Lab 2
First-principles calculations of the electronic properties of materials: The case study of bulk calcium oxide

Edward Linscott and Miki Bonacci

Paul Scherrer Institute

edward.linscott@psi.ch, miki.bonacci@psi.ch

March 27, 2025

This document contains the exercises that you will need to complete, each followed by some related hints. The exercises themselves are highlighted in red boxes. **Make sure you read the hints before attempting the exercises!**

In order to solve the problems, you will have to run dozens of PWscf calculations. You will find this lab a lot easier if you (a) systematically organise your calculations in separate directories and (b) use a script to automatically run multiple calculations at once. We have provided an example `bash` script that you can use for this purpose. It would also be wise to write scripts to extract results from the output files and plot them. Wherever possible, avoid doing things by hand!

Problem 1

Convergence of *total (absolute) energies* with respect to cutoff energies (10 points)

A Calculate the total energy of bulk CaO as a function of the kinetic-energy cutoff `ecutwfc`. Specify when you reach the level of convergence of 5 meV/atom.

B Do you see a trend in your calculated energies with respect to cutoff? If you see a trend, is this what you expect and why? If not, why? (Appeal to rigorous mathematical reasons where possible.)

C Here, we use the primitive cell, rather than the conventional cell with orthogonal lattice vectors. What are the advantages and disadvantages of both methods?

Start from a small value of `ecutwfc` (say, 10 Ry), and increase it in steps of 10 Ry. All other input parameters must be kept fixed. While doing so, observe how the total energy changes at various values of `ecutwfc`. Ensure you reach the specified convergence threshold.

   If you are using the provided `bash` script, set `LISTK` to only one value ('4'), and modify the content of `LISTECUT` to contain the values of `ecutwfc` you want to test. For example, you could start with 10 Ry and append the higher cutoffs up to 80 Ry with intervals of 10 Ry. Make sure you eventually test as large a cutoff as is required to reach convergence.

   The total energy of the system is reported in the output file in a line containing an "!". This means that it is easy to use tools such as `grep` to automatically extract this value from your input file. Note that PWscf reports the energy in units of Rydbergs and per unit cell.

   Think very carefully about how to define when a calculation is converged.

Problem 2

Convergence of *forces* with respect to cutoff energies (10 points)

In some cases, we are interested in quantities other than energies. In this problem, we will be calculating forces acting on atoms. Displace a Ca (or O) atom by $+0.05$ in the z direction (fractional coordinates). Keeping the other parameters fixed, calculate the forces on a Ca (or O) atom as a function of cutoff. Reach the convergence on forces to within 10 meV/Å. Use the **k** points mesh fixed to $4 \times 4 \times 4$ including the Γ point.

Forces are reported in the output file (in Ry/Bohr) after the total energies, e.g.

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

        atom    1 type  1    force =     0.00000000     0.00000000     0.02078255
        atom    2 type  2    force =    -0.00000000    -0.00000000    -0.02078255


        Total force =      0.029391     Total SCF correction =      0.000024
```

As an aside, it is interesting to think about why we must displace an atom for this convergence test.

Problem 3

Convergence of the *total (absolute) energies* with respect to the **k** points mesh (10 points)

  A Converge the total energy with respect to the **k** points mesh size. For each mesh, also record the number of the **k** points in the irreducible wedge of the first Brillouin zone.

  B Do you see a trend in your calculated energies with respect to size of the **k** points mesh? If you see a trend, is this what you expect and why? If not, why?

Use a converged value for the cutoff energy based on your results for problems 1 and 2.
   If you are using the provided `bash` script, change `LISTECUT` to only have a single entry, and change `LISTK` so that it is a list (e.g. '2 4 6 8'). Try larger grids if necessary. When changing the size of the **k** points mesh, make sure to keep all other input parameters fixed (lattice constant, energy cutoff, etc.).
   The number of irreducible **k** points is reported in the output file as follows:

```
number of k points=     16
```

The number of **k** points in the irreducible wedge gives a measure of how long your calculation will take — calculations scale linearly with the number of **k** points.

Problem 4

Convergence of *forces* with respect to the size of the **k** points mesh (10 points)

Calculate the force acting on a Ca (or O) atom displaced by +0.05 in the z direction (in fractional coordinates) as a function of size the **k** points mesh. Keep all other parameters fixed. Record all relevant input parameters (lattice parameter, energy cutoff, etc.). Specify when the forces are converged to within 10 meV/Å (convert this to Ry/Bohr, since PWscf gives forces in Ry/Bohr).

Problem 5

Convergence of *total energy differences* with respect to energy cutoff (5 points)

Calculate the total energy difference between two crystals at different lattice parameters, as a function of cutoff. Specifically, calculate the energy of CaO with the original lattice parameter, and then calculate the energy using a value 0.05 Å larger. Converge the energy difference to within 5 meV/atom.

Problem 6

Comparing Problems 1, 2, 3, 4, and 5 (10 points)

  A How do the energy cutoff requirements change when looking at total energies, looking at forces, and looking at total energy differences? How do the **k** points mesh requirements change? Can you explain this?

  B The pseudopotentials that you used in these calculations are norm-conserving pseudopotentials. How would your results change if we used ultrasoft pseudopotentials? Which other parameters would you run convergence tests for in this case?

Problem 7

Determination of the *equilibrium lattice parameter* (5 points)

Calculate the equilibrium lattice parameter of CaO by calculating its energy-versus-volume profile. How does the theoretical (computed) equilibrium lattice parameter a_0^{theor} compares with the experimental equilibrium lattice parameter a_0^{exp} =4.81 Å? Is this expected? Make sure to record all the relevant input parameters of the calculations (energy cutoff, **k** points mesh, etc.). Justify your choice of parameters using the results of Problems 1-6.

For this problem, you can use the bash script from earlier exercises with one value in both `LISTK` and `LISTECUT` (the converged values), and a range of values in `LISTA`.

Problem 8

Determination of the *bulk modulus* (20 points)

A Calculate the bulk modulus B of CaO using your data from Problem 7. The bulk modulus is a measure of the stiffness of a material. It is defined as

$$B = -V_0 \frac{\partial P}{\partial V},$$

where P is the pressure on the material, V is its volume, and V_0 is its equilibrium volume.

You will first need to derive a formula for the bulk modulus in terms of volumes and total energies. Write down your derivation in your report.

B Calculate the bulk modulus B of CaO using the third-order Birch-Murnaghan isothermal equation of state and your data from Problem 7.

C Compare your computed bulk modulus, obtained with two methods described above, between themselves and with values reported by experiments. What conclusions can you make? Explain your conclusions.

In the previous exercise you will have calculated the total energy as a function of the cell volume. By using the appropriate derivatives you can also calculate the pressure for each volume and bulk modulus of the material at hand. Such information is very important in solid state physics; it helps us identify different phases of matter and phase transitions between them. That said, if we can recast this relationship into a mathematical function instead of simply a set of individual datapoints, we would gain more predictive power about the properties of our material.

Part A of this problem uses the simplest possible approach, which is to approximate the energy-versus-volume relationship to second order and use the relation $P = -\partial E/\partial V$ to calculate $P(V)$. Remember that the PWscf program calculates energies per unit cell.

A more complicated approach is to use an *equation of state* — that is, a function that describes the relationship of state variables. There are several competing proposals for the precise shape of this function. Part B of this problem uses the *third-order Birch-Murnaghan isothermal equation of state*:

$$P(V) = \frac{3B_0}{2}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]\left\{1 + \frac{3}{4}(B_0' - 4)\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]\right\}, \tag{1}$$

where P is the pressure, V_0 is the equilibrium volume, V is the deformed volume, B_0 is the bulk modulus, and B_0' is the derivative of the bulk modulus with respect to pressure. Integration of this pressure expression with volume gives us the energy versus volume relationship as below:

$$E(V) = E_0 + \frac{9V_0B_0}{16}\left\{\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^3 B_0' + \left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^2\left[6 - 4\left(\frac{V_0}{V}\right)^{\frac{2}{3}}\right]\right\}. \tag{2}$$

To perform this fitting you can either implement it yourself (e.g. using `python`) or use the interactive `ev.x` program provided with QUANTUM ESPRESSO. This program works interactively: it expects that you specify units (`Ang` or `ANG` or `ang` indicates Ångstroms, while any other input will default to atomic units), the type of Bravais lattice that you used, the type of the equation of state that you want to use for a fit (in our case, `birch1`), and an input file. In the input file for `ev.x` you have to provide two columns for the case of an FCC lattice: the first one contains the lattice parameter and the second one the total energy obtained.

Because the Birch-Murnaghan EOS includes higher-order terms, you might need to take lattice parameter steps that are sufficiently large (e.g. steps of 0.1 Bohr).

Problem 9

The *elastic constants* of CaO (20 points)

Calculate the elastic constants C_{11}, C_{12}, and C_{44} of CaO. Use the conventional unit cell containing 8 atoms. You will need to compute the energetics of deformation, and fit the resulting energy curves.

 A Compute $C_{11} - C_{12}$, specifying the orthorhombic symmetry (`ibrav=8`) of the distorted lattice, and then use the relation $B = \frac{1}{3}(C_{11} + 2C_{12})$ to determine the elastic constants C_{11} and C_{12}.

 B Compute C_{44}, using the monoclinic (`ibrav=12`) Bravais lattice.

 C Compare the elastic constants you obtained with experimental data (be critical, find multiple sources and cite them appropriately)

Use the converged parameters that you obtained in problems 1-7. In principle, you should need fewer k points with the conventional supercell to get to convergence, but you are not required to test again.

How to calculate elastic constants is explained in the slides that cover this particular exercise. You can find these slides on Moodle.

Note that the cell symmetry changes upon strain. This means that the variable in your input that defines the symmetry (`ibrav`) in the cell should change accordingly. A list of all possible indications of `ibrav` can be found here. In this exercise you will have to start from the *conventional* unit cell with 8 atoms. You will need to work out the appropriate atomic positions. As for the cell, take the example of an orthorhombic cell (`ibrav=8`). Assume that the unit cell we aim to construct has the following lattice vectors (in cartesian coordinates, in Bohr)

```
v1=(a,0,0), v2=(0,b,0), v3=(0,0,c)
```

meaning that it is a Bohrs long in the x direction, b Bohrs along y, and c Bohrs along z. We can specify this cell in the following way:

```
ibrav = 8
celldm(1) = a
celldm(2) = b/a
celldm(3) = c/a
```

Enter the numerical result of the division, not the expression itself.

Also note that upon the application of strain, it may happen that not all atomic positions in the cell are fixed by symmetry, as there is more than one basis element (i.e. a Ca and a O atom). Therefore, when we apply the strain one of these atoms could move to another

relative position than the initial (1/2, 0, 0) and lower the total energy of the cell. This means that when we calculate the elastic constant of this system we should allow the cell to relax the atoms to their equilibrium positions instead of fixing them to relative positions. This is done very easily with QUANTUM ESPRESSO. The necessary modification is changing the `calculation` variable in `control` namelist, from `scf` to `relax`:

```
calculation="relax"
```

Since we will move the ions, QUANTUM ESPRESSO expects a new namelist called `ions`:

```
&ions
/
```

You can place this new namelist after the `electrons` namelist (after the slash). Because we will only use default parameters you do not need to specify anything in this namelist.