Solutions for excercise sheet 5

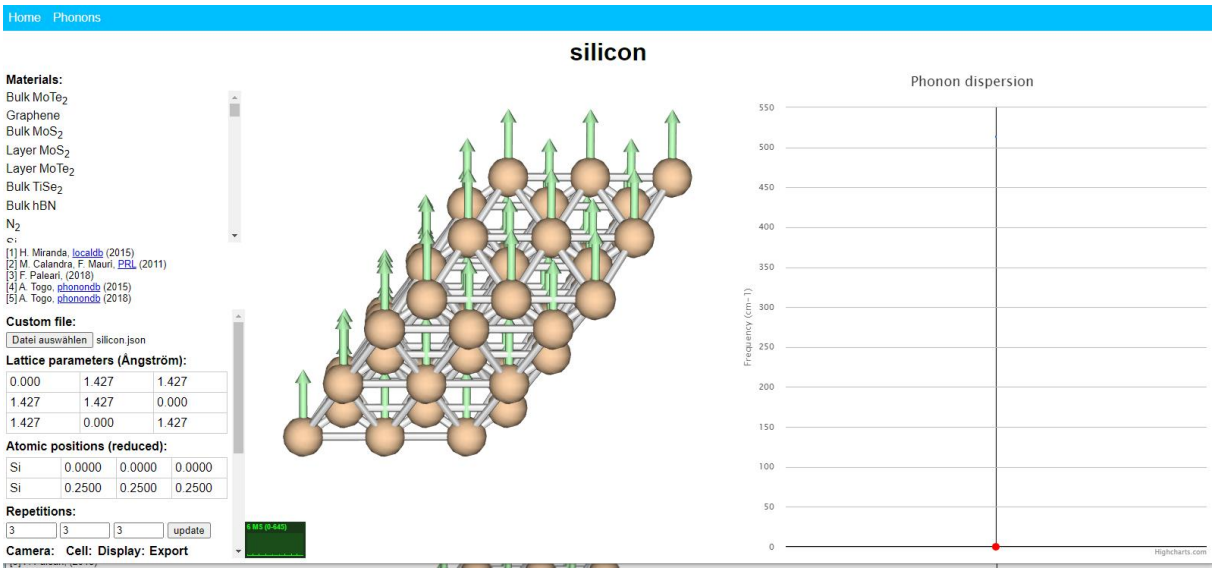
Exercise 1: Phonon spectrum of silicon

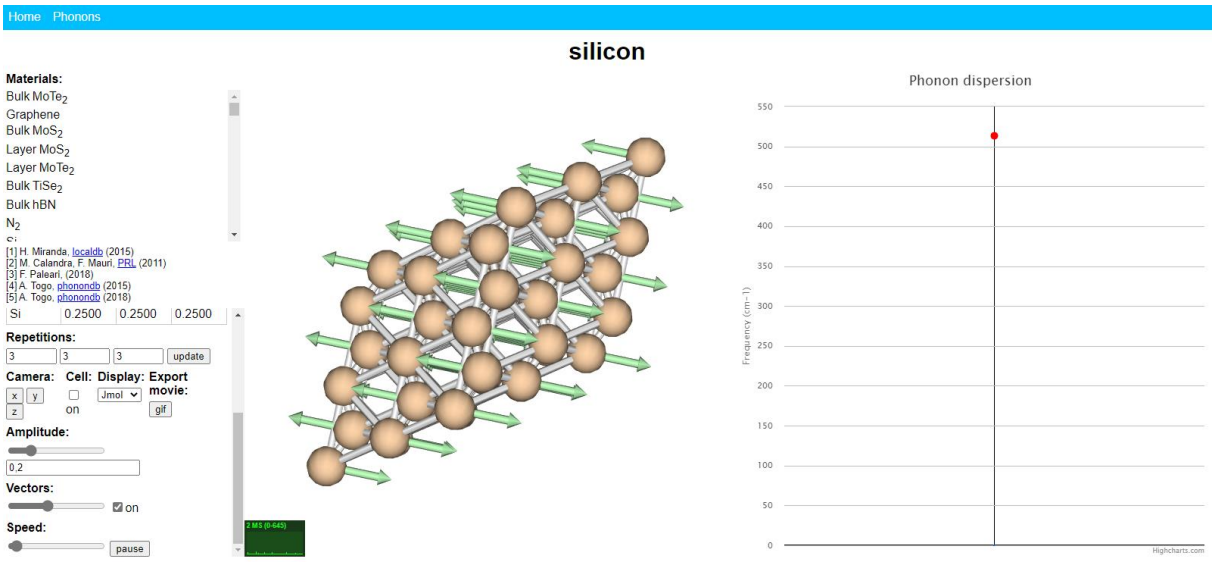
(a)

```
     Forces acting on atoms (cartesian axes, Ry/au):

     atom    1 type  1   force =     0.00000000    0.00000000    0.00000000
     atom    2 type  1   force =     0.00000000    0.00000000    0.00000000

     Total force =     0.000000     Total SCF correction =     0.000000


     Computing stress (Cartesian axis) and pressure

          total   stress  (Ry/bohr**3)                   (kbar)     P=   -0.00
  -0.00000002   0.00000000   0.00000000         -0.00      0.00      0.00
   0.00000000  -0.00000002   0.00000000          0.00     -0.00      0.00
  -0.00000000   0.00000000  -0.00000002         -0.00      0.00     -0.00

     Message from routine volume:
     axis vectors are left-handed

     bfgs converged in   4 scf cycles and   3 bfgs steps
     (criteria: energy <  1.0E-04 Ry, force <  2.0E-04Ry/Bohr, cell <  1.0E-02kbar)

     End of BFGS Geometry Optimization

     Final enthalpy =     -17.0557963653 Ry
Begin final coordinates
     new unit-cell volume =    264.90352 a.u.^3 (    39.25465 Ang^3 )
     density =      1.18445 g/cm^3

CELL_PARAMETERS (angstrom)
  -0.000000000   2.697451904   2.697451904
   2.697451904   2.697451904  -0.000000000
   2.697451904  -0.000000000   2.697451904

ATOMIC_POSITIONS (crystal)
Si       0.000000000  -0.000000000  -0.000000000
Si       0.250000000   0.250000000   0.250000000
End final coordinates
```

(b)

```
     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) =      15.389073 [THz] =     513.324233 [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) =      15.389073 [THz] =     513.324233 [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) =      15.389073 [THz] =     513.324233 [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   )
 **********************************************************************
```





(c) From ph.out:

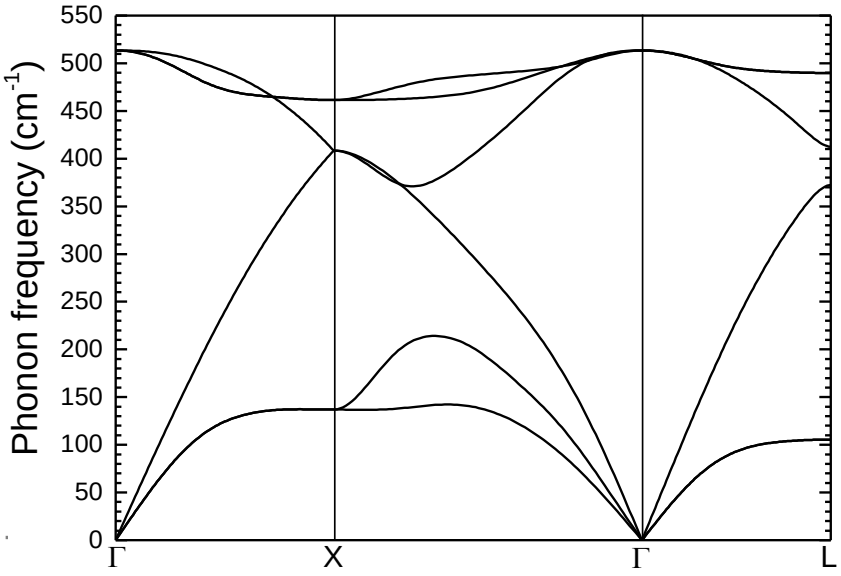
```
     q = (    0.000000000   0.000000000   0.000000000 )

 **************************************************************************
     freq (    1) =       -0.116354 [THz] =      -3.881160 [cm-1]
     freq (    2) =       -0.116354 [THz] =      -3.881160 [cm-1]
     freq (    3) =       -0.116354 [THz] =      -3.881160 [cm-1]
     freq (    4) =       15.393047 [THz] =     513.456787 [cm-1]
     freq (    5) =       15.393047 [THz] =     513.456787 [cm-1]
     freq (    6) =       15.393047 [THz] =     513.456787 [cm-1]
 **************************************************************************
```

Si.modes from dynmat.x:

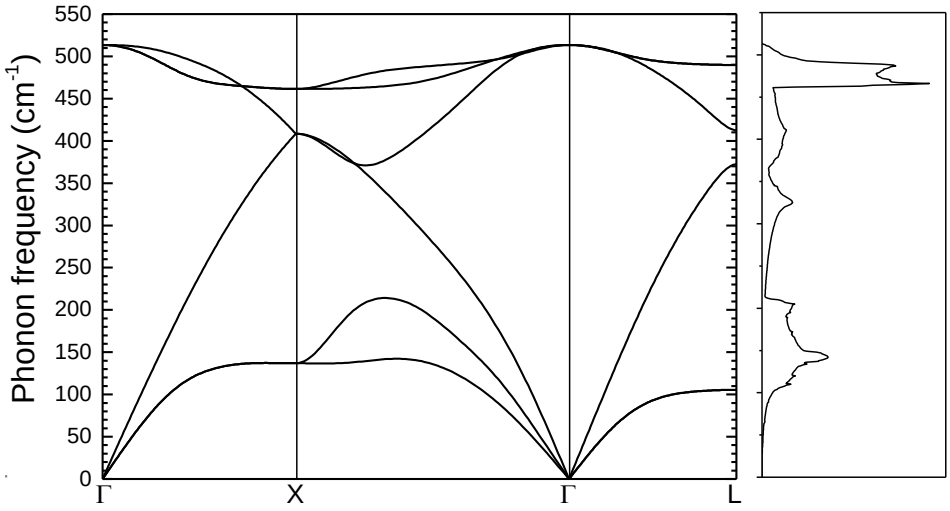
```
     diagonalizing the dynamical matrix ...

 q =       0.0000      0.0000      0.0000
 **********************************************************************************
     freq (    1) =       0.000000 [THz] =       0.000005 [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] =       0.000005 [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] =       0.000005 [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) =      15.393047 [THz] =     513.456786 [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) =      15.393047 [THz] =     513.456786 [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) =      15.393047 [THz] =     513.456786 [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   )
 **********************************************************************************
```

i.e. the FD and the DFPT methods give very similar results (with small deviations). The ASR correction yields zero frequency for the three acoustic modes.

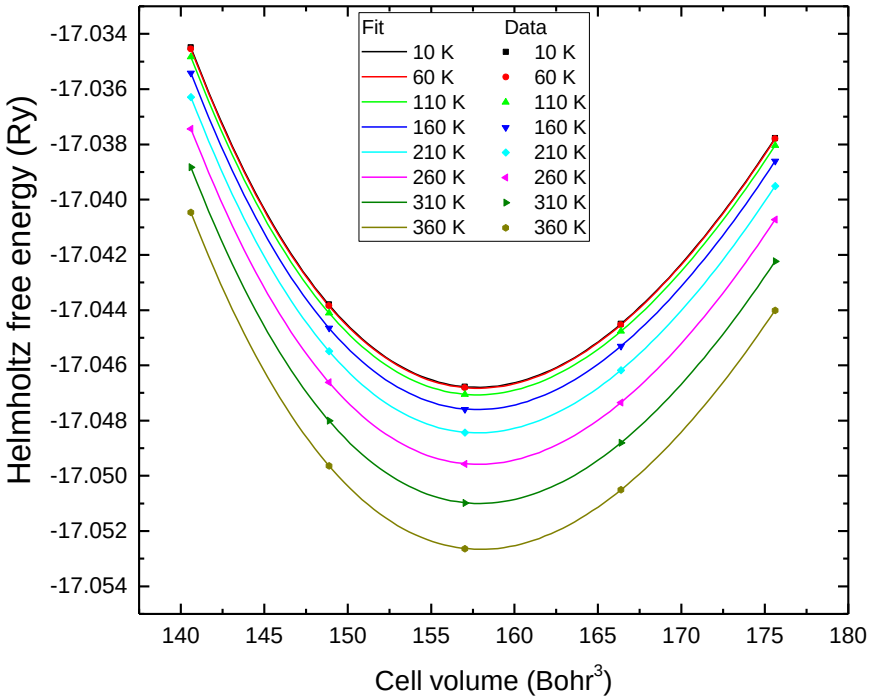
(d)



(e)

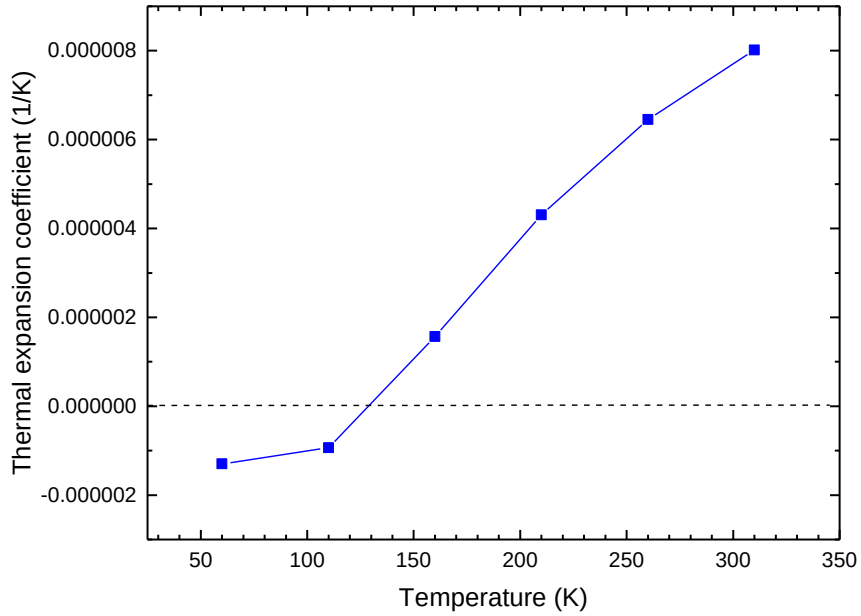


(f)



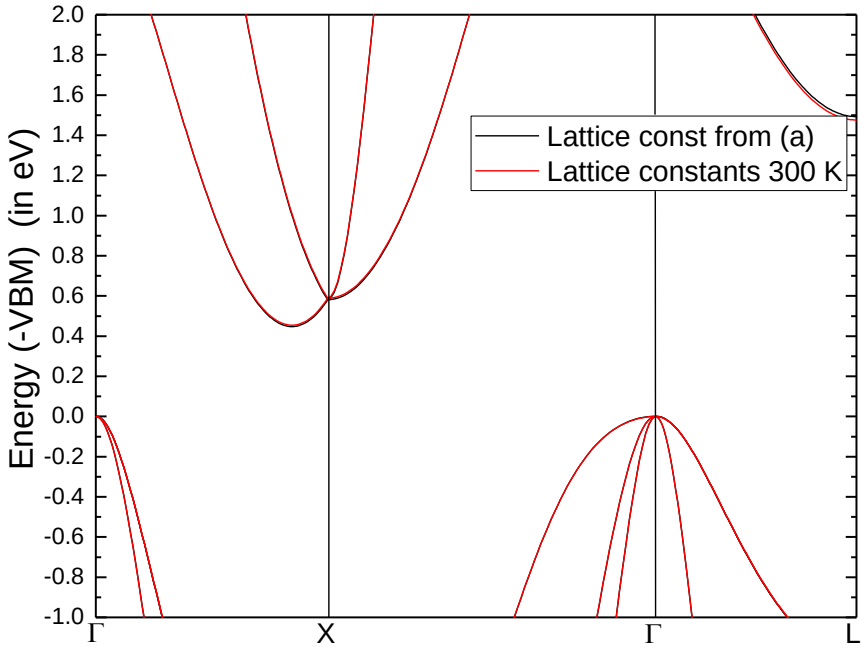
(For simplicity, the cell volume used here and in the fit.py script is that of the cubic conventional cell. Which has 4x the volume of the primitive cell.

Clearly, the vibrational contribution to the free energy slightly moves the volume for which the free energy is minimum and thus mimics the thermal lattice expansion)



(a better plot would have been achieved by using a denser temperature sampling)

(g)



The band gaps are predicted to be around 0.45 eV for both lattice constants. The small temperature-induced lattice expansion increases the band gap by about 0.01 eV.

Exercise 2: Phonon dispersion of monolayer PbO

(a)

```
     Forces acting on atoms (cartesian axes, Ry/au):

     atom    1 type  2   force =     0.00000000    0.00000000    0.00000000
     atom    2 type  2   force =     0.00000000    0.00000000    0.00000000
     atom    3 type  1   force =     0.00000000    0.00000000    0.00000039
     atom    4 type  1   force =     0.00000000    0.00000000   -0.00000039

     Total force =     0.000001     Total SCF correction =     0.000002
     SCF correction compared to forces is large: reduce conv_thr to get better values


     Computing stress (Cartesian axis) and pressure

          total   stress  (Ry/bohr**3)                   (kbar)     P=   -0.02
   0.00000002   0.00000000   0.00000000          0.00      0.00      0.00
   0.00000000   0.00000002   0.00000000          0.00      0.00      0.00
   0.00000000   0.00000000  -0.00000038          0.00      0.00     -0.06


     bfgs converged in  12 scf cycles and  11 bfgs steps
     (criteria: energy <  1.0E-04 Ry, force <  1.0E-03Ry/Bohr, cell <  1.0E-02kbar)

     End of BFGS Geometry Optimization

     Final enthalpy =    -345.8281272442 Ry
Begin final coordinates
     new unit-cell volume =   2082.05621 a.u.^3 (   308.52890 Ang^3 )
     density =      2.40258 g/cm^3

CELL_PARAMETERS (angstrom)
   3.927651304   0.000000000   0.000000000
   0.000000000   3.927651304   0.000000000
   0.000000000   0.000000000  20.000000000

ATOMIC_POSITIONS (crystal)
O        0.000000000   0.000000000   0.500000000
O        0.500000000   0.500000000   0.500000000
Pb       0.500000000   0.000000000   0.439957632
Pb       0.000000000   0.500000000   0.560042368
End final coordinates
```

(b)

```
     Diagonalizing the dynamical matrix

     q = (    0.000000000   0.000000000   0.000000000 )

 **************************************************************************
     freq (    1) =       -0.232095 [THz] =       -7.741846 [cm-1]
     freq (    2) =       -0.162218 [THz] =       -5.411007 [cm-1]
     freq (    3) =       -0.162218 [THz] =       -5.411007 [cm-1]
     freq (    4) =        2.460404 [THz] =       82.070229 [cm-1]
     freq (    5) =        2.460404 [THz] =       82.070229 [cm-1]
     freq (    6) =        4.491887 [THz] =      149.833213 [cm-1]
     freq (    7) =        8.324170 [THz] =      277.664438 [cm-1]
     freq (    8) =        8.324170 [THz] =      277.664438 [cm-1]
     freq (    9) =       10.727989 [THz] =      357.847198 [cm-1]
     freq (   10) =       12.693866 [THz] =      423.421807 [cm-1]
     freq (   11) =       12.693866 [THz] =      423.421807 [cm-1]
     freq (   12) =       14.588866 [THz] =      486.632200 [cm-1]
 **************************************************************************
```

	90 Ry	100 Ry	110 Ry	120 Ry	10x10x1
Frequency	486.632 cm^{-1}	486.633 cm^{-1}	486.674 cm^{-1}	486.637 cm^{-1}	486.63 cm^{-1}

(c) Without correction for LO-TO splitting (this is obtained by removing the line “q(1)=0.1, q(2)=0.0, q(3)=0.0“ from dynmat.in):

```
     Reading Dynamical Matrix from file PbO.dyn
     ...Force constants read
     ...epsilon and Z* read
     ...Raman cross sections read
     Acoustic Sum Rule: || Z*(ASR) - Z*(orig)|| =    2.112630E-04
     Acoustic Sum Rule: ||dyn(ASR) - dyn(orig)||=    9.606885E-04
     A direction for q was not specified:TO-LO splitting will be absent

     Polarizability (A^3 units)
     multiply by 0.764856 for Clausius-Mossotti correction
        30.052139    0.000000    0.000000
         0.000000   30.052139    0.000000
         0.000000    0.000000    7.828872

     IR activities are in (D/A)^2/amu units
     Raman activities are in A^4/amu units
     multiply Raman by 0.585005 for Clausius-Mossotti correction

# mode   [cm-1]    [THz]     IR          Raman   depol.fact
    1     -0.00   -0.0000   0.0000        0.0000   0.0298
    2      0.00    0.0000   0.0000        0.0000   0.0314
    3      0.00    0.0000   0.0000        0.0000   0.0107
    4     82.07    2.4604   0.0000        0.0545   0.7500
    5     82.07    2.4604   0.0000        0.0545   0.7500
    6    149.83    4.4919   0.0000      156.3574   0.0101
    7    277.31    8.3137  26.2163        0.0000   0.0720
    8    277.31    8.3137  26.2163        0.0000   0.2709
    9    357.85   10.7280   0.0000        0.2192   0.7500
   10    423.42   12.6939   0.0000        1.4295   0.7500
   11    423.42   12.6939   0.0000        1.4295   0.7500
   12    486.72   14.5914   0.6847        0.0000   0.0353
```

With correction for LO-TO splitting:

```
     Reading Dynamical Matrix from file PbO.dyn
     ...Force constants read
     ...epsilon and Z* read
     ...Raman cross sections read
     Acoustic Sum Rule: || Z*(ASR) - Z*(orig)|| =    2.112630E-04
     Acoustic Sum Rule: ||dyn(ASR) - dyn(orig)||=    9.606885E-04

     Polarizability (A^3 units)
     multiply by 0.764856 for Clausius-Mossotti correction
        30.052139    0.000000    0.000000
         0.000000   30.052139    0.000000
         0.000000    0.000000    7.828872

     IR activities are in (D/A)^2/amu units
     Raman activities are in A^4/amu units
     multiply Raman by 0.585005 for Clausius-Mossotti correction

# mode   [cm-1]    [THz]      IR          Raman   depol.fact
    1     -0.00   -0.0000    0.0000        0.0000    0.1117
    2      0.00    0.0000    0.0000        0.0000    0.7500
    3      0.00    0.0000    0.0000        0.0000    0.0165
    4     82.07    2.4604    0.0000        0.0545    0.7500
    5     82.07    2.4604    0.0000        0.0545    0.7500
    6    149.83    4.4919    0.0000      156.3574    0.0101
    7    277.31    8.3137   26.2163        0.0000    0.7495
    8    357.85   10.7280    0.0000        0.2192    0.7500
    9    397.98   11.9312   26.2163        0.0000    0.6448
   10    423.42   12.6939    0.0000        1.4295    0.7500
   11    423.42   12.6939    0.0000        1.4295    0.7500
   12    486.72   14.5914    0.6847        0.0000    0.7500
```

Extra-Exercise: Aluminum-doped SiO_2

Here, we continue the extra exercise from exercise sheet 4.

Remember to run the calculations in parallel on the HPC.

(d)

	$E_{tot}^{SiO2,q=0}$	$E_{tot}^{SiO2,q=0.001}$	E_{VBM}
(Total) Energy	-223.05808 Ry	-223.05821 Ry	0.1334 Ry

	$E_{tot}^{SiO2:Al,q=+1}$	$E_{tot}^{SiO2:Al,q=0}$	$E_{tot}^{SiO2:Al,q=-1}$
Total Energy	-1781.5 Ry	-1781.37 Ry	-1781.18 eV Ry

(e)

	Charge +1	Charge -1
Total energy of doped SiO_2, $E_{tot}^{SiO2:Al}$	-1781.5 Ry	-1781.18 Ry
Total energy of pristine SiO_2, E_{tot}^{SiO2}	-1784.46 Ry	-1784.46 Ry
Chemical potential of Si atom, μ_{Si}	-9.55266 Ry	-9.55266 Ry
Chemical potential of Al atom, μ_{Al}	-6.66477 Ry	-6.66477 Ry
Valence band maximum, E_{VBM}	0.13344 Ry	0.13344 Ry
Formation energy	2.838786 eV	3.635543 eV