Hands-on Tutorial on Electronic Structure Computations: Ab-initio molecular dynamics with the Car-Parrinello code (CP)

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The files for this tutorial can be found in the `archive`:
`/home/users/tutorial/user/public/Lab3_CP/lab3_cp.tar.gz`
Copy the content of this folder to your personal folder on the cluster; when you are inside your personal folder, type (WARNING, DO NOT CONFUSE THE BASH COMMAND COPY (cp), WITH THE QUANTUM ESPRESSO CODE EXECUTABLE cp.x; ONE IS A COMMAND OF THE UNIX SHELL OF THE CLUSTER, THE OTHER IS THE CAR PARRINELLO EXECUTABLE THAT WE ARE GOING TO USE):

```
cp /home/users/tutorial/user/public/Lab3_CP/lab3_cp.tar.gz ./
```

In your personal folder on the cluster, untar the archive with the command

```
tar -xzvf lab3_cp.tar.gz
```

This will create a folder `Lab3_CP in your personal folder.`

Do not use this way of calling executables! (Will cause trouble to the cluster)

The codes (`Quantum Espresso`) should be already in your path, to check this, issue the command:

```
which cp.x
which cppp.x
```

which, if everything is fine, should result in no error, but give you the path of the executable.

You will afterwards call these executables simply by typing:

```
cp.x
cppp.x
```

You can also run `cp` in parallel, if you want, by using (if you want to use 6 cpus):

```
mpiexec -np 6 cp.x
```

At the end of this file, you'll find also the link to the online input description of cp, and some suggestions for parameters.

Use this one instead!!!

Whenever calling cp.x < input.in > output.out, use the script (which is inside your directory):

```
./run_cp.sh input.in output.out
```

Whenever you might need to use gnuplot, there is a script also for this:

```
./run_gnuplot.sh
```

You can use the gnuplot instruction: `set terminal dumb` to plot files directly on the cluster shell, to have at least an idea of the function you are plotting.

The general plotting command is:

```
plot 'data.dat' u 1:2 w l, 'data2.dat' u 1:7 w l, ....
```

where the numbers 1:2 and 1:7 specify the columns to plot. You can plot as many files you want altogether.

Exercise 1 - H2 molecule

In this exercise we show different examples of electron and ion dynamics with CP; we investigate the effect of damping and of electron mass on the dynamics, we show that we can estimate the vibrational frequency of H2.

- Go to the `ex1` folder. Inspect the first files, e.g. the input file `H.erelax.start.in`. Check if you understand all parameters (you can use the web page
  http://www.quantum-espresso.org/wp-content/uploads/Doc/INPUT_CP.html
  for keywords that you do not know). The system consists in two Hydrogen atoms at a distance quite close, but not identical, to the equilibrium bond length of H2.

- There are two subdirectories in this folder (`ex1`), one is `pseudo`, and contains the pseudopotential file you will use for the calculation, as specified in all input files, the other one is `tmp`, and it is now empty, but you will use it as output directory (as also specified in the input files). Whenever giving paths and file names from now on, I will give them relative to the exercise folder `ex1`.

- The pseudopotential used for our calculations will be a LDA pseudopotential `./pseudo/H.pz-vbc.UPF`.

Step1: relaxation of the electronic wavefunction

- The first two calculations you need to perform are a relaxation of electronic degrees of freedom, at fixed ions; their input consists in the two files (a) `H.erelax.start.in` and (b) `H.erelax.restart.in`. Before running these two calculations, you need to fill missing input parameters in the two files. The missing input parameters are indicated by a triple X (`xxx`).

- Run the two calculations using the `cp.x` code of the Quantum Espresso suite:

      cp.x < H.erelax.start.in > H.erelax.start.out
      cp.x < H.erelax.restart.in > H.erelax.restart.out

You may want to use the parallelization to run the simulation faster, using (to use 6 processors)

      mpiexec -np 6 cp.x < H.erelax.start.in > H.erelax.start.out [./run_cp.sh H.erelax.start.in
  H.erelax.start.out]
      mpiexec -np 6 cp.x < H.erelax.restart.in > H.erelax.restart.out [./run_cp.sh H.erelax.restart.in
  H.erelax.restart.out]

- When the calculation finishes (you can see it with the command `tail ###.out`, where `###.out` is the output file), inspect the output files to check if there were any errors/warnings.

  - The most common error when there is more than one electron with the same spin, is "`ortho went bananas`", which means that one should use a smaller time step `dt` in input file b. In our case there is just one electron per spin, so that this error should be unlikely (it can still happen for very large time step, since the code still needs to normalize the electronic wavefunction). Another common error when `dt` is large is

        Error in routine ortho (101):
        max number of iterations exceeded
        You can correct this error by either decreasing `dt` (suggested in this case), or increasing `ortho_max`.

  - (*)If this or anything else went wrong, before re-running the two calculations above, one should DELETE THE FOLDER ./`tmp` AND CREATE A NEW ONE, TYPING

        rm -rf ./tmp
        mkdir tmp

  There is a script: `reset_tmp.sh,` which does this job when you do not want to type the two commands.

- If the calculation finished, enter the directory `tmp` and check that you have two directories and several files beginning with "cp". When you do not specify the `prefix` parameter, "cp" is the default `prefix`. Check what is the energy, by looking at the output file of the restart calculation (`H.erelax.restart.out`) or at the 5th column of file `./tmp/cp.evp`. You can try to make a plot where x is the eleventh column of `./tmp/cp.evp` (time in ps) and y is the fifth column of the same file (`etot`). You should see a monotonically decreasing curve, tending to a final energy which should be [-1.125708 Hartree] or smaller.

  - If the energy is larger (less negative), you might have used a too big value for `electron_damping`. You can decrease its value in input file b, and re-run the calculation, after emptying the folder `tmp` as shown above (see the * mark) in the case of errors.
  - If the energy is ok, but the curve plotted has some oscillations, your `electron_damping` might be too small. This does not affect the result, but the total time of the simulation, which will be longer than necessary. If you want you can re-run the calculation after changing input file b and after emptying the `tmp` folder as in *.

- Now that the energy is fine, make a copy of the directory `tmp`, let us call it `tmp_erelax`

  ```
  cp -r tmp tmp_erelax
  ```

- Before going to the next step, you can play with the values of `dt` and `electron_damping` in input file b; in general, increasing `dt` should speed up your calculation, but it may make the code crash (unlikely in this case). Changing the damping should not make the code crash, but it may result in incorrect energies, or unnecessarily long simulations. Every time you run a calculation with different parameters, remember to empty the `tmp` directory as in *.

Step2: relaxation of ionic coordinates

- (**) You are now ready for the second step, in which we would like to perform a relaxation of ionic coordinates using damped dynamics. Remove the `tmp` directory and copy `tmp_erelax` into `tmp`. Then clean the files `tmp/cp.evp` and `tmp/cp.pos`. You can do this as follows:

  ```
  rm -rf tmp
  cp -r tmp_erelax tmp
  rm -f tmp/cp.evp
  rm -f tmp/cp.pos
  ```

The above commands are inside the script `reset_from_erelax.sh,` so that you can call this script if you need to do the same thing later:

```
bash reset_from_erelax.sh
```

- Now you can open the file (c) `H.ionrelax.in`. Fill in the missing parameters (xxx) so as to setup the input file for an electron+ion damped dynamics. Then run the calculation

  ```
  cp.x < H.ionrelax.in > H.ionrelax.out [./run_cp.sh H.ionrelax.in H.ionrelax.out]
  ```

- Check that no errors/warnings occur in the output file, check the value of the final energy, both in the output file and in `./tmp/cp.evp`, by looking at the convergence of `etot` (the fifth column). The final energy should be [-1.125873] or smaller. If you have a larger (less negative) energy, you might need to adjust the damping parameters, or use a more strict convergence threshold. If anything went wrong, re-run the above simulation after re-initializing `tmp` as shown in **.

- (***)Once your energy is ok, check how large is, in electronvolts, the energy difference between the energy in the unrelaxed ionic configuration (obtained at Step1) and the one you found after ionic relaxation _____.

- You can also look at the position change of one of the two Hydrogens by using the auxiliary script `readpos.sh`

  ```
  bash readpos.sh
  ```

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which will read the file `./tmp/cp.pos`, extract the "time vs position" variables and store them in the file `plotpos.dat`. The ionic coordinate should evolve towards the equilibrium limit. Which final value of the coordinate do you find (Note that you can find the final coordinates also in the output file)? _____ .

Which is the bond length you find for H_2 with this LDA functional?_____

- Before proceeding, make a copy of `tmp`

      cp -r tmp tmp_ionrelax

- If you plot the file `plotpos.dat` file you will see either damped oscillations, or just a monotonic change of the ionic coordinate towards the equilibrium limit, this depends on the value you provided for `ion_damping`.   If you have time, you can re-run your calculation with a different value for ionic damping, and check the result. Every time you re-run, remember to re-initialize `tmp` as in **. Plot the evolution of ionic coordinates using the `readpos.sh` script.

- We can now proceed to estimate the frequency of H_2 molecular vibrations.

Step3: molecular dynamics simulation of H2 vibrations

- Re-initialize the `tmp` directory as in **

- Fill in the missing parameters (xxx) in file (d) `H.md.in,` and run the molecular dynamics calculation. The electronic mass has ben set to 500.

      cp.x < H.md.in > H.md.out [./run_cp.sh H.md.in H.md.out]

- Use the script `readpos.sh`***, to read and plot the positions of one of the hydrogens. You should see an oscillating behavior around the equilibrium value of the coordinate. Estimate the period of oscillation and compute the frequency; the total simulation time should be enough to see at least one full oscillation. Which is your estimated frequency?_____

- Backup the tmp directory (writing the value of electronic mass, in this case 500, in the name) as

      cp -r tmp tmp_md_m500

(****)Copy your input file and the positions file into this directory

      cp plotpos.dat tmp_md_m500
      cp H.md.in tmp_md_m500
      cp H.md.out tmp_md_m500

- Change the value for `emass` in `H.md.in` and re-run the calculation, after re-initializing `tmp` as shown in **. Estimate the period of oscillation and the frequency for a few values of the electronic mass between 50 and 1500 (a suggestion is 50,100, 1000, 1500). Backup the tmp directory at the end of every calculation, as done above****, so that you keep all your results for each value of the electronic mass. Explain the results _____.

- You can compare your estimate(s) for the oscillation frequency of the hydrogen molecule with the experimental value, whose exact value you might look up on the web (see NIST web-site), and which should be approximately 132 THz. Your largest estimate will probably be a bit smaller than this value.

Exercise 2 - Molecular dynamics simulation of Silicon

- Go to the `ex2` folder. We now deal with a Silicon bulk system, consisting in a cell of 16 atoms repeated periodically, and randomly displaced slightly away from their equilibrium positions. The content of the directory is similar to the one of the previous exercise, you have several input files, a pseudopotential directory `pseudo,` containing the file `Si.pz-vpc.UPF,` and a `tmp` directory.

Step1: relaxation of the electronic wavefunction

- As before, we have two input files for the relaxation of electronic degrees of freedom: (a) `Si.erelax.start.in` and (b) `Si.erelax.restart.in`. Enter the input files and fill in the missing parameters (xxx). You will have to fill in the number of bands. In order to understand the number of bands, you can check the number of valence electrons per Silicon atom by looking at the pseudopotential file. Remember that each band can accomodate two electrons. Then run the calculations:

  mpiexec -np 6 cp.x < Si.erelax.start.in > Si.erelax.start.out [./run_cp.sh Si.erelax.start.in Si.erelax.start.out]
  mpiexec -np 6 cp.x < Si.erelax.restart.in > Si.erelax.restart.out [./run_cp.sh Si.erelax.restart.in Si.erelax.restart.out]

- As in the previous exercise, check for errors. In this case the "`ortho went bananas`" error is very likely to appear for large `dt`, as well as "`maximum number of iterations exceeded`". You can correct the values of `dt` and `ortho_max` in file (b). In the event of errors, re-run the two calculations, after emptying the `tmp` directory as done in *. Check that your relaxed energy is not larger than [-62.6345 Hartree]. If not, modify your damping parameter, and convergence threshold. If you filled in the wrong number of bands, you might have also errors or wrong energy. Correct the number of bands. Then, then re-run after emptying `tmp`.

- When finished, empty the `tmp/cp.evp` and `tmp/cp.pos` files, and backup the `tmp` directory by typing

  ```
  cp -r tmp tmp_erelax
  rm -f tmp/cp.evp
  rm -f tmp/cp.pos
  ```

Step2: molecular dynamics simulation without thermostat

- Now edit file (c) `Si.md.in`. Fill in the missing parameters (xxx). Remember we would like to perform a molecular dynamics simulation, as in the last step of exercise 1.

- Run the calculation as

  cp.x < Si.md.in > Si.md.out [./run_cp.sh Si.md.in Si.md.out]

- If something wrong happens, you can re-run after restoring the directory tmp to the content of tmp_erelax (see ** in ex1, you have the same reset script in your directory).

- When the calculation is finished, you can make plots versus time of the different quantities inside `tmp/cp.evp`, these quantities are `etot` (5th column), `econs` (7th column) and `econt` (8th column). The first is the potential energy of the ions, the second is the sum of potential plus kinetic energy of the ions, the third is the constant of motion, which includes also the kinetic energy of the electrons (`ekinc`, which is stored in the 2nd column). Time is the 11th column of the file `tmp/cp.evp`.

  - Plot `econt`, `econs`, `etot` together and separately. Check that your constant of motion `econt` is truly approximately constant: its changes should be negligible with respect to those of `econs` or `etot`. Also check that `econs` is subject to variations which are smaller than those of `etot`.
  - Plot `ekinc`, check that it is small with respect to the above energies `econt`, `econs`, `etot`, and that it fluctuates around a more or less fixed average.
  - Plot the ionic temperature `tempp` (4th column) versus time: the temperature is not controlled by a thermostat, and its behavior with respect to time cannot be predicted.

- When finished, backup the tmp directory as

  ```
  cp -r tmp tmp_md
  cp Si.md.in tmp_md
  cp Si.md.out tmp_md
  ```

  and reinitialize `tmp` to the content of `tmp_erelax`, as in (**).

Step3: molecular dynamics simulation with thermostat

- The file for the simulation with thermostat is (d) `Si.md_th.in`. Fill in the missing parameters (xxx). Again, we would like to perform a molecular dynamics simulation, but now we need to decide the value of the frequency (in THz) of the thermostat (`fnosep`). If we choose the wrong value, the thermostat will not be able to exchange energy with our system in an efficient way.

- As a rule, one should choose the frequency of the thermostat to be in the middle of the phonon spectrum of the material.

  - You can therefore look on the internet for a phonon spectrum of silicon, and choose a frequency accordingly.
  - Another trick is to plot `etot` vs time for Step2 (the 5th vs 11th column of `./tmp_md/cp.evp`), and look at the potential energy fluctuations, which are a symptom of ionic vibrations. One should recognize, approximately, a characteristic frequency of oscillation (these are not harmonic oscillations, so there is no univocal value for it), and choose it as a frequency for the thermostat.

- Once this is chosen, run the calculation

    `mpiexec -np 6 cp.x < Si.md_th.in > Si.md_th.out [./run_cp.sh Si.md_th.in Si.md_th.out]`

- Check that everything is fine, that there are no errors, otherwise re-run after re-initializing (as for **).

- Plot `./tmp/cp.evp` using the temperature (4th) vs time (11th). Check if the system is reasonably thermalizing at 300 Kelvin. If not, try a smaller or larger frequency for the thermostat. For every value of the thermostat frequency, you can keep track of your results by copying `tmp` into `tmp_fxxx`, where xxx is the frequency of the thermostat.

The thermalization will never be perfect, since the number of atoms in our system is not very large.

Help and suggestions for parameters:

You can check the online help for default values of parameters. You can start using them when you do not know how to fill in the gaps (xxx):

http://www.quantum-espresso.org/wp-content/uploads/Doc/INPUT_CP.html

In general, reasonable time steps might be between `dt=1` and `dt=20`. For dampings, reasonable values might range from 0.005 to 0.5. Try choosing somethig in-between as a start. Electronic masses should not exceed the ionic mass, if they are too small you will have problems in integrating the equations of motion. In general for damped dynamics, the value should not influence the final result, but reasonable values might range from 30 to 800. The convergence threshold for energies in damped dynamics calculation might be set to `1.e-6`, for a start.