QE-2019: Hands-on session – Day-1

Topics of Day-1 hands-on session:

1. Installation/compilation of Quantum ESPRESSO (`example0.QE-compilation`)
2. How to run basic PWscf (`pw.x`) calculations
3. How to run post-processing calculations to plot molecular-orbitals and charge-density (`pp.x`), DOS (`dos.x`), and band-structure (`bands.x`)
4. How to calculate low-dimensional systems (`example1.benzene` and `example2.graphene`)
5. How to make basic convergence tests (`example3.Si`)
6. How to deal with metals (`example4.Al`)
7. How to deal with ultrasoft-pseudopotentials and with spin polarization (`example5.Fe`)

About Quantum ESPRESSO

More info about Quantum ESPRESSO can be found in:

- https://www.quantum-espresso.org/
- Quantum ESPRESSO (QE) documentation:
  - on-line manuals at www.quantum-espresso.org/resources/users-manual
  - Doc/ subdirectories in the QUANTUM ESPRESSO distribution
  - input data description: most programs contained in QE have their own input file description in the form of hyperlinked INPUT_***.html files (where *** stands for the name of the program)

Hands-on material

Hands-on material for each day is contained within its own directory:

- `Day-1/` – hands-on exercises for Day-1
- `Day-2/`, `Day-3/`, `Day-4/`, `Day-5/` – hands-on exercises for Day-2 to Day-5

Please go to `Day-1/` directory and execute: `git pull`
this will update the hands-on excercise to the latest version from the GitLab.

- The naming of files is described in `README-filenames.md` (in `Day-1/`).
- all directories contain `README.md` file with instructions how to run exercise(s)
- To help recognizing for which program a given input file in intended, the filename starts with the name of the program, i.e.:
  - `pw.*.in` – input file for `pw.x` program
  - `pp.*.in` – input file for `pp.x` program
  - etc.

0. Compilation of Quantum ESPRESSO

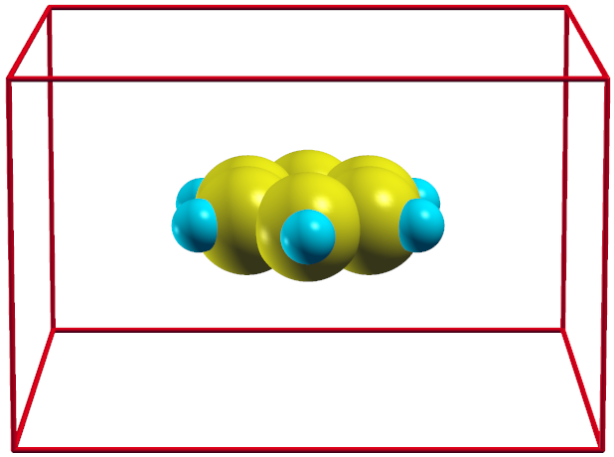
Please go to `Day-1/` directory.

- `cd example0.QE-compilation/`

TODO: please complete the slide ...

1. How to calculate a molecule with Quantum ESPRESSO

With Quantum ESPRESSO we can calculate a molecule by putting it in a big box.



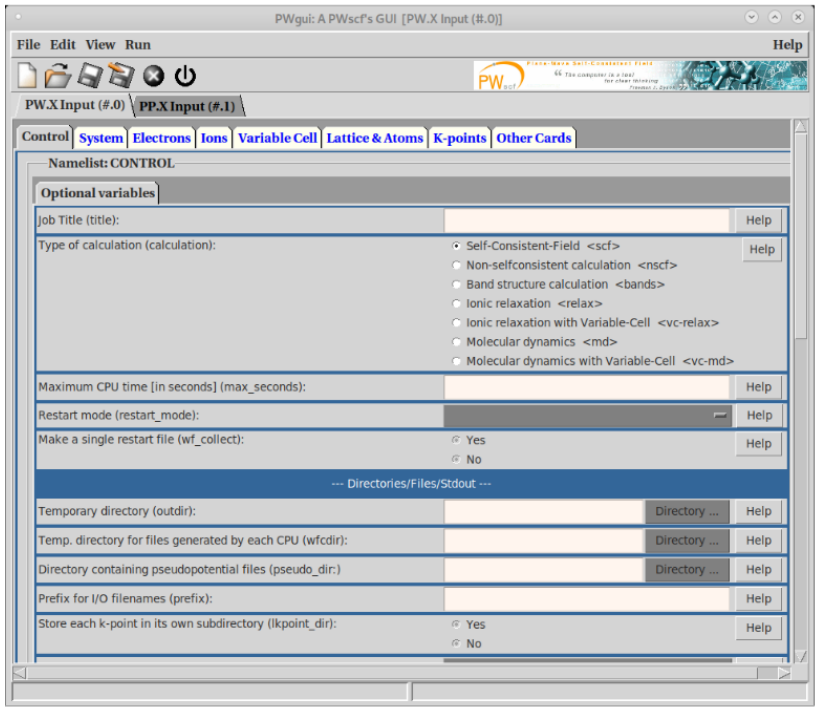
- move to `Day-1/example1.benzene/` directory
- look at the input file `pw.benzene.scf.in`. It is composed of three "namelists" `&CONTROL` (note that `calculation ='scf'` is the default value), `&SYSTEM`, `&ELECTRONS`, followed by three "cards" `ATOMIC_SPECIES`, `ATOMIC_POSITIONS`, `K_POINTS`
- instructions for how to run the example are in `README.md`

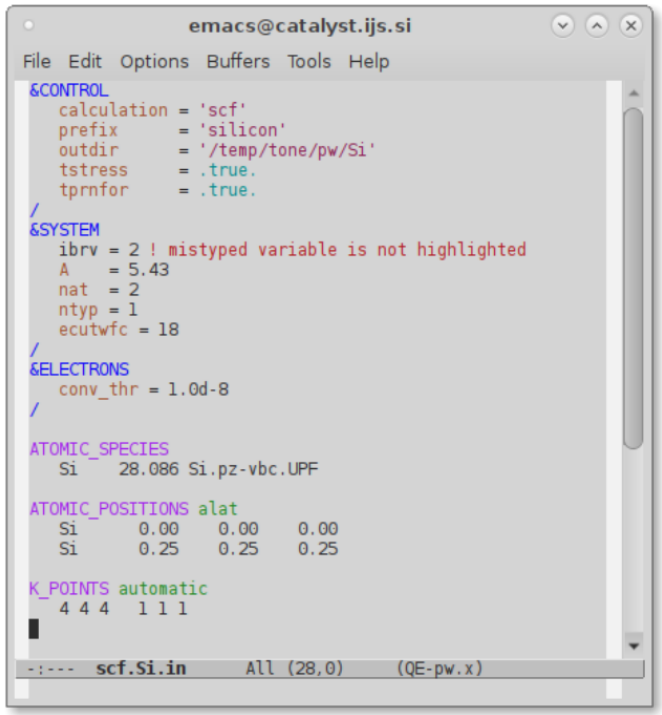
  Disclaimer: *box used in this example is very small as to speed-up calculations*

Preparation of input files

A few tools are available that aid at editing the Quantum ESPRESSO input files:

- `PWgui` – a QE input file builder GUI (`pwgui`)
- `QE-emacs-modes` – makes editing of input files easier with Emacs editor. It provides syntax highlighting, basic auto-indentation, and several utility commands; its manual is available in QE sub-directory `GUI/QE-modes/Doc/user_guide.pdf`



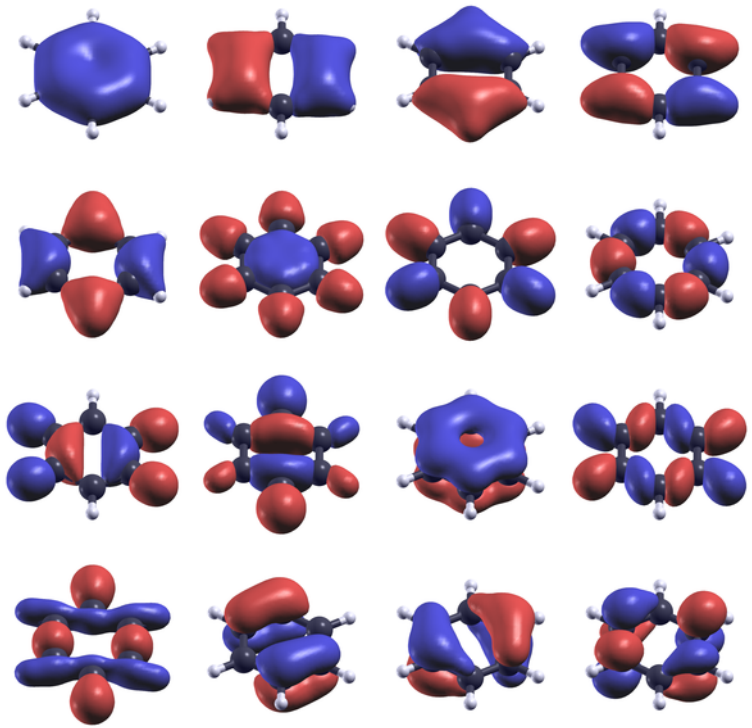


1. How to calculate and plot molecular orbitals

To plot molecular orbitals (actually the signed square modulus, $\mathrm{sign}(\psi(\boldsymbol{r}))|\psi(\boldsymbol{r})|^2$), we need to:

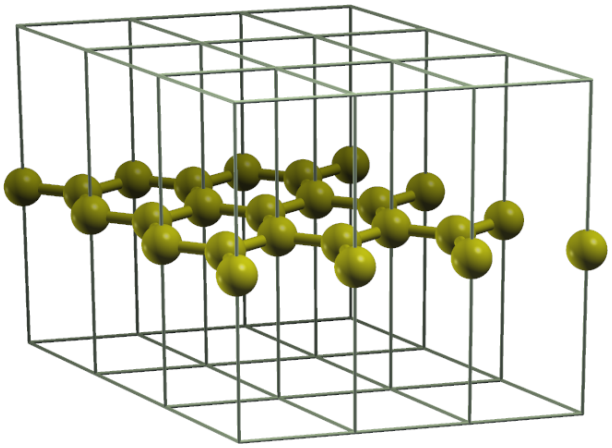
(see `README.md` for detailed instructions)

- calculate Kohn-Sham states with the `pw.x` (i.e. make an SCF calculation)
- instruct `pp.x` to write them in a suitable format to specified files
- plot orbitals with `xcrysden`



2. How to calculate a 2D-periodic system: graphene

A 2D-periodic system (e.g., a graphene sheet) is modelled by adding a vacuum layer in the 3rd direction.



- move to `Day-1/example2.graphene/` directory

- look at the input file `pw.graphene.scf.in`; graphene has a 2-atom hexagonal unit cell in the xy plane: `ibrav=4`, `celldm(1)=4.654`,
`celldm(3)=`*some suitably large value, e.g.* `3.0`;

(remember: `celldm(1)` in Bohr radii, `celldm(3)=c/a`; alternatively: `A=2.463`, `C=7.388` in Å)

- atomic positions:

```
ATOMIC_POSITIONS (alat)
C 0.000000 0.000000 0.000000
C 0.000000 0.5773503 0.000000
```

or, equivalently:

```
ATOMIC_POSITIONS (crystal)
C 0.000000 0.000000 0.000000
C 0.333333 0.666667 0.000000
```

- k-points: use a dense grid in the xy plane only, e.g.

```
K_POINTS (automatic)
9 9 1 0 0 0
```

(a uniform 9×9×1 grid, centered on $\mathbf{k} = (0, 0, 0)$)

2. Graphene: DOS and bands (spaghetti)

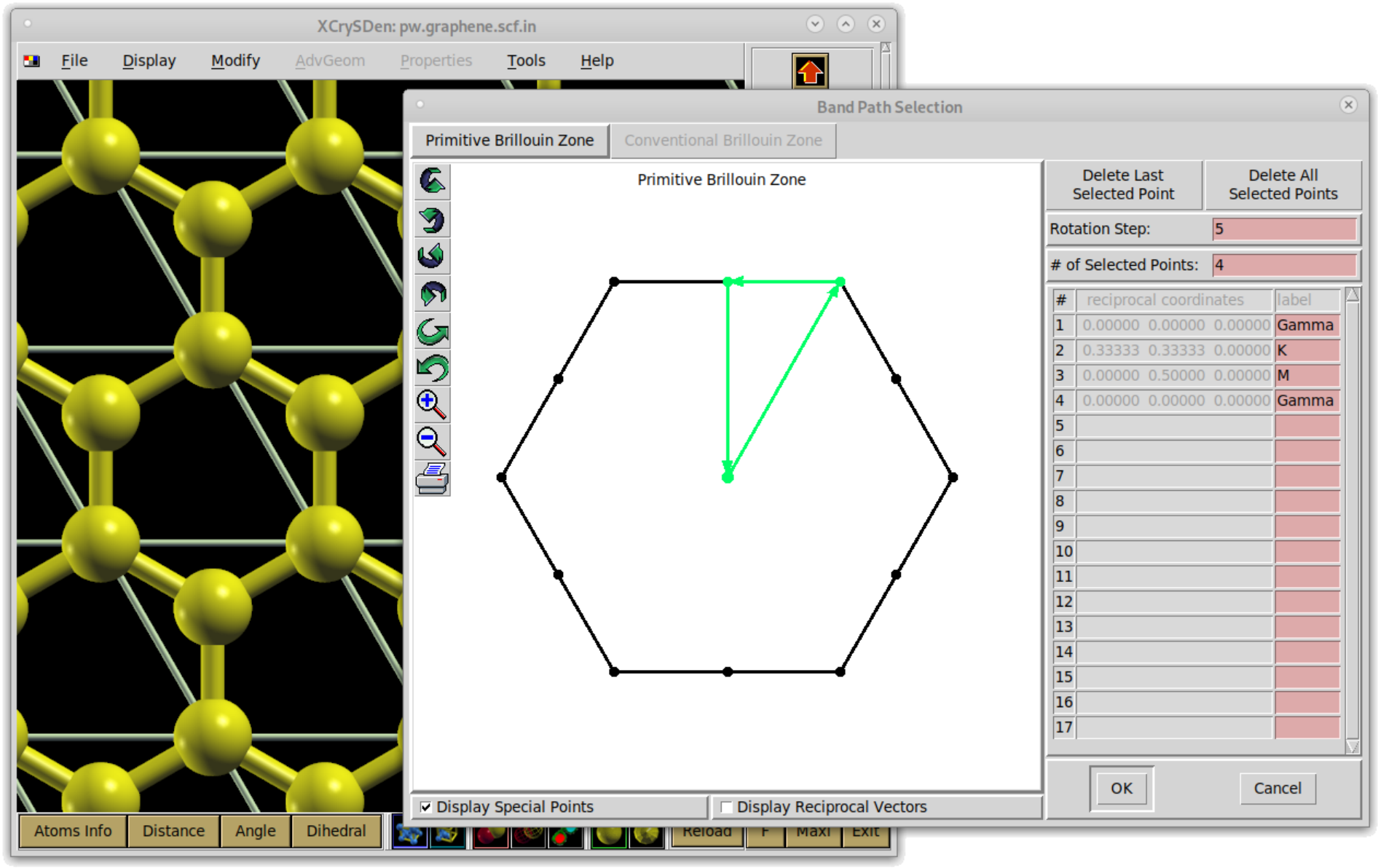
- DOS is typically calculated by `pw.x` SCF calculation followed by a `pw.x` non-SCF calculation (`calculation = 'nscf'`) with a denser k-point grid, and finally using the `dos.x` post-processing code.

- to calculate the bands (spaghetti plot), the `pw.x` SCF calculation is followed by a `pw.x` "bands"-type non-SCF calculation (`calculation = 'bands'`), for which we need a suitable path of k-points. The most difficult (?) part is to figure out a suitable path of k-points.

  You may either use the "k-path selection" tool of `xcrysden` or the `SeeK-path` web site at `http://materialscloud.org/tools/seekpath`.

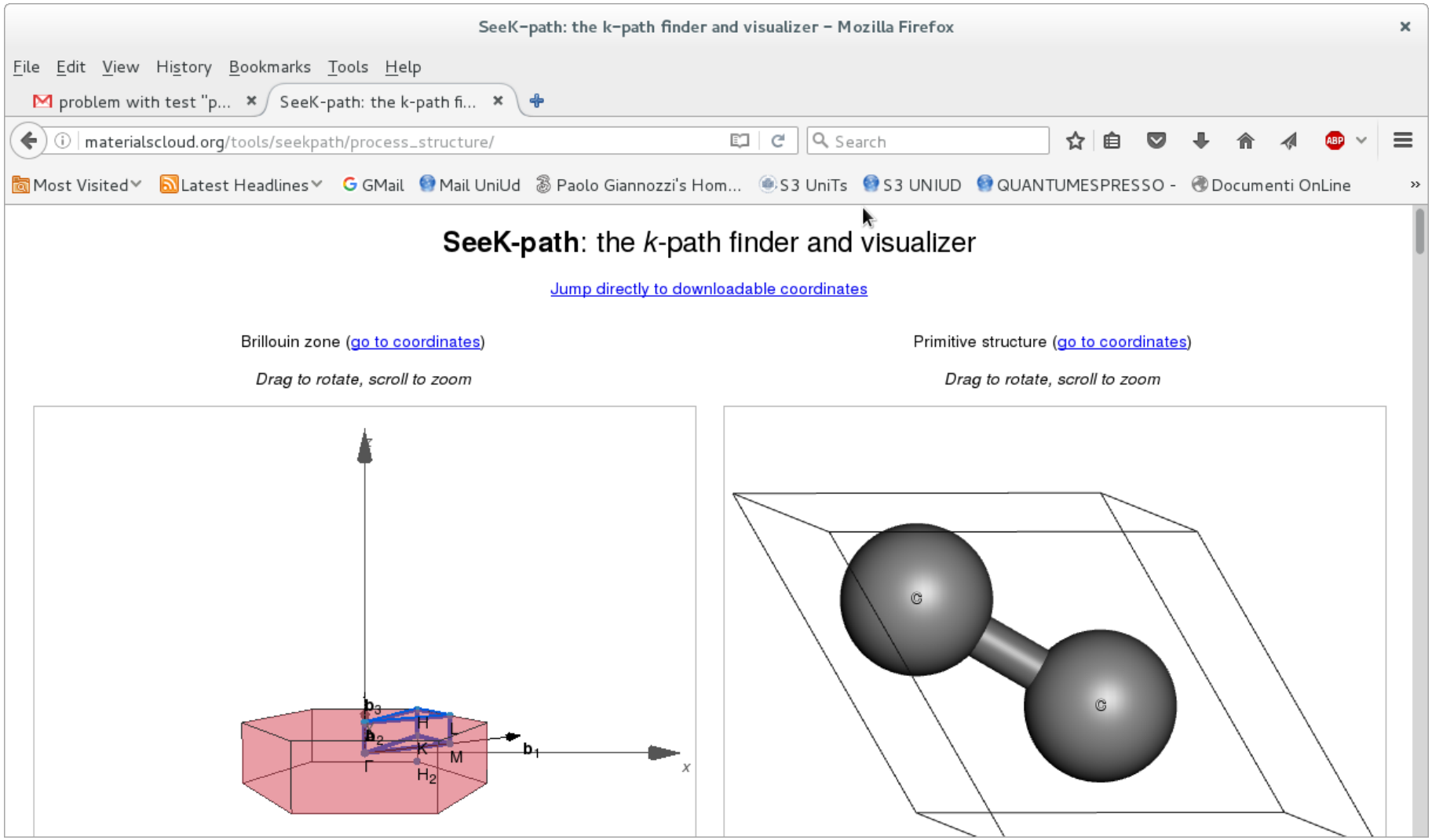
- instructions for how to calculate DOS and bands are in `README.md`

K-path selection tool of xcrysden



Example: `Day-1/example2.graphene`

SeeK-path @ http://materialscloud.org/tools/seekpath



Example: `Day-1/example2.graphene`

3. Bulk system: Silicon

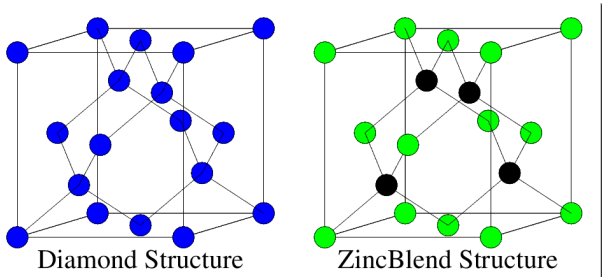
Self-consistent calculation (and a series of tests) for Silicon in the diamond structure:

- move to `Day-1/example3.Si` directory
- look at the input file `pw.si.scf.in`. It is composed of three "namelists" `&CONTROL` (note that `calculation = 'scf'` is the default value), `&SYSTEM`, `&ELECTRONS`, followed by three "cards" `ATOMIC_SPECIES`, `ATOMIC_POSITIONS`, `K_POINTS`
- in the `&CONTROL` namelist notice the following two variables (they are commented):
  - `outdir`: temporary directory for large files. Must be writable, will be created if not existent. You may set environment variable `ESPRESSO_TMPDIR` instead.
  - `pseudo_dir`: directory where pseudopotential (PP) files are kept. It must exist, be readable, and contain the required PP file (in this example, `Si.pz-vbc.UPF` for Silicon). You may set environment variable `ESPRESSO_PSEUDO` instead.

(note that for the hands-on exercises we rely on `ESPRESSO_TMPDIR` and `ESPRESSO_PSEUDO` enviromental variables, hence we don't need to set `outdir` and `pseudo_dir` variables)

Providing atomic structure in input

How is the crystal structure defined? This is a very simple case: diamond lattice is an fcc (face-centered cubic) lattice with two atoms per unit cell. You need to specify:



- What is the Bravais lattice?
  `ibrav=2`, meaning fcc lattice
- How many and which parameters are needed to completely define Bravais lattice?
  just one: `celldm(1)=10.2`, lattice parameter a in a.u.
- How many atoms there are in the unit cell?
  `nat=2`: two atoms
- How many different atomic species are present?
  `ntyp=1`: one species
- Which ones, described by which pseudopotential?
  See card `ATOMIC_SPECIES`
- Where the atoms are located in the unit cell?
  See card `ATOMIC_POSITIONS`: here, in Cartesian axis, in units of a ("`alat`")

Notice that there are several alternative methods to specify an atomic structure!

Brillouin zone (BZ) sampling

k-points are described in card `K_POINTS`. One has to choose

- Whether to provide a list of k-points, or a uniform grid

- If a list is chosen: list of k-points *in the Irreducible BZ* and corresponding symmetry weights; the latter do not need to add up to 1, they are normalized by the code

  Frequently Asked Question: where do I find special k-points and their weights? Answer: 1) in papers, 2) use auxiliary code `kpoints.x`, 3) use uniform grids

- If a uniform grid is chosen: Monkhorst-Pack parameters (H.J. Monkhorst and J.D. Pack, *Phys. Rev. B* **13**, 5188 (1976)), and offsets along the three directions

Running the pw.x code

For serial (single processor) execution you can use

```
$ pw.x -in pw.si.scf.in > pw.si.scf.out
```

(note: input redirection `pw.x < pw.si.scf.in` works but it is not recommended on parallel machines)

Look at the directory specified by `outdir` (in our case `$ESPRESSO_TMPDIR`) and its content:

```
$ ls $ESPRESSO_TMPDIR
silicon.save silicon.xml
```

The directory contains a data directory with binary data files for further processing and an XML file with general information on the run. The name of the various files is determined by the value of the `prefix` variable and by their content.

Do not run two instances of pw.x that access the same `outdir` with the same `prefix`! Unpredictable behavior may follow (the directory is used for temporary files as well). In case of trouble, clean `outdir`.

Running the pw.x code (II)

Examine output file `pw.si.scf.out`, look how self-consistency proceeds:

```
$ grep -e 'total energy' -e estimated pw.si.scf.out}
     total energy              =     -15.79103344 Ry
     estimated scf accuracy    <       0.06376674 Ry
     total energy              =     -15.79409289 Ry
     estimated scf accuracy    <       0.00230109 Ry
     total energy              =     -15.79447822 Ry
     estimated scf accuracy    <       0.00006291 Ry
     total energy              =     -15.79449510 Ry
     estimated scf accuracy    <       0.00000448 Ry
!    total energy              =     -15.79449593 Ry
     estimated scf accuracy    <       0.00000005 Ry
     The total energy is the sum of the following terms:
```

Notice that there are 8 electrons in the cell: 2 (pseudo-)atoms/cell with 4 electrons. The system is a non-magnetic insulator, so just the lowest 4=8/2 valence bands (Kohn-Sham states) are computed.

Convergence w.r.t. kinetic energy cutoff

The kinetic energy cutoff `ecutwfc` (in Ry) determines the size of the Plane-Wave (PW) basis set used to expand wavefunctions (i.e. Kohn-Sham orbitals)
(for Norm-Conserving PP, the PW set for charge density `ecutrho=4*ecutwfc`, do not specify it)

- A manual test of convergence w.r.t. kinetic energy cutoff entails the following tasks (**BEWARE: we will not do it manually**)

  1. change value of `ecutwfc` in `pw.si.scf.in` input to, e.g., 16, 20, 24, 28, 32 Ry
  2. for each value of `ecutwfc`, run `pw.x` and collect the final energy
  3. complete the data in a file, say `si.etot_vs_ecut` (i.e. each line should contain two values: `ecutwfc` and "total-energy")
  4. plot the energies collected in `si.etot_vs_ecut` using your preferred plotting program, for instance:

```
$ gnuplot
gnuplot> plot 'si.etot_vs_ecut' with lines
```

- because such a manual procedure is very cumbersome we use scripts instead

Convergence w.r.t. kinetic energy cutoff (II)

Because manual convergence tests are very cumbersome, scripts are used instead. Traditionally, Unix shell-scripts are used, yet there are other more "fancy" alternatives, e.g., PWTK scripts.

- Unix shell-script is located in `ex1.ecutwfc.classic/` sub-directory (file: `ecutwfc.sh`)
- PWTK scripts is located in `ex1.ecutwfc/` sub-directory (file: `ecutwfc.pwtk`)

Unix shell-script

```
#!/bin/sh

rm -f si.etot_vs_ecut.dat

for ecut in 12 16 20 24 28 32
do
    cat > pw.si.scf.$ecut.in << EOF
 &CONTROL
    prefix='silicon',
 /
 &SYSTEM
    ibrav =  2,
    celldm(1) = 10.2,
    nat =  2,
    ntyp = 1,
    ecutwfc = $ecut,
 /
 &ELECTRONS
 /
ATOMIC_SPECIES
   Si  28.086  Si.pz-vbc.UPF
ATOMIC_POSITIONS
   Si 0.00 0.00 0.00
   Si 0.25 0.25 0.25
K_POINTS automatic
   4 4 4   1 1 1
EOF

    pw.x -in pw.si.scf.$ecut.in > pw.si.scf.$ecut.out

    grep -e 'kinetic-energy cutoff' -e ! pw.si.scf.$ecut.out | \
        awk '/kinetic-energy/ {ecut=$(NF-1)}
             /!/              {print ecut, $(NF-1)}' >> si.etot_vs_ecut.dat

done
```

PWTK script

```
load_fromPWI ../pw.si.scf.in

set fid [open si.etot_vs_ecut.dat w]

foreach ecut {12 16 20 24 28 32} {
    SYSTEM "ecutwfc = $ecut"
    runPW pw.Si.scf.$ecut.in

    puts $fid "$ecut [::pwtk::pwo::totene pw.Si.scf.$ecut.out]"
}
close $fid
```

101 of PWTK scripting

Basic philosophy is to **keep the syntax close to original input syntax**!

pw.x input file

```
&CONTROL
   calculation = 'scf'
/
&SYSTEM
   ecutwfc = 25.0
   ecutrho = 200.0
   ...
/
ATOMIC_POSITIONS alat
   Si     0.00   0.00   0.00
   Si     0.25   0.25   0.25

K_POINTS automatic
   4 4 4    1 1 1
```

pw.Si.in

pwtk script

```
CONTROL {
   calculation = 'scf'
}
SYSTEM {
   ecutwfc = 25.0
   ecutrho = 8*25.0
   ...
}
ATOMIC_POSITIONS alat {
   Si     0.0   0.0   0.0
   Si     1/4   1/4   1/4
}
K_POINTS automatic {
   4 4 4    1 1 1
}

runPW pw.Si.in
```

Si_bulk.pwtk

Run from terminal as:

```
pw.x -in pw.Si.in > pw.Si.out
```

Run from terminal as:

```
pwtk Si_bulk.pwtk
```

101 of PWTK scripting

- PWTK script are basically Tcl-scripts, hence they use Tcl-syntax
- namelists and cards have the same names as in QE (with a few exceptions), but they are all written in **upper-case**. Their content is encapsulated with curly braces:

```
CONTROL { calculation = 'scf', outdir = '/tmp/pwscf/'}
ATOMIC_POSITIONS { ... }
```

- instead of curly braces, one can also use double-quotes (`"..."`), e.g.:

```
SYSTEM " celldm(1) = $a "
```

- difference between curly braces `{...}` and double-quotes `"..."` is that inside double-quotes the variable `$a` is substituted by its value, whereas inside curly braces the `$a` is treated literally (i.e. no substitution)
- real numbers can be specified as mathematical expressions (e.g. `ecutrho = 8*25.0`)
- indices of `ntyp`-type array variables, such as `starting_magnetization(i)`, can be specified with atomic labels, e.g.:

```
SYSTEM { starting_magnetization(Fe) = -0.8 }
```

  where Fe is one among atomic species defined by `ATOMIC_SPECIES` card.

- PWTK script are case sensitive, i.e., `CONTROL { ... }` is OK, whereas `control { ... }` is not; also namelist variables are case sensitive!
- namelist **variables can be set on-the fly** (we will use this heavily)
- to unset a namelist variable, set it to empty-value; for example to unset the `outdir` variable, use:

  ```
  CONTROL { outdir = }
  ```

- namelist and cards can be called many times, but there is a big difference how multiple calls are handled for namelists and cards: **cards** are handled in **overwrite mode**, whereas **namelists** are handled in *kind of* **append** mode. For example, the following is OK:

  ```
  CONTROL { calculation = 'scf' }
  CONTROL { outdir = '/tmp/qe' }
  ```

  and is equivalent to:

  ```
  CONTROL { calculation = 'scf' , outdir = '/tmp/qe' }
  ```

- the order of namelists and cards is not important; PWTK knows how to construct proper input files

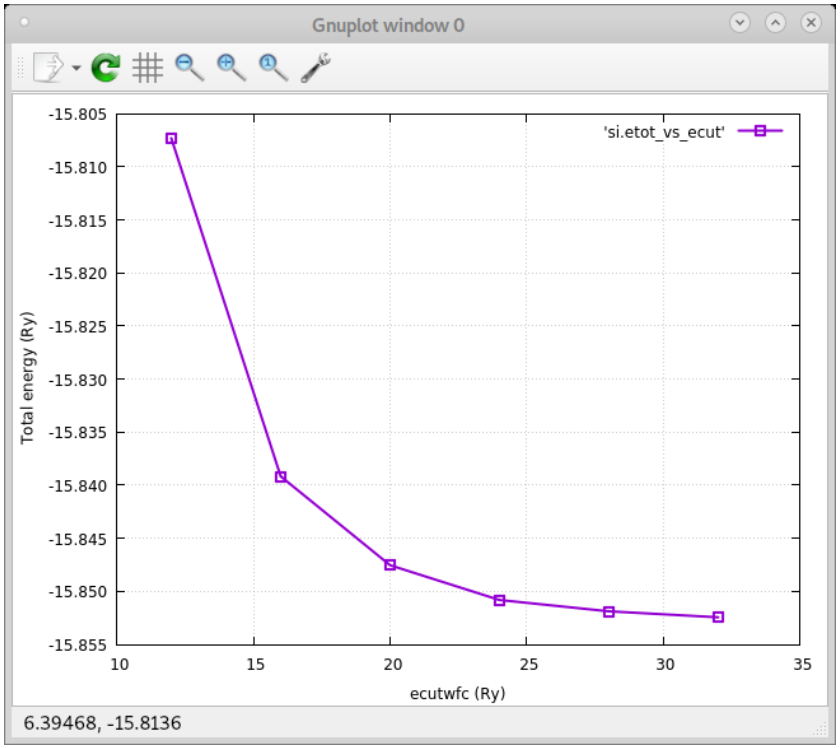
Convergence w.r.t. kinetic energy cutoff (III)

- To run the convergence test via Unix shell-script move to `ex1.ecutwfc.classic` sub-directory (read the `README.md` file) and execute

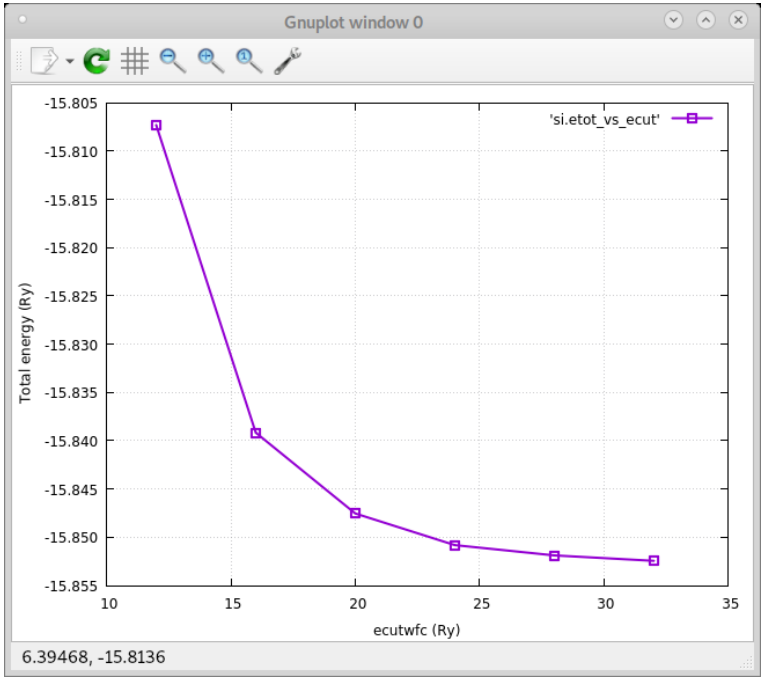
```
$ ./ecutwfc.sh
```

- To run the convergence test via PWTK script move to `ex1.ecutwfc` sub-directory (read the `README.md` file) and execute

```
$ pwtk ecutwfc.pwtk
```



Convergence w.r.t. kinetic energy cutoff (IV)



Reminder:

- Convergence w.r.t to cutoff is a property of the *pseudopotential(s) used*.
- Convergence of *absolute energy* is typically slower than convergence on *interesting physical properties*, e.g. structure.
- Absolute values of total energy do not have any physical meaning (and depend upon the specific PP): only energy *differences* do

Convergence w.r.t. k-points

A sufficiently dense grid of k-points is needed in order to account for *periodicity*.

To test the convergence w.r.t. k-points, you need to edit `K_POINTS` card and request *automatic* Monkhorst-Pack grids:

```
K_POINTS automatic
nk1 nk2 nk3   k1 k2 k3
```

then step-wise increase `nk1=nk2=nk3` to, e.g., `2, 4, 6, 8` (keep `k1=k2=k3=1`) and run `pw.x` calculation for each value of nk1, ...

For example, with PWTK this can be achieved with the following snippet:

```
load_fromPWI pw.si.scf.in

foreach k {2 4 6 8} {
   K_POINTS automatic "$k $k $k  1 1 1"
   runPW pw.si.scf.$k.in
}
```

Convergence w.r.t. k-points (II)

Description of `K_POINTS` card for *automatic* mode:

```
K_POINTS automatic
nk1 nk2 nk3   k1 k2 k3
```

The first three `nk1 nk2 nk3` numbers mean *"there are nk1,nk2,nk3 grid points along crystal axis 1,2,3"*; the second three `k1 k2 k3` numbers, either 0 or 1, mean *"grid starts from 0"* or *"displaced by half a step"* along crystal axis 1,2,3

Also note that:

- Convergence is not necessarily monotonic: there is no variational principle w.r.t. number of k-points
- The `2 2 2  1 1 1` Monkhorst-Pack grid is the same as the "two Chadi-Cohen points"

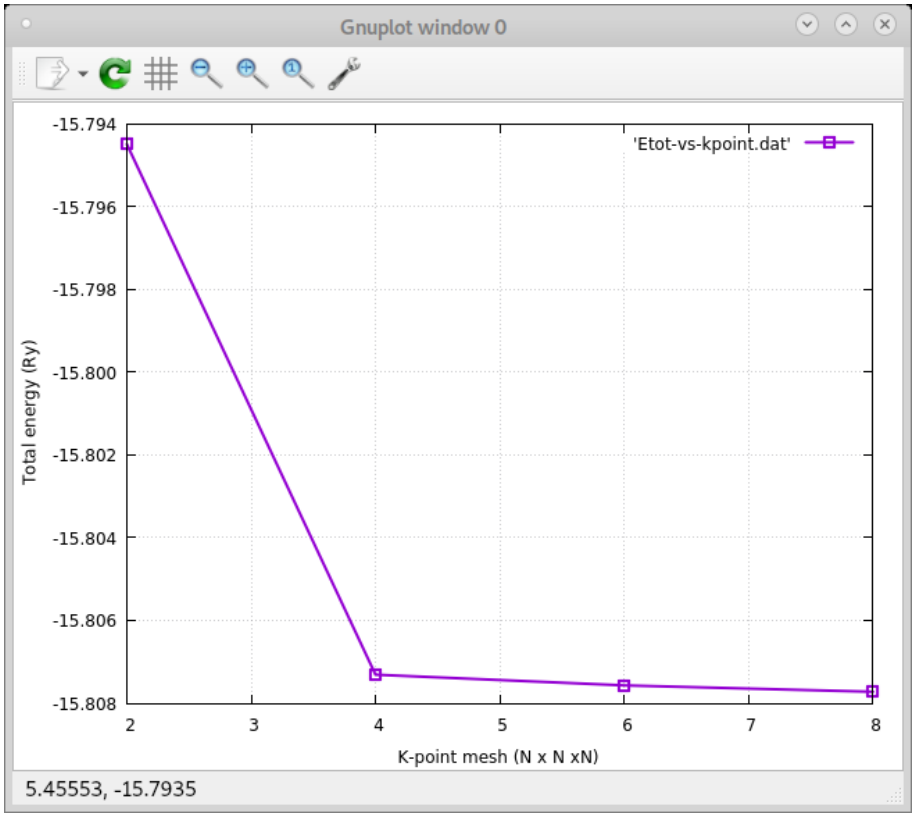
Convergence w.r.t. k-points (III)

PWTK script for testing the convergence with respect to k-points is located in `Day-1/example3.Si/ex2.kpoints` directory (see `README.md` for detailed instructions).

Within this directory execute:

```
$ pwtk kpoints.pwtk
```

You should get a plot like this one:



Equation of State: silicon

Equilibrium in Si is determined by the minimum-energy lattice parameter alone: there are no forces on atoms, by symmetry (you can verify this by setting `tprnfor=.true.` in namelist `&CONTROL` and looking for forces reprinted at the end).

To find the lattice parameter:

- Choose suitable values for `ecutwfc` and the k-point grid (e.g. `30` Ry and `4 4 4 1 1 1`)
- Run the `pw.x` for values of `celldm(1)` ranging from 9.7 to 10.7 in steps of 0.1 a.u.

With PWTK this can be achieved with the following snippet:

```
load_fromPWI pw.si.scf.in

foreach alat [seq 9.7 0.1 10.7] {
   SYSTEM "celldm(1) = $alat"
   runPW pw.si.scf.$alat.in
}
```

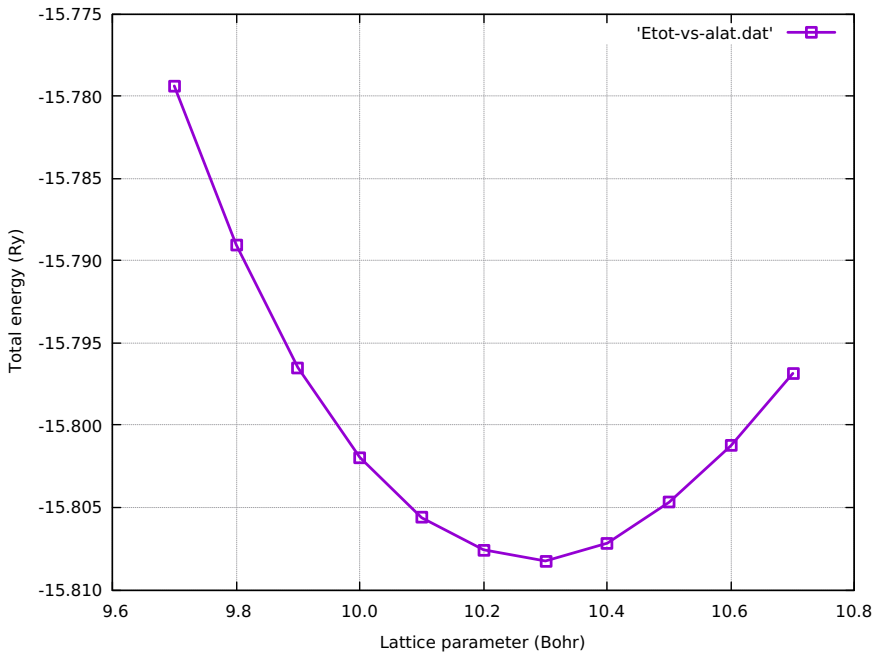
Equation of State: silicon (II)

The corresponding PWTK script is located in `Day-1/example3.Si/ex3.alat` directory (see `README.md` for detailed instructions).

Within this directory execute:

```
$ pwtk alat.pwtk
```

The experimental lattice parameter for Si is 5.47 Å or 10.26 a.u.. This is a case where plain simple LDA yields remarkable results. You may experiment changing cutoff, k-points, pseudopotential, ...



You should find that:

- The energy vs lattice parameter $E(a)$ curves are shifted down rather uniformly with increasing cutoff and are not strongly dependent on k-points.
- Structural properties and energy differences converge faster than total energies.

Equation of State: silicon (III)

Use the code `ev.x` to fit your results to a phenomenological equation-of-state (EOS, e.g. Murnaghan) and to get accurate values for the lattice parameter and for the bulk modulus.

The `ev.x` code prompts for some data and reads a data-file like the one produced by the `alat.pwtk` script (the data-file is `Etot-vs-alat.dat`). For cubic systems a data-file should contain the following rows:

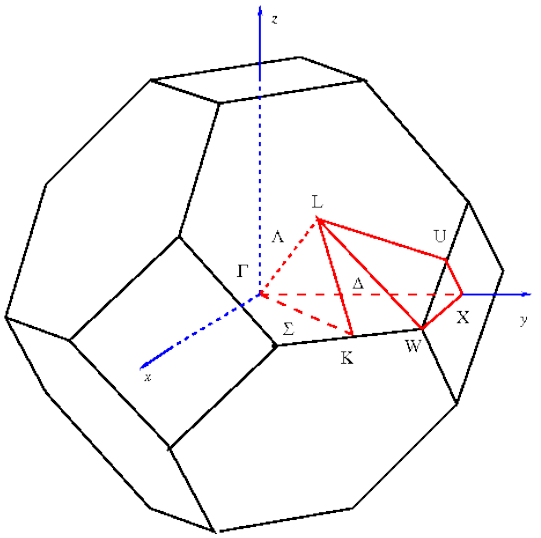
$$
\begin{array}{ll}
a_1 & E(a_1) \\
a_2 & E(a_2) \\
a_3 & E(a_3) \\
\ldots &
\end{array}
$$

Band Structure of Silicon

The scheme to calculate the bands (spaghetti plot) is the following:

1. SCF `pw.x` calculation (`calculation = 'scf'`)

2. "bands"-type non-SCF `pw.x` calculation (fixed-potential) with:
   - `calculation = 'bands'`
   - the number of Kohn-Sham states explicitly set (variable `nbnd`)
   - a suitable path of k-points specified in `K_POINTS` (in this example we use the $L-\Gamma-X-W-K-L$ path)



3. `bands.x` calculation, which, among others, produces data-files for spaghetti plot

Important: `outdir` and `prefix` must be the same for "bands" and "scf" `pw.x` calculations and for `bands.x` calculation
Important: the k-point path must be continuous in k-space

Band Structure of Silicon (II)

The input for the `bands.x` program is the following:

```
&BANDS
   prefix='...', outdir='...', filband = 'Si.bands.dat', lsym=.true.
/
```

Two files are produced: `Si.bands.dat.gnu`, directly plottable with `gnuplot`, and `Si.bands.dat`, for further processing by auxiliary command `plotband.x`.

If option `lsym=.true`, `bands.x` performs a symmetry analysis. An additional file `Si.bands.dat.rep` is generated, containing information on symmetry labels of the various bands.

The snippet for running all three calculations manually is:

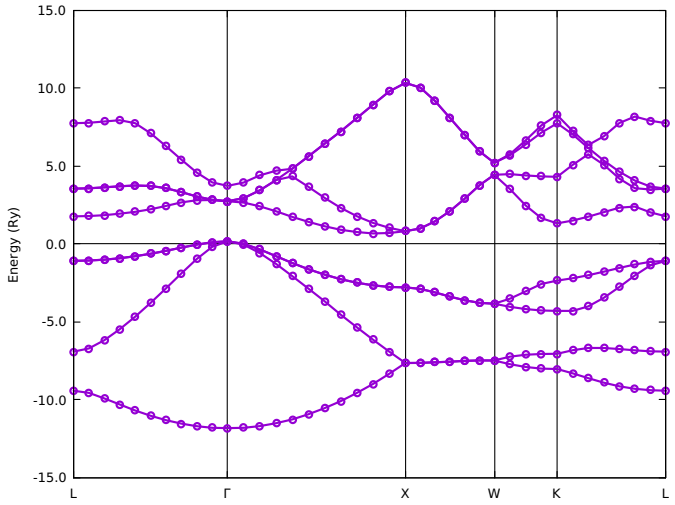
```
$ pw.x -in pw.Si.scf.in > pw.Si.scf.out
$ pw.x -in pw.Si.bands.in > pw.Si.bands.out
$ pw.x -in bands.Si.in > bands.Si.scf.out
```

but we will instead use a PWTK script instead.

Band Structure of Silicon (III)

To execute the PWTK script that will perform all the needed calculations to plot the bands, proceed as follows:

- move to directory `Day-1/example3.Si/ex4.bands` and read the `README.md` file
- set suitable values for `celldm(1)`, `ecutwfc`, and `K_POINTS`
- and execute: `pwtk bands.pwtk`
- you may set the `Efermi` value to the top of the occupied bands in gnuplot file `plot.gp` (see the instructions in `README.md`); then re-plot spaghetti with: `gnuplot plot.gp`



Remark: in PWTK, once `outdir` and `prefix` are set, they are automatically inherited for subsequent calculations.

Auxiliary program plotbands.x

`plotband.x` prompts for terminal input:

```
$ plotband.x
Input file > Si.bands.dat
Reading    8 bands at     39 k-points
Range:   -5.6940   16.4680eV  Emin, Emax > -5.6940   16.4680
high-symmetry point: -0.5000 0.5000 0.5000   x coordinate   0.0000
high-symmetry point:  0.0000 0.0000 0.0000   x coordinate   0.8660
high-symmetry point:  0.0000 0.0000 1.0000   x coordinate   1.8660
high-symmetry point:  0.0000 0.5000 1.0000   x coordinate   2.3660
high-symmetry point:  0.0000 0.7500 0.7500   x coordinate   2.7196
high-symmetry point: -0.5000 0.5000 0.5000   x coordinate   3.3320
output file (gnuplot/xmgr) > Si.bands.plot
bands in gnuplot/xmgr format written to file Si.bands.plot
output file (ps) > (press Return)
```

If symmetry analysis was performed in the previous step, the output is written to several plottable files `sibands.plot.`N`.`M, where N labels the high-symmetry lines, M labels irreducible representations.

4. A metallic example: Aluminum

Aluminum is even simpler than Silicon: one atom per unit cell in a fcc lattice.
BUT: it is a metal, valence bands only and a few k-points will not suffice.

- move to the `Day-1/example4.Al` directory
- read the `pw.x` input file `pw.al.scf.in`
- notice the presence of new variables: `occupations`, `smearing`, `degauss`;
- run `pw.x` as:

```
$ pw.x -in pw.al.scf.in > pw.al.scf.out
```

- notice in output file that
  - the number of bands (Kohn-Sham states) is automatically set to a value larger than the number of electrons divided by 2
  - the Fermi energy is computed.

Convergence with respect to k-points, degauss, and smearing

This is a *"three-dimensional"* convergence test, where we will vary the number of k-points and values of `degauss` and `smearing` variables. In particular, we will vary:

- variable `smearing`, possible values: `'gauss'` (or `'g'`), `'marzari-vanderbilt'` (or `'m-v'`), `'methfessel-paxton'` (or `'m-p'`)
- variable `degauss`, in range from 0.01 to 0.15
- k-points using the *automatic* grids of `6 6 6`, `12 12 12`, and `16 16 16`

With PWTK this can be achieved with the following snippet:

```
foreach nk {6 12 16} {
    foreach smear {'gauss'  'm-p'  'm-v'} {
        foreach degauss [seq 0.01 0.02 0.15] {
            SYSTEM " smearing = $smear
                     degauss  = $degauss "
            K_POINTS automatic "$nk $nk $nk   1 1 1"
            runPW pw.Al.scf.$nk.$smear.$degauss.in
        }
    }
}
```

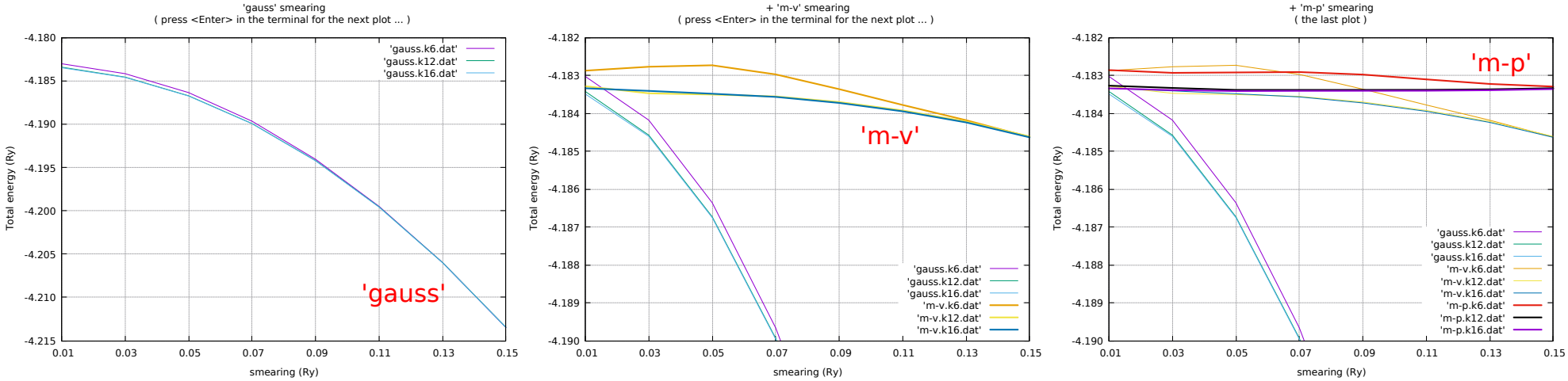
Convergence with respect to k-points, degauss, and smearing (II)

- move to `Day-1/example4.Al/ex1.degauss` directory

- execute: `pwtk degauss.pwtk`

Notice how much slower the convergence is for metals than for insulators!

Both `m-v` and `m-p` depend much less upon `degauss` and allow for faster and safer convergence than simple gaussian broadening. For Al and `m-v` or `m-p` smearing, good convergence is achieved for a `12 12 12` k-point grid and `degauss` $\sim 0.01 \div 0.05$ Ry.



Notice that you cannot reduce the broadening too much: the energy levels must have some overlap, or else the advantage of broadening is lost!

How to plot charge-density

Example `Day-1/example4.Al/ex2.chdens` shows how to calculate valence and all electron charge density (the latter requires PAW potential and very hard cutoff)

- move to `Day-1/example4.Al/ex2.chdens` directory (*chdens* is acronym for charge-density)

- execute: `pwtk 1-chdens.pwtk`
  this script calculates and plots the valence charge density; notice that electron charge is located mainly in interstitial regions (due to the use of pseudo-potential, there is *almost no* charge in close vicinity of nuclei; see next page);

- the scheme to calculate and plot charge-density is:

  1. make an SCF `pw.x` calculation
  2. make a post-processing `pp.x` calculation (`plot_num=0` for charge density) and instruct the program to write charge density in a suitable format
  3. plot the charge density by, e.g., `xcrysden`

How to plot charge-density (II)

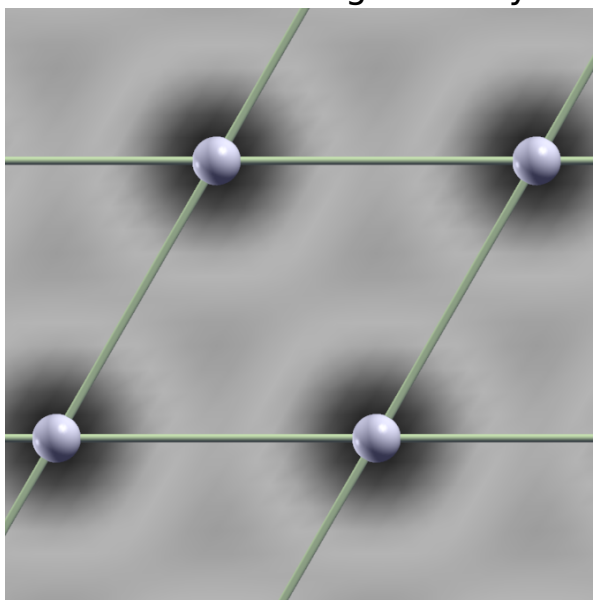
- to calculate all-electron **valence** and **total** charge densities, execute:

  ```
  $ pwtk 2-chdens-paw.pwtk
  ```

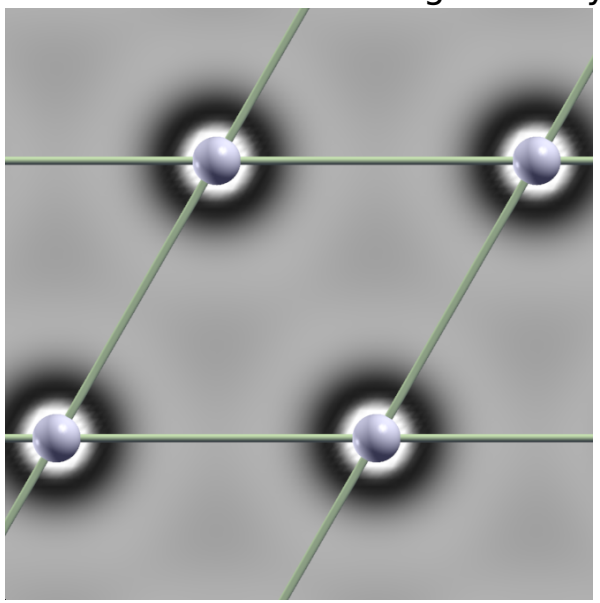
  (note that `plot_num=17` for all-electron valence density and `plot_num=21` for all-electron total density)

- comparison between PP valence-density vs. all-electron densities (valence and total):

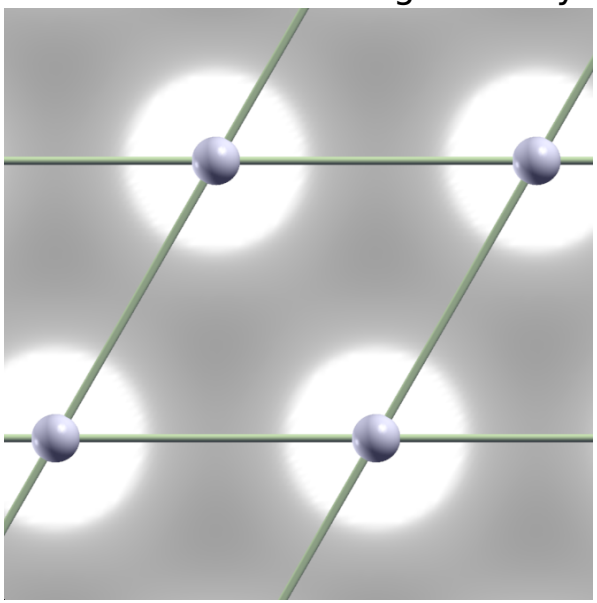
PP valence charge density



all-electron valence charge density



all-electron total charge density



5. A magnetic example: Iron

Iron has two remarkable features: it is magnetic and it requires Ultrasoft PP (USPP) since its localized 3d atomic states are very hard.

- move to the `Day-1/example5.Fe` directory and read the `pw.x` input file `pw.fe_fm.scf.in`
- the structure is bcc (`ibrav=3`) with one atom per unit cell
- notice the presence of variables `nspin` and of `starting_magnetization`, indicating LSDA (`nspin=2`) with unconstrained total magnetization and initial symmetry broken; plus, variables for *metallic* calculations
- notice that this calculation uses GGA (PBE): it is specified inside the PP file (can be guessed from the PP file name), reprinted on output as "Exchange-correlation"
- also notice that with USPP, it is typically needed to set `ecutrho` $> 4 \times$ `cutwfc` (it should be at least 8 to 12 times larger)

Magnetic structures

Run `pw.x` in the usual way (`pw.x -in pw.fe_fm.scf.in > pw.fe_fm.scf.out`). In the output, notice:

- the number of k-points is doubled w.r.t the non-magnetic case: the first set of k-points contains spin-up states, the second set spin-down states
  (use `verbosity='high'` in namelist `&CONTROL` if there are more than 100 k-points)

- in the output notice such lines:

```
total magnetization       =     2.41 Bohr mag/cell
absolute magnetization    =     2.60 Bohr mag/cell
```

  Since there is a single (magnetic) atom per unit cell, the only possible magnetic structure is ferromagnetic.

Magnetic structures: going antiferomagnetic

- in order to reach antiferromagnetic states, you need to:
  - introduce a supercell with two sublattices of different species of atoms (even if they are the same, it is important that they are labeled as different)
  - start with opposite initial magnetization for the two sublattices

- Can you write input data for an AFM structure?
  (hint: split bcc into two simple cubic sublattices, `ibrav=1`, with two atoms at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$).

As a convenience, an antiferromagnetic file is provided (`pw.fe_afm.scf.in`)

You can compare the ferromagnetic and antiferromagnetic files by:

```
$ diff pw.fe_fm.scf.in pw.fe_afm.scf.in
```

Convergence check for USPP

For computational efficiency, it is convenient to keep `ecutwfc` as low as possible, while `ecutrho` is less critical (look at the CPU time report at the end of an output: there are very many `fftw`, depending upon `ecutwfc`, while a much smaller number of `fft` depends upon `ecutrho`)

Set the `ecutrho/ecutwfc` ratio ($dual$) to 4, 8, 12 and compute the energy vs `ecutwfc` curve. For $dual = 4$ it will look funny: energy *increases* with increasing cutoff (see next page), but for higher dual (i.e. better description of augmentation charge) the normal behavior is observed.

The corresponding PWTK snippet is:

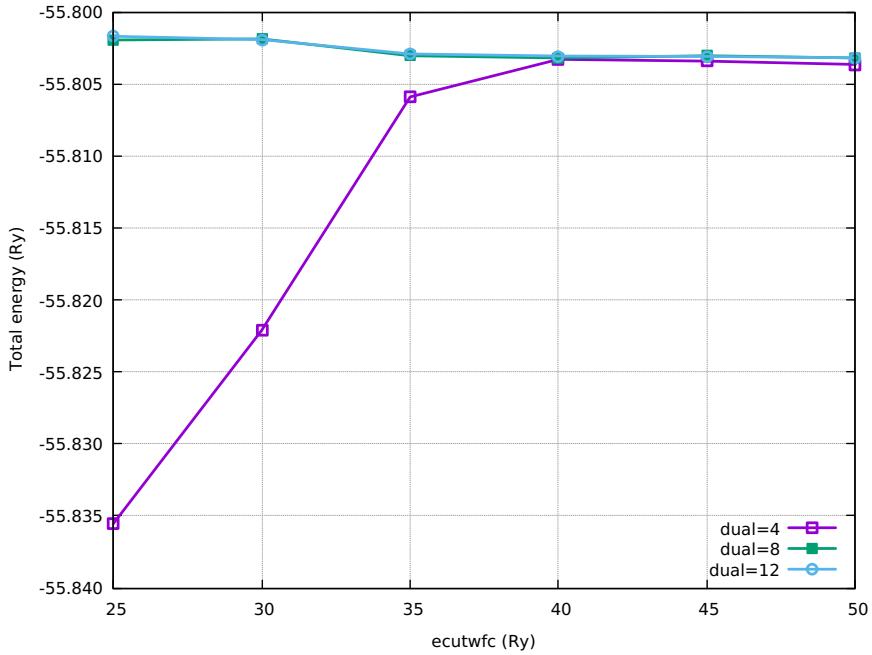
```
load_fromPWI pw.fe_fm.scf.in

foreach dual {4 8 12} {
   foreach ecut {25 30 35 40 45 50} {
      SYSTEM "ecutwfc = $ecut
              ecutrho = $ecut*$dual "
      runPW pw.fe_fm.scf.$dual.$ecut.in
   }
}
```

Convergence check for USPP (II)

A PWTK script to make convergence check for USPP is provided, i.e.:

- move to directory:
  `Day-1/example5.Fe/ex1.ecut`
- execute: `pwtk ecut.pwtk`
- you should obtain such a plot
  (notice that the curves for $dual = 8$ and 12 almost coincide)



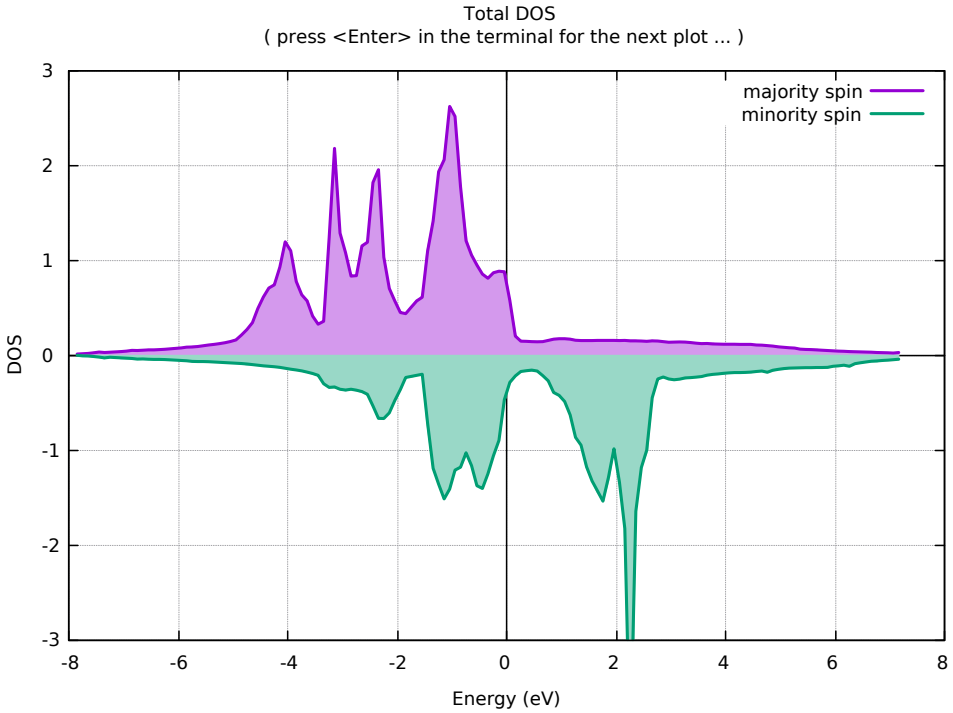
Homework: for converged values of both cutoffs and k-points, you may compare the stability of iron in the bcc, fcc, hcp phases (the latter being a slightly more complicated structure)

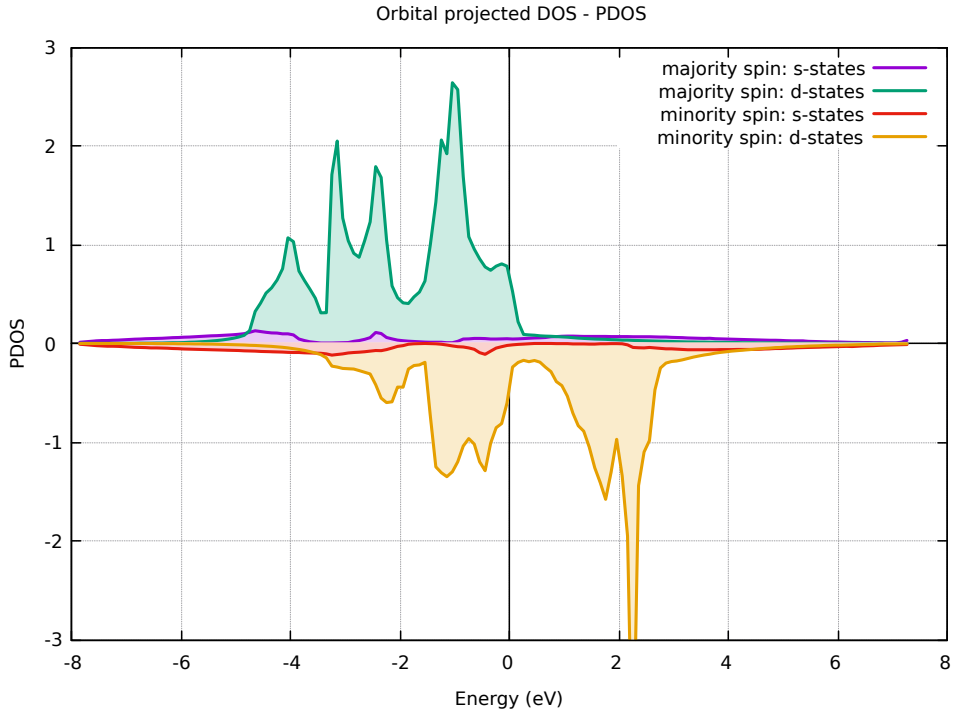
Density of States (DOS) and Projected DOS (PDOS)

1. move to `Day-1/example5.Fe/ex2.dos` directory and

2. edit the `dos.pwtk` script and set `ecutwfc` and `ecutrho` to appropriate values

3. execute: `pwtk dos.pwtk`
   (this script calculates both total DOS and DOS projected (PDOS) to atomic orbitals)





Density of States (DOS) and Projected DOS (PDOS)

The scheme to calculate DOS and PDOS consists of:

1. an SCF `pw.x` calculation (`calculation='scf'`)
2. a non-SCF `pw.x` calculation (`calculation='nscf'`), where:
   - the same `prefix` and `outdir` are used as preceding SCF calculation
   - a denser k-point mesh is specified
   - in this example *linear tetrahedron method* is used (variable `occupations='tetrahedra'`)
3. a `dos.x` calculation to calculated DOS (DOS is written to a file as specified by `fildos` variable in the `dos.x` input; also here the values `prefix` and `outdir` are the same as for SCF `pw.x` calculation)
4. a `projwfc.x` calculation to calculate PDOS projected to atomic states (this calculation is analogous to `dos.x` one, also inputs are very similar; you can compare them as:

   ```
   $ diff dos.Fe.in projwfc.Fe.in
   ```

   the difference is that `dos.x` uses `fildos` whereas `projwfc.x` uses `filpdos` variable)

Explore the content of `fildos` and `filpdos` files!