Hands on session:
PHONONS with Quantum ESPRESSO

Sharmila Shirodkar

Jawaharlal Nehru Centre for Advanced Scientific Research

Bangalore

Exercises

Exercise 1: To calculate phonon frequencies at the Brillouin Zone centre (Γ-point) for silicon.

Exercise 2: To calculate the phonon dispersion along high symmetry directions in the BZ for silicon.

Exercise 3: To calculate the phonon frequencies in a polar material (AlAs), accounting for the presence of macroscopic electric fields and LO-TO splitting.

Exercise 4: To calculate phonon dispersion of a metal (Al).

Exercise 1: phonon frequencies at Γ-point for silicon

- Executables: pw.x and ph.x
- Post processing: dynmat.x

Look in run.sh for the sequence

To run the script: nohup sh run.sh &

Step1: run a scf calculation on the equilibrium structure

```
&electrons
   mixing_mode = 'plain'
   mixing_beta = 0.5
   conv_thr =  1.0d-10
/
```

→ Smaller for scf calculations

Exercise 1: phonon frequencies at Γ-point for silicon

Step2: run a phonon calculation with ph.x

/usr/local/apps/espresso-5.1/bin/ph.x < si_ph_G.in > si_ph_G.out

```
&inputph
  outdir='./tmp/',
  prefix='si',
  fildyn='si.dynmat_G',
  tr2_ph=1.0d-14,
  amass(1)=28.086
/
0.0 0.0 0.0
```

- outdir='./tmp/', → Path to temporary folder of scf
- prefix='si', → Prefix used in scf calculation
- fildyn='si.dynmat_G', → Name of file for saving dynamical matrix
- tr2_ph=1.0d-14, → Minimum threshold for convergence or smaller
- amass(1)=28.086 → Atomic mass of each atomic type: If not specified it is read from the data file
- 0.0 0.0 0.0 → q point at which frequencies are calculated (in 2pi/a format)

Exercise 1: phonon frequencies at Γ-point for silicon

In the output of ph.x: si_ph_G.out

omega(1) =	0.437450 [THz] =	14.591747 [cm-1]	Acoustic modes
omega(2) =	0.437450 [THz] =	14.591747 [cm-1]	
omega(3) =	0.437450 [THz] =	14.591747 [cm-1]	
omega(4) =	14.994107 [THz] =	500.149581 [cm-1]	Optical modes
omega(5) =	14.994107 [THz] =	500.149581 [cm-1]	
omega(6) =	14.994107 [THz] =	500.149581 [cm-1]	

The frequencies of acoustic modes at BZ centre are supposed to be zero due to translational invariance

Exercise 1: phonon frequencies at Γ-point for silicon

In the si.dynmat_G file

```
   q = (    0.000000000   0.000000000   0.000000000 )
*****************************************************************************
   omega( 1) =       0.437450 [THz] =      14.591747 [cm-1]
(  0.294694  0.000000 -0.319422  0.000000 -0.557786  0.000000 )
(  0.294694  0.000000 -0.319422  0.000000 -0.557786  0.000000 )
   omega( 2) =       0.437450 [THz] =      14.591747 [cm-1]
( -0.445392  0.000000 -0.543899  0.000000  0.076157  0.000000 )
( -0.445392  0.000000 -0.543899  0.000000  0.076157  0.000000 )
   omega( 3) =       0.437450 [THz] =      14.591747 [cm-1]
(  0.463445  0.000000 -0.319599  0.000000  0.427873  0.000000 )
(  0.463445  0.000000 -0.319599  0.000000  0.427873  0.000000 )
   omega( 4) =      14.994107 [THz] =     500.149581 [cm-1]
( -0.053967  0.000000 -0.110628  0.000000  0.696311  0.000000 )
(  0.053967  0.000000  0.110628  0.000000 -0.696311  0.000000 )
   omega( 5) =      14.994107 [THz] =     500.149581 [cm-1]
(  0.635522  0.000000 -0.310019  0.000000  0.000000  0.000000 )
( -0.635522  0.000000  0.310019  0.000000  0.000000  0.000000 )
   omega( 6) =      14.994107 [THz] =     500.149581 [cm-1]
(  0.305286  0.000000  0.625819  0.000000  0.123090  0.000000 )
( -0.305286  0.000000 -0.625819  0.000000 -0.123090  0.000000 )
*****************************************************************************
```

} eigenvectors

Exercise 1: phonon frequencies at Γ-point for silicon

The acoustic sum rule (ASR):

Due to translational invariance, the zone centre dynamical matrix should allow a rigid translation of the solid as an eigenvector with zero eigenfrequency. This leads to the sum rule:

$$\sum_K C_{K\alpha,K'\beta} = 0$$

K is atom index
α, β= x, y, z

Numercal inaccuracies lead to violation of accoustic sum rules for force constant and effective charges.

Reasons:

- Insufficient k-point sampling.
- Large convergence thresholds.
- Small charge density cutoff (ecutrho) for ultrasoft PPs.

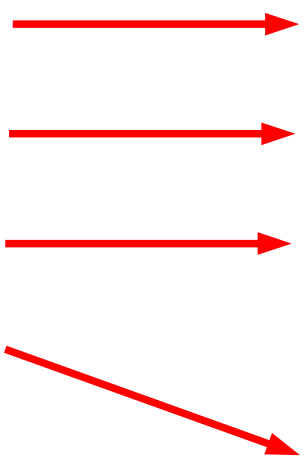
Exercise 1: phonon frequencies at Γ-point for silicon

Step 3: run dynmat.x with input file dynmat_Si_G.in

We apply ASR rule in this step

(skip step 3 for non-Γ q-point)

```
&input
    fildyn='si.dynmat_G',
    asr='simple',
    filout='dynmat.out',
    filxsf='dynmat.axsf',
/
```



Dynamical matrix file

Type of ASR rule

File that stores eigenvalues and eigenvectors

XSF file: open in Xcrysden to visualize the modes of vibration

/usr/local/apps/espresso-5.1/bin/dynmat.x < dynmat_Si_G.in > dynmat_Si_G.out

Exercise 1: phonon frequencies at Γ-point for silicon

Types of ASR in Quantum ESPRESSO

```
!  asr   character   indicates the type of Acoustic Sum Rule imposed
!                    - 'no': no Acoustic Sum Rules imposed (default)
!                    - 'simple':  previous implementation of the asr used
!                    (3 translational asr imposed by correction of
!                    the diagonal elements of the dynamical matrix)
!                    - 'crystal': 3 translational asr imposed by optimized
!                    correction of the dyn. matrix (projection).
!                    - 'one-dim': 3 translational asr + 1 rotational asr
!                    imposed by optimized correction of the dyn. mat. (the
!                    rotation axis is the direction of periodicity; it
!                    will work only if this axis considered is one of
!                    the cartesian axis).
!                    - 'zero-dim': 3 translational asr + 3 rotational asr
!                    imposed by optimized correction of the dyn. mat.
!                    Note that in certain cases, not all the rotational asr
!                    can be applied (e.g. if there are only 2 atoms in a
!                    molecule or if all the atoms are aligned, etc.).
!                    In these cases the supplementary asr are cancelled
!                    during the orthonormalization procedure (see below).
!                    Finally, in all cases except 'no' a simple correction
!                    on the effective charges is performed (same as in the
!                    previous implementation).
```

Exercise 1: phonon frequencies at Γ-point for silicon

dynmat.out file: Changes in eigenvalues and eigenvectors

```
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) =      14.987725 [THz] =     499.936680 [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) =      14.987725 [THz] =     499.936680 [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) =      14.987725 [THz] =     499.936680 [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 2: phonon dispersion for silicon

- Executables: pw.x and ph.x
- Post processing: q2r.x, matdyn.x, plotband.x

  To run the script: nohup sh run.sh &

Step1: run a scf calculation on the equilibrium structure

Same as step 1 in Exercise 1

Exercise 2: phonon dispersion for silicon

Step 2: run ph.x on a grid of q points

Look in si_ph.in file

```
 &inputph
   outdir='./tmp/',
   prefix='si',
   ldisp=.true.
   nq1=4,nq2=4,nq3=4
   fildyn='si.dynmat',
   tr2_ph=1.0d-14,
   amass(1)=28.086
 /
```

Specifies that phonon calculations are on a grid of q-points

4x4x4 grid of q-points

Run: nohup /usr/local/apps/espresso-5.1/bin/ph.x < si_ph.in > si_ph.out &

Exercise 2: phonon dispersion for silicon

ph.x generates si.dynmat0 to si.dynmat8 files

- si.dynmat0 consists of the q-point grid
- si.dynmat1 to si.dynmat8 consist of dynamical matrices for 4x4x4 grid of q-points

Step 3:

This step fourier transforms dynamical matrices from q-space (i.e. si.dynmat0 to si.dynmat8) to real space (R-space) force constant matrix (si444.fc). The q2r.in file

```
&input
 fildyn='si.dynmat'
 zasr='simple'
 flfrc='si444.fc'
/                    /usr/local/apps/espresso-5.1/bin/pw.xq2r.x < q2r.in > q2r.out
```

Exercise 2: phonon dispersion for silicon

Step 4:

This step involves generating the dynamical matrix (eigenvectors and eigenvalues) for an arbitrary q-point from the force constant matrix using Fourier interpolation.

Look in matdyn_Si_disp.in file

```
&input
  asr='simple',
  amass(1)=28.0855,
  flfrc='si444.fc',
  flfrq='si.freq',
  q_in_band_form=.true.
/
5
0.0000000   0.0000000   0.0000000 10
0.0000000   0.0000000   1.0000000 10
0.5000000   0.0000000   1.0000000 10
0.5000000   0.5000000   0.5000000 10
0.0000000   0.0000000   0.0000000 1
```

Force constant matrix file

Output file

For band calculations

List of high symmetry points in 2pi/a followed by number of points between two high symmetry q-points

Exercise 2: phonon dispersion for silicon

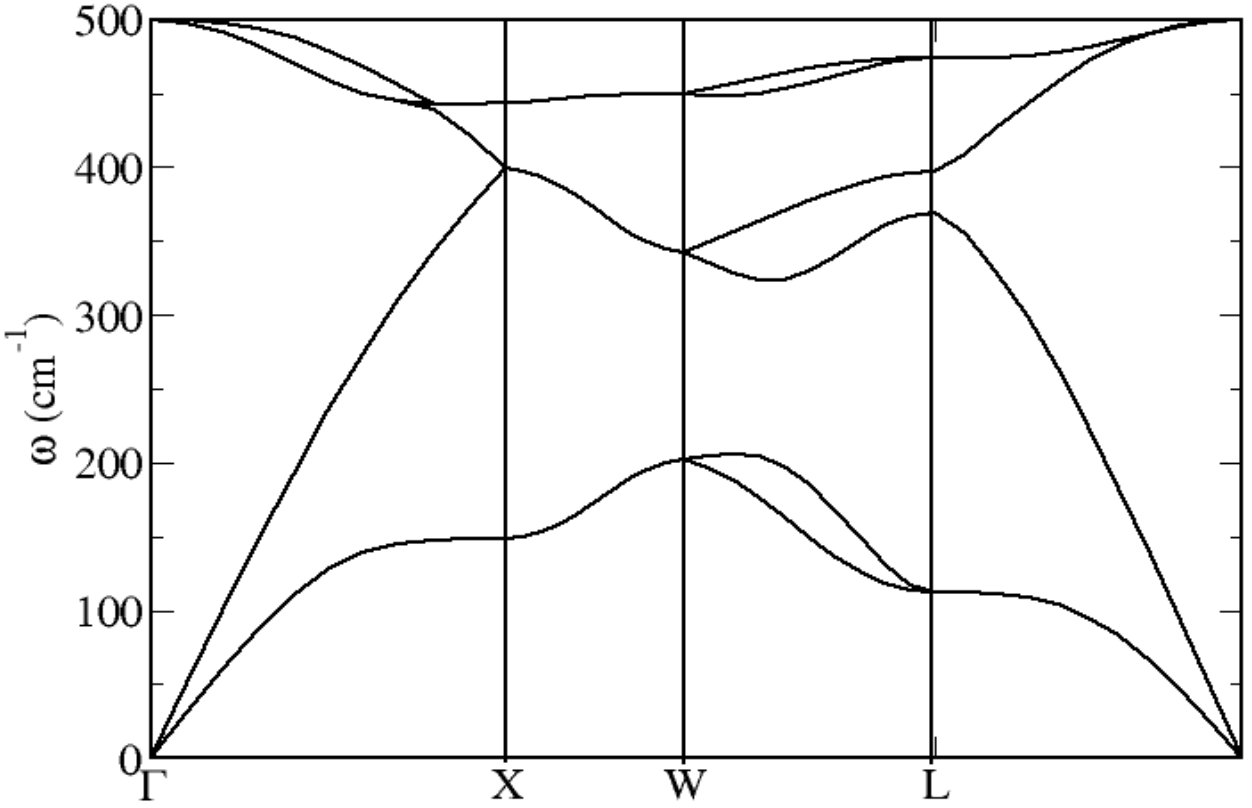
Step 5: Run plotband.x to generate a file which can be plotted

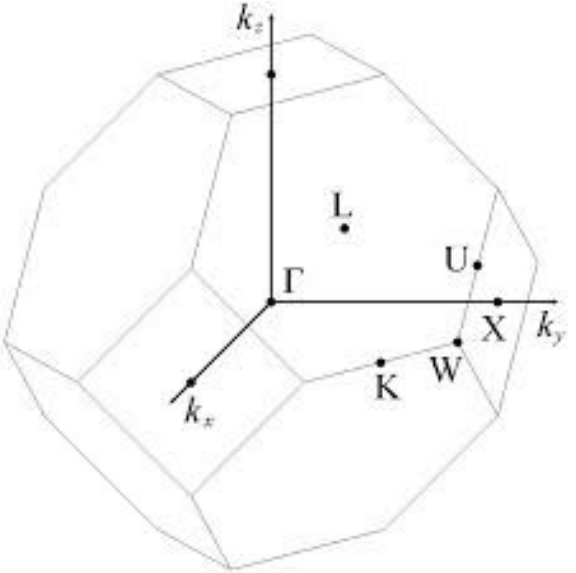
We will run plotband.x interactively

prompt> /usr/local/apps/espresso-5.1/bin/plotband.x

We plot the band structure using a plotting software

Exercise 2: phonon dispersion for silicon





BZ of FCC lattice

Exercise 2: phonon dispersion for silicon

Phonon density of states (DOS) using matdyn.x

The matdyn.x executable can also be used to calculate the phonon density of states

Look in matdyn_Si_dos.in file

```
 &input
    asr='simple',
    amass(1)=28.0855,
    flfrc='si444.fc', flfrq='si.freq.dos'
    dos=.true.,
    fldos='si.dos'
    deltaE=1.d0,
    nk1=4, nk2=4, nk3=4,
 /
```

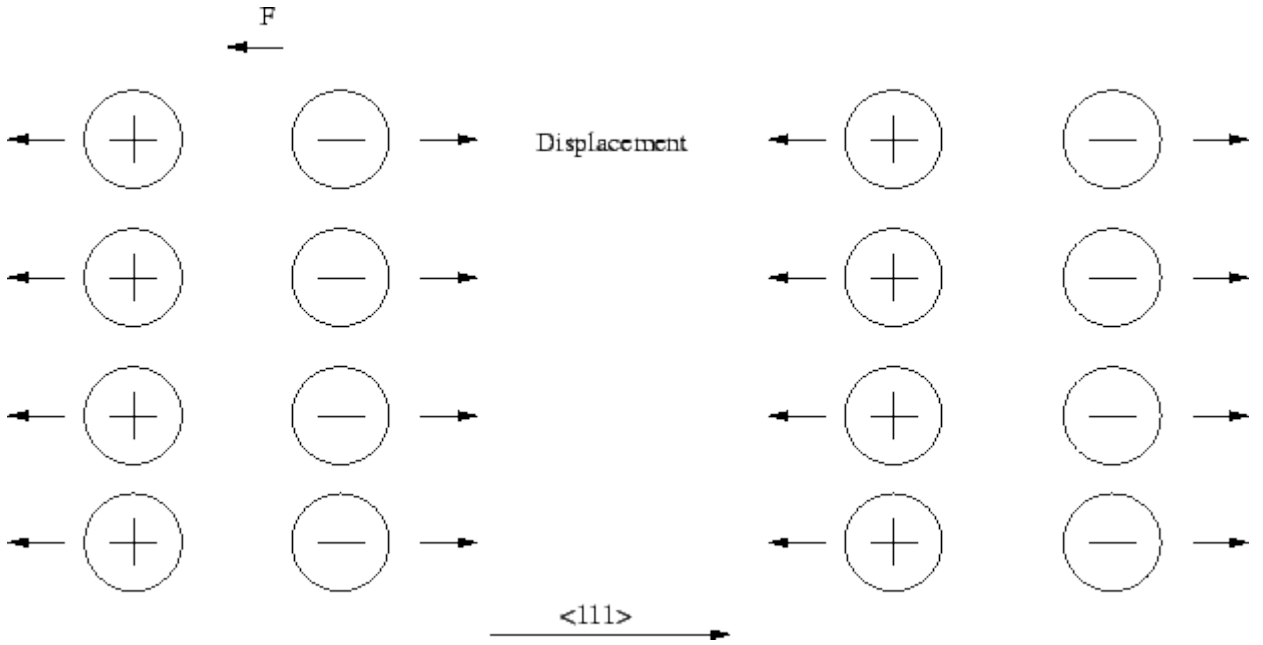
Tag for calculating DOS

File with phonon DOS

Energy interval

Exercise 3: LO-TO splitting for AlAs

- In polar crystals, long range macroscopic electric fields arise that are associated with long wave longitudinal optical (LO) phonons.



- The long range electric fields associated with long-wavelength LO phonons are responsible for removal of degeneracy between the LO and TO (Transverse Optical) phonons at the Brillouin zone centre (q= 0), and is known as LO-TO splitting.

Exercise 3: LO-TO splitting for AlAs

- A macroscopic electric field is incompatible with periodic boundary conditions (PBC).
- Force constants need to be modified in the case of PBC to account for the LO-TO splitting.
- A non-analytic term involving the effective charges (polarization induced by lattice distortion) and the dielectric tensor (polarization induced by electric field) is added to the force constants at gamma point.

$$na\tilde{C}_{st}^{\alpha\beta} = \frac{4\pi}{\Omega} \frac{\left(\mathbf{q}\cdot\mathbf{Z}^{\star}{}_{s}\right)_{\alpha}\left(\mathbf{q}\cdot\mathbf{Z}^{\star}{}_{t}\right)_{\beta}}{\mathbf{q}\cdot\boldsymbol{\epsilon}^{\infty}\cdot\mathbf{q}}$$

Exercise 3: LO-TO splitting for AlAs

- Executables: pw.x and ph.x
- Post processing: dynmat.x

To run the script: nohup sh run.sh &

Step1: run a scf calculation on the equilibrium structure

```
&system
   ibrav=  2,  nat=  2, ntyp= 2,celldm(1)=10.58997,
   ecutwfc =45, ecutrho=180
   occupations='fixed', nbnd=8
/
&electrons
   mixing_mode = 'plain'
   mixing_beta = 0.5
   conv_thr =  1.0d-10
/
```

Do a calculation with fixed occupations

Keep small covergence threshold

Exercise 3: LO-TO splitting for AlAs

Step2: run ph.x with alas_ph_G.in input file

```
&inputph
   outdir='./tmp/',
   prefix='alas',
   fildyn='alas.dynmat_G',
   epsil=.true.,
   tr2_ph=1.0d-14,
   amass(1)= 26.98,
   amass(2)= 74.92,
 /
0.0 0.0 0.0
```

To calculate born effective charges and dielectric constant

Exercise 3: LO-TO splitting for AlAs

Output in alas_G_ph.out

```
     Dielectric constant in cartesian axis
     (      9.224845161      0.000000000      0.000000000 )
     (      0.000000000      9.224845161      0.000000000 )
     (      0.000000000      0.000000000      9.224845161 )
     Effective charges (d Force / dE) in cartesian axis
      atom     1   Al
   Ex  (       2.15581       0.00000       0.00000 )
   Ey  (       0.00000       2.15581       0.00000 )
   Ez  (       0.00000       0.00000       2.15581 )
      atom     2   As
   Ex  (      -2.17069       0.00000       0.00000 )
   Ey  (       0.00000      -2.17069       0.00000 )
   Ez  (       0.00000       0.00000      -2.17069 )
     Diagonalizing the dynamical matrix
     q = (    0.000000000   0.000000000   0.000000000 )
**************************************************************************
     omega( 1) =       0.153627 [THz] =       5.124437 [cm-1]
     omega( 2) =       0.153627 [THz] =       5.124437 [cm-1]
     omega( 3) =       0.153627 [THz] =       5.124437 [cm-1]
     omega( 4) =      10.714684 [THz] =     357.403379 [cm-1]
     omega( 5) =      10.714684 [THz] =     357.403379 [cm-1]
     omega( 6) =      10.714684 [THz] =     357.403379 [cm-1]
**************************************************************************
```

ASR not satisfied

No LO-TO splitting

Exercise 3: LO-TO splitting for AlAs

Step3: run dynmat.x with dynmat_alas_G.in

```
&input
    fildyn='alas.dynmat_G',
    asr='simple',
    amass(1)= 26.98,
    amass(2)= 74.92,
    q(1)=1.0, q(2)=0.0, q(3)=0.00,
    filout='dynmat.out',
    filxsf='dynmat.axsf',
/
```

Direction for approaching Gamma point (q= 0)

Check output in dynmat_alas_G.out

#	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	357.40	10.7144	5.4432
	5	357.40	10.7144	5.4432
	6	395.39	11.8536	5.4432

LO-TO splitting

2 TO modes and 1 LO mode

Exercise 4: phonon dispersion of a metal (Al)

- Repeat exercise 2
- Notice the ecutwfc, ecutrho, conv_thr, kmesh
- Do you think they are converged?
- **Check how phonons converge with the above parameters.**