An introduction to density functional theory for experimentalists

Tutorial 3.1

We begin with a new folder as usual:

```
$ cd ~/scratch/summerschool ; mkdir tutorial-3.1 ; cd tutorial-3.1
```

In the first part of this tutorial we will say more on the determination of equilibrium structures of molecules and solids. In the second part we will attempt a calculation of elastic properties.

Automatic optimization of atomic coordinates

In Tutorial 2.1 we discussed how to calculate the potential energy surface of a molecule, and how to determine equilibrium structures by locating the minima of that surface.

In this section we consider an alternative route for finding the equilibrium geometry of Cl_2.

As a starter we copy over the input files that we used for the exercise on Cl_2 during Tutorial 2.1:

```
$ cp ../tutorial-2.1/cl2.in ./
$ cp ../tutorial-2.1/pw.x ./
$ cp ../tutorial-2.1/job.pbs ./
```

We check that everything is in place and that `job.pbs` is still reading in correctly `cl2.in` (in case this was modified during Tutorial 2.1). As usual we perform a test run in order to make sure that everything goes smoothly:

```
$ qsub job.pbs
```

For this job we must remember to use the submission flag `-npool 1`, otherwise the code will crash (can you explain why?). If everything is still fine, we should find `cl2.out` in the current folder, indicating that the run completed successfully.

Now let us take a look at the documentation of `pw.x`. As a reminder we need to go to:
http://www.quantum-espresso.org/wp-content/uploads/Doc/INPUT_PW.html

We look for the input variable `calculation`; we should find the following:

Namelist: CONTROL

calculation	CHARACTER
Default:	'scf'

```
a string describing the task to be performed:
    'scf',
    'nscf',
    'bands',
    'relax',
    'md',
    'vc-relax',
    'vc-md'

    (vc = variable-cell).
```

Until now we have used only one type of calculation, namely `calculation = 'scf'`. This means that we required the code to perform only a self-consistent DFT calculation with the ions clamped at the coordinates specified below the keyword `ATOMIC_POSITIONS`.

Another possibility is to set this variable to 'relax' inside cl2.in:

```
&control
 calculation = 'relax'
 prefix = 'Cl2',
 ...
```

This choice instructs `pw.x` to automatically determine the equilibrium structure, starting from the coordinates given below the keyword `ATOMIC_POSITIONS`. In practice the code calculates the **forces** acting on the ions, and updates the ionic positions in such a way as to minimize those forces. The equilibrium configuration will correspond to the situation where all forces are smaller than a certain threshold, and the total potential energy surface has changed less than a given threshold from the previous iteration.

The threshold on the forces is given by the variable `forc_conv_thr`:

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forc_conv_thr	REAL
Default:	1.0D-3

```
convergence threshold on forces (a.u) for ionic minimization:
the convergence criterion is satisfied when all components of
all forces are smaller than "forc_conv_thr".
See also "etot_conv_thr" - both criteria must be satisfied
```

The threshold on the total potential energy is specified by the variable `etot_conv_thr`:

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etot_conv_thr	REAL
Default:	1.0D-4

```
convergence threshold on total energy (a.u) for ionic
minimization: the convergence criterion is satisfied
when the total energy changes less than "etot_conv_thr"
between two consecutive scf steps. Note that "etot_conv_thr"
is extensive, like the total energy.
See also "forc_conv_thr" - both criteria must be satisfied
```

In principle we could perform calculations without specifying these parameters; in this case `pw.x` will use some preset default values. For the sake of completeness let us specify some rather stringent criterion in the input file cl2.in:

```
&control
 calculation = 'relax'
 prefix = 'Cl2',
 forc_conv_thr = 1.d-5,
 etot_conv_thr = 1.d-8,
 ...
```

When we perform the automatic optimization of the atomic coordinates we also need to add a 'card' for the ions, as follows:

```
...
&electrons
 conv_thr = 1.0d-8
/
&ions
/
ATOMIC_SPECIES
..
```

This extra card is to specify runtime parameters, but we can leave it empty for the time being.

As a starting point for the atomic coordinates let us use a very large Cl-Cl separation:

```
...
ATOMIC_POSITIONS bohr
 Cl 0.00 0.00 0.00
 Cl 5.00 0.00 0.00
...
```

We now execute `pw.x` and look at the output file `cl2.out` directly using . As a reminder, in order to search for a word in `vi` we simply press ⌷/⌷ and type the word. We search for 'Forces' and obtain:

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

    atom    1 type  1   force =     0.12392756    0.00000000    0.00000000
    atom    2 type  1   force =    -0.12392756    0.00000000    0.00000000

    Total force =    0.175260    Total SCF correction =    0.000022
```

These lines are telling us that, in the initial configuration, the two Cl atoms experience forces directed along the Cl-Cl axis, and pointing towards the other Cl atom. This was to be expected since we started with the atoms at a distance much larger than the equilibrium bond length.

Immediately below the forces we see the <u>updated</u> atomic positions which will be used at the next iteration:

```
    ATOMIC_POSITIONS (bohr)
    Cl       0.123927558    0.000000000    0.000000000
    Cl       4.876072442    0.000000000    0.000000000
```

Clearly the atoms are being displaced towards each other. At the end of the iterations we can see something like the following:

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

    atom    1 type  1   force =     0.00000147    0.00000000    0.00000000
    atom    2 type  1   force =    -0.00000147    0.00000000    0.00000000

    Total force =     0.000002    Total SCF correction =    0.000024
...
    Final energy   =     -59.9905957153 Ry
  Begin final coordinates
```

```
  ATOMIC_POSITIONS (bohr)
  Cl        0.637701785   0.000000000   0.000000000
  Cl        4.362298215   0.000000000   0.000000000
End final coordinates
```

Here we see that the forces are essentially vanishing, therefore we reached the equilibrium configuration. The total energy at equilibrium is -59.9905957153 Ry, and the bond length is 3.7246 bohr = 1.971 Å. These values are in agreement with what we had found in Tutorial 2.1 (pag. 4) by explicitly looking for the minimum of the potential energy surface.

If we want to see how the atomic coordinates evolved towards the equilibrium configuration, we can simply issue:

```
$ grep "Cl" cl2.out
```

There is also a way to directly visualize the evolution of the atomic coordinates: we can open xcrysden and go through the following steps:
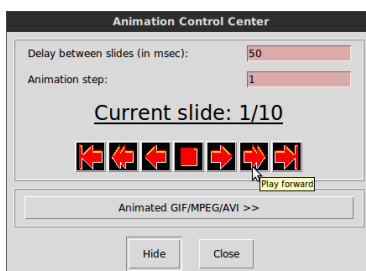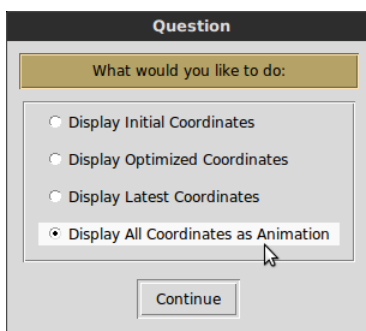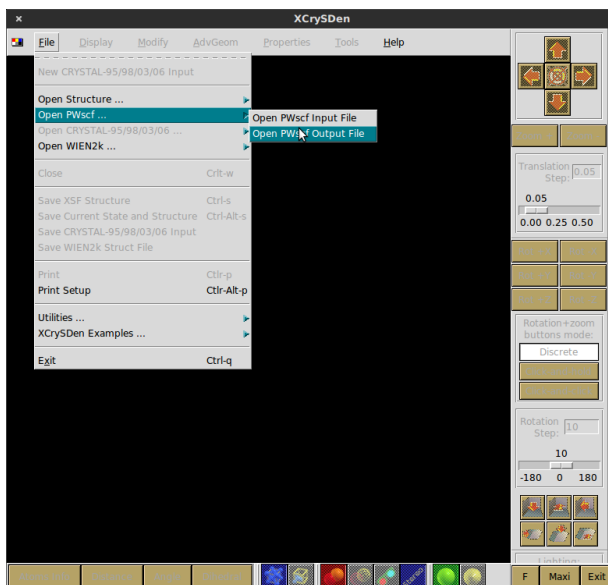
Automatic optimization of atomic coordinates and unit cell

In addition to the optimization of atomic coordinates, it is also possible to optimize the vectors of the primitive unit cell. This feature is activated in `pw.x` by setting the calculation type to `vc-relax`:

Namelist: CONTROL

calculation	CHARACTER
Default:	'scf'

```
a string describing the task to be performed:
   'scf',
   'nscf',
   'bands',
   'relax',
   'md',
   'vc-relax',
   'vc-md'

(vc = variable-cell).
```

Let us consider the case of **graphite** as in Tutorial 2.2. We can copy over the corresponding input file and the carbon pseudopotential:

```
$ cp ../tutorial-2.2/exercise3/graph.in ./
$ cp ../tutorial-2.2/exercise3/C.pz-vbc.UPF ./
```

Let us modify the input file is such a way as to start from a highly-compressed unit cell of graphite:

```
&control
 calculation = 'vc-relax'
 prefix = 'graphite',
 pseudo_dir = './',
 outdir = './'
/
&system
 ibrav = 4,
 celldm(1) = 4.0,
 celldm(3) = 2.0,
 nat = 4,
 ntyp = 1,
 ecutwfc = 100,
/
&electrons
 conv_thr = 1.0d-8
/
&ions
/
&cell
/
ATOMIC_SPECIES
 C 1.0 C.pz-vbc.UPF
ATOMIC_POSITIONS crystal
 C 0.00 0.00 0.25
 C 0.00 0.00 0.75
 C 0.333333 0.666666 0.25
 C 0.666666 0.333333 0.75
K_POINTS automatic
6 6 2 1 1 1
```

In the above input file we should note the 'cards' `ions` and `cell` which are required when running this kind of calculation. In this file the cards are left empty; generally they can be used to fine-tune the optimization procedure.

When instructred to execute a calculation of type `vc-relax`, `pw.x` evaluates the <u>stress tensor</u> of the system in the initial configuration, and updates the unit cell vectors so as to reduce the stress.

Let us execute `pw.x` using the above input file. At the end of the run we can look inside the output file using `vi` and search for the following words:

[/] `subroutine stress`

We will see something like:

```
    entering subroutine stress ...

          total   stress  (Ry/bohr**3)                   (kbar)     P= 4044.22
   0.03445761   0.00000000   0.00000000        5068.89     0.00      0.00
   0.00000000   0.03445761   0.00000000           0.00   5068.89     0.00
   0.00000000   0.00000000   0.01356098           0.00      0.00   1994.89
```

This indicates that, as expected, in the first iteration the system is under a very high pressure, precisely 4.04 Mbar. Following this initial iteration, `pw.x` modifies the lattice vectors in the direction of lower pressure.

We can note that in this case the <u>individual forces</u> on the atoms are all vanishing by symmetry:

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

    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 1   force =     0.00000000   0.00000000   0.00000000
    atom    4 type 1   force =     0.00000000   0.00000000   0.00000000
```

As a result this procedure will not modify the Wickoff positions of the 4 C atoms in the unit cell. The final optimized structure is found by looking for

[/] `Begin final coordinates`

```
Begin final coordinates
     new unit-cell volume =    200.62641 a.u.^3 (    29.72977 Ang^3 )

CELL_PARAMETERS (alat=  4.00000000)
   1.149452048   0.000000000   0.000000000
  -0.574726024   0.995454674   0.000000000
   0.000000000   0.000000000   2.739654388

ATOMIC_POSITIONS (crystal)
C        0.000000000   0.000000000   0.250000000
C        0.000000000   0.000000000   0.750000000
C        0.333333000   0.666666000   0.250000000
C        0.666666000   0.333333000   0.750000000
End final coordinates
```

In this output file we should note that the lattice vectors are given in units of the original lattice parameter in input, that is alat = 4.0 bohr. Therefore the optimized lattice parameter is now

$$a = 4.00000000 \cdot 1.149452048 = 4.59781 \, \text{bohr} = 2.433 \, \text{Å}$$

The optimized c/a ratio is

$$c/a = 2.739654388/1.149452048 = 2.383.$$

It is immediate to see that the lattice vectors correspond to an hexagonal lattice; for example the second line of CELL_PARAMETERS is $a(-1/2, \sqrt{3}/2, 0)$.

The total energy in the optimized configuration is -45.59332176 Ry.

> **Note**. From this calculation we have obtained a c/a ratio which is much smaller than the one determined in Tutorial 2.2 by studying the potential energy surface (2.383 here vs. 2.729 in T2.2). The interlayer separation is approximately 15% shorter in the present calculation.
>
> This result is a calculation artifact. What is happening is that the code modifies the structure so as to minimize the energy. Now, the Hamiltonian describing the system is expressed in a basis of planewaves, and the wavevectors of these planewaves alond the c axis are multiples of $2\pi/c$. If, during the optimization, the c parameter undergoes a significant change (as it is the case here, since we start from $c/a = 2$ and we end up with $c/a = 2.729$), then we are effectively reducing our planewaves cutoff at each iteration. As a result the calculation becomes less and less accurate. In order to avoid this problem, pw.x performs one additional calculation at the very end, after having redefined all the **G**-vectors according to the optimized structure. We can see that this step yields a residual pressure of 92.7 kbar along the c-axis. This indicates that the structure is not yet fully optimized. In order to avoid this problem we should run a new calculation, starting from the latest lattice parameters.

Elastic constants of diamond

Now we want study the elastic constants of diamond. As we have seen in Lecture 3.2, for a cubic system like diamond there are only three independent elastic constants, namely C_{11}, C_{12}, and C_{44}.

We can determine these constants by using the relations discussed in the lecture. In particular:

- We consider an **isotropic** deformation of the diamond structure. This corresponds to a uniform stretch of the lattice vectors:

$$\mathbf{a}_i' = (1 + \eta) \, \mathbf{a}_i \text{ for } i = 1, 2, 3$$

  The resulting change in the total potential energy from the equilibrium value U_0 is:

$$U - U_0 = \Omega \frac{3}{2} \left(C_{11} + 2C_{12} \right) \eta^2 \tag{1}$$

  The calculation of U and U_0 can be performed by using the following input file for diamond (taken from Tutorial 2.2, Exercise 2):

```
$ cat > scf.in << EOF
&control
 calculation = 'scf'
 prefix = 'diamond',
 pseudo_dir = './',
 outdir = './'
/
&system
 ibrav = 0,
 celldm(1) = 6.66405,
 nat = 2,
 ntyp = 1,
 ecutwfc = 100.0,
/
&electrons
 conv_thr = 1.0d-8
/
ATOMIC_SPECIES
 C 1.0 C.pz-vbc.UPF
ATOMIC_POSITIONS
 C 0.00 0.00 0.00
 C 0.25 0.25 0.25
K_POINTS automatic
 6 6 6 1 1 1
CELL_PARAMETERS
 -0.50 0.00 0.50
  0.00 0.50 0.50
 -0.50 0.50 0.00
EOF
```

In this version of the input file we are specifying that the unit cell vectors are given manually, ibrav = 0; these vectors are provided in units of the lattice parameter, celldm(1), after the keywoord CELL_PARAMETERS.

By running pw.x with the above input file we obtain the total energy in the ground state:

$U_0 = $ -22.80164823 Ry.

Furthermore we can read the volume of the unit cell by searching for: $\boxed{/}$ volume

This gives $\Omega = 73.9869$ bohr^3.

Now we can modify this input file in order to set in an isotropic deformation with $\eta = 0.002$:

```
$ more scf_iso.in

...
CELL_PARAMETERS
 -0.501 0.000 0.501
  0.000 0.501 0.501
 -0.501 0.501 0.000
...
```

With this new input file we find the total energy:

$U = $ -22.80159963 Ry

Using Eq. (1) with $\eta = 0.002$ we obtain

$$C_{11} + 2C_{12} = 0.10948 \text{ Ry/bohr}^3 = 1610.5 \text{ GPa} \qquad\qquad 1 \text{ Ry/bohr}^3 = 14710.5 \text{ GPa}$$

- We now consider a **tetragonal** deformation.

From Lecture 3.2 we have the relation:

$$U - U_0 = \Omega \, 3 \, (C_{11} - C_{12}) \, \eta^2 \tag{2}$$

and the tetragonal distortion of the unit cell can be realized by considering an expansion $(1+\eta)$ along x and y, and a contraction $(1 - 2\eta)$ along z. We modify the input file as follows:

```
$ more scf_tetra.in

...
CELL_PARAMETERS
 -0.501 0.000 0.498
  0.000 0.501 0.498
 -0.501 0.501 0.000
...
```

This calculation gives:

$U = $-22.80156418 Ry

Using Eq. (2) with $\eta = 0.002$ we obtain

$C_{11} - C_{12} = $0.094668 Ry/bohr^3 = 1392.6 GPa

By combining the two relations for C_{12} and C_{12} we obtain:

$C_{11} = 1465.6$ GPa, $C_{12} = 72.6$ GPa.

The corresponding experimental values are $C_{11} = 1079$ GPa, $C_{12} = 124$ GPa, from McSkimin & Andreatch, J. Appl. Phys. 43, 2944 (1972).

Note. These calculations are not fully converged, and by refining our setup we can obtain better agreement with experiment. In particular, we are determining elastic constants using only 2 calculations in each case. Since elastic constants are second derivatives of the total energy, a much more acurate approach is to evaluate such derivatives using 3 total energy calculations. See Exercise 6.4 of the Book for how to perform more refined calculations.

- Finally we can consider a **trigonal** deformation.

  From Lecture 3.2 we have the relation:

  $$U - U_0 = \Omega \frac{1}{2} C_{44} \eta^2 \qquad (3)$$

  and the trigonal distortion of the unit cell can be realized by considering the following distortion for $\eta = 0.002$:

```
$ more scf_trigo.in

...
CELL_PARAMETERS
  -0.5000  -0.0005   0.5000
   0.0005   0.5000   0.5000
  -0.4995   0.4995   0.0000
...
```

  This calculation gives:

  $U =$-22.80164338 Ry

  Using Eq. (3) with $\eta = 0.002$ we obtain

  $C_{44} = 0.0327761$ Ry/bohr^3 = 482.2 GPa

  The corresponding experimental value is $C_{44} = 578$ GPa [McSkimin & Andreatch, J. Appl. Phys. 43, 2944 (1972)].

Note. These calculations are not fully converged: in order to obtain accurate results we need to use higher-order finite difference formulas. See Exercise 6.4 of the Book.

We create a new folder as usual:

```
$ cd ~/scratch/summerschool; mkdir tutorial-3.2 ; cd tutorial-3.2
```

In this hands-on session we will first familiarize ourselves with calculations of elastic constants, using **diamond** as a test case. Then we will try to set up an entirely new calculation on **SrTiO₃**; here we will use the Materials Project database to find the initial geometry.

Exercise 1

► Calculate the elastic constants C_{11}, C_{12}, and C_{44} of diamond, by following the steps illustrated in Tutorial 3.1.

The **bulk modulus** B is a measure of the resistance of a materials to hydrostatic compression. This quantity can be obtained from the elastic constants as:

$$B = \frac{1}{3}(C_{11} + 2C_{12}).$$

► Calculate the bulk modulus of diamond, using the data obtained in the previous step, and compare your result with experiment.

► In Tutorial 3.1 we used a 'deformation' parameter $\eta = 0.002$ in all our calculations. Investigate the sensitivity of the calculated bulk modulus of diamond to the choice of η, by repeating the calculations for $\eta = 0.1$, 0.01, and 0.001.

Exercise 2

In this exercise we want to set up a simple input file to study SrTiO₃. In order to find an initial guess for the unit cell and atomic coordinates, we search the Materials Project database.

If you do not already have an account on the Materials Project, please go to https://www.materialsproject.org and click on Sign in or Register. The registration process only requires an email address and a password, this should take less than a minute to complete.
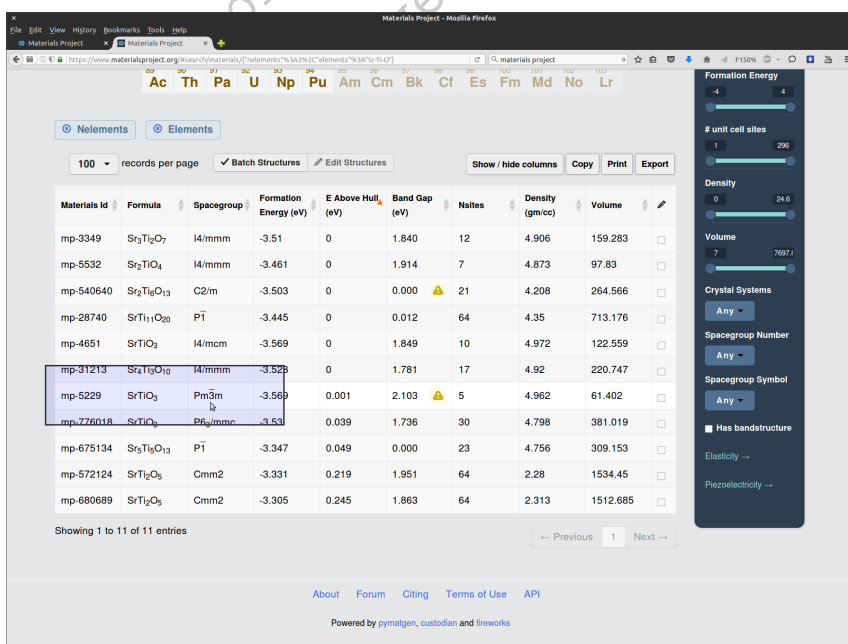
After logging-in you should be able to see a periodic table like the following:
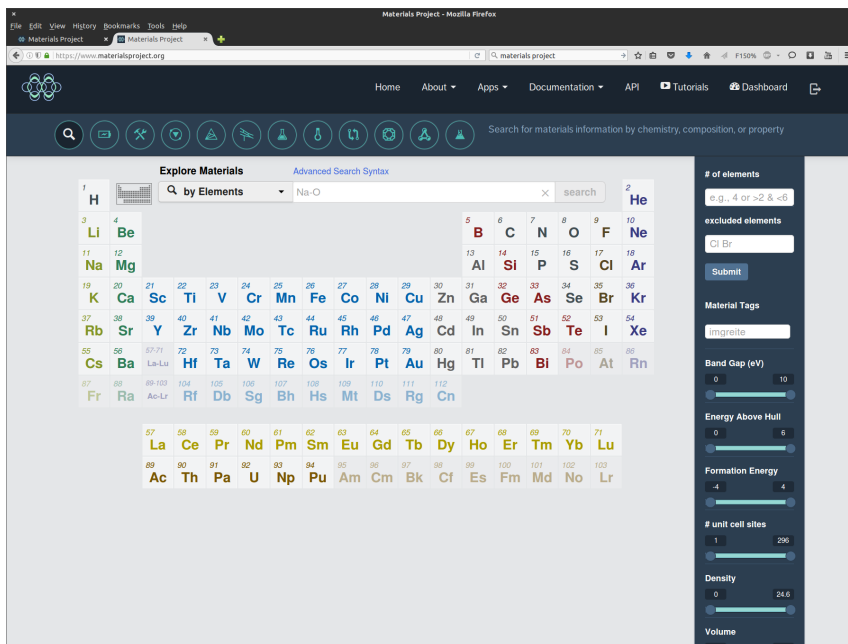
Now we can search for $SrTiO_3$ by entering Sr, Ti, and O in the search bar:
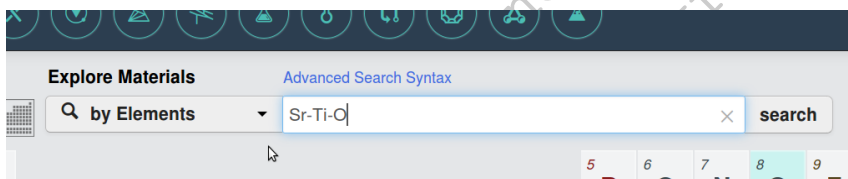
We are looking for the $Pm\overline{3}m$ structure of $SrTiO_3$, which is the high-temperature cubic phase. We will study the cubic phase since it only contains 5 atoms, therefore calculations are relatively easy.

By clicking on the $Pm\overline{3}m$ field we are shown the properties of this structures that have been uploaded in the database:

All we need from this page is the structural data, which can be found in the `poscar` file:

The 'poscar' format is the standard format of VASP, another widely used DFT package.

The 'poscar' file thus downloaded should look like the following:

```
1     Sr1 Ti1 O3
2    1.0
3    3.945130 0.000000 0.000000
4    0.000000 3.945130 0.000000
5    0.000000 0.000000 3.945130
6    Sr Ti O
7    1 1 3
8    direct
9    0.000000 0.000000 0.000000 Sr
10   0.500000 0.500000 0.500000 Ti
11   0.500000 0.000000 0.500000 O
12   0.500000 0.500000 0.000000 O
13   0.000000 0.500000 0.500000 O
```

Here the first line is a comment field, the second line contains the lattice parameter a in Å. Lines 3–5 contain the lattice vectors, scaled by the lattice parameter a: $\mathbf{a}_1/a$, $\mathbf{a}_2/a$, $\mathbf{a}_3/a$ (note that in this example the authors decided to set $a = 1$ and to give the lattice vectors directly in Å). Line 6 contains the list of atoms in the unit cell, followed by the number of atoms of each type on line 7,

in the same order. The keyword 'direct' on line 8 states that the atomic coordinates in lines 9-13 are expressed as fractional coordinates (units of 'direct' lattice), eg the Ti atom is at $(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)/2$.

▶ Construct the input file for a total energy calculation of $SrTiO_3$ using `pw.x`. For the time being we can leave the pseudopotential field blank. It is absolutely fine to start from an input file that you have from previous exercises.
If anything is unclear, please consult the documentation at
http://www.quantum-espresso.org/wp-content/uploads/Doc/INPUT_PW.html
Note: Remember that `celldm(1)` is to be given in atomic units. In order to specify that the atomic positions are in crystal coordinates we use the keyword: `ATOMIC_POSITIONS crystal`.

At this point we need pseudopotentials for Sr, Ti, O. For this exercise we want to use the LDA exchange and correlation functional, therefore we need to identify LDA pseudopotentials. We are looking for pseudos with the label `pz` (Perdew-Zunger) in the filename.
In order to make sure that we all obtain the same results, let us decide that we consider only pseudopotentials generated by Hartwigsen, Goedeker & Hutter.

▶ Download the required pseudopotential files from the QE library, using `wget` as in Tutorial 1.1.

▶ Using the input file just created, say `scf.in`, perform a test run using `calculation = 'scf'` in order to make sure that everything goes smoothly. For this test we can use some arbitrary convergence parameters, say `ecutwfc = 40` and a Brillouin-zone sampling 4 4 4 1 1 1.

Exercise 3

Now that we have a basic setup for $SrTiO_3$, we need to perform convergence tests.
▶ Determine the planewaves kinetic energy cutoff which is required to have the total energy converged to within 50 meV/atom. For this calculation you can use the same `K_POINTS` set of Exercise 2.
As a reminder, we performed a similar operation in Tutorial 1.2/Exercise 2.

▶ Using the cutoff just obtanied, determine the sampling of the Brillouin zone required to have the total energy converged to within 10 meV/atom.
You can find an example of such a test in Tutorial 1.2/Exercise 3.

Exercise 4

▶ Using the convergence parameters obtained in Exercise 3, determine the optimized lattice parameter of $SrTiO_3$ by using a calculation of type `vc-relax` (see Tutorial 3.1 for an example).

In this calculation you will note that the residual pressure at the end of the run is still nonzero. In order to fully optimize the lattice parameter it is convenient to perform one or two additional runs using the optimized parameter as a starting point.

▶ Compare your optimized lattice parameter with the experimental value from Cao et al, PSSA 181, 387 (2000).

Exercise 5

As a sanity check, at the end of Exercise 3 and 4 we should have obtained the following parameters:

```
...
celldm(1) = 7.18899,
ecutfwc = 210,
...
K_POINTS
4 4 4 1 1 1
```

▶ Use these parameters to calculate the bulk modulus of cubic $SrTiO_3$.

<u>Note</u>: In order to obtain reasonably accurate results it is convenient to use Eq. (1) of Tutorial 3.1, after rewriting as follows:

$$B = \frac{1}{3}(C_{11} + 2C_{12}) = \frac{1}{9}\frac{1}{\Omega}\frac{\partial^2 U}{\partial \eta^2} \simeq \frac{1}{9}\frac{1}{\Omega}\frac{U(+\eta) - 2U(0) + U(-\eta)}{\eta^2}$$

This expression shows that we can calculate the bulk modulus by using the second derivative of the total energy with respect to the deformation parameter. The second derivative is then approximated using a finite-difference formula involving 3 points $(+\eta, 0, -\eta)$.

For your reference, using $\eta = 0.01$ and considering the unit cell volume $\Omega = 360.5033\,\text{bohr}^3$, the value $B = 189$ GPa is obtained.

▶ Following the same lines as in the last step, calculate the elastic constants C_{11} and C_{12} of cubic $SrTiO_3$.
<u>Hint</u>: We already have the bulk modulus, therefore we know $C_{11} + 2C_{12} = 3B$. What we still need is the difference $C_{11} - C_{12}$, as discussed in Tutorial 3.1.
Also in this case we can rewrite Eq. (2) of Tutorial 3.1 as:

$$C_{11} - C_{12} \simeq \frac{1}{6}\frac{1}{\Omega}\frac{U(+\eta) - 2U(0) + U(-\eta)}{\eta^2}$$

and we perform three calculations corresponding to a tetragonal deformation of the lattice.

As a reference, you should obtain values in the range of $C_{11} = 360$ GPa and $C_{12} = 104$ GPa.

▶ Compare your calculated constants B, C_{11}, and C_{12} with the experimental values of Bell & Rupprecht, Phys. Rev. 129, 90 (1963).
You should find that the deviation from experiment is smaller than 10%.

▶ Can you think of possible strategies to improve your results?