QUANTUM ESPRESSO FOUNDATION

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MaX School on Advanced Materials and Molecular Modelling
with QUANTUM ESPRESSO

# QE-2021: Hands-on session - Day-5
## (Density Functional Perturbation Theory – Part 1)

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# Outline

1. Introduction

2. **Exercise 1a:** Phonons at Gamma in non-polar materials

3. **Exercise 1b:** Phonon dispersion in non-polar materials

4. **Exercise 2a:** Phonons at Gamma in polar materials

5. **Exercise 2b:** Phonon dispersion in polar materials

6. **Exercise 3:** Phonon dispersion of 2D materials (optional)

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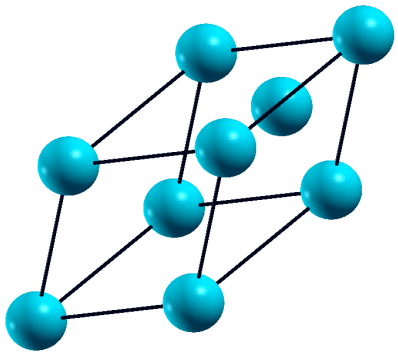
# Basic concepts

Let us consider a unit cell with $N_{at}$ atoms.



$s = 1 \ldots N_{at}$ index of an atom in the unit cell

$\alpha = x, y, z$ is the cartesian index

$\mathbf{R}$ is the point in the Bravais-lattice, identifying the position of a given unit cell

$N_{\mathbf{R}}$ is the number of unit cells in the crystal

$\mathbf{u}_{s\alpha}(\mathbf{R})$ is the $\alpha$ - component of the displacement of the **s**-th atom

$3 \times N_{at}$ variables

Interatomic Force Constants :

$$C_{s\alpha,s'\beta}(\mathbf{R},\mathbf{R}') = C_{s\alpha,s'\beta}(\mathbf{R}-\mathbf{R}') = \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{s\alpha}(\mathbf{R}) \partial \mathbf{u}_{s'\beta}(\mathbf{R}')}$$

# Basic concepts

Normal mode frequencies, $\omega$, and eigenvectors, $\mathbf{u}_{s\alpha}$ are determined by the secular equation:

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

where

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

**Interatomic Force Constants (IFC)**

is the ***dynamical matrix***.

Diagonalization of the dynamical matrix gives phonon modes at **q**.

# The phonon code works for a rather wide variety of systems and methods:

- **Insulators (also polar insulators, with LO-TO splitting)**
- **Metals**
- **Magnetic systems at the scalar relativistic collinear level (LSDA)**
- **Spin-orbit coupling (fully relativistic approach)**
- **Electric field calculations: Born effective charges, dielectric tensor**

**Recent developments:**

- **Phonons for magnetic systems in the fully relativistic non-collinear approach**
- **Phonons within the DFT+U approach**

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5. **Exercise 2b:** Phonon dispersion in polar materials
6. **Exercise 3:** Phonon dispersion of 2D materials (optional)

# Exercise 1a: Phonons at $\Gamma$ in non-polar materials

Go to the directory with the input files:

```
cd  ~/QE-2021/Day-5/example1a
```

In this directory you will find:

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

# Exercise 1a: Phonons at Γ 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.

**pw.Si.in**

Input file for the SCF calculation

```
&control
    calculation='scf'
    restart_mode='from_scratch',
!    pseudo_dir='../../pseudo'
!    outdir='./tmp'
    prefix='Si',
/
&system
    ibrav = 2,
    celldm(1) = 10.20,
    nat = 2,
    ntyp = 1,
    ecutwfc = 16
/
&electrons
    diagonalization = 'davidson'
    mixing_mode = 'plain',
    conv_thr =  1.0d-8
    mixing_beta = 0.7
/
ATOMIC_SPECIES
 Si  28.0855 Si.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
```

**pw.x -i pw.Si.in > pw.Si.out**

# Exercise 1a: Phonons at Γ in non-polar materials

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

**ph.Si.in**

Input file for the phonon calculation

```
Phonons at Gamma
 &inputph
  prefix = 'Si',
  tr2_ph = 1.0d-14,
  amass(1) = 28.0855,
!  outdir = './tmp'
  fildyn = 'Si.dyn',
 /
 0.0  0.0  0.0
```

← The same prefix as in the SCF calculation

← Threshold for self-consistency

← Atomic mass

← Directory for temporary files

← File containing the dynamical matrix

← Coordinates of the **q** point in units of 2*pi/a in the Cartesian reference system

**ph.x -i ph.Si.in > ph.Si.out**

# Exercise 1a: Phonons at Γ in non-polar materials

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

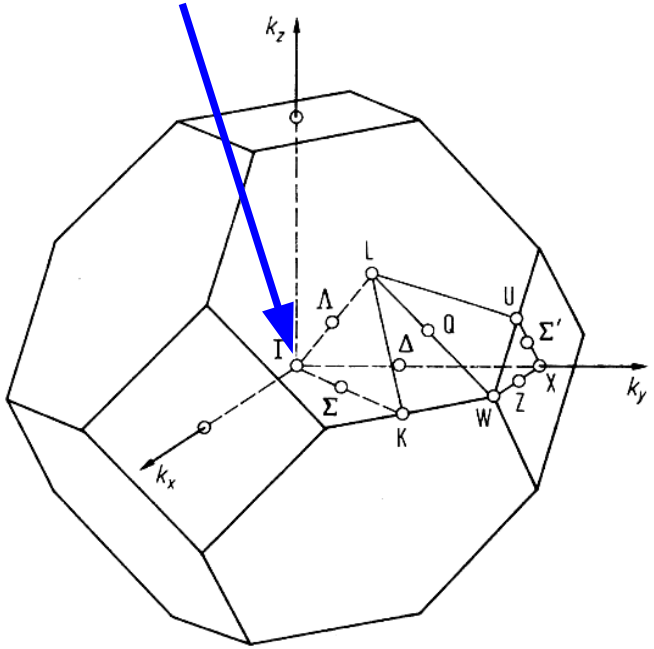
**ph.Si.in**

Input file for the phonon calculation

```
Phonons at Gamma
 &inputph
  prefix = 'Si',
  tr2_ph = 1.0d-14,
  amass(1) = 28.0855,
!  outdir = './tmp'
  fildyn = 'Si.dyn',
 /
 0.0  0.0  0.0
```

We consider only the Γ point:

**q** = 2*pi/a (0.0, 0.0, 0.0)




**Brillouin Zone**

# Exercise 1a: Phonons at Γ in non-polar materials

Dynamical matrix file **`Si.dyn :`**

```
**************************************************************************
     freq (    1) =       0.069949 [THz] =       2.333248 [cm-1]
(  0.006270  0.000000  0.104520  0.000000 -0.699311  0.000000 )
(  0.006270  0.000000  0.104520  0.000000 -0.699311  0.000000 )
     freq (    2) =       0.069949 [THz] =       2.333248 [cm-1]
(  0.644809  0.000000  0.286121  0.000000  0.048545  0.000000 )
(  0.644809  0.000000  0.286121  0.000000  0.048545  0.000000 )
     freq (    3) =       0.069949 [THz] =       2.333248 [cm-1]
(  0.290142  0.000000 -0.638130  0.000000 -0.092775  0.000000 )
(  0.290142  0.000000 -0.638130  0.000000 -0.092775  0.000000 )
     freq (    4) =      15.474501 [THz] =     516.173789 [cm-1]
( -0.534305  0.000000 -0.463023  0.000000 -0.011325  0.000000 )
(  0.534305  0.000000  0.463023  0.000000  0.011325  0.000000 )
     freq (    5) =      15.474501 [THz] =     516.173789 [cm-1]
( -0.202506  0.000000  0.217991  0.000000  0.641460  0.000000 )
(  0.202506  0.000000 -0.217991  0.000000 -0.641460  0.000000 )
     freq (    6) =      15.474501 [THz] =     516.173789 [cm-1]
(  0.416545  0.000000 -0.487944  0.000000  0.297322  0.000000 )
( -0.416545  0.000000  0.487944  0.000000 -0.297322  0.000000 )
**************************************************************************
```

**Acoustic modes**

**Optical modes**

# Exercise 1a: Phonons at $\Gamma$ in non-polar materials

## Acoustic sum rule at $\Gamma$

Because of the numerical inaccuracies the interatomic force constants do not strictly satisfy the acoustic sum rule (ASR).

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

As a consequence:

For each $\alpha$, $\beta$ and $i$: $$\sum_{\mathbf{L},j} C_{\alpha i,\beta j}(\mathbf{R_L}) = 0$$

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

# Exercise 1a: Phonons at Γ in non-polar materials

## Acoustic sum rule at Γ

Because of the numerical inaccuracies the interatomic force constants do not strictly satisfy the acoustic sum rule (ASR), hence the acoustic frequencies might be slightly different from zero.

However, the ASR can be imposed using the **`dynmat.x`** program.

The input file is **`dynmat.Si.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)

```
dynmat.x -i dynmat.Si.in > dynmat.Si.out
```

# Exercise 1a: 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.

```
     diagonalizing the dynamical matrix ...

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) =      15.474329 [THz] =     516.168042 [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) =      15.474329 [THz] =     516.168042 [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) =      15.474329 [THz] =     516.168042 [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   )
**********************************************************************
```

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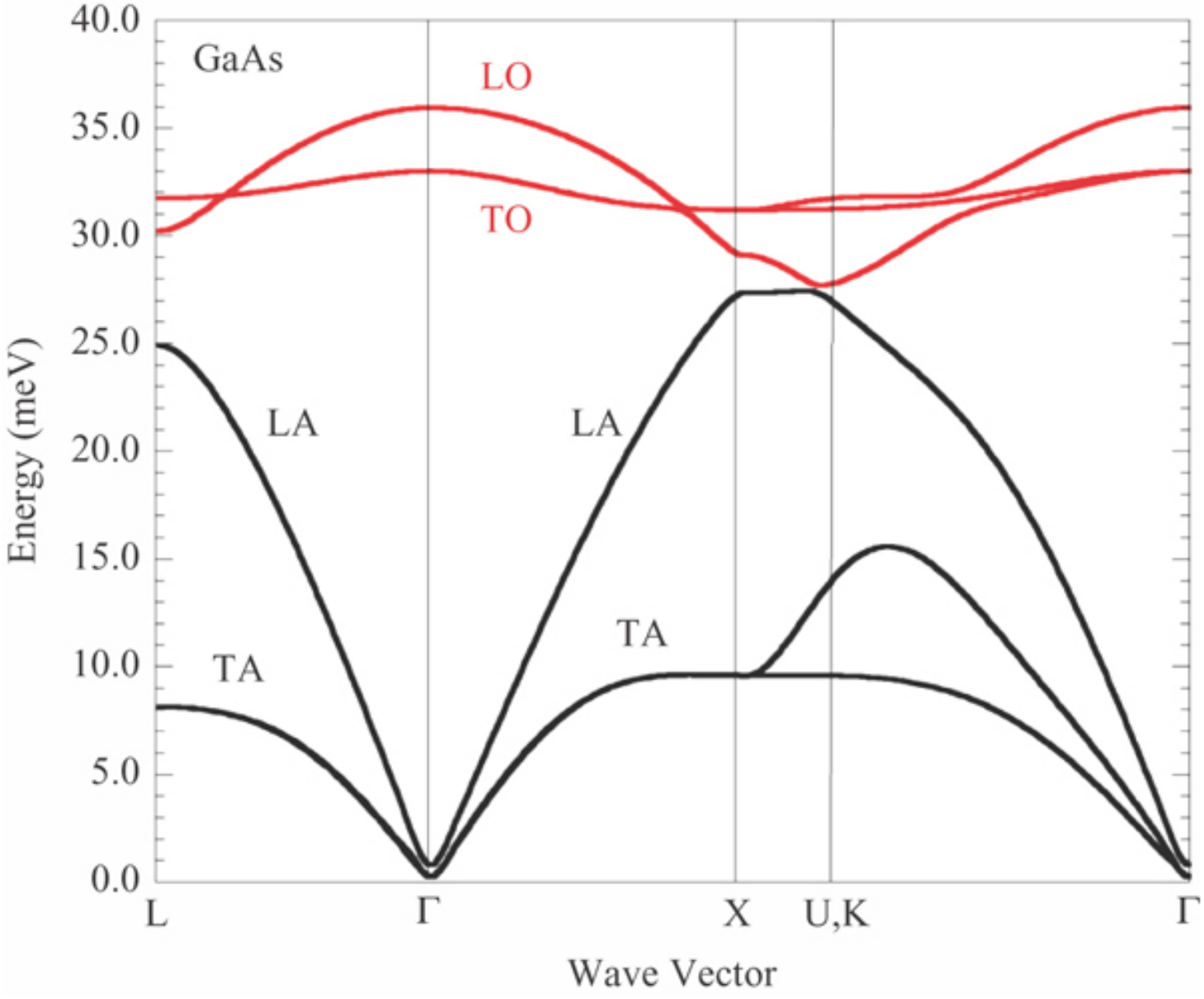
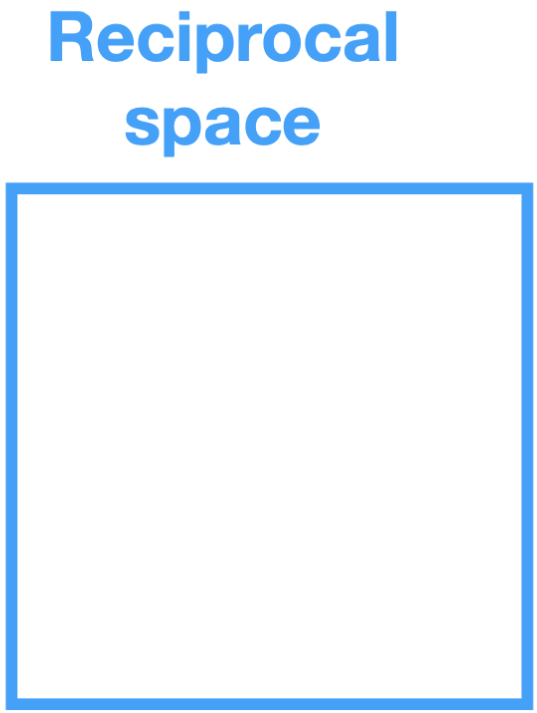
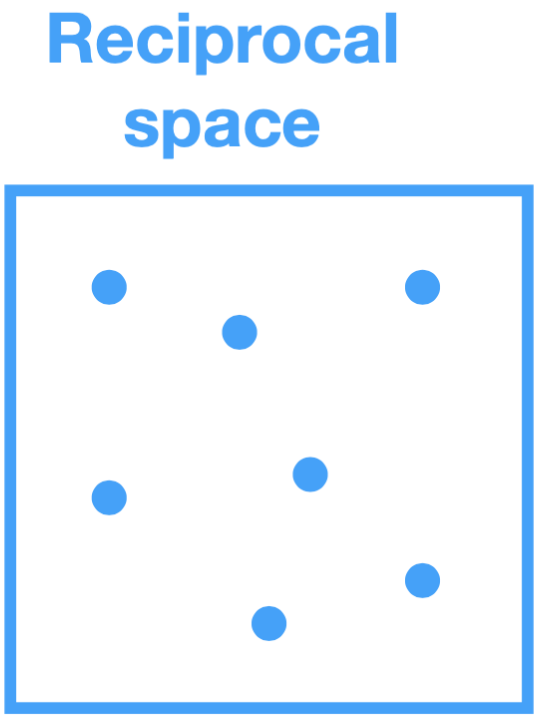
# Important concept: Fourier interpolation



# Important concept: Fourier interpolation

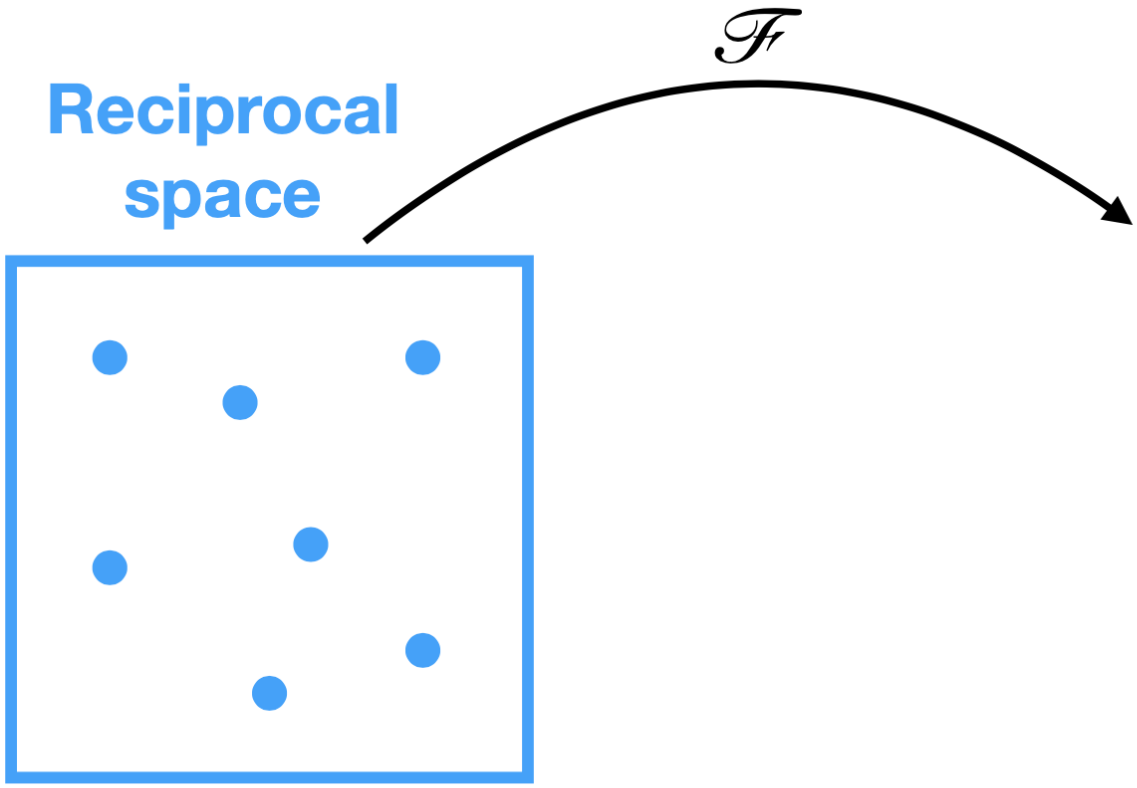


# Important concept: Fourier interpolation



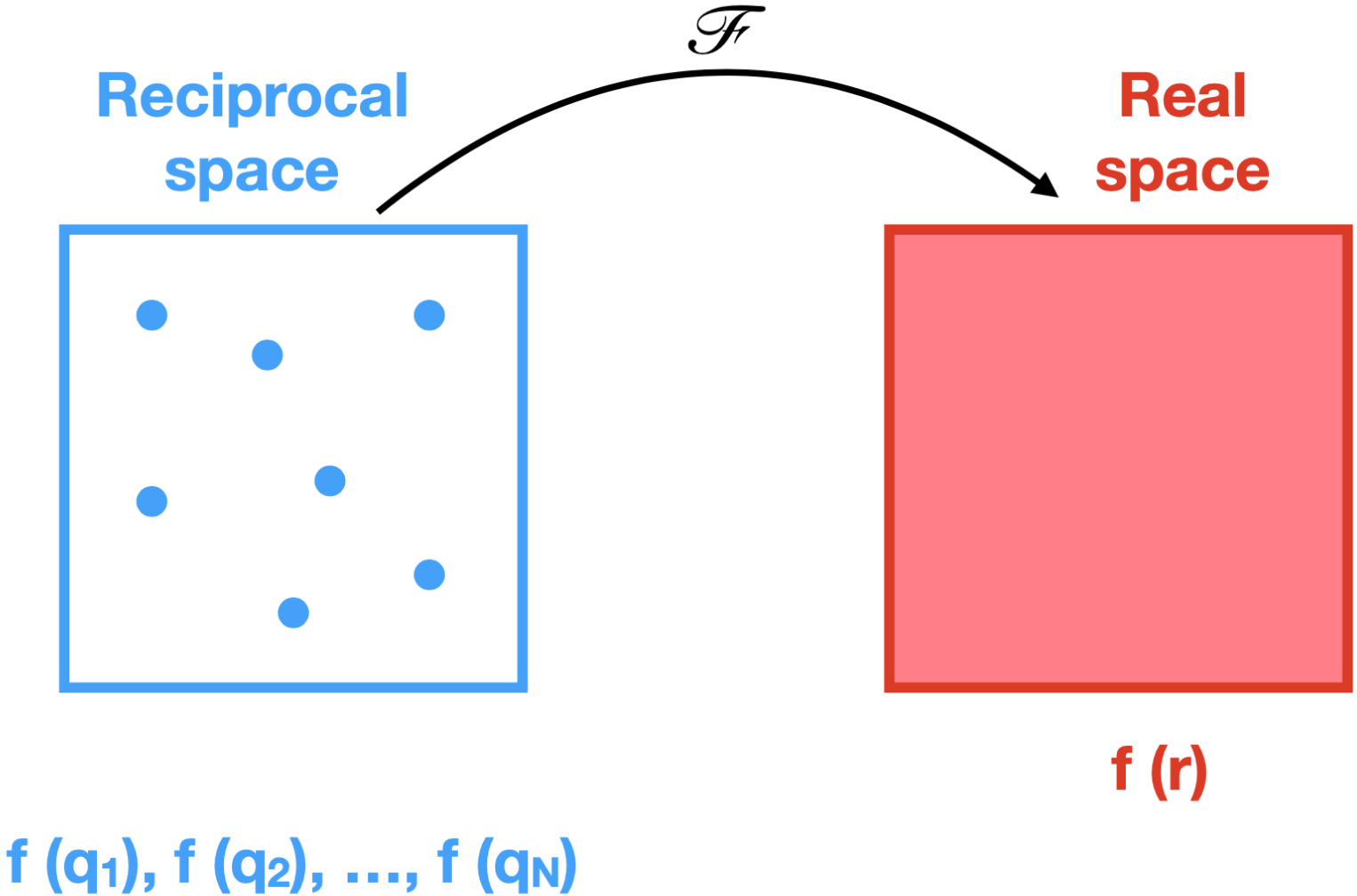

$f(q_1), f(q_2), \ldots, f(q_N)$

# Important concept: Fourier interpolation

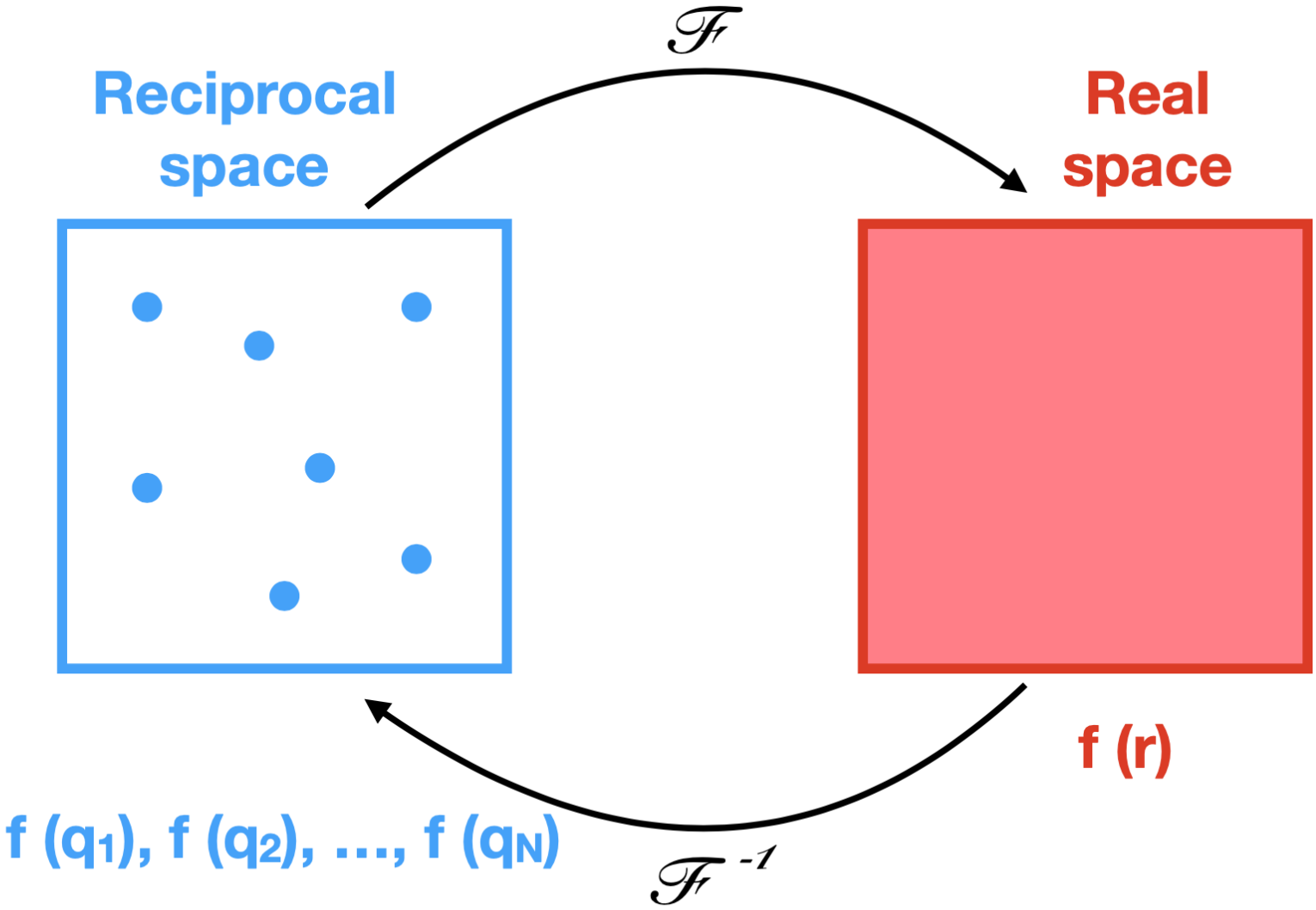



$f(q_1), f(q_2), \ldots, f(q_N)$

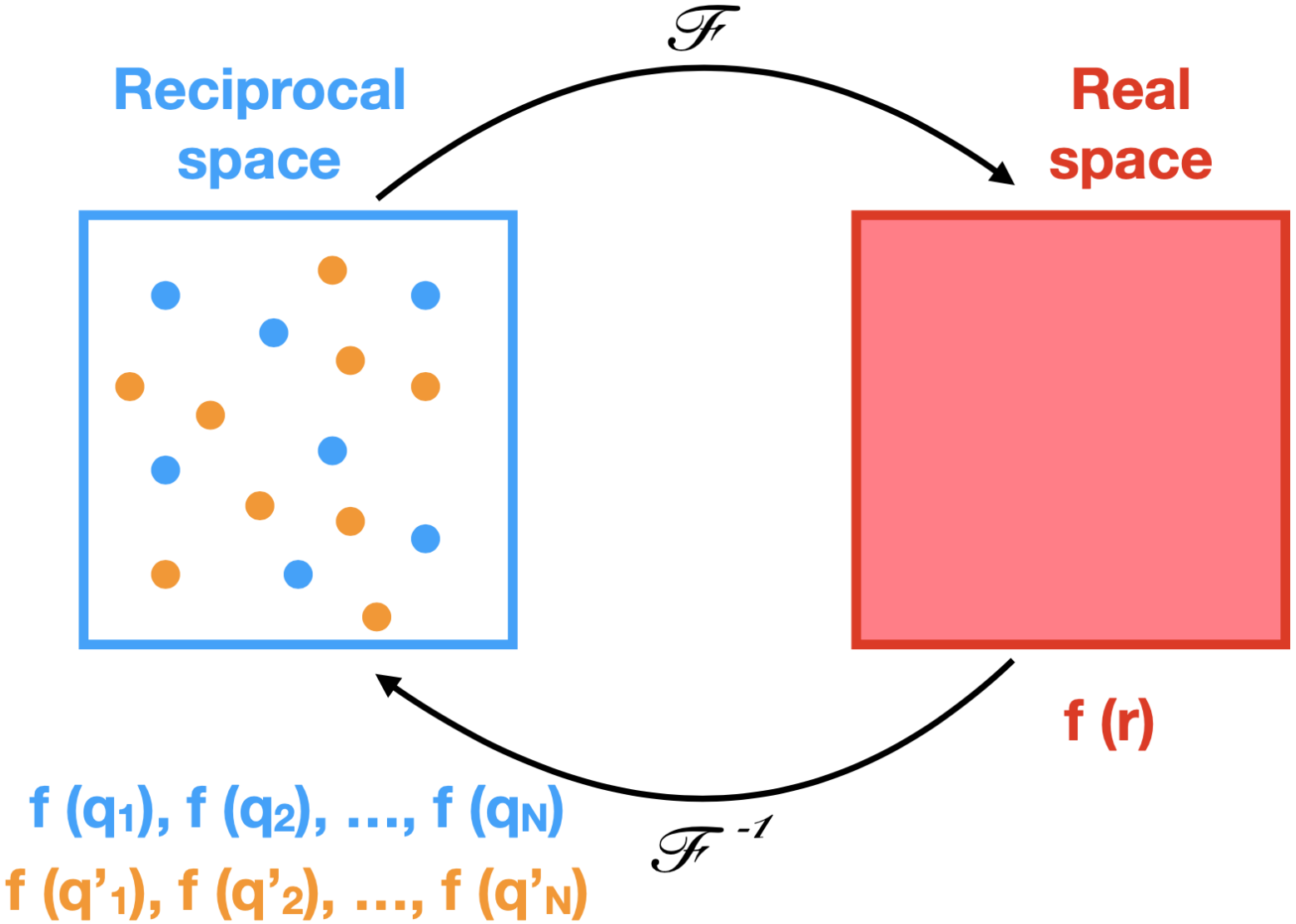
# Important concept: Fourier interpolation



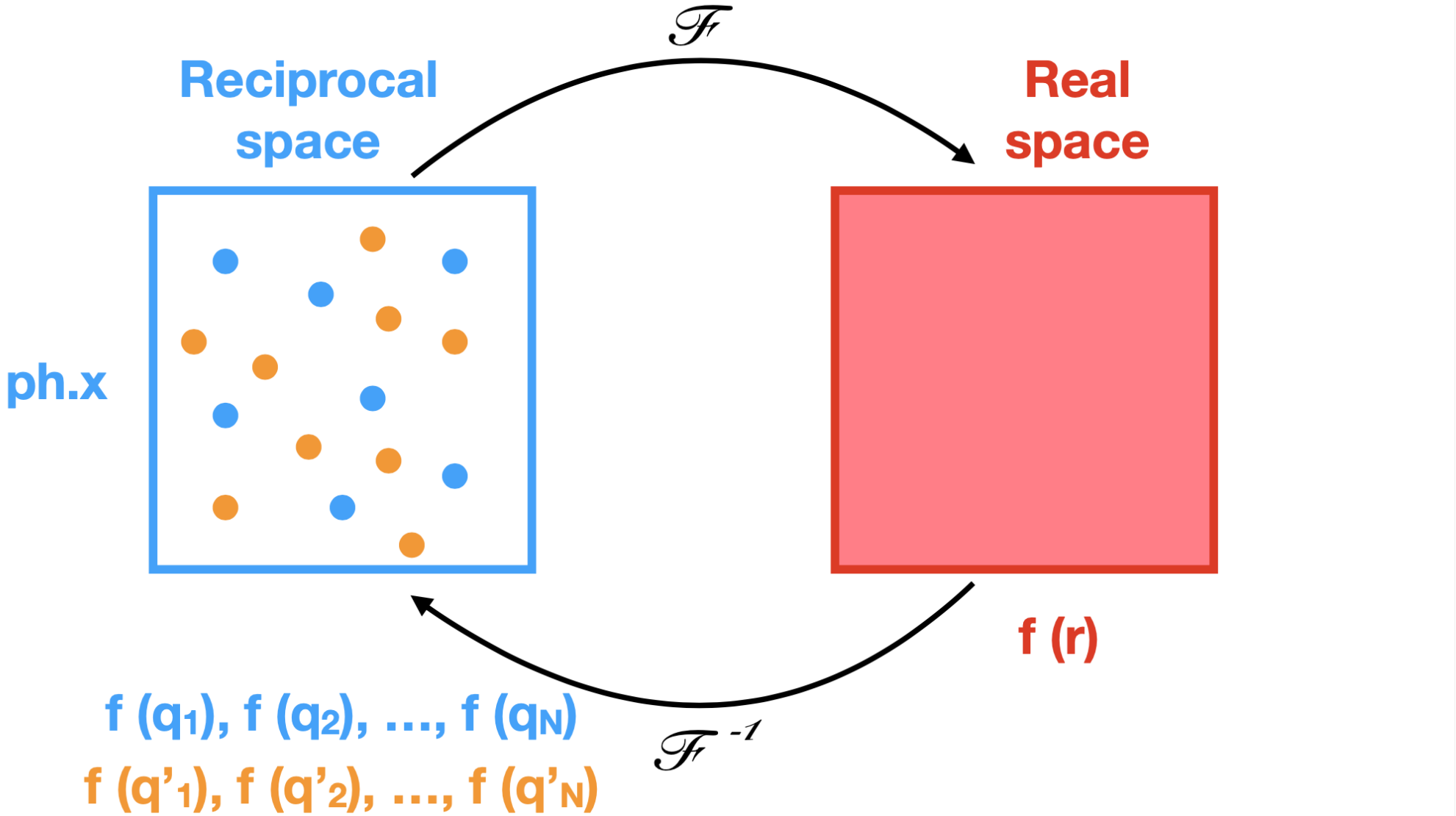
# Important concept: Fourier interpolation



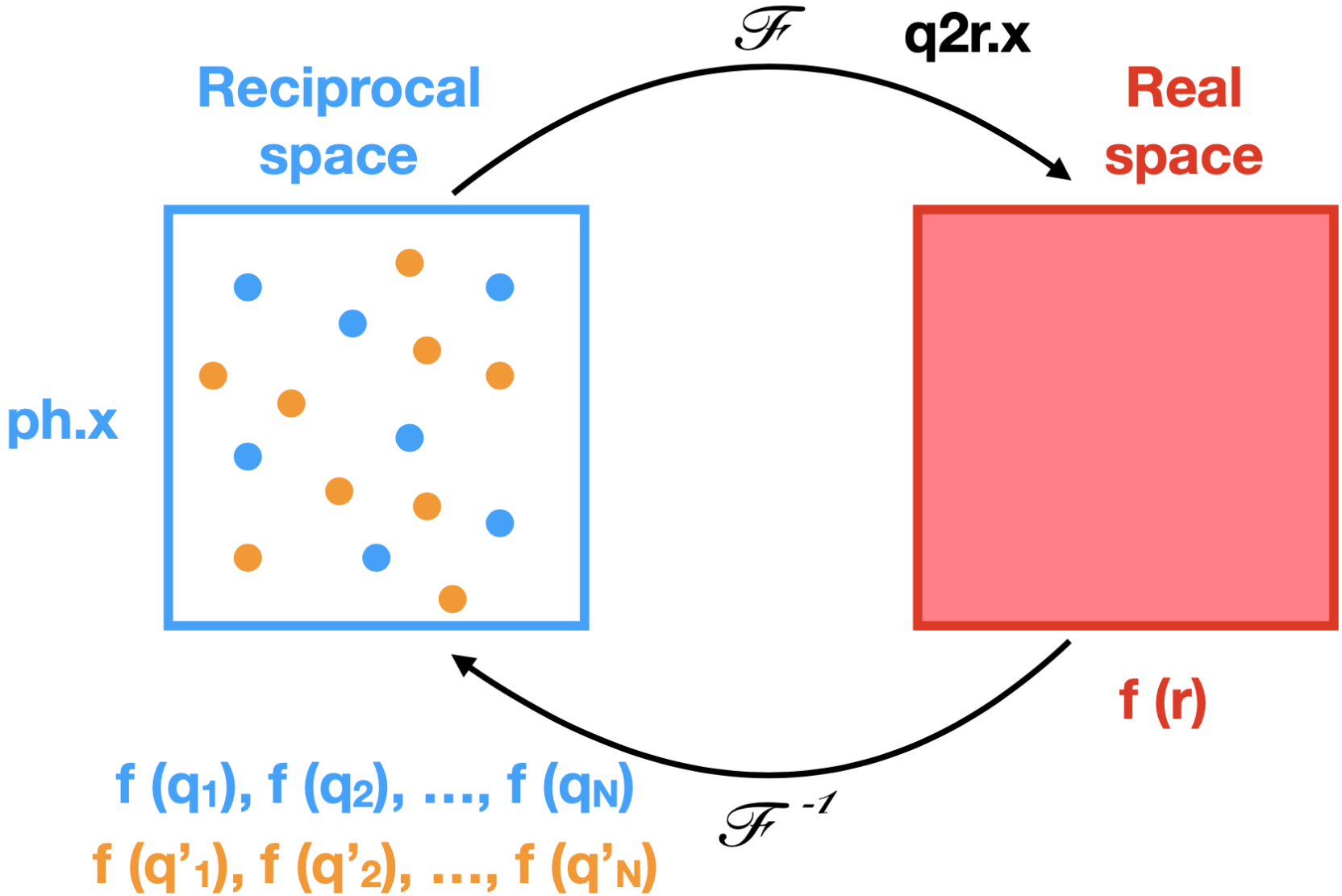
# Important concept: Fourier interpolation



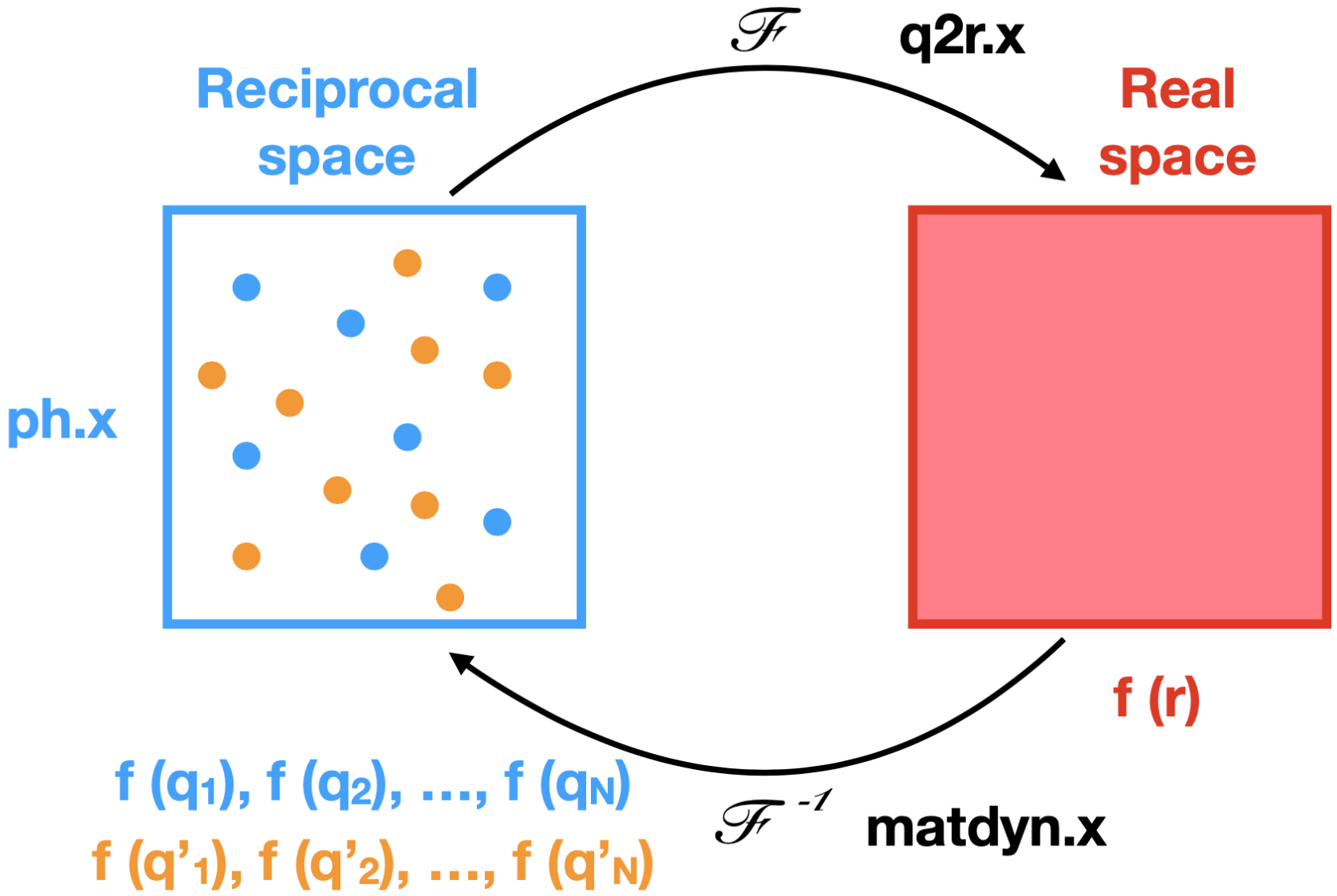
# Important concept: Fourier interpolation



# Important concept: Fourier interpolation



# Important concept: Fourier interpolation



# Exercise 1b: Phonon dispersion in non-polar materials

Go to the directory with the input files:

```
cd  ~/QE-2021/Day-5/example1b
```

In this directory you will find:

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

# Exercise 1b: Phonon dispersion in non-polar materials

Step 1. Perform a SCF calculation for silicon *at the equilibrium structure* using the **`pw.x`** program.

```
pw.x -i pw.Si.in > pw.Si.out
```

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

```
Phonons on a uniform q-grid
 &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',
 /
```

← Option for the calculation on a grid

← Uniform grid of **q** points

$$\mathbf{q}_{ijk} = \frac{i-1}{\mathrm{nq1}}\mathbf{G}_1 + \frac{j-1}{\mathrm{nq2}}\mathbf{G}_2 + \frac{k-1}{\mathrm{nq3}}\mathbf{G}_3$$

```
ph.x -i ph.Si.in > ph.Si.out
```

# Exercise 1b: Phonon dispersion in non-polar materials

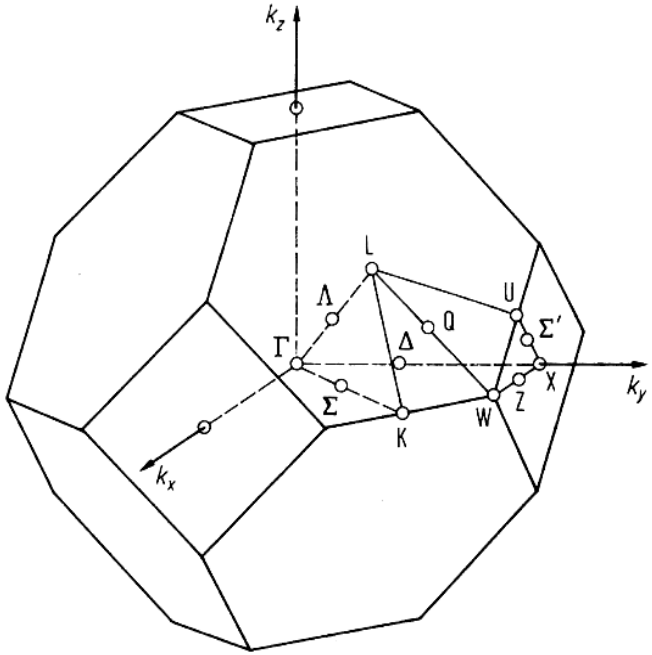
Step 1. Perform a SCF calculation for silicon *at the equilibrium structure* using the **`pw.x`** program.

```
pw.x -i pw.Si.in > pw.Si.out
```

Step 2. Perform a phonon calculation.

```
Phonons on a uniform q-grid
 &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',
 /
```

We sample the Brillouin zone with a uniform grid of 4x4x4 **q** points.



# Exercise 1b: Phonon 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    (q-grid)
      8             (number of non-equivalent q-points)
q1 =  0.0000000000000000E+00   0.0000000000000000E+00   0.0000000000000000E+00
q2 = -0.2500000000000000E+00   0.2500000000000000E+00  -0.2500000000000000E+00
q3 =  0.5000000000000000E+00  -0.5000000000000000E+00   0.5000000000000000E+00
q4 =  0.0000000000000000E+00   0.5000000000000000E+00   0.0000000000000000E+00
q5 =  0.7500000000000000E+00  -0.2500000000000000E+00   0.7500000000000000E+00
q6 =  0.5000000000000000E+00   0.0000000000000000E+00   0.5000000000000000E+00
q7 =  0.0000000000000000E+00  -0.1000000000000000E+01   0.0000000000000000E+00
q8 = -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 1b: Phonon dispersion in non-polar materials

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

Fourier transforms of IFC's :

$$\tilde{C}_{s\alpha,s'\beta}(\mathbf{q}_{ijk}) = \frac{\partial^2 E_{tot}}{\partial \tilde{\mathbf{u}}^*_{s\alpha}(\mathbf{q}_{ijk}) \partial \tilde{\mathbf{u}}_{s'\beta}(\mathbf{q}_{ijk})}$$

$\alpha, \beta$ are Cartesian components, and $s, s'$ are atomic indices.

$$C_{s\alpha,s'\beta}(\mathbf{R}_{lmn}) = \frac{1}{N_{\mathbf{q}}} \sum_{i,j,k} \tilde{C}_{s\alpha,s'\beta}(\mathbf{q}_{ijk}) e^{i\mathbf{q}_{ijk}\cdot\mathbf{R}_{lmn}}$$

$$\tilde{C}_{s\alpha,s'\beta}(\mathbf{q}_{ijk}) \longrightarrow C_{s\alpha,s'\beta}(\mathbf{R}_{lmn})$$

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

IFC's in a supercell nq1 x nq2 x nq3 in real space

# Exercise 1b: Phonon dispersion in non-polar materials

Input file **`q2r.Si.in`** :

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

← Dynamical matrices from the phonon calculation

← A way to impose the acoustic sum rule

← Output file of the interatomic force constants

The denser the grid of **q** points, the larger the vectors **R** for which the Interatomic Force Constants are calculated!

To perform the calculation:

```
q2r.x -i q2r.Si.in > q2r.Si.out
```

# Exercise 1b: Phonon dispersion in non-polar materials

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

$$\tilde{C}_{s\alpha,s'\beta}(\mathbf{q}') = \sum_{l,m,n} C_{s\alpha,s'\beta}(\mathbf{R}_{lmn}) e^{-i\mathbf{q}'\cdot\mathbf{R}_{lmn}}$$

$C_{s\alpha,s'\beta}(\mathbf{R}_{lmn})$ → **Fourier interpolation** → $\tilde{C}_{s\alpha,s'\beta}(\mathbf{q}')$

IFC's on a grid in real space

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

Input file **matdyn.Si.in** :

```
 &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
    ...         ...         ...         ...
```

- asr='simple', → Acoustic sum rule
- amass(1)=28.0855, → Atomic mass
- flfrc='Si444.fc', → File with IFC's
- flfrq='Si.freq' → Output file with the frequencies
- 396 → Number of **q** points
- 0.000000 0.000000 0.000000 0.000000 / 0.012658 0.000000 0.000000 0.012658 / ... ... ... ... → Coordinates of **q** points

**matdyn.x -i matdyn.Si.in > matdyn.Si.out**

# Exercise 1b: Phonon dispersion in non-polar materials

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

Input file **plotband.Si.in** :

```
Si.freq
0 600
freq.plot
freq.ps
0.0
100.0 0.0
```

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

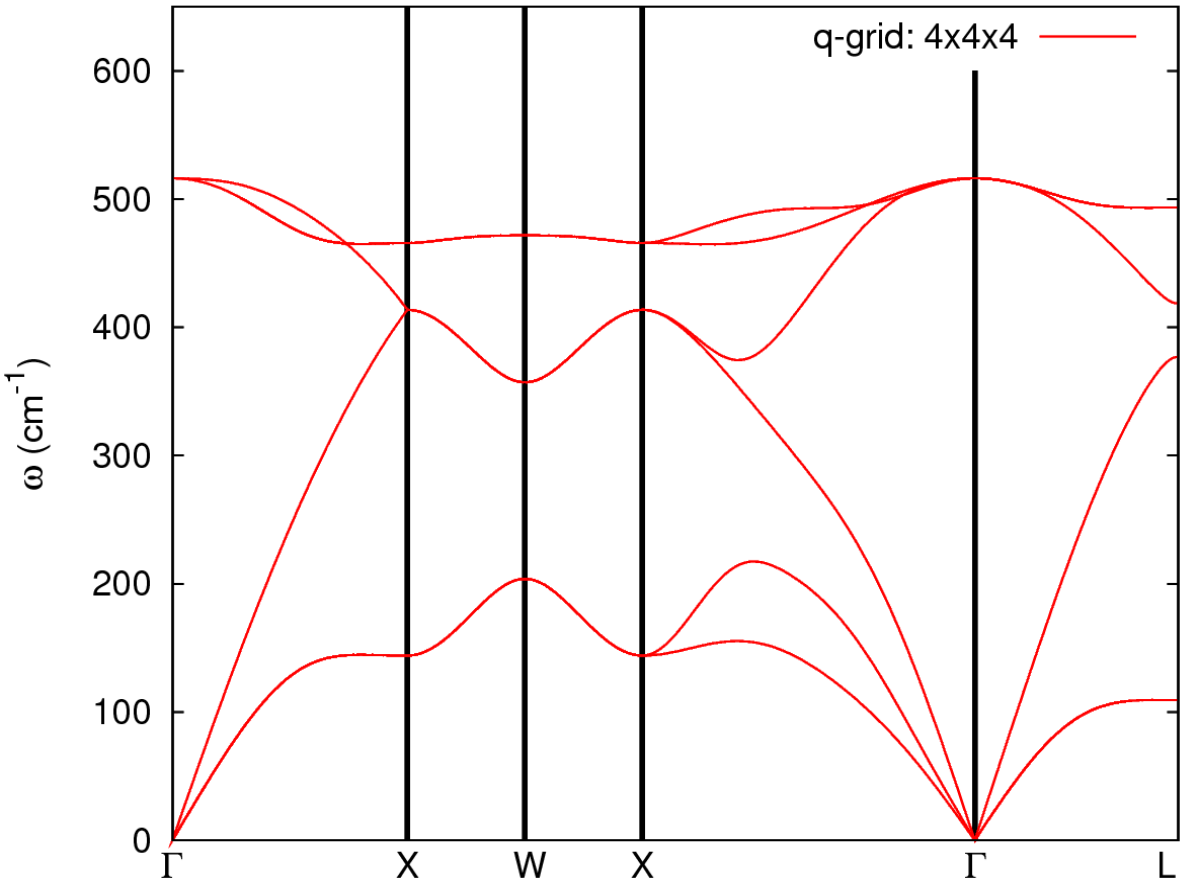
```
plotband.x < plotband.Si.in > plotband.Si.out
```

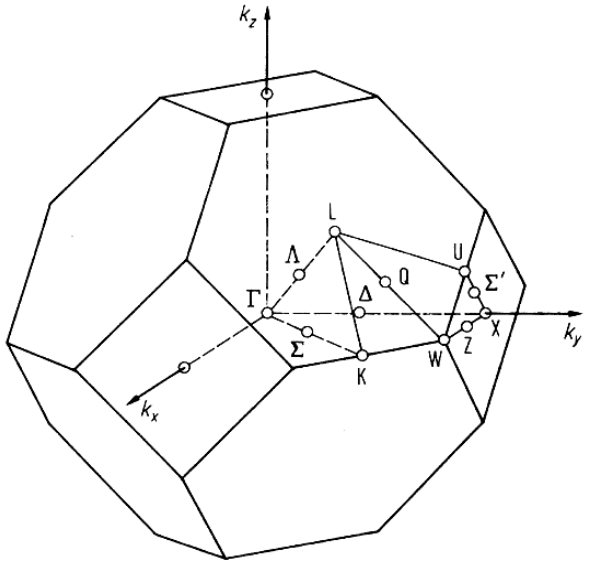
Use **gnuplot** and the file **plot_dispersion.gp** in order to plot the phonon dispersion of silicon (look at the file **experimental_data.dat** for the experimental reference).

You will get a postscript file **phonon_dispersion.eps** which you can visualize.

# Exercise 1b: Phonon dispersion in non-polar materials

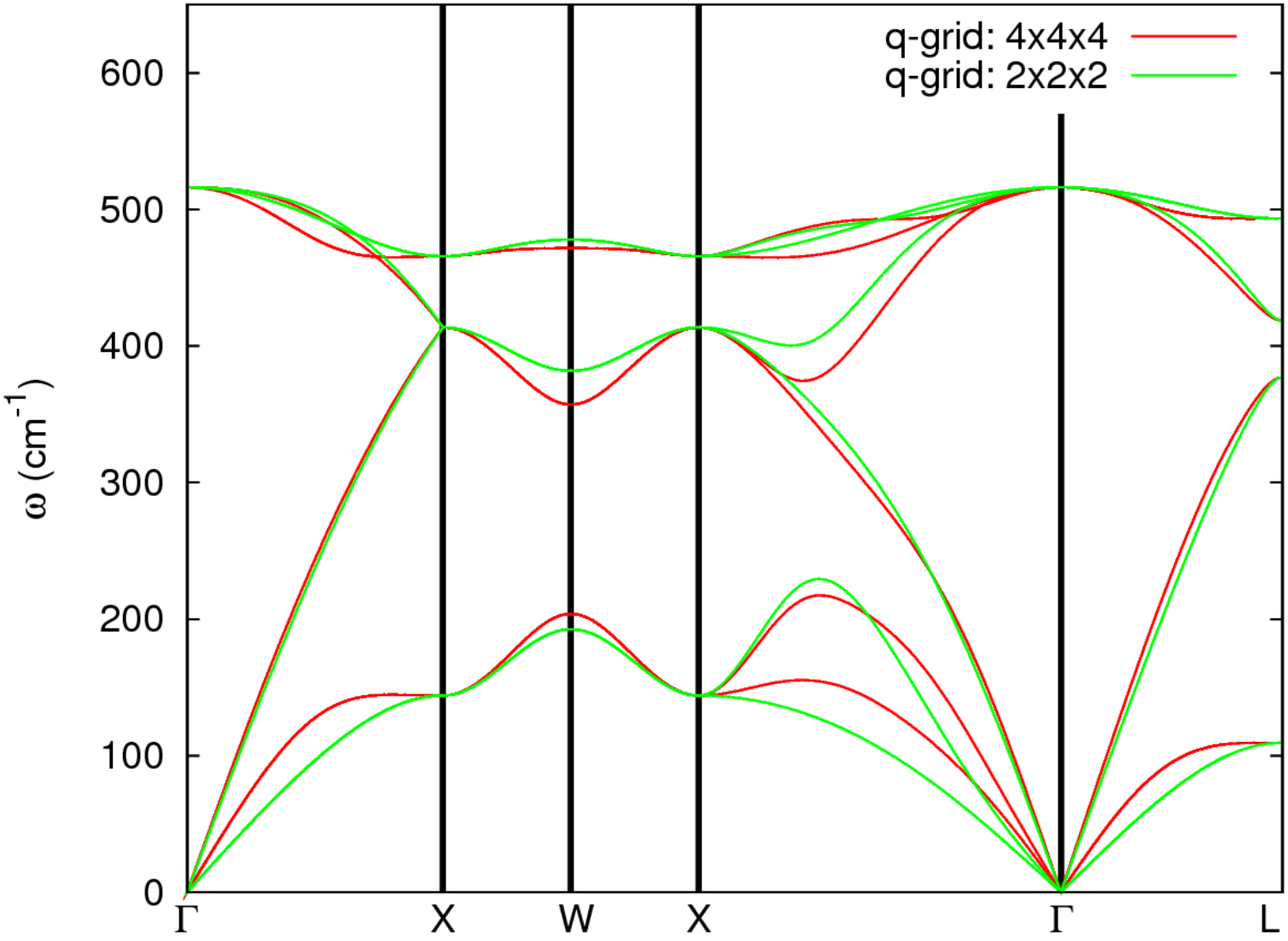
Phonon dispersion of silicon along some high-symmetry directions in the Brillouin zone (file **`phonon_dispersion.eps`**):



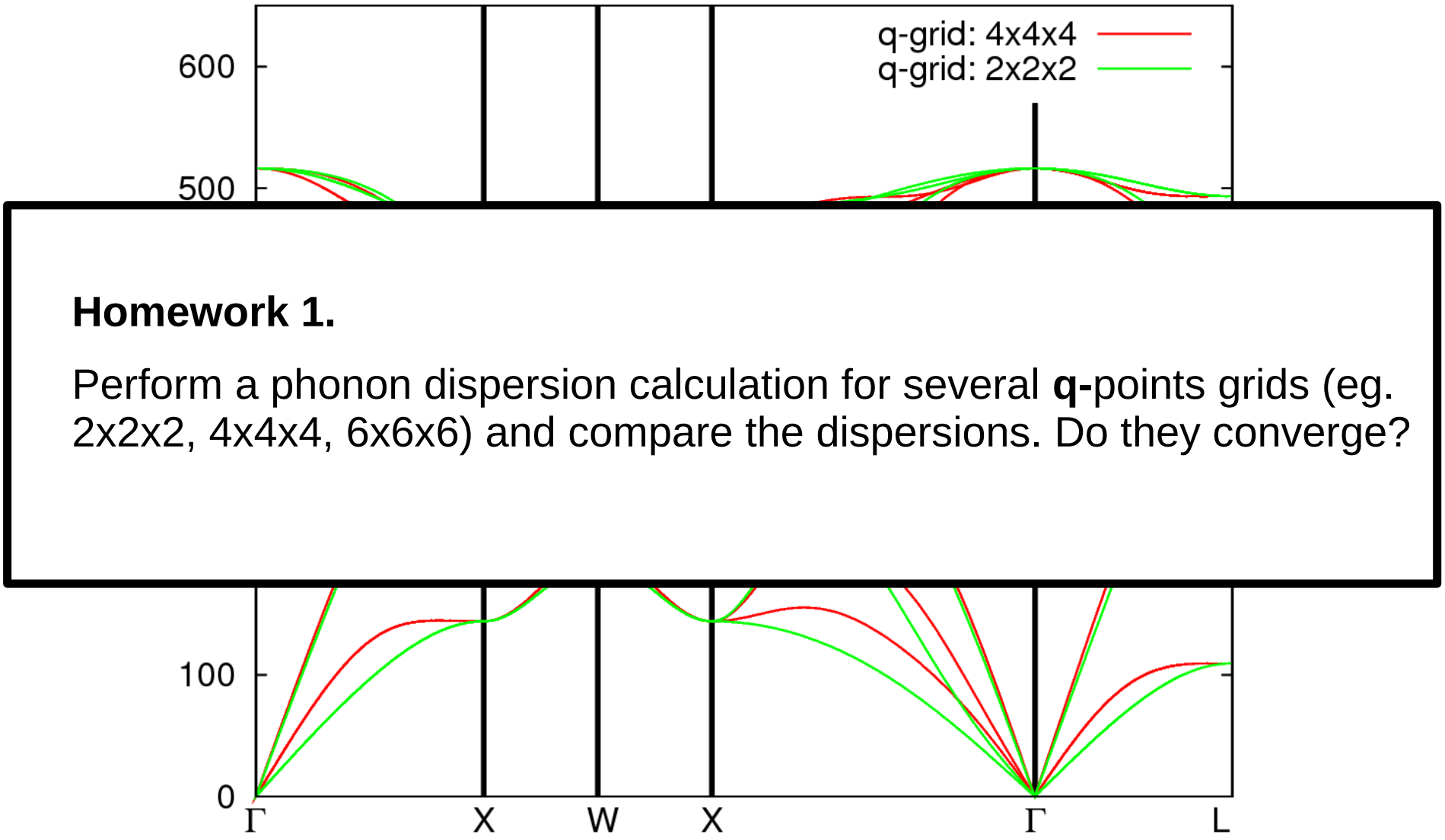
# Exercise 1b: Phonon dispersion in non-polar materials

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



# Exercise 1b: Phonon dispersion in non-polar materials

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

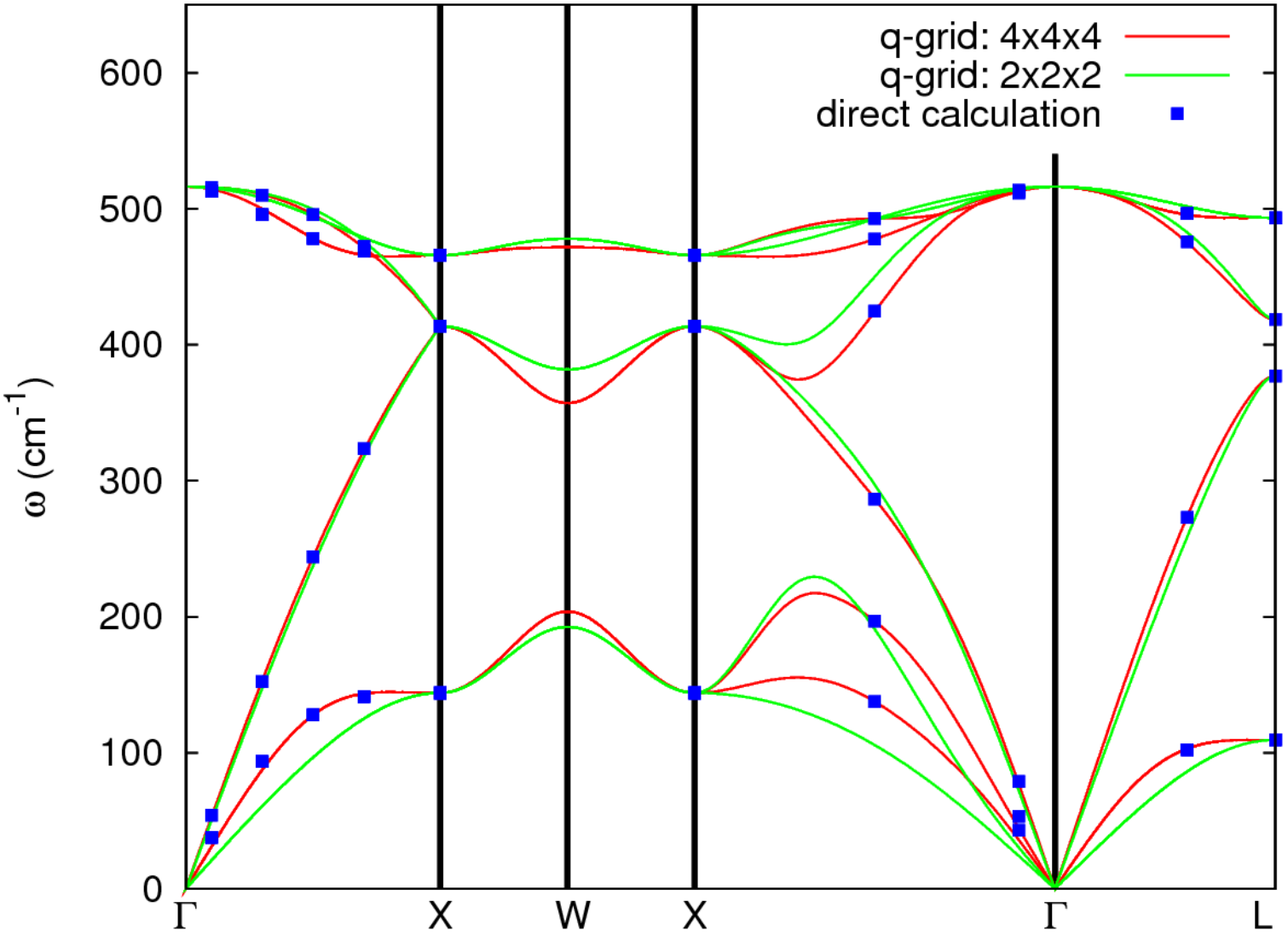



**Homework 1.**

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

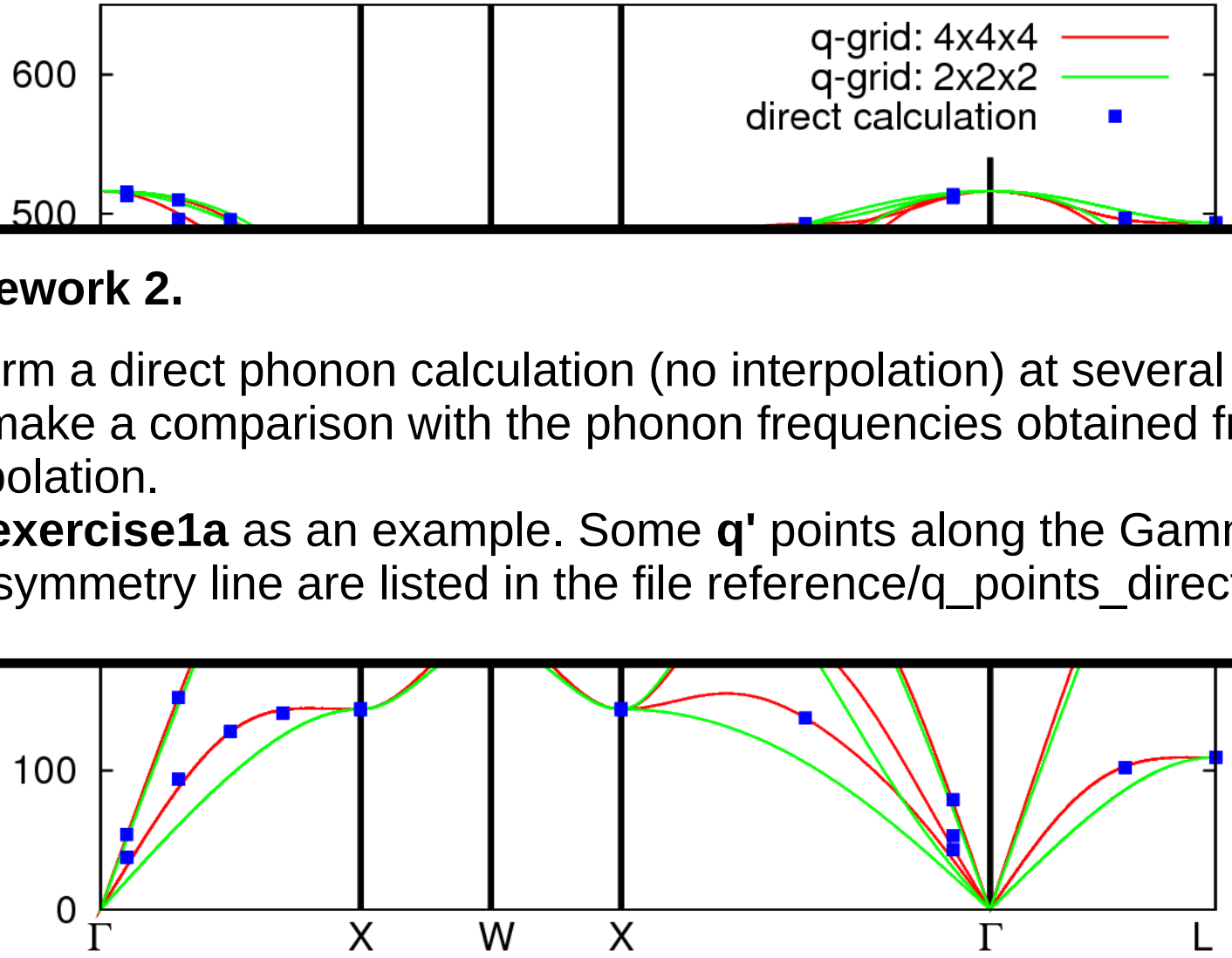
# Exercise 1b: Phonon dispersion in non-polar materials

Comparison of the phonon dispersion computed using the Fourier interpolation with the direct calculation at several **q** points. The Fourier interpolation for Si with the **q**-grid 4x4x4 is satisfactory.



# Exercise 1b: Phonon dispersion in non-polar materials

Comparison of the phonon dispersion computed using the Fourier interpolation with the direct calculation at several **q** points. The Fourier interpolation for Si with the **q**-grid 4x4x4 is satisfactory.

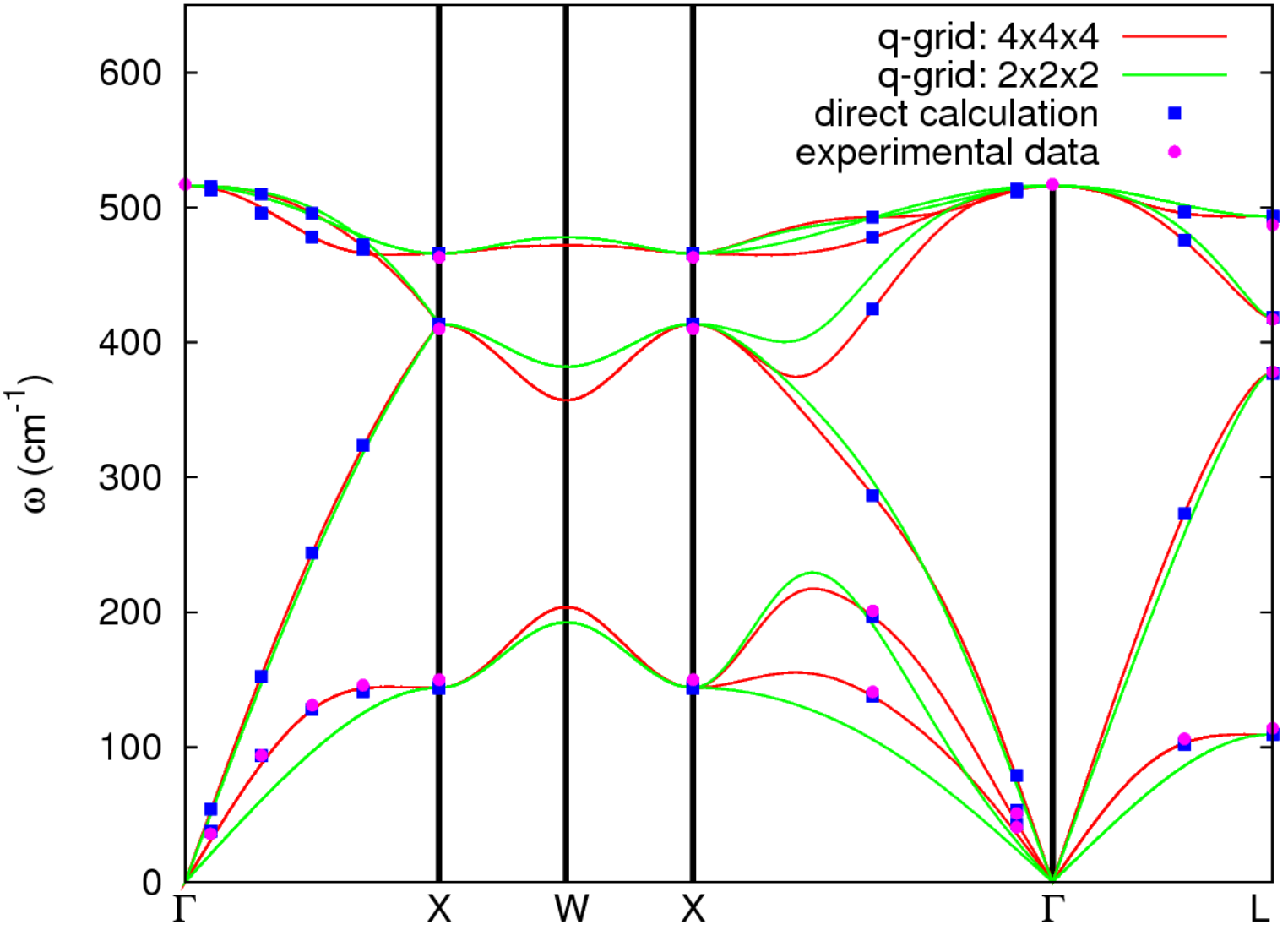



**Homework 2.**

Perform a direct phonon calculation (no interpolation) at several **q'** points and make a comparison with the phonon frequencies obtained from the interpolation.
Use **exercise1a** as an example. Some **q'** points along the Gamma-X high symmetry line are listed in the file reference/q_points_direct_calc.txt

# Exercise 1b: Phonon dispersion in non-polar materials

The agreement of *ab initio* calculation of the phonon dispersion with the experimental data is very good when we use the Fourier interpolation on a **q**-grid 4x4x4.

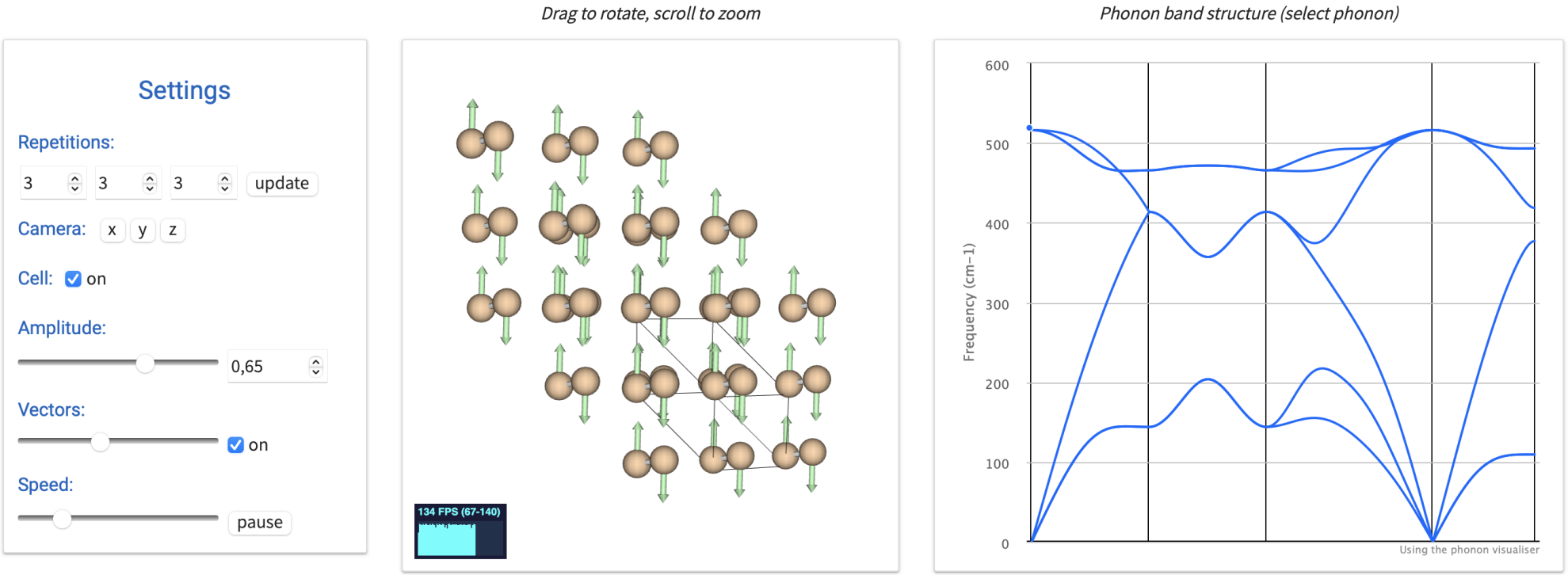


# Phonon modes visualizer

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

https://www.materialscloud.org/work/tools/interactivephonon

## Phonon dispersion: pw.Si.in & matdyn.modes



# Exercise 1b: Phonon dispersion in non-polar materials

The Fourier interpolation works well if the Interatomic Force Constants (IFC's) are known on a sufficiently large supercell, i.e. on a large enough mesh of **q** points in the phonon calculation.

<u>There are cases when the IFC's are long range and the Fourier interpolation does not work properly:</u>

- When there are Kohn anomalies in metals. In this case the dynamical matrices are not a smooth function of **q** and the IFC's are long range.
- In polar insulators, where the atomic displacements generate long range electrostatic interactions and the dynamical matrix is not analytical for $q \rightarrow 0$. However, this case can be addressed by calculating the Born effective charges and the dielectric tensor of the material.

# Outline

1. Introduction
2. **Exercise 1a:** Phonons at Gamma in non-polar materials
3. **Exercise 1b:** Phonon dispersion in non-polar materials
4. **Exercise 2a:** Phonons at Gamma in polar materials
5. **Exercise 2b:** Phonon dispersion in polar materials
6. **Exercise 3:** Phonon dispersion of 2D materials (optional)

# Exercise 2a: Phonons at $\Gamma$ 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**:

$$\tilde{C}_{s\alpha,s'\beta}(\mathbf{q}) = \tilde{C}^{\text{analytic}}_{s\alpha,s'\beta}(\mathbf{q}) + \frac{4\pi}{\Omega}\frac{(\mathbf{q}\cdot\boldsymbol{Z}^{\star}_{s})_{\alpha}(\mathbf{q}\cdot\boldsymbol{Z}^{\star}_{s'})_{\beta}}{\mathbf{q}\cdot\epsilon_{\infty}\cdot\mathbf{q}}$$

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

$$Z^{\star}_{s,\alpha\beta} = \Omega\frac{\partial \mathrm{P}_{\alpha}}{\partial u_{s\beta}}$$

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

$$\epsilon^{\alpha\beta}_{\infty} = \delta_{\alpha\beta} + 4\pi\left.\frac{\partial \mathrm{P}_{\alpha}}{\partial \mathrm{E}_{\beta}}\right|_{u_s(q=0)=0}$$

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

# Exercise 2a: Phonons at Γ in polar materials

Go to the directory with the input files:

```
cd  ~/QE-2021/Day-5/example2a
```

**Step 1.** Perform a Self-Consistent Field ground-state calculation for the polar semiconductor AlAs.

**Step 2.** Perform a phonon calculation at Gamma for AlAs.

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

If .true. will calculate and store the dielectric tensor and effective charges

# Exercise 2a: Phonons at $\Gamma$ in polar materials

In the file **`ph.AlAs.out`** you will find information about the dielectric tensor and effective charges:

```
     Dielectric constant in cartesian axis

     (      13.743494475      -0.000000000       0.000000000 )
     (      -0.000000000      13.743494475       0.000000000 )
     (       0.000000000       0.000000000      13.743494475 )

     Effective charges (d Force / dE) in cartesian axis

          atom      1   Al
      Ex  (         1.88274        0.00000        0.00000 )
      Ey  (         0.00000        1.88274       -0.00000 )
      Ez  (         0.00000       -0.00000        1.88274 )
          atom      2   As
      Ex  (        -3.23377       -0.00000        0.00000 )
      Ey  (        -0.00000       -3.23377        0.00000 )
      Ez  (        -0.00000        0.00000       -3.23377 )

    Diagonalizing the dynamical matrix

    q = (    0.000000000   0.000000000   0.000000000 )

**************************************************************************
    freq (    1) =       0.147836 [THz] =       4.931268 [cm-1]
    freq (    2) =       0.147836 [THz] =       4.931268 [cm-1]
    freq (    3) =       0.147836 [THz] =       4.931268 [cm-1]
    freq (    4) =      11.258207 [THz] =     375.533365 [cm-1]
    freq (    5) =      11.258207 [THz] =     375.533365 [cm-1]
    freq (    6) =      11.258207 [THz] =     375.533365 [cm-1]
**************************************************************************
```

**No LO-TO splitting**

# Exercise 2a: Phonons at Γ in polar materials

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

Input file **dynmat.AlAs.in** :

```
&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

Output file **dynmat.out** :

```
**********************************************
     freq (    1) =       -0.000000 [THz] =
(   0.538473   0.000000     -0.458309   0.000000
(   0.538473   0.000000     -0.458309   0.000000
     freq (    2) =       -0.000000 [THz] =
(   0.000000   0.000000      0.000000   0.000000
(   0.000000   0.000000      0.000000   0.000000
     freq (    3) =        0.000000 [THz] =
(  -0.458309   0.000000     -0.538473   0.000000
(  -0.458309   0.000000     -0.538473   0.000000
     freq (    4) =       11.257454 [THz] =
(   0.000000   0.000000      0.940852   0.000000
(  -0.000000   0.000000     -0.338817   0.000000
     freq (    5) =       11.257454 [THz] =
(   0.000000   0.000000      0.000000   0.000000
(   0.000000   0.000000      0.000000   0.000000
     freq (    6) =       12.307908 [THz] =
(   0.940852   0.000000     -0.000000   0.000000
(  -0.338817   0.000000      0.000000   0.000000
**********************************************
```

**LO-TO splitting**

**dynmat.x < dynmat.AlAs.in > dynmat.AlAs.out**

# Outline

1. Introduction
2. **Exercise 1a:** Phonons at Gamma in non-polar materials
3. **Exercise 1b:** Phonon dispersion in non-polar materials
4. **Exercise 2a:** Phonons at Gamma in polar materials
5. **Exercise 2b:** Phonon dispersion in polar materials
6. **Exercise 3:** Phonon dispersion of 2D materials (optional)

# Exercise 2b: Phonon dispersion in polar materials

Go to the directory with the input files:

```
cd  ~/QE-2021/Day-5/example2b
```

- Calculate phonon dispersion in AlAs following the same steps as in **exercise 1b**.

- Where necessary insert the missing information in the input files.

# Exercise 2b: Phonon dispersion in polar materials

Step 1. Perform a SCF ground-state calculation for AlAs using **`pw.x`**

Step 2. Perform a phonon calculation on a 4x4x4 **q**-grid using **`ph.x`**
(dielectric tensor and effective charges will be calculated)

Step 3. Perform Fourier Transforms (FT) of $\tilde{C}_{s\alpha,s'\beta}(\mathbf{q})$ in order to get Interatomic Force Constants in real space $C_{s\alpha,s'\beta}(\mathbf{R})$ using **`q2r.x`**.

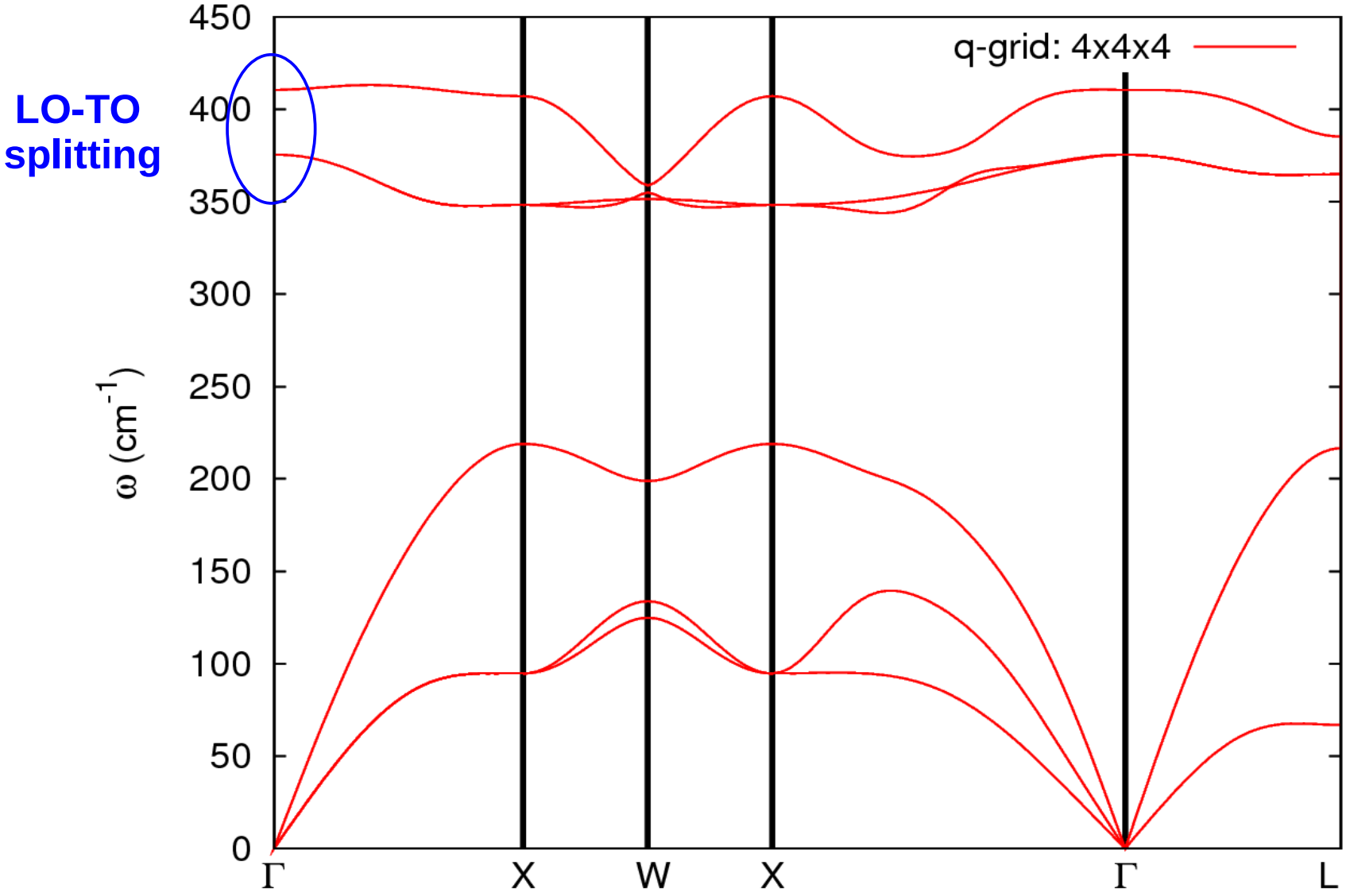
A term having the same behaviour for **q** -> **0** as the non-analytic term is subtracted from $\tilde{C}_{s\alpha,s'\beta}(\mathbf{q})$ before the FT and re-added to $C_{s\alpha,s'\beta}(\mathbf{R})$, so that no problem related to non-analytic behaviour and related long-rangeness arises in the FT.

Step 4. Calculate phonons at generic **q'** points using Interatomic Force Constants (including the non-analytic term) using the code **`matdyn.x`**

Step 5. Plot the phonon dispersion of AlAs using **`plotband.x`** and **`gnuplot`**.

# Exercise 2b: Phonon dispersion in polar materials

The phonon dispersion of AlAs:



# Outline

1. Introduction
2. **Exercise 1a:** Phonons at Gamma in non-polar materials
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5. **Exercise 2b:** Phonon dispersion in polar materials
6. **Exercise 3:** Phonon dispersion in 2D materials (optional)

# Exercise 3: Phonon dispersion in 2D materials

Go to the directory with the input files:

```
cd  ~/QE-2021/Day-5/example3
```

- Calculate phonon dispersion in 2D hexagonal BN following the same steps as in **exercise 1b** and **exercise 2b**.

- Notice that the options `assume_isolated='2D'` in `pw.bn.in` and `loto_2d=.true.` in `q2r.bn.in` and `matdyn.bn.in` have been set to properly deal with 2D materials.

# Exercise 3: Phonon dispersion in 2D materials

Step 1. Perform a SCF ground-state calculation for 2D h-BN using **`pw.x`**

Step 2. Perform a phonon calculation on a 6x6x1 **q**-grid using **`ph.x`**

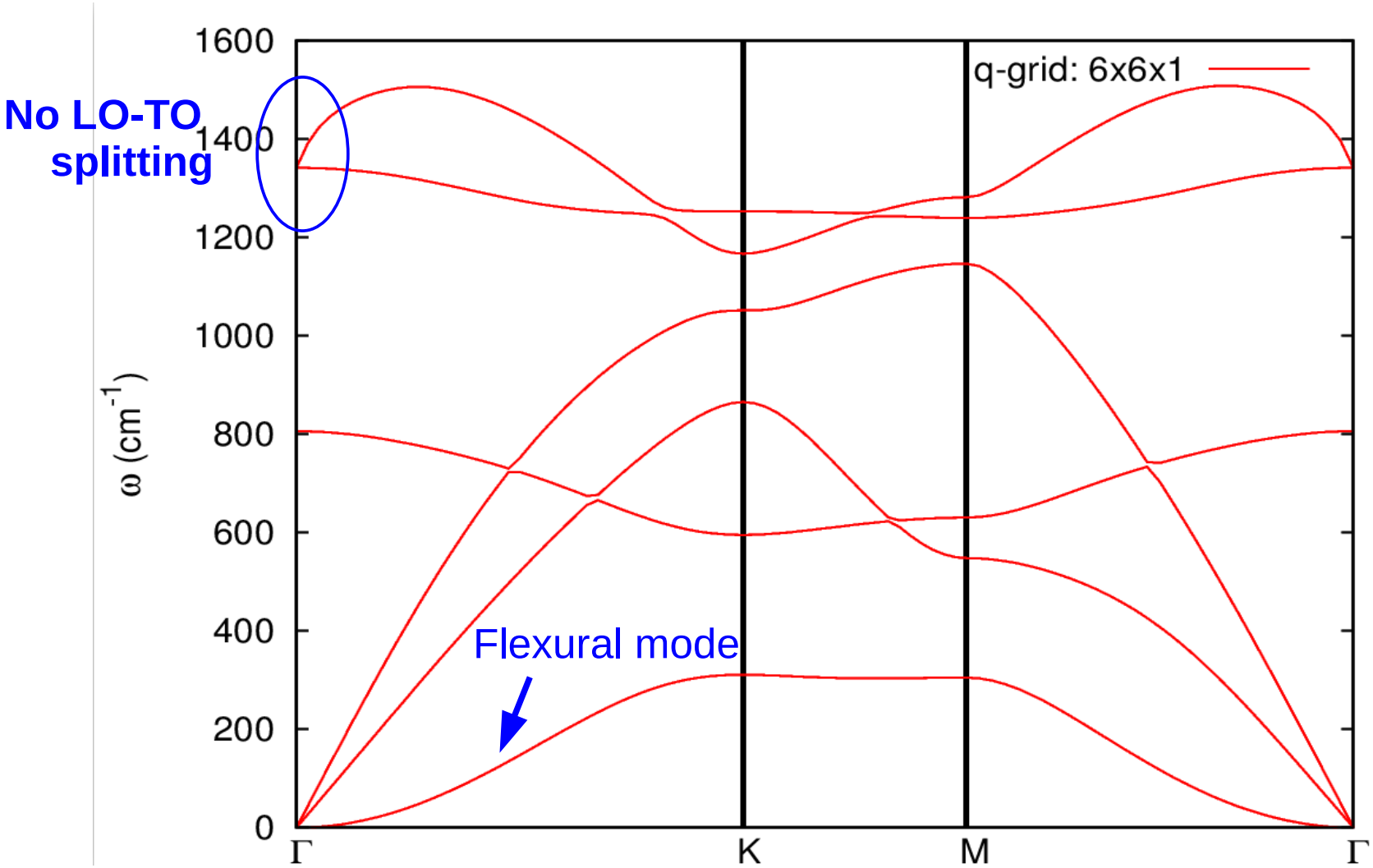
Step 3. Perform Fourier Transformations (FT) of $\tilde{C}_{s\alpha,s'\beta}(\mathbf{q})$ in order to obtain Interatomic Force Constants in real space $C_{s\alpha,s'\beta}(\mathbf{R})$ using **`q2r.x`**.

Step 4. Calculate phonons at generic **q'** points using Interatomic Force Constants using the code **`matdyn.x`**

Step 5. Plot the phonon dispersion of 2D h-BN using **`plotband.x`** and **`gnuplot`**.

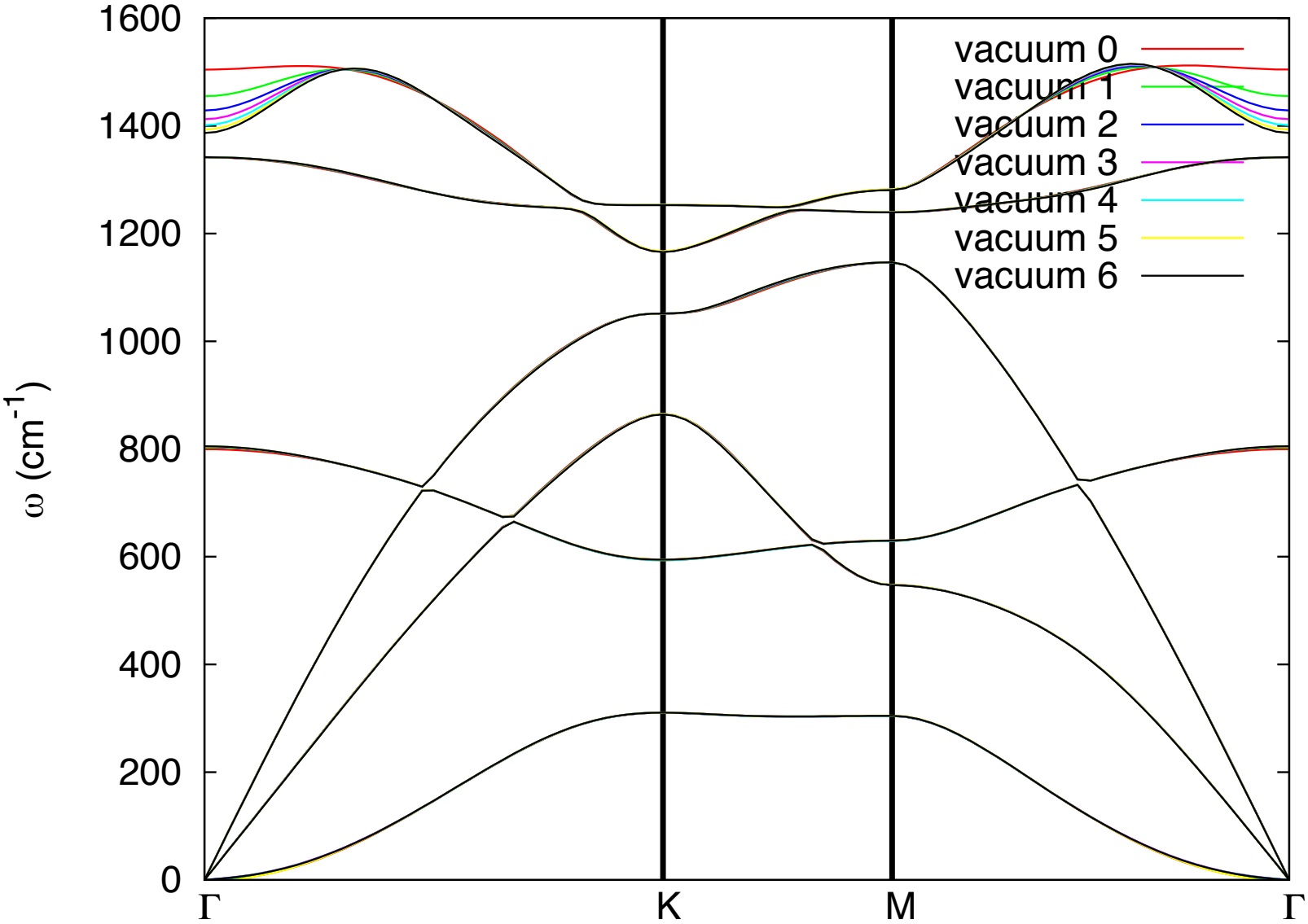
# Exercise 3: Phonon dispersion in 2D materials

The phonon dispersion of 2D hexagonal BN:



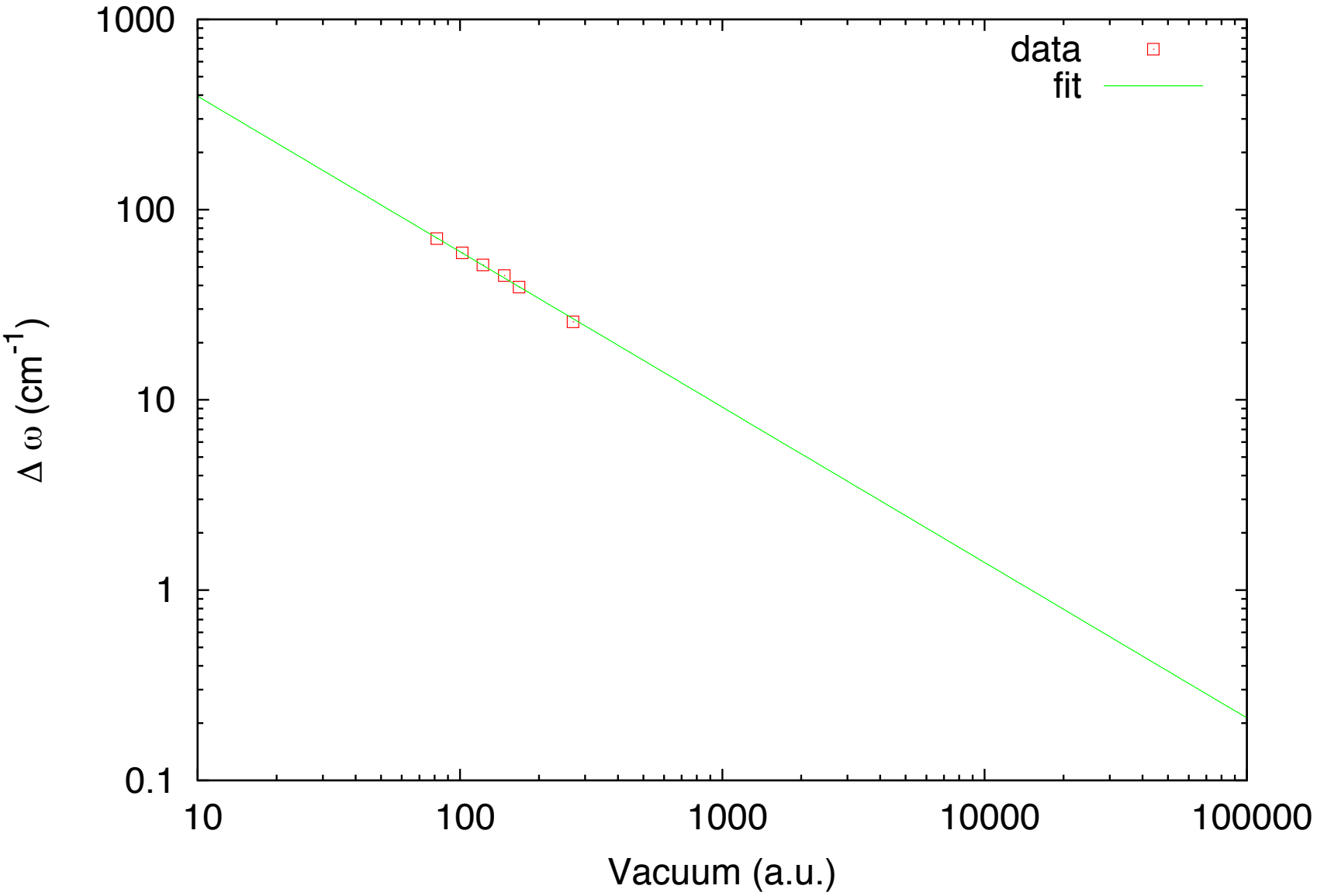
# Exercise 3: Phonon dispersion in 2D materials

Effect of vacuum



# Exercise 3: Phonon dispersion in 2D materials

Effect of vacuum



# Bibliography

## Books


**1**. N. W. Ashcroft, N. D. Mermin, Solid State Physics (for general discussion)

**2**. M. Fox, Optical properties of solids (a few words about LO-TO splitting)


## Papers


**1**. S. Baroni, P. Giannozzi, and A. Testa,
*Green's-function approach to linear response in solids*,
Phys. Rev. Lett. **58**, 1861 (1987).

**2**. P. Giannozzi, S. de Gironcoli, P. Pavone, and S. Baroni,
*Ab initio calculation of phonon dispersions in semiconductors*,
Phys. Rev. B **43**, 7231 (1991).

**3**. S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi,
*Phonons and related crystal properties from density-functional perturbation theory*, Rev. Mod. Phys. **73**, 515 (2001).

**4**. T. Sohier, M. Gibertini, M. Calandra, F. Mauri, and N. Marzari,
*Breakdown of Optical Phonons' splitting in Two-Dimensional Materials*,
Nano Lett. 2017, **17**, 6, 3758-3763.


"That's all Folks!"