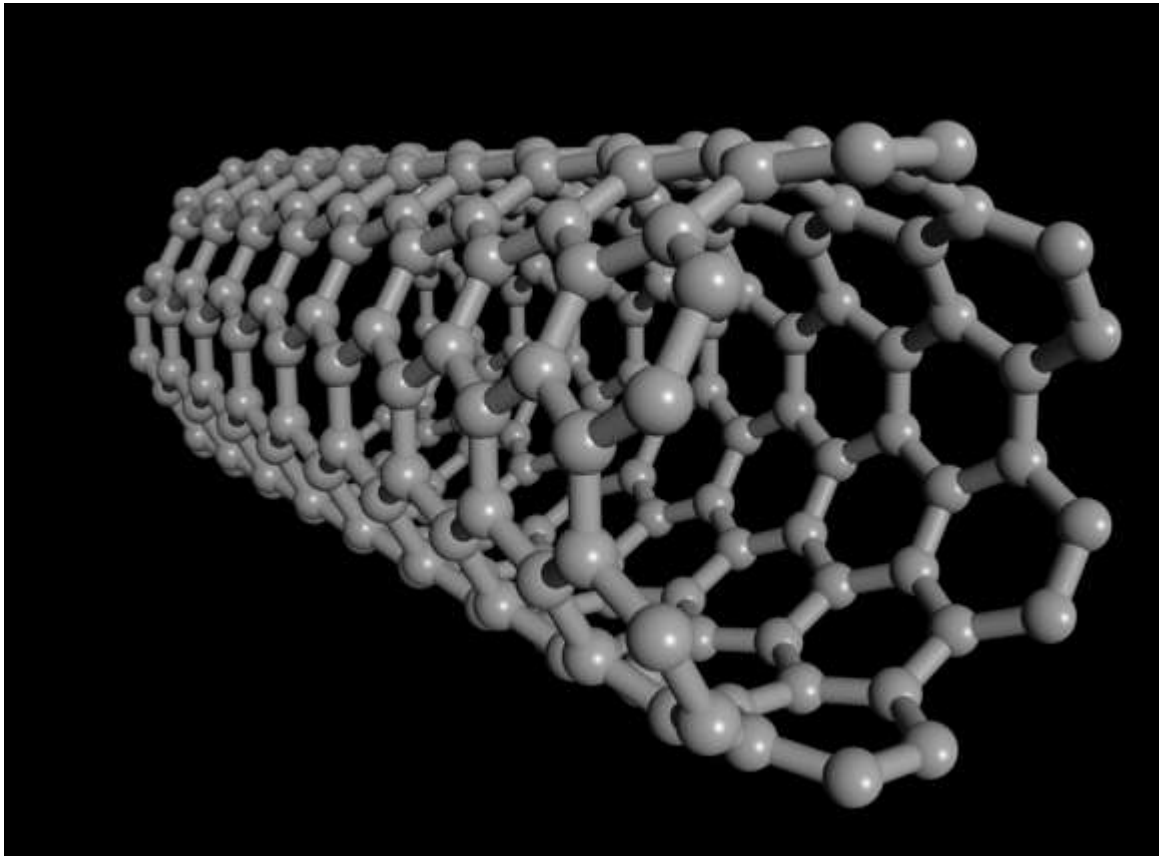
c.car

```
!BIOSYM archive 3
PBC=ON
Materials Studio Generated CAR File
!DATE Wed Nov 29 17:16:01 2017
PBC   3.5668   3.5668   3.5668  90.0000  90.0000  90.0000 (FD-3M)
C1     0.000000000   0.000000000   0.000000000 XXXX 1      xx      C   0.000
end
end
```

Or crystallgraphic information files .cif

Old fashion: write in hand or generate with code

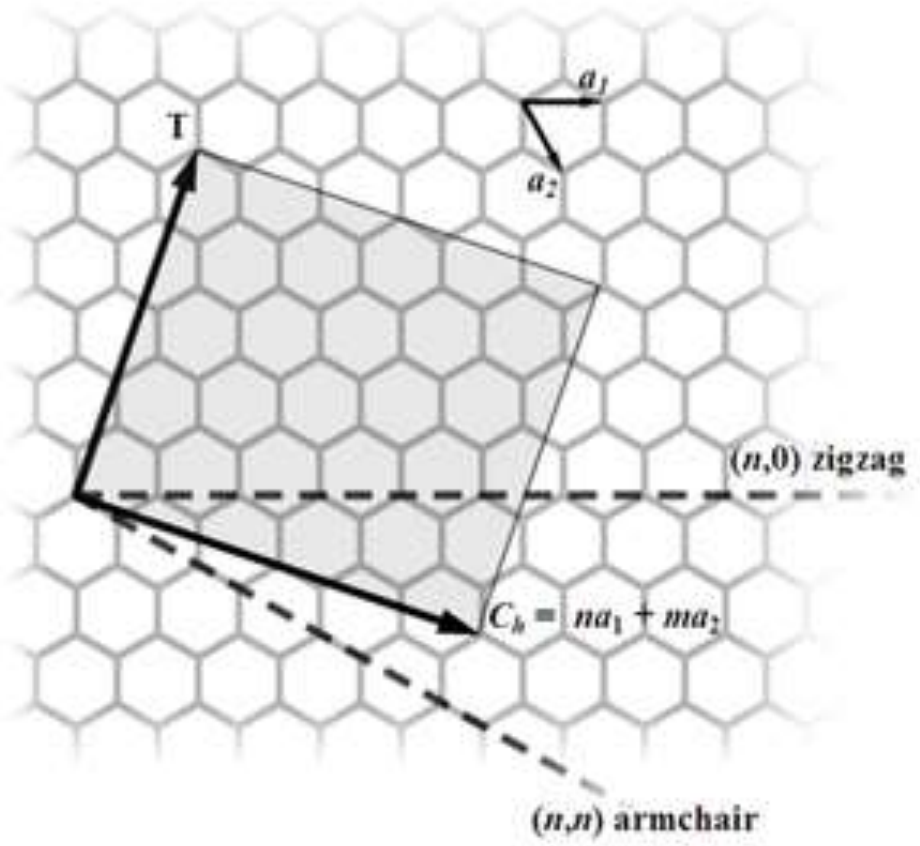
Carbon Nanotube



Hard to write down the coordination by hand

Old fashion: write in hand or generate with code

My C code for carbon nanotube structures




```
 for(i=0;(i*l1)<=s;i++)
and H atom*/
   {  for( j=0; (j*l7)<sl; j++)
              { u=r*cos(i*a2-j*a4);
                v=r*sin(i*a2-j*a4);
                w=i*l3-j*l9;
                if((w>=(g1-0.000001))&&(w<=g2))
                  {   maxc[numc].x=u;
                      maxc[numc].y=v;
                      maxc[numc].z=w;
                      numc++;
                      w=i*l3-j*l9-c1;
                      if(w<(g1-0.000001))
                                {maxh[numh].x=r*cos(i*a2-j*a4+b1);
                                 maxh[numh].y=r*sin(i*a2-j*a4+b1);
                                 maxh[numh].z=i*l3-j*l9-d1;
                                 numh++;
                                }
                      w=i*l3-j*l9-c5;
                      if(w<(g1-0.000001))
                                {maxh[numh].x=r*cos(i*a2-j*a4-b3);
                                 maxh[numh].y=r*sin(i*a2-j*a4-b3);
                                 maxh[numh].z=i*l3-j*l9-d5;
                                 numh++;
                                }
                      w=i*l3-j*l9+c3;
                      if(w>g2)
                                {maxh[numh].x=r*cos(i*a2-j*a4-b2);
                                 maxh[numh].y=r*sin(i*a2-j*a4-b2);
                                 maxh[numh].z=i*l3-j*l9+d3;
                                 numh++;
                                }
                                                          }
}
```

Just mathematic problem

New fashion: Generate by Click, Click, and Click or Import from Structure Database

Examples with Materials Studio

Different software use different file formats for structures

How to build a reasonable model

Molecule

Database, or generated by yourself with reasonable length and angle

Solid

Database, or generated by yourself with reasonable lattice constants and coordination

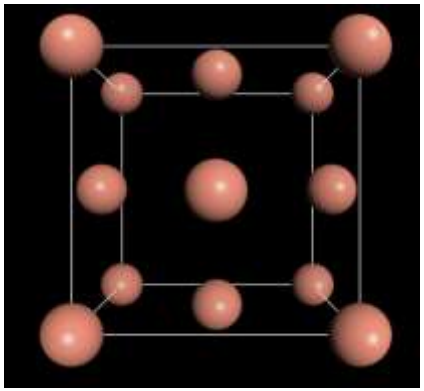
How to build a reasonable model

Surface

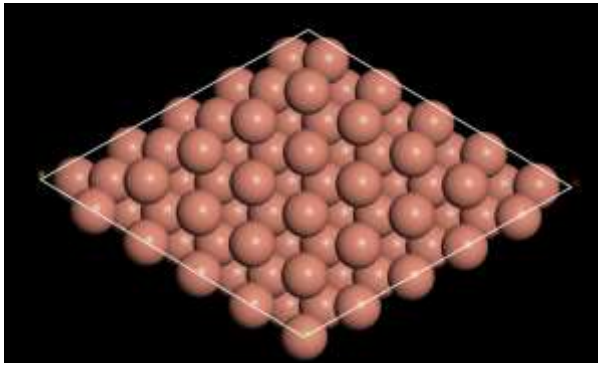
Ideal model: infinite in two dimensions and finite in one dimension
In practice: **slab model**

Simple metal

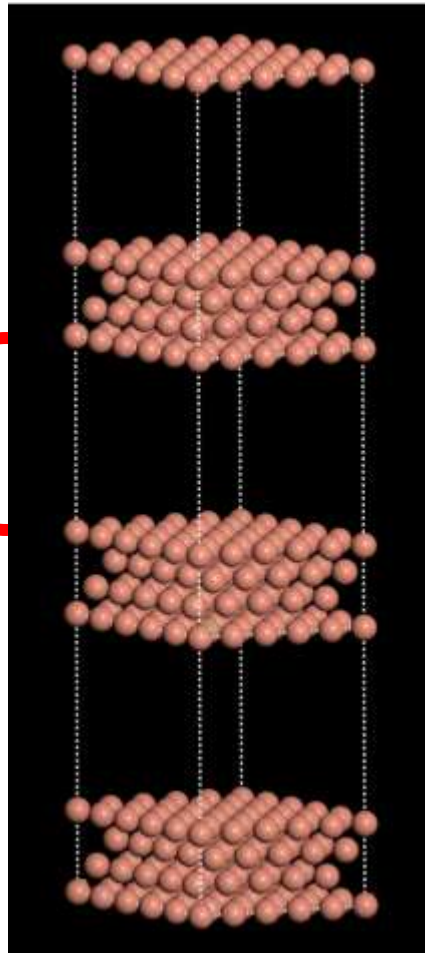
FCC Cu



Cu (111) Surface



Vacuum



How to build a reasonable model

Surface

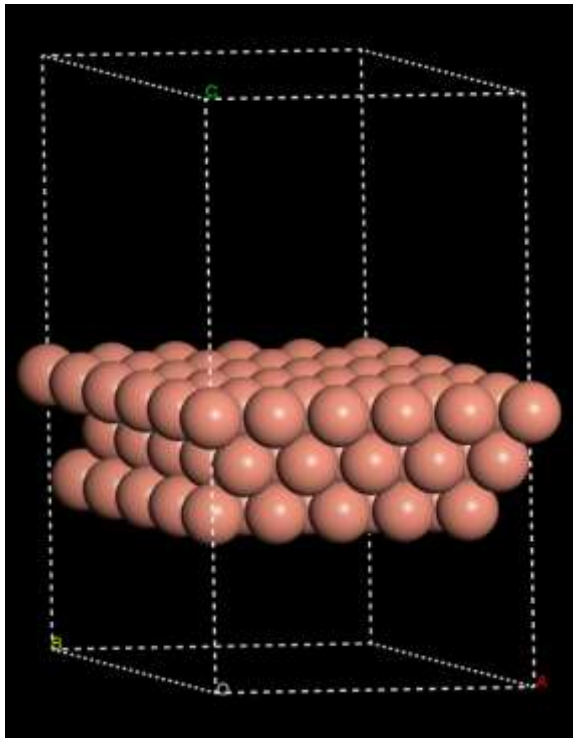
Simple system

Key points

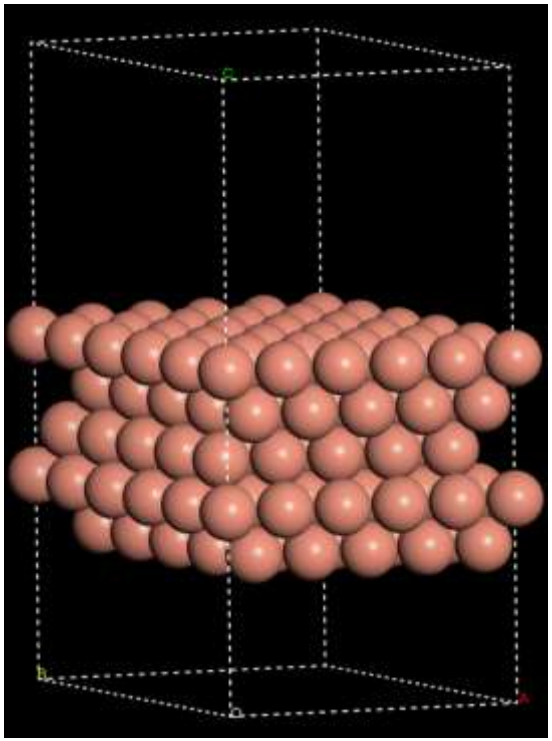
1. **The thickness of vacuum**
2. **The number of layers in slab model**
3. **Single or Double surface problem**

How to build a reasonable model

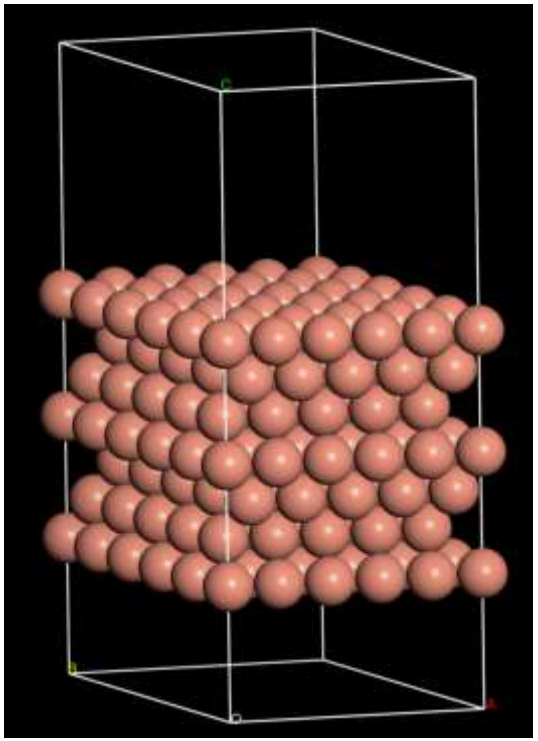
Surface



3 layers



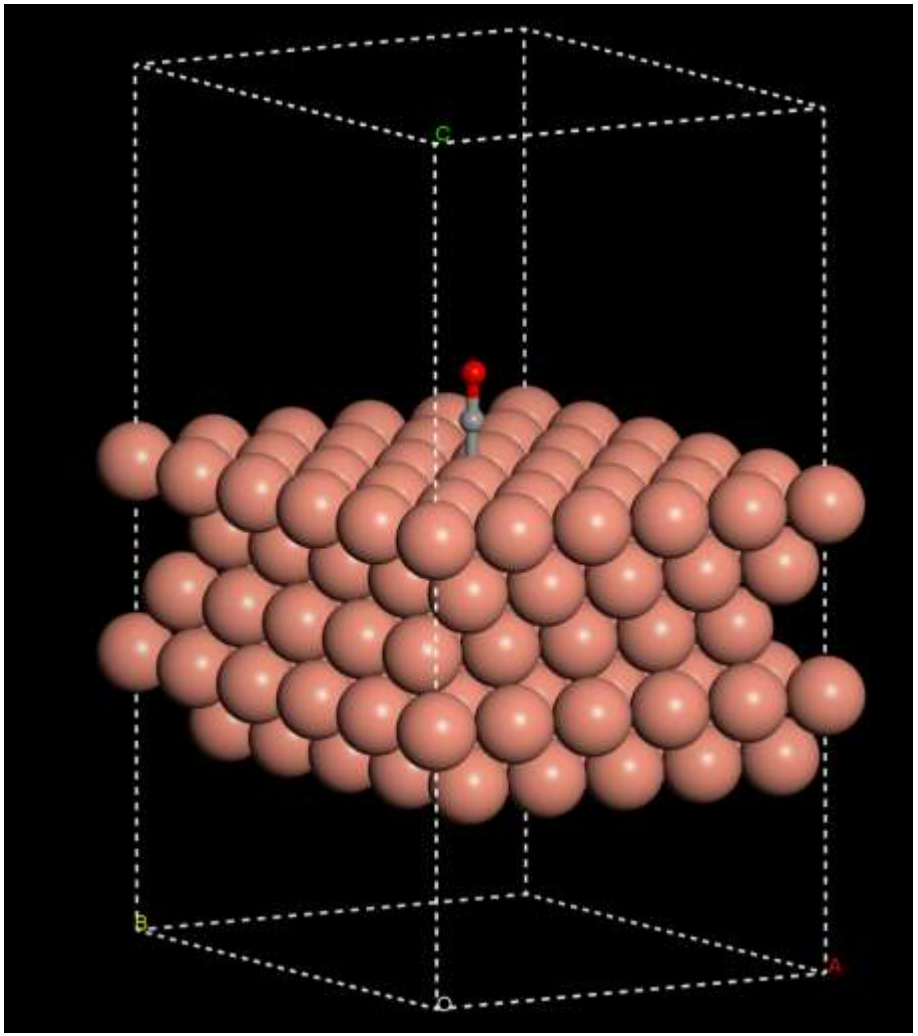
5 layers



7 layers

How to build a reasonable model

Surface



Fix bottom

Surface relaxation

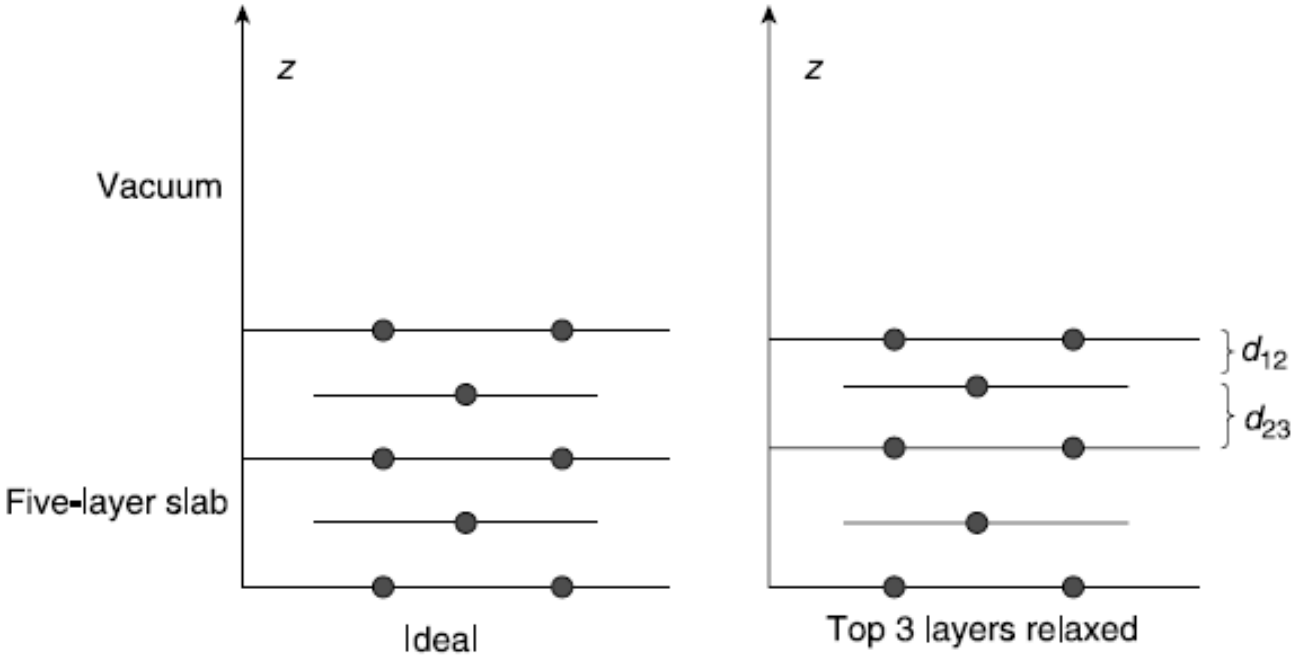
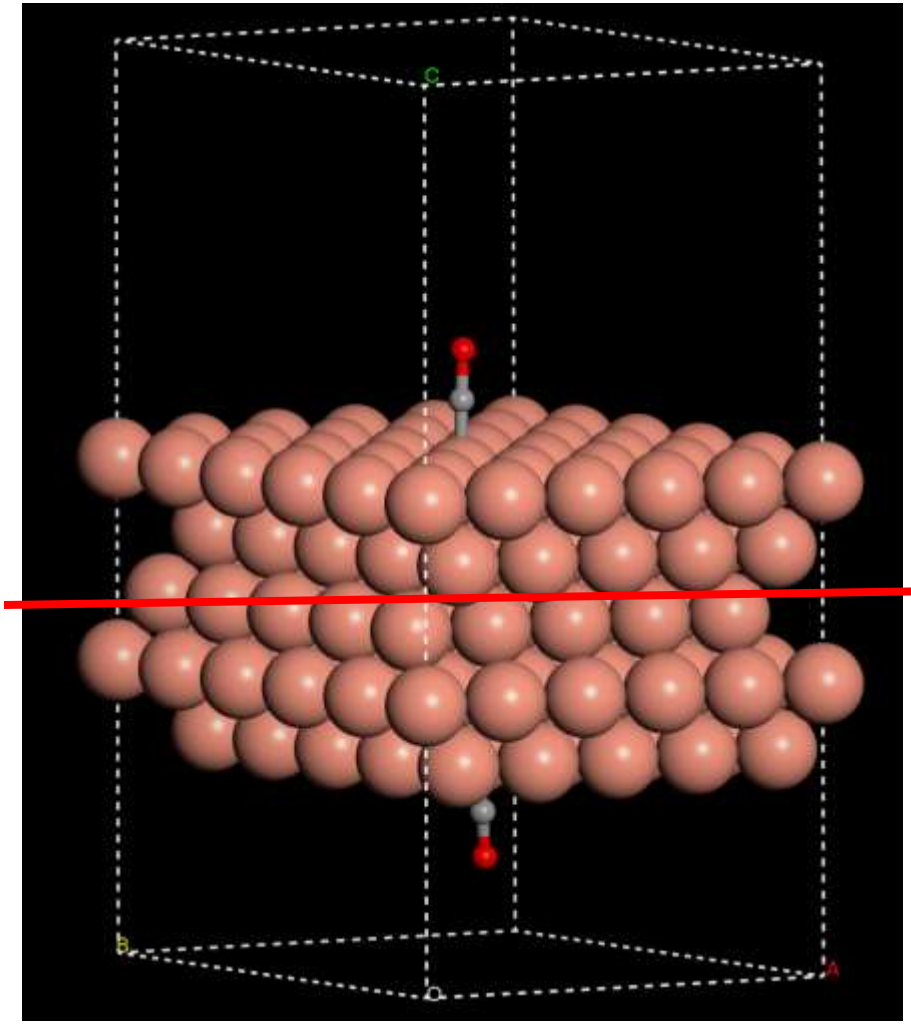


TABLE 4.1 Interlayer Relaxations in Cu(100) and Cu(111) Calculated Using DFT as Function of Slab Thickness

	Cu(001)			Cu(111)		
	δd_{12} (%)	δd_{23} (%)	δd_{34} (%)	δd_{12} (%)	δd_{23} (%)	δd_{34} (%)
5 layers	3.84	0.50	0.53	0.61	0.08	+0.08
6 layers	1.93	+0.83	+0.37	0.64	0.11	+0.27
7 layers	2.30	+0.55	0.25	0.56	0.04	+0.32
8 layers	2.14	+0.85	+0.00	0.59	0.32	+0.51
Expt.	2.0 ± 0.5^a	$+1.0 \pm 0.7^a$		0.7 ± 0.5^b		

How to build a reasonable model

Surface



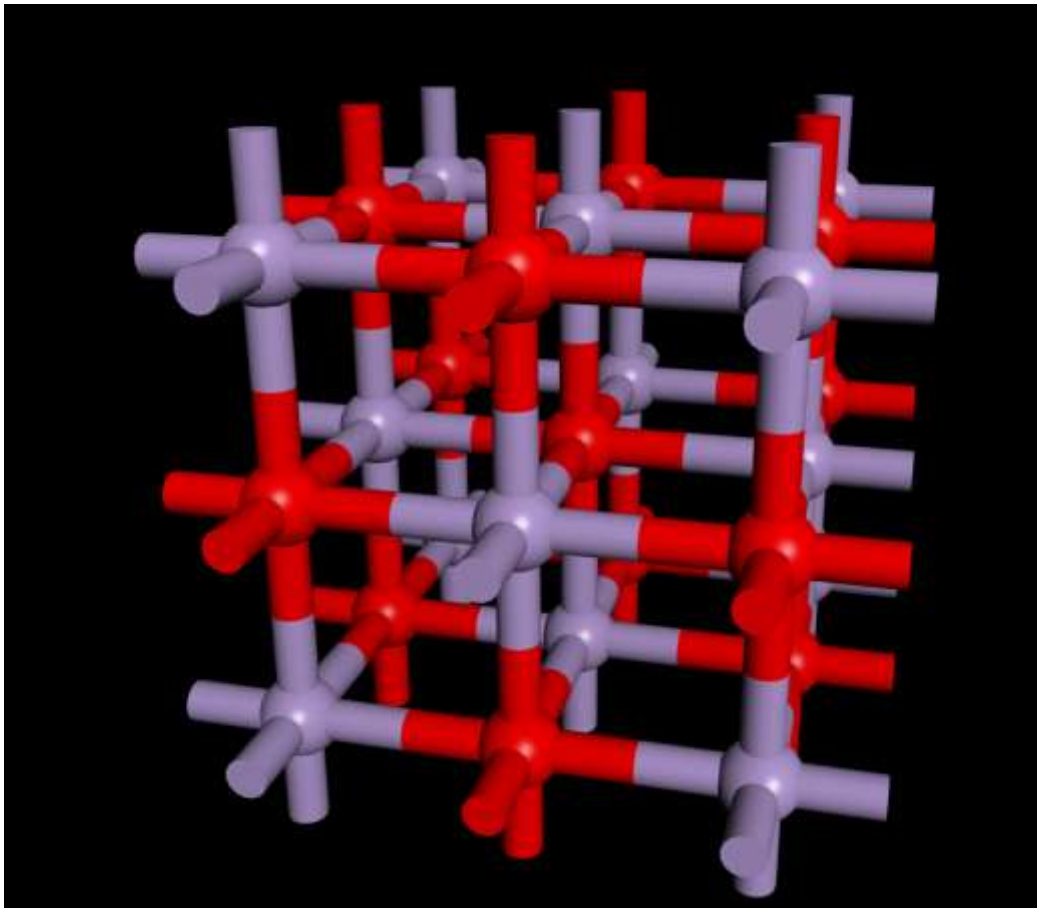
Fix middle

Mirror symmetry

How to build a reasonable model

Surface

Complex systems



MnO

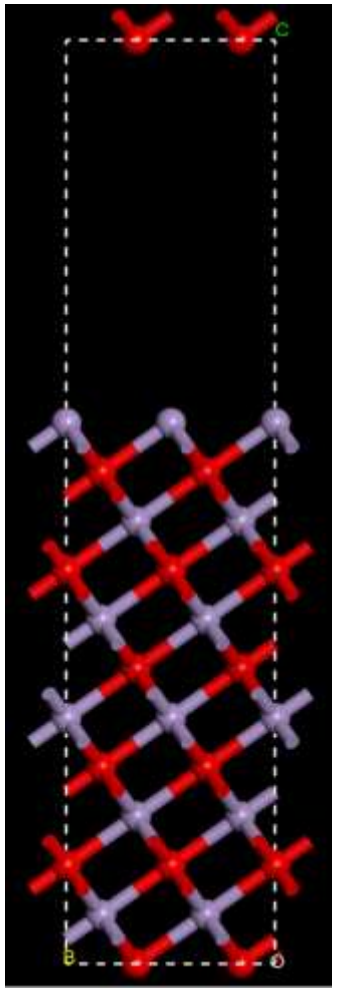
How to build a reasonable model

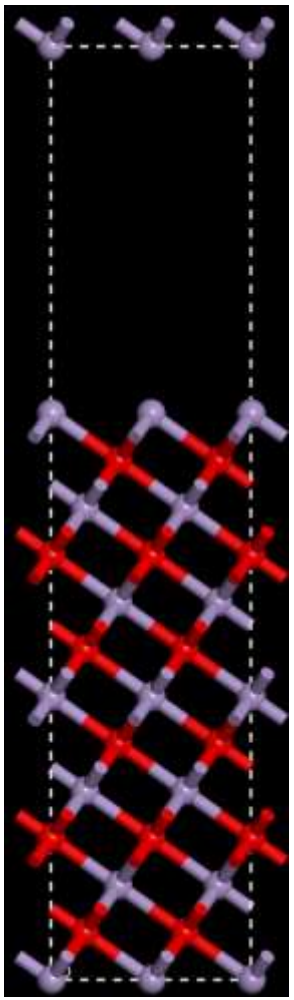
Surface

O-terminal

Mn-terminal

Mn:O = 1





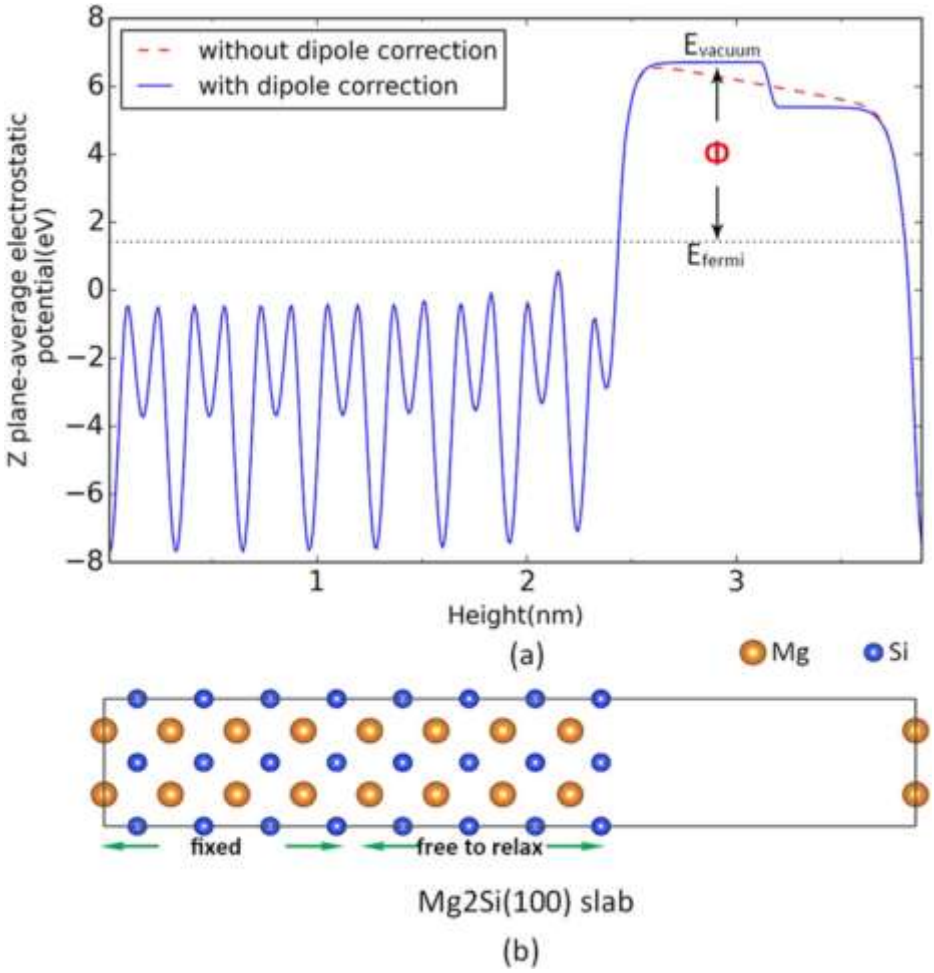
Mn-terminal

Mn-terminal

Mn:O > 1

Dipole correction for Slab model

Unphysical effect in slab model



The artificial potential affect the calculated adsorption energy and working function

Solutions:

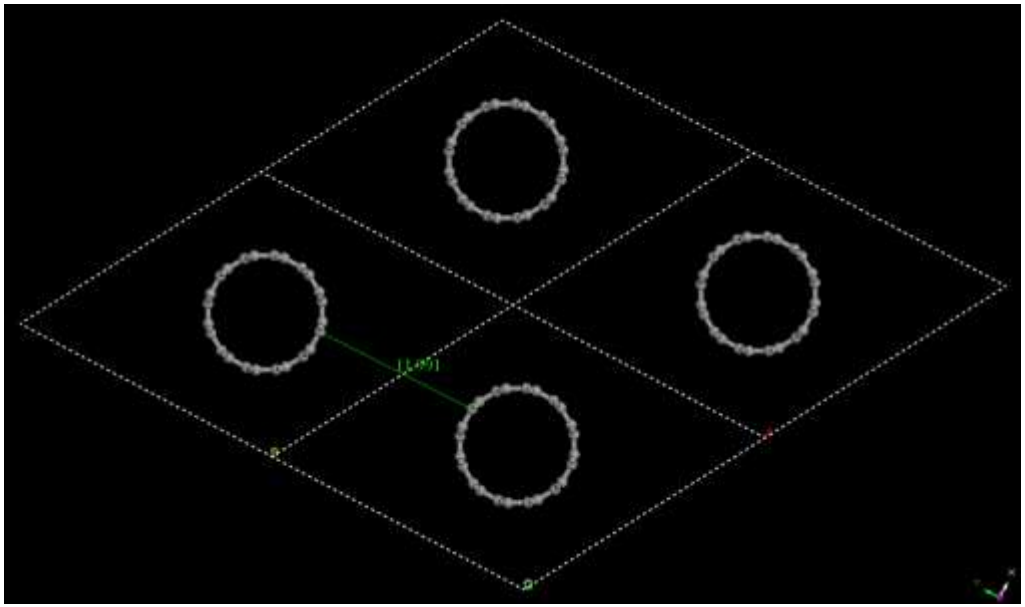
1. Dipole correction
2. Increase the vacuum thickness

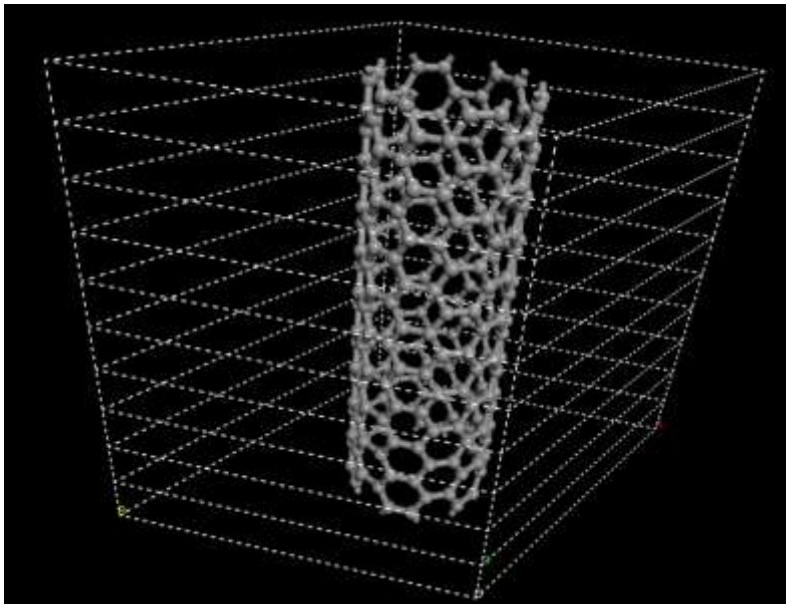
How to build a reasonable model

One-dimensional nanowires and nanotubes

one dimension infinite; two dimensions finite

(6,6) carbon nanotube



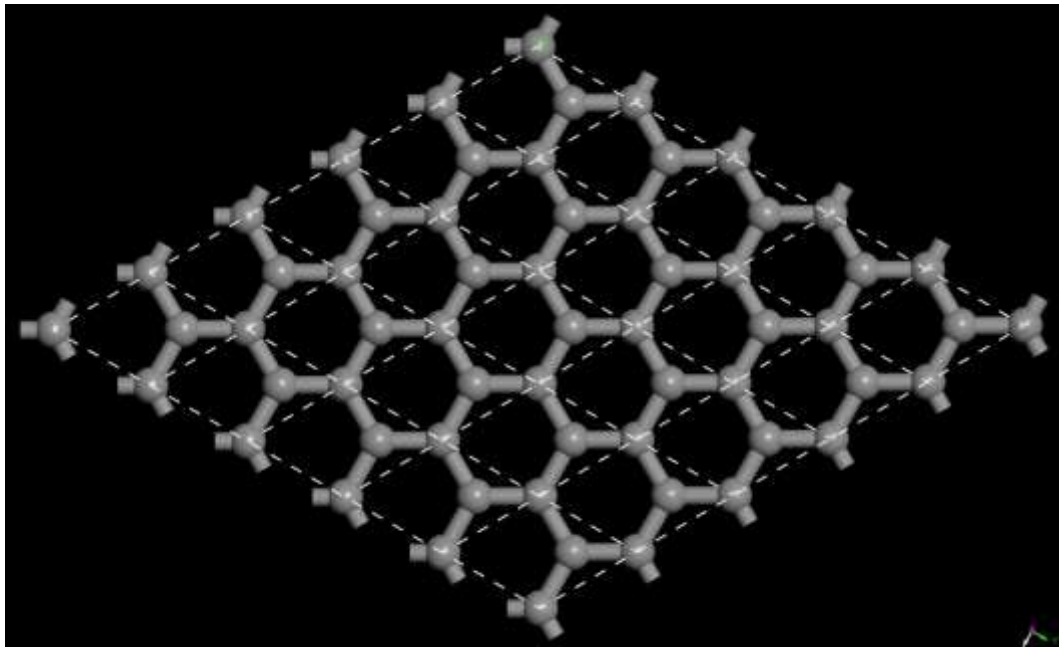


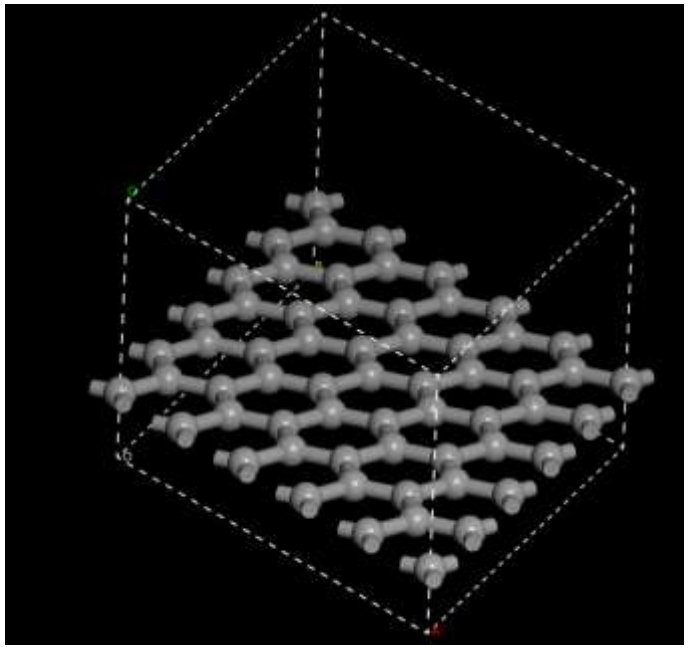
How to build a reasonable model

Two-dimensional monolayer

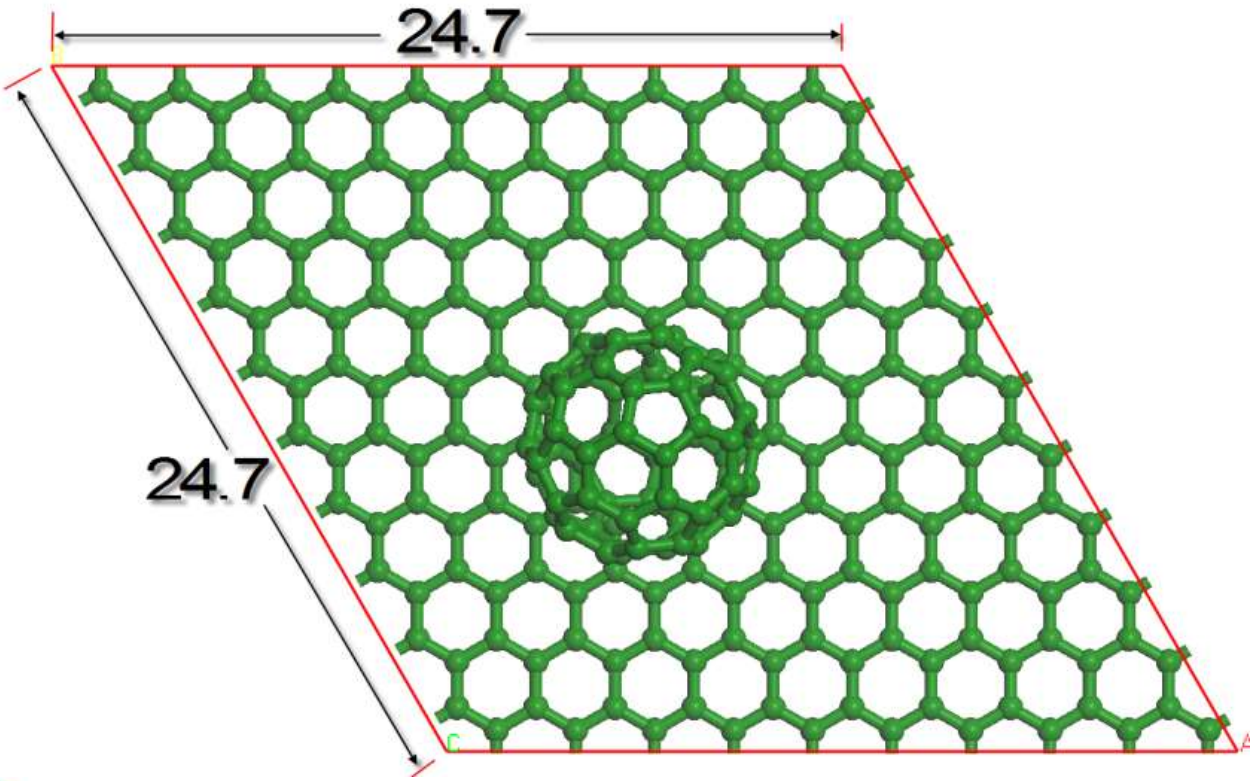
same as surface

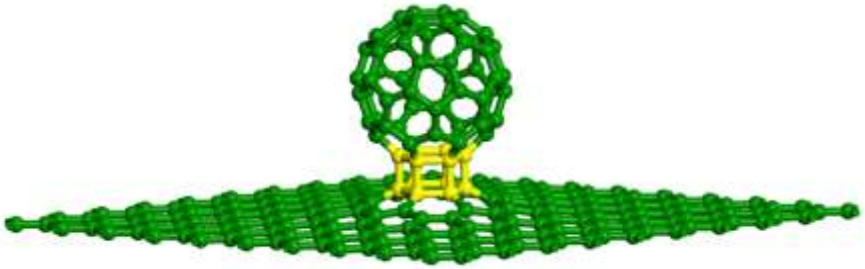
Graphene





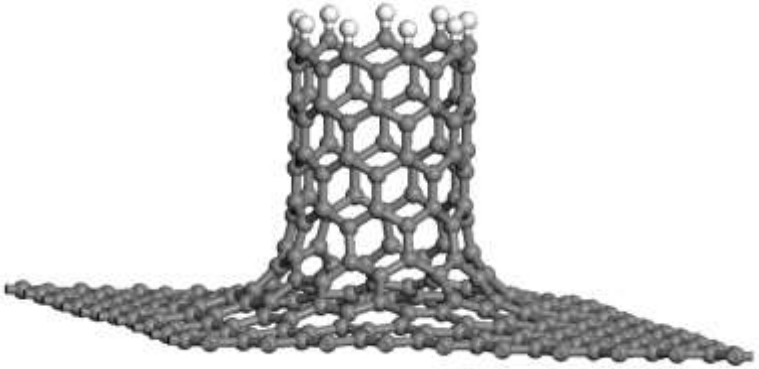
Build model for your problem and Control it

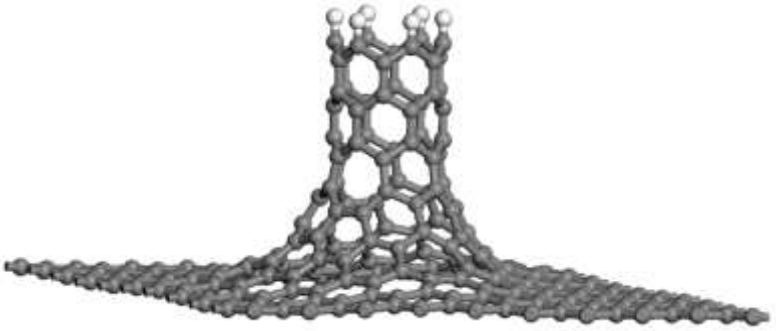


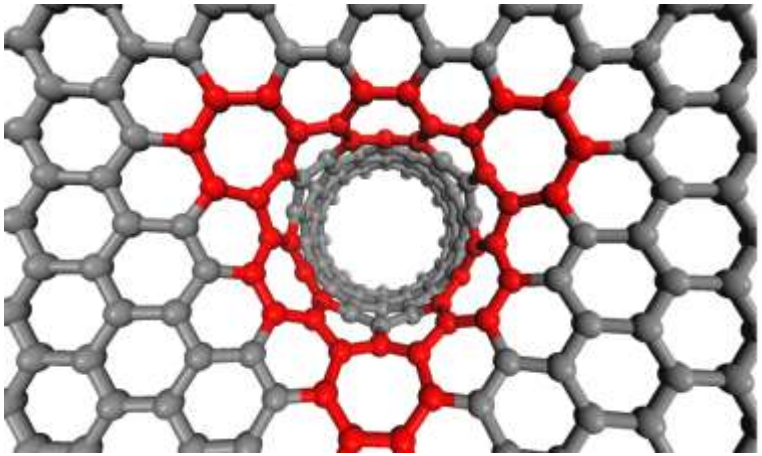


Build model for your problem and Control it

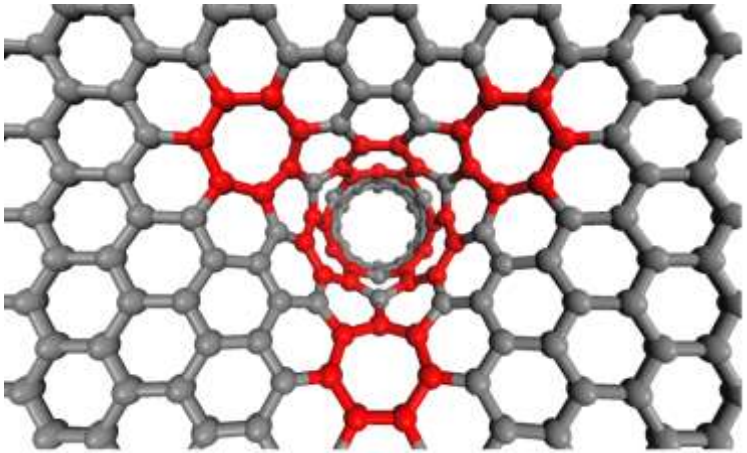
Carbon Nano-Funnel







（9，0） Funnel



（6，0） Funnel

Control and Conditions

- We can manipulate the model system: complete control
  - Move and place atoms
  - Apply strain
  - Try configurations
- Any conditions and situations are accessible
  - High pressure and temperature
  - Interfaces, porous medium, nanostructures
  - … …
  - Any reasonable things you can imagine