Phonons by QE + visualizer

This document[1] is a step-by-step guide on how to use Quantum Espresso, using Density Functional Perturbation Theory (DFPT), to calculate the phonon spectra for hexagonal Si. Under extreme conditions, Si in the cubic diamond phase transforms into a hexagonal wurtzite crystal, known as lonsdaleite. First step is to acquire an appropriate CIF, for example from the Crystallography Open Database:

```
wget https://www.crystallography.net/cod/1100044.cif
```

Next is to convert the CIF to Quantum Espresso input, this can be done by hand, using the online input generator or with cif2cell, as here:

```
cif2cell 1100044.cif -p quantum-espresso -o 01_Si-lonsdaleite.in
```

The CIF correspond to the correct structure, but not the correct elements. So, edit the input file (01_Si-lonsdaleite.in) by changing all elements to Si. XCrysDen can be used to visualize the structure:

```
xcrysden --pwi 01_Si-lonsdaleite.in
```

In general, appropriate convergence testing for pseudopotentials, k-mesh, cut-off energies and other relevant parameters should be carried out. For this example, ecutwfc=50, ecutrho=200, k-mesh=8×8×4, and the Si.pbe-n-kjpaw_psl.1.0.0.UPF pseudopotential will be used:

```
wget http://pseudopotentials.quantum-espresso.org/upf_files/Si.pbe-n-kjpaw_psl.1.0.0.UPF
```

The QE scf input file is shown below:

```
&CONTROL
  calculation = 'scf',
  outdir = './',
  prefix = 'Si-lonsdaleite',
  pseudo_dir = './',
  tprnfor = .true.,
  tstress = .true.,
  verbosity = 'low',
/
&SYSTEM
  ibrav = 0,
  A = 3.82270,
  nat = 4,
  ntyp = 1,
  ecutwfc = 50,
  ecutrho = 200,
  occupations = 'smearing',
  smearing = 'mv',
  degauss = 0.005d0,
/
&ELECTRONS
  conv_thr = 1d-08,
  mixing_beta = 0.7d0,
/
CELL_PARAMETERS {alat}
  0.866025403784439  -0.500000000000000   0.000000000000000
  0.000000000000000   1.000000000000000   0.000000000000000
  0.000000000000000   0.000000000000000   1.637769116069794
ATOMIC_SPECIES
  Si   28.08500  Si.pbe-n-kjpaw_psl.1.0.0.UPF
ATOMIC_POSITIONS {crystal}
  Si   0.333333333333333   0.666666666666667   0.000000000000000
  Si   0.666666666666667   0.333333333333333   0.500000000000000
  Si   0.333333333333333   0.666666666666667   0.374800000000000
  Si   0.666666666666667   0.333333333333333   0.874800000000000
K_POINTS automatic
8 8 4 0 0 0
```

Listing 1: 01_Si-lonsdaleite.in

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[1] Made by José Núñez for the Computational Materials Physics course by Stefaan Cottenier. 21.09.25

which is run (approx. 1 minute) with:

```
pw.x -in 01_Si-lonsdaleite.in > 01_Si-lonsdaleite.out
```

The description for every variable can be found in the QE pw.x documentation. Observing the output (.out file) a pressure of 29.65 kbar is found. In this example, phonons for the ground-state without external pressure will be calculated, so a full structural relaxation is conducted. A second QE input file is created (02_Si-lonsdaleite.in) and adapted for the structural relaxation. The calculation is ‘vc-relax’ (instead of ‘scf’) and the following lines are added above the cell parameters card (CELL_PARAMETERS):

```
&IONS
  ion_dynamics = ’bfgs’,
/
&CELL
  cell_dynamics = ’bfgs’,
  press = 0.0d0,
  press_conv_thr = 0.5d0,
/
```

Listing 2: Instructions included in 02_Si-lonsdaleite.in

which is run (approx. 10 minutes) with:

```
pw.x -in 02_Si-lonsdaleite.in > 02_Si-lonsdaleite.out
```

resulting in relaxed structural parameters (atomic positions and cell dimensions). A new file has to be created (03_Si-lonsdaleite.in) with the updated structural information:

```
CELL_PARAMETERS {alat}
   0.872654024  -0.503827036   0.000000000
   0.000000000   1.007654072  -0.000000000
   0.000000000   0.000000000   1.664298618
ATOMIC_SPECIES
  Si   28.08500  Si.pbe-n-kjpaw_psl.1.0.0.UPF
ATOMIC_POSITIONS {crystal}
  Si  0.3333333333  0.6666666667  0.0003053389
  Si  0.6666666667  0.3333333333  0.5003053389
  Si  0.3333333333  0.6666666667  0.3744946611
  Si  0.6666666667  0.3333333333  0.8744946611
```

Listing 3: Updated structural parameters in 03_Si-lonsdaleite.in

which is run (approx. 1 minute) with:

```
pw.x -in 03_Si-lonsdaleite.in > 03_Si-lonsdaleite.out
```

ensuring to have the ground-state atomic and electronic state. The next step is to calculate the dynamical matrices. A new file is needed (04_Si-lonsdaleite_q01.in):

```
&INPUTPH
  prefix = ’Si-lonsdaleite’,
  outdir = ’./’,
  low_directory_check = .true.,
  amass(1) = 28.08500,
  ldisp = .true.,
  lqdir = .true.,
  nq1 = 4,
  nq2 = 4,
  nq3 = 2,
  start_q=01, last_q=01,
  fildyn=’Si-lonsdaleite.dyn’,
/
```

Listing 4: First q-point calculation, 04_Si-lonsdaleite_q01.in

The description for every variable can be found in the QE ph.x documentation. The prefix and outdir variables need the same values as in the ground-state calculation (03_Si-lonsdaleite.in). The Monkhorst-Pack grid (nq1, nq2 and nq3) has to be commensurate with the k-mesh (this means that the k-grid should be an integer multiple of the q-grid, e.g. 8×8×4 = 2*(4×4×2)), and convergence testing has to be performed. In this example, q-mesh=4×4×2. The first q-point is run (approx. 25 minutes) with:

```
ph.x -in 04_Si-lonsdaleite_q01.in > 04_Si-lonsdaleite_q01.out
```

which calculates the phonon frequencies (written in Si-lonsdaleite.dyn1) for the specified q-point, in this case q=01. Also, ph.x generates the file .dyn0 (Si-lonsdaleite.dyn0) containing the list of q-vectors needed for the complete phonon dispersion:

```
   4   4   2
   8
   0.000000000000000E+00   0.000000000000000E+00   0.000000000000000E+00
   0.000000000000000E+00   0.000000000000000E+00  -0.300426855248403E+00
   0.143241189019030E+00   0.248101016952971E+00   0.000000000000000E+00
   0.143241189019030E+00   0.248101016952971E+00  -0.300426855248403E+00
  -0.286482378038059E+00  -0.496202033905941E+00   0.000000000000000E+00
```

```
 -0.286482378038059E+00  -0.496202033905941E+00  -0.300426855248403E+00
   0.429723567057089E+00   0.248101016952971E+00   0.000000000000000E+00
   0.429723567057089E+00   0.248101016952971E+00  -0.300426855248403E+00
```

Listing 5: q-point list, Si-lonsdaleite.dyn0

A calculation is needed for every q-point in the list. The first q-point listed always correspond to the $\Gamma-$point. So, construct and run the remaining 7 input files (04_Si-lonsdaleite_qXX.in, approx 12 hours in total), changing the start_q and last_q variables accordingly, in this case from q=02 to q=08. Phonon calculations are computationally demanding, and performing them one q-point at the time provides the advantage of being able to restart from an interrupted run if necessary. One can directly check the phonon frequencies in the .dynX files, it has to correspond to $3\times N$, where N is the number of different atoms in the unit cell, in this case $N = 4$, so there are 12 frequencies. Once all force constant matrices (in q-space) have been obtained, the interatomic force constants (IFCs) can be derived. A new file is needed (05_Si-lonsdaleite.in):

```
&INPUT
  fildyn = 'Si-lonsdaleite.dyn',
  flfrc = 'Si-lonsdaleite.fc',
  zasr = 'simple',
/
```

Listing 6: 05_Si-lonsdaleite.in

which is run (approx. 1 minute) with:

```
q2r.x -in 05_Si-lonsdaleite_q01.in > 05_Si-lonsdaleite_q01.out
```

where a simple sum rule (zasr variable) was used. The .fc file contains the IFCs in real space. More information can be found in the QE q2r.x documentation. The dynamical matrix for any q-point is needed to know the phonon dispersion for a chosen path. A new file has to be created (06_Si-lonsdaleite.in):

```
&INPUT
  amass(1) = 28.08500,
  flfrc = 'Si-lonsdaleite.fc',
  flfrq = 'Si-lonsdaleite.freq',
  fldyn = 'Si-lonsdaleite.matdyn',
  flvec = 'Si-lonsdaleite.modes',
  asr = 'simple',
  q_in_cryst_coord = .true.,
  q_in_band_form = .true.,
/
10
0.0000000000  0.0000000000  0.0000000000  20  !G
0.5000000000  0.0000000000  0.0000000000  15  !M
0.3333333333  0.3333333333  0.0000000000  19  !K
0.0000000000  0.0000000000  0.0000000000  20  !G
0.0000000000  0.0000000000  0.5000000000  20  !A
0.5000000000  0.0000000000  0.5000000000  15  !L
0.3333333333  0.3333333333  0.5000000000  19  !H
0.0000000000  0.0000000000  0.5000000000  20  !A
0.5000000000  0.0000000000  0.0000000000  20  !M
0.3333333333  0.3333333333  0.0000000000   1  !K
```

Listing 7: 06_Si-lonsdaleite.in

which is run (approx. 1 minute) with:

```
matdyn.x -in 06_Si-lonsdaleite.in > 06_Si-lonsdaleite.out
```

where the standard path was used, gathered from SeeK-path using the scf input file (03_Si-lonsdaleite.in). More information is available at the QE matdyn.x documentation. At this stage, the phonon dispersion (ph-disp) can be plotted. For a quick view, use plotband.x and introduce the relevant data:

```
plotband.x
  Si-lonsdaleite.freq
  0 500
  Si-lonsdaleite-phdisp.gnu
  Si-lonsdaleite-phdisp.ps
  0
  100 0
```

The dispersion is plotted in the Si-lonsdaleite-phdisp.ps file, while the raw data is in the Si-lonsdaleite-phdisp.gnu file. The phonon density of states (ph-DOS) also can be calculated, from a new file (07_Si-lonsdaleite.in):

```
&INPUT
  flfrc = 'Si-lonsdaleite.fc',
  flfrq = 'Si-lonsdaleite.freq',
  flvec = 'Si-lonsdaleite.modes',
  fldos = 'Si-lonsdaleite.phdos',
  asr = 'simple',
  dos = .true.,
  nk1 = 50, nk2 = 50, nk3 = 50,
```

```
/
```

Listing 8: 07_Si-lonsdaleite.in

which is run (approx. 15 minutes) with:

```
matdyn.x -in 07_Si-lonsdaleite.in > 07_Si-lonsdaleite.out
```

The ph-disp and ph-DOS are plotted in figure 1, using gnuplot and converting the units from cm^{-1} to meV. This result can be compared with the one reported by Materials Project (mp-165), or in the literature with the band calculation of lonsdaleite Ge.

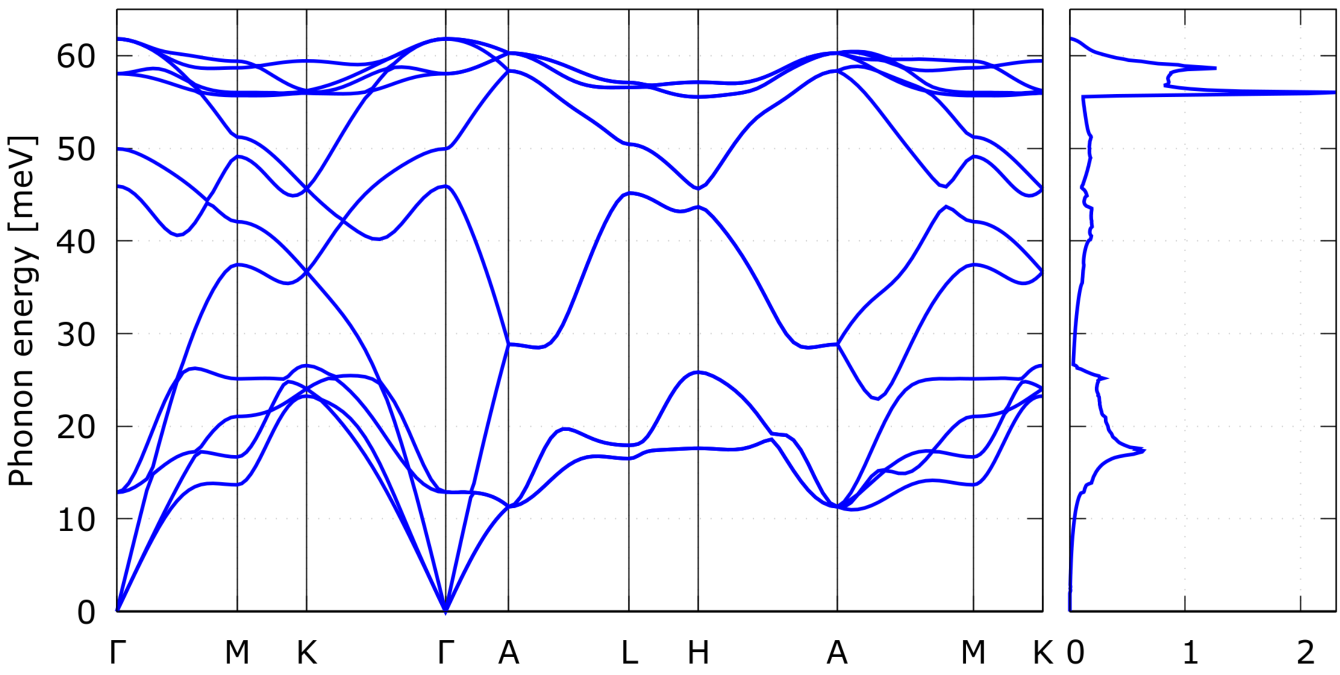

Figure 1: Phonon dispersion and density of states for Si-lonsdaleite.

Interactive Phonon Visualizer

The Interactive Phonon Visualizer serves to visualize the motion of the atoms for any q-point in the Brilliouin zone. It requires three input files, in this example: 03_Si-lonsdaleite.in, 03_Si-lonsdaleite.out and Si-lonsdaleite.modes. More information is available in the website by Henrique Miranda.

Visualizing specific modes

To visualize specific vibrational modes for the calculated q-points, a new file is needed for each q-point (08_Si-lonsdaleite.in):

```
&INPUT
  fildyn = 'Si-lonsdaleite.dyn2',
  filout = 'Si-lonsdaleite_q02.out',
  filxsf = 'Si-lonsdaleite_q02.axsf',
  filmol = 'Si-lonsdaleite_q02.mold',
  asr = 'no',
  q(1) = 0.000000000000000E+00,
  q(2) = 0.000000000000000E+00,
  q(3) = -0.300426855248403E+00,
/
```

Listing 9: 08_Si-lonsdaleite.in

which is run (approx. 1 minute) with:

```
dynmat.x -in 08_Si-lonsdaleite_q02.in > 07_Si-lonsdaleite_q02.out
```

More information is available at the QE dynmat.x documentation. In this example, the A-point was selected by using the corresponding dynamical matrix file (Si-lonsdaleite.dyn2) and q-vector (from Si-lonsdaleite.dyn0). XCrysDen can be used to visualize and animate the vibrational modes:

```
xcrysden --axsf Si-lonsdaleite_q02.axsf
```

To see as vectors, select ‘Display’, then ‘Forces’. Another option is to use VESTA. For that, a script to split the .axsf file into individual .xsf files is needed:

```
git clone https://github.com/ikuhamada/axsf2xsf
./axsf2xsf/src/axsf2xsf.sh Si-lonsdaleite_q02.axsf
```

Run VESTA and load the respective file for each mode of the selected q-point. Figure 2 show the 12 modes for the A-point. Note that there are degenerancies due to symmetry.

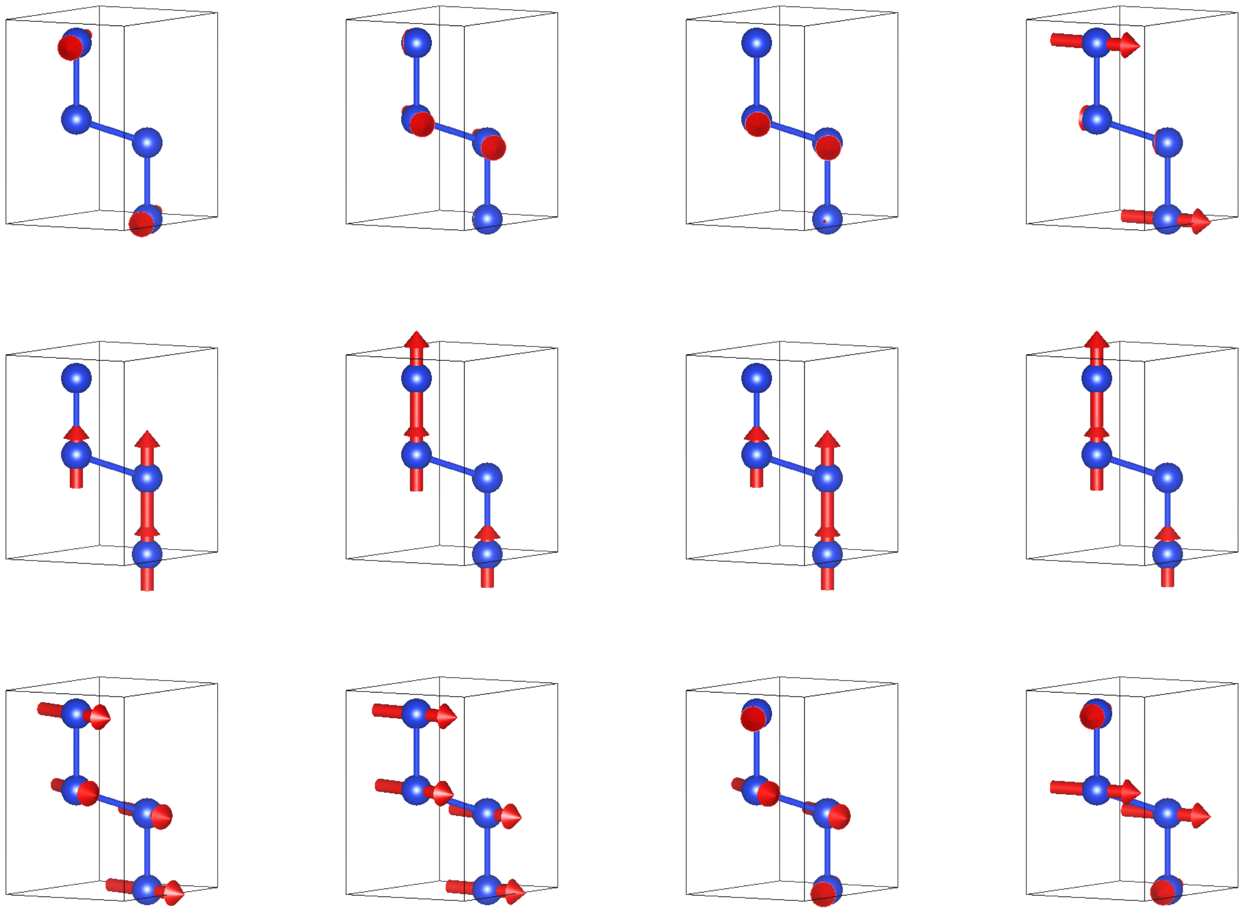

Figure 2: Phonon modes for the A-point.