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/ sub-directories 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 the `Day-1/` directory and execute: `git pull`
this will update the hands-on exercises to the latest version from the GitLab.

- All directories contain a `README.md` file with instructions how to run exercise(s)
- Naming of files is described in `README-filenames.md` (in `Day-1/`).
- To help recognizing for which program a given input file is 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.

Disclaimer: *many examples use lousy convergence thresholds to speed-up calculations*

0. Compilation of Quantum ESPRESSO

Please go to the `Day-1/` directory, then execute:

```
$ cd example0.QE-compilation/
$ tar zxvf q-e-qe-6.4.1.tar.gz
$ cd q-e-qe-6.4.1/
```

Now read the `README.md` file. It contains installation (compilation) instructions. In essence, compilation consists of:

```
$ ./configure [options]
$ make target
```

(remark: `make` alone prints a list of acceptable targets)

Today we will only compile `pw.x` program to speed-u, hence:

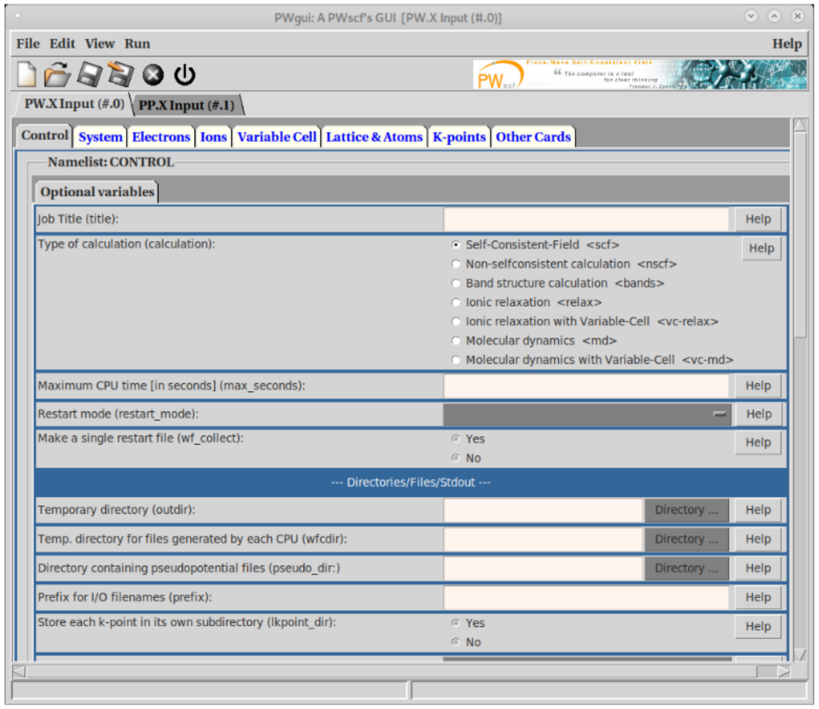
```
$ ./configure
$ make pw
```

... and wait for a while as compilation takes some time. If all went OK, the compiled `pw.x` program (along with some other executables) is now located in `bin/` directory.

Preparation of Quantum ESPRESSO input files

A few tools are available that aid at editing 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 the QE sub-directory `GUI/QE-modes/Doc/user_guide.pdf`



Namelist: CONTROL

Optional variables

Job Title (title):

Type of calculation (calculation): [✓ Self-Consistent-Field <scf>] Non-selfconsistent calculation <nscf> Band structure calculation <bands> Ionic relaxation <relax> Ionic relaxation with Variable-Cell <vc-relax> Molecular dynamics <md> Molecular dynamics with Variable-Cell <vc-md>

Maximum CPU time [in seconds] (max_seconds):

Restart mode (restart_mode):

Make a single restart file (wf_collect): Yes No

--- Directories/Files/Stdout ---

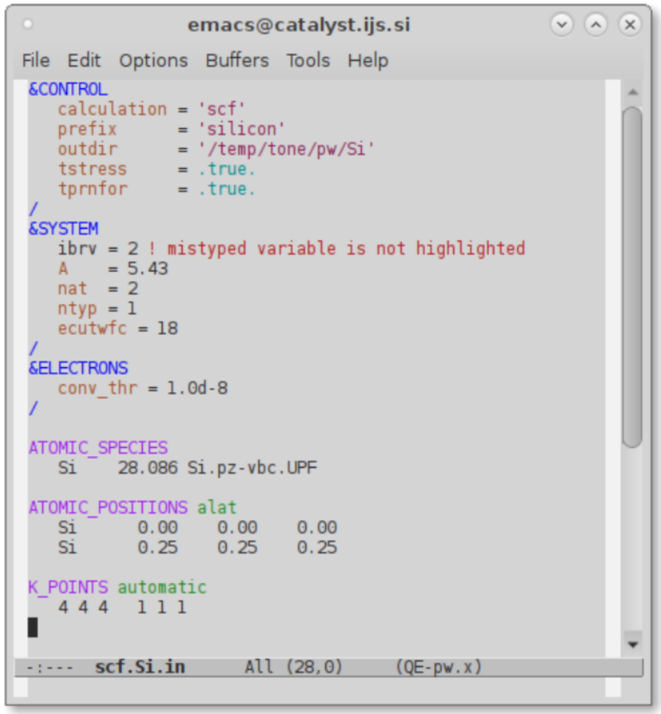
Temporary directory (outdir):

Temp. directory for files generated by each CPU (wfcdir):

Directory containing pseudopotential files (pseudo_dir:)

Prefix for I/O filenames (prefix):

Store each k-point in its own subdirectory (lkpoint_dir): Yes No



```
&CONTROL
   calculation  = 'scf'
   prefix       = 'silicon'
   outdir       = '/temp/tone/pw/Si'
   tstress      = .true.
   tprnfor      = .true.
/
&SYSTEM
   ibrv = 2 ! mistyped variable is not highlighted
   A    = 5.43
   nat  = 2
   ntyp = 1
   ecutwfc = 18
/
&ELECTRONS
   conv_thr = 1.0d-8
/

ATOMIC_SPECIES
   Si     28.086 Si.pz-vbc.UPF

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

-:---  scf.Si.in      All (28,0)      (QE-pw.x)
```

About QE-emacs-modes

`QE-emacs-modes` package provides syntax highlighting, auto-indentation, and several utility commands, in particular:

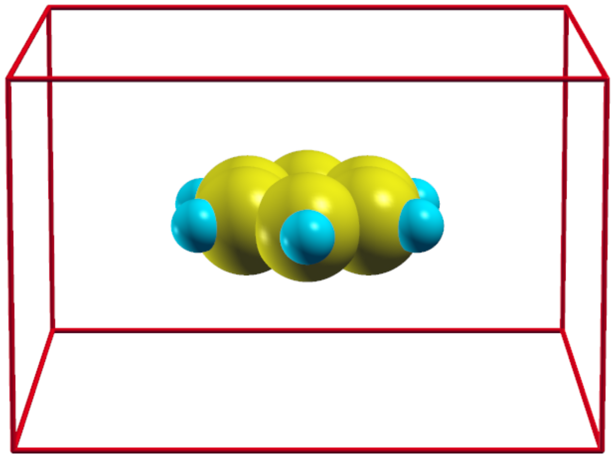
- `Alt-x` *`prog`*`-insert-template` – inserts a respective input file template
- `Alt-x` *`prog-NAMELIST`* – inserts a blank namelist named *NAMELIST*
- `Alt-x` *`prog-CARD`* – inserts a blank namelist named *CARD*
- `Alt-x` *`prog-variable`* – inserts a namelist variable named *variable*
- `Alt-x` *`prog`*`-mode` – toggles the respective mode
- `Alt-x indent-region` – indents region

where

- *`prog`* is one of `qe`, `pw`, `neb`, `cp`, `ph`, `ld1`, or `pp` (these stands for `pw.x`, `neb.x`, ... Quantum ESPRESSO (QE) programs)
- *`NAMELIST`* is the uppercase name for a given QE namelist
- *`CARD`* is the uppercase name for a given QE card
- *`variable`* is the lowercase name for a given namelist variable

1. How to describe a molecule with Quantum ESPRESSO

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

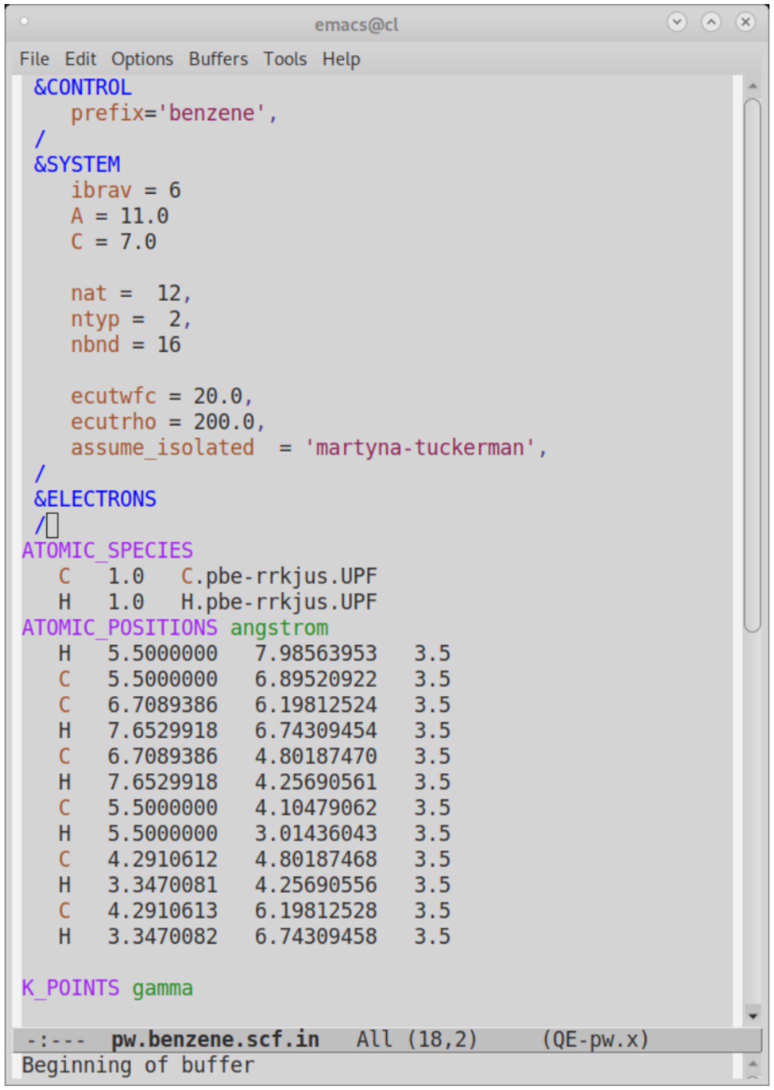


- move to `Day-1/example1.benzene/` directory
- look at the input file `pw.benzene.scf.in`. It is composed of three "namelists" `&CONTROL` (note that `calculation ='scf'` is the default value), `&SYSTEM`, `&ELECTRONS`, followed by three "cards" `ATOMIC_SPECIES`, `ATOMIC_POSITIONS`, `K_POINTS`
- instructions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

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

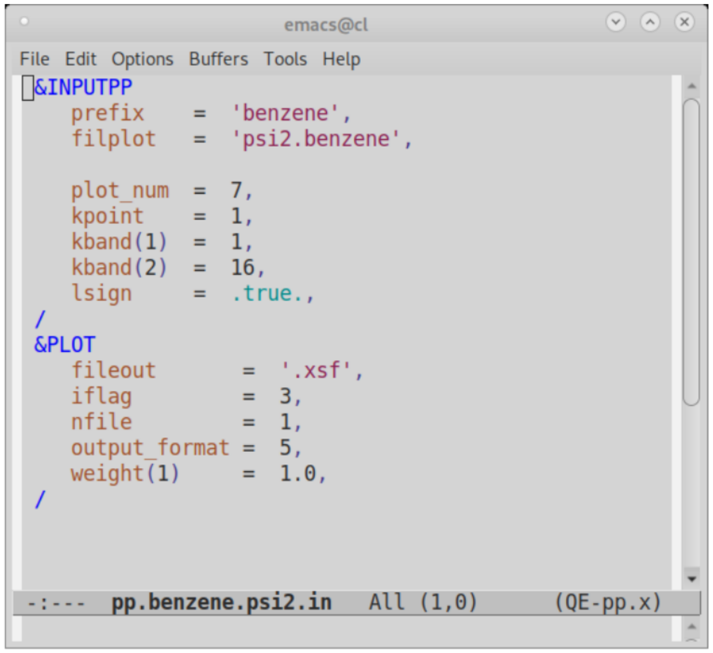
1. How to calculate and plot molecular orbitals

Here are the two needed input files for calculation of molecular orbitals of benzene (actually, $\mathrm{sign}(\psi(\boldsymbol{r}))|\psi(\boldsymbol{r})|^2$), opened with `emacs` using `QE-emacs-modes`:



```
 &CONTROL
    prefix='benzene',
 /
 &SYSTEM
    ibrav = 6
    A = 11.0
    C = 7.0

    nat =  12,
    ntyp =  2,
    nbnd = 16

    ecutwfc = 20.0,
    ecutrho = 200.0,
    assume_isolated  = 'martyna-tuckerman',
 /
 &ELECTRONS
 /
ATOMIC_SPECIES
   C   1.0    C.pbe-rrkjus.UPF
   H   1.0    H.pbe-rrkjus.UPF
ATOMIC_POSITIONS angstrom
   H   5.5000000   7.98563953   3.5
   C   5.5000000   6.89520922   3.5
   C   6.7089386   6.19812524   3.5
   H   7.6529918   6.74309454   3.5
   C   6.7089386   4.80187470   3.5
   H   7.6529918   4.25690561   3.5
   C   5.5000000   4.10479062   3.5
   H   5.5000000   3.01436043   3.5
   C   4.2910612   4.80187468   3.5
   H   3.3470081   4.25690556   3.5
   C   4.2910613   6.19812528   3.5
   H   3.3470082   6.74309458   3.5

K_POINTS gamma
```

```
-:---  pw.benzene.scf.in   All (18,2)     (QE-pw.x)
Beginning of buffer
```



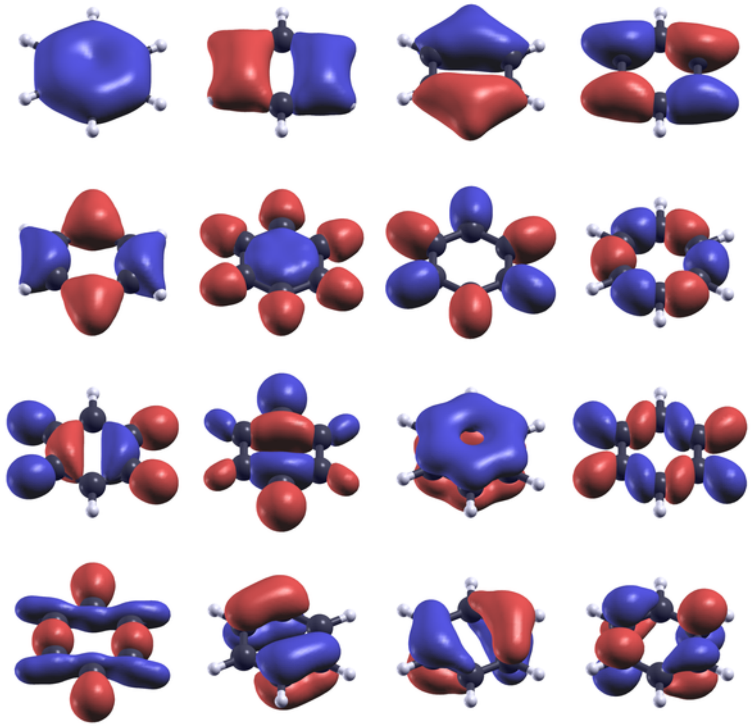
```
&INPUTPP
   prefix     =  'benzene',
   filplot    =  'psi2.benzene',

   plot_num   =  7,
   kpoint     =  1,
   kband(1)   =  1,
   kband(2)   =  16,
   lsign      =  .true.,
/
&PLOT
   fileout        =  '.xsf',
   iflag          =  3,
   nfile          =  1,
   output_format  =  5,
   weight(1)      =  1.0,
/
```

```
-:---  pp.benzene.psi2.in   All (1,0)      (QE-pp.x)
```

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:

- calculate Kohn-Sham states with `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`



See `README.md` for detailed instructions.

1. How to plot molecular orbitals with xcrysden

- Execute in the terminal:

```
$ pw.x < pw.benzene.scf.in > pw.benzene.scf.out
$ pp.x < pp.benzene.scf.in > pp.benzene.scf.out
```

  The resulting molecular orbitals (i.e., $\mathrm{sign}(\psi(\boldsymbol{r}))|\psi(\boldsymbol{r})|^2$) are written to `psi2.benzene_*.xsf`

- Plot one of the generated XSF files with `xcrysden`, e.g.:

```
$ xcrysden --xsf psi2.benzene_K001_B006.xsf
```

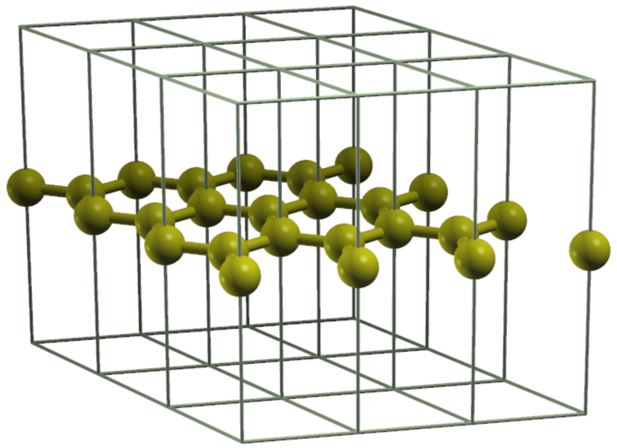
  and follow these instructions:
  - use the menu `Tools-->Data Grid`; a new window opens, press `[OK]`
  - an isosurface-control window appear; specify the `Isovalue`, say `0.005` and press `[Submit]`
  - click the `Render +/- isovalue` radiobutton and again press `[Submit]`
  - rotate and zoom the structure according to your preference
  - save the displayed *state* via the menu `File-->Save Current State` (e.g., save to `my-display.xcrysden`)
  - try this with other orbitals, e.g.:

```
$ xcrysden --xsf psi2.benzene_K001_B005.xsf --script my-display.xcrysden
```

- To plot all orbitals, execute: `./plot-psi2.sh`

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)

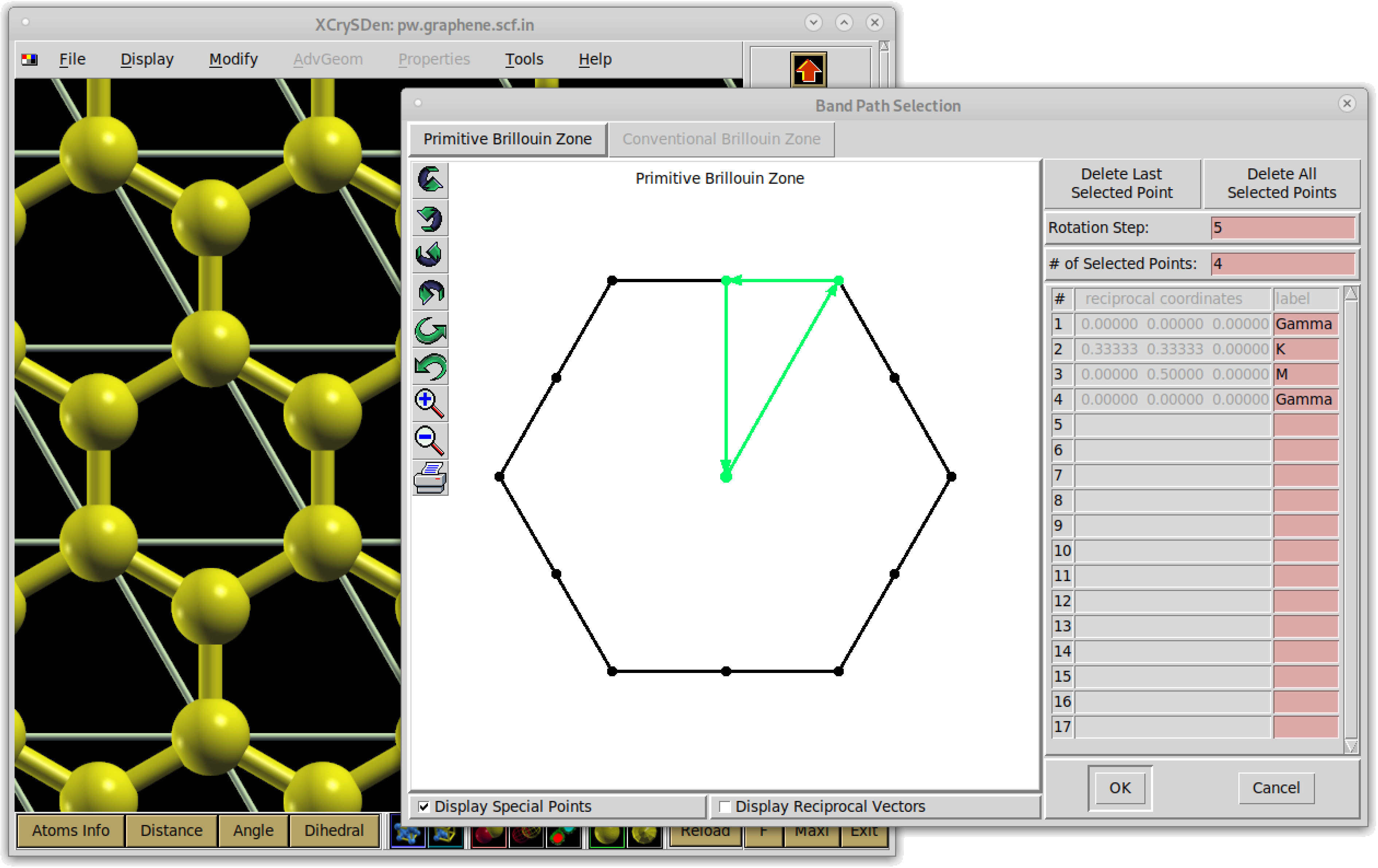
- DOS is typically calculated by a `pw.x` SCF calculation followed by a `pw.x` non-SCF calculation (`calculation = 'nscf'`) with a denser k-point grid, and finally using `dos.x` post-processing code.

- 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



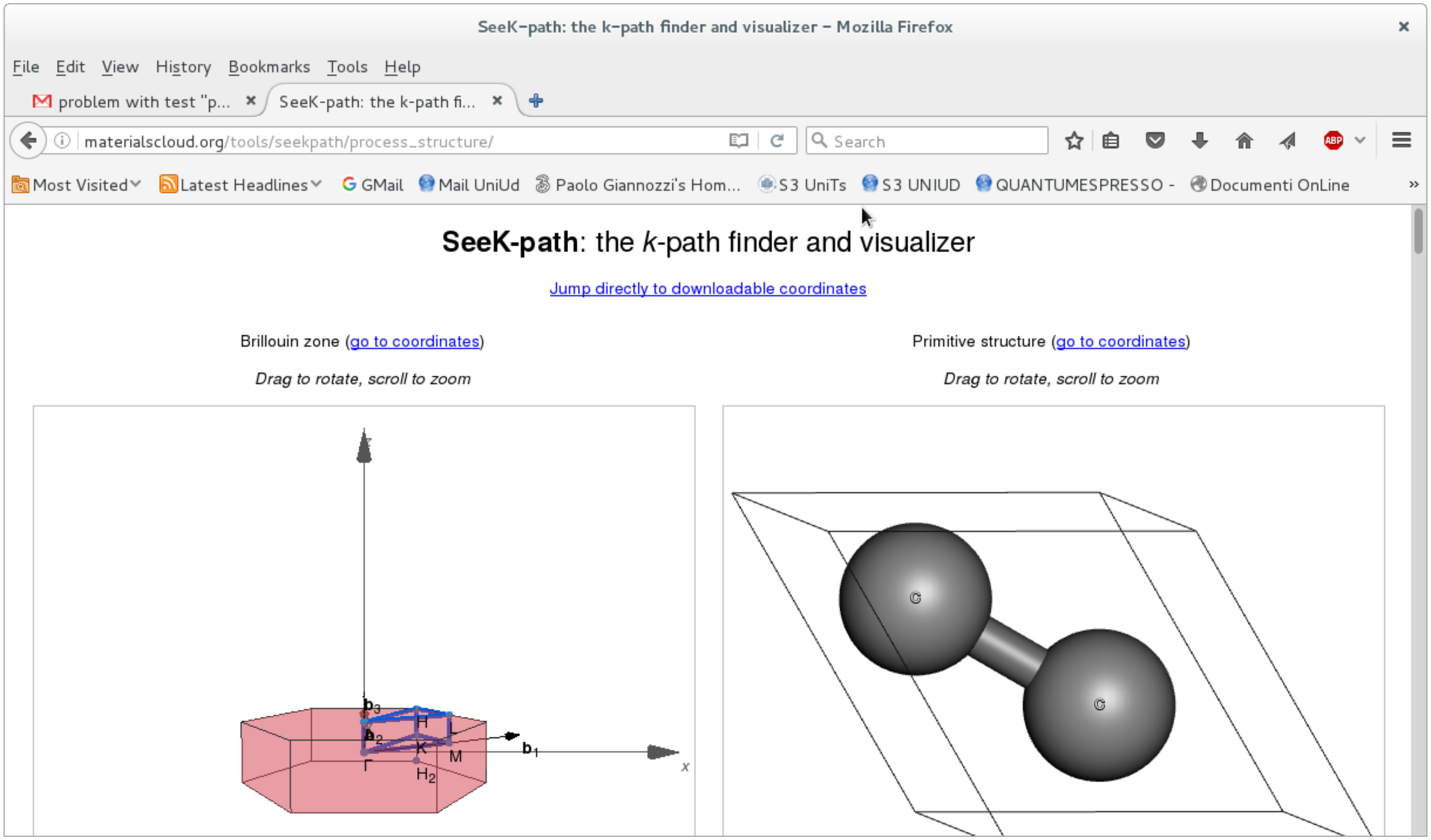
Rotation Step: 5

# of Selected Points: 4

#	reciprocal coordinates	label
1	0.00000 0.00000 0.00000	Gamma
2	0.33333 0.33333 0.00000	K
3	0.00000 0.50000 0.00000	M
4	0.00000 0.00000 0.00000	Gamma
5		
6		
7		
8		
9		
10		
11		
12		
13		
14		
15		
16		
17		

(**important:** to save k-path in Quantum ESPRESSO format, explicitly specify the `*.pwscf` extension)

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


SeeK-path: the k-path finder and visualizer – Mozilla Firefox

File Edit View History Bookmarks Tools Help

problem with test "p... SeeK-path: the k-path fi...

materialscloud.org/tools/seekpath/process_structure/

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SeeK-path: the *k*-path finder and visualizer

Jump directly to downloadable coordinates

Brillouin zone (go to coordinates)

Drag to rotate, scroll to zoom

Primitive structure (go to coordinates)

Drag to rotate, scroll to zoom

3. Bulk system: Silicon

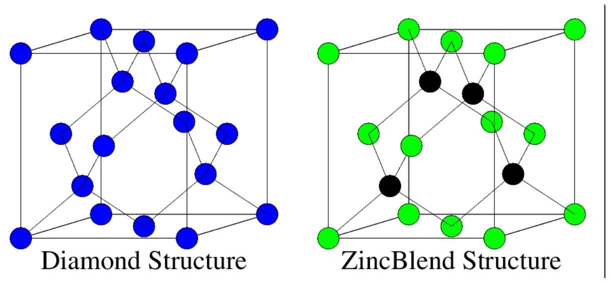
Self-consistent calculation (and a series of tests) for Silicon in the diamond structure:

- 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` environmental 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: the 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 axes, 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 the `K_POINTS` card. One has to choose

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

- If a list is chosen: provide a 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 an 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
```

(to see only these files, you may need to use `ls $ESPRESSO_TMPDIR/silicon.*`)

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. the kinetic energy cutoff

The kinetic energy cutoff `ecutwfc` (in Ry) determines the size of the Plane-Wave (PW) basis set used to expand wave-functions (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. collect 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)

To make convergence tests easier and faster, scripts are commonly used. To this end, Unix shell-scripts have been traditionally used, yet there are other more "fancy" alternatives, e.g., PWTK scripts.

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

PWTK scripting: basics

The 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
```

PWTK scripting: basics

- PWTK scripts 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 in 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 "
```

- the 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 in the `ATOMIC_SPECIES` card.

- PWTK script are case sensitive, i.e., `CONTROL { ... }` is OK, but `control { ... }` is not; namelist variables are also case sensitive!

- namelist **variables can be set on-the fly** (we will use this heavily)

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

- 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 a *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' }
  ```

- to unset a namelist variable, set it to an empty-value; for example to unset the `outdir` variable, use:

  ```
  CONTROL { outdir = }
  ```

- today we will use the following PWTK functions:
  - `load_fromPWI` – loads input data from an existing `pw.x` input file
  - `::pwtk::pwo::totene` – returns the converged total energy from `pw.x` output
  - `seq` – like the Unix `seq` command (returns a sequence of numbers)
  - `runPW` – constructs `pw.x` input file and runs a calculation
  - `runPP` – similar as `runPW` but for the `pp.x` program
  - `runDOS` – ... for the `dos.x` program
  - `runPROJWFC` – ... for the `projwfc.x` program

- the PWTK web-site is:
  `http://pwtk.ijs.si/` or `http://pwtk.quantum-espresso.org/`

- PWTK documentation is available at:
  `http://pwtk.ijs.si/toc_index.html`

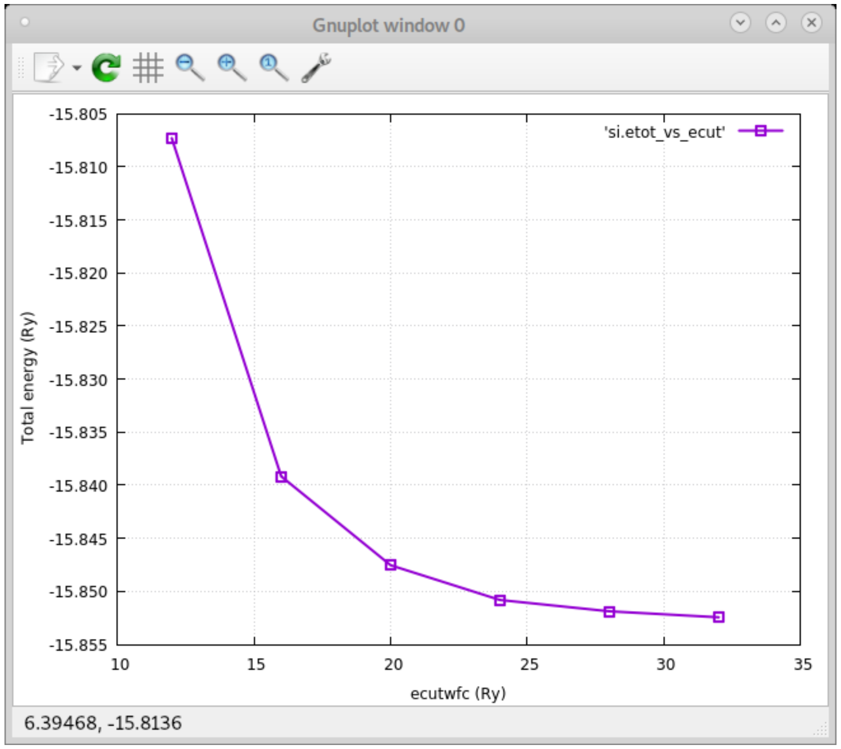
Convergence w.r.t. the kinetic energy cutoff (III)

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

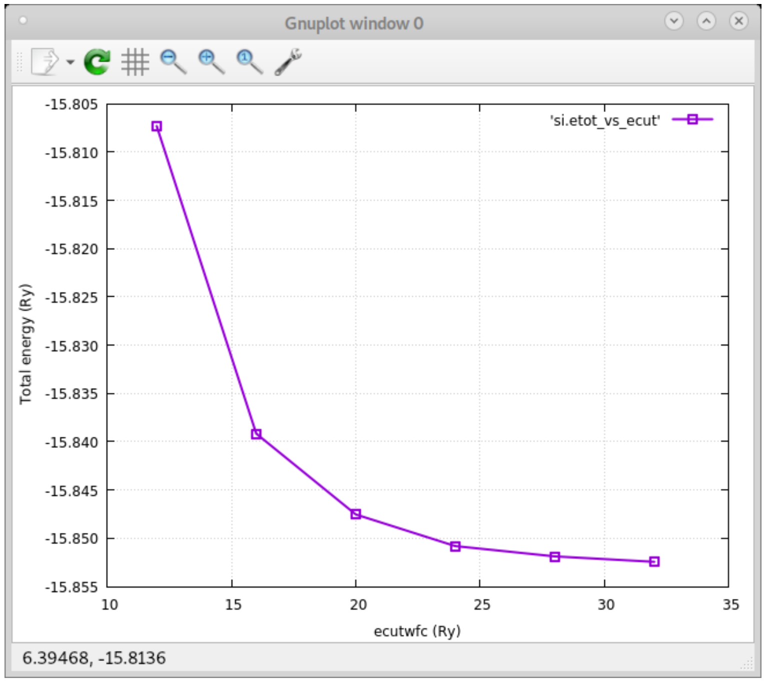
```
$ ./ecutwfc.sh
```

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

```
$ pwtk ecutwfc.pwtk
```



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



Reminder:

- Convergence w.r.t the cutoff is a property of the *pseudopotential(s) used*.
- Convergence of the *absolute energy* is typically slower than convergence of *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 the `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 a run `pw.x` calculation for each value of `nk1=nk2=nk3`.

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 the `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" (see: D.J. Chadi and M.L. Cohen, Phys. Rev. B **8**, 5747 (1973))

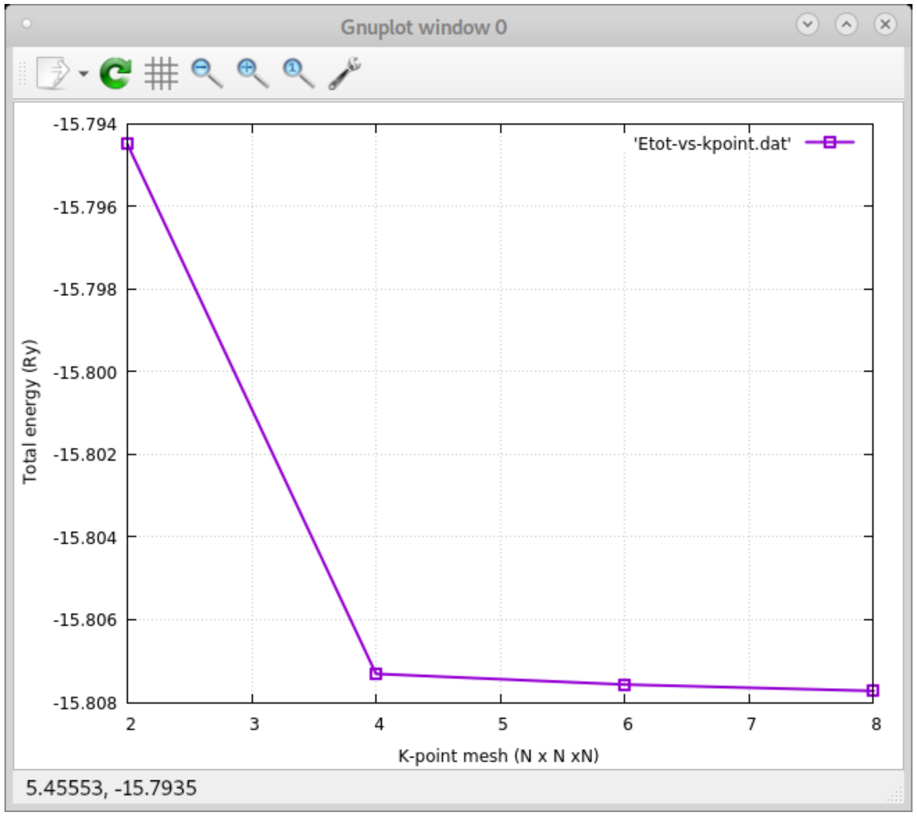
Convergence w.r.t. k-points (III)

The 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 `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:

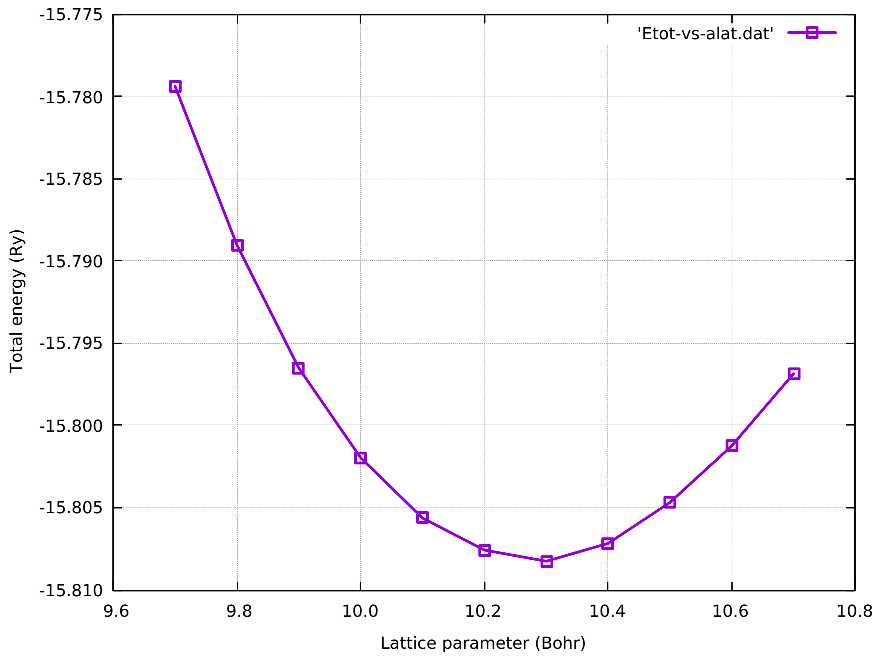
```
load_fromPWI pw.si.scf.in

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:

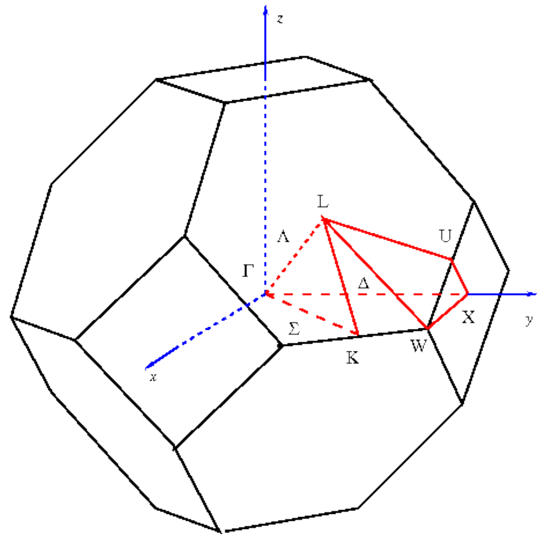
$$\begin{array}{ll} a_1 & E(a_1) \\ a_2 & E(a_2) \\ a_3 & E(a_3) \\ \ldots & \end{array}$$

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 the spaghetti plot

Important: `outdir` and `prefix` must be the same for "bands" and "scf" `pw.x` calculations and for the `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 the 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:

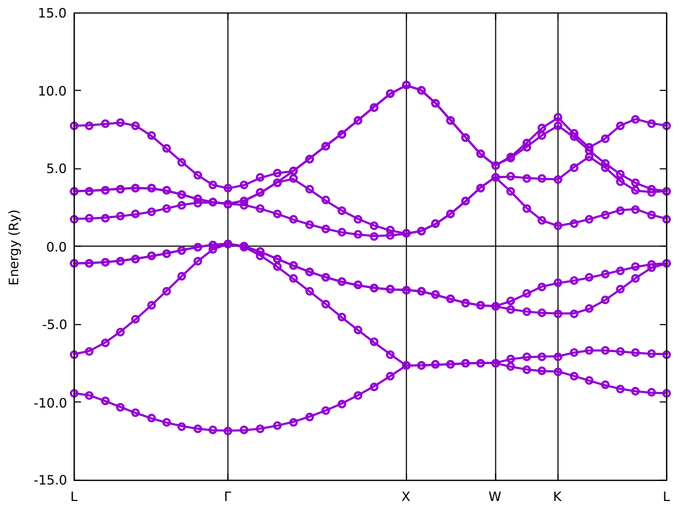
```
   $ pw.x -in pw.Si.scf.in > pw.Si.scf.out
   $ pw.x -in pw.Si.bands.in > pw.Si.bands.out
   $ pw.x -in bands.Si.in > bands.Si.scf.out
```

but we will 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 the 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 `Si.bands.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, only valence bands 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
```

- in the output file notice 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:

- `smearing` variable, possible values: `'gauss'` (or `'g'`), `'marzari-vanderbilt'` (or `'m-v'`), `'methfessel-paxton'` (or `'m-p'`)
- `degauss` variable, 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:

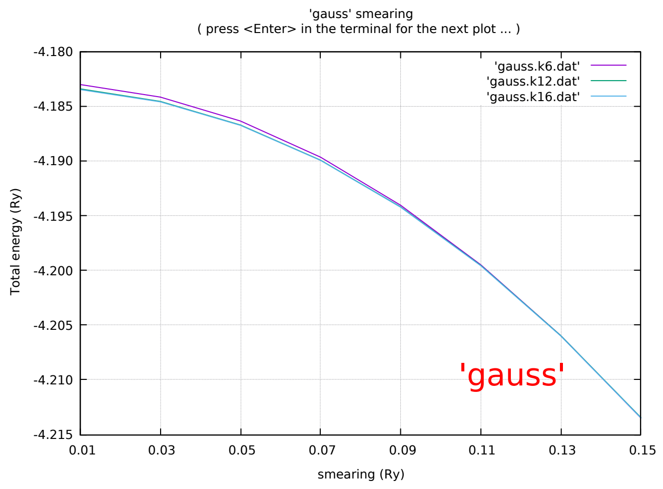
```
foreach nk {6 12 16} {
    foreach smear {'gauss'  'm-p'  'm-v'} {
        foreach degauss [seq 0.01 0.02 0.15] {
            SYSTEM " smearing = $smear
                     degauss  = $degauss "
            K_POINTS automatic "$nk $nk $nk   1 1 1"
            runPW pw.Al.scf.$nk.$smear.$degauss.in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

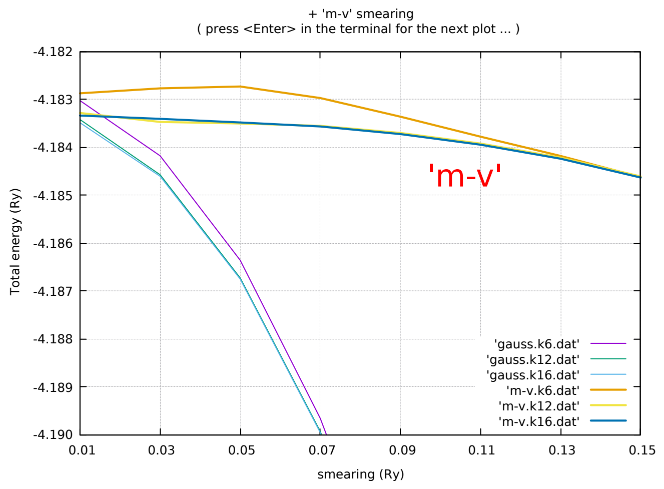
Convergence with respect to k-points, degauss, and smearing (II)

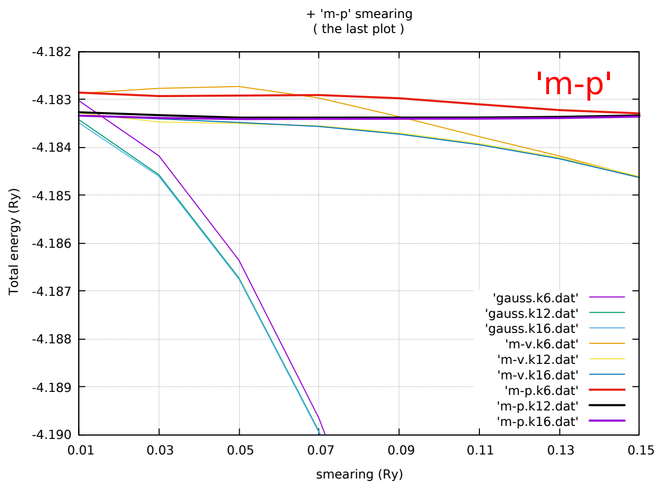
- move to `Day-1/example4.Al/ex1.degauss` directory
- execute: `pwtk degauss.pwtk`

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` ~ 0.01 to 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 the valence and the all electron charge density (the latter requires PAW a potential and a very large cutoff energy)

- move to `Day-1/example4.Al/ex2.chdens` directory (*chdens* is an acronym for charge-density)
- execute: `pwtk 1-chdens.pwtk`
  this script calculates and "plots" the valence charge density; notice that the electron charge is located mainly in interstitial regions (due to the use of a pseudo-potential, there is *almost no* charge in close vicinity of nuclei; see next page);
- the scheme to calculate and plot the 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 `xcrysden` (let's plot density in contour/colorplane style; follow the instructions of tutor and select density range from `0.0` to `0.05`)

How to plot charge-density (II)

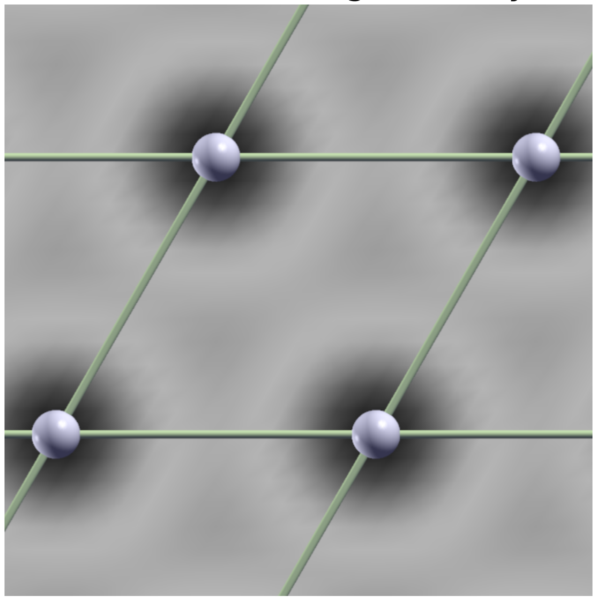
- to calculate all-electron **valence** and **total** charge densities, execute:

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

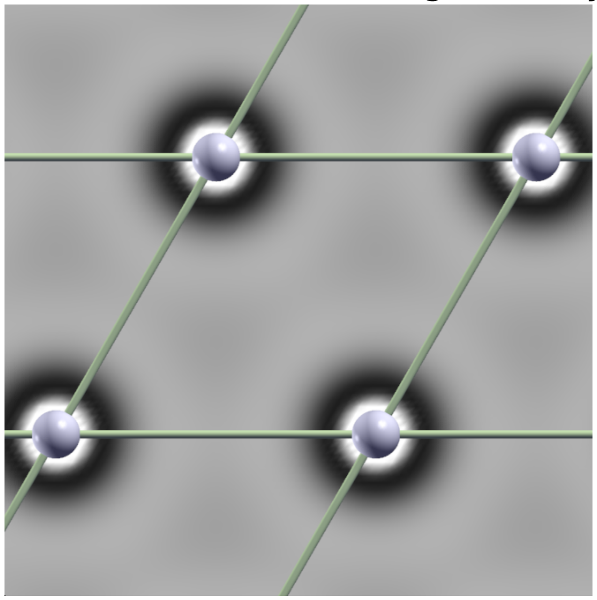
  (note that `plot_num=17` for all-electron valence density and `plot_num=21` for all-electron total density)

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

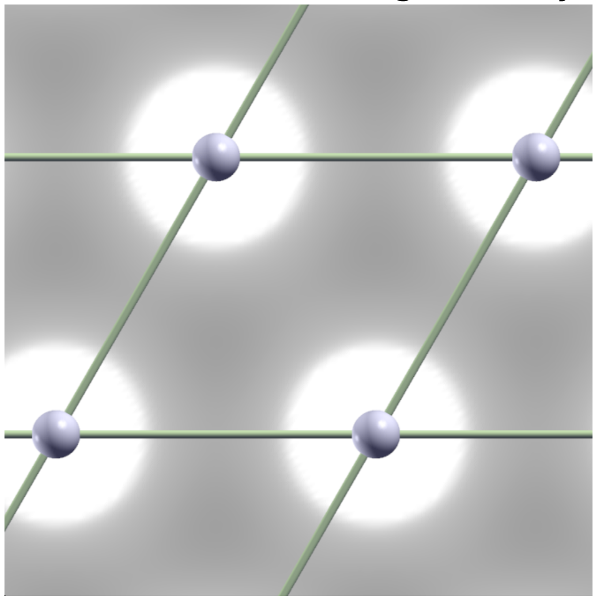
PP valence charge density



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 an 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` $> 4\times$`ecutwfc` (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 antiferromagnetic

- 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 a higher $dual$ (i.e. better description of augmentation charge) the normal behavior is observed.

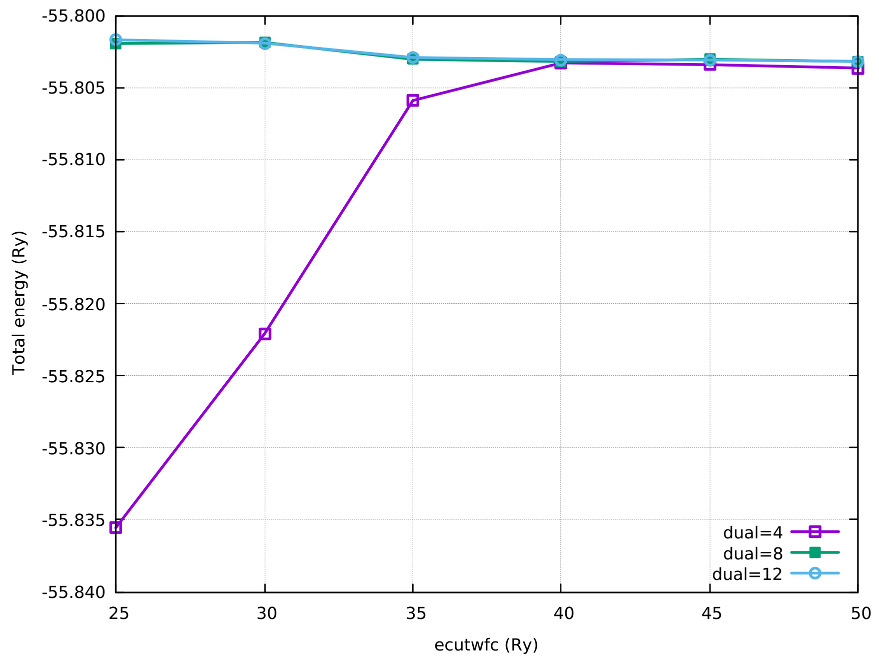
The corresponding PWTK snippet is:

```
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 curves for $dual = 8$ and 12 almost coincide)



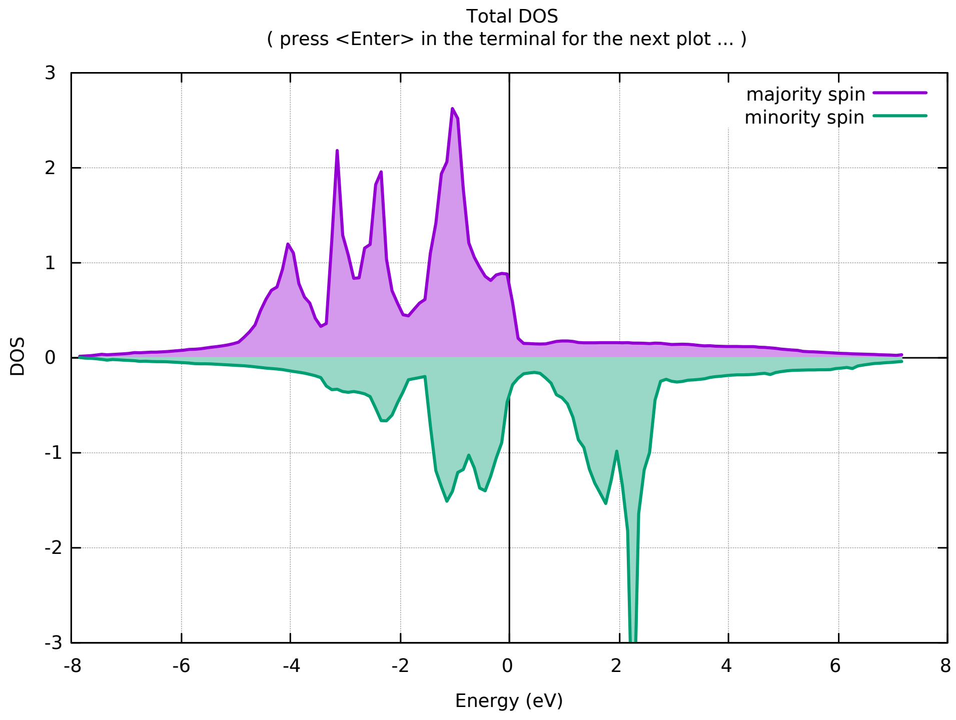
Homework: for converged values of both cutoffs and k-points, you may compare the stability of iron in the bcc, fcc, hcp phases (the latter being a slightly more complicated structure)

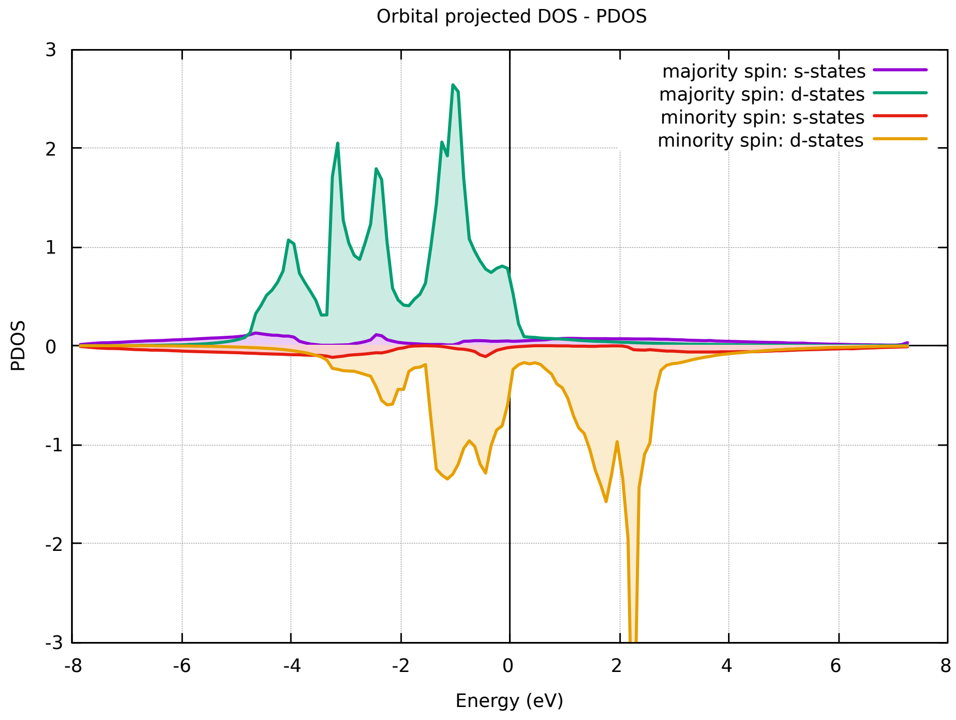
Density of States (DOS) and Projected DOS (PDOS)

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 in the preceding SCF calculation
   - a denser k-point mesh is specified
   - in this example the *linear tetrahedron method* is used (variable `occupations='tetrahedra'`)
3. a `dos.x` calculation to calculate DOS (DOS is written to a file as specified by the `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, inputs are also very similar; you can compare them as:

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

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

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