Day 4 Hands on: Forces and phonons

Tutors: Chiara Cignarella / Alberto Carta / Nelson Dzade / George Manyali / James Sifuna / Fatema Mohamed / Omamuyovwi Rita Jolayemi / Maram Ali Ahmed Musa

Today's theme:
1) Relaxations: adsorption of oxygen on graphene and automatic lattice constant optimization
2) Phonons: compute phonon in Γ and along the BZ, for Si and AlAs

Exercise 1:

Learning Goals: optimize atomic position and lattice constants

Exercise 1

Topics of the exercise:

1. How to perform relaxation of atomic structure (graphane and oxygen adsorption)

2. Understanding forces.

3. Optimizing the lattice constant of Silicon and comparing with total energy approaches

4. Understanding stresses.

Exercise 1.1: graphane and O adsorption

Input file scf calculation

```
&CONTROL
calculation = 'scf',
prefix = 'Graphane',
outdir = '/tmp',
pseudo_dir = '../../pseudo',
/

&SYSTEM
….
….
/

&ELECTRONS
conv_thr = 1.0d-8
/

ATOMIC_SPECIES
C 12.0107 C.pbe-rrkjus.UPF
H 1.00007 H.pbe-rrkjus.UPF


ATOMIC_POSITIONS alat
...

K_POINTS automatic
991 000
```

Input file for relaxation

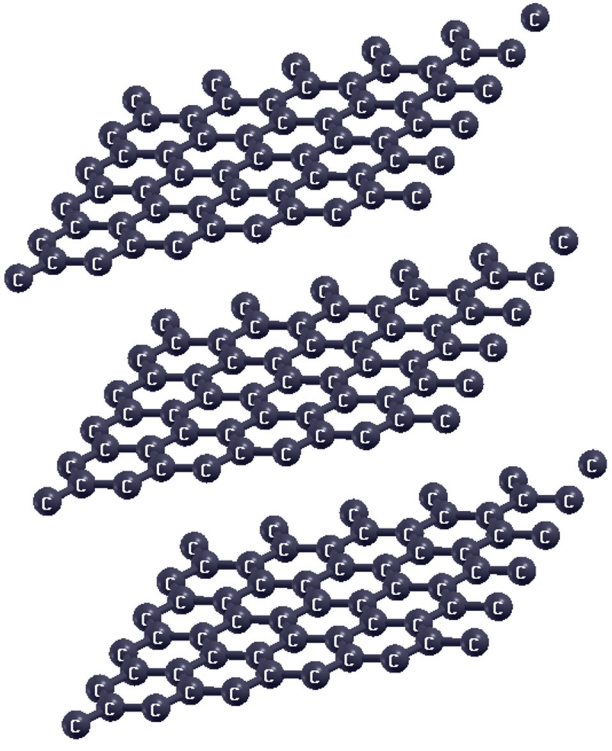
```
&CONTROL
calculation = 'relax',
prefix = 'Graphane',
outdir = '/tmp',
pseudo_dir = '../../pseudo',
/

&SYSTEM
….
….
/

&ELECTRONS
conv_thr = 1.0d-8
/

&IONS
/


ATOMIC_SPECIES
C 12.0107 C.pbe-rrkjus.UPF
H 1.00007 H.pbe-rrkjus.UPF


ATOMIC_POSITIONS alat
...

K_POINTS automatic
991 000
```

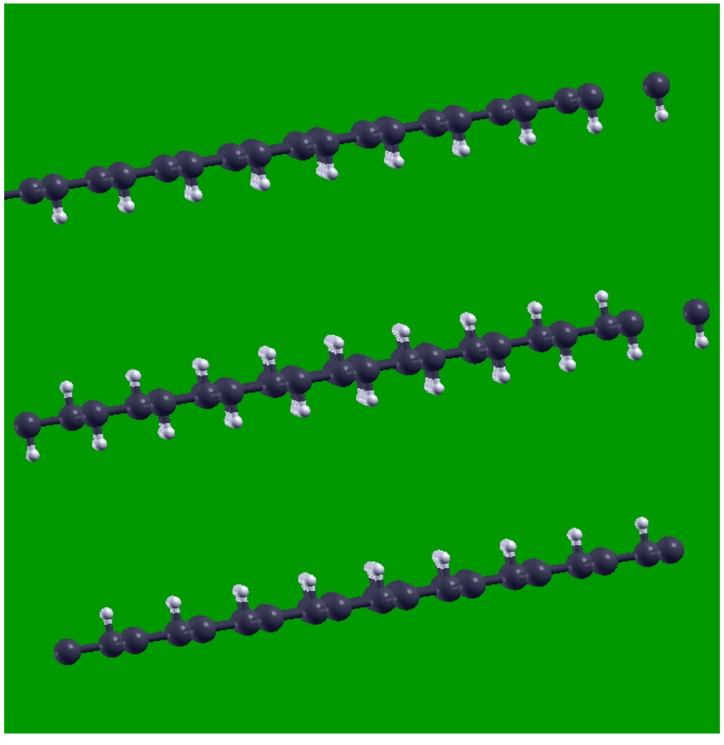
This relaxes **only** the **atomic positions**

Ions is jargon for atoms, this cell must appear!

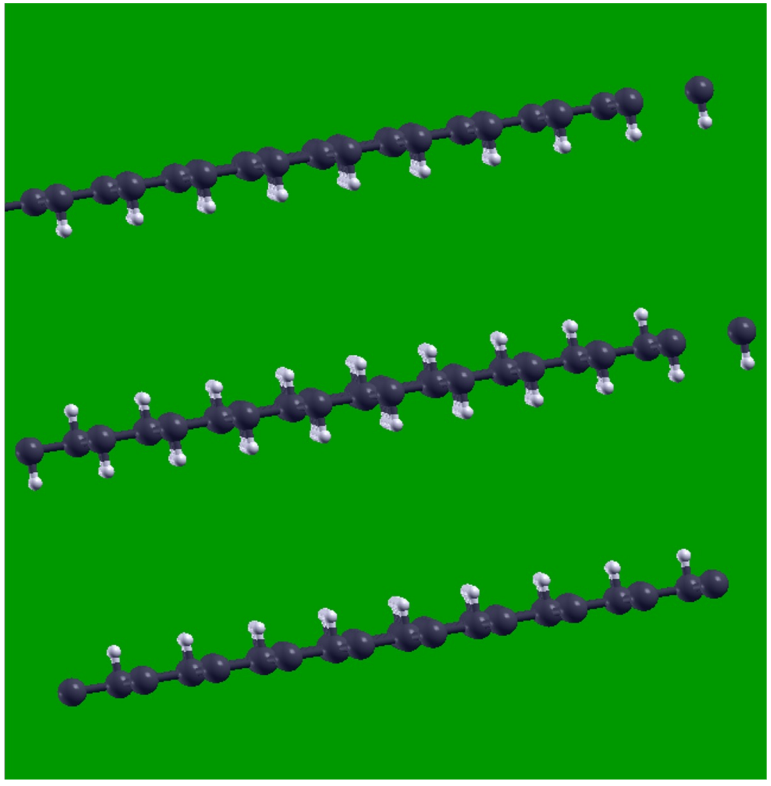
Exercise 1.1: graphane

Graphane is hydrogenated graphene:
→ H saturates double-bonds and destroys the pi-delocalized cloud
→ remove tendency to be planar (why?)



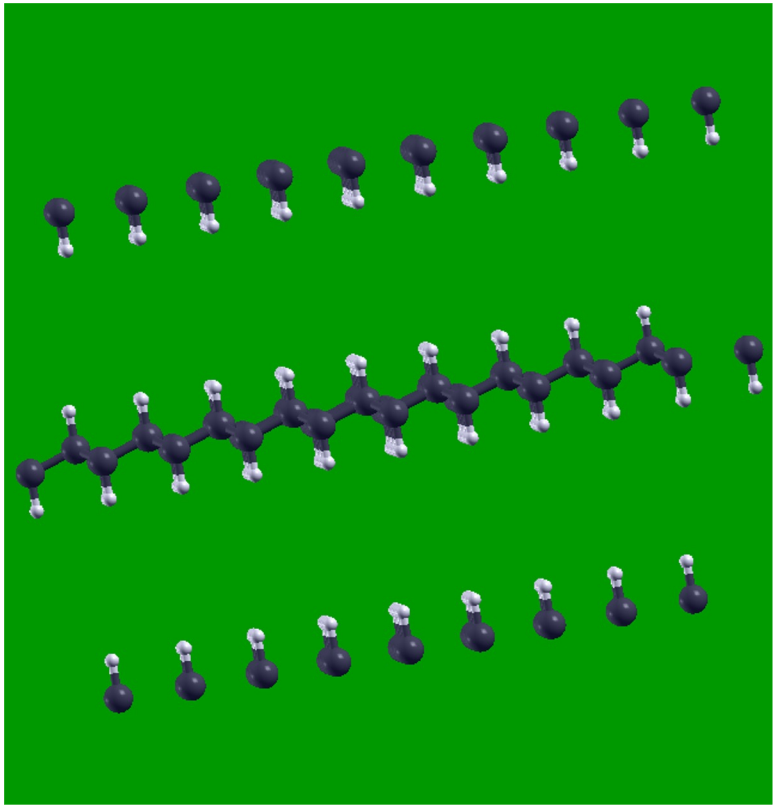


Exercise 1.1: graphane buckling



Relax

→



Exercise 1.1: finding forces

Output relaxation file

Iteration #1

Forces acting on atoms (cartesian axes, Ry/au):

```
atom    1 type  2   force =    -0.00000000   -0.00000000    0.29668613
atom    2 type  1   force =     0.00000000    0.00000000    0.24378433
atom    3 type  1   force =     0.00000000    0.00000000   -0.24378433
atom    4 type  2   force =     0.00000000    0.00000000   -0.29668613

Total force =     0.543053     Total SCF correction =     0.000031
```

What is the condition on forces for the material to be in equilibrium?

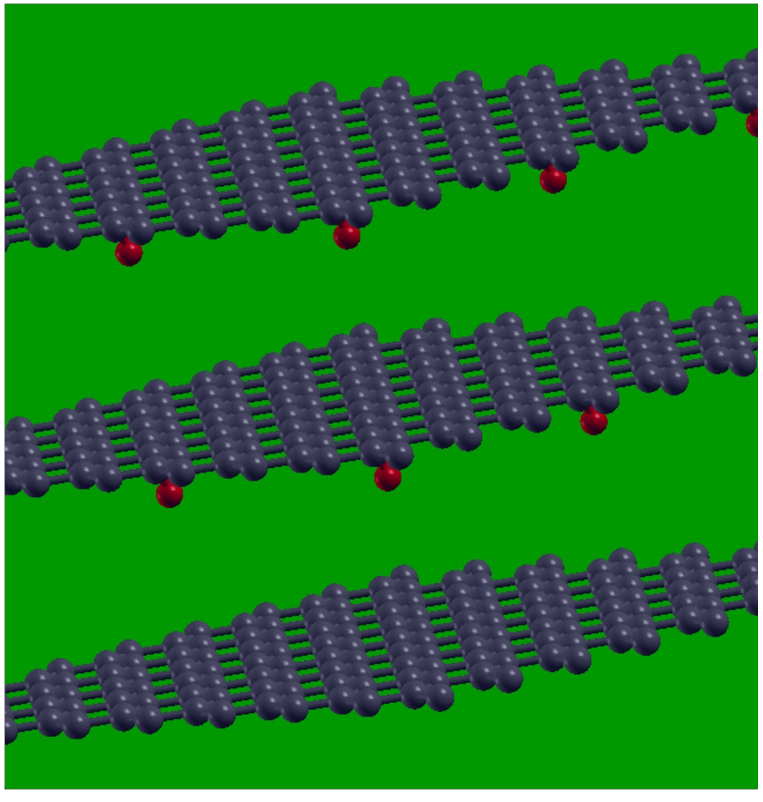
Iteration #6

Forces acting on atoms (cartesian axes, Ry/au):

```
atom    1 type  2   force =     0.00000000    0.00000000    0.00017761
atom    2 type  1   force =     0.00000000    0.00000000   -0.00064644
atom    3 type  1   force =     0.00000000    0.00000000    0.00064644
atom    4 type  2   force =     0.00000000   -0.00000000   -0.00017761

Total force =     0.000948     Total SCF correction =     0.000003
Energy error          =      2.7E-05 Ry
Gradient error        =      6.5E-04 Ry/Bohr
```

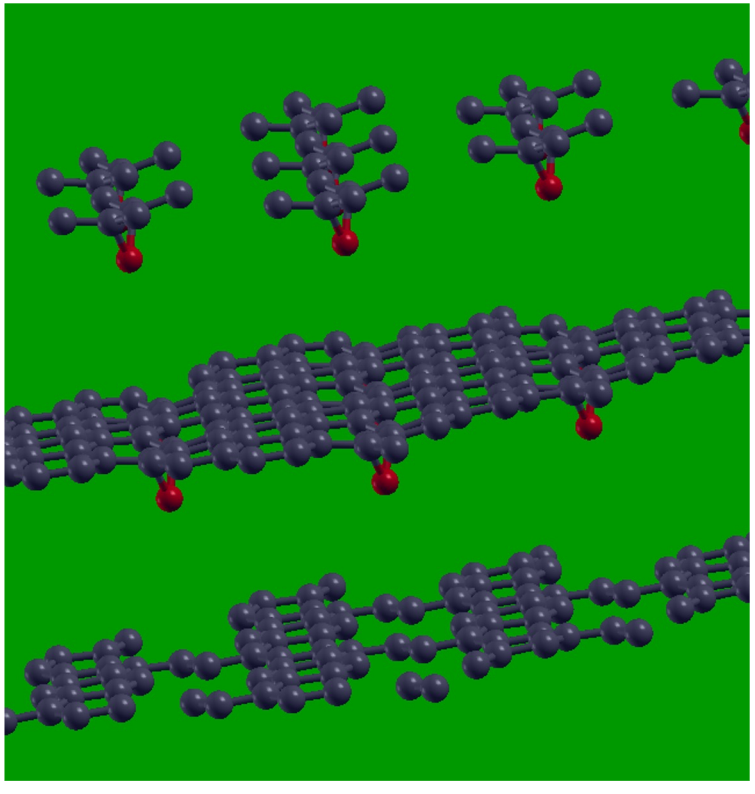
Exercise 1.1: O adsorption on graphene

Oxygen is strongly electronegative → electron acceptor



Relax

→



Exercise 1.1: optimizing silicon

Input file for cell relaxation

```
&CONTROL
   calculation='vc-relax',
   prefix='silicon',
   pseudo_dir='../../pseudo/',
   outdir='./tmp'
/
&SYSTEM
   ibrav =  2,
   celldm(1) = 10.6,
   nat =  2,
   ntyp = 1,
   nbnd=10,
   ecutwfc = 36,
/
&ELECTRONS
/
&IONS
/
&CELL
/
ATOMIC_SPECIES
   Si  28.086  Si.pz-vbc.UPF
ATOMIC_POSITIONS
   Si 0.00 0.00 0.00
   Si 0.25 0.25 0.25
K_POINTS automatic
   6 6 6   1 1 1
```

This relaxes **both cell and atomic positions**

We need also a CELL section

Exercise 1.1: finding stresses

Output relaxation file

```
Iteration #1
     Forces acting on atoms (cartesian axes, Ry/au):

     atom    1 type  1   force =     0.00000000   0.00000000   0.00000000
     atom    2 type  1   force =     0.00000000   0.00000000   0.00000000

     Total force =     0.000000     Total SCF correction =     0.000000

     Computing stress (Cartesian axis) and pressure

          total   stress  (Ry/bohr**3)                  (kbar)     P=      -85.01
  -0.00057789  -0.00000000   0.00000000         -85.01       -0.00        0.00
  -0.00000000  -0.00057789   0.00000000          -0.00      -85.01        0.00
   0.00000000   0.00000000  -0.00057789           0.00        0.00      -85.01

Iteration #6
     Forces acting on atoms (cartesian axes, Ry/au):

     atom    1 type  1   force =    -0.00000000  -0.00000000  -0.00000000
     atom    2 type  1   force =     0.00000000   0.00000000  -0.00000000

     Total force =     0.000000     Total SCF correction =     0.000000


     Computing stress (Cartesian axis) and pressure

          total   stress  (Ry/bohr**3)                  (kbar)     P=        0.29
   0.00000194   0.00000000  -0.00000000           0.29        0.00       -0.00
   0.00000000   0.00000194  -0.00000000           0.00        0.29       -0.00
  -0.00000000  -0.00000000   0.00000194          -0.00       -0.00        0.29
```

End of exercise 1

Questions?

Topics of the following session: Phonons

- Exercise 2: Phonons at Gamma in non-polar materials
- Exercise 3: Phonons dispersion in non-polar materials
- Exercise 4: Phonon at Gamma in polar materials

Optional:

- Exercise 5: Phonon dispersion in polar materials

Introduction: Phonons

Normal mode frequencies, , and eigenvectors, are determined by the secular equation:

$$\sum_{s',\beta} \widetilde{D}_{s\alpha,s'\beta}(\boldsymbol{q})\widetilde{\boldsymbol{u}}_{s'\beta}(\boldsymbol{q}) = \omega_{\boldsymbol{q}}^2 \widetilde{\boldsymbol{u}}_{s\alpha}(\boldsymbol{q})$$

where $$\widetilde{D}_{s\alpha,s'\beta}(\boldsymbol{q}) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{\boldsymbol{R},\boldsymbol{R}'} \frac{\partial^2 \mathrm{E}_{\mathrm{tot}}}{\partial u_{s\alpha}(\boldsymbol{R}) \partial u_{s'\beta}(\boldsymbol{R}')} e^{i\boldsymbol{q}(\boldsymbol{R}-\boldsymbol{R}')}$$

is the dynamical matrix.

Interatomic Force Constant (IFC)

This Matrix can be calculated from linear response and diagonalized to get phonon modes at **q**.

Exercise 2:
Phonons at Gamma in non-polar materials

Exercise 2: Phonons at Γ in non-polar materials

Go to the directory with the input files:

cd ~/ASESMA2025/Day4/example2.phonon.Gamma.Si/

In this directory you will find:

- *README.md* – File describing how to do the exercise
- *Si.scf.in* – Input file for the SCF ground-state calculation
- *Si.ph.in* – Input file for the phonon calculation at Γ
- *Si.dynmat.in* – Input file to impose the acoustic sum rule
- **reference** – Directory with the reference results

Exercise 2: Phonons at Γ in non-polar materials

```
&CONTROL
calculation = 'scf',
prefix = 'si',
pseudo_dir = '../pseudo/',
outdir = '../tmp'
/
&SYSTEM
ibrav = 2,
celldm(1) = 10.2,
nat = 2,
ntyp = 1,
ecutwfc = 60,
ecutrho = 720
/
&ELECTRONS
mixing_beta=0.7,
conv_thr=1d-10,
/
ATOMIC_SPECIES
Si 28.086  Si.pz-vbc.UPF
ATOMIC_POSITIONS
Si              0.00.   0.00.   0.00
Si              0.25.   0.25    0.25
K_POINTS automatic
4 4 4    1 1 1
```

Smaller than for simple total energy!

Step 1: Perform a Self-Consistent Field ground-state calculation for silicon at the equilibrium structure using the pw.x program.

```
mpirun –np 4 pw.x –in Si.scf.in > Si.scf.out
```

Input Output

Exercise 2: Phonons at Γ in non-polar materials

Input file for phonon at Gamma

```
&inputph
prefix = 'si',
tr2_ph = 1.0d-14,
amass(1) = 28.0855,
epsil = .true.
outdir = './tmp'
fildyn = 'Si.dyn',
/
0.0 0.0 0.0
```

Step 2: Perform a phonon calculation at Γ using the ph.x program.

```
mpirun –np 4 ph.x –in Si.ph.in > Si.ph.out
```

- The same prefix as in the SCF calculation
- Threshold for self-consistency
- Atomic mass
- To calculate the dielectric tensor and effective charges
- Directory for temporary files
- File containing the dynamical matrix
- Coordinates of the q point (Γ) in units of 2*pi/a in the Cartesian reference system

Exercise 2: Phonons at Γ in non-polar materials

Dynamical matrix file: **Si.dyn**

```
Dielectric Tensor:

    13.581468280806          -0.000000000000          -0.000000000000
     0.000000000000          13.581468280806           0.000000000000
    -0.000000000000           0.000000000000          13.581468280806

Effective Charges E-U: Z_{alpha}{s,beta}

atom #    1
    -0.069382139635          -0.000000000000          -0.000000000000
    -0.000000000000          -0.069382139635          -0.000000000000
    -0.000000000000          -0.000000000000          -0.069382139635
atom #    2
    -0.069382139635           0.000000000000           0.000000000000
     0.000000000000          -0.069382139635          -0.000000000000
     0.000000000000          -0.000000000000          -0.069382139635
```

Dielectric constant and Born effective charges (BECs)

$$Z^*_{s,\alpha\beta} = \frac{V}{e}\frac{\partial P_\alpha}{\partial u_{s,\beta}(\boldsymbol{q}=0)} = \frac{1}{e}\frac{\partial F_{s\beta}}{\partial \mathcal{E}_\alpha(\boldsymbol{q}=0)}$$

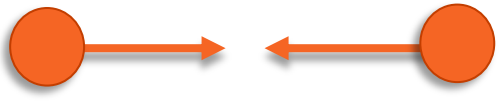
Exercise 2: Phonons at Γ in non-polar materials

Dynamical matrix file: **Si.dyn**

```
     Diagonalizing the dynamical matrix

     q = (    0.000000000   0.000000000   0.000000000 )

**************************************************************************
     freq (    1) =       0.369224 [THz] =      12.315990 [cm-1]
(  -0.502437   0.000000   0.469222   0.000000   0.165492   0.000000 )
(  -0.502437   0.000000   0.469222   0.000000   0.165492   0.000000 )
     freq (    2) =       0.369224 [THz] =      12.315990 [cm-1]
(  -0.186720   0.000000   0.040185   0.000000  -0.680824   0.000000 )
(  -0.186720   0.000000   0.040185   0.000000  -0.680824   0.000000 )
     freq (    3) =       0.369224 [THz] =      12.315990 [cm-1]
(   0.461186   0.000000   0.527462   0.000000  -0.095350   0.000000 )
(   0.461186   0.000000   0.527462   0.000000  -0.095350   0.000000 )
     freq (    4) =      15.306901 [THz] =     510.583264 [cm-1]
(   0.700260  -0.000000  -0.059885   0.000000  -0.077779   0.000000 )
(  -0.700260   0.000000   0.059885  -0.000000   0.077779   0.000000 )
     freq (    5) =      15.306901 [THz] =     510.583264 [cm-1]
(   0.067676   0.000000   0.700365   0.000000   0.070066   0.000000 )
(  -0.067676   0.000000  -0.700365   0.000000  -0.070066   0.000000 )
     freq (    6) =      15.306901 [THz] =     510.583264 [cm-1]
(  -0.071103   0.000000   0.076832   0.000000  -0.699315   0.000000 )
(   0.071103   0.000000  -0.076832   0.000000   0.699315   0.000000 )
**************************************************************************
```

Acoustic modes (in-phase)

Optical modes (out-of-phase)



Exercise 2: Phonons at Γ in non-polar materials

Acoustic sum rule at Γ

Problems with the frequency of the acoustic phonon mode at Γ and with effective charges.
Because of the numerical inaccuracies the interatomic force constants (IFC) and effective charges (Z^*) do not strictly satisfy the acoustic sum rule (ASR).

ASR comes directly from the continuous translational invariance of the crystal:
if we translate the whole solid by a uniform displacement, the forces acting on the atoms must be zero

$\Longrightarrow$ for each cartesian direction α, β and s,s'-th atom:

$$\sum_{\boldsymbol{R}j} C_{s\alpha\,,s'\beta}\,(\boldsymbol{R}) = 0, \qquad \sum_{j} Z^*_{s\alpha\beta} = 0$$

As a consequence, the frequencies of the acoustic modes at Gamma must be zero.

Exercise 2: Phonons at Γ in non-polar materials

Acoustic sum rule at Γ

Reason for numerical inaccuracy:

- Insufficiently accurate SCF thresholds (in pw.x and/or ph.x)
- XC energy is computed in real space. More problematic for GGA than in LDA, for US pseudopotentials it could require large *ecutrho*.
- K-points sampling not accurate enough (especially, BECs and dielectric constant required denser k-point sampling).

Exercise 2: Phonons at Γ in non-polar materials

Acoustic sum rule at Γ

The acoustic sum rule (ASR) can however be imposed after the phonon calculations. To do this we use the dynmat.x program that imposes the ASR on the elements of the dynamical matrix and diagonalize it.

Step 3: Run a dynmat.x calculation to impose the ASR

```
mpirun –np 4 dynmat.x –in Si.dynmat.in > Si.dynmat.out
```

The input file is Si.dynmat.in :

```
&input
fildyn = 'Si.dyn',
asr = 'simple',
/
```

File containing the dynamical matrix

A way to impose the acoustic sum rule (simple, crystal, one-dim, zero-dim, all)

Exercise 2: Phonons at Γ in non-polar materials

The program dynmat.x produces the file **dynmat.out** which contains the new acoustic frequencies, which are exactly equal to zero

```
q =       0.0000      0.0000      0.0000
 **************************************************************************
     freq (    1) =       0.000000 [THz] =       0.000000 [cm-1]
(  0.000000   0.000000     0.707107   0.000000     0.000000   0.000000  )
(  0.000000   0.000000     0.707107   0.000000     0.000000   0.000000  )
     freq (    2) =       0.000000 [THz] =       0.000000 [cm-1]
( -0.707107   0.000000     0.000000   0.000000     0.000000   0.000000  )
( -0.707107   0.000000     0.000000   0.000000     0.000000   0.000000  )
     freq (    3) =       0.000000 [THz] =       0.000000 [cm-1]
(  0.000000   0.000000     0.000000   0.000000     0.707107   0.000000  )
(  0.000000   0.000000     0.000000   0.000000     0.707107   0.000000  )
     freq (    4) =      15.302447 [THz] =     510.434704 [cm-1]
(  0.000000   0.000000     0.707107   0.000000     0.000000   0.000000  )
(  0.000000   0.000000    -0.707107   0.000000     0.000000   0.000000  )
     freq (    5) =      15.302447 [THz] =     510.434704 [cm-1]
(  0.000000   0.000000     0.000000   0.000000    -0.707107   0.000000  )
(  0.000000   0.000000     0.000000   0.000000     0.707107   0.000000  )
     freq (    6) =      15.302447 [THz] =     510.434704 [cm-1]
( -0.707107   0.000000     0.000000   0.000000     0.000000   0.000000  )
(  0.707107   0.000000     0.000000   0.000000     0.000000   0.000000  )
 **************************************************************************
~
```

Exercise 3:
Phonons dispersion in non-polar materials

Exercise 3: Phonons dispersion in non-polar materials

Go to the directory with the input files:

cd ~/ASESMA2025/Day4/example3.phonon.dispersion.Si/

In this directory you will find:

- *README.md* – File describing how to do the exercise
- *Si.scf.in* – Input file for the SCF ground-state calculation
- *Si.ph.in* – Input file for the phonon calculation at Γ
- *Si.q2r.in* – Input file for calculation of Interatomic Force Constants
- *Si.matdyn.in* – Input file for Fourier Interpolation for various q points
- *Si.plotband.in* - Input file for plotting a phonon dispersion
- **reference** – Directory with the reference results

Exercise 3: Phonons dispersion in non-polar materials

Step 1: Perform a Self-Consistent Field ground-state calculation for silicon at the equilibrium structure using the pw.x program.

```
mpirun –np 4 pw.x –in Si.scf.in > Si.scf.out
```

Step 2: Perform a phonon calculation on a uniform grid of q points the ph.x program.

```
mpirun –np 4 ph.x –in Si.ph.in > Si.ph.out
```

Flags for the calculation on a grid
Uniform grid of q points:

$$q_{ijk} = \frac{i-1}{nq1}\boldsymbol{G_2} + \frac{j-1}{nq2}\boldsymbol{G_1} + \frac{k-1}{nq3}\boldsymbol{G_1}$$

```
&inputph
prefix = 'si',
tr2_ph = 1.0d-14,
amass(1) = 28.0855,
ldisp = .true.,
nq1 = 4,
nq2 = 4,
nq3 = 4,
outdir = './tmp'
fildyn = 'Si.dyn',
/
```

Exercise 3: Phonons dispersion in non-polar materials

4x4x4 = 64 **q**-points => **Use of symmetry** => 8 non-equivalent **q** points

The file Si.dyn0 contains a list of the non-equivalent q points (8, in this case).

```
 4   4   4
 8
 0.0000000000000000E+00   0.0000000000000000E+00   0.0000000000000000E+00
-0.2500000000000000E+00   0.2500000000000000E+00  -0.2500000000000000E+00
 0.5000000000000000E+00  -0.5000000000000000E+00   0.5000000000000000E+00
 0.0000000000000000E+00   0.5000000000000000E+00   0.0000000000000000E+00
 0.7500000000000000E+00  -0.2500000000000000E+00   0.7500000000000000E+00
 0.5000000000000000E+00   0.0000000000000000E+00   0.5000000000000000E+00
 0.0000000000000000E+00  -0.1000000000000000E+01   0.0000000000000000E+00
-0.5000000000000000E+00  -0.1000000000000000E+01   0.0000000000000000E+00
```

The phonon code ph.x generates a file for every non-equivalent q point (Si.dyn1, Si.dyn2, ..., Si.dyn8), which contain information about dynamical matrices, phonon frequencies and atomic displacements

Exercise 3: Phonons dispersion in non-polar materials

Step 3: Calculation of the Interatomic Force Constants (IFC) using the q2r.x program

IFCs in reciprocal space (Fourier transform of IFCs):

$$\tilde{C}_{s\alpha,s'\beta}(\boldsymbol{q}) = \frac{\partial^2 \mathrm{E}_{\mathrm{tot}}}{\partial \tilde{\boldsymbol{u}}_{s\alpha}(\boldsymbol{q}) \partial \tilde{\boldsymbol{u}}_{\beta}(\boldsymbol{q})}$$

where α, β are the cartesina direction and s,s' the atomic index

$$C_{s\alpha,s'\beta}(\boldsymbol{R}) = \sum_{\boldsymbol{q_n}} \tilde{C}_{s\alpha,s'\beta}(\boldsymbol{q}) e^{i\boldsymbol{q_n}(\boldsymbol{R}-\boldsymbol{R'})}$$

$\tilde{C}_{s\alpha,s'\beta}(\boldsymbol{q})$ ⟶ $C_{s\alpha,s'\beta}(\boldsymbol{R})$

Fourier transforms of IFCs on a grid of **q** points nq1 x nq2 x nq3 in reciprocal space

IFCs in a supercell nq1 x nq2 x nq3 in real space

Exercise 3: Phonons dispersion in non-polar materials

Step 3: Calculation of the Interatomic Force Constants (IFC) using the q2r.x program

```
mpirun –np 4 q2r.x –in Si.q2r.in > Si.q2r.out
```

```
&input
fildyn = 'Si.dyn',
zasr = 'simple',
flfrc = 'Si444.fc',
/
```

File containing the dynamical matrix

A way to impose the acoustic sum rule (simple, crystal, one-dim, zero-dim, all)

Output file of the interatomic force constants

Note: The denser the grid of q points, the larger the vectors R for which the IFCs are calculated.

Exercise 3: Phonons dispersion in non-polar materials

Step 4: Calculate phonons at generic **q'** points using IFC using the matdyn.x code

$$\tilde{C}_{s\alpha,s'\beta}(\boldsymbol{q}) = \sum_{\boldsymbol{R}} C_{s\alpha,s'\beta}(\boldsymbol{R}) e^{-i\boldsymbol{q}'\boldsymbol{R}}$$

$C_{s\alpha,s'\beta}(\boldsymbol{R})$ → $\tilde{C}_{s\alpha,s'\beta}(\boldsymbol{q}')$

Fourier interpolation

IFC's on a grid in real space

Fourier transforms of IFC's at generic q' points in reciprocal space

```
&input
asr = 'simple',
amass(1) = 28.0855,
flfrc = 'Si444.fc',
flfrq = 'Si.freq'
/
396
0.000000 0.000000 0.000000 0.000000
0.012658 0.000000 0.000000 0.012658...
```

```
mpirun –np 4 matdyn.x –in Si.matdyn.in > Si.matdyn.out
```

File containing the the interatomic force constants from q2r.x

Output file with the interpolated frequencies

Number of q points

Coordinates of the q points

Exercise 3: Phonons dispersion in non-polar materials

Step 5: Plot the phonon dispersion using the plotband.x program and gnuplot.

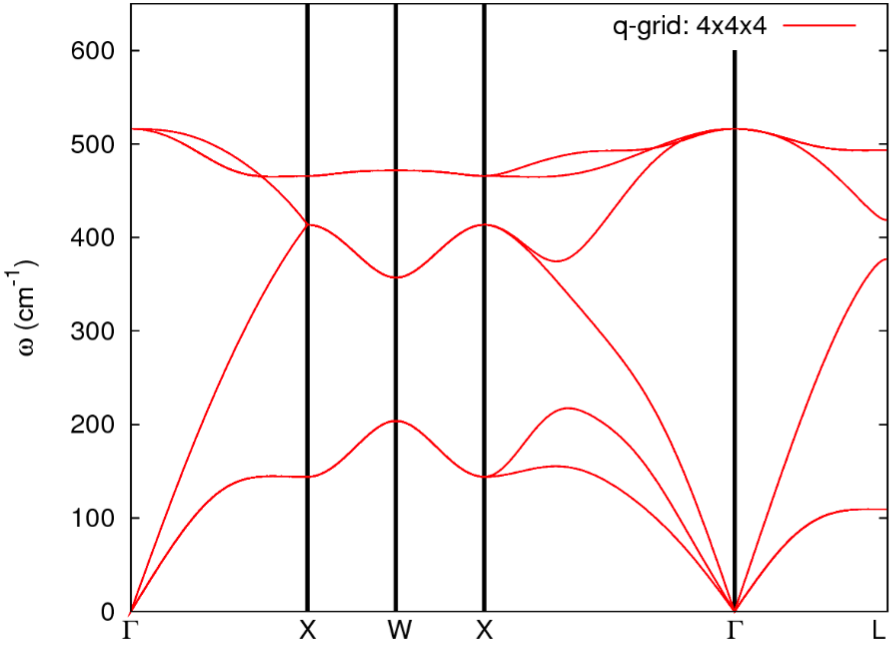
```
plotband.x < Si.plotband.in > Si.plotband.out
```

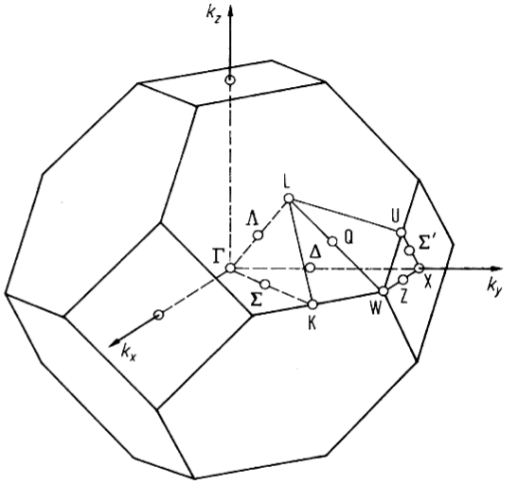
Si.freq	Input file with the frequencies at various q' points
0 600	Range of frequencies for a visualization
freq.plot	Output file with frequencies which will be used for plot
freq.ps	Plot of the dispersion (we will produce another one)
0.0	Fermi level (needed only for band structure plot)
100.0 0.0	Freq. step and reference freq. on the plot freq.ps

Use gnuplot and the file **plot_dispersion.gp** in order to plot the phonon dispersion of silicon (look at the file experimental_data.dat for the experimental reference).
You will get a postscript file phonon_dispersion.eps which you can visualize.

Exercise 3: Phonons dispersion in non-polar materials

Phonon dispersion of silicon along some high-symmetry directions in the Brillouin zone (file phonon_dispersion.eps).





Exercise 3: Phonons dispersion in non-polar materials

How to determine whether the quality of the Fourier interpolation is satisfactory? Compare with the direct calculation (no interpolation)!

Homework-1: Perform a direct phonon calculation (no interpolation) at several **q**' points and make a comparison with the phonon frequencies obtained from the interpolation. (Use exercise2 as an example).
Some **q**' points along the Gamma-X high symmetry line are listed in the file reference/q_points_direct_calc.txt

Homework-2: Perform a phonon dispersion calculation for several q-points grids (eg. 2x2x2, 4x4x4, and 6x6x6) and compare the dispersions. Do they converge?

Exercise 3: Phonons dispersion in non-polar materials

The phonon modes are not always easy to visualize, especially if we are not at Γ. An online phonon visualizer is very helpful in this regard.

https://interactivephonon.materialscloud.io

Let’s click on the link and look at your phonons.

Exercise 4:
Phonons at Gamma in polar materials

Phonons in polar materials

Polar materials in the q = 0 limit: a macroscopic electric field appears as a consequence of the long-range character of the Coulomb interaction (incompatible with Periodic Boundary Conditions).
A non-analytic term must be added to Interatomic Force Constants at **q** = 0:

$$\tilde{C}_{s\alpha,s'\beta}(\boldsymbol{q}) = \tilde{C}^{analytic}_{s\alpha,s'\beta} + \frac{4\pi}{V}\frac{(\boldsymbol{q}\cdot\boldsymbol{Z}^*_s)_\alpha(\boldsymbol{q}\cdot\boldsymbol{Z}^*_s)_\beta}{\boldsymbol{q}\cdot\varepsilon_\infty\cdot\boldsymbol{q}}$$

Effective charges Z^*_s are related to polarization P induced by a lattice

$$Z^*_{s,\alpha\beta} = V\frac{\partial P_\alpha}{\partial u^\beta_s}$$

Dielectric tensor $\varepsilon^{\alpha\beta}_\infty$ is related to polarization P induced by an electric field E:

$$\varepsilon^{\alpha\beta}_\infty = \delta_{\alpha\beta} + 4\pi\left.\frac{\partial P_\alpha}{\partial E_\beta}\right|_{u_s(\boldsymbol{q}=0)=0}$$

All of the above can be calculated from (mixed) second order derivatives of the total energy.

Exercise 4: Phonons at Gamma in polar materials

Go to the directory with the input files:

cd ~/ASESMA2025/Day4/example4.phonon.Gamma.AlAs/

In this directory you will find:

- *README.md* – File describing how to do the exercise
- *AlAs.scf.in* – Input file for the SCF ground-state calculation
- *AlAs.ph.in* – Input file for the phonon calculation at Γ
- *AlAs.dynmat.in* – Input file for Fourier Interpolation for various q points
- ***reference*** – Directory with the reference results

Exercise 4: Phonons at Gamma in polar materials

Step 1: Perform a Self-Consistent Field ground-state calculation for AsAl at the equilibrium structure using the pw.x program.

```
mpirun –np 4 pw.x –in AlAs.scf.in > AlAs.scf.out
```

Step 2: Perform a phonon calculation in Gamma using ph.x.

```
mpirun –np 4 ph.x –in AlAs.ph.in > AlAs.ph.out
```

```
Phonons at Gamma
&inputph
prefix = 'AlAs',
tr2_ph = 1.0d-14,
amass(1) = 26.98,
amass(2) = 74.92,
epsil = .true.
outdir = './tmp'
fildyn = 'AlAs.dyn',
/
0.0 0.0 0.0
```

Exercise 4: Phonons at Gamma in polar materials

In the file **ph.AlAs.out** you will find information about the dielectric tensor and effective charges (BECs)

```
     Effective charges (d Force / dE) in cartesian axis with asr applied:
          atom      1   Al Mean Z*:        4.43445
     E*x (        4.43445         0.00000        -0.00000 )
     E*y (        0.00000         4.43445        -0.00000 )
     E*z (       -0.00000        -0.00000         4.43445 )
          atom      2   As Mean Z*:       -4.43445
     E*x (       -4.43445        -0.00000         0.00000 )
     E*y (       -0.00000        -4.43445         0.00000 )
     E*z (        0.00000         0.00000        -4.43445 )

    Diagonalizing the dynamical matrix

    q = (    0.000000000   0.000000000   0.000000000 )

 **************************************************************************
    freq (    1) =      -0.062455 [THz] =      -2.083289 [cm-1]
    freq (    2) =      -0.062455 [THz] =      -2.083289 [cm-1]
    freq (    3) =      -0.062455 [THz] =      -2.083289 [cm-1]
    freq (    4) =      11.807415 [THz] =     393.852972 [cm-1]
    freq (    5) =      11.807415 [THz] =     393.852972 [cm-1]
    freq (    6) =      11.807415 [THz] =     393.852972 [cm-1]
 **************************************************************************
```

$$Z^*_{s,\alpha\beta} = \frac{V}{e}\frac{\partial P_\alpha}{\partial u_{s,\beta}(\boldsymbol{q}=0)} = \frac{1}{e}\frac{\partial F_{s\beta}}{\partial \mathcal{E}_\alpha(\boldsymbol{q}=0)}$$

No LO-TO splitting

Exercise 4: Phonons at Gamma in polar materials

Step 3: Impose Acoustic Sum Rule and add the non analytic LO-TO splitting using the dynmat.x program

```
mpirun –np 4 dynmat.x –in AlAs.dynmat.in > AlAs.dynmat.out
```

```
&input
  fildyn = 'AlAs.dyn',
  asr='simple',
  amass(1)=26.98,
  amass(2)=74.92
  q(1) = 1.0,
  q(2) = 0.0,
  q(3) = 0.0
/
```

Direction in the Brillouin zone along which we want to compute the LO-TO splitting

```
     IR activities are in (D/A)^2/amu units

# mode    [cm-1]     [THz]       IR
    1     -0.00    -0.0000    0.0000
    2      0.00     0.0000    0.0000
    3      0.00     0.0000    0.0000
    4    393.86    11.8075   22.8709
    5    393.86    11.8075   22.8709
    6    430.19    12.8969   22.8709
```

LO-TO splitting

Exercise 4: Phonons at Gamma in polar materials

Step 3: Impose Acoustic Sum Rule and add the non analytic LO-TO splitting using the dynmat.x program

```
mpirun –np 4 dynmat.x –in AlAs.dynmat.in > AlAs.dynmat.out
```

```
&input
  fildyn = 'AlAs.dyn',
  asr='simple',
  amass(1)=26.98,
  amass(2)=74.92
  q(1) = 1.0,
  q(2) = 0.0,
  q(3) = 0.0
/
```

IR activities are in (D/A)^2/amu units

# mode	[cm-1]	[THz]	IR
1	-0.00	-0.0000	0.0000
2	0.00	0.0000	0.0000
3	0.00	0.0000	0.0000
4	393.86	11.8075	22.8709
5	393.86	11.8075	22.8709
6	430.19	12.8969	22.8709

IR intensities $$I_{IR}(\nu) = \sum_{\alpha} \left| \sum_{s\beta} Z^{*\alpha\beta}_{s} u^{\beta}_{s}(\nu) \right|^2$$

can be calculated directly from effective charges and phonon displacement patterns

Exercise 5 (Optional):
Phonons dispersion in polar materials

Exercise 5: Phonons dispersion in polar materials

Go to the directory with the input files:

cd ~/ASESMA2025/Day4/example5.phonon.dispersion.AlAs/

In this directory you will find:

- *README.md* – File describing how to do the exercise
- *AlAs.scf.in* – Input file for the SCF ground-state calculation
- *AlAs.ph.in* – Input file for the phonon calculation at Γ
- *AlAs.q2r.in* – Input file for calculation of Interatomic Force Constants
- *AlAs.matdyn.in* – Input file for Fourier Interpolation for various q points
- *AlAs.plotband.in* – Input file for plotting a phonon dispersion
- ***reference*** – Directory with the reference results

Exercise 5: Phonons dispersion in polar materials

Step 1: Perform a Self-Consistent Field ground-state calculation at the equilibrium structure using the pw.x program.

```
mpirun –np 4 pw.x –in AlAs.scf.in > Si.scf.out
```

Step 2: Perform a phonon calculation on a uniform grid of q points the ph.x program.

```
mpirun –np 4 ph.x –in AlAs.ph.in > AlAs.ph.out
```

Step 3: Calculation of the Interatomic Force Constants (IFC) using the q2r.x program

```
mpirun –np 4 q2r.x –in AlAs.q2r.in > AlAs.q2r.out
```

Step 4: Calculate phonons at generic **q**' points using IFC using the matdyn.x code

```
mpirun –np 4 matdyn.x –in AlAs.matdyn.in > AlAs.matdyn.out
```

Step 5: Plot the phonon dispersion using the plotband.x program and gnuplot.

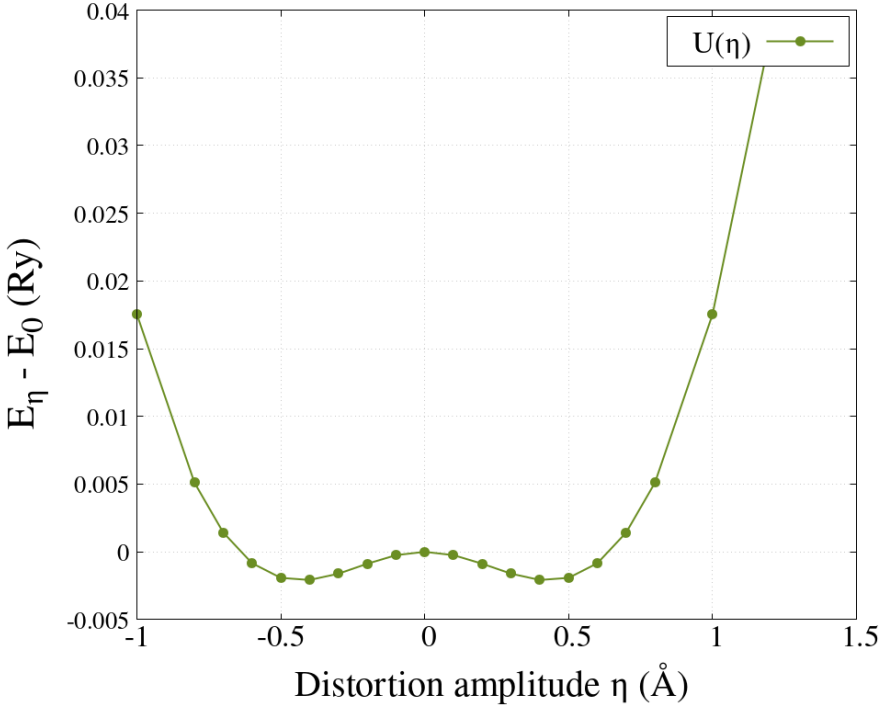
```
plotband.x < AlAs.plotband.in > AlAs.plotband.out
```

(Note: some parts of the input files are left empty for you to fill !

Exercise 6 (Optional):
Phonons dispersion of unstable materials

Negative phonon frequencies

Phonons are the solution of the secular equation: $\sum_{s',\beta} \tilde{D}_{s\alpha,s'\beta}(\boldsymbol{q})\tilde{\boldsymbol{u}}_{s'\beta}(\boldsymbol{q}) = \omega_{\boldsymbol{q}}^2 \tilde{\boldsymbol{u}}_{s\alpha}(\boldsymbol{q})$



$$\tilde{D}_{s\alpha,s'\beta}(\boldsymbol{q}) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{\boldsymbol{R},\boldsymbol{R'}} \frac{\partial^2 \mathrm{E_{tot}}}{\partial u_{s\alpha}(\boldsymbol{R}) \partial u_{s'\beta}(\boldsymbol{R'})} e^{i\boldsymbol{q}(\boldsymbol{R}-\boldsymbol{R'})}$$

If you are not in the minimum of the PES, you will get **negative phonons frequencies** (imaginary values of $\omega_{\mathbf{q}}$)

(where η *is* : $\eta \boldsymbol{u}_k = \eta \boldsymbol{\epsilon}_k e^{i\boldsymbol{q}\boldsymbol{R}_l}$)

Exercise 6: Negative phonons

Go to the directory with the input files:

cd ~/ASESMA2025/Day4/example6.negative.phonon/

In this directory you will find:

- *README.md* – File describing how to do the exercise
- *Si.scf.in* – Input file for the SCF ground-state calculation
- *Si.ph.in* – Input file for the phonon calculation at Γ
- *Si.q2r.in* – Input file for calculation of Interatomic Force Constants
- *Si.matdyn.in* – Input file for Fourier Interpolation for various q points
- *Si.plotband.in* – Input file for plotting a phonon dispersion
- ***reference*** – Directory with the reference results

Exercise 6: Negative phonons

Step 1: Perform a Self-Consistent Field ground-state calculation at the equilibrium structure using the pw.x program.

```
mpirun –np 4 pw.x –in Si.scf.in > Si.scf.out
```

Step 2: Perform a phonon calculation on a uniform grid of q points the ph.x program (here we use 2x2x2).

```
mpirun –np 4 ph.x –in Si.ph.in > Si.ph.out
```

Step 3: Calculation of the Interatomic Force Constants (IFC) using the q2r.x program

```
mpirun –np 4 q2r.x –in Si.q2r.in > Si.q2r.out
```

Step 4: Calculate phonons at generic **q**' points using IFC using the matdyn.x code

```
mpirun –np 4 matdyn.x –in Si.matdyn.in > Si.matdyn.out
```

Step 5: Plot the phonon dispersion using the plotband.x program and gnuplot.

```
plotband.x < Si.plotband.in > Si.plotband.out
```

Exercise 6: Negative phonons

- Look at the results of the phonon dispersion: can you explain what you see? What is the difference with the band dispersion in exercise3?

Thank you!

Questions?