Supercells, forces, and structural optimizations

- Setting up supercells
- Atomic forces
- Structural minimizations

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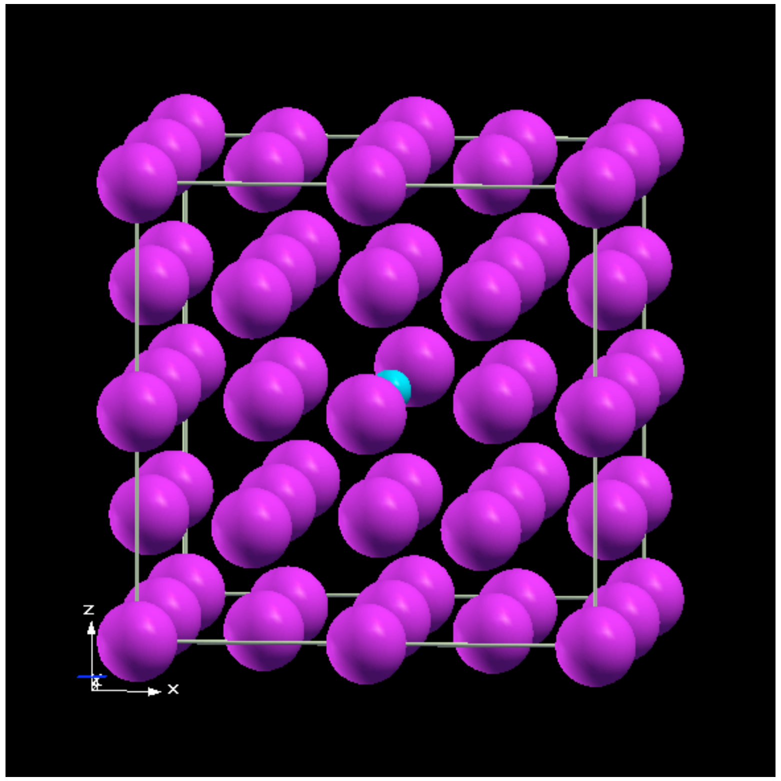
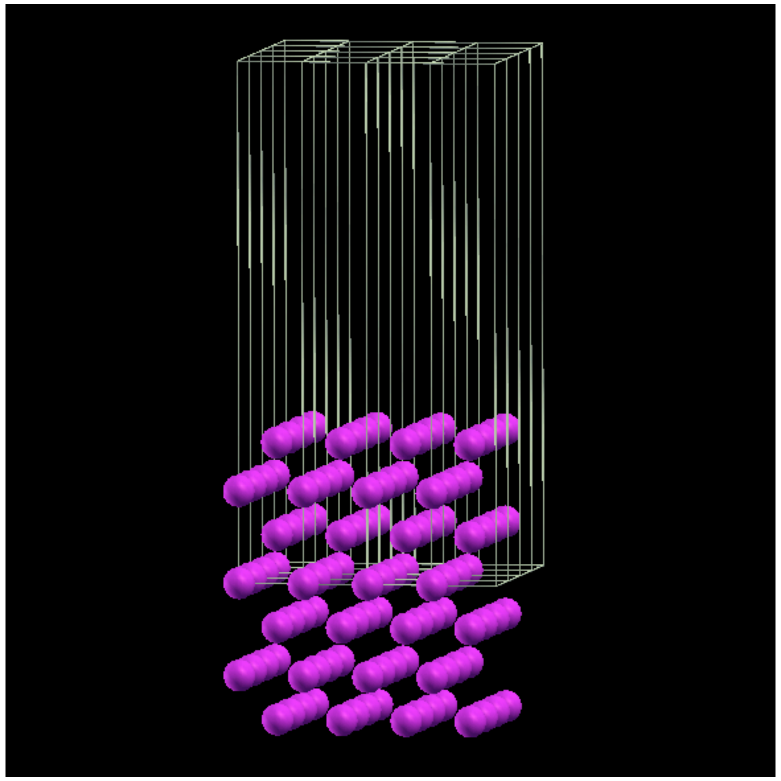
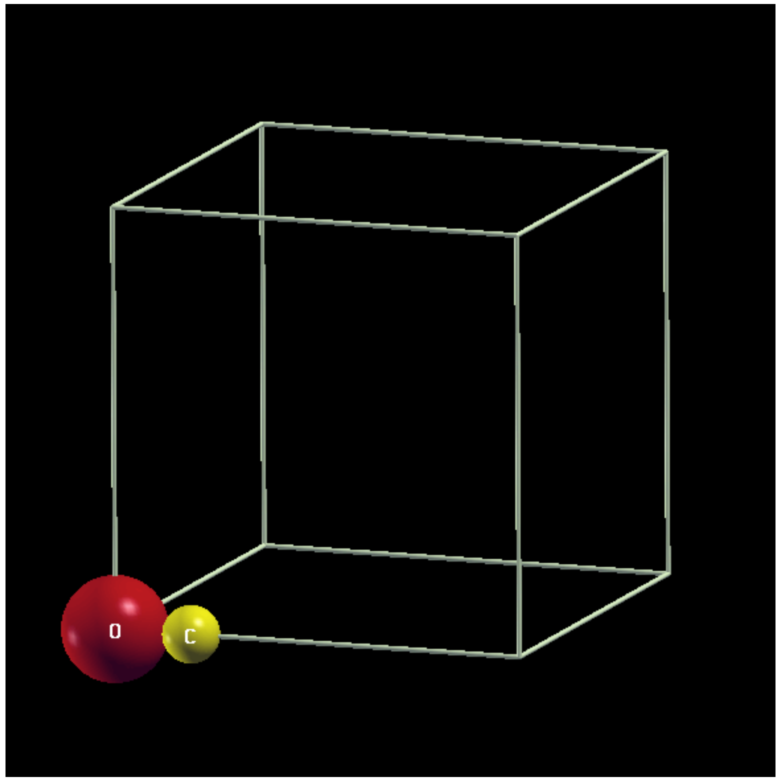
Supercells



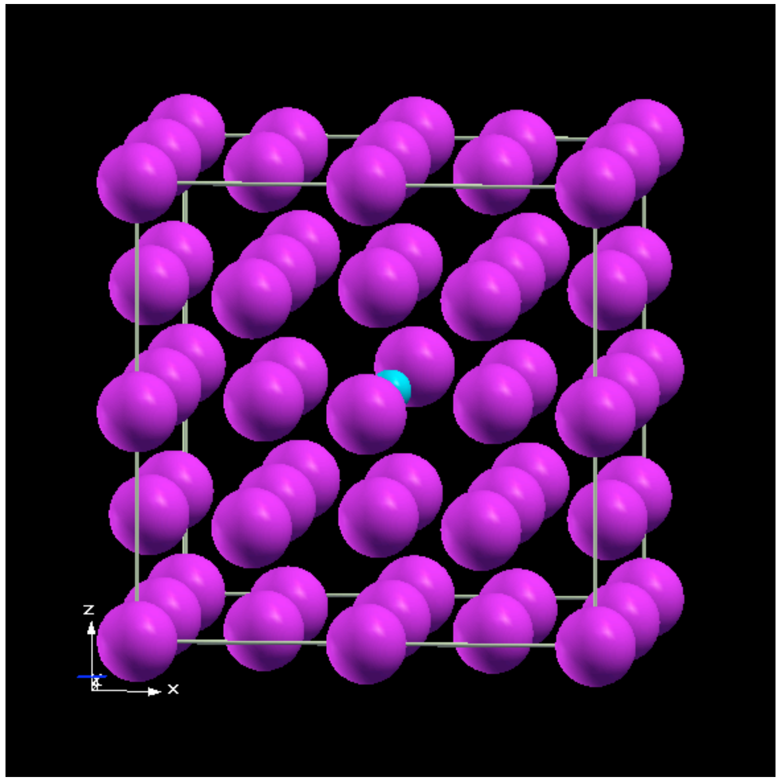


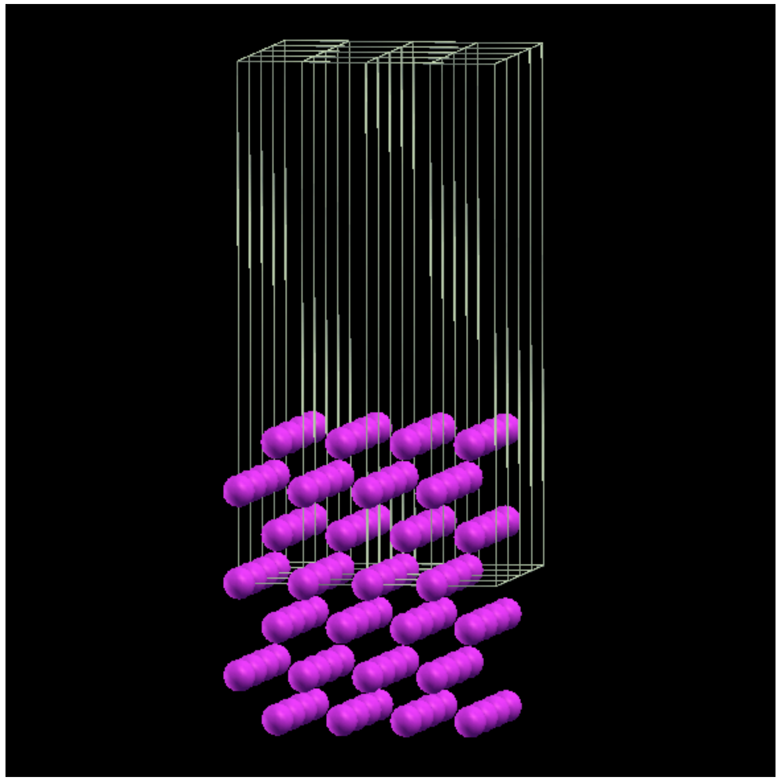


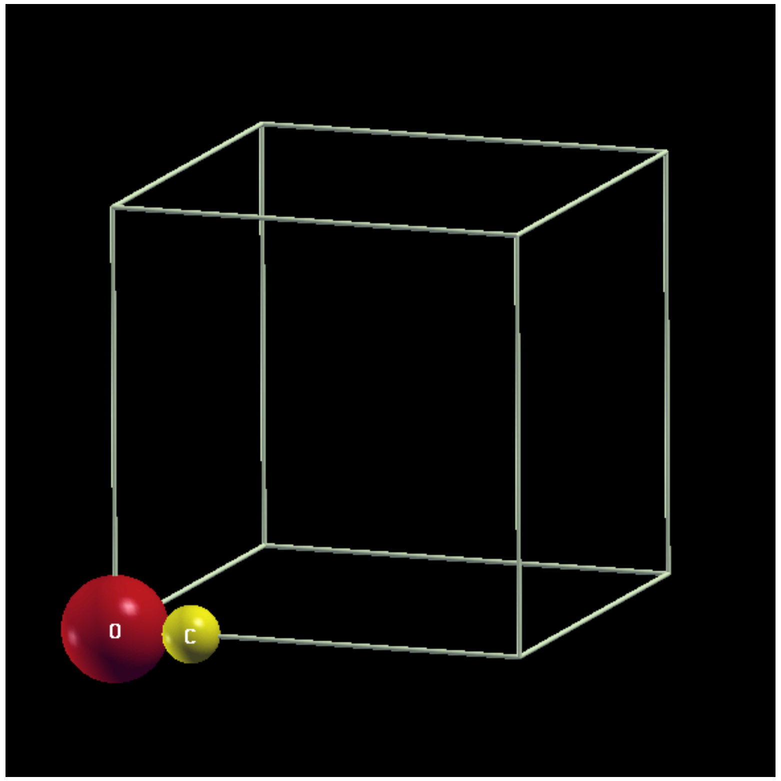
Supercells

- The simulation of many material properties in the plane waves framework often requires the supercell method.

- Typical cases are the study of crystalline defects, surface or molecular properties.







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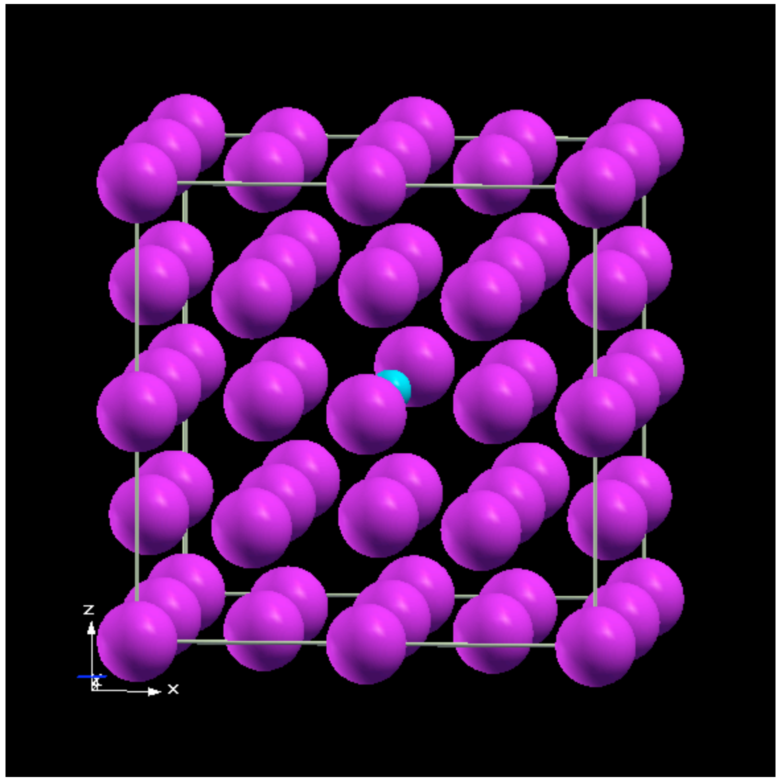
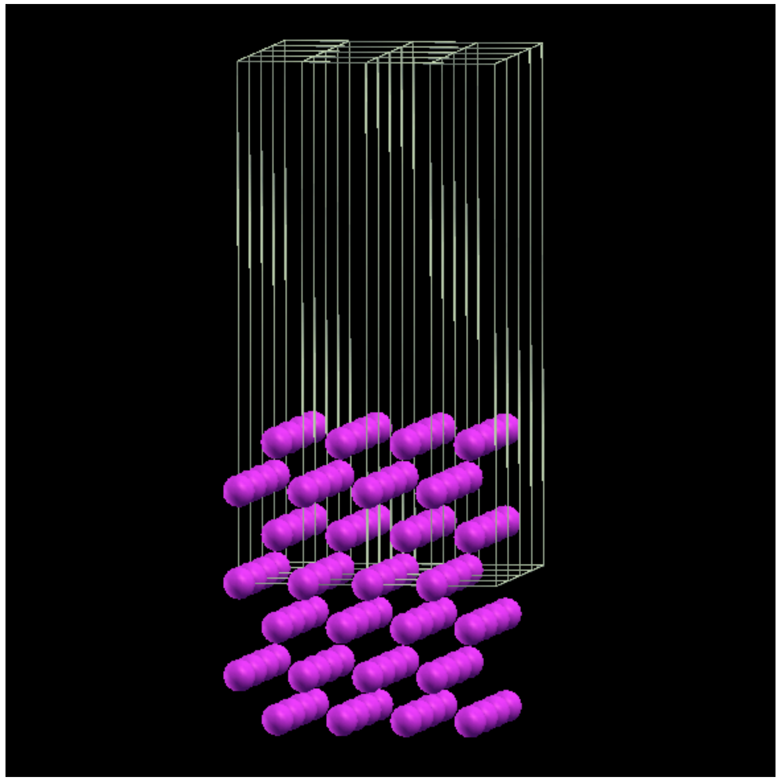
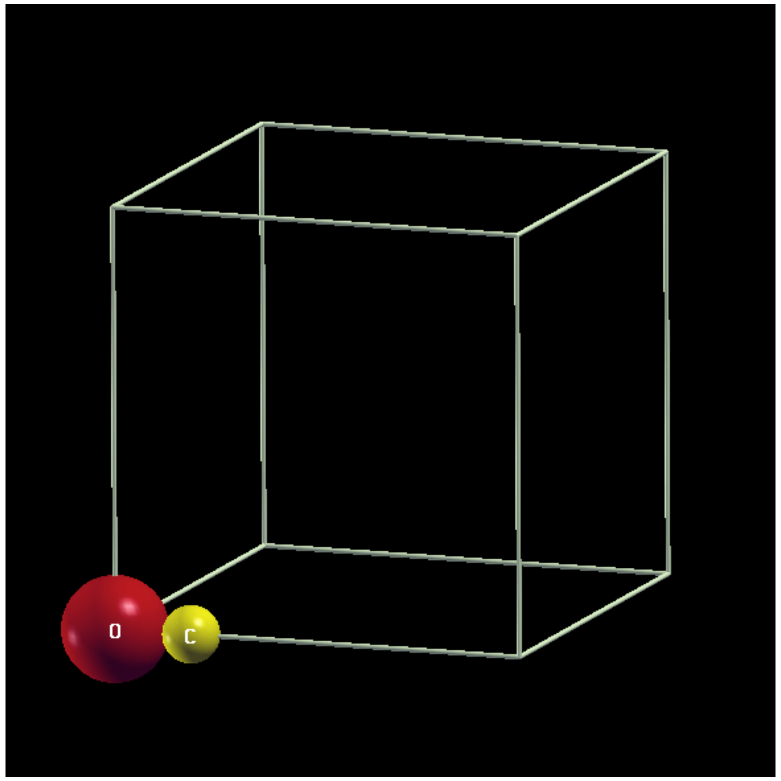
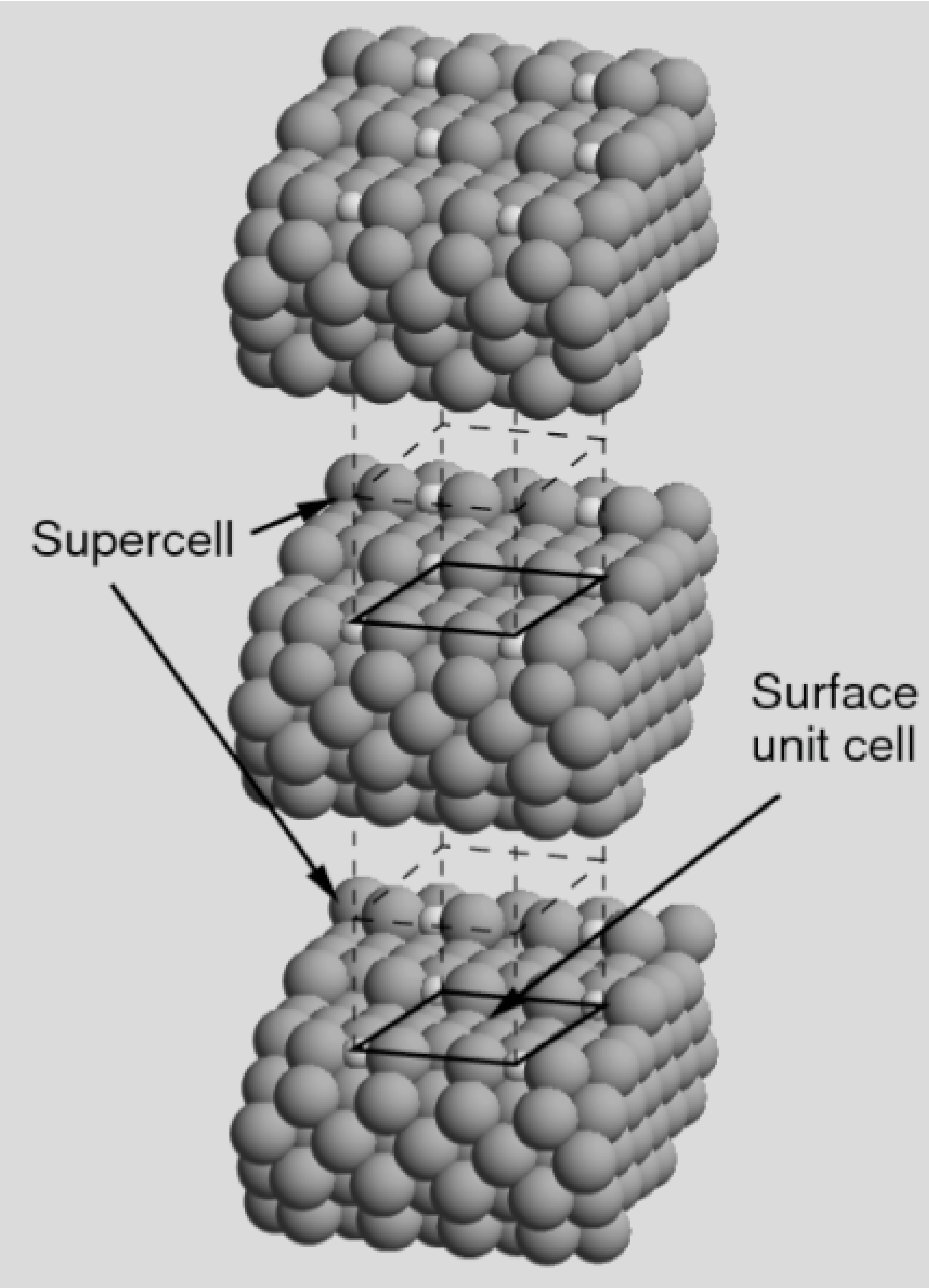






The correct choice of supercell size and shape is determinant for an accurate description of the properties under analysis

Supercells vs. clusters



SUPERCELL METHOD

+ 2D periodicity --> Bloch electron states

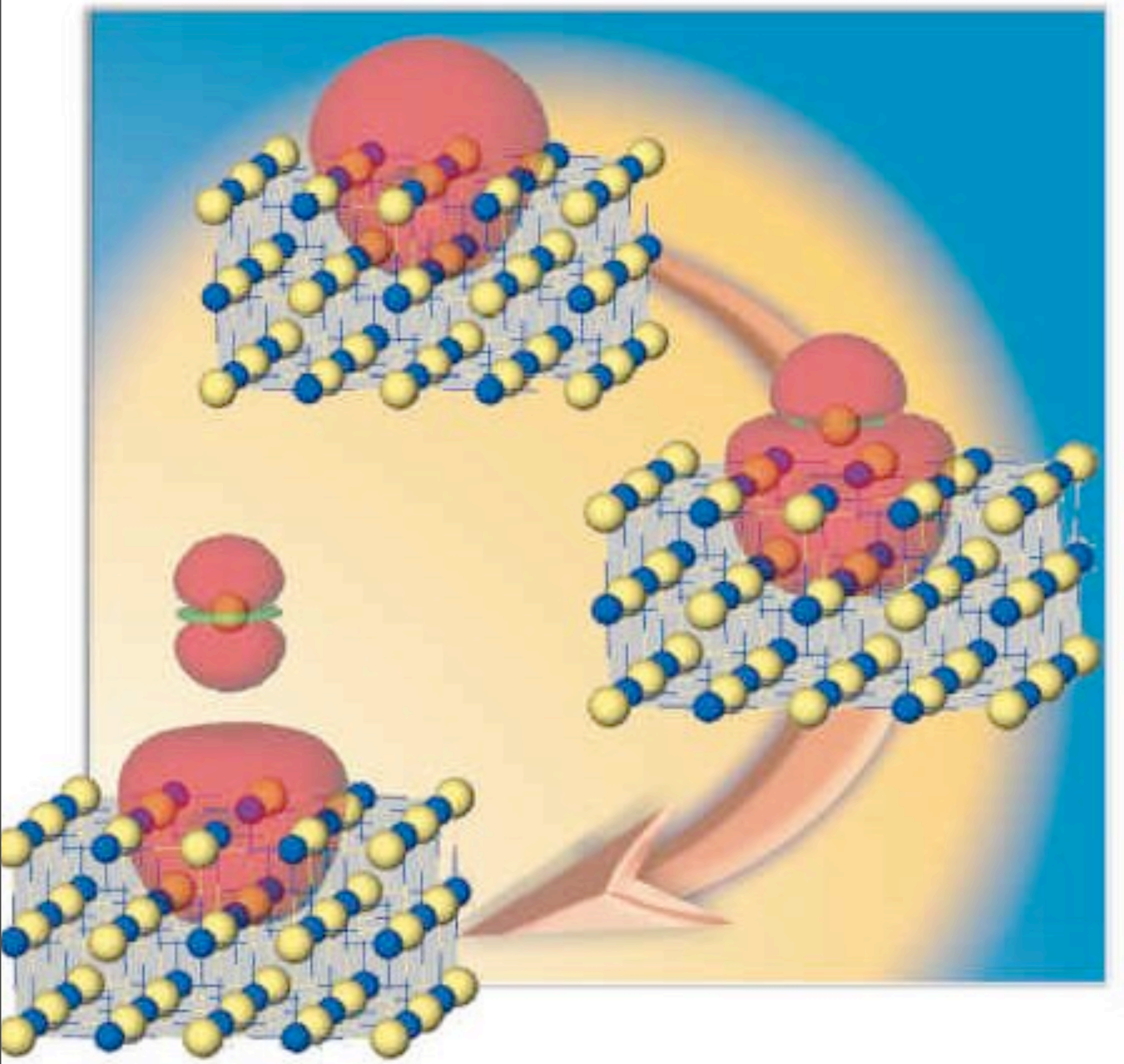
+ fast convergence with slab thickness

+ compatible with all basis set, particularly with PW

Finite size effects - lateral interaction with periodic images

- Computationally expensive

Supercells vs. clusters



CLUSTER METHOD

+ Good representation of isolated defects or adsorbates

+ Computationally efficient

- Very slow convergence with cluster size

- Compatible only with localized basis set

- Poor description of Bloch states

Setting up the supercell

The main variables used to set up a supercell are specified in the &SYSTEM namelist and by the ATOMIC_POSITIONS card of the input file

Setting up the supercell

The main variables used to set up a supercell are specified in the &SYSTEM namelist and by the ATOMIC_POSITIONS card of the input file

➡ ibrav is the structure index:

ibrav	structure	celldm(2)-celldm(6)
0	"free", see above	not used
1	cubic P (sc)	not used
2	cubic F (fcc)	not used
3	cubic I (bcc)	not used
4	Hexagonal and Trigonal P	celldm(3)=c/a
5	Trigonal R	celldm(4)=cos(alpha)
6	Tetragonal P (st)	celldm(3)=c/a
7	Tetragonal I (bct)	celldm(3)=c/a
…	…	…

… see file “espresso-x.y/Doc/INPUT_PW.txt”

ATOMIC POSITIONS

ATOMIC POSITIONS

➡ There are 4 possibilities to specify the atomic positions in the input file:

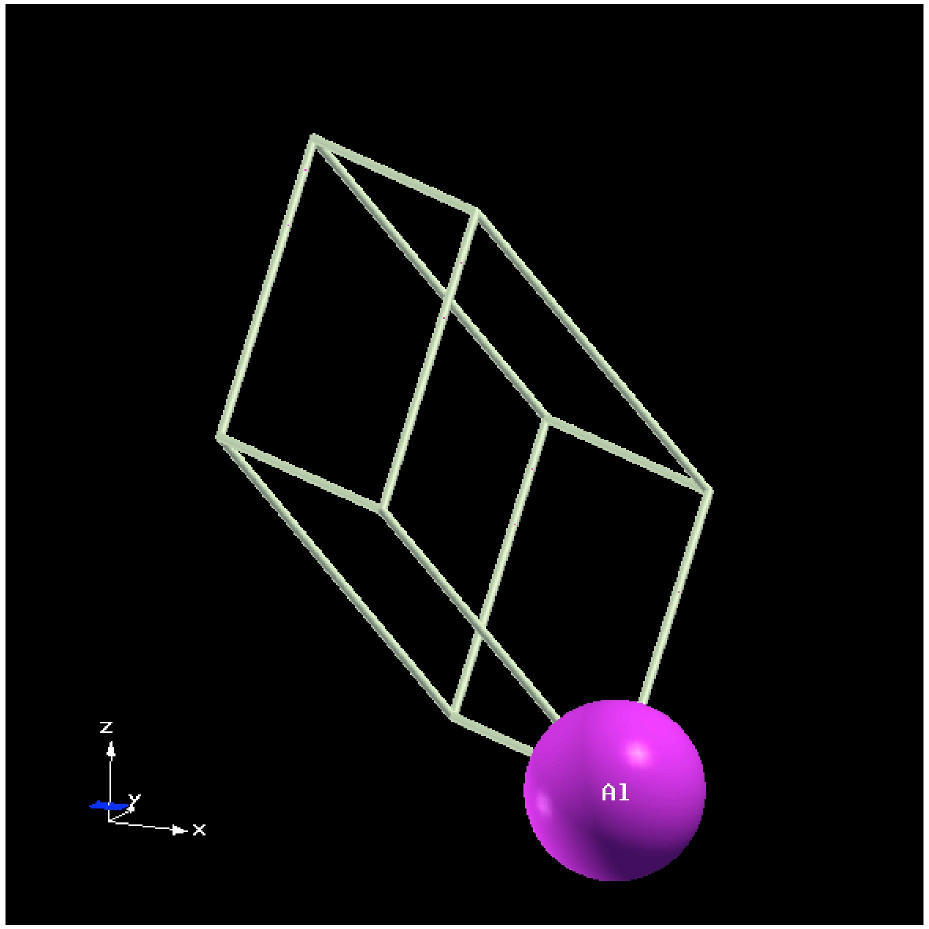
```
ATOMIC_POSITIONS { alat | bohr | crystal | angstrom }

alat     : atomic positions are in units of alat (default)
bohr     : atomic positions are in a.u.
crystal  : atomic positions are in crystal coordinates
angstrom: atomic positions are in A

There are "nat" cards like the following:
X x y z
where:
X    label of the atom as specified in ATOMIC_SPECIES
x, y, z atomic positions
```

… see file "espresso-xxx/Doc/INPUT_PW"

Ex1: bulk Cu
the primitive fcc cell

1) Edit the input file (run-cu.fcc)

```
&system
    ibrav=  XX,
    celldm(1) =XXX,
    nat=  xx,
    ntyp= xx,
```



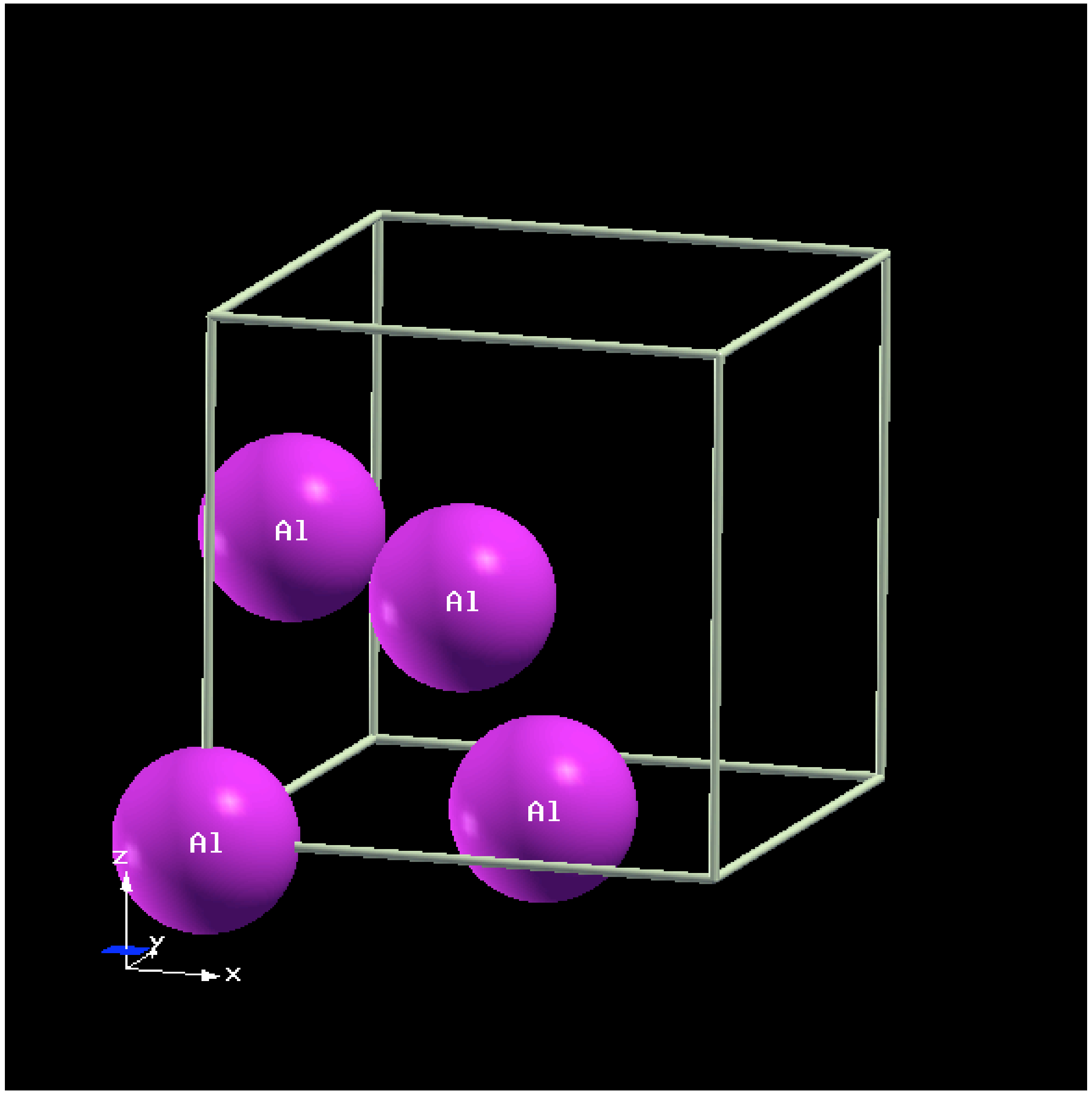
2) Run the scf calculation for bulk Cu described by the primitive fcc cell (pw.x):

```
./run-cu.scf
```

Ex2: bulk Cu - sc

1) Modify the input file (`run-cu.sc`) for describing bulk cupper with a simple cubic supercell (4 atoms/cell)

```
&system
    ibrav=  XX,
    celldm(1) =XXX,
    nat=  xx,
    ntyp= xx,
...
ATOMIC_POSITIONS
 Cu 0.0 0.0 0.0
 Cu xx xx xx
 Cu xx xx xx
 Cu xx xx xx
```

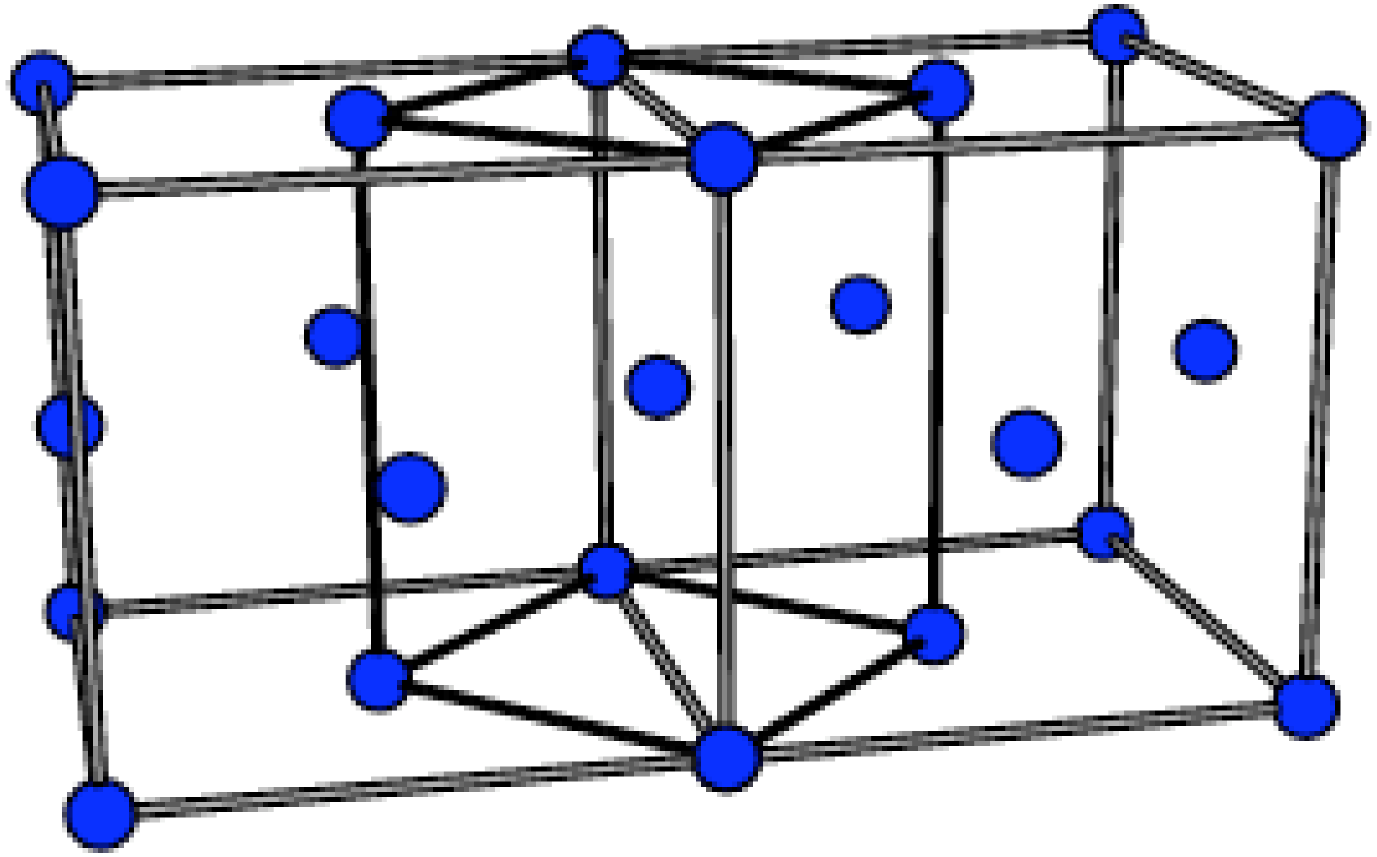


2) Run the scf calculation for bulk sc Cu

Ex3: bulk Cu - tetragonal alat

1) Modify the input file (**run-cu.tet**) for describing Cu bulk with a tetragonal supercell (2 atoms/cell). Atomic positions in "alat" units.

```
&system
    ibrav=  XX,
    celldm(1) =XXX,
    nat=  xx,
    ntyp= xx,
...
ATOMIC_POSITIONS {alat}
 Cu 0.0 0.0 0.0
 Cu xx xx xx
```

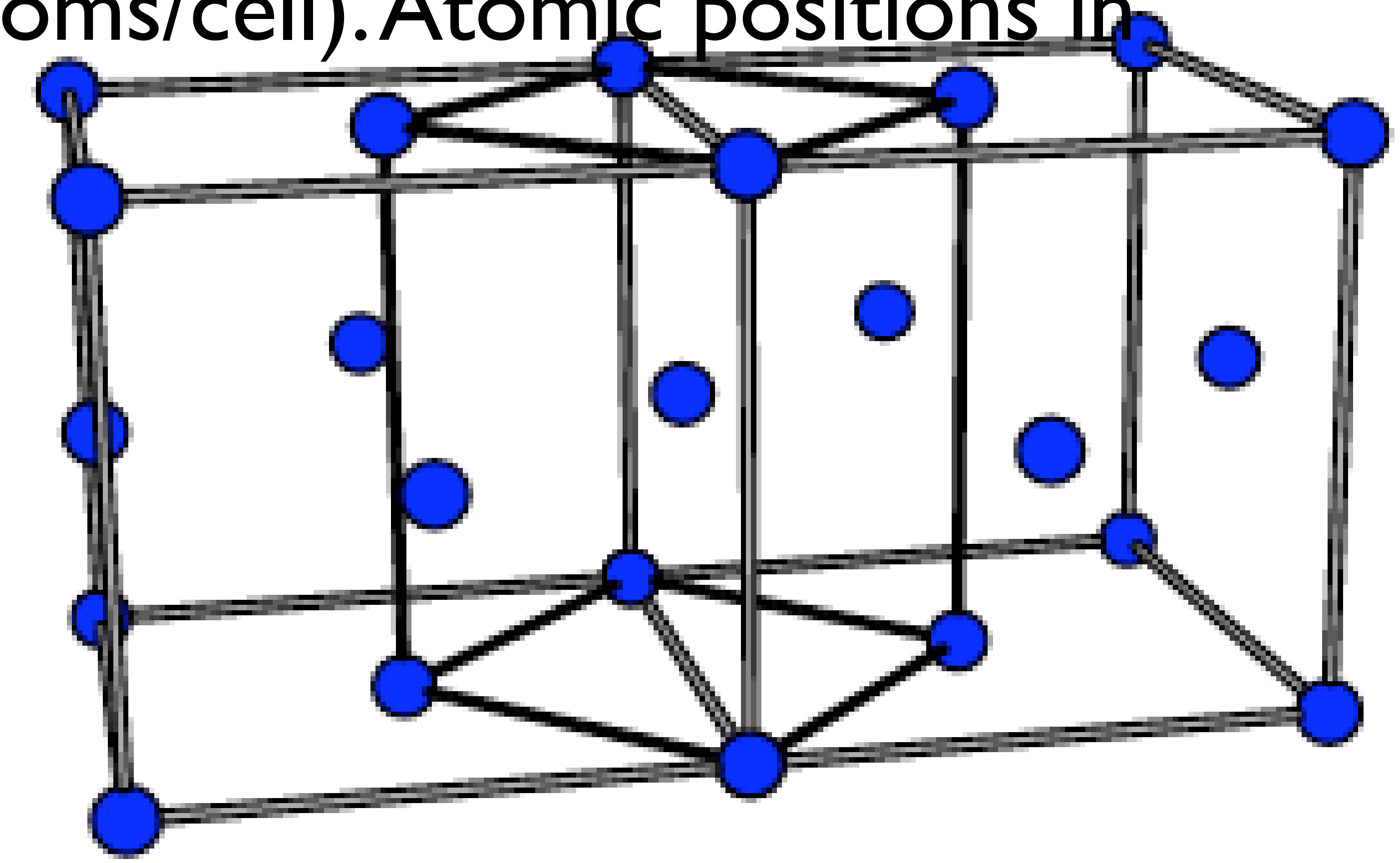


```
simple tetragonal (p)
====================
   v1 = a(1,0,0),  v2 = a(0,1,0),  v3 = a(0,0,c/a)
```

2) Run the scf calculation

Ex4: bulk Cu - tetragonal crystal

1) Modify the input file (`run-cu.tet-c`) for describing Cu bulk with a tetragonal supercell (2 atoms/cell). Atomic positions in "crystal" units.



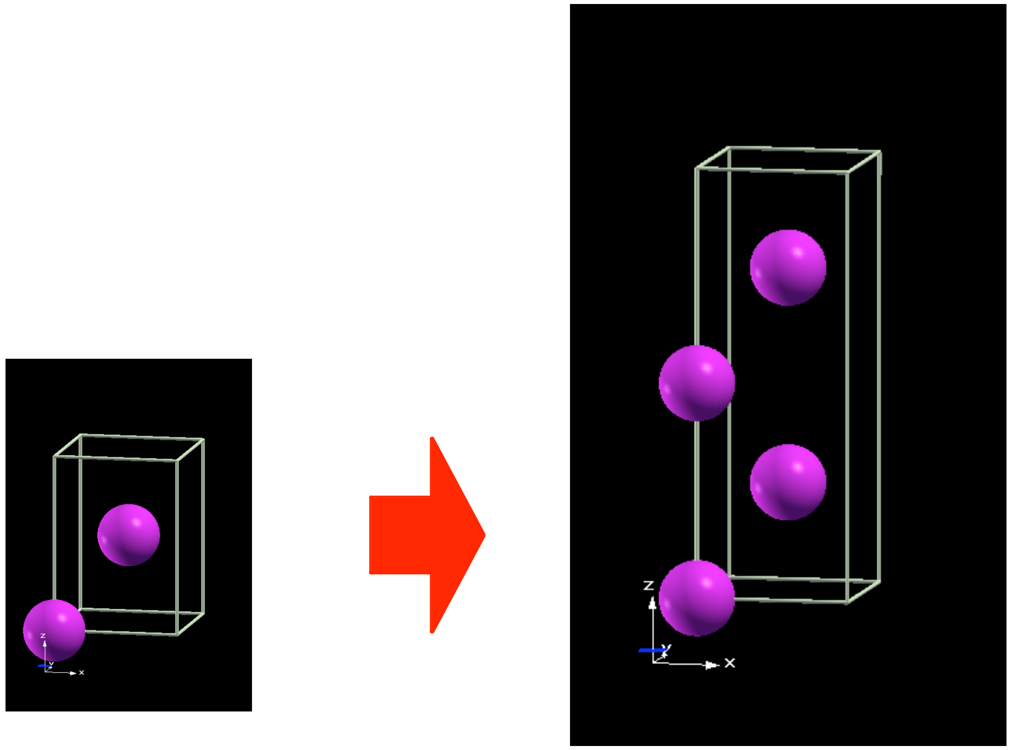
```
&system
    ibrav=  XX,
    celldm(1) =XXX,
    nat=  xx,
    ntyp= xx,
...
ATOMIC_POSITIONS {crystal}
 Cu 0.0 0.0 0.0
 Cu xx xx xx
```

2) Run the scf calculation

Ex4: bulk Cu - tet 1x1x2

1) Double the previous unit cell along the z direction. Modify the input file (run-cu.tet-c2) for describing Cu bulk with a 1x1x2 tetragonal supercell (4 atoms/cell). Atomic positions in “crystal” units.

```
&system
    ibrav=  XX,
    celldm(1) =XXX,
    nat=  xx,
    ntyp= xx,
...
ATOMIC_POSITIONS {crystal}
 Cu 0.0 0.0 0.0
 Cu xx xx xx
```



2) Run the scf calculation

Supercells and k-point sampling

➡Collect the total energies obtained with the tetragonal supercells:

```
> grep ! cu.tet*.out
cu.tet2.out:!    total energy       =   -xxx Ry
cu.tet.out:!    total energy        =    -yy Ry
```

… and make a Table in which you enter the supercell used, the kpoint mesh, and the total energy per Cu atom.

Supercells and k-point sampling

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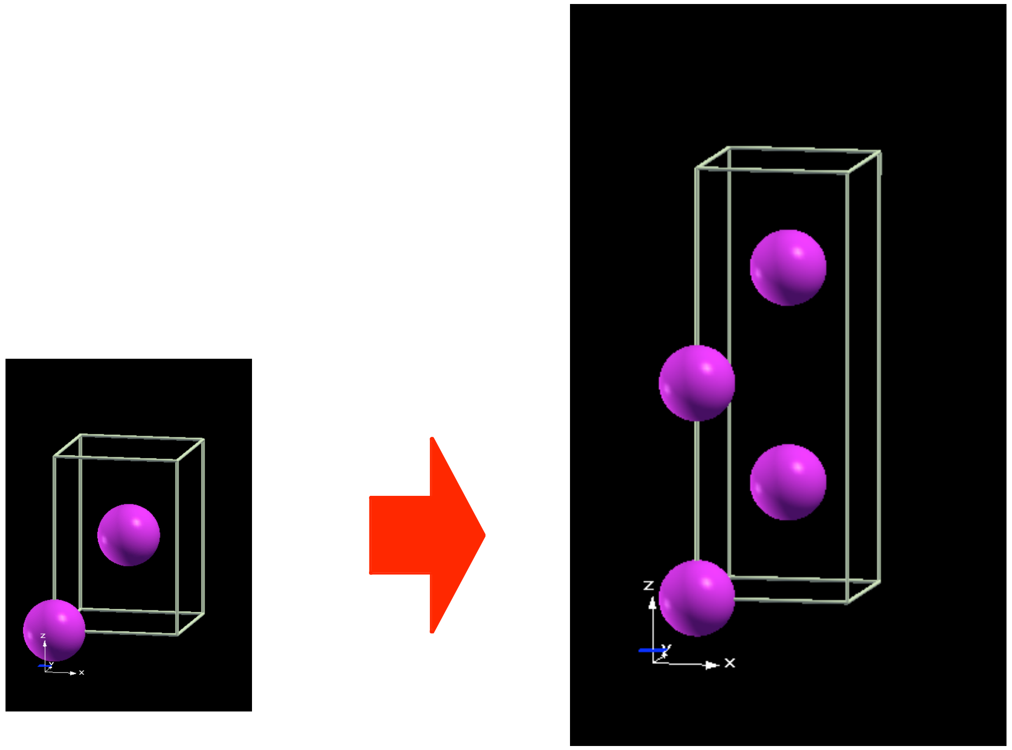
… and make a Table in which you enter the supercell used, the kpoint mesh, and the total energy per Cu atom.

➡ Are the calculated energies per Cu atom the same? Why (or why not)? (hint: we have used the same k-point mesh ...)

Ex5: supercell and k-points

1) Edit the input file (`run-cu.tet-c2k`) for describing Cu bulk with a 1x1x2 tetragonal supercell (4 atoms/cell). Atomic positions in "crystal" units.

```
&system
    ibrav=  XX,
    celldm(1) =XXX,
    nat=  xx,
    ntyp= xx,
...
ATOMIC_POSITIONS {crystal}
 Cu 0.0 0.0 0.0
 Cu xx xx xx
```



2) Select a k-point mesh that provides an sampling of the BZ equivalent to the one in the 1x1x1 tetragonal body centered supercell.

```
K_POINTS (automatic)
x x x 1 1 1
```

Ex5: supercell and k-points

3) Run the calculation

4) Compare again the total energies obtained with the tetragonal supercells:

```
> grep ! cu.tet*.out
cu.tet3.out:!     total energy          =    -zzz Ry
cu.tet2.out:!     total energy          =    -xxx Ry
cu.tet.out:!     total energy           =     -yy Ry
```

… and make a Table in which you enter the supercell used, the kpoint mesh, and the total energy per Cu atom.

5) Which k-point sampling yields the same total energies per Cu atom? Why it is so?

Ex6: the Cu(001) surface

Model the Cu(001) surface with a supercell slab having 4 atomic layers separated by a region of vacuum along the z direction.

1) Edit the input file (**run-cu001**) to obtain a tetragonal supercell (4 atoms/cell). Select a sufficiently large c/a ratio (i.e. 2 times the c/a ratio of the 1x1x2 tetragonal supercell). Atomic positions in “alat” units (do you see why in this case it is more practical than “crystal”?).

2) How many k-points along the K_z? Why?

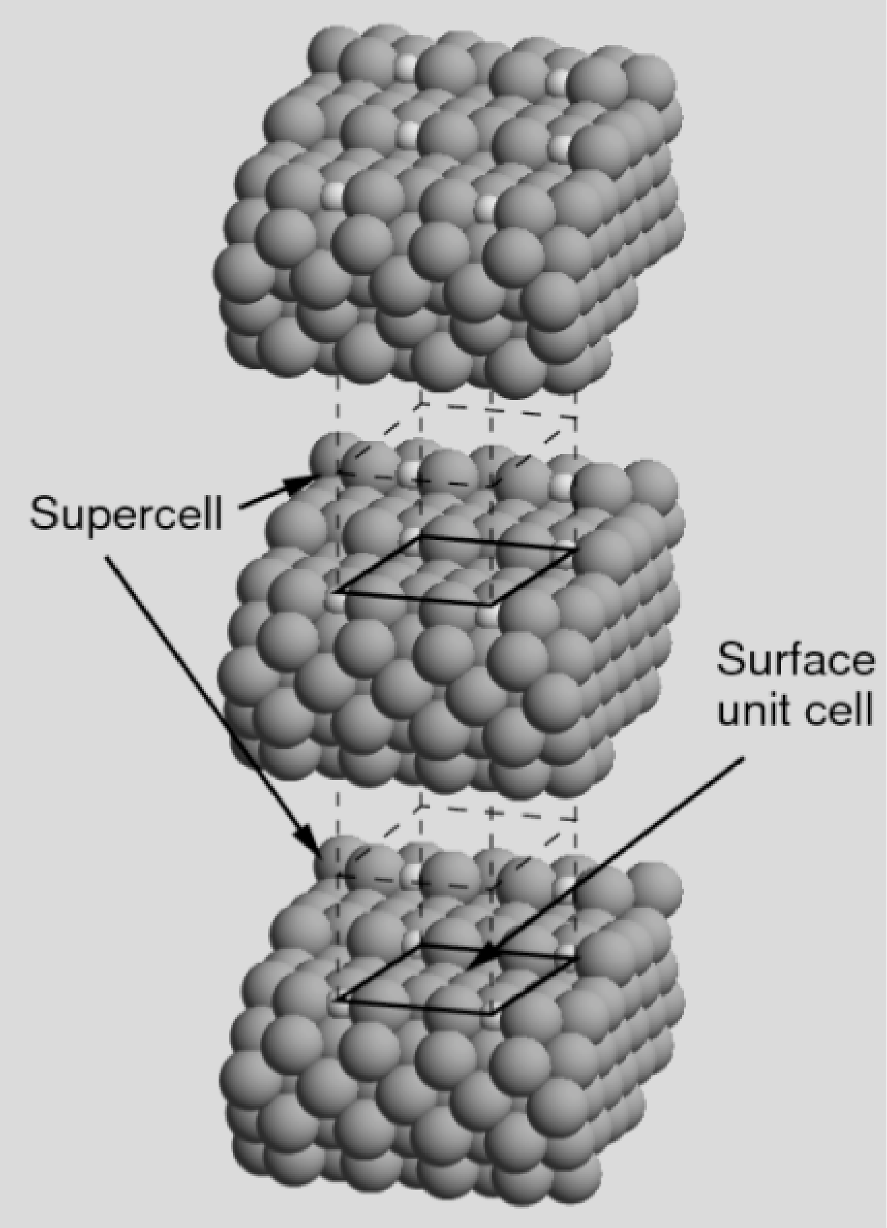
```
K_POINTS (automatic)
8 8 x 1 1 1
```

3) Visualize the supercell with XCrysDen and check that the interlayer distances have the bulk value. Check the size of the vacuum region separating the slab surfaces.

4)Run the calculation

Modeling surfaces with the supercell method

In periodic boundary conditions, surfaces are modeled by 2D slabs separated by a vacuum region



➡Vacuum thickness

- Minimize interaction of opposite sides of the slabs through vacuum

➡!! check convergence !!

- Surface energy
- Electronic properties: layer resolved PDOS
- Structural properties: atomic relaxation
- ...

Modeling surfaces with the supercell method

In periodic boundary conditions, surfaces are modeled by 2D slabs separated by a vacuum region

➡Slab thickness

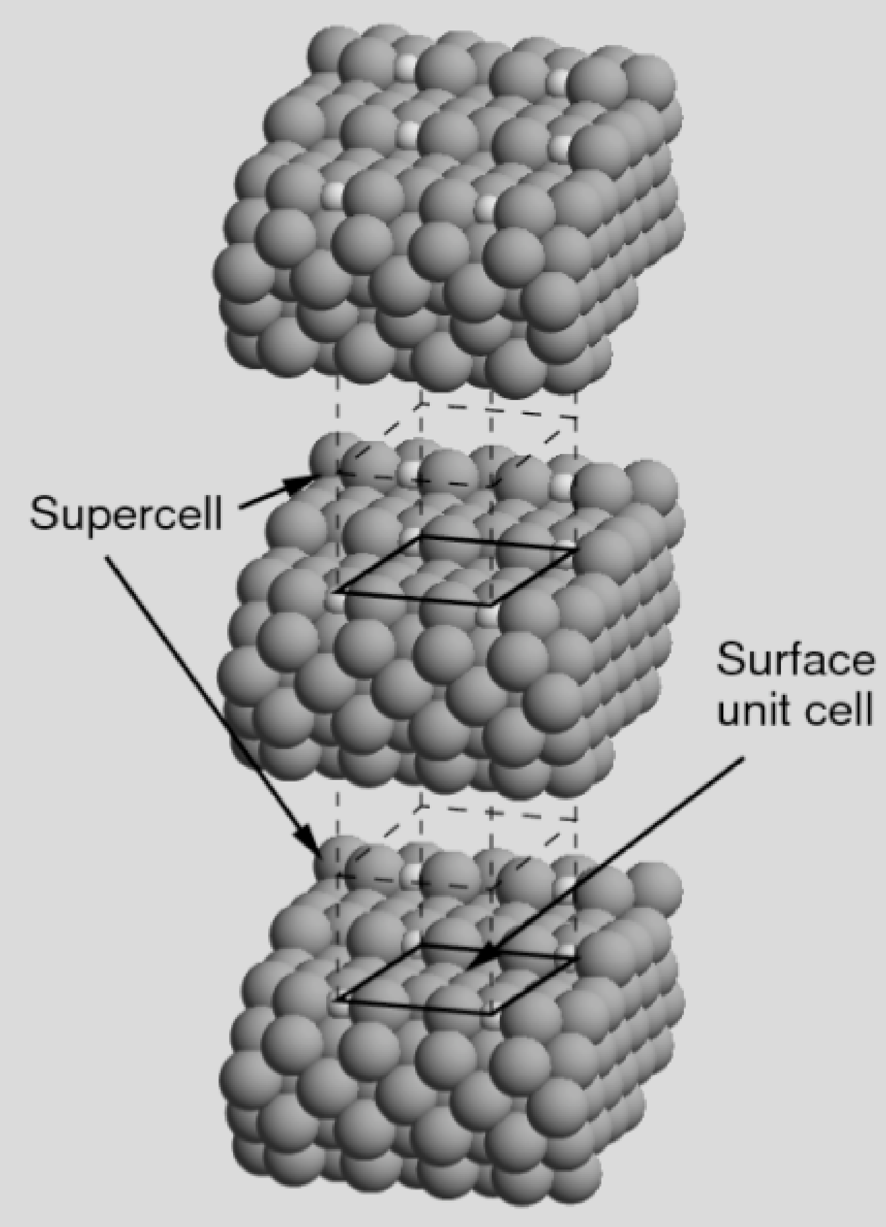
- •Bulk environment for innermost layers
- •Minimize interaction of opposite sides of the slabs

➡Vacuum thickness

- •Minimize interaction of opposite sides of the slabs through vacuum

➡!! check convergence !!

- •Surface energy
- •Electronic properties: layer resolved PDOS
- •Structural properties: atomic relaxation
- • ...



Atomic forces

•The loss of symmetry due to the surface make arise atomic forces which determine surface relaxation and/or reconstruction

$$\mathbf{F}_I = -\frac{\partial E}{\partial \mathbf{R}_I}$$

• Forces acting on atomic nuclei can be calculated with the Hellmann-Feynman theorem

$$\frac{\partial E}{\partial \lambda} = \langle \Psi_\lambda | \frac{\partial H}{\partial \lambda} | \Psi_\lambda \rangle$$

•Given the ground state density, the atomic forces are determined by classical electrostatics

$$\frac{\partial E[\rho]}{\partial \mathbf{R}_I} = \int \rho \frac{\partial V_{\mathrm{ext}}}{\partial \mathbf{R}_I} d\mathbf{r} + \frac{\partial E_{ZZ}}{\partial \mathbf{R}_I}$$

Ex7: forces on the Cu(001) surface

Model the Cu(001) surface with a supercell slab having 4 atomic layers separated by a region of vacuum along the z direction.

1) Edit the input file (`run-cu001`) so that atomic forces are calculated at the end of the scf loop and printed in the output file (see Doc/INPUT_PW.txt - &CONTROL namelist)

2) Run the scf calculation and check the forces in the output file. Will the surface expand or contract with respect to the bulk-like termination?

3) Visualize the forces with XCrysDen.

Atomic forces and Potential Energy Surfaces

- Atomic forces can be used to find and predict the equilibrium ionic structure of a crystal or molecule.

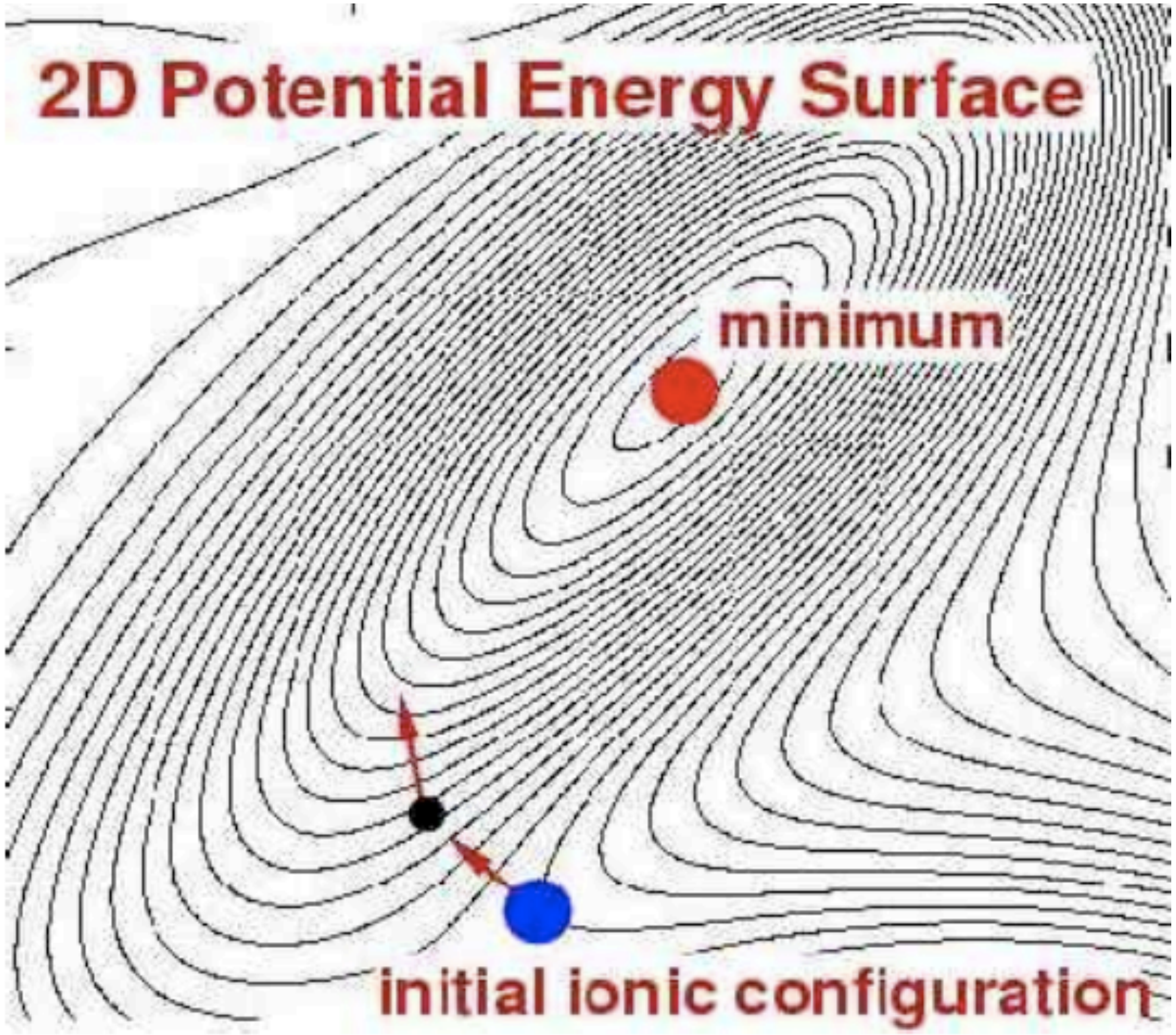
- The total energy is a parametric function of the ionic coordinates and defines a 3N-dimensional iper-space named Potential Energy Surface (PES).

- Equilibrium ionic configurations corresponds to minima (local or absolute) of the PES

$$F(X_I^{3N}) = -\frac{\partial E\left[X_I^{3N}, \rho(X_I^{3N})\right]}{\partial X_I^{3N}} = 0$$

Atomic forces and Potential Energy Surfaces

•Given an initial ionic configuration, the minimum of the PES can be identified with iterative methods



- Steepest descent:

$$\dot{X}_I^{3N} = F(X_I^{3N})$$

discretisation

$$X_{k+1} = X_k - \lambda \frac{g_k}{|g_k|}$$

gradient versor

Ex8: structural relaxation of the Cu(001) surface

Relax the Cu(001) surface and find the equilibrium configuration of the outermost atomic layers. Use a supercell slab having 7 atomic layers separated by a region of vacuum along the z direction.

1) Edit the input file (`run-cu001-7lay`) to perform a structural relaxation of the ionic positions with the BFGS algorithm (see Doc/INPUT_PW.txt - &CONTROL and &IONS namelists).

```
&CONTROL
   calculation  = "XXX",
   dt           = 20.D0,
...
&ELECTRONS
   conv_thr    = 1.D-8,
...
&IONS
   ion_dynamics        = "xxxx",
   pot_extrapolation = "second_order",
   wfc_extrapolation = "second_order",
```

Ex8: structural relaxation of the Cu(001) surface

1) constrain the z coordinate of the two lowermost layers.

```
&CONTROL
   calculation  = "XXX",
   dt           = 20.D0,
...
&ELECTRONS
   conv_thr    = 1.D-8,
...
&IONS
   ion_dynamics      = "damp",
   pot_extrapolation = "second_order",
   wfc_extrapolation = "second_order",
```

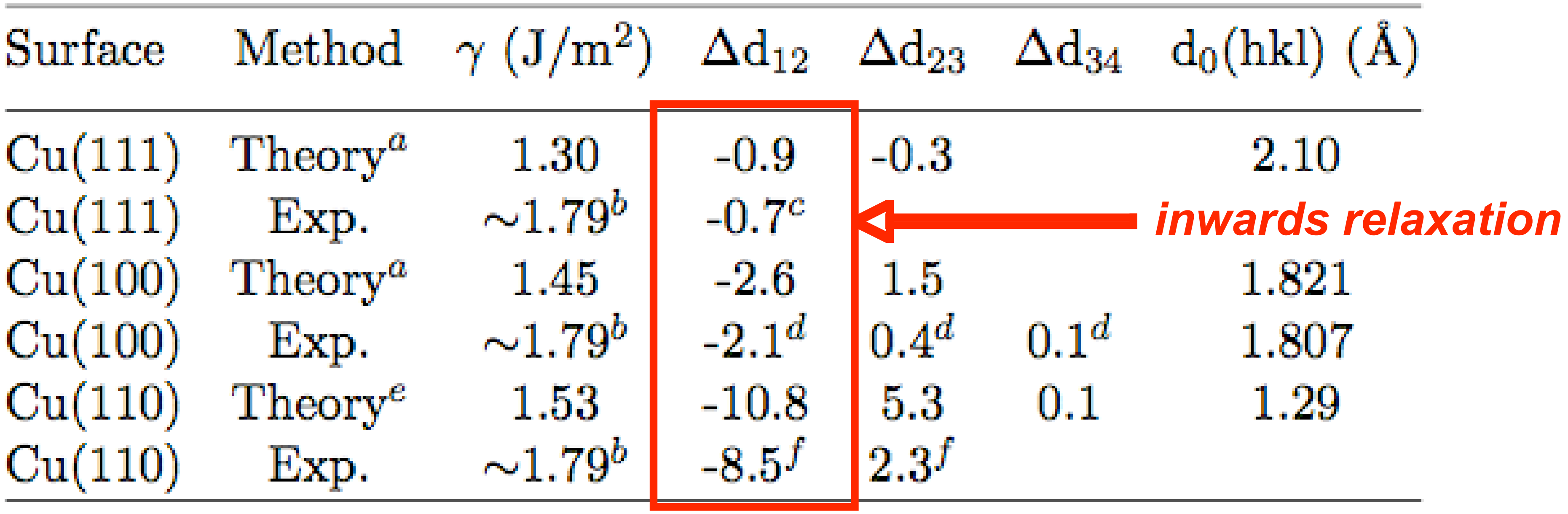
2) Run the scf calculation and check the forces in the output file. Does the surface expand or contract with respect to the bulk-like termination?

3) Visualize the forces and the resulting equilibrium structure with XCrysDen.

Ex8: structural relaxation of the Cu(001) surface

4) The forces must be small at convergency.

5)Compare your results with the experiment and with the literature:



Surface	Method	γ (J/m^2)	Δd_{12}	Δd_{23}	Δd_{34}	d_0(hkl) (Å)
Cu(111)	Theory^a	1.30	-0.9	-0.3		2.10
Cu(111)	Exp.	~1.79^b	-0.7^c			
Cu(100)	Theory^a	1.45	-2.6	1.5		1.821
Cu(100)	Exp.	~1.79^b	-2.1^d	0.4^d	0.1^d	1.807
Cu(110)	Theory^e	1.53	-10.8	5.3	0.1	1.29
Cu(110)	Exp.	~1.79^b	-8.5^f	2.3^f		

inwards relaxation

6) Notice that some innermost ionic positions have been constrained. Do you have any idea why this was done?

Ex9: structural relaxation of acetylene

Find the equilibrium structure of the C2H2 molecule by using the damped dynamics algorithm.

1) Edit the input file (`run-c2h2-scf`) to perform a scf calculation. How many (and which) K points do you select? Why? Constrain the position of one C atom.

2) Visualize the initial guessed structure with XCrysDen and run the calculation. Check the forces.

```
     Forces acting on atoms (Ry/au):

      atom    1 type  2   force =     0.04222638   -0.07117288    0.00000000
      atom    2 type  2   force =    -0.29084207    0.14204759    0.00000000
      atom    3 type  1   force =    -0.50882979    0.10564908   -0.00000000
      atom    4 type  1   force =     0.75744548   -0.17652379   -0.00000000
```

```
cp run-c2h2-scf run-c2h2-damp
```

Ex9: structural relaxation of acetylene

3) Edit the input file (**run-c2h2-damp**) to perform a relaxation of the atomic positions with the damped dynamics method (see Doc/INPUT_PW.txt - &CONTROL and &IONS namelists)

```
&CONTROL
   calculation  = "XXX",
   dt           = 20.D0,
...
&ELECTRONS
   conv_thr    = 1.D-8,
...
&IONS
   ion_dynamics      = "damp",
   pot_extrapolation = "second_order",
   wfc_extrapolation = "second_order",
 /
...
 H  1.0  H.US_PBE.RRKJ3.UPF
 C  1.0  C.US_PBE.RRKJ3.UPF
```

4) Run the calculation

Ex9: structural relaxation of acetylene

5) Check that at convergence the forces are smaller than the specified (or default) threshold

```
Forces acting on atoms (Ry/au):

atom    1 type  2   force =    -0.00052248   -0.00030500    0.00000000
atom    2 type  2   force =     0.00031278    0.00021916   -0.00000000
atom    3 type  1   force =     0.00006239   -0.00020314    0.00000000
atom    4 type  1   force =     0.00014731    0.00028898    0.00000000

Total force =      0.000544     Total SCF correction =      0.000039
```

6) Examine the equilibrium molecular structure with XCrysDen

7) Put to file the scf total energy at calculated at each minimization step:

```
grep ! c2h2-damp.out | nl > etot-damp.dat
```

Ex9: structural relaxation of acetylene

8) `cp run-c2h2-damp run-c2h2-bfgs`

9)Edit the input file to perform a relaxation of the atomic positions with the BFGS algorithm

```
&IONS
   ion_dynamics      = "XXXX",
   pot_extrapolation = "second_order",
   wfc_extrapolation = "second_order",
 /
```

10) Run the calculation

11) Check if the two algorithms predict the same equilibrium structure

Ex9: structural relaxation of acetylene

12) Put to file the scf total energy at calculated at each minimization step:

```
grep ! c2h2-bfgs.out | nl > etot-bfgs.da
```

13) Compare the performance of the two algorithms: plot the total energy as a function of the step number

14)
```
cp run-c2h2-damp run-c2h2-damp-constr
```

Ex9: structural relaxation of acetylene

15) Edit the input file (`run-c2h2-damp-constr`) to perform a relaxation of the atomic positions (damped dynamics) that constrain the C-C distance to be 2.1 a.u. (see Doc/INPUT_PW.txt - CONSTRAINS card)

```
CONSTRAINTS
NN
XXXX N M YYY
```

16) Run the calculation

17) Verify that the C-C distance is effectively constrained during the optimization procedure.

Ex10: structural relaxation of the Si(001) surface

Find the equilibrium structure of the Si(001) surface

1) Edit the input file (`run-si001`) to perform a structural relaxation of the Si(001) surface with the bfgs algorithm.

2) Run the calculation and check the final configuration.

3) Collect the total energies along the minimization procedure and plot them as a function of the ionic step. What do you notice?