DFT Hands-on

- Solid LiF
  - Plane wave cutoff convergence
  - Determination of equilibrium lattice constant
  - DFT Band Structure
- CO molecule
  - Equilibrium geometry (Plane wave cutoff and supercell size convergence)
  - Plot of HOMO LUMO wfns
- Si(111) surface
  - Equilibrium geometry
  - DFT band structure

Check installation & basic usage

```
cdhogan$ tar -xvf EsercitazioneDFT_2015-16.tar

cdhogan$ cd EsercitazioneDFT/Lezione

cdhogan$ ls
CO      ENVIRONMENT_VARIABLES  LiF    Si111         Test_PW
Doc     Graphene               Pseudo Sibulk

cdhogan$ cd Test_PW

Cdhogan$ cat si.scf.in
Cdhogan$ cat si.pp.in
Cdhogan$ which pw.x
/usr/local/applications/qe-5.2.1—gfortran-mp-4.9_parallel/bin/pw.x

Cdhogan$ pw.x < si.scf.in
Cdhogan$ pw.x < si.scf.in > si.scf.out
Cdhogan$ less si.scf.out       (or view/vi/more/cat etc)
Cdhogan$ pp.x < si.pp.in > si.pp.out
Cdhogan$ xcrysden --xsf psi2.xsf

Tools > Data grid (OK) > (Isovalue = 0.01) (Submit)
```

Initialization of environment

```
cdhogan$ cd ../
cdhogan$ ls
CO      ENVIRONMENT_VARIABLES  LiF    Si111        Test_PW
Doc     Graphene     Pseudo       Sibulk

cdhogan$ cat ENVIRONMENT_VARIABLES

#The ABSOLUTE PATH of the bin folder containing the QE executables (pw.x, pp.x)
BIN_DIR='/usr/local/applications/qe-5.2.1--gfortran-mp-4.9_parallel/bin/'
#The ABSOLUTE PATH of the folder containing the Pseudopotential files .UPF
PSEUDO_DIR='/Users/cdhogan/LINUX/EsercitazioneDFT/Lezione/Pseudo/'
#The RELATIVE PATH of the folder to contain temporary/restart QE files
TMP_DIR='./tmp'
#For parallel execution uncomment this
RUN_COMMAND="mpirun -np 2"
#For serial execution uncomment this
#RUN_COMMAND=""


                    EDIT THIS FILE (vi) AND SET UP FOR YOUR SYSTEM!

cdhogan$ cd LiF/Ecut
```

Use of shell scripts to automate tasks

It's a text file containing a list of commands that are run by the shell (sh or bash)
If file permissions are set to executable, you can launch it directly: ./run_ecut
Otherwise launch it with: sh run_ecut

```
cdhogan$ vi run_ecut
```

```
#!/bin/sh

source ../../ENVIRONMENT_VARIABLES
echo "BIN_DIR:" $BIN_DIR
echo "PSEUDO_DIR:" $PSEUDO_DIR
echo "TMP_DIR:" $TMP_DIR
echo "Parallel command:" $RUN_COMMAND
echo "Started at: " `date`

for ecut in  10 20 30 40 50 60 70 80 90 100
do

# self-consistent calculation
cat > LiF.scf.in << EOF
&CONTROL
  calculation  = "scf",

 […....................................]

   0.3750000  0.3750000  0.6250000   3.00
EOF

$RUN_COMMAND $BIN_DIR/pw.x < LiF.scf.in > LiF.scf.out_ecut$ecut
echo "Run completed at: " `date`

done
```

Reads settings

Loop over variable ecut

Creation of input file …

… to EOF (end-of-file)

Run code and continue loop

Input file structure

```
margherita@Kenni:~/Lezione/LiF/Ecut$ vi run_ecut
```

```
&CONTROL
...
/
&SYSTEM
...
/
&ELECTRONS
...
/
ATOMIC_SPECIES
...
ATOMIC_POSITIONS
...
K_POINTS
...
```

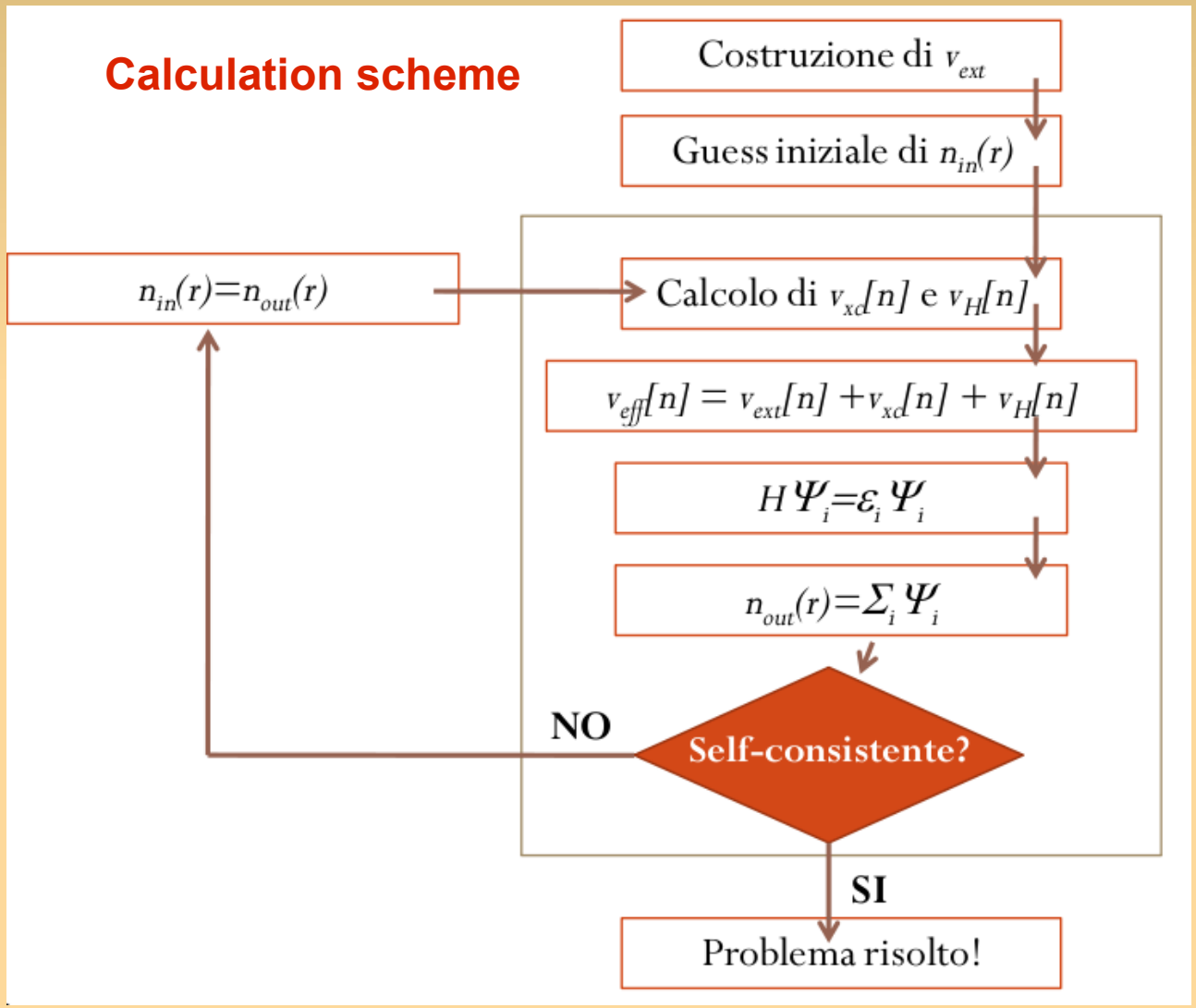
The input file is organized in **namelists** (&CONTROL; &SYSTEM, etc …) and **cards** (ATOMIC_SPECIES, ATOMIC_POSITIONS, etc...).

You can find the meaning of the input variables in the website. In this moment you can find an (old) list in your directory:
~/Lezione/Doc

Input file structure

```
margherita@Kenni:~/Lezione/LiF/Ecut$ vi run_ecut
```

```
&CONTROL
...
/
&SYSTEM
...
/
&ELECTRONS
...
/
ATOMIC_SPECIES
...
ATOMIC_POSITIONS
...
K_POINTS
...
```

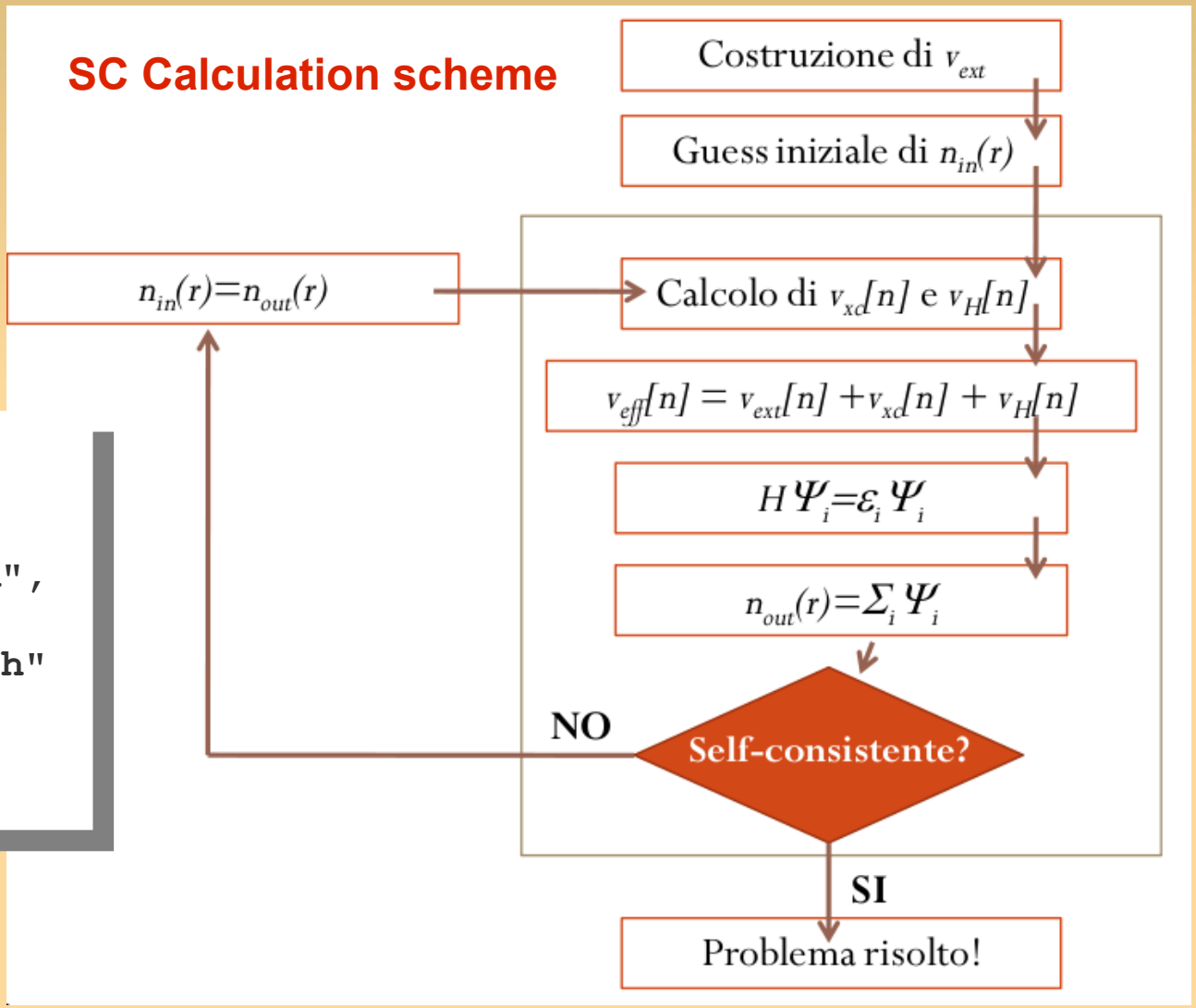


Input file structure

```
margherita@Kenni:~/Lezione/LiF/Ecut$ vi run_ecut
```

This namelist provides indication on what kind of calculation we want to perform and how to manage the input and ouput files.

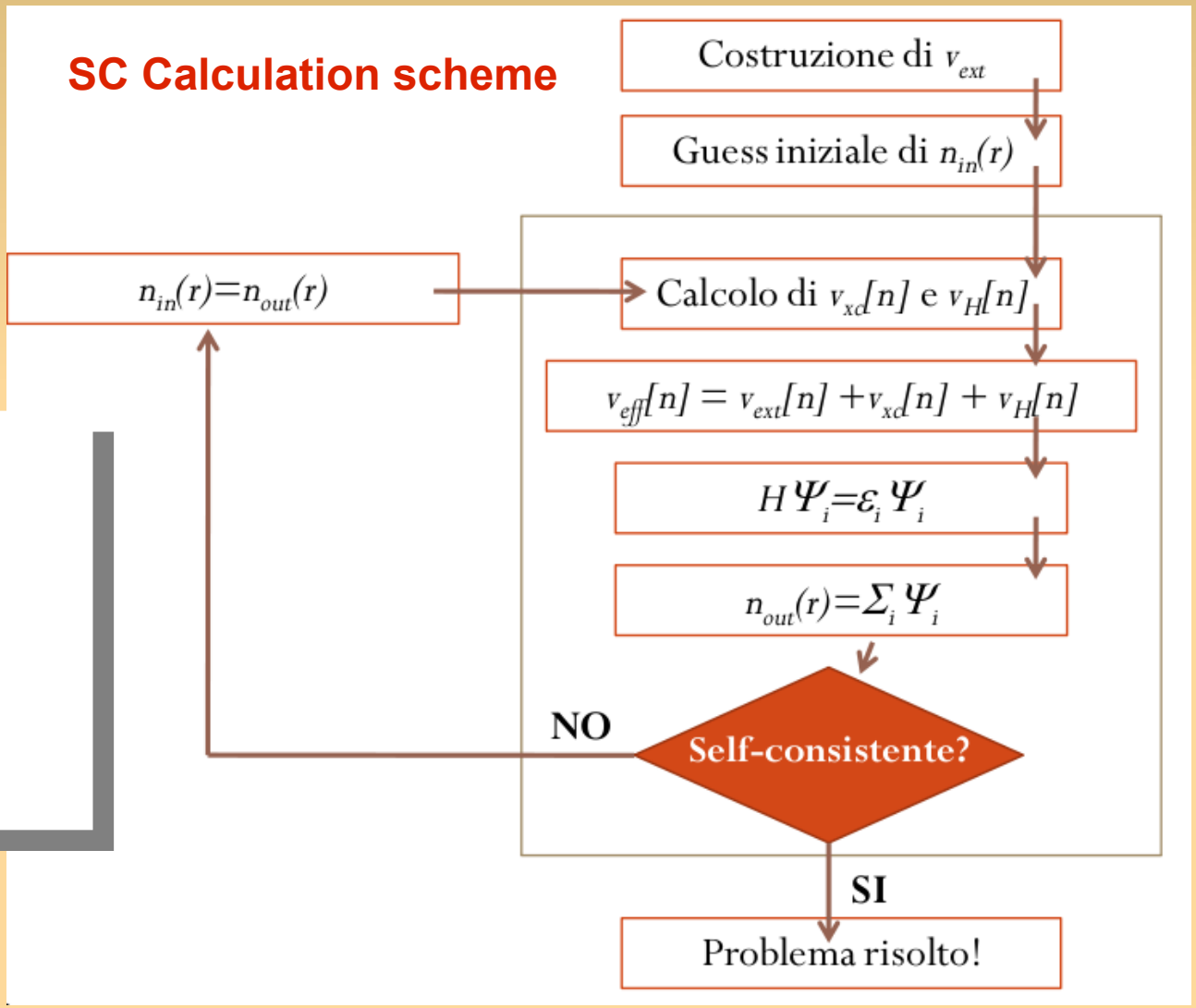
```
&CONTROL
  calculation   = "scf",
  prefix        = "LiF",
  pseudo_dir    = "$PSEUDO_DIR",
  outdir        = "$TMP_DIR",
  restart_mode  = "from_scratch"
  tprnfor = .true.
  wf_collect=.true.
/
```



Input file structure

```
margherita@Kenni:~/Lezione/LiF/Ecut$ vi run_ecut
```

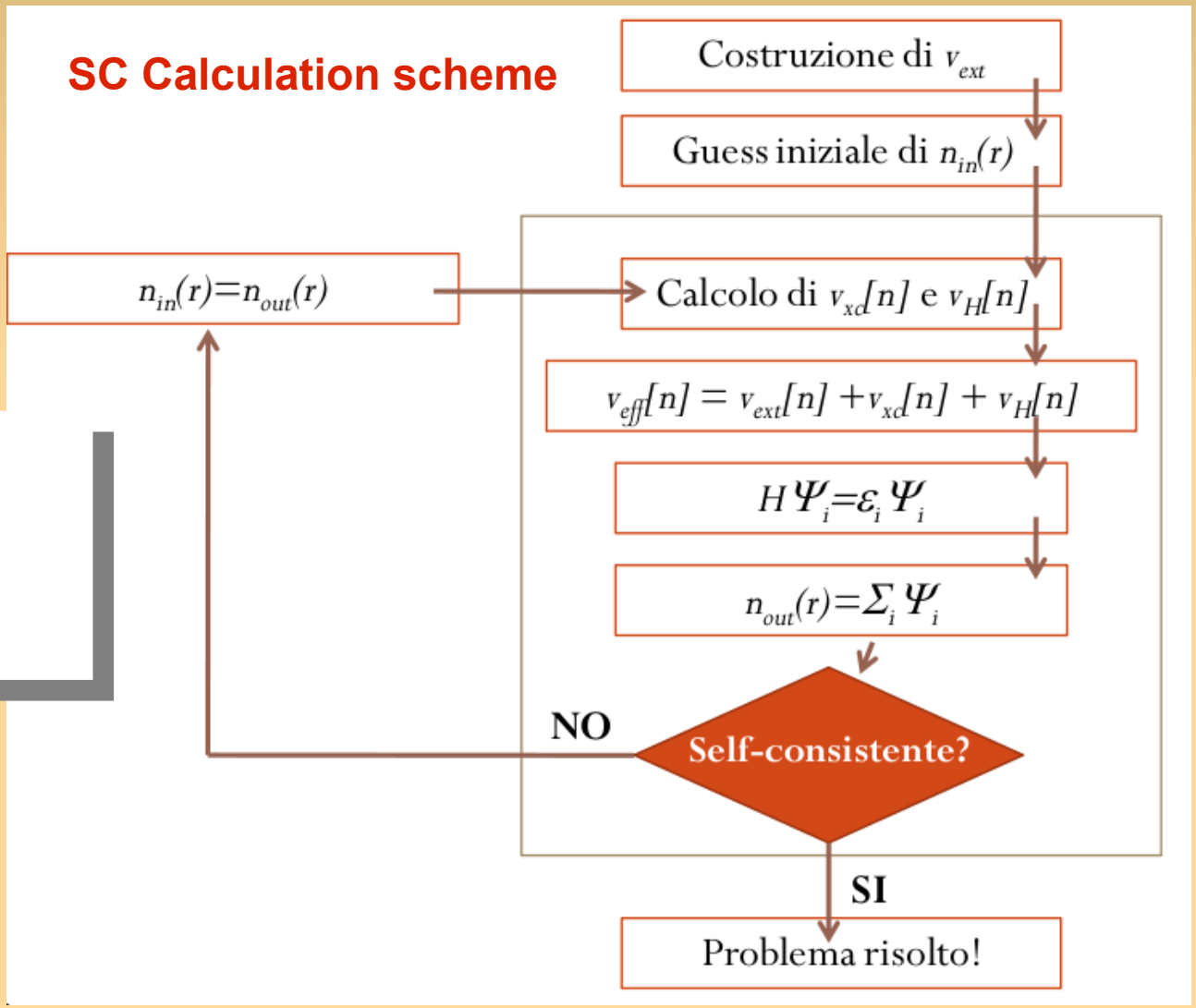
```
&SYSTEM
  ibrav      = 2,
  celldm(1)  = 7.7034756,
  nat        = 2,
  ntyp       = 2,
  ecutwfc    = $ecut
  nbnd       = 5
/
```



Input file structure

```
margherita@Kenni:~/Lezione/LiF/Ecut$ vi run_ecut
```

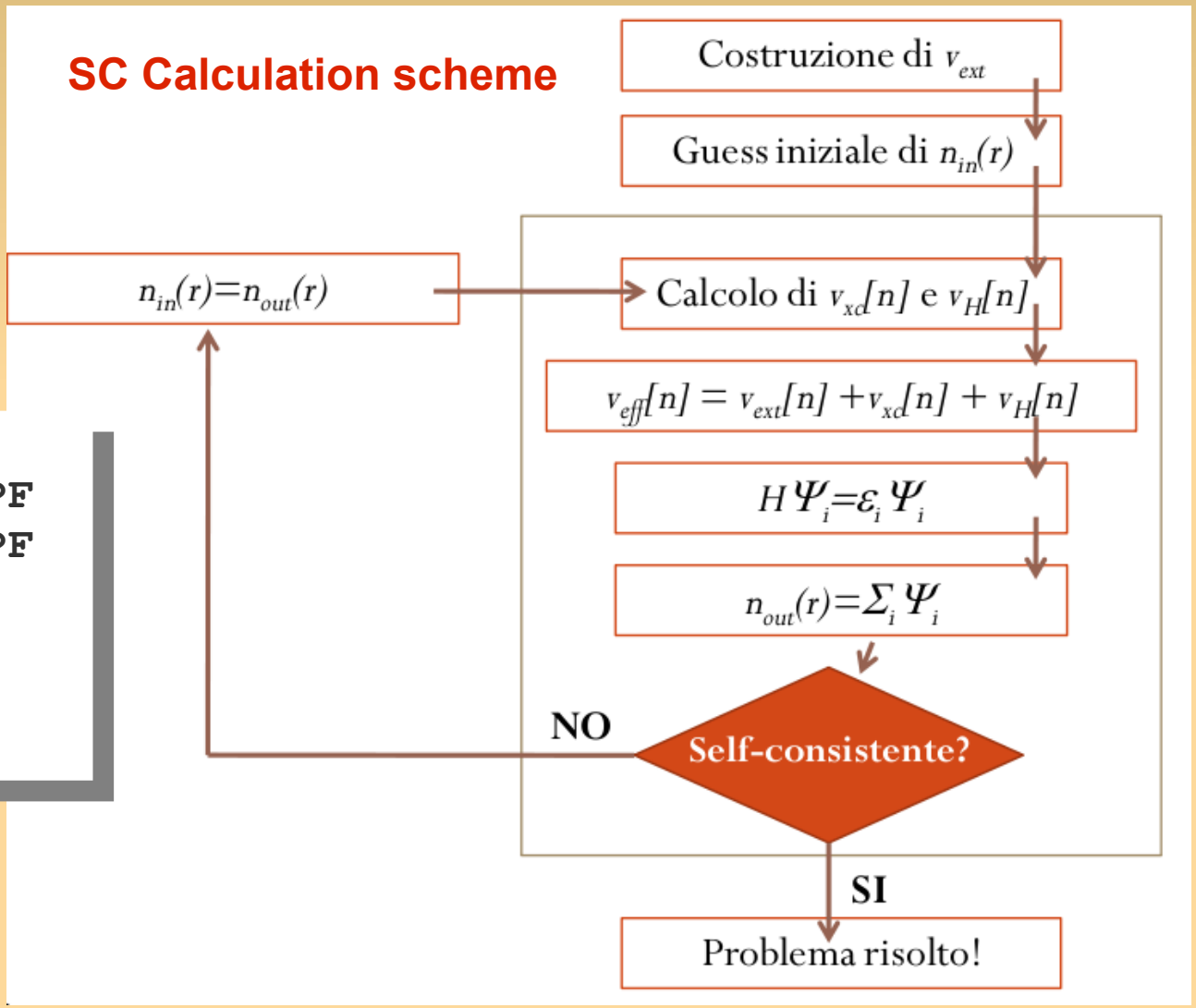
```
&ELECTRONS
  conv_thr     = 1.D-8,
  mixing_beta = 0.7D0    ,
/
```



Input file structure

```
margherita@Kenni:~/Lezione/LiF/Ecut$ vi run_ecut
```

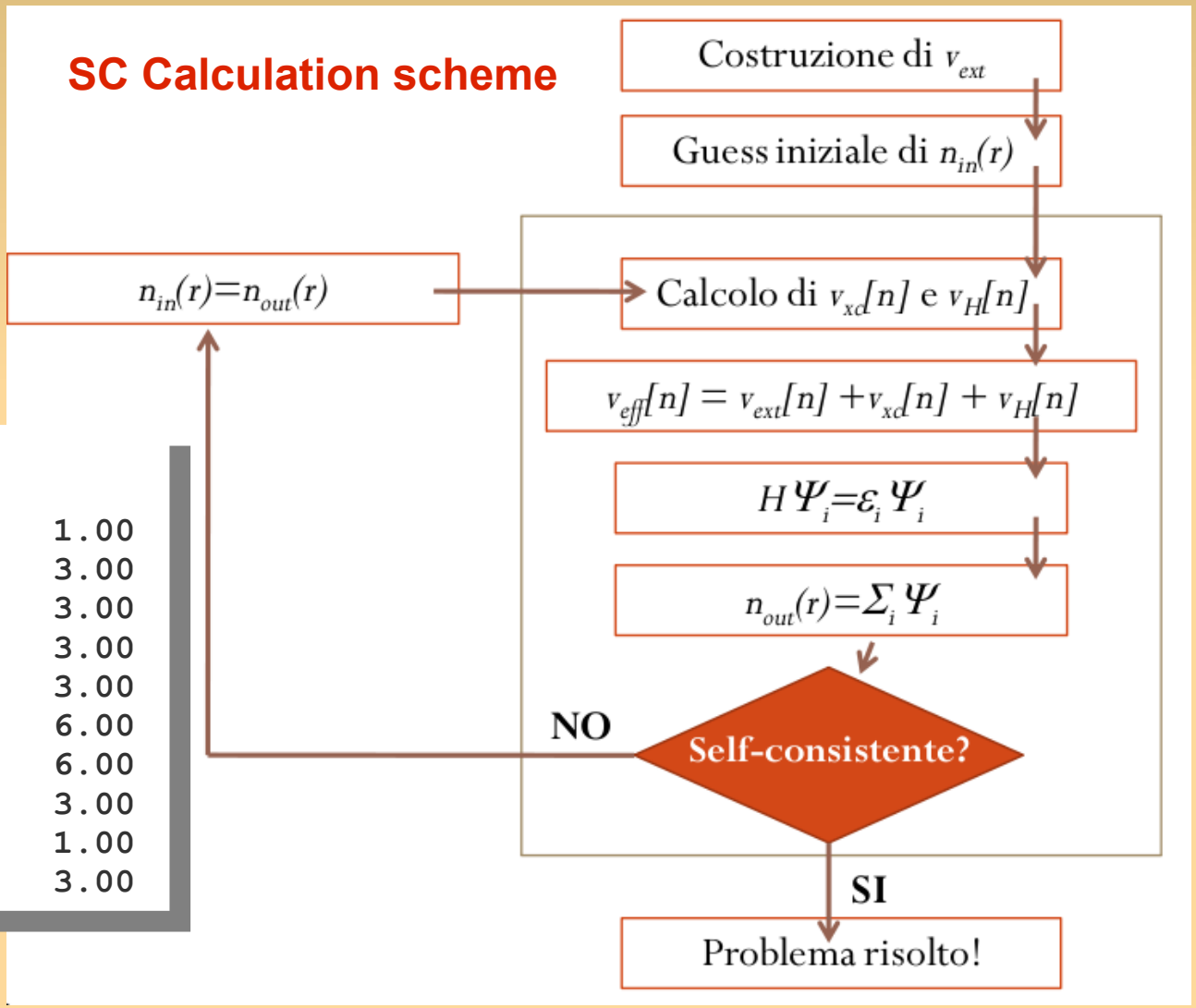
```
ATOMIC_SPECIES
Li   6.941 Li.pbe-mt_fhi.UPF
F    18.998 F.pbe-mt_fhi.UPF
ATOMIC_POSITIONS
Li   0.0   0.0   0.0
F    0.5   0.0   0.0
```



Input file structure

```
margherita@Kenni:~/Lezione/LiF/Ecut$ vi run_ecut
```

```
K_POINTS
  10
   0.1250000   0.1250000   0.1250000   1.00
   0.1250000   0.1250000   0.3750000   3.00
   0.1250000   0.1250000   0.6250000   3.00
   0.1250000   0.1250000   0.8750000   3.00
   0.1250000   0.3750000   0.3750000   3.00
   0.1250000   0.3750000   0.6250000   6.00
   0.1250000   0.3750000   0.8750000   6.00
   0.1250000   0.6250000   0.6250000   3.00
   0.3750000   0.3750000   0.3750000   1.00
   0.3750000   0.3750000   0.6250000   3.00
```



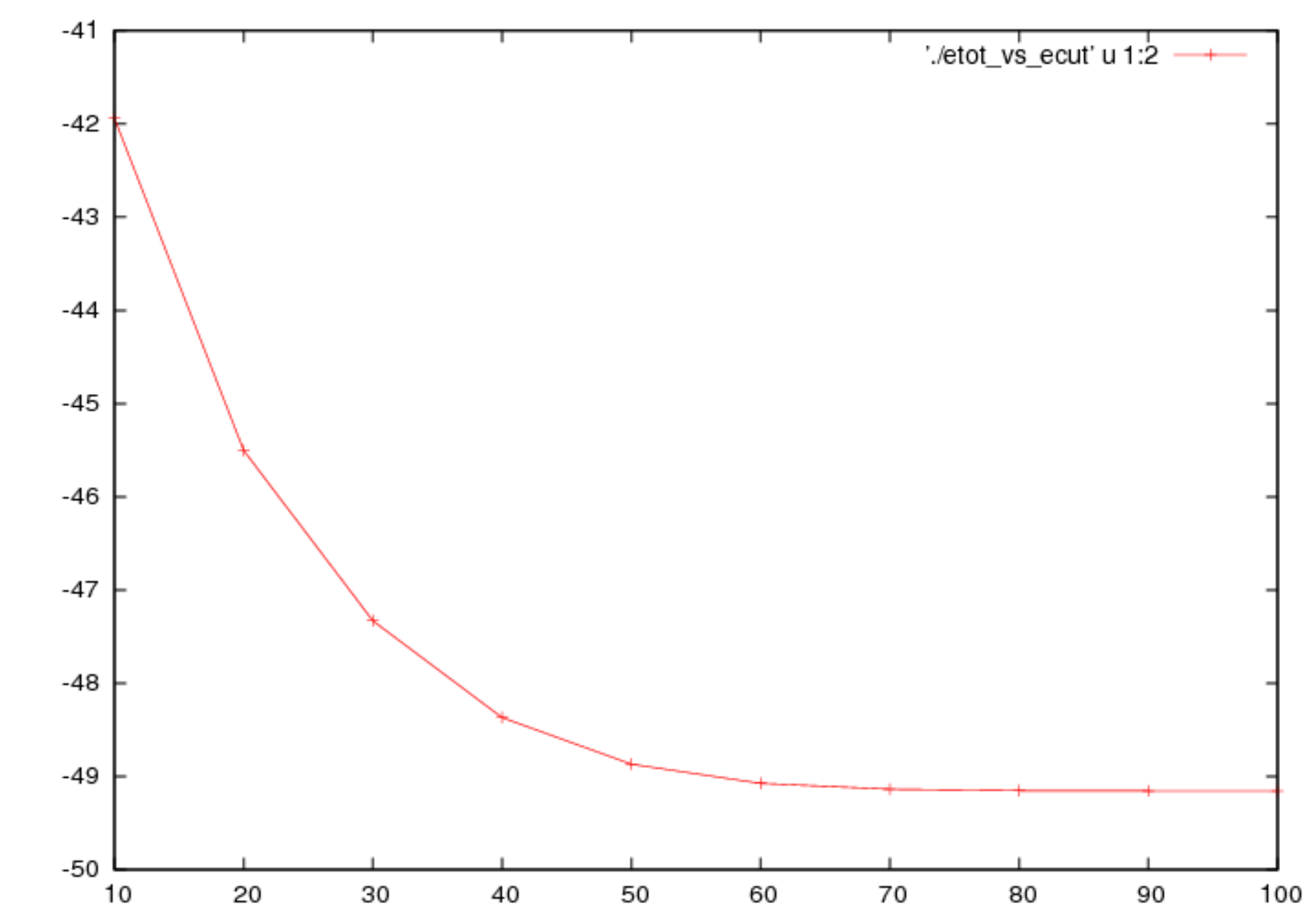
LiF (1): pw cutoff convergence

```
margherita@Kenni:~/Lezione/LiF/Ecut$ ./run_ecut
```

```
margherita@Kenni:~/Lezione/LiF/Ecut$ grep ! *out*
LiF.scf.out_ecut10:!    total energy              =     -41.94033271 Ry
LiF.scf.out_ecut100:!    total energy              =     -49.15553155 Ry
LiF.scf.out_ecut20:!    total energy              =     -45.50468801 Ry
LiF.scf.out_ecut30:!    total energy              =     -47.33046132 Ry
LiF.scf.out_ecut40:!    total energy              =     -48.36980705 Ry
LiF.scf.out_ecut50:!    total energy              =     -48.86924616 Ry
LiF.scf.out_ecut60:!    total energy              =     -49.07471103 Ry
LiF.scf.out_ecut70:!    total energy              =     -49.13795709 Ry
LiF.scf.out_ecut80:!    total energy              =     -49.15318351 Ry
LiF.scf.out_ecut90:!    total energy              =     -49.15538390 Ry
```

```
margherita@Kenni:~/Lezione/LiF/Ref_results$ gnuplot
gnuplot> p './etot_vs_alat' u 1:2 w lp
```

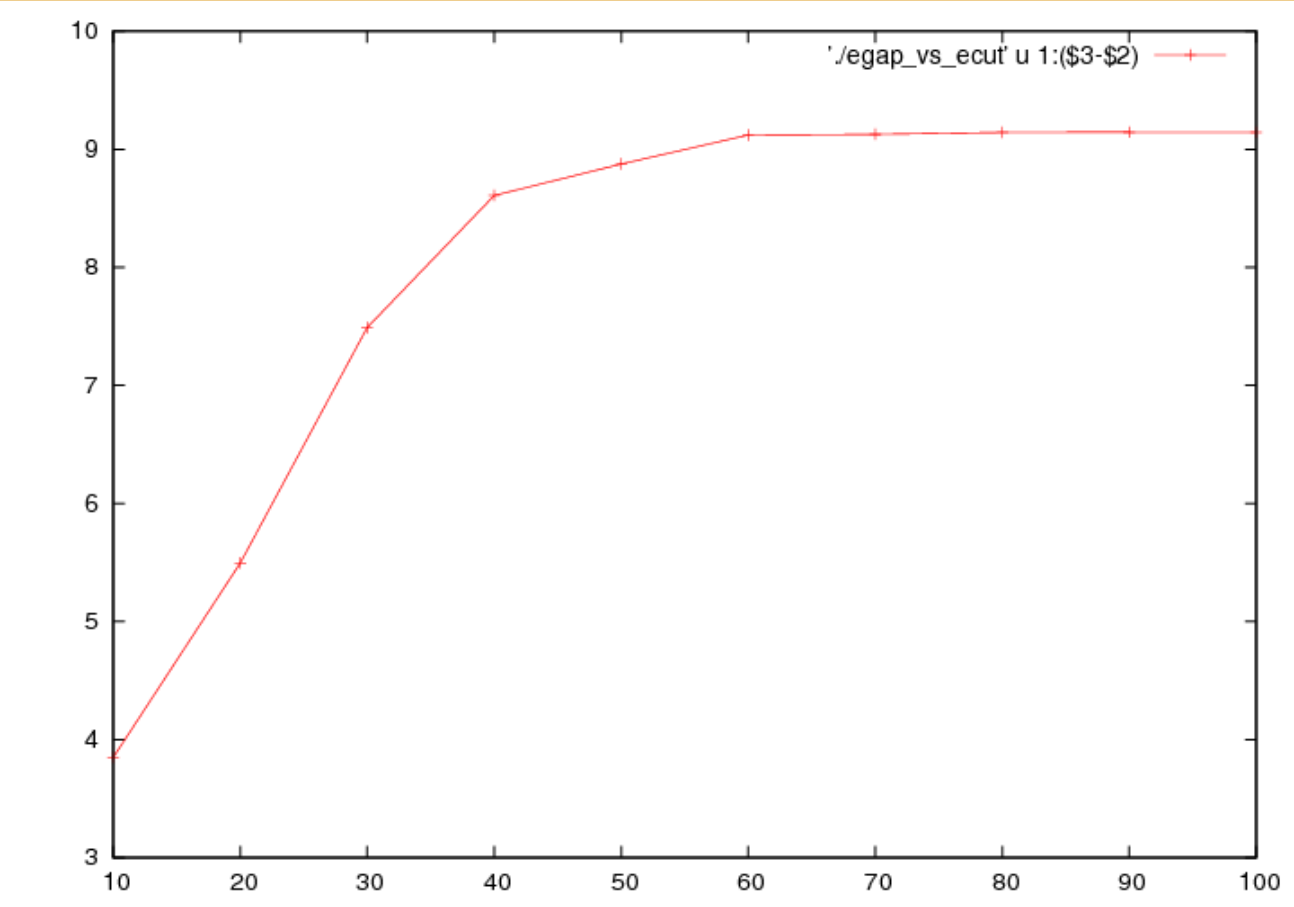
LiF (1): pw cutoff convergence



LiF (1): pw cutoff convergence

```
margherita@Kenni:~/Lezione/LiF/Ecut$ grep hest LiF.scf.out_ecut10
highest occupied, lowest unoccupied level (ev):     4.4577    8.3053
```

```
margherita@Kenni:~/Lezione/LiF/Ref_results$ gnuplot
gnuplot> p './egap_vs_ecut' u 1:($3-$2) w lp
```



LiF (2): equilibrium lattice constant

```
&SYSTEM
  ibrav      = 2,
  celldm(1)  = $alat,
  nat        = 2,
  ntyp       = 2,
  ecutwfc    = 60
  nbnd       = 5
/
```

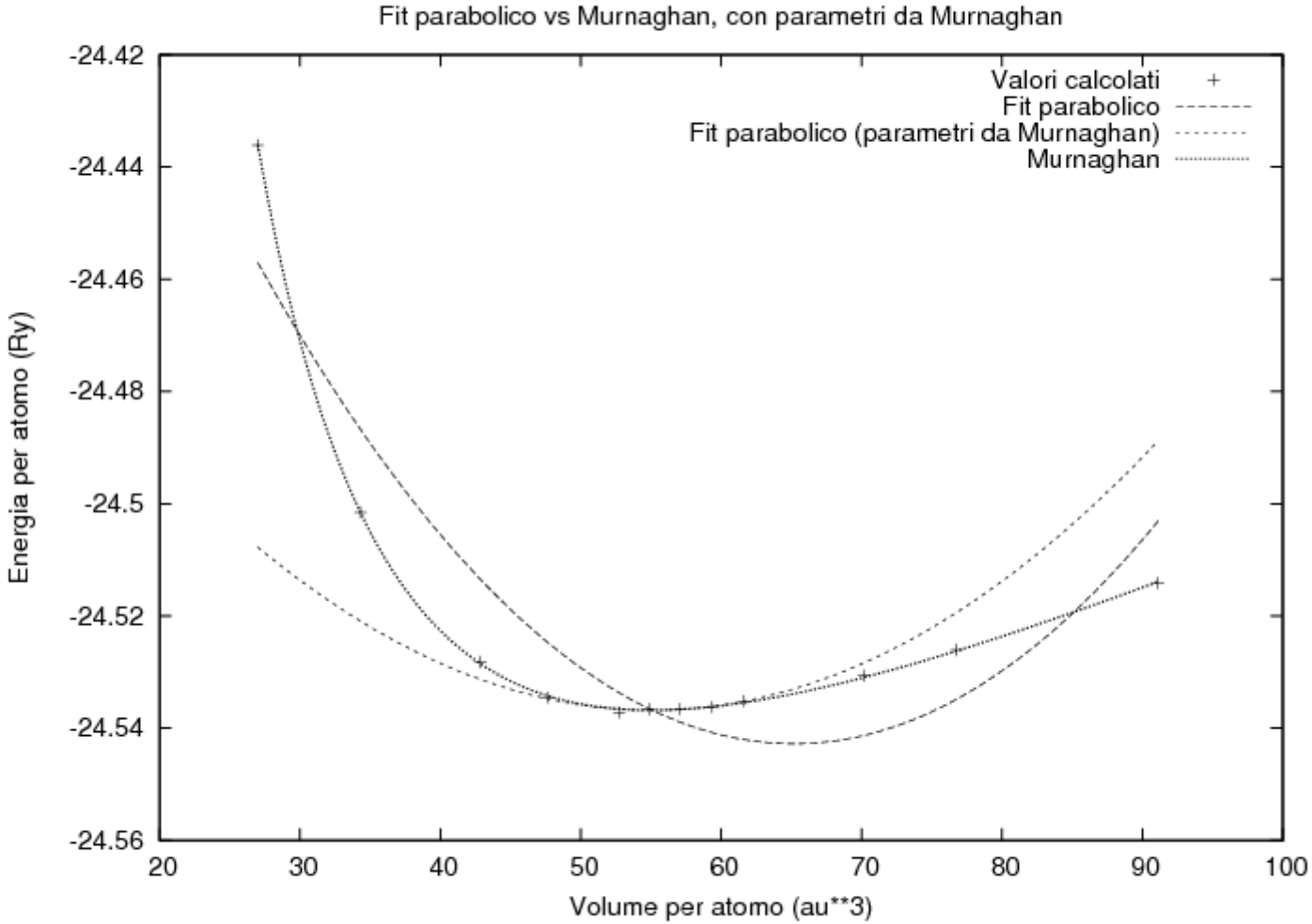
1) With the converged pw cutoff we vary the lattice parameter and collect the total energy.

2) We perform a fit to extrapolate the value of the lattice constant for which the total energy is minimum.

REMEMBER TO EDIT THE SCRIPT FILE WITH THE CORRECT PATH!

```
margherita@Kenni:~/Lezione/LiF/Alat$ ./run_alat
margherita@Kenni:~/Lezione/LiF/Alat$ grep ! *out*
LiF.scf.out_alat6:!    total energy              =     -48.87218303 Ry
LiF.scf.out_alat6.5:!    total energy              =     -49.00308119 Ry
margherita@Kenni:~/Lezione/LiF/Alat$ vi E_vs_cell.dat
margherita@Kenni:~/Lezione/LiF/Alat$ gnuplot
gnuplot> load './DoFit.gnu'
```

LiF (2): equilibrium lattice constant




```
* Energia al minimo    = -24.5367910676349 Ry
* Volume al minimo     = 55.052772735607 au^3/atomo
* Costante reticolare = 7.60833677668143 au
```

LiF (3): band structure

```
&CONTROL
  calculation  = "bands",
  prefix       = "LiF",
  pseudo_dir   = "$PSEUDO_DIR",
  outdir       = "$TMP_DIR",
/
(...)
K_POINTS {tpiba_b}
 7
   0.0 0.0 0.0 5
   0.0 1.0 0.0 5
   0.5 1.0 0.0 5
   0.75 0.75 0.0 5
   0.0 0.0 0.0 5
   0.5 0.5 0.5 5
   0.5 1.0 0.0 5
```

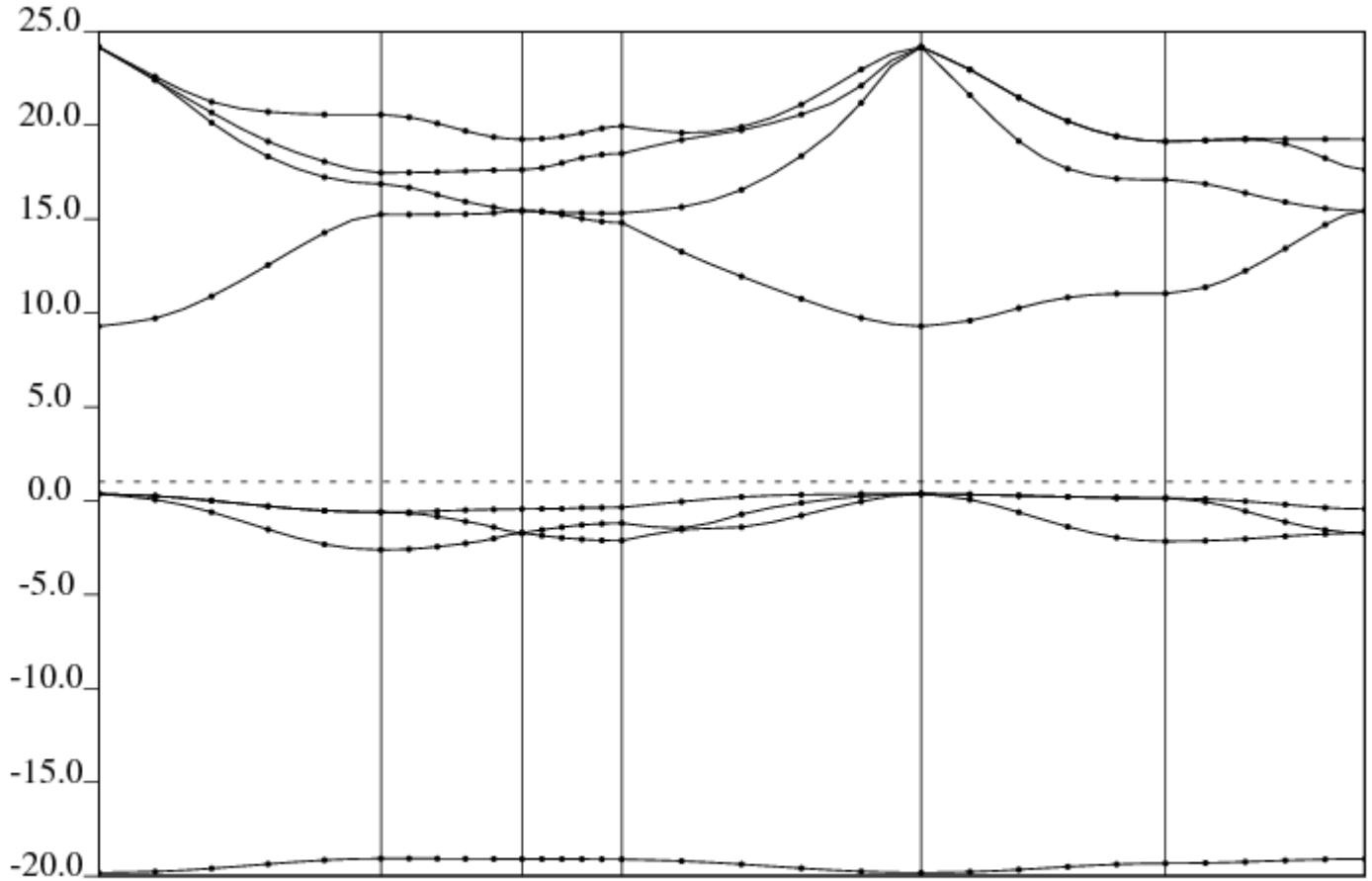
1) With the converged pw cutoff and at the equilibrium lattice constant we compute the charge density.

2) With this charge density we compute the single-particle KS levels for a set of high-symmetry k-points

3) We run a post-processing program to plot the band structure.

```
margherita@Kenni:~/Lezione/LiF/Band_structure$ ./run_scf
margherita@Kenni:~/Lezione/LiF/Band_structure$ ./run_nscf
margherita@Kenni:~/Lezione/LiF/Band_structure$ ./run_pp
```

LiF (3): band structure



Some homework!

Per casa:

Calcolare la costante reticolare del Si bulk.

Trovate lo pseudopotenziale nella directory ~/Lezione/Pseudo
Attenzione al tipo di reticolo e alla base!

CO pw cutoff convergence

```
&CONTROL
  calculation = "relax",
  prefix      = "CO",
  pseudo_dir  =
"/home/margherita/Lezione/Pseudo",
  outdir      = "./",
  etot_conv_thr = 1.0D-4
  forc_conv_thr = 1.0D-3
/
&SYSTEM
  ibrav     = 0,
  nat       = 2,
  ntyp      = 2,
  nbnd      = 6,
  ecutwfc   = 50
/
&ELECTRONS
  conv_thr    = 1.D-7,
  mixing_beta = 0.7D0,
```

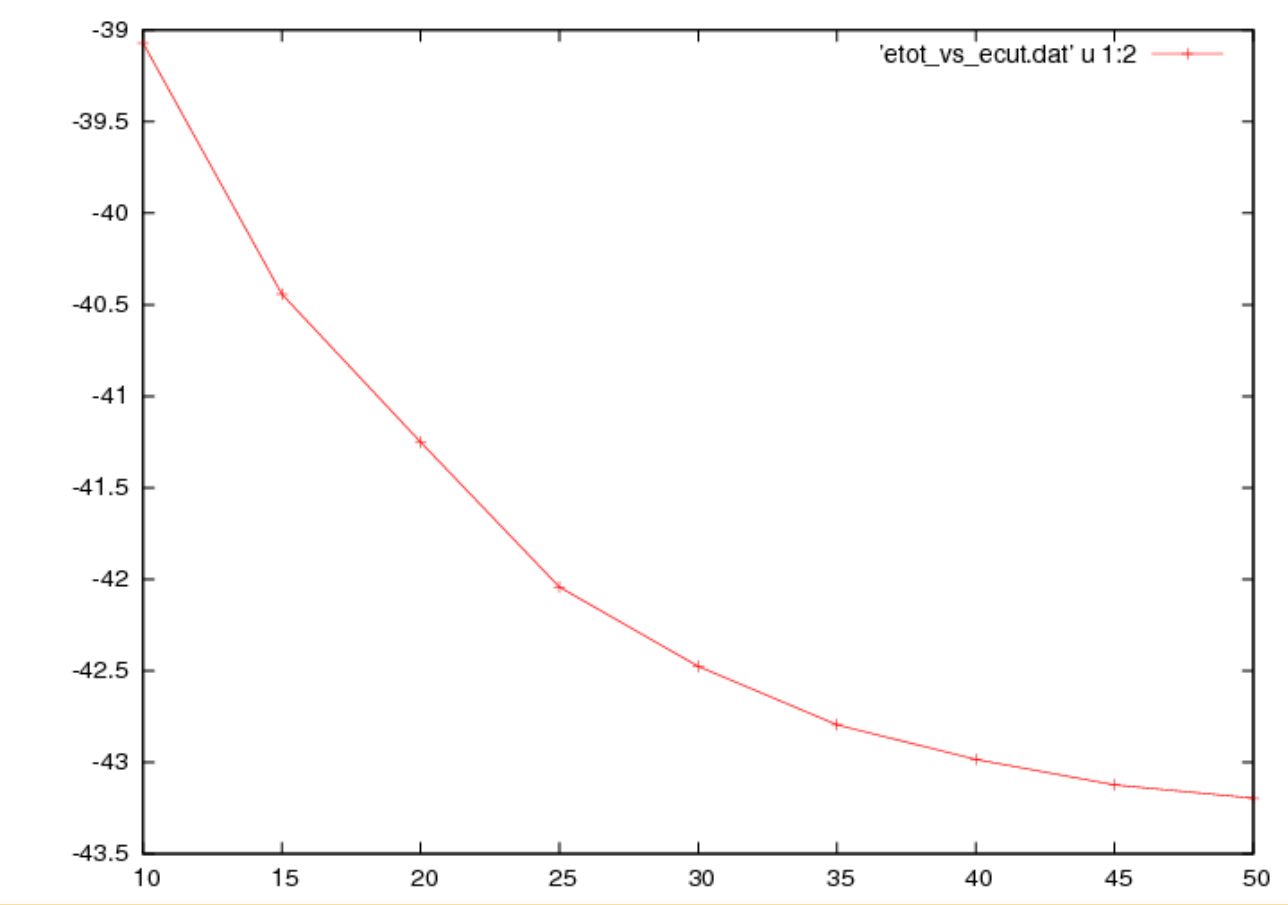
```
&IONS
  ion_dynamics = "bfgs"
/
CELL_PARAMETERS {bohr}
12.0  0.0  0.0
 0.0 12.0  0.0
 0.0  0.0 12.0
ATOMIC_SPECIES
O  1.00  O.pw-mt_fhi.UPF
C  1.00  C.pw-mt_fhi.UPF
ATOMIC_POSITIONS {bohr}
C  2.256  0.0  0.0
O  0.000  0.0  0.0  0 0 0
K_POINTS {Gamma}
```

INPUT FILE FOR A RELAXATION RUN

CO pw cutoff convergence

```
margherita@Kenni:~/Lezione/CO/Ecut$ ./run_ecut
margherita@Kenni:~/Lezione/CO/Ecut$ grep ! *out*
margherita@Kenni:~/Lezione/CO/Ecut$ grep hest *out*
```

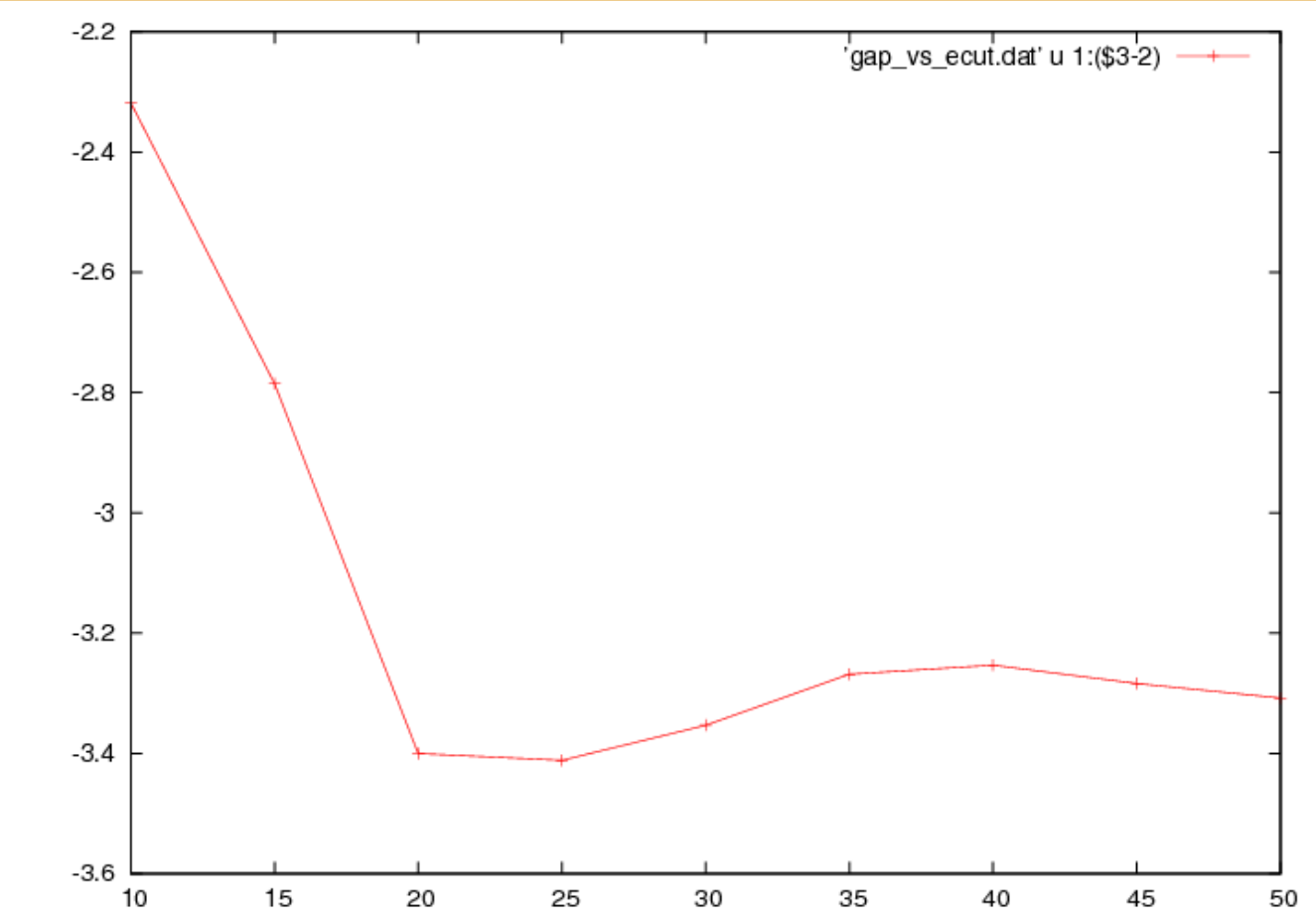
Pay attention to select the last value of total energy and HOMO LUMO levels of each calculation!



CO pw cutoff convergence

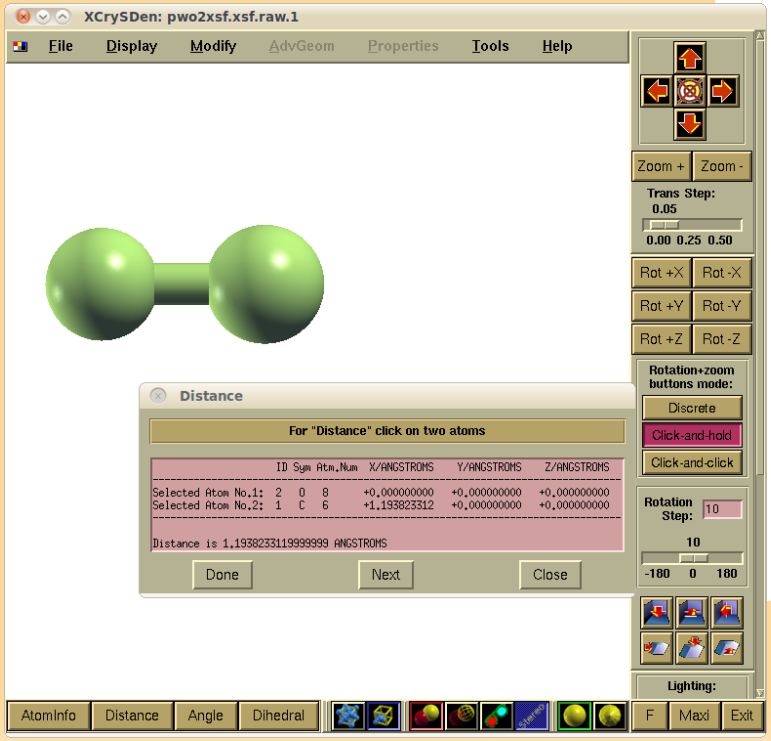
```
margherita@Kenni:~/Lezione/CO/Ecut$ ./run_ecut
margherita@Kenni:~/Lezione/CO/Ecut$ grep ! *out*
margherita@Kenni:~/Lezione/CO/Ecut$ grep hest *out*
```

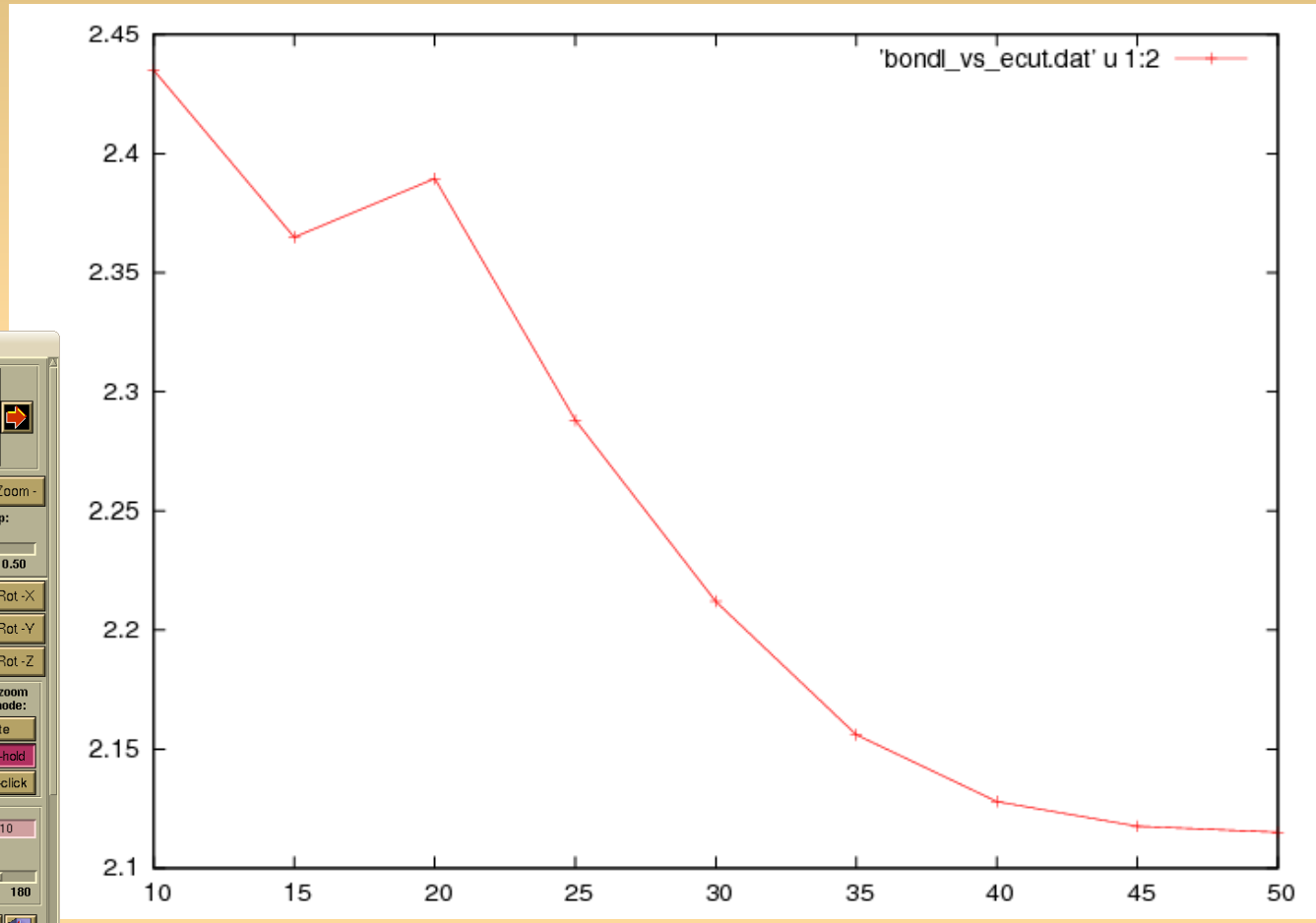
Pay attention to select the last value of total energy and HOMO LUMO levels of each calculation!



CO pw cutoff convergence

Collect the bond length as a function of pw cutoff using xcrysden.
We can also see how the atoms are moving within the relaxation run!





CO box size convergence

```
&CONTROL
  calculation  = "bands",
  prefix       = "LiF",
  pseudo_dir   = "$PSEUDO_DIR",
  outdir       = "$TMP_DIR",
/
(...)
K_POINTS {tpiba_b}
 7
   0.0 0.0 0.0 5
   0.0 1.0 0.0 5
   0.5 1.0 0.0 5
   0.75 0.75 0.0 5
   0.0 0.0 0.0 5
   0.5 0.5 0.5 5
   0.5 1.0 0.0 5
```

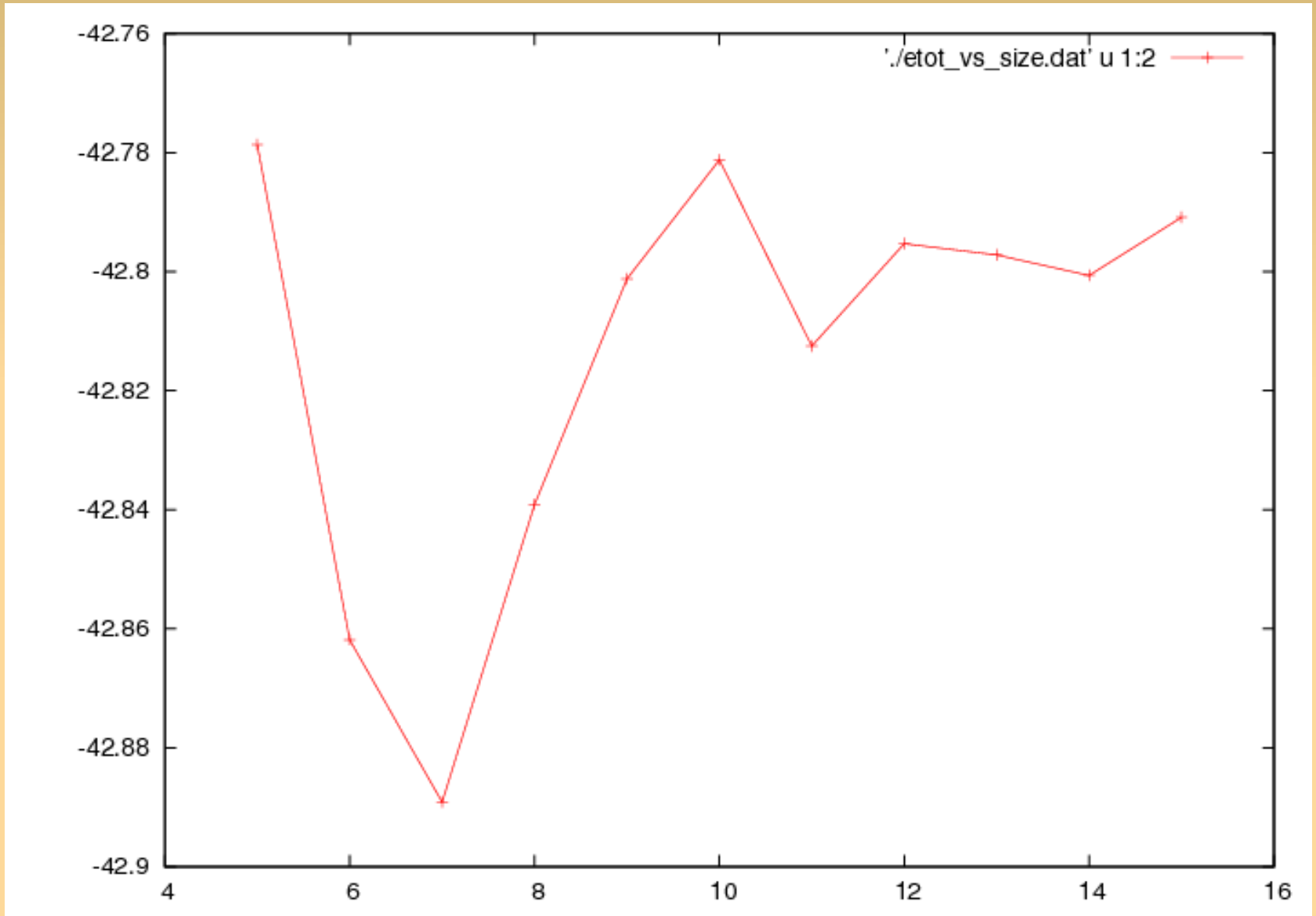
1) With the converged pw cutoff we now change the size of the box.

2) We look at the total energy, HOMO_LUMO gap and bond length vs box size.

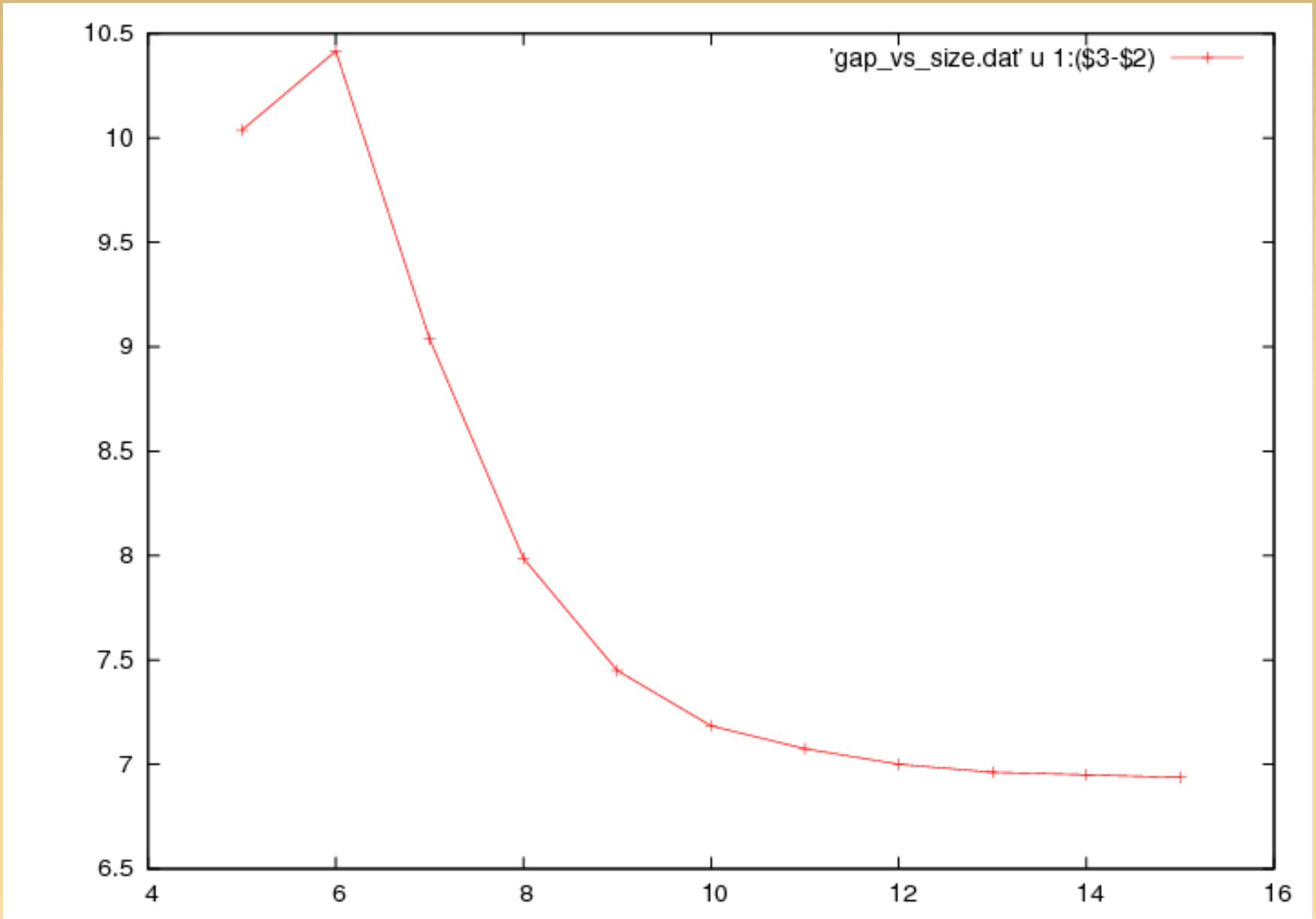
3) Using a post processsing tool and xcrysden we look at the single-particle wavefunction.

```
margherita@Kenni:~/Lezione/LiF/Band_structure$ ./run_scf
margherita@Kenni:~/Lezione/LiF/Band_structure$ ./run_nscf
margherita@Kenni:~/Lezione/LiF/Band_structure$ ./run_pp
```

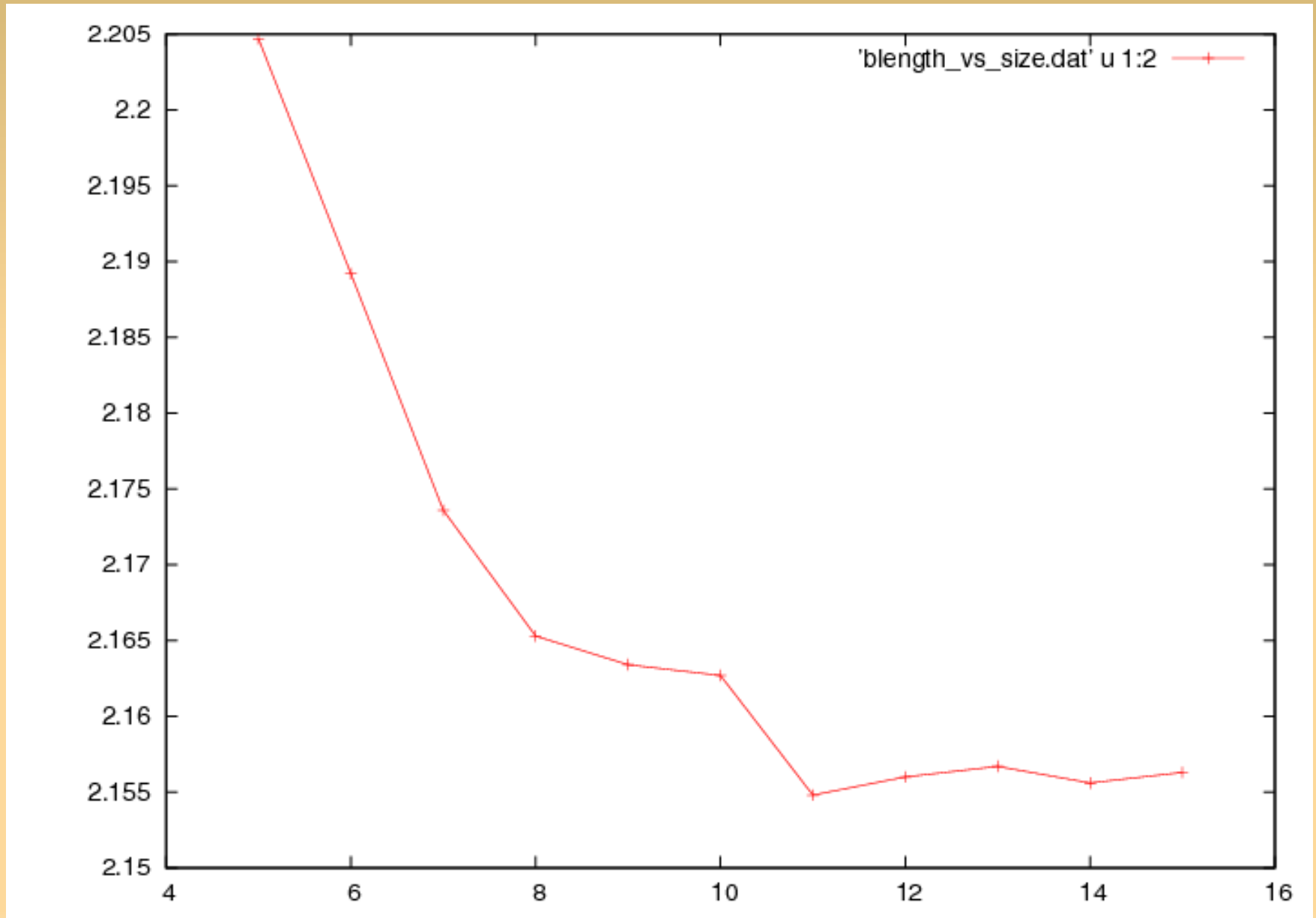
CO box size convergence



CO box size convergence

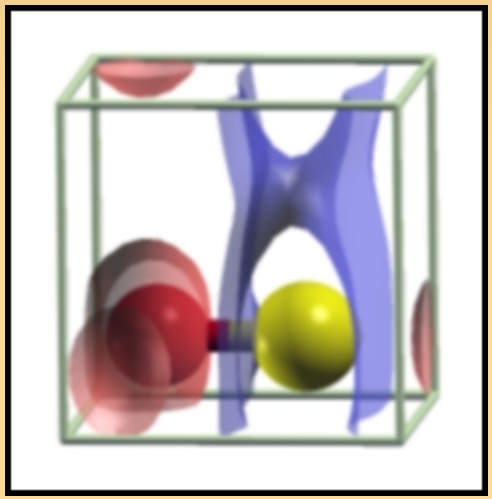


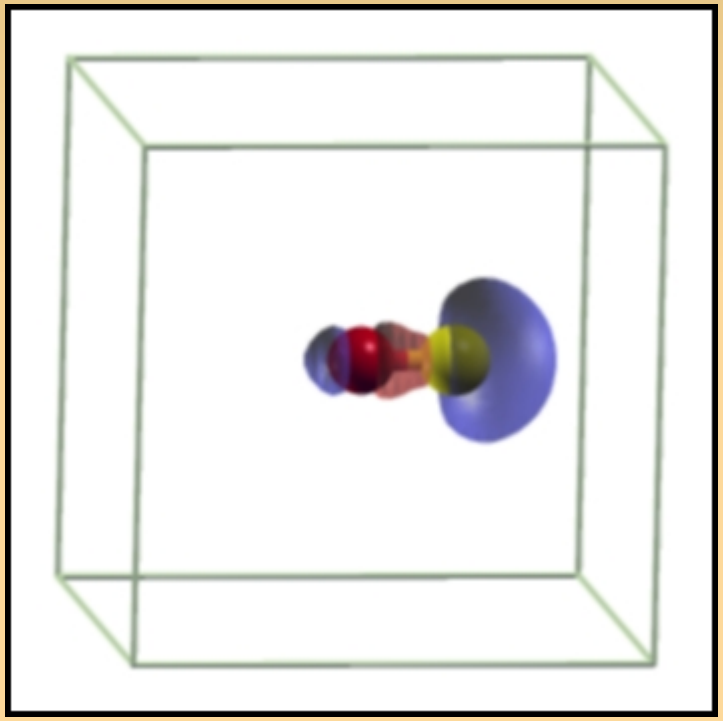
CO box size convergence



CO box size convergence

Using xcrysden we plot the HOMO level for the the 12 au and 5 au cell size.



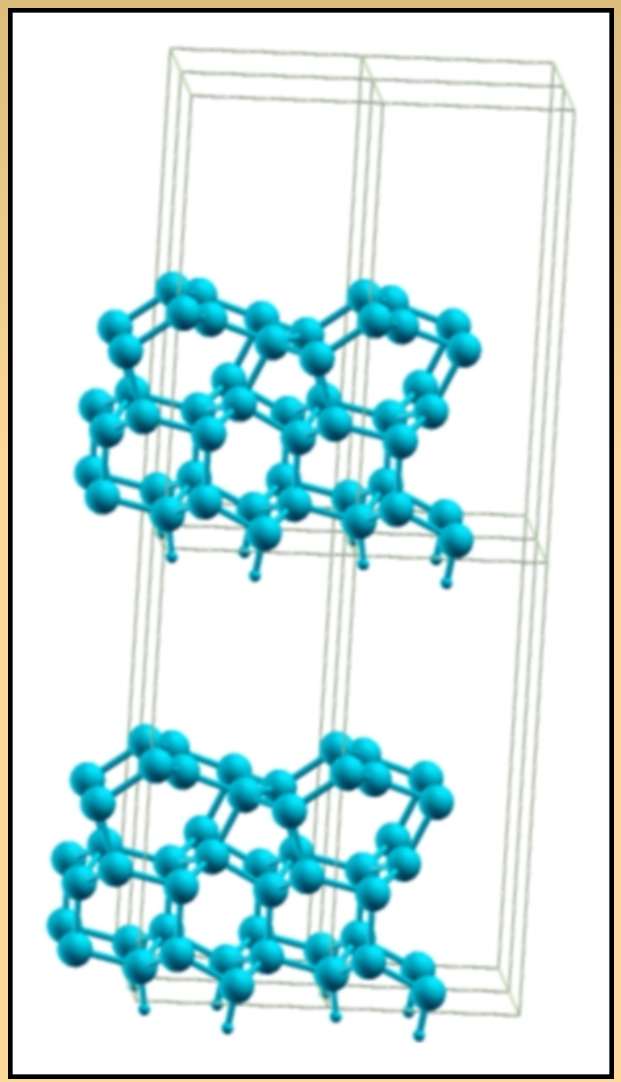


Some homework (2)!

Per casa:

Calcolare la distanza di legame della molecola di H2.

Si(111)

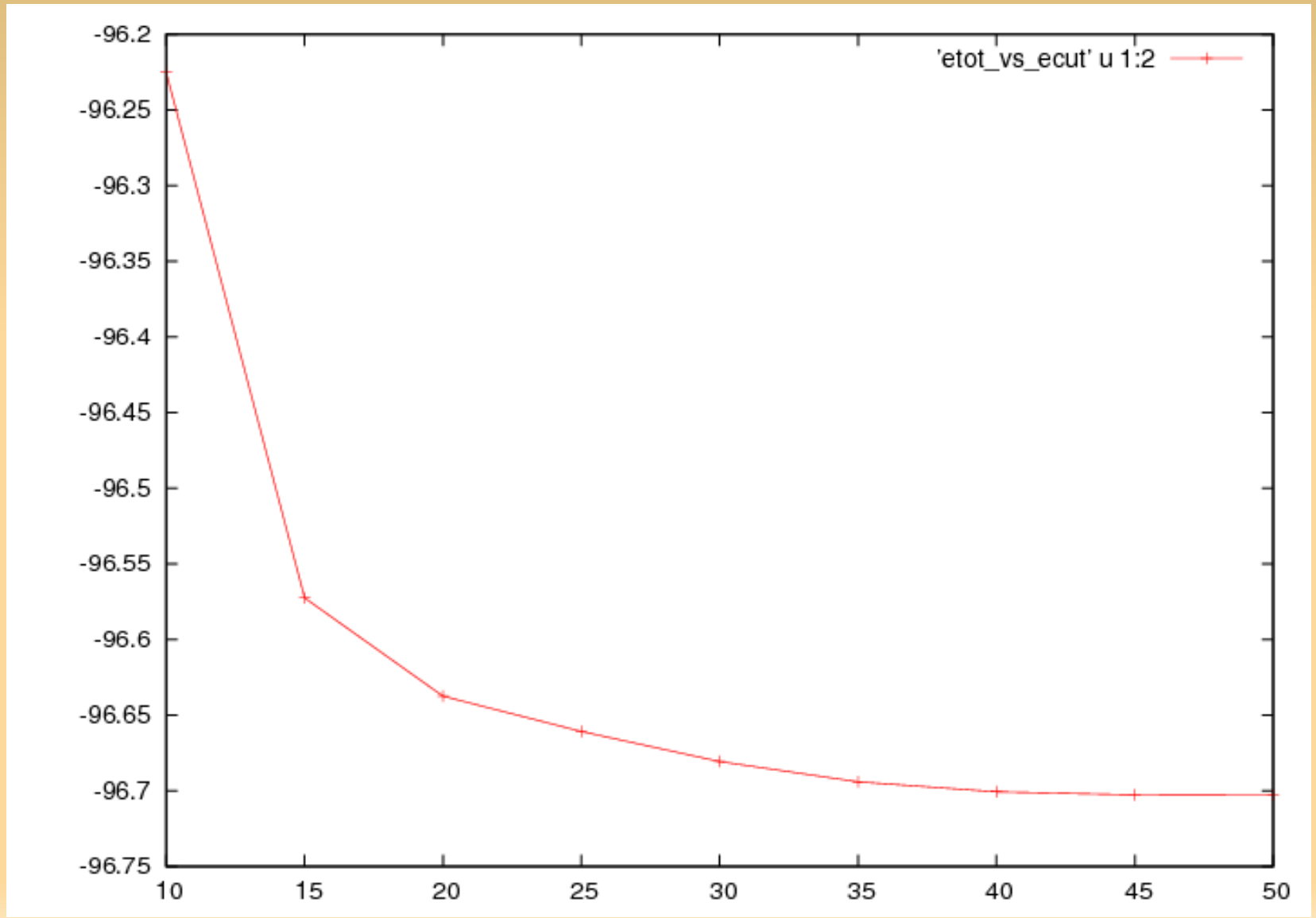


The surface is model as a supercell made by atomic layers and empty space.
(1) the number of atomic layers should be high enough to act as a bulk
(2) the empty space should be enough to avoid spurious interaction between replicas.

We will
(1) Find the good pw cutoff
(2) Relax the surface to obtain its ground state geometry.
(3) Obtain the DFT band structure and see how it is connected to the details of the geometry.

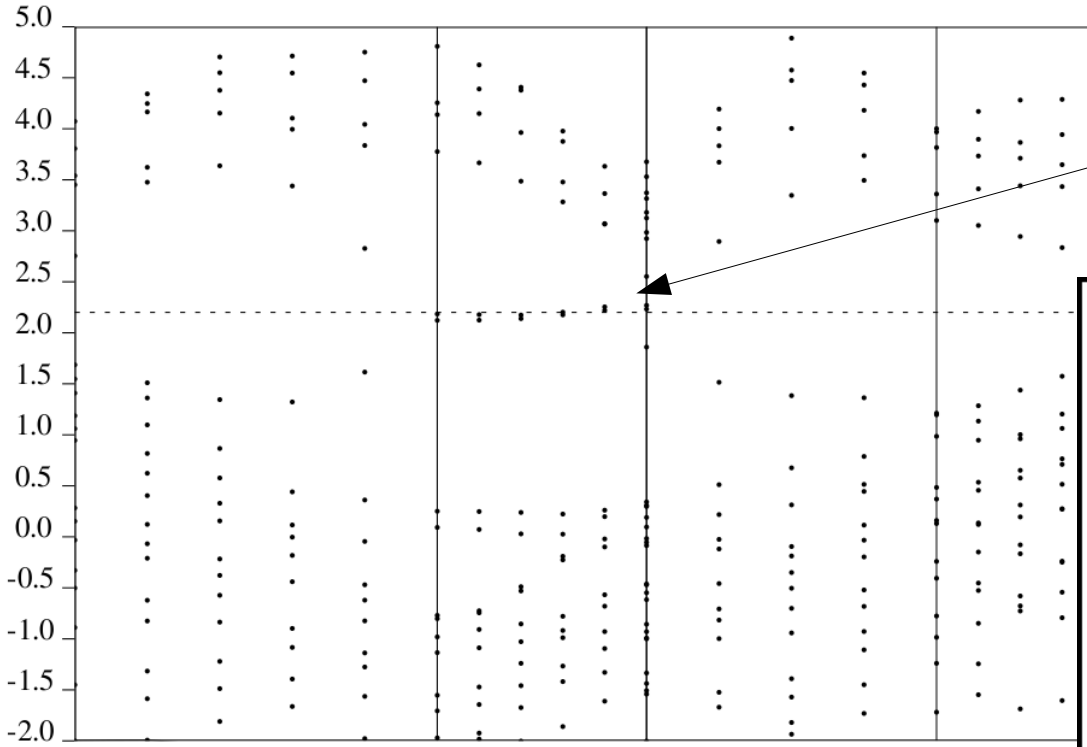
Si(111): pw cutoff

```
margherita@Kenni:~/Lezione/Si111/Ideal$ ./run_scf
```

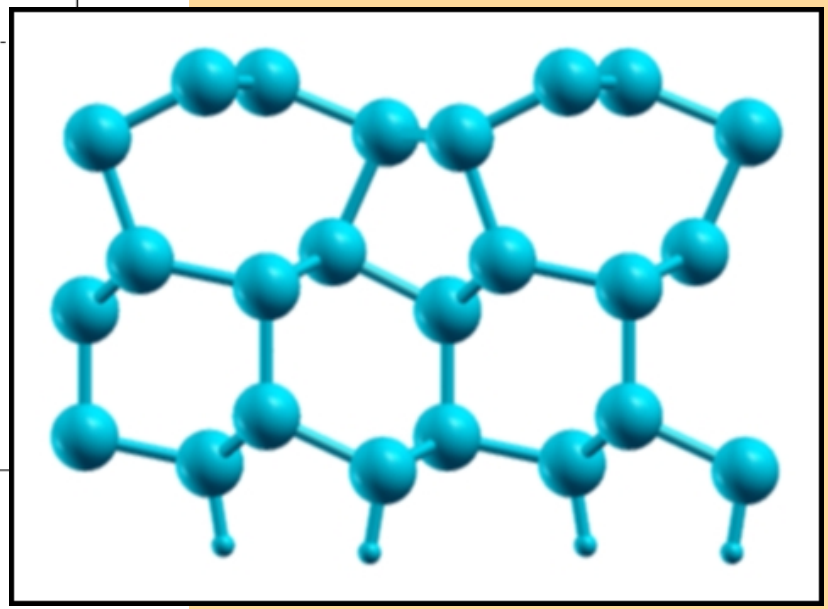


Si(111): band structure

```
margherita@Kenni:~/Lezione/Si111/Band_structure$ ./run_ideal_scf
margherita@Kenni:~/Lezione/Si111/Band_structure$ ./run_ideal_band
margherita@Kenni:~/Lezione/Si111/Band_structure$ ./run_ideal_pp
```

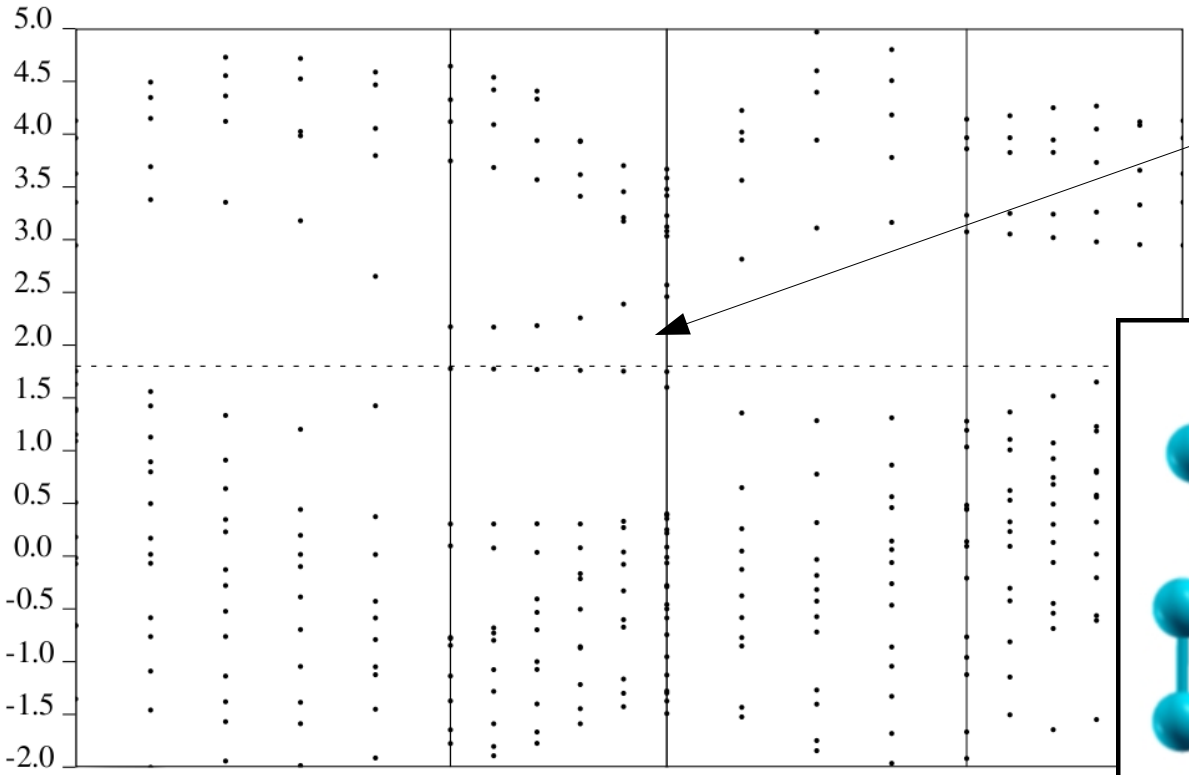


Superficie non rilassata ha una struttura a bande METALLICA.



Si(111): band structure

```
margherita@Kenni:~/Lezione/Si111/Band_structure$ ./run_relaxed_scf
margherita@Kenni:~/Lezione/Si111/Band_structure$ ./run_relaxed_band
margherita@Kenni:~/Lezione/Si111/Band_structure$ ./run_relaxed_pp
```



Superficie non rilassata ha una struttura a bande ISOLANTE.