geometry optimization : towards the ground state

This document explains how Quantum Espresso can be used to find the ground state geometry of a given type of crystal (it will be explained what is meant by 'ground state geometry'). This is a powerful and largely automatized process. There will be another document with a somewhat longer procedure, which will lead to the same result yet which will give additional information on top of the ground state geometry (elastic information via the equation of state).

The few crystals we calculated so far in this course (silicon, halite,…), had very high symmetry. Actually, *one single number* was sufficient to nail down the position of every atom in the infinite perfect crystal. If we say 'silicon in the diamond structure', then we need to know the lattice parameter only (=a single number) and we know exactly where every atom is. The same holds true for 'NaCl in the rocksalt structure'.

For the majority of crystals, more information is needed. Let us have a look at lead monoxide (PbO) in its mineral form that is knows as litharge. The shape of the crystal unit cell is not cubic, it is tetragonal. That means that *two numbers* must be specified to determine this unit cell: the a=b lattice parameters and the c lattice parameter. In the most general case, *6 numbers* need to be given (three lattice parameters and three angles – for a tetragonal cell, all angles are 90°).

Get the experimental crystal structure for litharge in the following way: go to COD, select 'Search', enter Pb and O in the element boxes, and 2 and 2 in the boxes for the minimal and maximal number of elements (i.e. you ask for exactly these two elements), then press 'Send'. You will get a list of over 40 crystals made exclusively from Pb and O (several pages of twenty each). We'll work with the one that has a cell volume of 79.327 $Å^3$, which is a room temperature measurement. Download the cif file to your computer.

Alternatively, the direct download of this cif file is via this link.

If you inspect the cif file, you see that the a=b lattice parameter is 3.9744 Å, while the c lattice parameter is 5.022 Å. Two numbers, indeed. You'll see coordinate lines near the end of the file:

```
_atom_site_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
Pb 0.00000 0.50000 0.23510 0.01520
O 0.00000 0.00000 0.00000 0.01013
```

The oxygen atoms in the unit cell are at a set of coordinates that looks very simple: (0, 0, 0). The lead atoms are at (0, 0.5, 0.23510). Those "0" and "0.5" are nice fractions, whereas the "0.23510" looks like a random number. That is no coincidence. We'll see in the crystallography lecture of this course that the former two are determined by symmetry, while the latter one is a "free coordinate" : you can assign any value to it, and the overall symmetry of the crystal will not change. Therefore, if we say "PbO in the litharge structure with a=b=3.9744 Å and c=5.022 Å", the crystal is not entirely

determined yet. We need to tell that the z-coordinate for the Pb-atom is 0.23510. That means we need three numbers to fully specify this crystal.

Imagine we know all information about the symmetry of this crystal, but we do not know the values for these 3 numbers from experiment (this situation often arises in practice). Can we get these numbers from DFT? This document will tell you how. The result will be a prediction for the full specification of a crystal *in its ground state*, i.e. in the absence of external perturbations as pressure and temperature. DFT will predict how the crystal would be like at 0 K.

1. preparation

Use cif2cell to convert the structure to a *.in file for QE, and add the other required information as done before. Regarding the pseudopotentials, take this one for Pb and this one for O.

We'll focus on the geometry aspect in this exercise, so let's assume you have done the convergence testing already. These are good settings for basis set size and k-mesh:

```
  ecutwfc=60,
  ecutrho=240,

K_POINTS {automatic}
  5 5 5 0 0 0
```

These settings guarantee a numerical precision of 2 kB on stress tensor components and 1 mRy/au on forces (if you're not familiar with these quantities: they will be shortly explained underneath, as well as in the lecture on geometry optimization).

Run this calculation, which will take somewhat less than 2 minutes (depending on the speed of your computer). For later reference, take note of the total energy:

```
!    total energy              =   -1824.46682511 Ry
```

And these are the stress tensor felt by the crystal and the forces on all atoms:

```
     Forces acting on atoms (Ry/au):

     atom    1 type  2   force =     0.00000000    0.00000000    0.02154389
     atom    2 type  2   force =     0.00000000    0.00000000   -0.02154389
     atom    3 type  1   force =     0.00000000    0.00000000   -0.00000000
     atom    4 type  1   force =     0.00000000    0.00000000    0.00000000

     Total force =     0.030494     Total SCF correction =     0.000129


     entering subroutine stress ...

          total   stress  (Ry/bohr**3)                   (kbar)      P=   52.50
   0.00038269   0.00000000   0.00000000         56.40      0.00      0.00
   0.00000000   0.00038269   0.00000000          0.00     56.40      0.00
   0.00000000   0.00000000   0.00030323          0.00      0.00     44.70
```

2. positions of the atoms

If symmetry does not dictate it, how does nature choose the value for the z-coordinate of Pb? Why is it 0.2351 and nothing else? The DFT answer is: because this is the value that minimizes the total energy of the crystal. Indeed, you could make a few calculations with different values for this z-coordinate, and search for the value that minimizes the energy[1]. More complex crystals will easily have 5, 10 or more such degrees of freedom, which will make such an explicit calculation procedure rapidly too expensive. QE has an automatic procedure to search efficiently the minimum of this high-dimensional energy function. We'll apply this to litharge :

Make the following changes/additions to your QE input file, starting from the file you used for the previous static calculation (the new &IONS block should come after the &ELECTRONS block):

```
  calculation='relax',

&IONS
  ion_dynamics='bfgs',
/
```

Run this calculation (expect about 5 minutes), and inspect the output file:

```
     Final energy   =   -1824.4681413711 Ry

Begin final coordinates

ATOMIC_POSITIONS (crystal)
Pb       0.000000000   0.500000000   0.241551287
Pb       0.500000000   0.000000000   0.758448713
O        0.000000000   0.000000000   0.000000000
O        0.500000000   0.500000000  -0.000000000
End final coordinates

     Forces acting on atoms (Ry/au):

     atom    1 type  2   force =     0.00000000    0.00000000    0.00003019
     atom    2 type  2   force =     0.00000000    0.00000000   -0.00003019
     atom    3 type  1   force =     0.00000000    0.00000000    0.00000000
     atom    4 type  1   force =     0.00000000    0.00000000    0.00000000
```

You observe here that the total energy is indeed lower than in the previous calculation. The optimal z-coordinate is 0.24155. The force on the Pb-atoms has reduced from 21.5 mRy/au to 0.03 mRy/au (which is basically zero). This z-coordinate value is only slightly different from the experimental value

[1] It is instructive to test this explicitly. Take a few values for z within the interval 0.21 – 0.26 (in steps of 0.1), and compute and plot the total energy as a function of z. Compare this graph with the z-value and corresponding energy you get later in Sec. 2 using the automatic procedure.

z=0.23510 that was in the initial cif file. If we wouldn't have known the experimental value at all, this would have been an excellent prediction. Actually, internal coordinates are not easily determined experimentally, their error bars can be large. In many cases, a DFT prediction of internal coordinates is the fastest way to get fairly accurate values.

3. shape of the unit cell

We are now ready to search for the optimal values of the a=b and c lattice parameters. One way to do this, is to do DFT calculations for all possible values of a=b and c, and find out which value gives the lowest total energy (ideally, for every single choice of a=b and c, the z-value has to be optimized too) . An alternative (and faster) way is to use an automatic optimization procedure within QE that searches for the set of lattice parameters, unit cell angles and internal positions that makes the stress tensor zero (which corresponds automatically to a minimal total energy).

At the end of your previous calculation, you found the stress tensor (for the experimental lattice parameters with the optimal z-coordinate):

```
     entering subroutine stress ...

          total   stress  (Ry/bohr**3)                   (kbar)      P=   34.54
   0.00027768   0.00000000   0.00000000         40.84       0.00       0.00
   0.00000000   0.00027768   0.00000000          0.00      40.84       0.00
   0.00000000   0.00000000   0.00014937          0.00       0.00      21.95
```

It tell us that in order to adopt the given (experimental) lattice parameters, the crystal should – according to DFT – be subject to an applied stress of about 41 kbar in the horizontal plane and 22 kbar in the vertical direction. The ground state lattice parameters at zero pressure should therefore be a little bit larger then these experimental values (at least, according to the PBE XC-functional). The required stress is not isotropic, implying that the c/a ratio of the PBE-optimized crystal is slightly different from the ratio for the experimental unit cell.

Make the following changes/additions to your *.in file (note that we start from the optimized z-coordinate), and let the calculation run. This will take a while, roughly 1.5 hours :

```
  calculation='vc-relax',

&IONS
  ion_dynamics='bfgs',
/

&CELL
  cell_dynamics='bfgs',
  press=0.d0,
  press_conv_thr=0.5d0,
/

ATOMIC_POSITIONS {crystal}
  Pb   0.0000000000d0   0.5000000000d0   0.2415512870d0
```

```
  Pb   0.5000000000d0   0.0000000000d0   0.7584487130d0
   O   0.0000000000d0   0.0000000000d0   0.0000000000d0
   O   0.5000000000d0   0.5000000000d0   0.0000000000d0
```

The new &CELL block tells which optimization scheme will be used to change the unit cell shape and volume ('bfgs'), it states that the target for the applied pressure is zero (if the applied pressure is zero, then the stress tensor will be zero), and it tells that we consider it to be zero as soon as it is smaller than 0.5 kbar (for a computer, 'zero' is always 'zero within a given treshold').

Inspect the output file after the calculation has finished, to see what are the optimal lattice parameters and their corresponding energy and stress tensor:

```
Begin final coordinates
     new unit-cell volume =    615.80088 a.u.^3 (    91.25227 Ang^3 )

CELL_PARAMETERS (alat=  7.51052751)
   1.022364802   0.000000000   0.000000000
   0.000000000   1.022364802   0.000000000
   0.000000000   0.000000000   1.390647962

ATOMIC_POSITIONS (crystal)
Pb       0.000000000   0.500000000   0.215741137
Pb       0.500000000   0.000000000   0.784258863
O        0.000000000   0.000000000   0.000000000
O        0.500000000   0.500000000  -0.000000000
End final coordinates
```

The lattice parameters are expressed in terms of 'alat', which itself is given in bohr units (1 bohr unit = 1 atomic unit = 0.529177 Å). After conversion, you conclude that the DFT(PBE) prediction for the lattice parameters of litharge is a=b=4.0633 Å and c=5.5270 Å. For many, many crystals such a DFT(PBE) prediction will be in very good agreement with experiment (we'll talk more about the kind of deviations you can expect later). Litharge is a somewhat exceptional case (there are good reasons for that, see later), as the experimental values of a=b=3.9744 Å and in particular c=5.022 Å are quite a bit off.

Note as well that the z-coordinate of Pb has changed too: it is not independent from the volume.

The total energy has lowered as well. When sticking to the PBE XC-functional, this is the lowest possible energy you can achieve by varying lattice parameters and the Pb z-coordinate:

```
!    total energy              =   -1824.47526831 Ry
```

The forces are obviously zero:

```
     Forces acting on atoms (Ry/au):

     atom    1 type  2   force =     0.00000000    0.00000000    0.00006979
     atom    2 type  2   force =     0.00000000    0.00000000   -0.00006979
     atom    3 type  1   force =     0.00000000    0.00000000    0.00000000
     atom    4 type  1   force =     0.00000000    0.00000000    0.00000000

     Total force =     0.000099     Total SCF correction =     0.000003
```

And the stress tensor is zero too (remember that our precision settings guaranteed a precision of 2 kB on stress tensor components – everything below 2 kB is therefore indistinguishable from zero):

```
          total   stress  (Ry/bohr**3)                   (kbar)      P=   -0.30
 -0.00000079   0.00000000   0.00000000         -0.12      0.00       0.00
  0.00000000  -0.00000079   0.00000000          0.00     -0.12       0.00
  0.00000000   0.00000000  -0.00000462          0.00      0.00      -0.68
```

Make sure you can reproduce the three calculations in this document. Also, make sure you understand why the keywords in each section are added/modified. It might be helpful to search their definition in the keyword list of QE.