Quantum-ESPRESSO

PHONONS by DFPT

Vibartional Properties with DFPT

Download the examples_phonon.tgz file from the web site and unpack it (on the machine used for computations) this will create an examples_phonon directory

Move to the examples_phonon directory

A quick summary of the DFPT formulas can found in summary_DFPT.pdf A longer account of DFPT and its applications is given in RMP-73-515-2001.pdf

This tutorial can be found in README

Phonons at Gamma

Edit si.scf.in in order to set outdir and pseudo_dir according to your need.

Run the scf calculation for Silicon

$espresso_dir/bin/pw.x < si.scf.in > si.scf.out

Have a look to the si.phG.in file.
Notice that the prefix is the same as the previous calculation and set outdir as before.
Mass value will overwrite the value given in si.scf.in (1.0).
The line after the namelist is the q-point to be computed (gamma)

Run the phonon calculation at gamma point for Silicon
$espresso_dir/bin/ph.x < si.phG.in > si.phG.out

Examine the output:
The code determines a number of irreducible representations and performs a scf (linear response) calculation for each of them.
At the end, the dynamical matrix is computed and diagonalized.
The dynamical matrix is also written in the file si.dynG [the variable fildyn in si.phG.in input file]
It also contains eigenvalues and a description of the eigenvectors.

```
( re_x_atom1 im_x_atom1 re_y_atom1 im_y_atom1 re_z_atom1 im_z_atom1 )
   ...          ...          ...          ...          ...          ...
   ...          ...          ...          ...          ...          ...
( re_x_atomN im_x_atomN re_y_atomN im_y_atomN re_z_atomN im_z_atomN )
```

Notice that there are 3 frequencies close to zero (should be exactly zero due to traslational symmetry $\longrightarrow$ Acoustic Sum Rule (ASR)) and 3 degenerate non zero frequencies (cubic system).

Notice that the degeneracy of the modes $[\,3 + 3\,]$ corresponds to the dimensionality of the irreducible representations.

It is a property related to symmetry.

There is a small program (dynmat.x) that diagonalizes the matrix and, among other things, writes the eigenvalues in XCrySDen format. Have a look to si.dynmat.in and run.
$espresso_dir/bin/dynmat.x < si.dynmat.it

Visualize the modes with XCrySDen

Phonons NOT at Gamma

In order to perform a phonon calculation at a q-point $<> 0$ it is necessary to run a nscf calculation to (re)construct electronic states at k and k+q.

Edit si.nscfX.in and define outdir and pseudo_dir .
Notice that calculation='phonon' and there is an additional namelist (&phonon) where q-point can be defined ...
in this case q = (1,0,0) 2pi/a = X

Run the nscf calculation.
$espresso_dir/bin/pw.x < si.nscfX.in > si.nscfX.out

Notice that the calculation is non self-consistent (potential is computed from the scf density, only one iteration is performed)

Notice that the number of symmetry operations is reduced and that the number of points is increased ..

Notice that k's and k+q's (with zero weight) are alternating .

Data are saved in the save directory in outdir.

Copy si.phG.in to si.phX.in, edit it and modify the title (if you wish), the fildyn variable (si.dynG -> si.dynX) and the line defining the q-point [(0.0 0.0 0.0) $\longrightarrow$ (1.0 0.0 0.0)]

Run the phonon code for X point

$espresso_dir/bin/ph.x < si.phX.in > si.phX.out

Have a look to the output:
Notice that the number of irreducuble representations is different (depends on the symmetry $\longrightarrow$ the small group of q)

File si.phX contains now 3 matrices (the three equivalent X points)

Repeat the same for L point = (0.5,0.5,0.5) 2pi/a

```
grep omega si.dyn*

si.phG.out:     omega( 1) =        0.065068 [THz] =        2.170443 [cm-1]
si.phG.out:     omega( 2) =        0.065068 [THz] =        2.170443 [cm-1]
si.phG.out:     omega( 3) =        0.065068 [THz] =        2.170443 [cm-1]
si.phG.out:     omega( 4) =       15.476572 [THz] =      516.246292 [cm-1]
si.phG.out:     omega( 5) =       15.476572 [THz] =      516.246292 [cm-1]
si.phG.out:     omega( 6) =       15.476572 [THz] =      516.246292 [cm-1]

si.phL.out:     omega( 1) =        3.282186 [THz] =      109.482656 [cm-1]
si.phL.out:     omega( 2) =        3.282186 [THz] =      109.482656 [cm-1]
si.phL.out:     omega( 3) =       11.304627 [THz] =      377.084280 [cm-1]
si.phL.out:     omega( 4) =       12.549798 [THz] =      418.618979 [cm-1]
si.phL.out:     omega( 5) =       14.788129 [THz] =      493.282157 [cm-1]
si.phL.out:     omega( 6) =       14.788129 [THz] =      493.282157 [cm-1]

si.phX.out:     omega( 1) =        4.318264 [THz] =      144.042741 [cm-1]
si.phX.out:     omega( 2) =        4.318264 [THz] =      144.042741 [cm-1]
si.phX.out:     omega( 3) =       12.401427 [THz] =      413.669814 [cm-1]
si.phX.out:     omega( 4) =       12.401427 [THz] =      413.669814 [cm-1]
si.phX.out:     omega( 5) =       13.964039 [THz] =      465.793300 [cm-1]
si.phX.out:     omega( 6) =       13.964039 [THz] =      465.793300 [cm-1]
```

Compare with the results you can find in
P. Giannozzi, S. deGironcoli, P. Pavone, and S. Baroni,
Phys. Rev. B 43, 7231 (1991)
[there is a copy of this paper in this directory]

TABLE II. Phonon frequencies calculated at the high-symmetry points Γ, X, and L, for the six materials considered in this work (cm^{-1}). Experimental data are in parentheses. Data tagged with an asterisk are from Ref. 33.

	Si[a]	Ge[b]	GaAs[c]	AlAs[d]	GaSb[e]	AlSb[f]
Γ_{TO}	517 (517)	306 (304)	271 (271)	363 (361)	230 (224)*	316 (323)*
Γ_{LO}	517 (517)	306 (304)	291 (293)	400 (402)	237 (233)*	334 (344)*
X_{TA}	146 (150)	80 (80)	82 (82)	95 (109)	57 (57)	64 (70)
X_{LA}	414 (410)	243 (241)	223 (225)	216 (219)	162 (166)	153 (155)
X_{TO}	466 (463)	275 (276)	254 (257)	337 (333)	210 (212)	290 (296)
X_{LO}	414 (410)	243 (241)	240 (240)	393 (399)	211 (212)	343 (341)
L_{TA}	111 (114)	62 (63)	63 (63)	71	45 (46)	49 (56)
L_{LA}	378 (378)	224 (222)	210 (207)	212	157 (153)	149 (148)
L_{TO}	494 (487)	291 (290)	263 (264)	352	203 (205)	306 (308)
L_{LO}	419 (417)	245 (245)	238 (242)	372	221 (216)	327 (320)

[a] Experimental data from Ref. 28.
[b] Experimental data from Ref. 29.
[c] Experimental data from Ref. 30.
[d] Experimental data from Ref. 31.
[e] Experimental data from Ref. 32.
[f] Experimental data from Ref. 11.

Electric Fields and Acoustic Sum Rule

Let us study a little more in detail the Gamma case.

In insulating materials the system can sustain macroscopic electric fields and these can be coupled with vibrations.
The physical properties that describe these properties are epsilon and zstar
[In metals there are no macroscopic electric fields => epsilon=∞]

Edit si.phG.in and add epsil=.true. in the name list.
THIS is only available if q=(0.0 0.0 0.0), code complains otherwise

Run again the scf calculation (to get the original k-point sampling in outdir) and then the phonon calc.

$espresso_dir/bin/pw.x < si.scf.in > si.scf.out
$espresso_dir/bin/ph.x < si.phG.in > si.phG.out

Notice in the output that an additional scf (linear response) calculation for electric fields in 3 independent directions is performed, and dielectric constant and effective charges are calculated.
Also in the si.dynG matrix these quantities are written.

Translational symmetry requires (ASR) that acoustic modes have zero frequencies AND $\sum_i z_i^* = 0$

This is not verified exactly by the calculation because:

– not sufficiently accurate scf threshold (in pw.x and/or ph.x part). Usually pw.x takes very little w.r.t. ph.x $=>$ Do not use lousy thresholds in pw.x in order to spare some time.

– XC energy is computed on a real-space grid that assume an explicit origin. More problematic for GGA (than for LDA)

– k-point sampling is not accurate enough (for z^* and epsil): electric fields can be seen as the limit for q-> 0 and requires a denser grid of k-points.

Let us see that explicitly:
change samplig in si.scf.in with

```
> 28 monkhorst-pack points :
  K_POINTS automatic
    6 6 6 1 1 1
```

Run again pw+ph save the output for later comparison

$espresso_dir/bin/pw.x < si.scf.in > si.scf.out-28k
$espresso_dir/bin/ph.x < si.phG.in > si.phG.out-28k

repeat for

```
> 2 chiadi-cohen / monkhorst-pack points :
  K_POINTS automatic
   2 2 2 1 1 1
> 6 monkhorst-pack points :
  K_POINTS automatic
   3 3 3 1 1 1
> 10 chadi-cohen / monkhorst-pack points
                        (*** THIS IS WHAT WE ALREADY HAVE **
  K_POINTS automatic
   4 4 4 1 1 1
```

Notice that

– ASR for effective charges improves by improving BZ sampling.

– ASR for acoustic mode improves but does not go to zero . => k-point sampling is not an issues for ASR for acoustic modes.

– Optical modes are practically unaffected.

You could try to improve scf thresholds for pw.x (tr2=1.d-12) and ph.x (tr2_ph=1.d-18) and repeat ...
It does not really get better.

What really would make it vanish would be to remove XC functional ... But obviously this is not what you want.

Edit si.dynmat and add asr='simple' to the name list and run again
$espresso_dir/bin/dynmat.x < si.dynmat.it

Notice that acoustic frequency is zero but optical frequency does not change.

Phonons in Polar Materials

In polar materials the macroscopic electric fields that are present in the long wavelenght limit induce the so called LO-TO splitting. This can be computed from the knowledge of epsilon, z^* and the propagation direction q.

Create an input for scf calculation in alas using the following data:

```
ATOMIC_SPECIES
 Al   26.98   Al.vbc.UPF
 As   74.92   As.gon.UPF
```

and alat $= 10.6$

$espresso_dir/bin/pw.x $<$ alas.scf.in $>$ alas.scf.out

Create an input for phonon at Gamma for alas (including electric fields)

$espresso_dir/bin/ph.x < alas.phG.in > alas.phG.out

Notice that the optical phonon frequencies are 3-fold degenerate.

Create an input for dynmat for alas and specify the additional variables
&input ... q(1)=1.0, q(2)=0.0, q(3)=0.0 /

$espresso_dir/bin/dynmat.x < alas.dynmat.in

Notice that the 3-fold degenerate optical modes are split [LO-TO splitting]
Notice again that asr='simple' makes the frequency of acoustic phonons vanish but has no effect on the other modes.

In cubic system, such as AlAs, the frequencies (NOT the eigenvalues) are independent on the q-direction. In lower symmetries both eigenvales and eigenvectors depend on the phonon propagation direction.

Phonons in a Molecular System

Edit sih4.scf.in and define outdir and pseudo_dir
Notice that Gamma only sampling is performed for this molecule.

$espresso_dir/bin/pw.x < sih4.scf.in > sih4.scf.out
Verify that the molecule is in equilibrium.

Edit sih4.nm.in and define outdir

$espresso_dir/bin/phcg.x < sih4.nm.in > sih4.nm.out

This code can only be used for gamma-only calculations (molecules and very rarge system) and exploit the symmetry in a diffrent way.

In a molecule one would expect 6 zero-frequency modes (3 translations + 3 rotations) but the Rotational Sum Rule (RSR) is not satisfied due to the finite size of the cell that induce interactions between periodic replicas.

$espresso_dir/bin/dynmat.x < sih4.dyn.in
shows that it is possible to enforce ASR + RSR sum rules .
This is done in a least square way that minimizes the effect on the other modes.

However this may still be inaccurate if RSR violation is too large.

Modify sih4.scf.in file changing the box-size to 20 bohrs and repeat the scf and ph calculation.

Notice that the RSR is still very poorly satisfied. Why?

Look at the forces on atoms !

RELAX the structure and repeat the phonon calculation.

Now RSR is much better satisfied. Why ?
Hint: consider a dimer in two-dim with a sombrero-hat PES and think of the normal modes when the bond lenght does not have the equlibrium value.

THE END