Tutorial on phonon calculations with Quantum-Espresso

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Outline

Phonons and related quantities

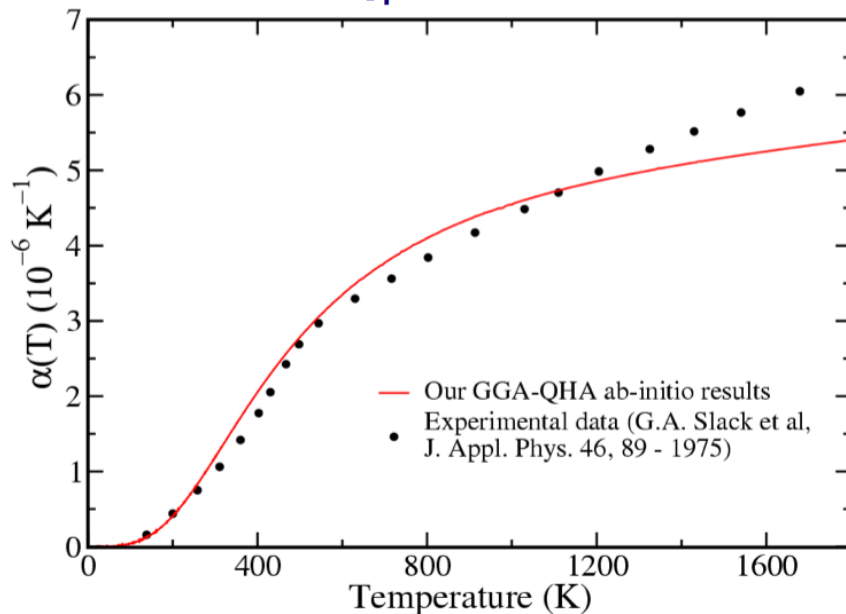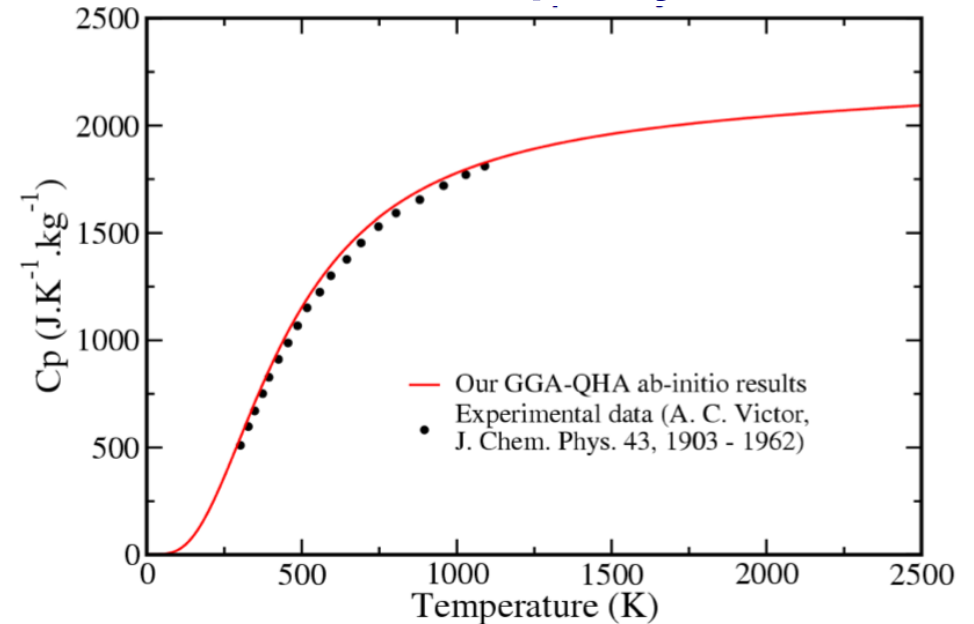## Phonon dispersion of diamond
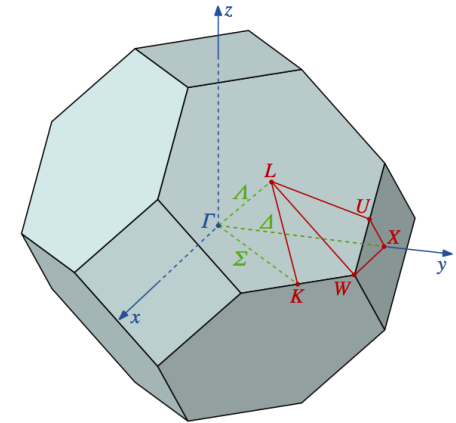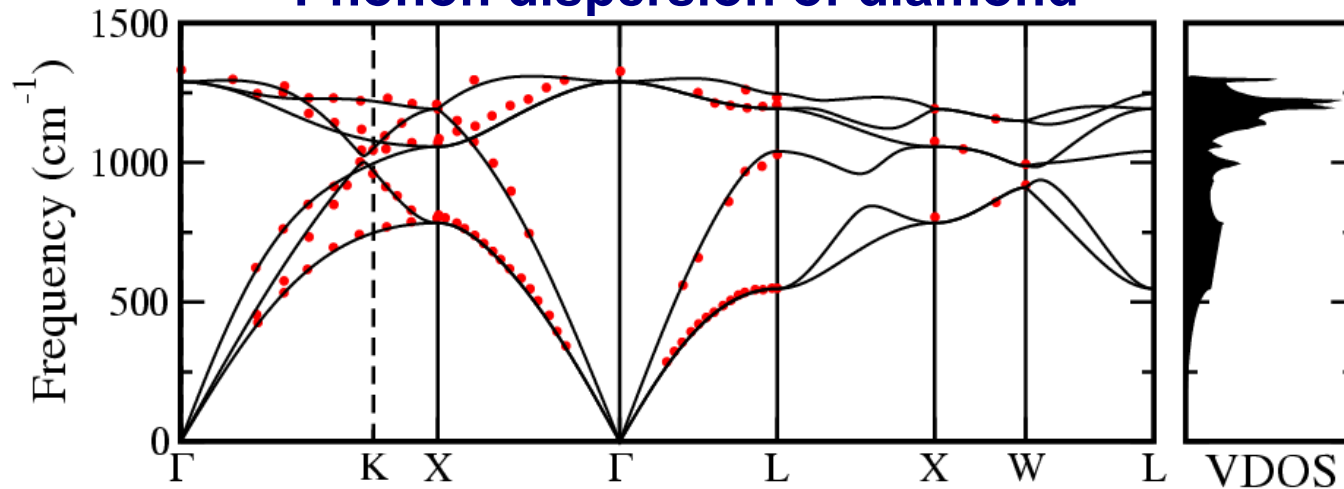
Brillouin zone of a FCC

Thermal expansion coefficient

Heat capacity

N.Mounet and N.Marzari, PRB **71**, 205214 (2005)

Phonons

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

$$\sum_{s'\beta} D_{s\alpha s'\beta}(\boldsymbol{q}) \, \boldsymbol{u}_{s'\beta}(\boldsymbol{q}) = \omega_q^2 \, \boldsymbol{u}_{s\alpha}(\boldsymbol{q})$$

where

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

Interatomic force constants (IFC)

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

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

    epsil=.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 )
      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 )
 **************************************************************
```

Acoustic modes

●→ ●→

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:

Translational rules
$$\sum_{L,j} C_{\alpha i, \beta j}(\mathbf{R_L}) = 0 \qquad \forall \; \alpha, \beta \text{ and } i$$

$$\sum_{j} Z^*_{j,\alpha \beta} = 0 \qquad \forall \; \alpha, \beta$$

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 dyagonalizes 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 $\mathbf{q} = 0$:

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

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

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

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

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

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:

$$I_{IR}(\nu) = \sum_{\alpha} \left| \sum_{s\beta} Z^{\star\alpha\beta}_s U^\beta_s(\nu) \right|^2$$

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 ../exercise1/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.              Option for the calculation on a grid
   fildyn='dyn',
   nq1=4,
   nq2=4,                    Uniform grid of q points
   nq3=4,
   tr2_ph=1.0d-14,
 /
```
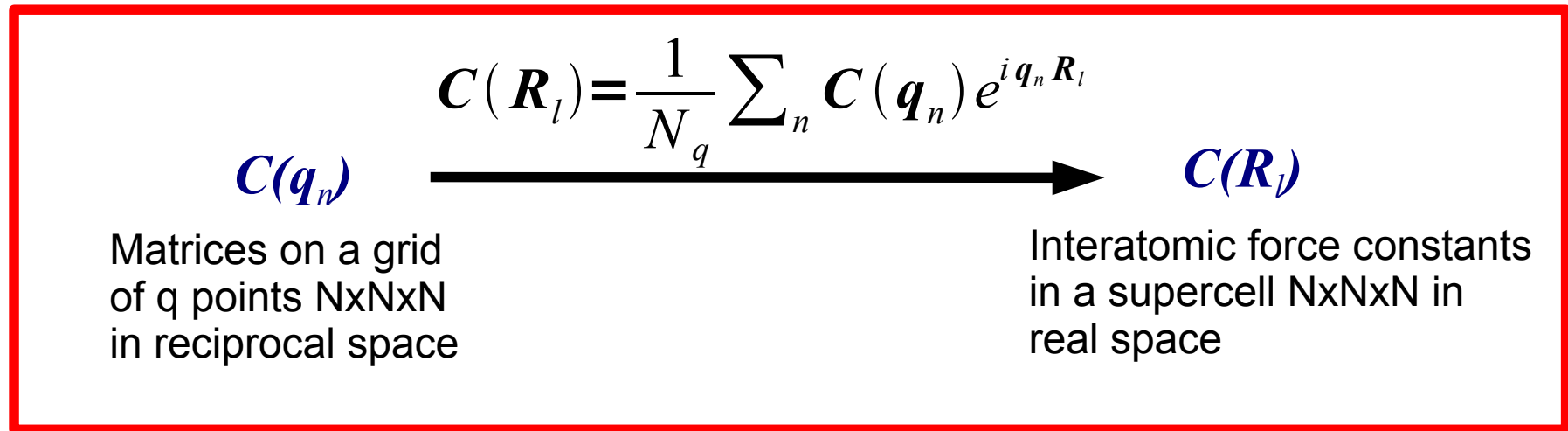
$$q_{ijk} = \frac{i-1}{n_1}\mathbf{G}_1 + \frac{j-1}{n_2}\mathbf{G}_2 + \frac{k-1}{n_3}\mathbf{G}_3$$

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

$$C(R_l) = \frac{1}{N_q} \sum_n C(q_n) e^{i q_n R_l}$$

$C(q_n)$ ───────────────▶ $C(R_l)$

Matrices on a grid
of q points NxNxN
in reciprocal space

Interatomic force constants
in a supercell NxNxN in
real space

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

```
&input
  fildyn='dyn',
  zasr='simple',
  flfrc='si.444.fc'
/
```
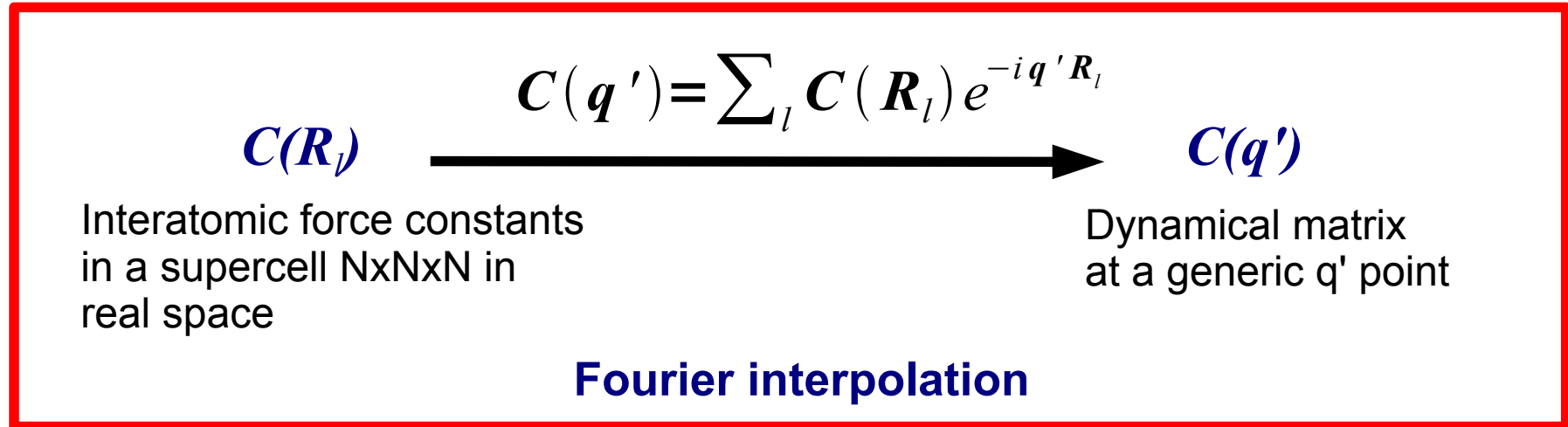
Dynamical matrices from the phonon
calculation

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

$$C(q') = \sum_l C(R_l) e^{-i q' R_l}$$

$C(R_l)$ $\longrightarrow$ $C(q')$

Interatomic force constants
in a supercell NxNxN in
real space

Dynamical matrix
at a generic q' point

Fourier interpolation

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

```
&input
   asr='simple',
   amass(1)=28.0855,
   flfrc='si.444.fc',          ← IFC input file
   flfrq='si.freq'             ← Output file of the frequencies
 /
1                              ← Number of q points
 0.300000     0.200000     0.050000  ← 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)
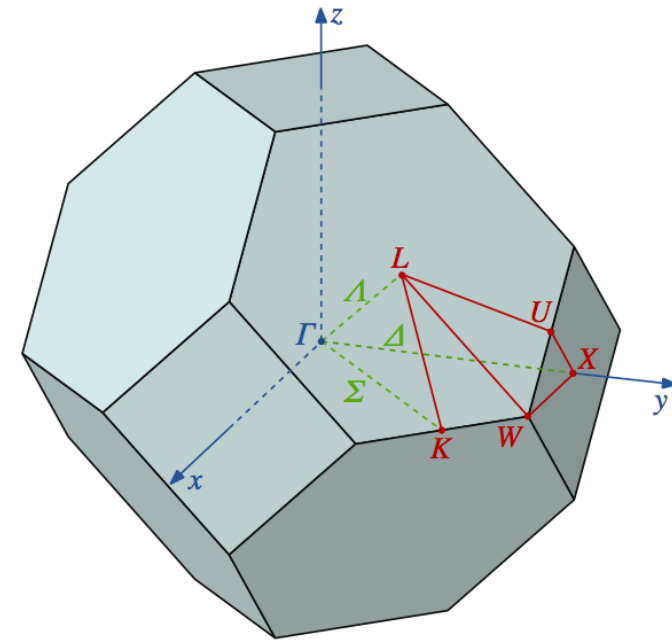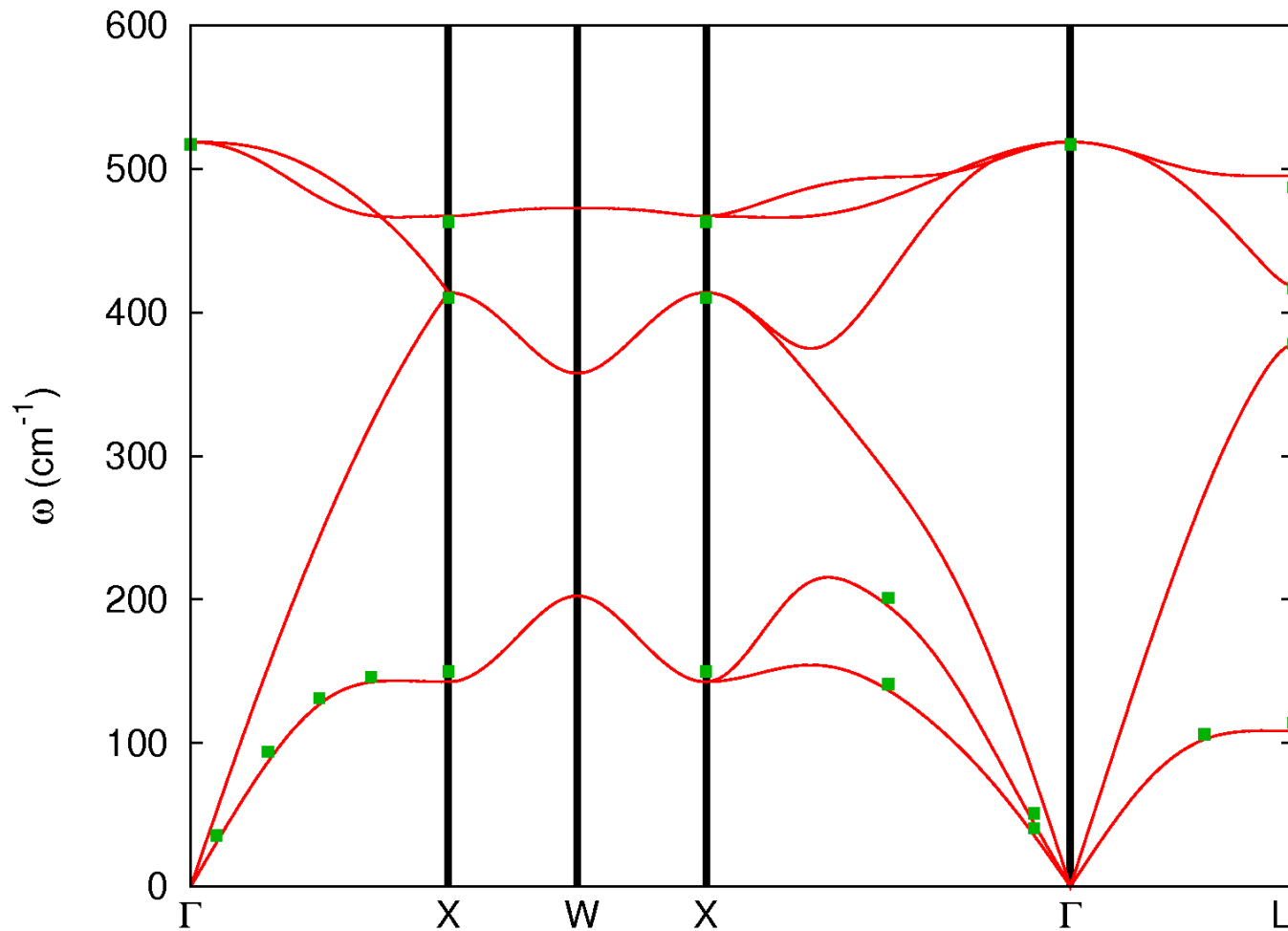
Brillouin zone of a FCC

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.,                      ⟵ Option for a DOS calculation
   fldos='si.dos'
   deltaE=1.d0,                     ⟵ Energy interval
   nk1=4, nk2=4, nk3=4,             ⟵ Grid of q points for the DOS
 /                                     calculation
```
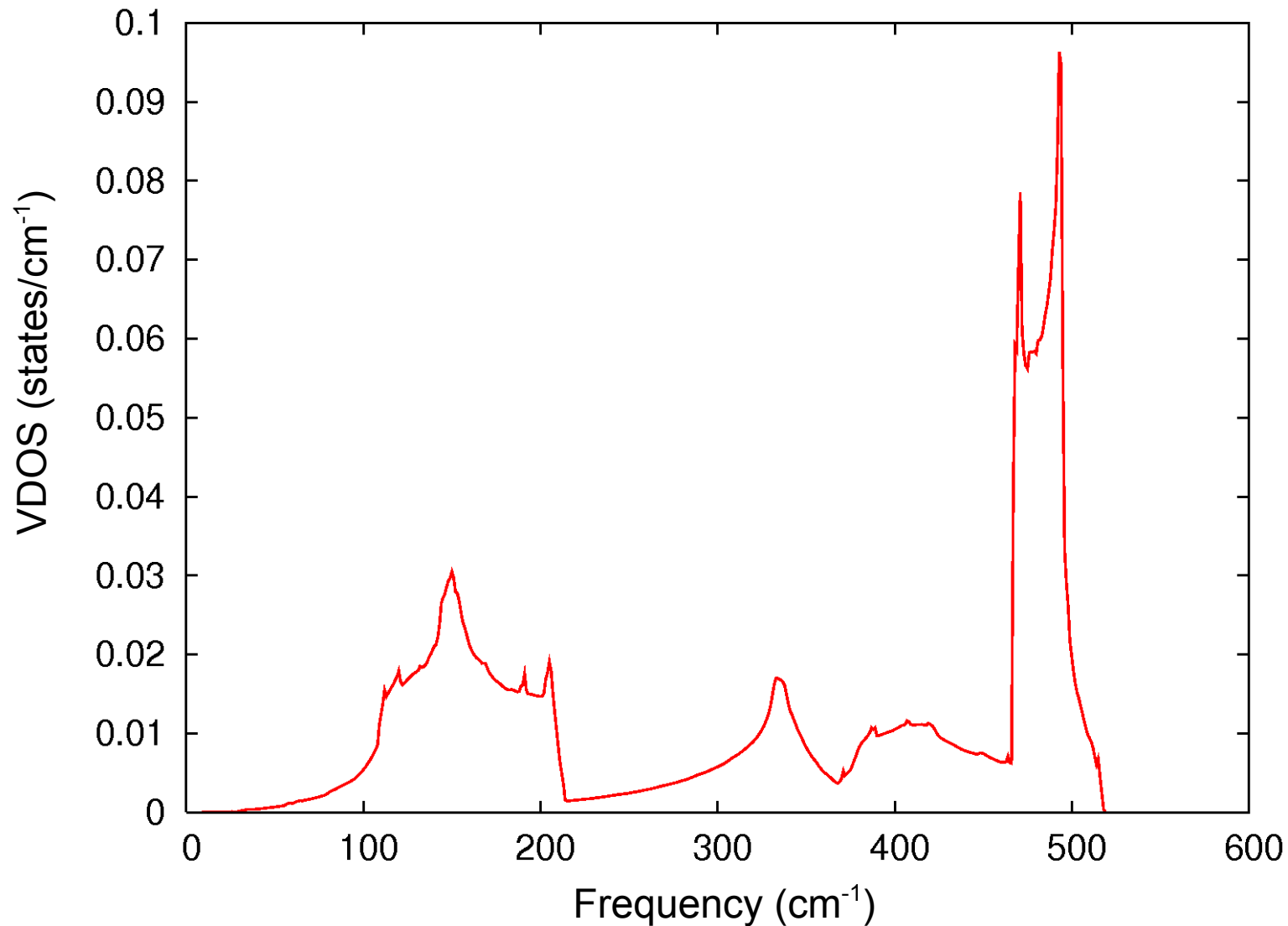
Modify the matdyn.x input file and perform the calculation.
You can use the gnuplot script plot_dos.gnu to generate a picture.

    prompt> gnuplot plot_dos.gnu

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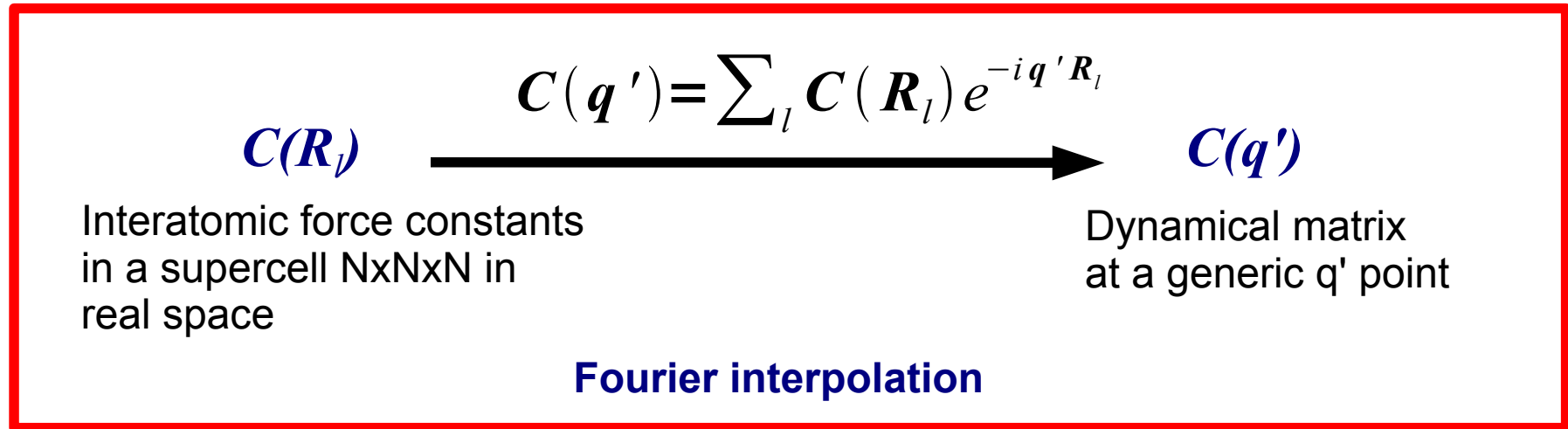Which grid gives a converged result?

Exercise 3: phonon dispersion calculations

Si vibrational density of states

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

Exercise 4: checking the Fourier interpolation

$$C(\boldsymbol{q}') = \sum_l C(\boldsymbol{R}_l) e^{-i\boldsymbol{q}'\boldsymbol{R}_l}$$

$C(R_l)$ $C(q')$

Interatomic force constants in a supercell NxNxN in real space   Dynamical matrix at a generic q' point

Fourier interpolation

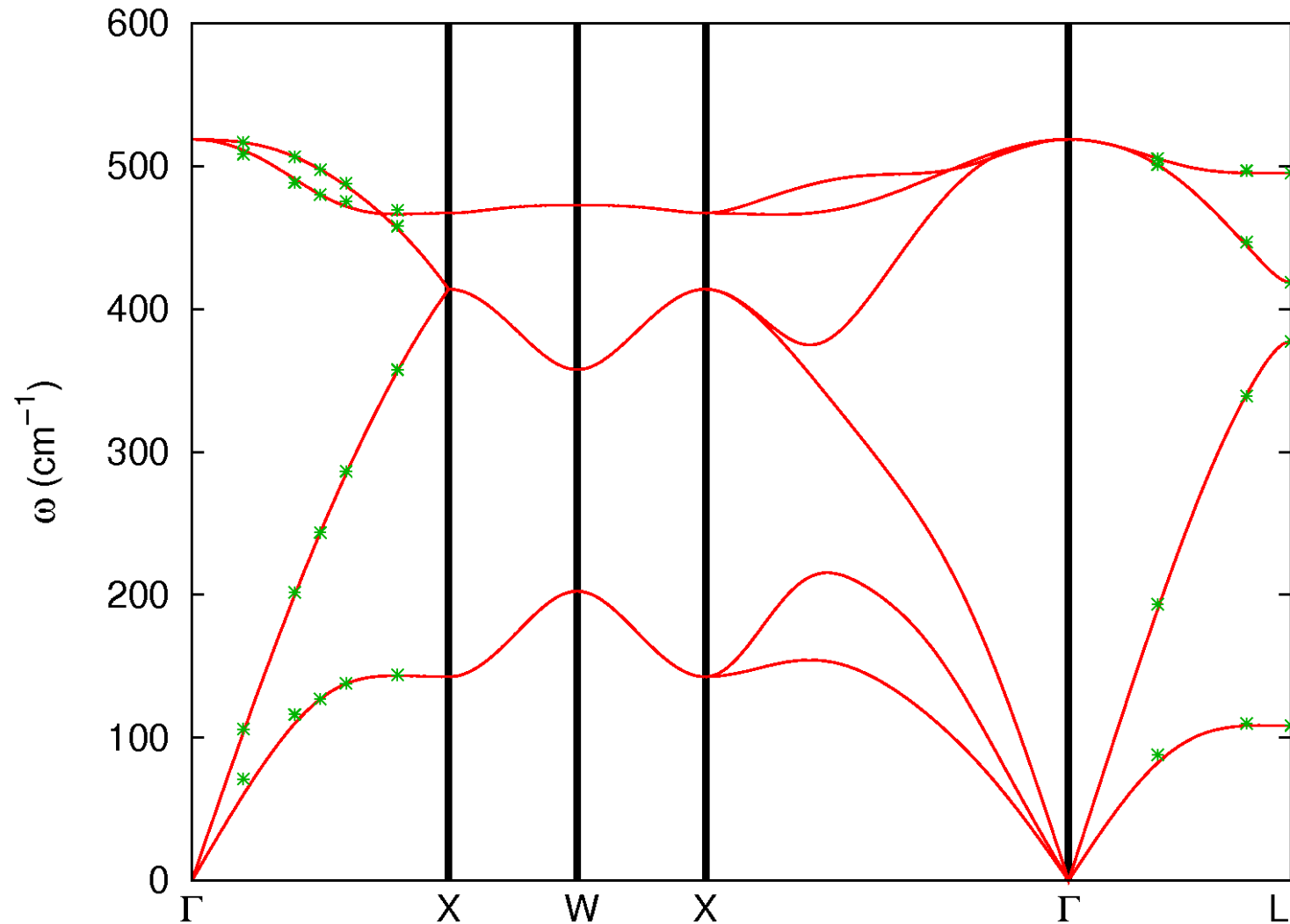We need to check if the Fourier interpolation works properly.
To do that we can calculate:

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 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 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 q → 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.

Extra slides...

Phonons and thermo-mechanical properties

Phonons are determined by this secular equation:

$$\sum_{t,\beta} \left(\widetilde{C}_{st}^{\alpha\beta}(\mathbf{q}) - M_s\omega^2(\mathbf{q})\delta_{st}\delta_{\alpha\beta} \right) U_t^{\beta}(\mathbf{q}) = 0$$

Free energy in quasi-harmonic approximation:

$$F(\{a_i\},T) = E(\{a_i\}) + F_{vibr}(\{a_i\},T)$$

$$= E(\{a_i\}) + \sum_{q,j} \frac{\hbar\omega_{q,j}(\{a_i\})}{2} + k_BT \sum_{q,j} \ln\left(1 - \exp\left(-\frac{\hbar\omega_{q,j}(\{a_i\})}{k_BT} \right) \right)$$

$$\boxed{\alpha_i = \frac{1}{a_i}\frac{\partial a_i}{\partial T}}$$ Thermal expansion coefficient

And also: heat capacity, temperature dependence of the elastic constants....

Density functional perturbation theory (1)

Let us assume that the external potential depends on some parameter λ

$$V_\lambda(\mathbf{r}) \simeq V(\mathbf{r}) + \lambda\frac{\partial V(\mathbf{r})}{\partial \lambda} + \frac{1}{2}\lambda^2\frac{\partial^2 V(\mathbf{r})}{\partial \lambda^2} + \ldots$$

(all derivatives calculated at $\lambda = 0$) and expand the charge density

$$n_\lambda(\mathbf{r}) \simeq n(\mathbf{r}) + \lambda\frac{\partial n(\mathbf{r})}{\partial \lambda} + \frac{1}{2}\lambda^2\frac{\partial^2 n(\mathbf{r})}{\partial \lambda^2} + \ldots$$

and the energy functional into powers of λ:

$$E_\lambda \simeq E + \lambda\frac{\partial E}{\partial \lambda} + \frac{1}{2}\lambda^2\frac{\partial^2 E}{\partial \lambda^2} + \ldots$$

The first-order derivative $\partial E/\partial \lambda$ does not depend on any derivative of $n(\mathbf{r})$ (*Hellmann-Feynman theorem*):

$$\frac{\partial E}{\partial \lambda} = \int n(\mathbf{r})\frac{\partial V(\mathbf{r})}{\partial \lambda}d\mathbf{r}$$

Density functional perturbation theory (2)

The second-order derivative $\partial^2 E/\partial\lambda^2$ depends on the first-order derivative of the charge density, $\partial n(\mathbf{r})/\partial\lambda$:

$$\frac{\partial^2 E}{\partial\lambda^2} = \int \frac{\partial V(\mathbf{r})}{\partial\lambda}\frac{\partial n(\mathbf{r})}{\partial\lambda}d\mathbf{r} + \int n(\mathbf{r})\frac{\partial^2 V(\mathbf{r})}{\partial\lambda^2}d\mathbf{r}$$

The result can be generalized to mixed derivatives:

$$\frac{\partial^2 E}{\partial\lambda\partial\mu} = \int \frac{\partial V(\mathbf{r})}{\partial\lambda}\frac{\partial n(\mathbf{r})}{\partial\mu}d\mathbf{r} + \int n(\mathbf{r})\frac{\partial^2 V(\mathbf{r})}{\partial\lambda\partial\mu}d\mathbf{r}$$

(the order of derivatives can be exchanged)

In general, the $(2n+1)-$th derivative of energy depends only on derivatives up to order n of the charge density ($(2n+1)$ *theorem*).

Density functional perturbation theory (3)

The first-order derivative of the charge density can be obtained as in traditional linear-response theory, by applying perturbation theory to the KS Hamiltonian:

$$\frac{\partial \psi_v(\mathbf{r})}{\partial \lambda} = \sum_c \psi_c(\mathbf{r}) \frac{1}{\epsilon_v - \epsilon_c} \langle \psi_c | \frac{\partial V_{KS}}{\partial \lambda} | \psi_v \rangle = \frac{1}{\epsilon_v - H_{KS}} P_c \frac{\partial V_{KS}(\mathbf{r})}{\partial \lambda} \psi_v(\mathbf{r})$$

(v denotes occupied KS states, c empty states, P_c is the projector over empty states). The self-consistent potential response $\partial V_{KS}/\partial \lambda$:

$$\frac{\partial V_{KS}(\mathbf{r})}{\partial \lambda} = \frac{\partial V(\mathbf{r})}{\partial \lambda} + \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial n(\mathbf{r}')}{\partial \lambda} d\mathbf{r}' + \int \frac{\delta V_{xc}(\mathbf{r})}{\delta n(\mathbf{r}')} \frac{\partial n(\mathbf{r}')}{\partial \lambda} d\mathbf{r}'$$

depends on the first-order variation $\partial n(\mathbf{r})/\partial \lambda$ of the charge density:

$$\frac{\partial n(\mathbf{r})}{\partial \lambda} = 2\mathrm{Re} \sum_v \psi_v^*(\mathbf{r}) \frac{\partial \psi_v(\mathbf{r})}{\partial \lambda}$$

The quantities $\partial \psi_v(\mathbf{r})/\partial \lambda$ and all other needed quantities are thus determined by the solution of a self-consistent set of *linear equations*.

Frozen phonons vs DFPT

Frozen phonons is an older and alternative way to calculate phonons. The monochromatic perturbation is *frozen in* with a finite amplitude in the system, which is described by a *supercell* having **q** as reciprocal lattice vector.

Fourier transform of force constants at **q** are calculated from *finite differences of forces* induced on all the atoms of the supercell by the monochromatic perturbation.

Advantages:

- straightforward to implement

Disadvantages:

- limited to small supercells, i.e. $\mathbf{q} = \mathbf{G}/n$, where $\mathbf{G}$ is a reciprocal lattice vector of the original cell, $n = 2, 3, 4, ...$, but in any case a small number.

Note that this is *not* the algorithm used by Quantum-Espresso!
What if we want the entire dispersions for all **q**-vectors in the Brillouin Zone?

Calculation of IR and Raman intensities

Infrared Intensities:

$$I_{IR}(\nu) = \sum_\alpha \left| \sum_{s\beta} Z^{\star\alpha\beta}_s U^\beta_s(\nu) \right|^2 \qquad \boxed{Z^{\star\alpha\beta}_s = \Omega \frac{\partial P_\alpha}{\partial u^\beta_s(\mathbf{q}=0)}}$$

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

Non-resonant Raman intensities:

$$I_{\text{Stokes}}(\nu) \propto \frac{(\omega_i - \omega_\nu)^4}{\omega_\nu} r_{\alpha\beta}(\nu), \qquad \boxed{r_{\alpha\beta}(\nu) = \left| \frac{\partial \chi_{\alpha\beta}}{\partial U(\nu)} \right|^2}$$

where χ is the electric polarizability of the system.

Raman coefficients are third-order derivatives of the energy that can be calculated in various ways. The most convenient way is to use second-order response to an electric field: M.Lazzeri and F.Mauri, Phys. Rev. Lett. 90, 036401 (2003).