

Outline

Introduction

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Phonons

Normal mode frequencies, ω , and eigenvectors, \mathbf{u} , are determined by the secular equation:

$$\sum_{s'\beta} D_{s\alpha s'\beta}(\mathbf{q}) \mathbf{u}_{s'\beta}(\mathbf{q}) = \omega_{\mathbf{q}}^2 \mathbf{u}_{s\alpha}(\mathbf{q})$$

where

$$D_{s\alpha s'\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{\nu} \boxed{\frac{\partial^2 E_{tot}}{\mathbf{u}_{\mu s\alpha} \mathbf{u}_{\nu s'\beta}}} e^{i\mathbf{q}(\mathbf{R}_{\nu} - \mathbf{R}_{\mu})}$$

Interatomic force constants (IFC)

is the **dynamical matrix** of the solid.

This matrix can be calculated from the linear response $\partial n(\mathbf{r}) / \partial \mathbf{u}_{s\alpha}(\mathbf{q})$ and diagonalized to get phonon modes at \mathbf{q} .

Exercise 1: phonon calculations at Γ

Part 1: Calculation of the phonon frequencies of silicon at Γ

To perform the calculation use the script `run_ph_G_Si.sh` in the directory `exercise1`:

```
prompt> ./run_ph_G_Si.sh &
```

The script allows you to perform:

- 1) A scf calculation for silicon *at the equilibrium structure* using `pw.x`
- 2) A phonon calculation at Γ using `ph.x`

Exercise 1: phonon calculations at Γ

1) A scf calculation for silicon *at the equilibrium structure* using pw.x

```
&control
  calculation='scf'
  restart_mode='from_scratch',
  prefix='si',
  pseudo_dir = '../',
/
&system
 ibrav= 2,
  celldm(1) =10.187,
  nat= 2,
  ntyp= 1,
  ecutwfc =16
/
&electrons
  conv_thr = 1.0d-10
/
ATOMIC_SPECIES
Si 0.0 Si.pz-rrkj.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



Exercise 1: phonon calculations at Γ

2) Phonon calculation at Γ using ph.x

Input file si.phG.in of *ph.x*:

```
phonons at Gamma
&inputph
```

```
  prefix='si',
```

```
  epsilon=.true.,
```

```
  fildyn='dyn.G',
```

```
  tr2_ph=1.0d-14,
```

```
/
0.0 0.0 0.0
```

← Same prefix as in the scf calculation
(and same outdir)

← To calculate the dielectric tensor and
the effective charges

← File containing the dynamical matrix

← Threshold

↑
q point (Γ)

Exercise 1: phonon calculations at Γ

Output file si.phG.out :

Dielectric constant in cartesian axis

```
(      13.99782      0.00000      0.00000 )
(      0.00000      13.99782      0.00000 )
(      0.00000      0.00000     13.99782 )
```

Effective charges (d Force / dE) in cartesian axis

```
  atom      1      Si
Ex (      -0.07434      0.00000      0.00000 )
Ey (      0.00000     -0.07434      0.00000 )
Ez (      0.00000      0.00000     -0.07434 )

  atom      2      Si
Ex (      -0.07434      0.00000      0.00000 )
Ey (      0.00000     -0.07434      0.00000 )
Ez (      0.00000      0.00000     -0.07434 )
```

Diagonalizing the dynamical matrix

```
q = (      0.000000000      0.000000000      0.000000000 )
```

```
omega( 1) =      0.081752 [THz] =      2.726975 [cm-1]
omega( 2) =      0.081752 [THz] =      2.726975 [cm-1]
omega( 3) =      0.081752 [THz] =      2.726975 [cm-1]
omega( 4) =     15.549026 [THz] =     518.663131 [cm-1]
omega( 5) =     15.549026 [THz] =     518.663131 [cm-1]
omega( 6) =     15.549026 [THz] =     518.663131 [cm-1]
```

Exercise 1: phonon calculations at Γ

Dynamical matrix file dyn.G :

Diagonalizing the dynamical matrix

q = (0.000000000 0.000000000 0.000000000)

```
omega( 1) = 0.081752 [THz] = 2.726975 [cm-1]
( 0.400413 0.000000 -0.325855 0.000000 -0.483206 0.000000 )
( 0.400413 0.000000 -0.325855 0.000000 -0.483206 0.000000 )
omega( 2) = 0.081752 [THz] = 2.726975 [cm-1]
( 0.578307 0.000000 0.294894 0.000000 0.280354 0.000000 )
( 0.578307 0.000000 0.294894 0.000000 0.280354 0.000000 )
omega( 3) = 0.081752 [THz] = 2.726975 [cm-1]
( 0.072322 0.000000 -0.553946 0.000000 0.433490 0.000000 )
( 0.072322 0.000000 -0.553946 0.000000 0.433490 0.000000 )
```

**Acoustic
modes**



```
omega( 4) = 15.549026 [THz] = 518.663131 [cm-1]
( -0.445151 0.000000 0.547867 0.000000 0.041012 0.000000 )
( 0.445151 0.000000 -0.547867 0.000000 -0.041012 0.000000 )
omega( 5) = 15.549026 [THz] = 518.663131 [cm-1]
( -0.535639 0.000000 -0.444530 0.000000 0.124435 0.000000 )
( 0.535639 0.000000 0.444530 0.000000 -0.124435 0.000000 )
omega( 6) = 15.549026 [THz] = 518.663131 [cm-1]
( 0.122195 0.000000 0.047270 0.000000 0.694863 0.000000 )
( -0.122195 0.000000 -0.047270 0.000000 -0.694863 0.000000 )
```

**Optical
modes**



Exercise 1: phonon calculations at Γ

Problems with the frequency of the acoustic phonon modes at Γ and with the effective charges.

Because of numerical inaccuracies the interatomic force constants and the effective charges do not strictly satisfy the following rules due to the translational invariance of the system:

$$\text{Translational rules} \quad \sum_{\mathbf{L}, j} C_{\alpha i, \beta j}(\mathbf{R}_{\mathbf{L}}) = 0 \quad \forall \alpha, \beta \text{ and } i$$

$$\sum_j Z_{j, \alpha}^* \beta = 0 \quad \forall \alpha, \beta$$

Reasons for numerical inaccuracies:

- Insufficiently accurate scf thresholds (in pw.x and/or in ph.x).
DO NOT USE large thresholds in pw.x to save time !!
- XC energy is computed in real space. More problematic for GGA than in LDA. For US pseudopotentials it could require large *ecutrho*.
- k point sampling not accurate enough (in particular Z^* and ϵ require a very dense k-point sampling).

Exercise 1: phonon calculations at Γ

The ***acoustic sum rules*** can however be imposed after the phonon calculation.

To do this we use the code *dynmat.x* which imposes the acoustic sum rules on the elements of the dynamical matrix and diagonalizes it.

The input of *dynmat.x* in this case is:

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

← File containing the dynamical matrix
← A way to impose the acoustic sum rules
(if you put 'no' instead of 'simple'
the code does not impose the asr)

To submit the calculation:

```
prompt> dynmat.x < si.dynmat.in > si.dynmat.out
```

Exercise 1: phonon calculations at Γ

Dynmat.x produces the file *dynmat.out* which contains the new frequencies:

```
diagonalizing the dynamical matrix ...
q =          0.0000          0.0000          0.0000
*****
      omega( 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   )
      omega( 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   )
      omega( 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   )
      omega( 4) =         15.548811 [THz] =        518.655959 [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   )
      omega( 5) =         15.548811 [THz] =        518.655959 [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   )
      omega( 6) =         15.548811 [THz] =        518.655959 [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   )
*****
```

Dynmat.x creates also the file *dynmat.axsf* which contains the phonon eigendisplacements. You can use xcrysden to visualize them:

```
prompt> xcrysden -axsf dynmat.axsf &
```

Exercise 2: phonons in polar materials

Polar materials in the $\mathbf{q}=0$ limit: a macroscopic electric field appear as a consequence of long-rangeness of Coulomb interactions. Incompatible with Periodic Boundary Conditions! A non-analytic term must be added to force constants at $\mathbf{q} = 0$:

$${}^{na}\tilde{C}_{st}^{\alpha\beta} = \frac{4\pi (\mathbf{q} \cdot \mathbf{Z}_s^*)_{\alpha} (\mathbf{q} \cdot \mathbf{Z}_t^*)_{\beta}}{\Omega \mathbf{q} \cdot \boldsymbol{\epsilon}^{\infty} \cdot \mathbf{q}}$$

Effective charges \mathbf{Z}^* are related to polarization \mathbf{P} induced by a lattice distortion:

$$Z_s^{\alpha\beta} = \Omega \frac{\partial P_{\alpha}}{\partial u_s^{\beta}(\mathbf{q} = 0)}.$$

Dielectric tensor $\epsilon_{\infty}^{\alpha\beta}$ are related to polarization induced by an electric field \mathbf{E} :

$$\epsilon_{\infty}^{\alpha\beta} = \delta_{\alpha\beta} + 4\pi \left. \frac{\partial P_{\alpha}}{\partial E_{\beta}} \right|_{\mathbf{u}_s(\mathbf{q}=0)=0}.$$

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

Exercise 2: phonons in polar materials

Part 2: Phonons in polar materials

Use the script `run_ph_G_AlAs.sh` to calculate the phonons at Γ :

prompt> ./run_ph_G_AlAs.sh &

```
Dielectric constant in cartesian axis
(      9.33612      0.00000      0.00000 )
(      0.00000      9.33612      0.00000 )
(      0.00000      0.00000      9.33612 )
Effective charges (d Force / dE) in cartesian axis
  atom      1      Al
Ex (      2.12370      0.00000      0.00000 )
Ey (      0.00000      2.12370      0.00000 )
Ez (      0.00000      0.00000      2.12370 )
  atom      2      As
Ex (     -2.17270      0.00000      0.00000 )
Ey (      0.00000     -2.17270      0.00000 )
Ez (      0.00000      0.00000     -2.17270 )
Diagonalizing the dynamical matrix
q = (      0.000000000      0.000000000      0.000000000 )
*****
omega( 1) =      0.155039 [THz] =      5.171595 [cm-1]
omega( 2) =      0.155039 [THz] =      5.171595 [cm-1]
omega( 3) =      0.155039 [THz] =      5.171595 [cm-1]
omega( 4) =     11.220317 [THz] =     374.271992 [cm-1]
omega( 5) =     11.220317 [THz] =     374.271992 [cm-1]
omega( 6) =     11.220317 [THz] =     374.271992 [cm-1]
*****
```

**No LO-TO
splitting**

Exercise 2: phonons in polar materials

To add the non-analytic term to the force constants and recalculate the frequencies we use dynmat.x.

In this case the input for dynmat.x is:

```
&input
  fildyn='dyn.G',
  asr='simple',
  q(1)=1.d0, q(2)=0.d0, q(3)=0.d0
```

← Direction for the LO-TO splitting.

Re-calculate the phonons at Γ :

```
prompt> dynmat.x < alas.dynmat.in > alas.dynmat.out
```

Check the output file :

#	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		374.24	11.2195	5.3672
5		374.24	11.2195	5.3672
6		410.67	12.3115	5.3672

**LO-TO
splitting**

Exercise 2: phonons in polar materials

#	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		374.24	11.2195	5.3672
5		374.24	11.2195	5.3672
6		410.67	12.3115	5.3672

Infrared Intensities:

$$I_{IR}(\nu) = \sum_{\alpha} \left| \sum_{s\beta} Z_s^{\star\alpha\beta} U_s^{\beta}(\nu) \right|^2$$

can be calculated directly from effective charges and phonon displacement patterns.

Exercise 3: phonon dispersion calculations

Phonon calculation for $q \neq 0$

The procedure to calculate phonons for $q \neq 0$ is the same as the one for a calculation at Γ .

Modify the script `run_ph_G_Si.sh` and calculate the phonons at $X = (0,0,1)$:

- 1) `prompt> cp ../exercisel/run_ph_G_Si.sh run_ph_X_Si.sh`
- 2) Use your favorite editor to remove `epsil=.true.` (that works only at Γ), change the q point and the name of the dynamical matrix.
- 3) Execute the new script:

```
prompt> ./run_ph_X_Si.sh &
```

Notice that the output file for the phonon calculation is slightly different from the one at $q=0$. It is because for $q \neq 0$ the code has to calculate also the wavefunctions ψ_{k+q} (in addition to the ψ_k 's in the scf calculation).

Notice also that the symmetry of the *small group of q* is used (not the crystal symmetry).

Exercise 3: phonon dispersion calculations

First step: Phonon calculation on a grid of q points

Modify the script `run_ph_X_Si.sh` as described below.

1) **prompt> cp run_ph_X_Si.sh run_ph_Si.sh**

2) The script should allow you to perform both scf and phonon calculations.
The input file for the phonon calculations should be like this:

```
phonons on a grid
&inputph
  prefix='si',
  epsil=.true.,
  ldisp=.true.,
  fildyn='dyn',
  nq1=4,
  nq2=4,
  nq3=4,
  tr2_ph=1.0d-14,
/
```

Option for the calculation on a grid

Uniform grid of q points

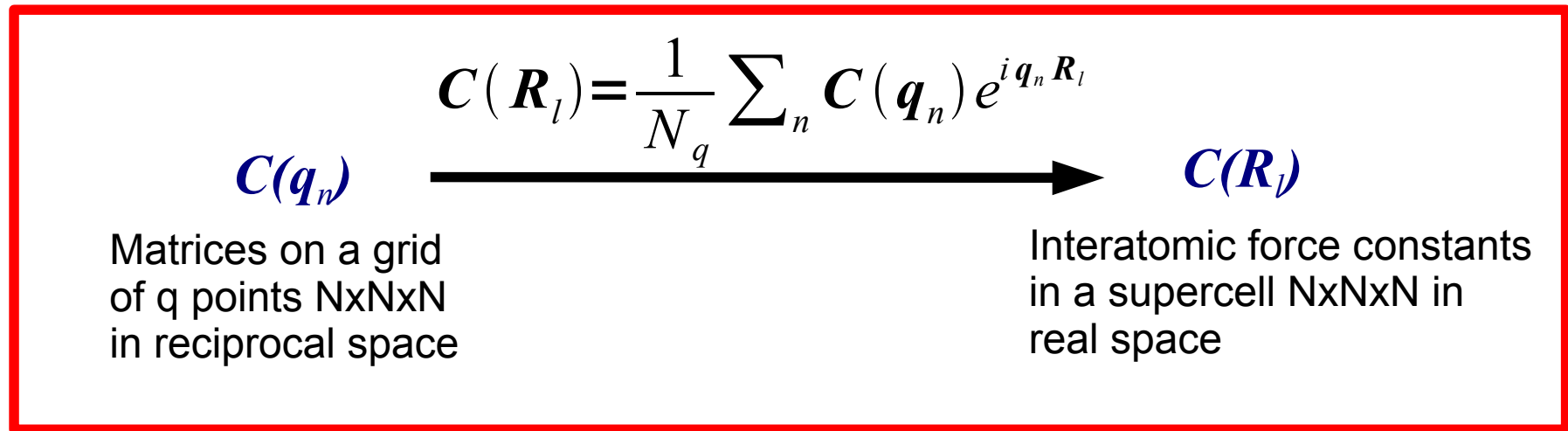
$$\mathbf{q}_{ijk} = \frac{i-1}{n_1}\mathbf{G}_1 + \frac{j-1}{n_2}\mathbf{G}_2 + \frac{k-1}{n_3}\mathbf{G}_3$$

The phonon code generates the files of the dynamical matrices on the specified grid of points. The files are **dyn1**, **dyn2**, ... **dyn8**.

The file **dyn0** contains the list of the inequivalent q points (8, in this case).

Exercise 3: phonon dispersion calculations

Second step: calculation of the interatomic force constants



We use the code q2r.x. The input file for q2r.x is:

```
&input  
  fildyn='dyn',  
  zasr='simple',  
  flfrc='si.444.fc'  
/
```

← Dynamical matrices from the phonon calculation

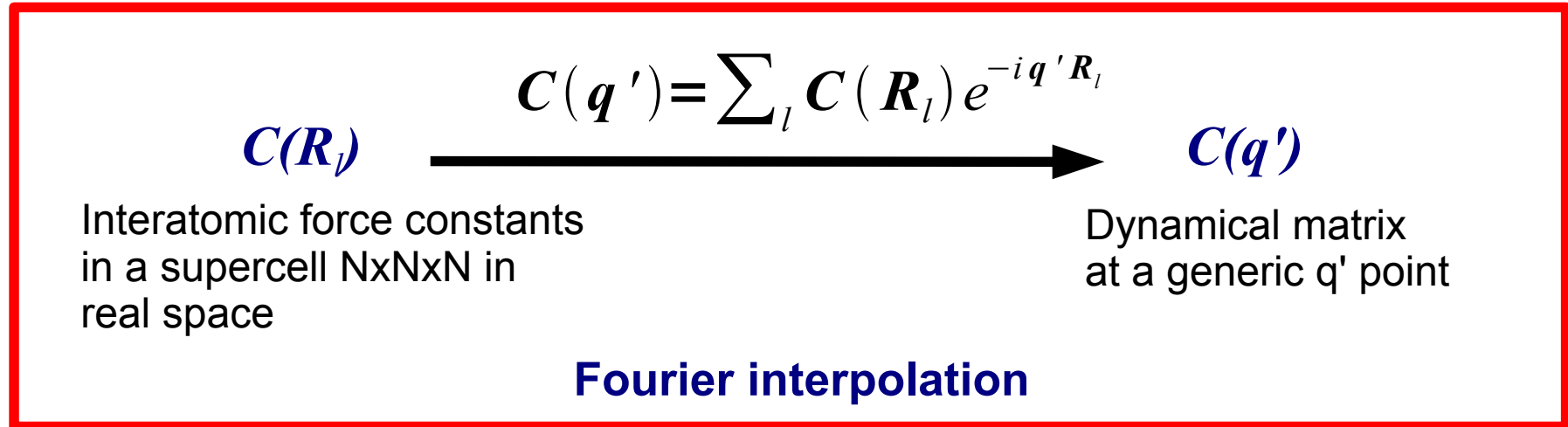
← Output file of the interatomic force constants

To perform the calculation:

```
prompt> q2r.x < q2r.in > q2r.out
```

Exercise 3: phonon dispersion calculations

Third step: phonons at a generic q' point using the IFC



We use the code `matdyn.x`. The input file for `matdyn.x` is:

```
&input
  asr='simple',
  amass(1)=28.0855,
  flfrc='si.444.fc',
  flfrq='si.freq'
/
1
0.300000 0.200000 0.050000
```

IFC input file
Output file of the frequencies
Number of q points
List of q points

To perform the calculation:

```
prompt> matdyn.x < matdyn_ex.in > matdyn_ex.out
```

Exercise 3: phonon dispersion calculations

Si phonon dispersion

Using the script `run_dispersion_Si.sh` you can calculate and generate a plot of the phonon dispersion:

```
prompt> ./run_dispersion_Si.sh &
```

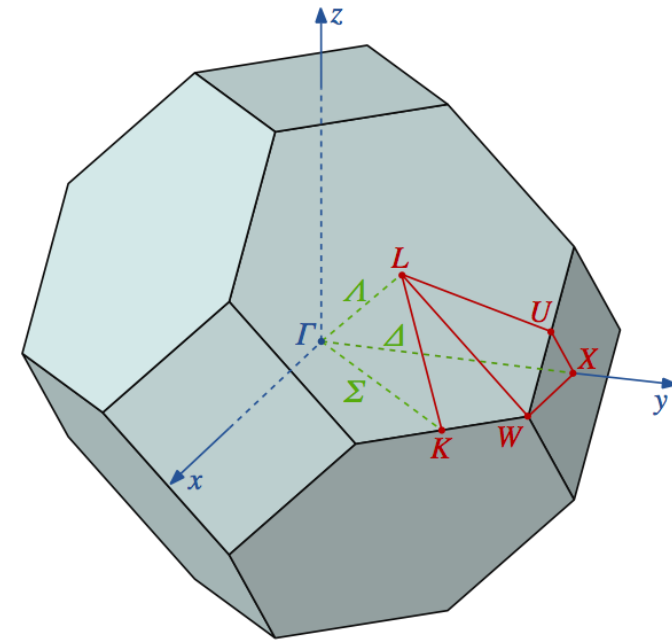
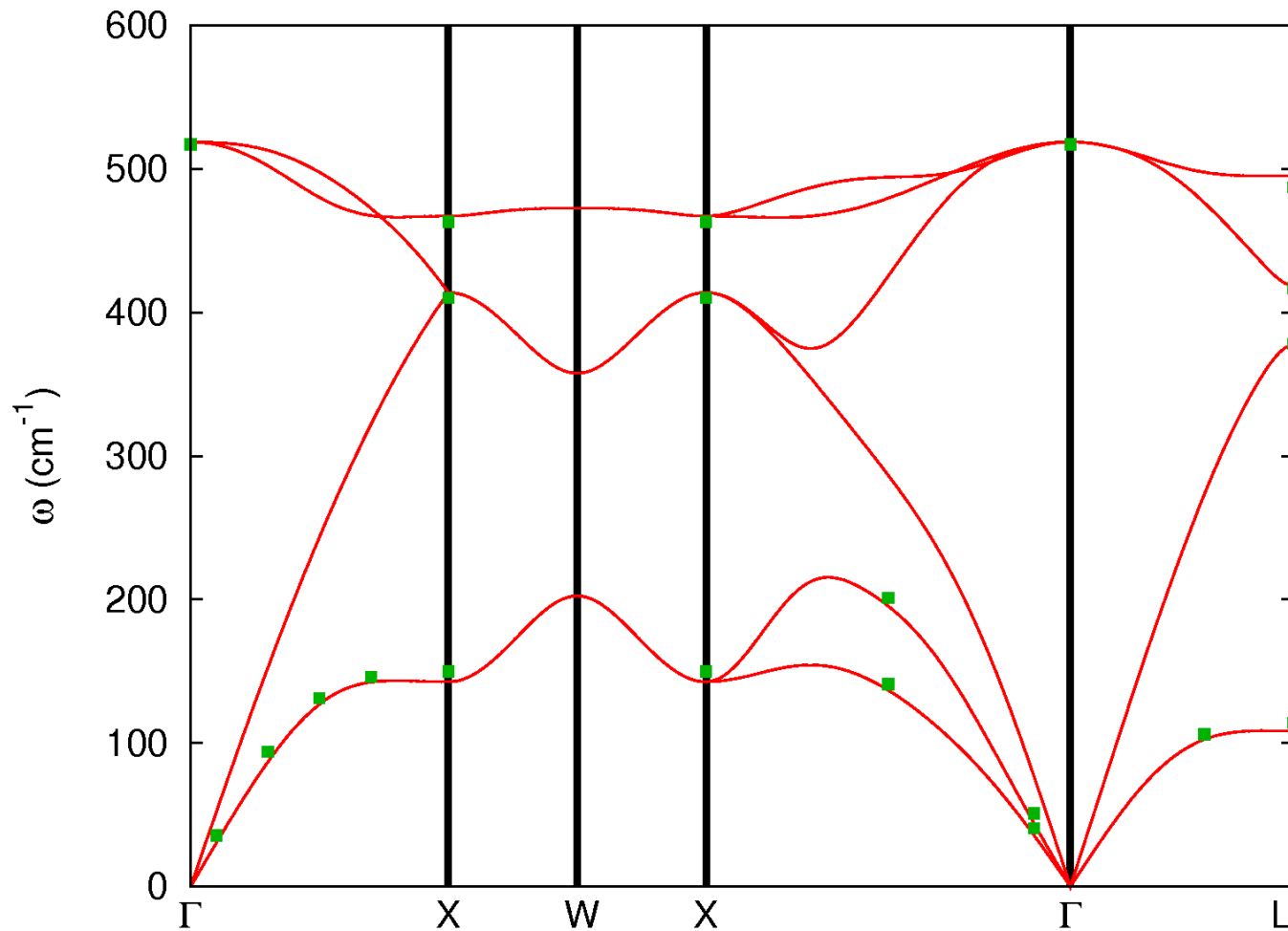
The script includes a *matdyn.x* calculation on a list of q points (along particular lines in the Brillouin zone) and a *plotband.x* post-processing calculation that generates a user-friendly file of the frequencies and a postscript figure.

Using a gnuplot script (*plot_dispersion.gnu*) you can plot the theoretical results together with some experimental data (exp.dat):

```
prompt> gnuplot plot_dispersion.gnu
```

Exercise 3: phonon dispersion calculations

Si phonon dispersion (file gnuplot_dispersion.eps)



Brillouin zone of a FCC

Exercise 3: phonon dispersion calculations

Si vibrational density of states

The code matdyn.x can also be used to calculate the phonon density of states. In this case the input file should be like this:

```
&input
  asr='simple',
  amass(1)=28.0855,
  flfrc='si.444.fc',
  flfrq='si.dos.freq'
  dos=.true.,
  fldos='si.dos'
  deltaE=1.d0,
  nk1=4, nk2=4, nk3=4,
/
```

← Option for a DOS calculation

← Energy interval

← Grid of q points for the DOS calculation

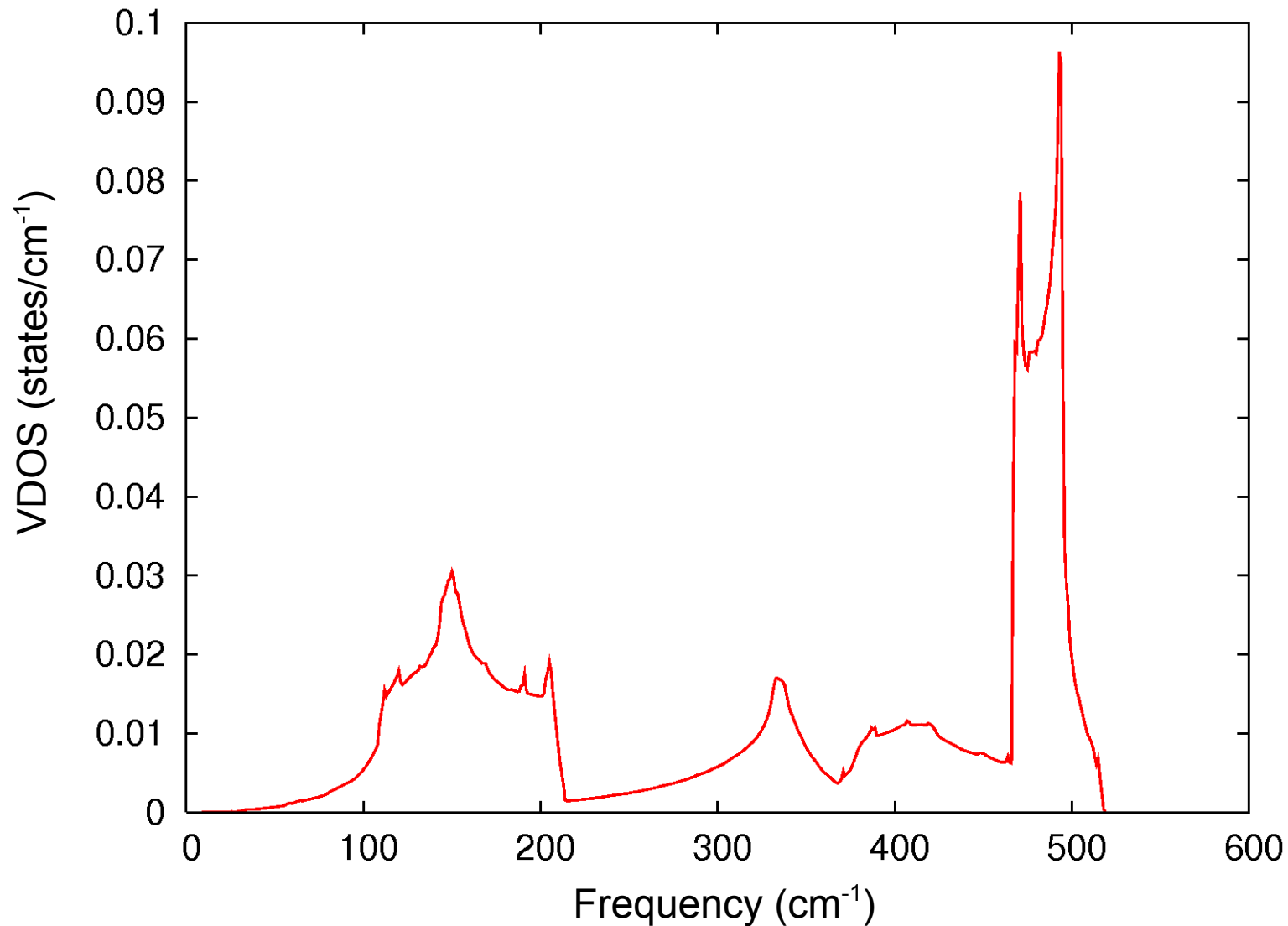
Modify the matdyn.x input file and perform the calculation.
You can use the gnuplot script plot_dos.gnu to generate a picture.

prompt> gnuplot plot_dos.gnu

Calculate the phonon density of states using different grid of q points.
Which grid gives a converged result?

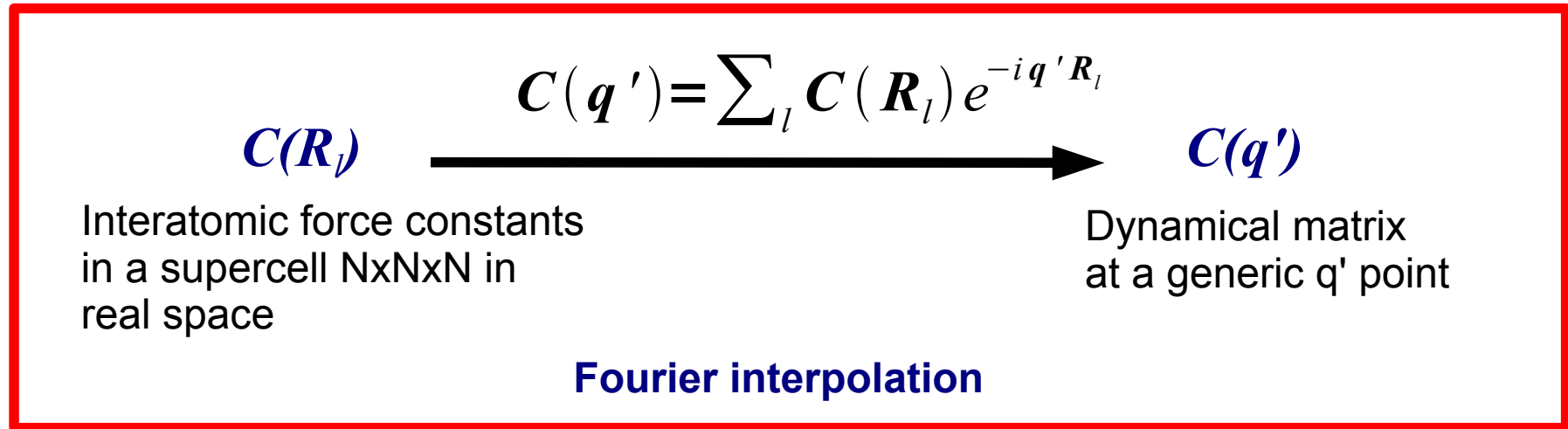
Exercise 3: phonon dispersion calculations

Si vibrational density of states



Notice that the VDOS is normalized to $3N_{\text{at}}$, where N_{at} is the number of

Exercise 4: checking the Fourier interpolation



We need to check if the Fourier interpolation works properly.

To do that we can calculate:

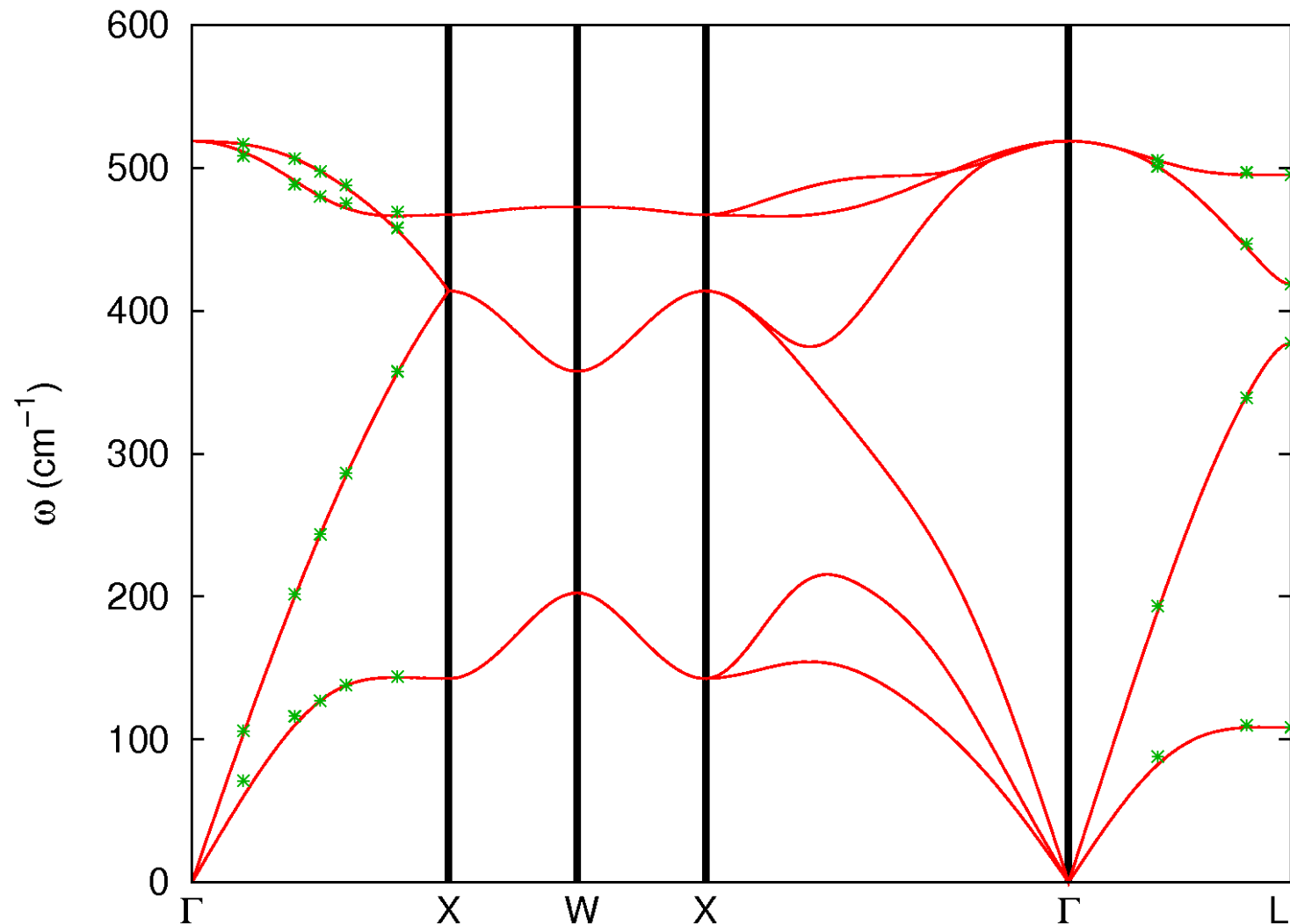
- 1) the phonon frequencies at a certain q point (not belonging to the grid on which we calculated the dynamical matrices) using `matdyn.x` and our file of the interatomic force constants (from exercise3).
- 2) the phonon frequencies at the same point using `ph.x` (i.e. performing the *ab initio* calculation).

and compare the results.

You can run a `ph.x` calculation modifying the script of exercise3 and perform a `matdyn.x` calculation as in exercise3.

Exercise 4: checking the Fourier interpolation

You can use the script `run_check_Si.sh` and use `plot_check.gnu`
Where the comparison is done automatically for a few q points.



Exercise 4: checking the Fourier interpolation

The Fourier interpolation works if the interatomic force constants are known on a sufficiently large supercell (i.e, large enough grid of \mathbf{q} points in the phonon calculation).

There are cases in which the interatomic force constants are long range and the Fourier interpolation does not work properly:

- 1) When there are Kohn anomalies in metals. In this case the dynamical matrices are not a smooth function of \mathbf{q} and the interatomic force constants are long range.
- 2) In polar insulators where the atomic displacements generate long range electrostatic interactions and the dynamical matrix is non analytic for $\mathbf{q} \rightarrow 0$. As we have seen, this case, however, can be dealt with by calculating the Born effective charges and the dielectric tensor of the material.