



THERMO_PW Tutorial (v.1.5.0)

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1 Introduction

This guide gives a brief overview of the `thermo_pw` package. It gives you the minimal information needed to accomplish a given task. It assumes that you have already downloaded and compiled `QUANTUM ESPRESSO` and `thermo_pw` and you want to calculate some material property but you do not know where to start. The ultimate reference for the use of `thermo_pw` is its user's guide, however the capabilities of the code are rapidly expanding and the user's guide is becoming long, so if you do not want to read it entirely you can find here where the relevant information are. There might be some limitations on the type of functionals that you can use or the electronic structure scheme available to compute a given quantity. Please refer to the `QUANTUM ESPRESSO` documentation for this.

2 People

This tutorial has been written by Andrea Dal Corso (SISSA - Trieste).

3 Overview

In order to make a calculation with `thermo_pw` you need to be able to produce an input file for the `pw.x` code of QUANTUM ESPRESSO. This input file requires mainly five information:

- The Bravais lattice.
- The position of the atoms inside the unit cell.
- The type of atoms and the pseudopotentials files that you want to use.
- The cut-off energies.
- The \mathbf{k} -point mesh used to make integration over the Brillouin zone. The smearing parameter for metals.

The Bravais lattice is specified by an integer number `ibrav` and by the crystal parameters `celldm` (up to six numbers). You can find information on the `ibrav` code and on the required crystal parameters in the file `PW/Doc/INPUT_PW` of the QUANTUM ESPRESSO distribution. In QUANTUM ESPRESSO you can use `ibrav=0` and give the primitive lattice vectors of the Bravais lattice. Presently `thermo_pw` needs to know the Bravais lattice number so this form of input is not recommended. If you use it, `thermo_pw` writes on output the `ibrav`, the `celldm` and the atomic coordinates needed to simulate the same cell and stops. You can therefore just cut and paste `ibrav`, `celldm` and the atomic coordinates in the input of `pw.x`. Alternatively you can set the flag `find_ibrav=.TRUE.` in the `thermo_pw` input and `thermo_pw` will make the conversion for you and run the job. After setting the correct `ibrav` and `celldm`, `thermo_pw` might still tell you that the Bravais lattice is not compatible with the point group. This can happen, for instance, if you have isolated molecules, amorphous solids, defects, or supercells. In these cases you can still continue but symmetry will not be used to reduce the number of components of the physical quantities tensors. In order to use the residual symmetry, you have to use one of the suggested `ibrav`, adjusting the `celldm` to the parameters of your cell. For instance if you have a cubic cell, but the symmetry requires a tetragonal lattice, you have to use a tetragonal lattice with `celldm(3)=1.0`. In rare cases, with lattices such as the face-centered orthorhombic some symmetry operations might be incompatible with the FFT grid found by `pw.x`. The choice made in QUANTUM ESPRESSO is to discard these symmetries making the lattice incompatible with the point group. In these cases the code needs `nr1=nr2=nr3`. Set these three parameters in the `pw.x` input equal to the largest one.

The positions of the atoms inside the unit cell are defined by an integer number `nat` (the number of atoms) and by `nat` three-dimensional vectors as explained in the file `PW/Doc/INPUT_PW`. You can use several units, give the coordinates in the Cartesian or in the crystal basis or you can give the space group number and the coordinates of the nonequivalent atoms. These options

are supported by `thermo_pw`. See the `pw.x` manual for details.

The number of different types of atoms is given by an integer number `ntyp` and for each atomic type you need to specify a pseudopotential file. Pseudopotential files depend on the exchange and correlation functional and can be found in many different places. There is a pseudopotential page in the QUANTUM ESPRESSO website, or you can consider generating your pseudopotentials with the `pslibrary` inputs. You can consult the web page

<https://dalcorso.github.io/pslibrary/>

for more information.

The kinetic energies cut-offs depend on the pseudopotentials and on the accuracy of your calculation. You can find some hints about the required cut-offs inside the pseudopotentials files, but you need to check the convergence of your results with the cut-off energies. Many tests of the kinetic energy cut-offs can be found also at <https://www.materialscloud.org/discover/sssp/>.

The **k**-point mesh is given by three integer numbers and possible shifts (0 or 1) in the three directions. The convergence of the results with this mesh should be tested. For metals you have also to specify a smearing method (for instance `occupations='smearing'`, `smearing='mp'`) and a value of the smearing parameter (in Ry) (see the variable `degauss` in the file `PW/Doc/INPUT_PW`). Note that the convergence with respect to the **k**-points depends on the value of `degauss` and must be tested for each `degauss`.

Once you have an input for `pw.x`, in order to run `thermo_pw` you have to write a file called `thermo_control` that contains a namelist called `INPUT_THERMO`. This namelist contains a keyword `what` that controls the calculation performed by `thermo_pw`. Ideally you need to set only `what` and call `thermo_pw.x` instead of `pw.x`, giving as input the input prepared for `pw.x`.

4 How do I make a self-consistent calculation?

Use `what='scf'`. See `example01`. The calculation is equivalent to a call to `pw.x` and is controlled by its input. In particular in the input of `pw.x` you can choose a single self-consistent calculation using `calculation='scf'`, an atomic relaxation using `calculation='relax'`, or a cell relaxation using `calculation='vc-relax'`. The use of `calculation='nscf'` and `calculation='bands'` is not supported by `thermo_pw` and could give unpredictable results. There is no advantage to use `thermo_pw` to do a molecular dynamic calculation.

5 How do I plot the band structure?

Use `what='scf_bands'`. See `example02`. With this option `thermo_pw` calls twice `pw.x` making first a self-consistent calculation with the parameters given in the `pw.x` input and then a band calculation along a path chosen by `thermo_pw`, or along a path given by the user after the `INPUT_THERMO` namelist. The path can be given as in the `pw.x` input, but see the user's guide for additional details. There are a few parameters that you can give in the `INPUT_THERMO` namelist to control the band plot. The most useful are `emin_input` and `emax_input` that allow you to plot the bands in a given energy range. At the end of the run, the figure of the bands is in a file called `output_band.ps`, if you do not change the name of the postscript file in the `thermo_pw` input. Check also the option `what='scf_2d_bands'` if you need to plot the surface band structure.

6 How do I plot of the electronic density of states?

Use `what='scf_dos'`. See `example18`. With this option `thermo_pw` calls twice `pw.x` making first a self-consistent calculation followed by a non self-consistent calculation on a uniform **k**-point mesh. This mesh can be specified in the `thermo_pw` input (if none is given `thermo_pw` uses the default values). At the end of the run, the figure of the density of states is in a file called `output_eldos.ps` if you do not specify the name of the postscript file in the `thermo_pw` input.

7 How can I see the crystal structure?

`thermo_pw` is not a crystal structure viewer, but you can use the code `XCrySDen` that reads the `pw.x` input to see the crystal structure. If you use `what='plot_bz'`, `thermo_pw` produces a `.xsf` file that contains the structure given in input and can be read directly by `XCrySDen`. This could be useful when you give the space group number and the nonequivalents atomic positions since this input is presently not readable by `XCrySDen`. The generated `.xsf` file contains all the symmetry equivalent atomic positions. For the same purpose you could also use the output of `pw.x`.

8 How can I see the Brillouin zone?

Use `what='plot_bz'`. See `example12`. With this option `thermo_pw` does not call `pw.x`, it just produces a script for the `asymptote` code with the instructions to plot the Brillouin zone and the standard path (or the path that you have given in the `thermo_pw` input).

9 How can I plot the X-ray powder diffraction spectrum?

Use `what='plot_bz'` to see the spectrum corresponding to the geometry given in the `pw.x` input. You can also see the spectrum corresponding to a relaxed structure using for instance `what='scf'`, asking for an atomic (cell) relaxation in the `pw.x` input and using `lxrpd=.TRUE.` variable in the `thermo_pw` input. The X-ray powder diffraction spectrum is shown in a file called `output_xrpd.ps`, if the name of the postscript file is not given in the `thermo_pw` input. The scattering angles and intensities are also written in a file called `output_xrpd.dat`, if the filename is not given in the `thermo_pw` input.

10 How can I find the space group of my crystal?

Use `what='plot_bz'` and look at the output. The space group is identified. In the case you have a structure with `ibrav=0` and the primitive lattice vectors use the option `find_ibrav=.TRUE.` in the `thermo_pw` input (see the `thermo_pw` user's guide in the subsection *Coordinates and structure*). This option has presently some limitations. It does not work for noncollinear magnetic system, or for supercells, or when the Bravais lattice and the point group are incompatible.

11 How do I plot the phonon dispersions?

Use `what='scf_disp'`. See `example04`. In this case you have to prepare an input for the `ph.x` code that must be called `ph_control`. The required information in this input is the \mathbf{q} -point mesh on which the dynamical matrices are computed and the name of the files where the dynamical matrices are written. See the `ph.x` guide if you need information on this point. At the end of the run, the phonon dispersions are found in a file called `output_disp.g1.ps`, if the name of the postscript file is not given in the `thermo_pw` input. The vibrational density of states is found in a file called `output_dos.g1.ps`, if the name of the postscript file is not given in the `thermo_pw` input.

12 How do I calculate the vibrational energy, free energy, entropy, and heat capacity?

Use `what='scf_disp'`. See `example04`. These quantities are calculated after the phonon dispersion calculation for the default temperature range (1 K - 800 K) or for the range given in the `thermo_pw` input. The figure of these quantities is in the file `output_therm.g1.ps`. Note that they are calculated at the geometry given in the input of `pw.x`.

13 How do I calculate the atomic B-factor of a solid?

Use `what='scf_disp'` as in `example04` and add the flag `with_eigen=.TRUE..` These quantities are calculated after the phonon dispersion calculation for the default temperature range (1 K - 800 K) or for the range given in the `thermo_pw` input. The figure of these quantities is in the file `output_therm.g1_dw.ps`. Note that they are calculated at the geometry given in the input of `pw.x`.

14 How do I calculate the elastic constants?

Use `what='scf_elastic_constants'`. See `example13`. The elastic constants appear in the output of `thermo_pw` and also in a file called `output_el_cons.dat`, if the name of the file is not given in input. This file can be read by `thermo_pw` for the options that require the knowledge of the elastic constants.

15 How do I calculate the Debye temperature?

Use `what='scf_elastic_constants'`. See `example13`. The Debye temperature appears in the output of `thermo_pw`. A file called `output_therm.ps_debye` contains plots of the vibrational energy, free energy, entropy, and heat capacity computed within the Debye model.

16 How do I calculate the equilibrium structure?

Use `what='mur_lc'`. See `example05`. Refer to the user's guide for anisotropic solids. The crystal parameters are written in the `thermo_pw` output file. Note that the structure is searched interpolating with a polynomial or with the Murnaghan equation the energy calculated for several geometries close to the geometry given in the input of `pw.x` so the closer this structure is to the actual equilibrium structure the better the fit is and the closer the value found by `thermo_pw` to the real minimum. If the equilibrium structure is very different from the one given in the `pw.x` input you might want to repeat the calculation starting from the new equilibrium structure. You can also check with the file `output_mur.ps` (when `lmur=.true.`) or `output_energy.ps` (when `lmur=.false.`) if the minimum found is within the range of calculated structures. If this is not the case the minimum has probably a non negligible error. Note also that almost all options can be specified using `what='mur_lc_...'` instead of `what='scf_...'`. In this case they are calculated at the equilibrium geometry instead of the geometry given in the `pw.x` input. This holds also if a finite pressure is specified in the `thermo_pw` input and the equilibrium structure corresponds to the given pressure (See below).

17 How do I calculate the equilibrium structure at a given pressure?

Use `what='mur_lc'` and specify `pressure=value in kbar` in the `thermo_pw` input. Note that in the input of `pw.x` you should give a geometry which is as close as possible to the equilibrium value found by the code at the given pressure (see above).

18 How do I specify the temperature range

See the `thermo_pw` user's guide in the subsection *Temperature and Pressure*.

19 How do I calculate the crystal parameters as a function of temperature?

Use `what='mur_lc_t'`. See `example09`. Note that for this option you need to give also the `ph.x` input. For anisotropic solids you need to specify `lmurn=.FALSE.`, otherwise you calculate only the volume as a function of temperature varying `celldm(1)` but keeping all the other crystal parameters constant. The crystal parameters are plotted as a function of temperature in the standard temperature range if not given in input, in the file `output_anharm.ps` for cubic solids and `output_anharm.ps_celldm` for anisotropic solids if the name of the postscript file is not given in input.

20 How do I calculate the thermal expansion?

Use `what='mur_lc_t'`. See `example09`. The thermal expansions are shown as a function of temperature in the file `output_anharm.ps`.

21 How do I calculate the Helmholtz (or Gibbs) free energy as a function of temperature keeping into account the thermal expansion?

Use `what='mur_lc_t'`. The Helmholtz (or Gibbs at finite pressure) free energy is shown as a function of temperature in the file `output_anharm.ps`. Note that the absolute value of this energy depends on the pseudopotentials as the total energy. You can however compare the free energies for different crystal structures and predict if a phase transition occurs and at which temperature (also as a function of pressure).

22 How do I calculate the bulk modulus as a function of temperature?

Use `what='mur_lc_t'` and the option `lmurn=.TRUE..` This approach is rigorously valid only for cubic solids, for anisotropic solid it is only an approximation in which only `celldm(1)` is changed while the other crystal parameters are kept constant.

23 How do I calculate the constant pressure heat capacity?

Use `what='mur_lc_t'` and the option `lmurn=.TRUE..` This approach is rigorously valid only for cubic solids, for anisotropic solid it is only an approximation in which only `celldm(1)` is changed while the other crystal parameters are kept constant.

24 How do I calculate the elastic constants as a function of temperature?

There are two ways. Both of them are a two step calculation. The fastest method uses the “quasi-static” approximation but it is less accurate. First use `what='elastic_constants_t'`. This option computes the elastic constants at $T = 0$ for all the geometries used by `what='mur_lc_t'` and saves them in the directory `elastic_constants`. In the second step use the same input for `pw.x` and run again `thermo_pw` with `what='mur_lc_t'` after copying in your working directory the directory `elastic_constants` obtained in the previous step. Elastic constants are read only when `lmurn=.FALSE..` The “quasi-static” approximation means that the code interpolates the elastic constants at $T = 0$ K found in the first step at the geometry that minimizes the Helmholtz (or Gibbs at finite pressure) free energy at temperature T .

The second method uses the “quasi-harmonic” approximation and requires many phonon calculations at many geometries. First use `what='elastic_constants_t'` and set `use_free_energy= .TRUE..` This option computes the temperature dependent elastic constants taking as unperturbed geometries those used by `what='mur_lc_t'` and saves them in the directory `anhar_files`. In the second step use the same input for `pw.x` and run again `thermo_pw` with `what='mur_lc_t'` after copying in your working directory the directory `anhar_files` obtained in the previous step. Elastic constants are read only when `lmurn=.FALSE..` The “quasi-harmonic” approximation means that the code interpolates the temperature dependent elastic constants found in the first step as second derivatives of the Helmholtz free energy (corrected to give the stress-strain elastic constants), at the geometry that minimizes the Helmholtz free energy.

The plot of the elastic constants will be found in `output_anhar.el_cons.ps`. Note that these approaches used with the option `lmurn=.FALSE.` can calculate the thermodynamic properties of non-cubic solids, but the second method is still experimental and should be limited to cubic solids.

25 How do I calculate the electronic heat capacity of a metal?

Use `what='scf_dos'`. See `example18`. In the metallic case in addition to a plot of the density of states this option produces also a plot of the electronic energy, free energy, entropy, heat capacity, and chemical potential in the standard temperature range if this range is not given in the `thermo_pw` input. These quantities are found in the file `output_eltherm.ps` if the name of the postscript file is not given in the `thermo_pw` input. Please keep the default value of `deltae` or the electronic thermodynamic properties could be wrong at low temperatures.

26 How do I calculate the thermal expansion of a metal accounting for the free energy due to the electronic excitations?

This is a two step calculations. First use `what='mur_lc'` and the flag `lel_free_energy=.TRUE.` to write on files the electronic thermodynamic properties for each geometry used by `what='mur_lc'`. Then copy the files with the electronic thermodynamic properties in the `therm_files` directory and run `thermo_pw` with `what='mur_lc_t'` and the flag `lel_free_energy=.TRUE..` The electronic free energy is read from files and added to the vibrational free energy before computing the equilibrium crystal structure. See `example24` for this case.

27 How do I calculate the elastic constants of a metal accounting for the free energy due to the electronic excitations?

This is a four step procedure. First use `what='mur_lc'` and the flag `lel_free_energy=.TRUE.` as in the previous point in order to get the electronic thermodynamic properties for all the unperturbed geometries. Then use `what='elastic_constant_t'` with the flag `lel_free_energy=.TRUE.` and the flag `use_free_energy=.FALSE.` to write on file the electronic thermodynamic properties for all strained geometries. Then use `what='elastic_constant_t'` with `lel_free_energy=.TRUE.` and `use_free_energy=.TRUE.` after copying the electronic thermodynamic properties obtained at previous point in the `therm_files` directory, so the free energy derived in this step to obtain the elastic constants has also the electronic contribution. Finally use `what='mur_lc_t'` with `lel_free_energy=.TRUE.` and `use_free_energy=.TRUE.` after copying the elastic constants obtained at previous step in the `anhar_files` directory and the electronic thermodynamic properties obtained in the first step in the `therm_files` directory.

28 How do I calculate the frequency dependent dielectric constant of a material?

Use `what='scf_ph'`. See `example16` and `example20`. Please note that this calculation is made by the extended version of the phonon code available in `thermo_pw`, so you have to provide specific flags to the phonon input. See the user's guide for details. The dielectric constant is in the file `output_epsilon.ps`. Note that for metals you need to specify a finite wave-vector \mathbf{q} and you cannot plot the dielectric constant when \mathbf{q} is the Γ point. See `example17` and `example21` for this case.

29 How do I calculate the frequency dependent reflectivity of a material?

The calculation of this quantity is implemented only for isotropic (cubic) solids. It is plotted together with the frequency dependent dielectric constant in insulating cubic solids when \mathbf{q} is the Γ point. In this case the code plots also the absorption coefficient. Both quantities can be plotted as a function of the frequency or of the wavelength.

30 Which is the meaning of the colors in the electronic bands and phonon dispersions plots?

Different colors correspond to different irreducible representations of the point co-group of the \mathbf{k} or \mathbf{q} wavevector. To see the correspondence color-representation see the `point_groups.pdf` manual. The point group used for each \mathbf{k} or \mathbf{q} point is written in the `thermo_pw` output and also in the plot if you set `enhance_plot=.TRUE..` In the output you can also find, close to each band energy or phonon frequency value, the name of the irreducible representation. Relevant character tables are given in the `point_groups.pdf` manual, in the `thermo_pw` output, or by the `crystal_point_group.x` tool.