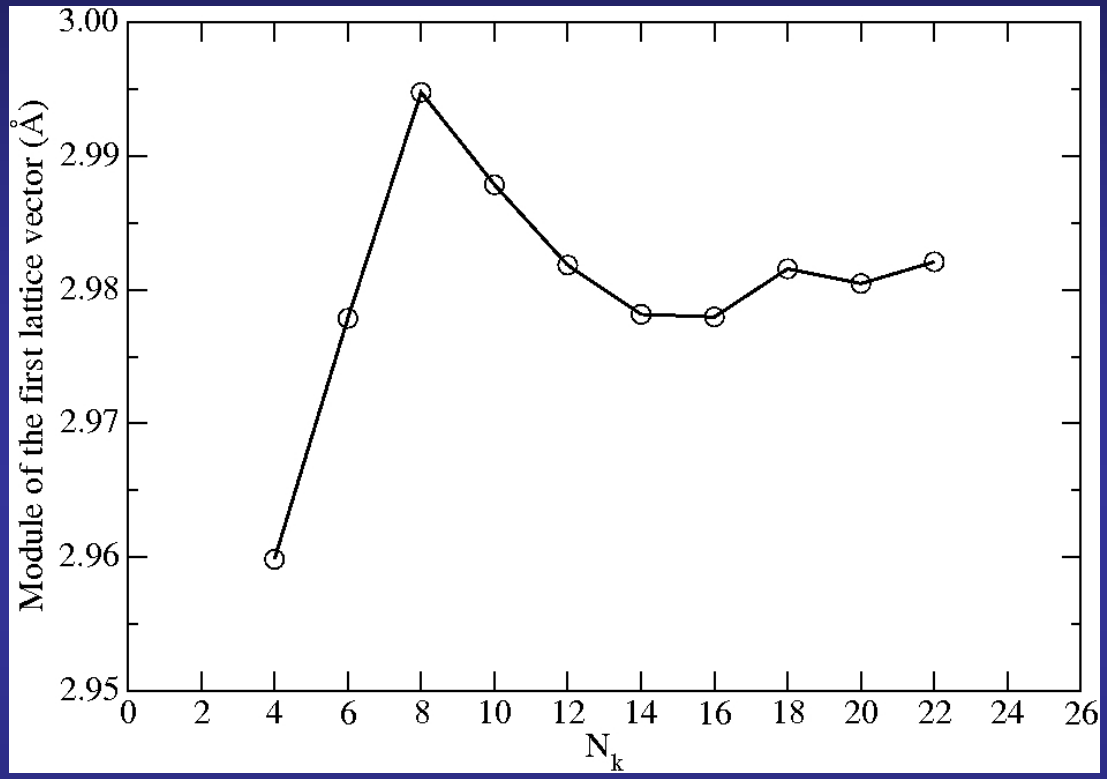
Convergence of electronic and structural properties of a metal with respect to the k-point sampling: bulk Al



Objectives

- Study the convergence of the structural and electronic properties of a metal with respect the first Brilloin-zone sampling

Bulk Al, a metal that crystallizes in the fcc structure

Go to the directory with the exercise on the convergence with respect to the k-point sampling

Inspect the input file, Al_bulk.fdf

```
#
# General system descriptors
#

SystemName          FCC Al
SystemLabel         Al
NumberOfAtoms       1
NumberOfSpecies     1

#
# Lattice, coordinates, k-sampling
#

%block ChemicalSpeciesLabel
 1   13 Al                      # Species index, atomic number, species label
%endblock ChemicalSpeciesLabel

LatticeConstant 4.05 Ang       # Experimental lattice parameter 4.05 Ang

%block LatticeVectors
  0.000  0.500  0.500
  0.500  0.000  0.500
  0.500  0.500  0.000
%endblock LatticeVectors

AtomicCoordinatesFormat  ScaledCartesian

%block AtomicCoordinatesAndAtomicSpecies
  0.000  0.000  0.000  1
%endblock AtomicCoordinatesAndAtomicSpecies

%block kgrid_Monkhorst_Pack
  18   0   0  0.5
   0  18   0  0.5
   0   0  18  0.5
%endblock kgrid_Monkhorst_Pack
```

More information at the Siesta web page http://www.icmab.es/siesta and follow the link Documentations, Manual

As starting point, we assume the theoretical lattice constant of bulk Al

FCC lattice

Sampling in k in the first Brillouin zone to achieve self-consistency

For each k-point sampling in the first-Brillouin zone, a relaxation of the unit cell is performed

Variables to control the Conjugate Gradient minimization

```
#
# Molecular dynamics and relaxations
#

MD.TypeOfRun       CG                  # We are going to perform a
                                       #   Conjugate Gradient (CG) minimization
MD.VariableCell    .true.              # Is the lattice relaxed together with
                                       #   the atomic coordinates?
MD.NumCGsteps      50                  # Number of CG steps for
                                       #   coordinate optimization
MD.MaxStressTol    0.0005 eV/Ang**3 # Tolerance in the maximum
                                       #   stress in a MD.VariableCell CG optimi.
%block GeometryConstraints             # Constraints impossed on
   position   1                        #   the position of atom 1
   stress     4   5   6                #   the shear stresses
%endblock GeometryConstraints
```

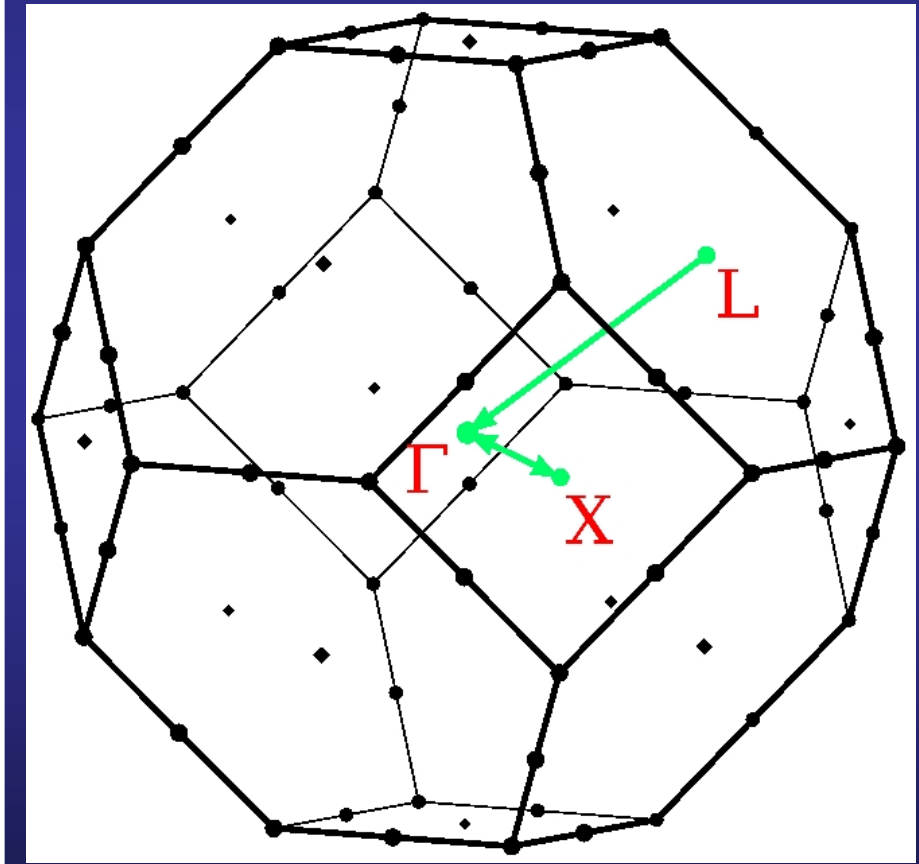
Two constraints in the minimization:

- the position of the atom in the unit cell (fixed at the origin)

- the shear stresses are nullified to fix the angles between the unit cell lattice vectors to 60°, typical of a fcc lattice

Once SCF has been achieved, we compute the bands along the high symmetry points in the first-Brillouin zone

First-Brillouin zone of a FCC , with the high symmetry points



Variables to plot the band structure

```
#
# Output (Band structure calculation)
#

BandLinesScale pi/a

%block BandLines
1    1.0000 1.0000 1.0000  L       # Begin at L
20   0.0000 0.0000 0.0000  \Gamma  # 20 points from L to gamma
25   2.0000 0.0000 0.0000  X       # 25 points from gamma to X
30   2.0000 2.0000 2.0000  \Gamma  # 30 points from X to gamma
%endblock BandLines
```

The band structure is dumped in a file called Al.bands

Relax the lattice constant and compute the electronic band structure for different k-point Monkhorst-Pack samplings

Run the code for different k-point samplings

```
siesta < Al_bulk.fdf > Al.diagonal_number_in_the_MP_mesh.out
```

The name of the output file is free, but since we are running bulk Al for different k-point samplings, this seems very sensible…

Save the file with the band structure in a different file to avoid overwrite it

```
mv Al.bands Al.diagonal_number_in_the_MP_mesh.bands
```

Study the convergence of the structural and electronic properties with respect to the k-point sampling

Inspect the output files and search for

the relaxed structure

```
outcoor: Relaxed atomic coordinates (scaled):
    0.00000000    0.00000000    0.00000000   1       1  Al

outcell: Unit cell vectors (Ang):
        0.000000    2.108295    2.108295
        2.108295    0.000000    2.108295
        2.108295    2.108295    0.000000

outcell: Cell vector modules (Ang)   :    2.981580    2.981580    2.981580
outcell: Cell angles (23,13,12) (deg):     60.0000     60.0000     60.0000
outcell: Cell volume (Ang**3)        :     18.7424
```

After relaxation, the system remains in a fcc lattice

Study the convergence of the structural and electronic properties with respect to the k-point sampling

Inspect the output files and search for

the converged Free energy for the relaxed structure

```
siesta: Program's energy decomposition (eV):
siesta: Eions   =        88.830648
siesta: Ena     =        22.933098
siesta: Ekin    =        21.117956
siesta: Enl     =         7.733159
siesta: DEna    =         1.567599
siesta: DUscf   =         0.037632
siesta: DUext   =         0.000000
siesta: Exc     =       -20.999449
siesta: eta*DQ  =         0.000000
siesta: Emadel  =         0.000000
siesta: Emeta   =         0.000000
siesta: Emolmec =         0.000000
siesta: Ekinion =         0.000000
siesta: Eharris =       -56.440653
siesta: Etot    =       -56.440653
siesta: FreeEng =       -56.441578
```

We are interested in this number

Study the convergence of the structural and electronic properties with respect to the k-point sampling

Inspect the output files and search for

the converged Free energy for the relaxed structure

We are interested in the free energy because we have introduced an electronic temperature and, in this case, the functional that has to be minimized is the Free energy, defined as

$$F(\boldsymbol{R}_I, \psi_i(\boldsymbol{r}), n_i) = E^{KS}(\boldsymbol{R}_I, \psi_i(\boldsymbol{r}), n_i) - \mu \sum_i n_i$$
$$- k_B T \sum_i (n_i \log n_i + (1 - n_i) \log(1 - n_i)).$$

$n_i \equiv$ Occupation of state i

J. M. Soler et al., J. Phys.: Condens. Matter 14, 2745 (2002), page 2761

Study the convergence of the structural and electronic properties with respect to the k-point sampling

With your favorite text editor, edit a file with the following three columns:

Al.convergencek.dat

# Diagonal # MP mesh	Module of the first lattice vector Ang	Free Energy eV
4	2.959837	-56.406617
6	2.977869	-56.429728
8	2.994786	-56.439394
10	2.987873	-56.443370
12	2.981853	-56.443295
14	2.978168	-56.442584
16	2.977970	-56.441362
18	2.981580	-56.441578
20	2.980470	-56.442095
22	2.982099	-56.442299

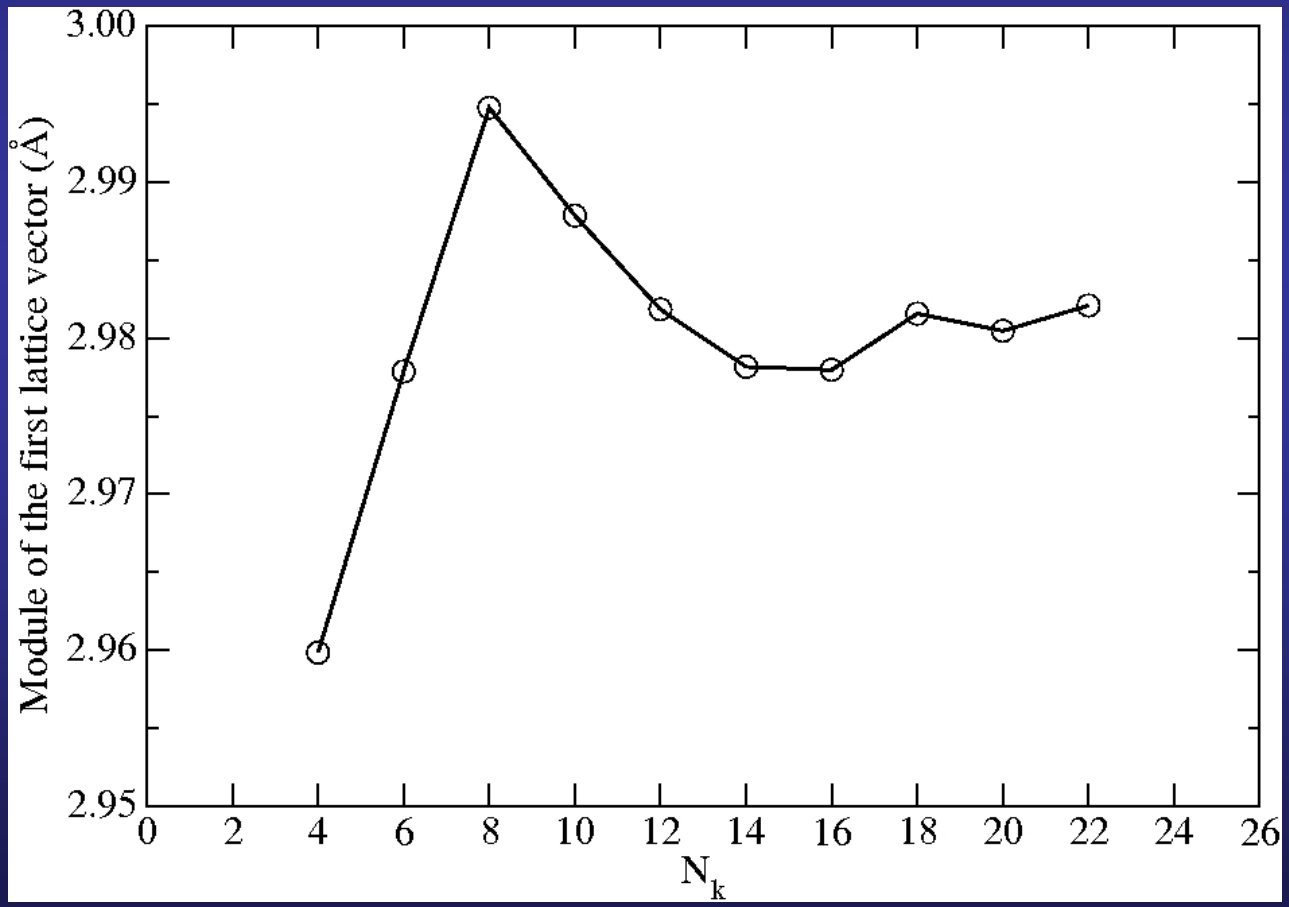
These numbers have been obtained with siesta-3.0-b, compiled with the g95 compiler and double precision in the grid.

Numbers might change slightly depending on the platform, compiler and compilation flags

Plot the lattice constant as a function of the k-point sampling

gnuplot

plot “Al.convergencek.dat” using 1:2 with lines

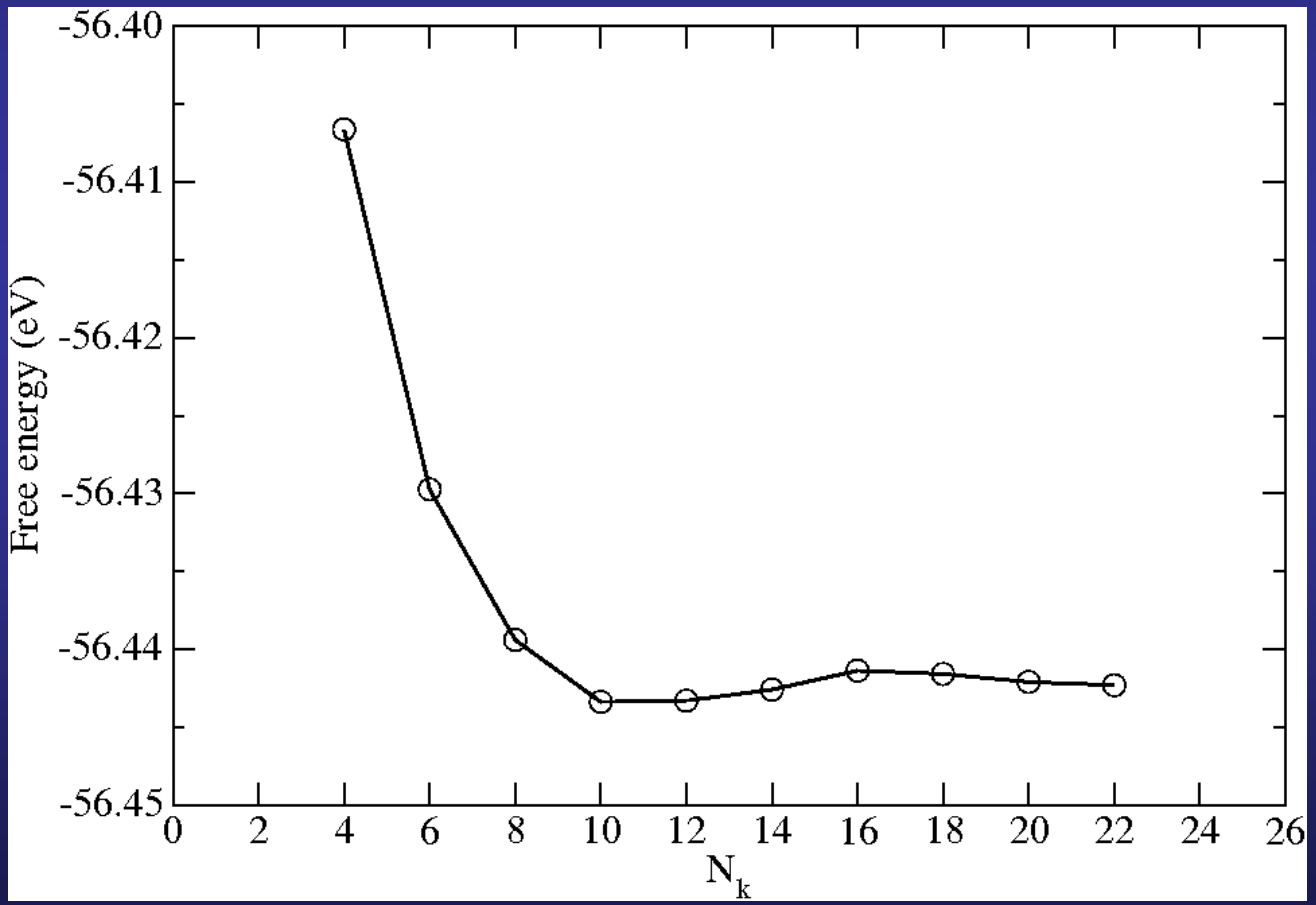


To compute the lattice constant, multiply this number by $\sqrt{2}$

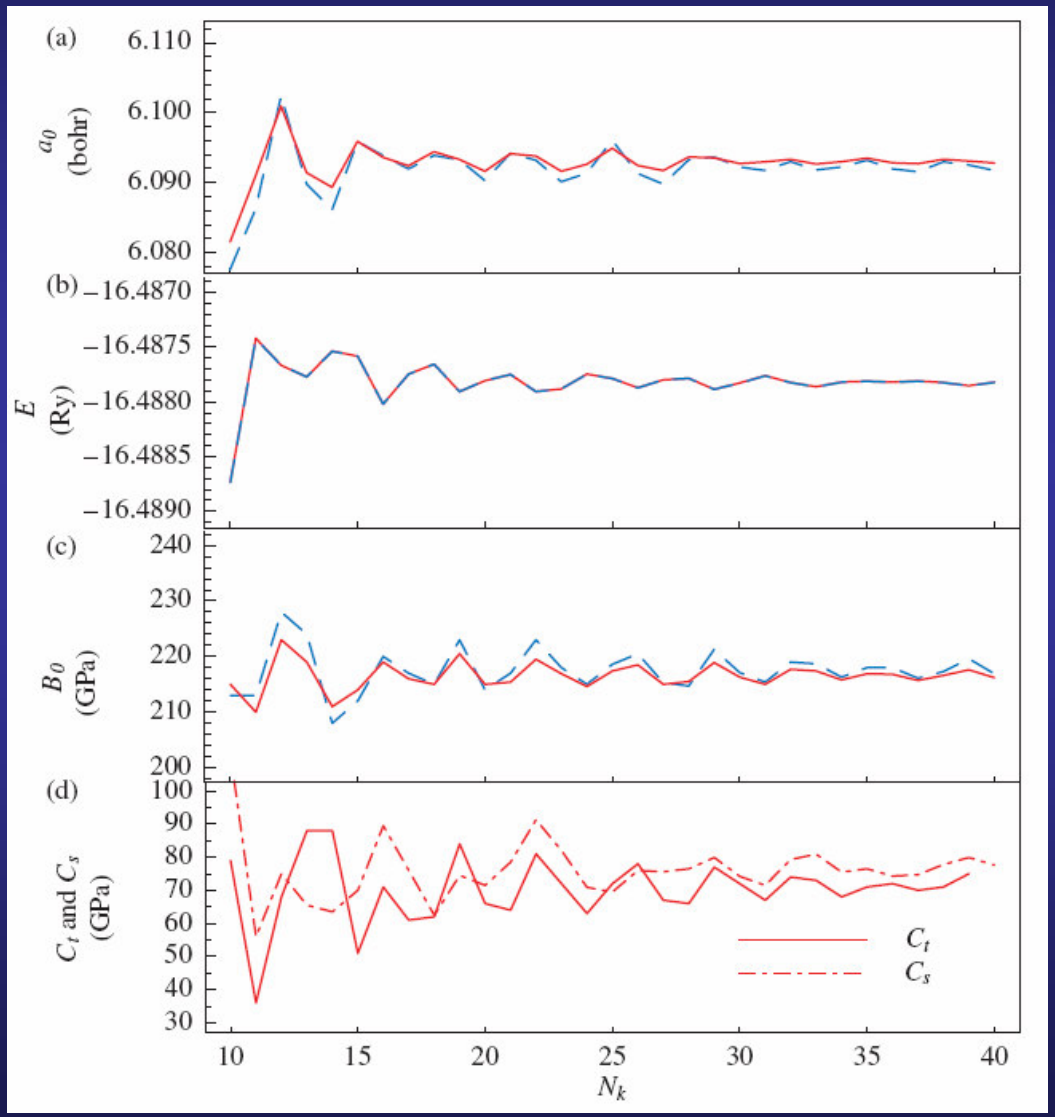
Plot the free energy as a function of the k-point sampling

gnuplot

plot “Al.convergencek.dat” using 1:3 with lines



Some quantities are more sensitive to the k-point sampling than others



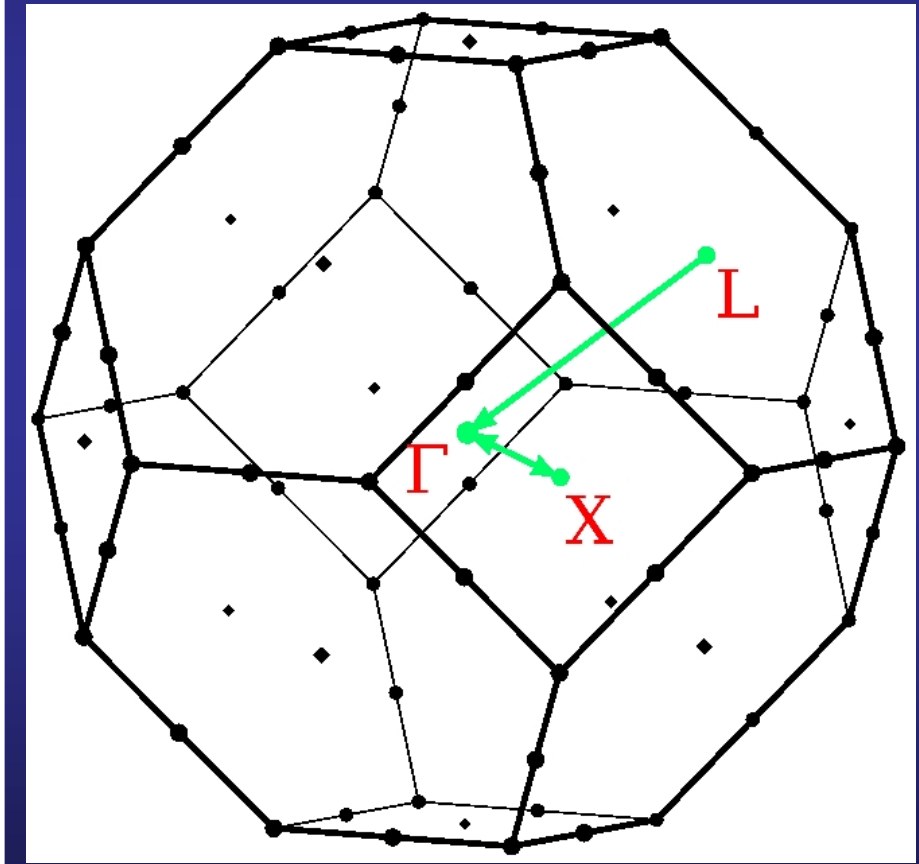
Bulk bcc Ta

Although lattice parameter, total energy and bulk modulus appear to be converged, if slowly, the computed shear moduli are much more sensitive to the k-sample, and still varying over a range of 5 GPa at a k grid of 40^3

A. E. Mattson *et al.*, Modelling Simul. Mater. Sci. Eng. 13, R1 (2005)

Once SCF has been achieved, we compute the bands along the high symmetry points in the first-Brillouin zone

First-Brillouin zone of a FCC , with the high symmetry points



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20   0.0000 0.0000 0.0000  \Gamma  # 20 points from L to gamma
25   2.0000 0.0000 0.0000  X       # 25 points from gamma to X
30   2.0000 2.0000 2.0000  \Gamma  # 30 points from X to gamma
%endblock BandLines
```

The band structure is dumped in a file called Al.bands

Once SCF has been achieved, we compute the bands along the high symmetry points in the First-Brillouin zone

Let us make a tour around the Al.bands file

If you inspect this file, you will find something like

```
-4.012232514613835
0.  2.586573561185123
-14.749629873316438 8.649105958283496
4  1  76
 0.000000      -8.5534      -8.4974       6.1582       6.1582 ...
 ...
```

Energy of the Fermi level

Minimum and maximum length of the path in k-space

Minimum and maximum eigenvalues

Number of orbitals in the unit cell, number of different spin polarization, and number of k-points in the walk through the 1BZ

Coordinate of the k-point in the path, and eigenvalues (in eV). There are as many eigenvalues as orbitals in the unit cell.

Once SCF has been achieved, we compute the bands along the high symmetry points in the First-Brillouin zone

To plot the band structure, there is a Utility in the directory Util, called gnubands.f

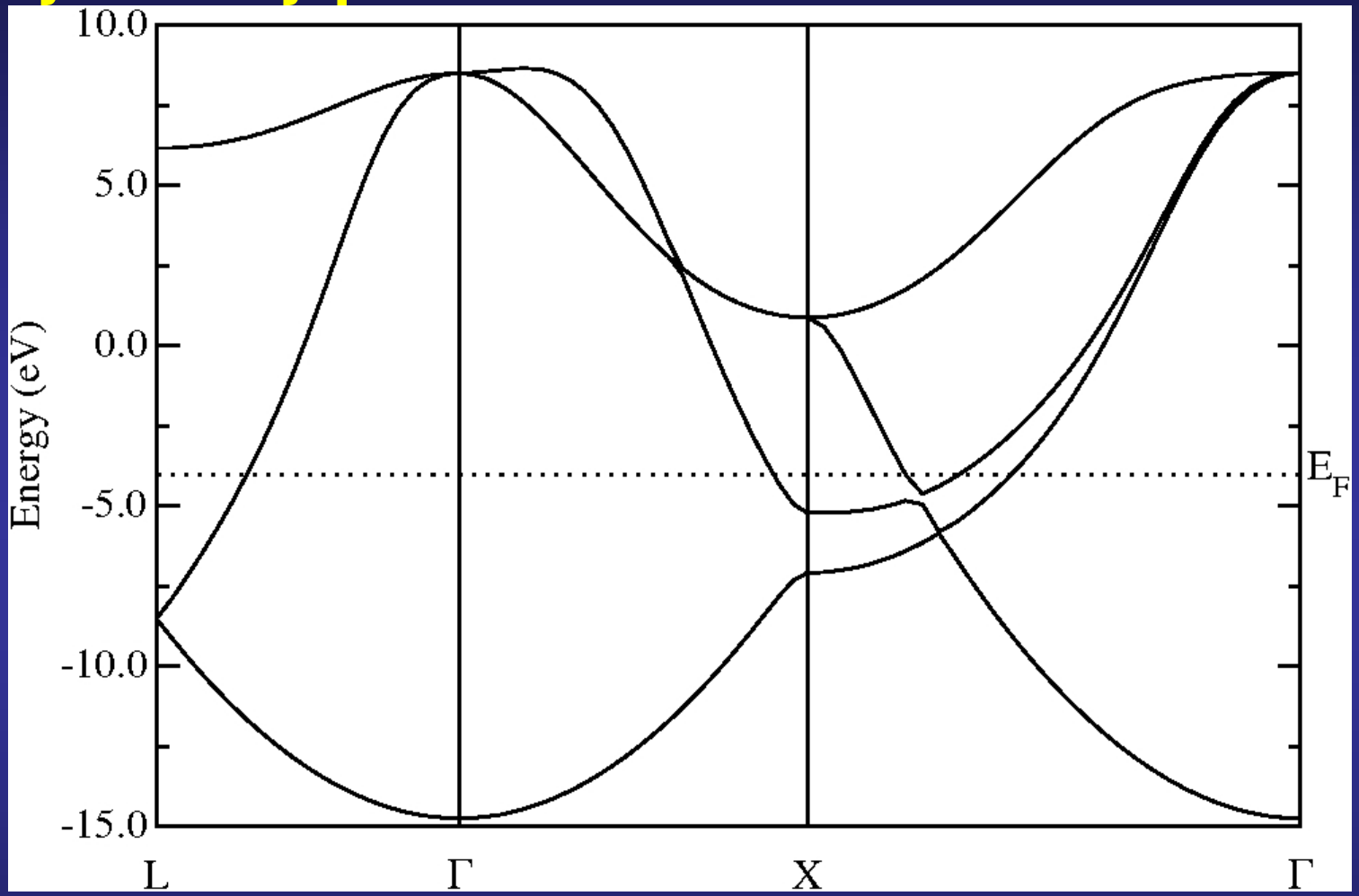
To use it:

```
cp ~/siesta/Util/gnubands.f .
<your_fortran_compiler> -o gnubands.x gnubands.f
gnubands.x < Al.bands > Al.bands.dat
```

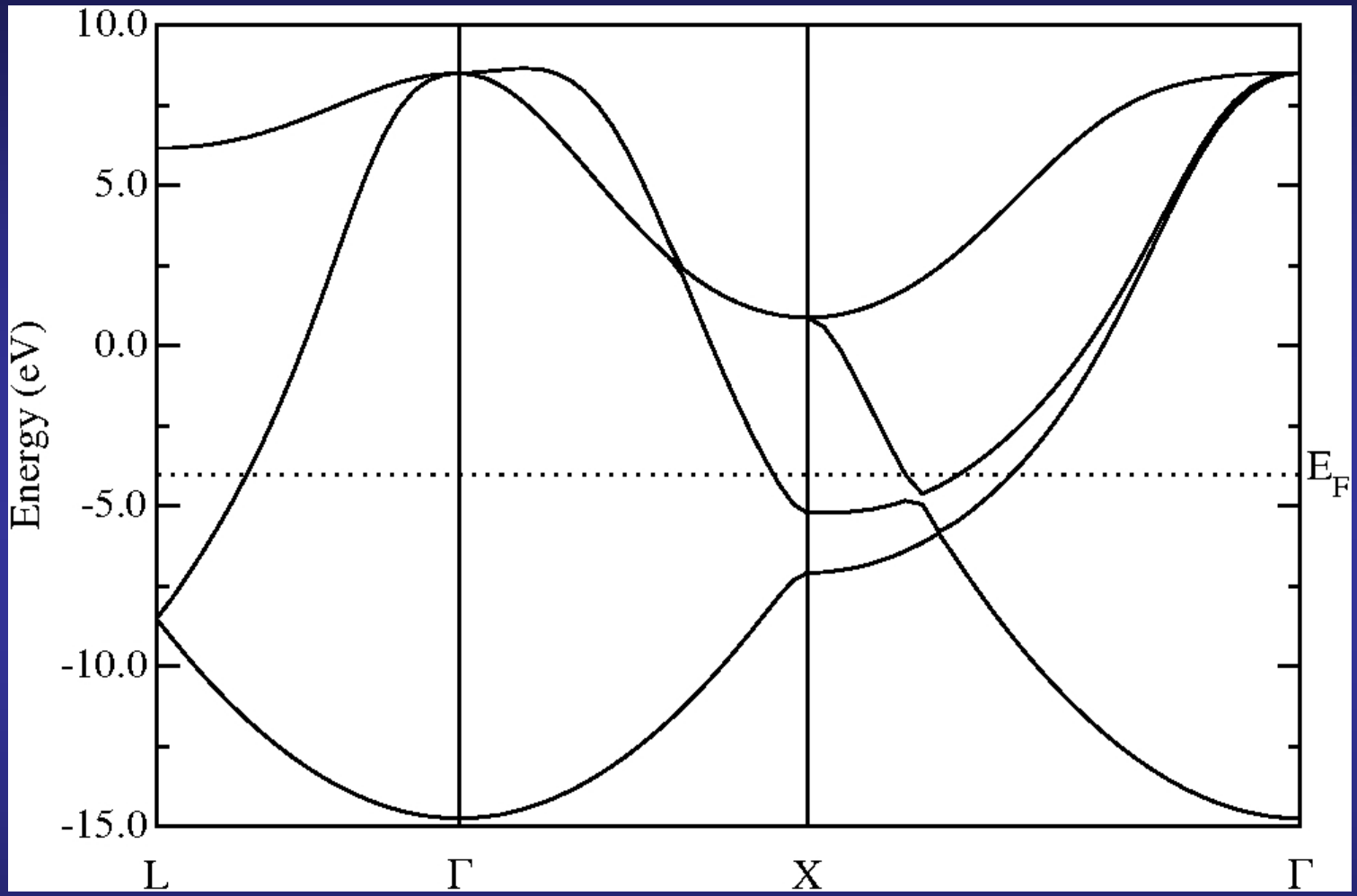
The name of this output file is free

```
gnuplot
plot “Al.bands.dat” using 1:2 with lines
```

Once SCF has been achieved, we compute the bands along the high symmetry points in the First-Brillouin zone



The most important point: analyze your results



The bands cross the Fermi level

(metallic character)

Bands look like parabollas,

(Al resembles a free electron gas)

How to compute the Density Of States (DOS)

For a deeper explanation on how to compute the DOS,
see the talk on “Visualization”

Here, we have prepared an input file, Al_bulk_dos.fdf,
with the relaxed structure at 18 ×18× 18 Monkhorst-Pack mesh.
Pay particular attention to

```
#
# Output (Density Of States, DOS)
#

%block PDOS.kgrid_Monkhorst_Pack
    30  0  0  0.5
     0 30  0  0.5
     0  0 30  0.5
%endblock PDOS.kgrid_Monkhorst_Pack

%block ProjectedDensityOfStates
   -20.00  10.00  0.200  500  eV
%endblock ProjectedDensityOfStates
```

How to compute the Density Of States (DOS)

```
#
# Output (Density Of States, DOS)
#

%block PDOS.kgrid_Monkhorst_Pack
    30  0  0  0.5
     0 30  0  0.5
     0  0 30  0.5
%endblock PDOS.kgrid_Monkhorst_Pack

%block ProjectedDensityOfStates
   -20.00  10.00  0.200  500  eV
%endblock ProjectedDensityOfStates
```

Run the code for different sampling in the Monkhorst-Pack meshes while computing the DOS

siesta < Al_bulk_dos.fdf

mv Al.DOS Al.diagonal_number_in_PDOS_MP_mesh.DOS

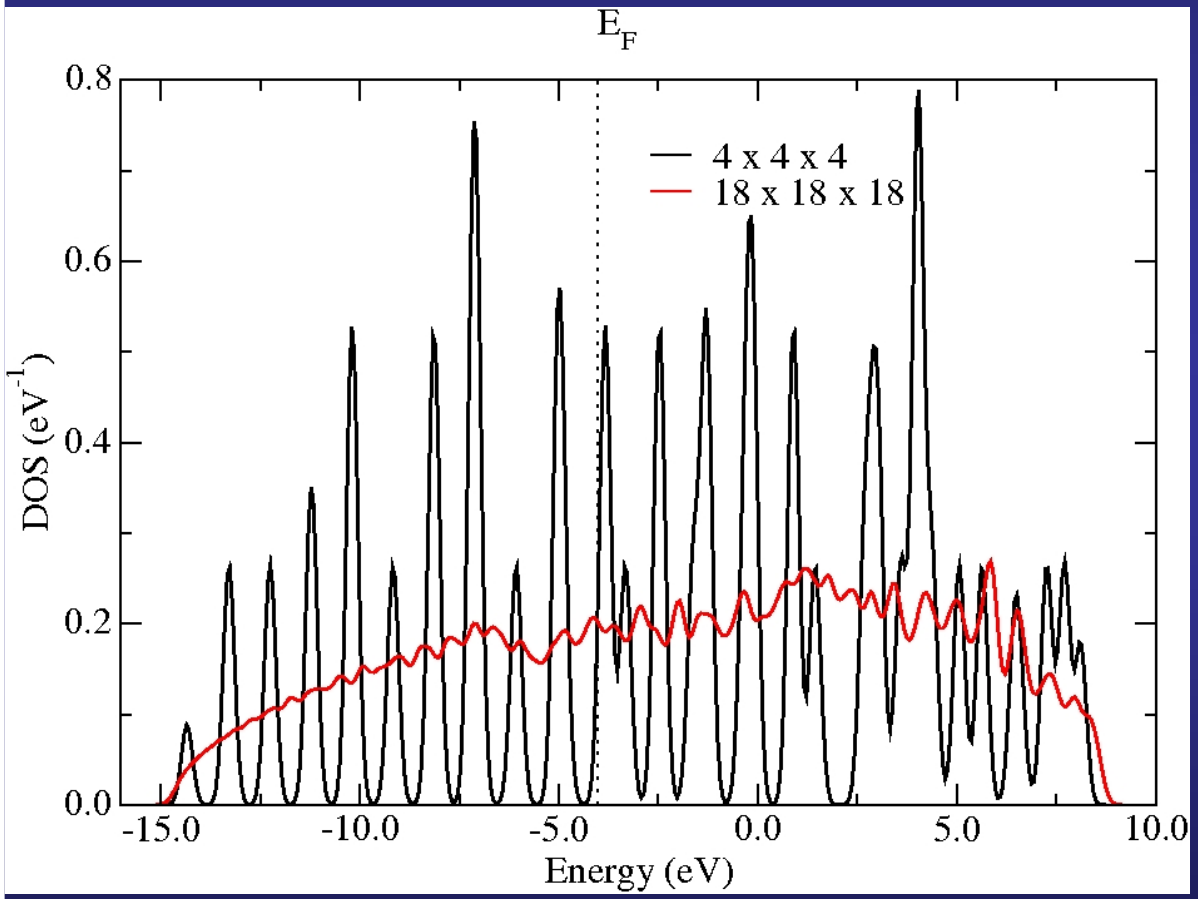
Plot the Density Of States

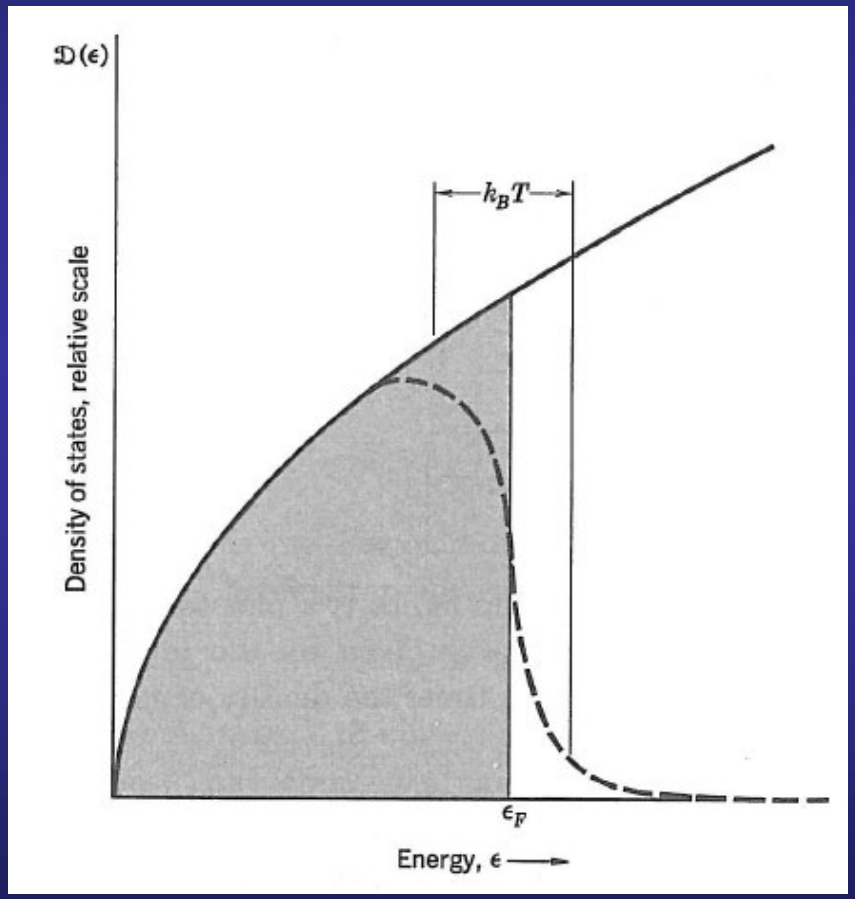
gnuplot

plot “Al.444.DOS” using 1:2 with lines, “Al.181818.DOS” using 1:2 with lines

Convergence of the Density Of States (DOS) with respect the k-point sampling

Ch. Kittel, Introduction to Solid State Physics, Chapter 6





The computed density of states has the form of $\sqrt{E}$, as is typical in a three-dimensional free electron gas

$$\mathcal{D}(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{E}$$