Advanced Quantum ESPRESSO tutorial

Day2: Basic PHONON workflow

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Introduction to phonon workflows:

We will learn how to compute dynamical matrices, dielectric tensors, and vibrational modes and frequencies with `ph.x` Exercises:

1. Computation of Zone Center phonons and dielectric tensors:
   - Non polar case (fcc-Si) `Day2/PHONON/Exercise1.1/`
   - Polar case (fcc AlAs) `Day2/PHONON/Exercise1.2/`

2. Calculation of phonons on $\mathbf{q}$-point meshes and Fourier Interpolation technique `Day-2/PHONON/Exercise2`:
   - Calculation of phonon dispersion for fcc AlAs
   - Calculation of VDOS for fcc AlAs

About Quantum ESPRESSO

More info about Quantum ESPRESSO can be found in:

- https://www.quantum-espresso.org/
- Quantum ESPRESSO (QE) documentation:
  - on-line manuals at www.quantum-espresso.org/resources/users-manual
  - Doc/ sub-directories in the QUANTUM ESPRESSO distribution
  - input data description: most programs contained in QE have their own input file description in the form of hyperlinked **INPUT_***.html** files (where *** stands for the name of the program)

Hands-on material

Hands-on material for these exercises is in `/home/max/QuantumESPRESSO-school-2023/Day2/PHONON/`:

- `Exercise1.1` – Γ modes for fcc-Si
- `Exercise1.2/` – Gamma modes for fcc-AlAs
- `Exercise2` – Dispersion and VDOS for fcc-AlAs

- All directories contain a `README.md` with instructions how to run exercise(s)
- To help recognizing for which program a given input file is intended, the filename starts with the name of the program, i.e.:
  - `<prefix>.scf*.in` – input file for `pw.x` program for the starting scf step
  - `<prefix>.ph*.in` – input file for `ph.x` program for performing the DFPT calculations
  - `<prefix>.<executable>.in` –input file for post-processing programs.

Disclaimer: *many examples use lousy convergence thresholds to speed-up calculations*

Reminder of conditions and definitions

- Interatomic Force Constants:
  - Ground state is a structural local minimum: forces are vanishing;
  - We consider only small displacements around minimum:

$$\mathbf{R}_\mathrm{I} = \mathbf{R}_\mathrm{I}^0 + \mathbf{u}_\mathrm{I}$$

  - Forces have a linear dependence on small displacements:

$$\mathbf{F}_\mathrm{I}(\{\mathbf{u}_\mathrm{I}\}) = -\sum_J \frac{\partial^2 \mathrm{E}}{\partial \mathbf{u}_\mathrm{I} \partial \mathbf{u}_\mathrm{J}} \cdot \mathbf{u}_\mathrm{J}$$

  - The set of force constants $\mathrm{K}_{I,\alpha,J,\beta}$ thus describes the dynamics of the harmonic system:

$$\mathrm{K}_{I,\alpha,J,\beta} = \frac{\partial^2 \mathrm{E}}{\partial \mathrm{u}_{I,\alpha} \partial \mathrm{u}_{J,\beta}}$$

  - Because of the periodicity we can rewrite K in a translationally invariant form:

$$\mathrm{K}_{I_\kappa,\alpha,J_\sigma,\beta} = \mathrm{K}_{\kappa,\alpha,\sigma,\beta}(\mathbf{R}_\kappa - \mathbf{R}_\sigma)$$

Reminder of conditions and definitions

- Monochromatic displaclemt patterns .
  - For infinite periodic systems it is necessary to decompose the dynamics into separate finite monochromatic modes:

$$\tilde{\mathbf{u}}(\mathbf{q})i \cdot e^{i\mathbf{q}\cdot\mathbf{r}}$$

  - The generic monochromatic mode is described by the generalized amplitude:

$$\tilde{\mathrm{u}}_{\kappa,\alpha} = \sqrt{\mathrm{M}_{\kappa}}\mathrm{u}^{0}_{\kappa,\alpha}$$

    with κ running on the atomic indexes of the lattice basis and α the cartesian indexes.
  - and a wavevector $\mathbf{q}$ within the Brillouin zone

Reminder of conditions and definitions

- Dynamical matrices:
  - At each $\mathbf{q}$ the equation of motion are recast into a symmetric eigenvalue problem for the generalized amplitude:

$$\sum_{\sigma,\beta} D_{\kappa,\alpha;\sigma,\beta} \cdot \tilde{u}_{\sigma,\beta} = \omega^2 \tilde{u}_{\kappa,\alpha}$$

  - Where $\mathbf{D}$ is the mass symmetrized Fourier transform of the interatomic force constant matrix:

$$D_{\kappa,\alpha;\sigma,\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_\kappa M_\sigma}} \sum_{\mathbf{R}} K_{\kappa,\alpha,\sigma,\beta}(\mathbf{R}) e^{i\mathbf{q}\cdot\mathbf{R}}$$

  - Alternatively, more useful for plane-wave formalism, the dynamical matrices can be computed directly as mixed second derivatives of the energy with respect to the monochromatic displacements.

Exercise 1: Calculation of Zone center phonons.

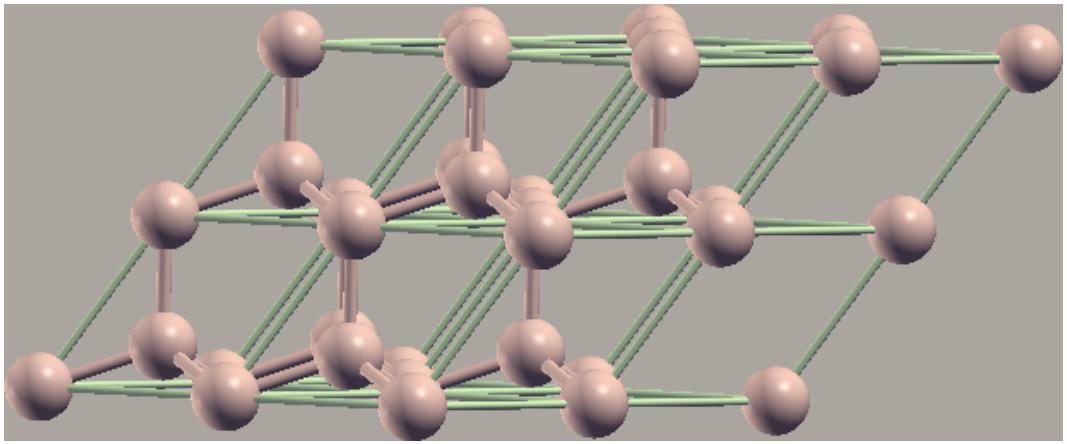
We start computing the dynamical matrices and dielectric properties of fcc-Si

- Go to Exercise1.1 directory and start running the preliminary SCF calculation:

```
> cd Exercise1.1
> mpirun -np 2 pw.x < Si.scf.in > Si.scf.out
```

- let's run our first phonon calculation:

```
> mpirun -np 2 ph.x -i Si.phG.in > Si.phG.out
```



Exercise1.1 input

- `ph.x` has only one namelist `&inputph`
- `prefix` and `tmp` must match those used by `pw.x` for the scf calculation.
- `tr2_ph` defines the convergence threshold for the self consistent solution of the Sternheimer equations.
- `epsilon` asks the program to compute the Electric Field perturbation as well
- `fildyn` defines the prefix for the files where the dynamical matrices are saved
- After the namelist we indicate the coordinates of the wavevector for which we want compute the dynamical matrix.

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

Exercise1.1 output

`ph.x` writes types of output:

- Standard output (`Si.phG.out`) with logging info and summary of the main results of the calculation.
- Files with dynamical matrices (`Sy.dyn`)
- Detailed data for recover and post-processing in `tmp/_ph0/Si.phsave` directory.

Exercise1.1 results

Inspecting the content of `Si.phG.out` we find:

- Symmetry analysys of the system, wavevector and summary of the perturnations that will be computed
- log of the Self Consistent calculation of the density responses for each perturbation
- Summary of the general results

```
Mode symmetry, O_h (m-3m)  point group:


Electric field:
Dielectric constant
Born effective charges as d Force / d E


Atomic displacements:
There are    2 irreducible representations

Representation     1      3 modes -  To be done

Representation     2      3 modes -  To be done
```

Exercise1.1 results

Inspecting the content of `Si.phG.out` we find:

- Symmetry analysys of the system, wavevector and summary of the perturnations that will be computed
- log of the Self Consistent calculation of the density responses for each perturbation
- Summary of the general results

```
Electric Fields Calculation

 iter #   1 total cpu time :     0.6 secs   av.it.:   5.5
 thresh= 1.000E-02 alpha_mix =  0.700 |ddv_scf|^2 =  8.876E-07

 iter #   2 total cpu time :     0.8 secs   av.it.:   9.3
 thresh= 9.421E-05 alpha_mix =  0.700 |ddv_scf|^2 =  3.366E-08

 iter #   3 total cpu time :     1.0 secs   av.it.:   9.2
 thresh= 1.835E-05 alpha_mix =  0.700 |ddv_scf|^2 =  3.540E-10

 iter #   4 total cpu time :     1.1 secs   av.it.:   9.3
 thresh= 1.881E-06 alpha_mix =  0.700 |ddv_scf|^2 =  1.516E-12

 iter #   5 total cpu time :     1.3 secs   av.it.:   9.0
 thresh= 1.231E-07 alpha_mix =  0.700 |ddv_scf|^2 =  1.889E-15

End of electric fields calculation
```

Exercise1.1 results

Inspecting the content of `Si.phG.out` we find:

- Symmetry analysys of the system, wavevector and summary of the perturnations that will be computed
- log of the Self Consistent calculation of the density responses for each perturbation
- Summary of the general results

```
     Dielectric constant in cartesian axis

     (      13.806605797      -0.000000000       0.000000000 )
     (      -0.000000000      13.806605797      -0.000000000 )
     (       0.000000000      -0.000000000      13.806605797 )

     Effective charges (d Force / dE) in cartesian axis without acoustic sum rule applied (asr)

      atom      1   Si Mean Z*:       -0.07570
  Ex  (       -0.07570        0.00000        0.00000 )
  Ey  (        0.00000       -0.07570        0.00000 )
  Ez  (        0.00000        0.00000       -0.07570 )
      atom      2   Si Mean Z*:       -0.07570
  Ex  (       -0.07570       -0.00000        0.00000 )
  Ey  (       -0.00000       -0.07570       -0.00000 )
  Ez  (        0.00000       -0.00000       -0.07570 )

     Effective charges Sum: Mean:       -0.15140
        -0.15140        0.00000        0.00000
         0.00000       -0.15140       -0.00000
         0.00000       -0.00000       -0.15140

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

 Diagonalizing the dynamical matrix

 q = (    0.000000000   0.000000000   0.000000000 )

**************************************************************************
  freq (    1) =       0.070175 [THz] =       2.340773 [cm-1]
  freq (    2) =       0.070175 [THz] =       2.340773 [cm-1]
  freq (    3) =       0.070175 [THz] =       2.340773 [cm-1]
  freq (    4) =      15.292434 [THz] =     510.100699 [cm-1]
  freq (    5) =      15.292434 [THz] =     510.100699 [cm-1]
  freq (    6) =      15.292434 [THz] =     510.100699 [cm-1]
```

Exercise1.1 results

- The acustic sum rules for the rigid translations and for the Born Charges are not exaclty fullfilled. In the next step we will see that (if the deviation is small) we can correct them on the post-processing phase. It is also possible to obtain smaller deviation improving the convergence of our ground state and perturbative calculations.

Exercise1.1 results

- The acustic sum rules for the rigid translations and for the Born Charges are not exaclty fullfilled. In the next step we will see that (if the deviation is small) we can correct them on the post-processing phase. It is also possible to obtain smaller deviation improving the convergence of our ground state and perturbative calculations.

- Rigid translation energies:
  - Use tighter thresholds for both `pw.x` and `ph.x` steps: set `conv_thr` to 1.d-13 in `Si.scf.in` and `tr2_ph` to 1.d-26 in `Si.phG.in` and repeat the calculation.
  - Use a finer FFT mesh increasing the cutoff: compare results with `ecutwfc` set to 30 40 and 50 Ry respectively.

Exercise1.1 results

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  - Use a finer FFT mesh increasing the cutoff: compare results with `ecutwfc` set to 30 40 and 50 Ry respectively.

- Electric field perturbation is more sensitive to convergence w.r.t. the k-point mesh used. In our case deviation from the ASR is significant, which usually means that also the dielectric tensor is inaccurate. Try to see what happens improving the k-point sampling.

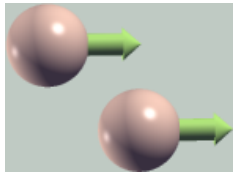
Exercise1.1: postprocessing with dynmat.x

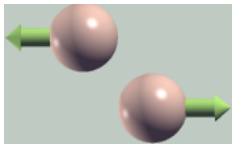
We now use dynmat.x to refine our analysis.

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

- fildyn is used to indicate where the program finds the Dynamical matrix data, we put the name of the file just printed by ph.x
- asr selects if enforcing the ASR and how.
- lperm is true if we want to printout the dielectric tensor (electronic and ionic part)
- filout, filxsf, etc. select the filename for saving displacements and frequencies in various formats.

```
&input
fildyn = 'Si.dyn',
lperm = .true.
asr = 'simple'
filout = 'Si-dynmat.out'
fileig = 'Si-dynmat.eig'
filmol = 'Si-dynmat.mold'
filxsf = 'Si-dynmat.xsf'
/
```





Exercise1.2: AlAs Zone Center modes

We now do the same exercise for fcc-AlAs:

- go to the working directory

```
> cd Day2/PHONON/Exercise1.2
```

- run in sequence `pw.x`, `ph.x`, and `dynmat.x` as in the previous exercise:

```
> mpirun -np 2 pw.x -i AlAs.scf.in > AlAs.scf.out
> mpirun -np 2 ph.x -i AlAs.phG.in > AlAs.phG.out
> dynmat.x -i AlAs.dynmat.in > AlAs.dynmat.log
```

- Now let us inspect files `AlAs.dyn` and `AlAs.dynmat.log`

Exercise1.2: Results

- Inspecting the dielectric tensors in `AlAs.dyn` we find that Born charges are now finite with a value of $\sim$ 2.15 for Al and -2.15 for As

- From `dynmat.x` output (`AlAs.dynmat.log`) we find the 3 optical modes are Infrared active and they give a sizeable contribution to the static dielectric constant tensor.

- The dielectric tensor mantains the cubic symmetry because the 3 optical modes for a degenerate triplet with mutually orthogonal dipole directions.

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

atom #    1
     2.122399401758         -0.000000000000         -0.000000000000
    -0.000000000000          2.122399401758         -0.000000000000
     0.000000000000         -0.000000000000          2.122399401758
atom #    2
    -2.177419719160         -0.000000000000          0.000000000000
    -0.000000000000         -2.177419719160         -0.000000000000
     0.000000000000         -0.000000000000         -2.177419719160

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

atom #    1
 0.212249409755E+01      0.000000000000E+00     -0.333066907388E-15
 0.555111512313E-16      0.212249409755E+01     -0.166533453694E-15
-0.222044604925E-15     -0.333066907388E-15      0.212249409755E+01
atom #    2
-0.217694240795E+01      0.000000000000E+00      0.133226762955E-14
 0.133226762955E-14     -0.217694240795E+01      0.399680288865E-14
 0.133226762955E-14      0.222044604925E-14     -0.217694240795E+01
```

Exercise1.2: Results

- Inspecting the dielectric tensors in `AlAs.dyn` we find that Born charges are now finite with a value of $\sim$ 2.15 for Al and -2.15 for As

- From `dynmat.x` output (`AlAs.dynmat.log`) we find the 3 optical modes are Infrared active and they give a sizeable contribution to the static dielectric constant tensor.

- The dielectric tensor mantains the cubic symmetry because the 3 optical modes for a degenerate triplet with mutually orthogonal dipole directions.

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

# mode   [cm-1]    [THz]      IR
    1     -0.00   -0.0000    0.0000
    2     -0.00   -0.0000    0.0000
    3     -0.00   -0.0000    0.0000
    4    374.23   11.2190    5.3758
    5    374.23   11.2190    5.3758
    6    374.23   11.2190    5.3758

Electronic dielectric permittivity tensor (relati
         9.376325    0.000000    0.000000
         0.000000    9.376325   -0.000000
         0.000000    0.000000    9.376325

 ... with zone-center polar mode contributions
        11.285370    0.000000    0.000000
         0.000000   11.285370    0.000000
         0.000000    0.000000   11.285370
```

Exercise1.2: Results

- Inspecting the dielectric tensors in `AlAs.dyn` we find that Born charges are now finite with a value of $\sim$ 2.15 for Al and -2.15 for As

- From `dynmat.x` output (`AlAs.dynmat.log`) we find the 3 optical modes are Infrared active and they give a sizeable contribution to the static dielectric constant tensor.

- The dielectric tensor mantains the cubic symmetry because the 3 optical modes for a degenerate triplet with mutually orthogonal dipole directions.

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

# mode   [cm-1]    [THz]      IR
    1     -0.00   -0.0000    0.0000
    2     -0.00   -0.0000    0.0000
    3     -0.00   -0.0000    0.0000
    4    374.23   11.2190    5.3758
    5    374.23   11.2190    5.3758
    6    374.23   11.2190    5.3758

Electronic dielectric permittivity tensor (relati
         9.376325    0.000000    0.000000
         0.000000    9.376325   -0.000000
         0.000000    0.000000    9.376325

 ... with zone-center polar mode contributions
        11.285370    0.000000    0.000000
         0.000000   11.285370    0.000000
         0.000000    0.000000   11.285370
```

Exercise1.2: evaluate the LO-TO splitting

(We now use `dynmat.x` and the data in Γ dynamical matrix to estimate the long wave limit of the the IR active phonons. We use the modified input `AlAs.dynmat-LO-TO.in`:

```
> dynmat.x -i AlAs.dynmat-LO-TO.in > AlAs-dynmat-LO-TO.log
```

- To evaluate the splitting we need to specify a direction with `q(1`, `q(2)`, and `q(3)`.
- In this case any direction is equivalent, the LO mode has a dipole oriented in the selected direction.
- The LO - TO splitting is the one expected by the Lyddane-Sachs-Teller relation:

$$\omega_{LO} = \sqrt{\frac{\epsilon_0}{\epsilon_\infty}} \cdot \omega_{TO} = \sqrt{\frac{11.3}{9.4}} \cdot 374 = 410$$

```
&input
fildyn = 'AlAs.dyn',
asr='simple',
amass(1)=26.98,
amass(2)=74.92
filout='AlAs-dynmatLOTO.out'
fileig='AlAs-dynmatLOTO.modes'
filmol='AlAs-dynmatLOTO.mold'
filxsf='AlAs-dynmatLOTO.xsf'
q(1) = 1.0,
q(2) = 1.0,
q(3) = 0.0
/
```

Exercise2: phonon dispersion in fcc-AlAs

In this exercise we will compute the phonon dispersion and the VDOS of AlAs. The material for this exercise is in `../../Day2/PHONON/Exercise2` directory. First step will be computing the dynamical matrices for a uniform mesh of wavevectors with `ph.x`

- We first execute the scf calculations:
  ```
  > mpirun -np 2 pw.x -i AlAs.scf.in > AlAs.scf.out
  ```
- We now execute the phonon calculation, as we are running the calculation for many $\mathbf{q}$s it is usually more efficient to use the image parallelism as much as possible:
  ```
  > mpirun -np 2 ph.x -ni 2 -i AlAs.ph.in > AlAs.ph_images.out
  ```
- After using the image parallelism one has to execut a further single image `ph.x` run to collect data and print the dynamical matrices.
  - Check that `recover` is set to `.true.` in `AlAs.ph.in`
  - Execute with a single image the recover run:
    ```
    > mpirun -np 2 ph.x -i AlAs.ph.in > AlAs.ph_recover.out
    ```

Exercize2: Phonon input

- We `ldisp` to `.true.` to activate the calculation on a uniform mesh
- `nq1`, `nq2`, and `nq3` are used to set the uniform mesh used.
- Symmetries will be used to reduce the number of $\mathbf{q}$ computed.
- `recover` must be set to `.true.` whenever restarting the calculation.
- `fildyn` in this case indicates the suffix for the dynamical matrix files, a separate file will be produced for each q-point computed.

```
Phonons on uniform q-grid
&inputph
prefix='AlAs',
tr2_ph = 1.0d-14,
recover = .false.
ldisp = .true.,
nq1 = 4
nq2 = 4
nq3 = 4
outdir='./tmp'
fildyn='AlAs.dyn',
/
```

Exercise 2: Fourier interpolation of dynamical matrices

- We use the dynamical matrices on the $\mathrm{nq}_1 \times \mathrm{nq}_2 \times \mathrm{nq}_3$ mesh to generate the force constants for a $\mathrm{nq}_1 \times \mathrm{nq}_2 \times \mathrm{nq}_3$ supercell.

```
> q2r.x -i AlAs.q2r.in > AlAs.q2r.log
```

- We need to specify the suffix of the dynamical matrix files in `fildyn`
- The force constants are saved in the file specified by `flfrc`.

```
&input fildyn='AlAs.dyn',
zasr='simple',
flfrc='AlAs444.fc'
/
```

Exercise 2: Fourier interpolation

- Fourier transforming back the force constants we estimate the dynamical matrices at any $\mathbf{q}$ force constants.
- The long-range dipole-dipole interaction has been removed by `q2r.x` and will be readded by `matdyn.x`.
- The range of the remaing ion-ion interaction is assumed to be shorter than the chosen supercell.

- We first compute the phonon dispersion

```
> matdyn.x -i AlAs.matdyn.in
```

- For the dispersion we set `q_in_band_form` to `.true.` and use band form for indicating the BZ path.
- coordinates can be indicated in $2\pi/a$ units, or setting `q_in_cryst_coord` to `.true.` in fractional coordinated of the reciprocal lattice.

```
&input
asr = 'simple'
q_in_band_form = .true.
flfrc='AlAs444.fc',
flfrq='AlAs_dispersion.freq'
/
6
0.00 0.00 0.00 18
0.75 0.75 0.00 22
0.50 1.00 0.00 17
0.00 1.00 0.00 34
0.00 0.00 0.00 29
0.50 0.50 0.50 1
```

Exercise 2: Fourier interpolation

- Fourier transforming back the force constants we estimate the dynamical matrices at any $\mathbf{q}$ force constants.
- The long-range dipole-dipole interaction has been removed by `q2r.x` and will be readded by `matdyn.x`.
- The range of the remaing ion-ion interaction is assumed to be shorter than the chosen supercell.

- We first compute the phonon dispersion

  ```
  > matdyn.x -i AlAs.matdyn.in
  ```

- For the dispersion we set `q_in_band_form` to `.true.` and use band form for indicating the BZ path.
- or directly using special labels; using `point_label_type` flag one can chose between the notation of Setyawan-Curtarolo paper (`'SC'`) or the one of Bilbao Crystallographic Server (`'BI'`)

```
&input
asr = 'simple'
q_in_band_form = .true.
flfrc='AlAs444.fc',
flfrq='AlAs_dispersion.freq'
point_label_type = 'SC'
/
6
gG 18
K 22
W 17
X 34
gG 29
L 1
```

Exercise 2: Fourier interpolation

- Fourier transforming back the force constants we estimate the dynamical matrices at any $\mathbf{q}$ force constants.
- The long-range dipole-dipole interaction has been removed by `q2r.x` and will be readded by `matdyn.x`.
- The range of the remaing ion-ion interaction is assumed to be shorter than the chosen supercell.

- We then compute the VDOS

```
> matdyn.x -i AlAs_dos.matdyn.in
```

- For the VDOS we set `dos` to `.true.` and indicate values for k-mesh with `nk1`, `nk2`, `nk3`, and `deltaE` for the VDOS step
- remember to rename all printout files and indicate with `fldos` a filename for the VDOS printout

```
&input
asr = 'simple'
dos = .true.
deltaE = 1.0
flfrc='AlAs444.fc',
nk1 = 8
nk2 = 8
nk3 = 8
flfrq = 'AlAs_dos.freq'
flvec = 'AlAS_dos.modes'
fleig = 'AlAS_dos.eig'
fldos = 'AlAs_vdos'
/
```