Basic DFT and NMR with Quantum-Espresso

Day 2, Afternoon

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Welcome to the first hands-on session of the GIPAW tutorial! This afternoon we will become familiar with running QE and QE-GIPAW. The activity is divided into 8 parts, some of them are optional. If you are already familiar with QE, the best has still to come in the next days.

1. Basic SCF calculation: beta-cristobalite (½ hour)
2. Converging the plane wave cutoff (½ hour)
3. Converging the k-points (½ hour)
4. (optional) Band structure and density of states (½ hour)
5. Geometry and cell relaxation (1 hour)
6. Coffe break/merenda (½ hour)
7. NMR chemical shift convergence (1 hours)
8. (optional) From crystal structure to input file (½ hour)

In order to save time, activity 5 and 6 can be carried out in parallel. Activity 8 does not require calculations and can be performed while activity 7 is running.

0. Practical information

The calculations and the scripts are meant to be performed into a UNIX-like environment, such as Linux, Mac OS X, Windows+Cygwin. Additional software tools such as *bc*, *perl*, *python* will be very useful, but not required for this tutorial. For visualization purposes we will use *gnuplot*, *Xcrysden* and *VESTA*. If you need to compile QE and GIPAW, you will need a working Fortran90 compiler (such as *gfortran*) and optionally, installed mathematically libraries (*blas*, *lapack*, *FFTW3*).

If you are not familiar with the UNIX environment and commands, here is a brief list of useful commands:

ls	list files in the current directory
ls -l	list files - but give more details than plain ls
exit	to close the terminal when you are finished
pwd	print current working directory
mkdir	make a new directory (aka folder)

cd	change directory (aka folder) eg 'cd directory'
mv	rename (or move) a file eg ‘mv oldfile newfile’
cp	copy a file eg ‘mv original copy’
cp fred/* jim/	copy all the files in the folder fred into the folder jim
cp ../myfile ./	copy the file myfile in the folder below to the current folder
cp ~/myfile ./	copy the file myfile in your home folder to the current folder
rm	remove file eg 'rm filename' beware: no possibility to undelete!
cat, more, less	show contents of a text file eg 'more output.txt'
nano	a file editor eg ‘nano filename’ to exit: Ctrl-X note you can use this to edit an existing file, or to create a new file. eg ‘nano mynewfile’ will create a new file called ‘mynewfile’
vi	a file editor (*only the brave*) to exit: ESC : q ! ENTER
emacs	another file editor, opens a new window

Setting the environment and copy day-2 files

This notes, the input files (day2.tar.gz) can be downloaded from tutorial website at CECAM, as well as from the public Google drive folder: https://drive.google.com/folderview?id=0BxmE1NC-2O4wRXVmeXJFdHUwZDg&usp=sharing

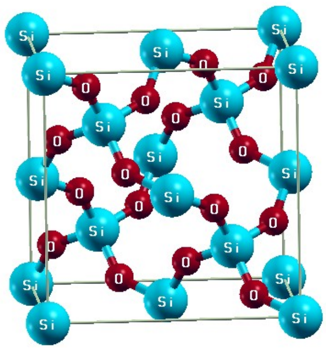
To expand the input files:

```
tar zxfv day2.tar.gz
```

If you need an updated version of QE, expand, *configure* and compile the *espresso-10460.tar.gz* archive.

1. Basic SCF calculation: beta-cristobalite

The purpose of this example is to learn how to perform a basic SCF calculation with the PW code, and how to understand the output. We will use the cubic *fcc* beta-cristobalite structure with lattice spacing 7.1315 Å:



Go to directory day2/01-betacrist, and have a look at the input file betacrist-scf.in:

```
&control
    calculation = 'scf'                             !type of calculation: 'scf', 'relax',
                                                    !'vc-relax, 'nscf', 'bands'
    restart_mode = 'from_scratch'                   !'from_scracth' or 'restart'
    prefix = 'betacrist'                            !basename for all binary files
    pseudo_dir = './pseudo/'                        !directory containing pseudopotentials
    outdir = './scratch/'                           !scratch directory for large binary files
    tstress = .true.                                !if .true., print stress tensor
    tprnfor = .true.                                !if .true., print forces
/
&system
```

```
    ibrav = 2                                       !see manual, ibrav=2 means fcc
    a = 7.1315                                      !conventional lattice spacing in Å
    nat = 6                                         !number of atoms
    ntyp = 2                                        !number of different atomic speciec
    ecutwfc = 35                                    !plane wave cutoff in Ry
    ecutrho = 350                                   !density cutoff in Ry
    spline_ps = .true.                              !useful for NMR
/
&electrons
    diagonalization = 'david'                       !'davidson' (faster, more memory) or 'cg'
    diago_thr_init = 1e-4                           !eigenvalue accuracy at first diagonalization
    mixing_mode = 'plain'
    mixing_beta = 0.7                               !0.3-0.7 in insulators, <0.1 in metals
    conv_thr = 1e-10                                !SCF accuracy
/

ATOMIC_SPECIES
Si  28.086  Si.pbe-tm-new-gipaw-dc.UPF              !atom mass pseudopotential
O   15.999  O.pbe-rrkjus-gipaw-dc.UPF

K_POINTS automatic
4 4 4 0 0 0                                         !4x4x4 not-shifted Monrkhorst-Pack mesh

ATOMIC_POSITIONS alat                               !alat=cartesian in units of 'a'
Si      0.000000000  0.000000000  0.000000000       !other possibilities: crystal (=fractional)
Si      0.250000000  0.250000000  0.250000000       !or angstrom (=cartesian, in Å)
O       0.075458128  0.174541872  0.125000000
O       0.424541872  0.325458128  0.125000000
O       0.174541872  0.424541872  0.375000000
O       0.325458128  0.075458128  0.375000000
```

You can find the complete description of input parameters and the numeric codes for the Bravais lattices at: http://www.quantum-espresso.org/input-syntax/INPUT_PW.html

Now let's run the SCF calculation. The SCF is performed by the pw.x code of QE. Pw.x can read from standard input:

```
pw.x <betacrist-scf.in >betacrist-scf.out
```

or from command line:

```
pw.x -in betacrist-scf.in >betacrist-scf.out
```

In both cases, the output is sent to the standard output (the terminal), and must be redirected to a file.

Now, let's have a look at the output file betacrist-scf.out. Here the most significant sections are highlighted:

```
     Program PWSCF v.5.0.2 (svn rev. 10449) starts on 16Sep2013 at 11:38:38

     Parallel version (MPI), running on     1 processors                  PARALLELIZATION

     bravais-lattice index     =            2                             SUMMARY OF INPUT
     lattice parameter (alat)  =      13.4766  a.u.
     unit-cell volume          =     611.8983 (a.u.)^3
     number of atoms/cell      =            6
     number of atomic types    =            2
     number of electrons       =        32.00
     number of Kohn-Sham states=           16
     kinetic-energy cutoff     =      35.0000  Ry
     charge density cutoff     =     350.0000  Ry
     convergence threshold     =      1.0E-10
     mixing beta               =       0.7000
     number of iterations used =            8  plain     mixing
     Exchange-correlation      =  SLA  PW   PBX  PBC ( 1  4  3  4 0)

     celldm(1)=  13.476582  celldm(2)=   0.000000  celldm(3)=   0.000000
     celldm(4)=   0.000000  celldm(5)=   0.000000  celldm(6)=   0.000000
```

```
     crystal axes: (cart. coord. in units of alat)                       CELL VECTORS
               a(1) = (  -0.500000   0.000000   0.500000 )
               a(2) = (   0.000000   0.500000   0.500000 )
               a(3) = (  -0.500000   0.500000   0.000000 )

     8 Sym. Ops. (no inversion) found ( 4 have fractional translation)    SYMMETRY INFO

   Cartesian axes

     site n.     atom                  positions (alat units)            ATOMIC POSITIONS
         1           Si  tau(   1) = (   0.0000000   0.0000000   0.0000000  )
         2           Si  tau(   2) = (   0.2500000   0.2500000   0.2500000  )
         3           O   tau(   3) = (   0.0754581   0.1745419   0.1250000  )
         4           O   tau(   4) = (   0.4245419   0.3254581   0.1250000  )
         5           O   tau(   5) = (   0.1745419   0.4245419   0.3750000  )
         6           O   tau(   6) = (   0.3254581   0.0754581   0.3750000  )

     number of k points=    13
                       cart. coord. in units 2pi/alat                     K-POINTS
        k(    1) = (   0.0000000   0.0000000   0.0000000), wk =   0.0312500
        k(    2) = (  -0.2500000   0.2500000  -0.2500000), wk =   0.2500000
        k(    3) = (   0.5000000  -0.5000000   0.5000000), wk =   0.1250000
        k(    4) = (   0.0000000   0.5000000   0.0000000), wk =   0.1250000
        k(    5) = (   0.7500000  -0.2500000   0.7500000), wk =   0.5000000
        k(    6) = (   0.5000000   0.0000000   0.5000000), wk =   0.2500000
        k(    7) = (   0.0000000  -1.0000000   0.0000000), wk =   0.0625000
        k(    8) = (  -0.5000000  -1.0000000   0.0000000), wk =   0.1250000
        k(    9) = (   0.0000000   0.0000000   0.5000000), wk =   0.0625000
        k(   10) = (  -0.7500000   0.7500000  -0.2500000), wk =   0.2500000
        k(   11) = (  -0.5000000   0.5000000   0.0000000), wk =   0.1250000
        k(   12) = (   0.0000000   0.0000000  -1.0000000), wk =   0.0312500
        k(   13) = (   0.0000000   1.0000000  -0.5000000), wk =   0.0625000

     Self-consistent Calculation                                          START OF SCF

     iteration #  1     ecut=    35.00 Ry     beta=0.70
     Davidson diagonalization with overlap
     ethr =  1.00E-04,  avg # of iterations =  4.0

     total cpu time spent up to now is        8.2 secs

     total energy              =    -144.29523942 Ry
     Harris-Foulkes estimate   =    -144.67178153 Ry
     estimated scf accuracy    <       0.61397905 Ry                      SCF ACCURACY

     iteration #  2     ecut=    35.00 Ry     beta=0.70
     Davidson diagonalization with overlap
     ethr =  1.92E-03,  avg # of iterations =  2.0
```

more scf steps
The total energy should converge and the estimated scf accuracy should gradually decrease. When it's lower than conv_thr, the SCF is converged!

```
!    total energy              =    -144.51637306 Ry                      FINAL ENERGY
     Harris-Foulkes estimate   =    -144.51637306 Ry
     estimated scf accuracy    <          1.7E-11 Ry

     The total energy is the sum of the following terms:

     one-electron contribution =     -97.26391384 Ry
     hartree contribution      =      63.59679082 Ry
     xc contribution           =     -33.81947251 Ry
     ewald contribution        =     -77.02977753 Ry

     convergence has been achieved in  10 iterations

     Forces acting on atoms (Ry/au):                                      FORCES

     atom    1 type  1   force =     0.00000000    0.00000000    0.00000000
     atom    2 type  1   force =     0.00000000   -0.00000000   -0.00000000
     atom    3 type  2   force =     0.00026673   -0.00026673    0.00000000
     atom    4 type  2   force =    -0.00026673    0.00026673   -0.00000000
     atom    5 type  2   force =    -0.00026673   -0.00026673   -0.00000000
```

```
     atom    6 type  2   force =     0.00026673    0.00026673    0.00000000

     Total force =     0.000754     Total SCF correction =     0.000002


          total   stress  (Ry/bohr**3)                   (kbar)     P= -110.37   STRESS
  -0.00079697   0.00000000   0.00000000       -117.24      0.00      0.00        TENSOR
   0.00000000  -0.00079697   0.00000000          0.00   -117.24      0.00
   0.00000000   0.00000000  -0.00065698          0.00      0.00    -96.65

     PWSCF        :    41.21s CPU        41.59s WALL                      TIMING INFO
```

2. Converging the plane wave cutoff

The *rrkjus-gipaw-dc* pseudopotentials are a little harder than the normal *rrkjus* pseudopotentials you can find on the QE webpage. In fact, O.pbe-rrkjus.UPF can be used at 35 Ry cutoff without problems. In our case, we need to converge the total energy, stress and forces with respect to plane wave cutoff.

Go to directory day2/02-betacrist-ecut. There you will find a template input file betacrist-scf.in.tmpl. Edit it and change *ecutwfc* from 20 to 60 Ry, in increments of 5 Ry. Always set ecutrho to ten times *ecutwfc* (with ultrasoft pseudopotentials, ecutrho is typically 8-12 times ecutwfc). Run SCF calculations for each value of ecutwfc and annotate total energy, stress and force acting on oxygen atom. If you are familiar with scripting, you can automate the procedure.

Useful commands:

```
grep ! *.out
grep P= *.out
grep -A8 “Forces acting” *.out
```

Here are the results (actual number may vary a little):

Ecutwfc (Ry)	Total energy (Ry)	Pressure (kbar)	Force//x at. 3 (Ry/au)
20	-142.06406291	-1456.46	-0.01381274
25	-143.66883205	-762.57	-0.00788271
30	-144.30121777	-325.22	-0.00269678
35	-144.51637306	-110.37	0.00026673
40	-144.57967751	-20.28	0.00004484
45	-144.59394204	10.19	-0.00115035
50	-144.59580714	16.84	-0.00112849
55	-144.59615670	16.27	-0.00107879
60	-144.59717572	14.77	-0.00035145

Usually we declare the system “converged” when total energy changes is ~ 1 mRy, pressure change is ~1 kbar and forces change by less than 1%. In this case, the optimal cutoffs are 50/500 Ry but also 45/450 Ry will do a good job.

3. Converging k-points

Now that we have converged the plane wave cutoffs, we need to converge the sampling of reciprocal space. The k-points convergence affects dramatically the accuracy of NMR shifts!

Go to directory day2/03-betacrist-kpoints. There you will find a template input file betacrist-scf.in.tmpl. Cutoffs have been set to 45/450 Ry. The input file lacks the k-points card. Append to the input file a string such as “n n n 0 0 0” for an unshifted mesh, and “n n n 1 1 1” for a shitfed mesh, n=2..6. Again you can make the all procedure automatic by running a script.

Here are the results:

n, shift	**Total energy (Ry)**	**Pressure (kbar)**	**Force//x at. 3 (Ry/au)**
2, no	-144.59275863	10.28	-0.00155057
3, no	-144.59390504	10.19	-0.00116080
4, no	-144.59394204	10.19	-0.00115035
5, no	-144.59392645	10.14	-0.00115018
6, no	-144.59393669	10.17	-0.00115040
2, yes	-144.59393481	10.16	-0.00115252
3, yes	-144.59394596	10.20	-0.00114994
4, yes	-144.59389989	10.07	-0.00115058
5, yes	-144.59393857	10.18	-0.00115022
6, yes	-144.59391257	10.10	-0.00115057

For beta-cristobalite (a wide band-gap insulator), even a 3x3x3 unshifted mesh is sufficient. However, we'll see later that this mesh is not sufficient for accurate NMR calculations.

4. (optional) Band structure and density of states

In this activity we will calculate the band structure and projected-density of states of beta-cristobalite. The procedure is a bit involved with QE, and I have prepared a series of scripts to help post-processing the results.

Go to day2/04-betacrist-bandos. In order to calculate the band structure and density of states, you must first perform a well-converged *scf* calculation, then a *bands* calculation to obtain the eigenvalues of the SCF-potential along the symmetry lines of the Brillouin zone (BZ), finally a non-scf (*nscf*) on a very fine mesh of k-points, in order to sample the BZ. To save time, we will use 35/350 Ry cutoffs. In this case, the results are not too much affected by plane wave cutoff.

In detail:

```
pw.x <betacrist-scf-35.in >betacrist-scf-35.out
pw.x <betacrist-bands-35.in >betascrist-bands-35.out
bands.x <pp_bands.in >/dev/null
../scripts/bands2gnuplot.pl pp_bands.tmp >bands.dat
pw.x <betacrist-nscf-35.in >betacrist-nscf-35.out
projwfc.x <pp_projwfc.in >pp_projwfc.out
```

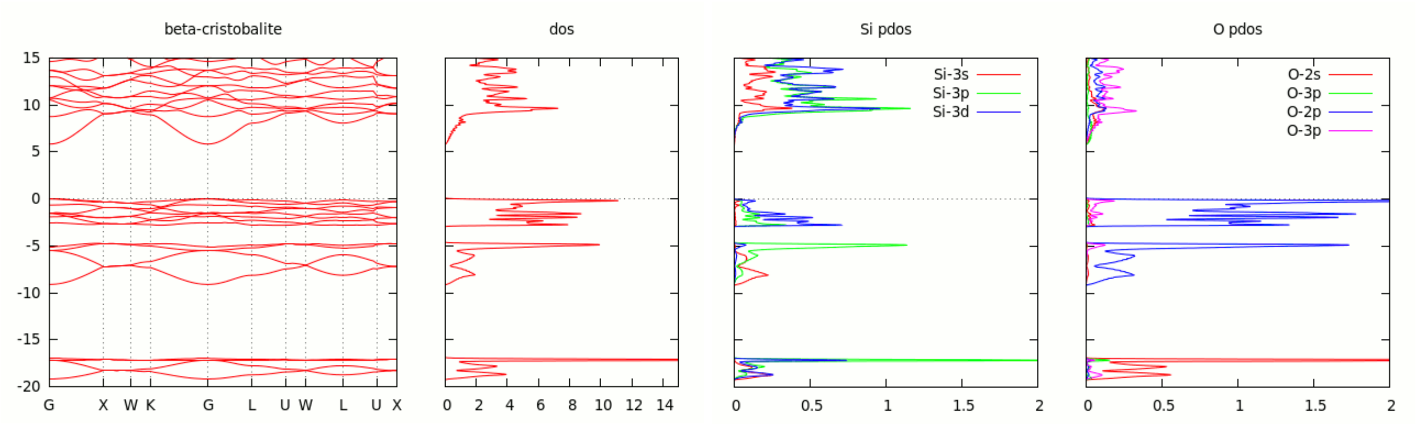
The k-point path along the Brillouine zone has been generated by the (incomplete) ../scripts/generate_kpoints_path.py script by typing: *FCC, [enter], [ente]r, kpoints.out*. The file kpoints.out has been appended to betacrist-bands-35.in. Note that we set *nbnd=32*, in order to include 16 occupied + 16 empty states.

Next, '*grep occupied betacrist-scf-35.out*' to get the highest occupied orbital, and set the value of the Fermi energy to the highest occupied orbital, in file the *bandos.gplot*.

Finally, if gnuplot is installed and working:

```
gnuplot -persist bandos.gplot
[enter]
[enter]
```

Here is how they should look like:



5. Geometry and cell relaxation

If coordinates and/or cell parameters are not known accurately, we should *relax* them, in order to find the minimum of energy/enthalpy.

Go to day2/05-betacrist-relax, and inspect the betacrist-relax.in file. The main changes are:

```
&electrons
   calculation = 'relax'
...
&ions
    ion_dynamics = 'bfgs'
/
```

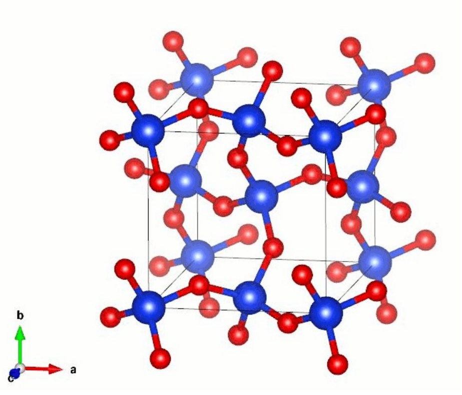
Also, notice that initial coordinates are different from the previous activities. The calculation should run in ~10 minutes and it should converge to nearly the same structure and energy as before.

In case you want to relax simultaneously the positions and cell parameters, have a look at the betacrist-vcrelax.in input file:

```
&electrons
   calculation = 'vc-relax'
...
&system
   nosym = .true.                                  ! to switch off symmetry detection
...
&ions
    ion_dynamics = 'bfgs'
/
&cell
    cell_dynamics = 'bfgs'
/
```

This calculation will take ~30 minutes and it can be a good idea to run in while moving to activity 6 (coffee break/merenda).

The final structure is no longer cubic and the *findsym* code (http://stokes.byu.edu/isotropy.html) reports a body centered tetragonal $I\bar{4}2d$. This space group has been reported for beta-cristobalite, however there is still some debate on the true ground state structure of beta-cristobalite (see e.g. http://arxiv.org/abs/0806.3737):



6. Coffee break/merenda

Enjoy!

7. NMR chemical shift convergence

In this part we will calculate the NMR shielding of cubic beta-cristobalite as a function of k-points sampling. For each k-point mesh (2x2x2 to 6x6x6, unshifted) you must first run the SCF calculation, then the NMR calculation:

```
pw.x <betacrist-scf-2x2x2.in >betacrist-scf-2x2x2.out
gipaw.x <betacrist-nmr.in >betacrist-nmr-2x2x2.out
```

The betacrist-nmr.in input file is very simple and the input variables are self-explaining. The NMR output file instead consists of several sections. The most important are:

1. f-sum rule
2. susceptibility
3. total sigma

The f-sum rule should be fulfilled as much as possible. In order to improve the f-sum rule one can increase plane wave cutoff and (more important) k-points sampling. The total sigma reports the NMR absolute isotropic shielding, together with the full tensor, anisotropy, eta (according to the SIMPSON convention) and tensor principal axis.

If you report the convergence of f-sum rule and total sigma as a function of k-points you should get numbers like:

Cutoff (Ry)	**K-points**	**f-sum**	**Total sigma Si**	**Total sigma O**
30	2	-30.7307	437.03	211.32
30	3	-30.6281	434.85	231.20
30	4	-30.6200	434.64	232.30
30	5	-30.6190	434.58	232.35
30	6	-30.6196	434.56	232.33
45	2	-30.8077	434.71	204.81
45	3	-30.7122	432.55	223.91

45	4	-30.7055	432.35	225.05
45	5	-30.7050	432.33	225.12
45	6	-30.7050	432.32	225.13

Note that a k-point mesh of 3x3x3 is not sufficient for converging the NMR shielding of oxygen. More important, increasing the cutoff from 30 to 45 yields a large change of the NMR shielding. however, we don't have time to test for higher cutoff in this tutorial.

In the directory extra, I've calculated NMR shielding of quartz. They are 429.26 for Si and 218.20 for O. The experimental chemical shifts (with respect to TMS and liquid water) are the following:

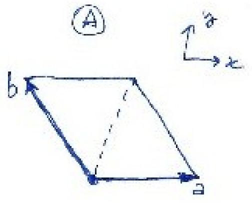
beta-cristobalite	$\delta(^{29}\mathrm{Si}) = -108.50$ ppm	$\delta(^{17}\mathrm{O}) = 37.2$ ppm
quartz	$\delta(^{29}\mathrm{Si}) = -107.73$ ppm	$\delta(^{17}\mathrm{O}) = 40.8$ ppm

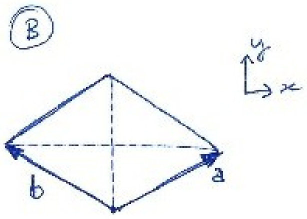
Thus, the difference in NMR *shielding* between beta-cristobalite and quartz is: +0.77 ppm for Si and +3.6 ppm for O. Our calculations at 45 Ry slightly overestimates the experimental data: +3.06 ppm for Si and +6.93 ppm for O.

9. (optional) From crystal structure to input file

The purpose of this exercise is to write an input file starting from a CIF structure, and to help you choosing the best ibrav/coordinates format combination.

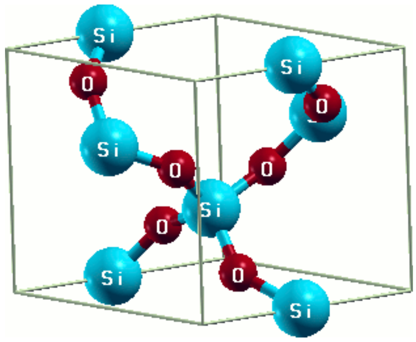
The first system is quartz. The crystal cell is hexagonal, but the standard QE setup (*ibrav=4*) will place the *a* vector along *x* (Fig. A). However, GIPAW requires that all symmetry operations must transform cartesian axes into themselves. To this end, it is better to use *ibrav=0* and to setup CELL_PARAMETERS like in Fig. B.

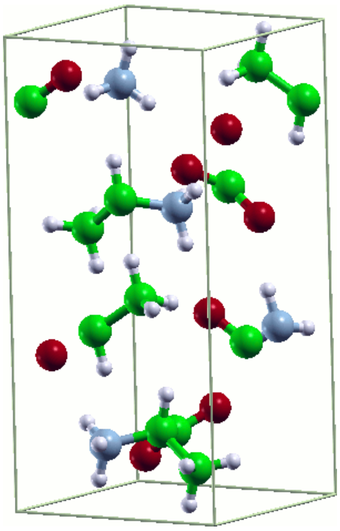




Then, you have to take fractional coordinates from the CIF file and apply the symmetry operations of the group, also listed into the CIF file. The easy way is to use VESTA: open the CIF file, Edit → Edit data → Unit cell → Remove symmetry. Then File → Export data → quartz_P1.cif. Alternatively you can modify the generate_coordinates.py script.

The second system is solid L-alanine. The resulting input file will contain 52 atoms. They should look like:





Links and documentation

Google drive link: https://drive.google.com/folderview?id=0BxmE1NC-2O4wRXVmeXJFdHUwZDg&usp=sharing

Quantum Espresso homepage: http://www.quantum-espresso.org

Input data description: http://www.quantum-espresso.org/wiki/index.php/Input_Data_Description

Pseudopotentials: http://www.quantum-espresso.org/pseudo.php

Gipaw pseudopotentials: https://sites.google.com/site/dceresoli/pseudopotentials

QE Forge: http://qe-forge.org

Bilbao Crystallographic Server: http://www.cryst.ehu.es

Xcrysden: http://www.xcrysden.org/

VESTA: http://jp-minerals.org/vesta/en/