First steps with a periodic DFT code : Quantum Espresso

The Quantum Espresso distribution comes with an examples subdirectory where several scripts and reference results are collected. If $espresso_dir is the directory were the distribution is located (espresso-4.3.1 in the $home/QE/ directory for instance) the example directory is simply $espresso_dir/examples

```
% ls  $espresso_dir/examples
autopilot-example       example05  example18  example32     Recover_example
check_failure.sh        example06  example19  example33     Restart_example
CLS_FS_example          example07  example20  example34     run_all_examples
CLS_IS_example          example08  example21  example35     save_results
cluster_example         example09  example22  example36     VCSexample
daily_test              example10  example23  example_vwdDF WAN90_example
dipole_example          example11  example24  EXX_example   WannierHam_example
environment_variables   example12  example25  GRID_example  WorkFct_example
ESM_example             example13  example26  GWW_examples  XSpectra_example
example01               example14  example27  log
example02               example15  example29  make_clean
example03               example16  example30  QExml_example
example04               example17  example31  README
```

Here we describe in detail the study of the adsorption of a CO molecule on the Pt (100) surface.

This study will allow to review the different phases needed in a generic project:

- determination of the electronic structure of a simple molecule

- building of the fundamental Bravais lattice of a 3D crystalline solid

- convergence of the total energy and geometrical optimization of a chemical system

- determination of the bulk modulus of a 3D solid,

- building of a slab model for a surface

- determination of the surface energy

- study of the surface reconstruction

- characterization of adsorption sites, calculation of vibrational frequencies

- electronic structure analysis (DOS, pDOS, band-structure, charge density)

The chosen system is deliberately small so that all the relevant phases needed in the study are relatively fast and can be studied in detail.

A similar tutorial has been developed for Vasp

Let's start by the study of an isolated CO molecule.

We can create a working directory for this example by

% mkdir CO

and move in it by

% cd CO

The directory is initially empty as can be verified by

% ls

Input structure in Quantum Espresso pw.x / cp.x codes

The main Quantum Espresso [QE] codes, pw.x (Plane Wave Self-Consistent Field) and cp.x (Car-Parrinello), share a common input structure and a common way of storing data for further post-processing analysis and/or additional calculation like in the study of vibrational properties or nuclear magnetic resonance via Density Functional Perturbation Theory [DFPT].

This single input file is organized in a number of namelists and input cards.

Some of the namelists are mandatory and define the main flow of the calculation and the I/O control (&control namelist), the system under study (&system namelist), the strategy used to optimize the electrons (&electrons namelist); some of the namelists are optionals and are used when ions (&ions) and/or the cell (&cell namelist) are optimized.

Three input cards are mandatory and are used to define

ATOMIC_SPECIES

ATOMIC_POSITIONS

K_POINTS

A full description of the the input for pw.x can be found in $espresso_dir/Doc/INPUT_PW.html.

An example for a single point calculation of an isolated CO molecule in a simple cubic box follows

```
% cat > co.pw.in  << EOF
&CONTROL
 calculation  = "scf",   ! single point calculation (default, could be omitted)
 prefix  = "CO",    ! all auxiliary files will have filename beginning by prefix
 pseudo_dir  ="/directory/where/pseudopotentials/are/to/be/found"
 outdir      = "/directory/where/large/auxiliary/files/are/written/",
 tprnfor      = .true.
/
&SYSTEM
 ibrav      = 0,  ! Bravais lattice defined by user in CELL_PARAMETERS card
 celldm(1)= 1.88972687,  ! define length  unit as 1 AA= 1/0.529177 bohr
 ntyp      = 2, ! number of atomic species (see later ATOMIC_SPECIES)
 nat       = 2, ! number of atoms in the unit cell (see later ATOMIC_POSITIONS)
 ecutwfc   = 24.D0,
 ecutrho   = 144.D0,
/
&ELECTRONS
 conv_thr    = 1.D-7, ! convergence threshold on total energy , in Rydberg
/
CELL_PARAMETERS cubic
10.0  0.0  0.0
 0.0 10.0  0.0
```

```
 0.0  0.0 10.0
ATOMIC_SPECIES
O  1.00  O.pbe-rrkjus.UPF
C  1.00  C.pbe-rrkjus.UPF
ATOMIC_POSITIONS    angstrom
C  1.152  0.0  0.0
O  0.000  0.0  0.0
K_POINTS gamma
EOF
```

Variable ibrav in &system namelist define the Bravais lattice. Value ibrav=0 is used to provide the three fundamental lattice vectors in via the CELL_PARAMETERS card, as in the example above.

Values from 1 to 14 are used to select the Bravais lattice according to the following list (see INPUT_PW.html for details). The needed cell dimesions are defined via celldm(1)-celldm(6).

Celldm(1) is always the length unit (also called "a" lattice parameter or alat in the code)

```
Bravais-lattice index:

  ibrav         structure                 celldm(2)-celldm(6)

   0            "free", see CELL_PARAMETERS      not used
   1            cubic P (sc)                     not used
   2            cubic F (fcc)                    not used
   3            cubic I (bcc)                    not used
   4            Hexagonal and Trigonal P      celldm(3)=c/a
   5            Trigonal R                    celldm(4)=cos(alpha)
   6            Tetragonal P (st)             celldm(3)=c/a
   7            Tetragonal I (bct)            celldm(3)=c/a
   8            Orthorhombic P                celldm(2)=b/a,celldm(3)=c/a
   9            Orthorhombic base-centered(bco) celldm(2)=b/a,celldm(3)=c/a
  10            Orthorhombic face-centered    celldm(2)=b/a,celldm(3)=c/a
  11            Orthorhombic body-centered    celldm(2)=b/a,celldm(3)=c/a
  12            Monoclinic P                  celldm(2)=b/a,celldm(3)=c/a,
                                              celldm(4)=cos(ab)
  13            Monoclinic base-centered      celldm(2)=b/a,celldm(3)=c/a,
                                              celldm(4)=cos(ab)
  14            Triclinic                     celldm(2)= b/a,
                                              celldm(3)= c/a,
                                              celldm(4)= cos(bc),
                                              celldm(5)= cos(ac),
                                              celldm(6)= cos(ab)
```

Some input cards can have many alternative formats (see INPUT_PW.html for details).

In particular atomic positions can be given in cartesian coordinates in unit of the lattice parameter alat,

in cartesian coordinates in bohr radii or in angstrom, or as fractions of the crystal lattice vectors

```
ATOMIC_POSITIONS { alat | bohr | angstrom | crystal }
```

Similarly K-points can be given in cartesian coordinates in unit of 2pi/alat (tpiba), as an automatically generated grid of points, as fractions of the reciprocal lattice vectors, just the gamma point (as in the example above) or in special formats useful to calculate electronic band structure along high symmetry

lines.

```
K_POINTS { tpiba | automatic | crystal | gamma | tpiba_b | crystal_b }
```

Pseudopotentials: where to find them ?

Verify that the directories defined in pseudo_dir and outdir are correctly set and that pseudo_dir contains the two pseudopotential defined in the input.

You are ready to run the pw.x calculation.

How to submit your QE calculation ?

To run the code interactively with the above input saving the output in a file named co.pw.out issue the command

```
% pw.x < co.pw.in > co.pw.out
```

The executable is located in $espresso_dir/bin. This directory has been added to the path in .bashrc

In general you may need to specify the full path when calling the execulatable.

To run the code in background "Ctrl-z" and then "bg" or submit it with and "&" at the line end

```
% pw.x < co.pw.in > co.pw.out &
```

To see if the job is runnig: "qstat -f", or "top"

```
%qstat -f
```
(see instruction on "Linux & installation")

Output

The main output of the code is sent to the standard output (redirected in the example above to file co.pw.out). Additional files are created (with name beginning with the specified prefix) in the directory define in the outdir variable.

```
% ls /directory/where/large/auxiliary/files/are/written/
CO.save  CO.wfc
```

Edit the output file and look for the way the input data have been reported on output.

In particular search for

– cutoff energies, XC functional used

– system definition (cell, number of atoms, their positions)

– pseudopotential information (norm-conserving ? ultra-soft ? paw ?)

– k-point sampling

Find the final self-consistent total energy searching "convergence has been achieved".

An alternative way to find the final self-consistent energy is by looking for the single line beginning with an exclamation mark in the output.

```
% grep -e !  co.pw.out
```

Because tprnfor=.true. was defined in &control namelist the code computed the forces even if only a single point calculation was defined. By examining the forces displayed in output at the end of the scf prcocedure, given in Ry/Bohr units(1 Ry/Bhor = 25.71 eV/A), it can be seen that the molecule is not in its equilibrium structure.

Optimization of the structural properties

Copy file co.pw.in to co.rx.in and etid this one to define calculation="relax" in &control namelist and add an additional, empty, &ions namelist after the &electron one. All other input parameters can be left unchanged (tprnfor=.true. can be removed as it is automatically implied by the relaxation request).

Relaxation algorithms implemented in pw.x

By default when calculation="relax" the relaxation is performed using the BFGS quasi-Newton algorithm (ion_dynamics='bfgs'). This algorithm does not require additional variables. Relaxation proceeds until subsequent total energy evaluations differ by less than 1.0d-4 Ry and each force component is less than 1.0d-3 Ry/bohr. These dedault values can be changed by defining variables

etot_conv_thr and forc_conv_thr in &control namelist, respectively.

Another minimization strategy that is implemented in the pw.x is damped dynamics (ion_dynamics='damp') where atoms move according to Newton equation (Verlet algorithm) with the additional condition that at each time step velocity components orthogonal, or anti-parallel, to forces are projected out thus removing energy from the system..

This algorithm require also the definition of a time step (variable dt in &control namelist) and make use of the masses defined in the ATOMIC_SPECIES card.

For both relaxation algorithms some components of the atomic positions can be fixed by adding three integer values (0/1) after the atomic coordinates. A value of 1 means that the coresponding componet is left free to vary, a value of 0 means that component is fixed.

For instance in the CO example the following lines

```
ATOMIC_POSITIONS    angstrom
C  1.152  0.0  0.0    1 0 0
O  0.000  0.0  0.0    0 0 0
```
mean that only the x component of the carbon atom is allowed to relax, all other component are fixed.

NB: if atomic coordinates are given in crystal units, the constraints are applied to this set.

More elaborated type of constraints are compatible with damped dynamics, check file $espresso_dir/Doc/INPUT_PW.html

To run the relaxation

% pw.x < co.rx.in > co.rx.out

This run will use the same outdir as the previous one, with the same prefix. Existing files will be therefore overwritten. If you wish to keep them just use a different outdir directory or define a different prefix.

Analyze the output file: how many minimization steps have been performed?

Compare the optimized C-O distance with the experimental results for the molecule in the gas phase (1.14 A). d(CO)th = _____A.

Convergence tests

As in the determination of the ground state of any system we need to check that the results are converged with respect to several thecnical parameters:

- the completeness of the plave wave expansion (parameters ecutwfc and ecutrho in &system)

- the completeness of the Brillouin zone sampling (K_POINTS card)

- la possibility of magnetism in the system

- the converge threshold in structural optimization (etot_conv_thr, forc_conv_thr)

All these parameters have to be verified by repeating the calculation by varying the parameters one by one.

a) Convergence with respect to cutoff

Previous calculations have been done with a cutoff for the wavefunctions of 24 Ry and a cutoff for the density of 144 Ry. If ecutrho is not specified it is assumed to be 4 times the cutoff used for the wavefunctions because this is the minimum needed to expand correctly the square wavefunctions.

In general an higher cutoff for the density can be necessary because *i)* an ultra-soft pseudopotential is used with localized augmentation charges, *ii)* integrals needed to evaluate exchange-correlation energy and potential can involve higher order powers of the density.

In order to determine the optimal working values of ecutwfc and ecutrrho one can proceed as follows.

In a first phase monitor the convergence of the interesting quantity (total energy, structural property, stress on the cell) with respect to ecutwfc keeping ecutrho at its default value (4 x ecutwfc). This will define an ecutrho large enough that all the higher order Fourier components introduced by the augmentation charges and/or the xc functional are integrated correctly. Keeping fixed the so determined value for ecutrho one can then attempt to reduce the value of ecutwfc to see if a smaller plane-wave basis set can be used for the wavefunction.

The needed value of ecutwfc and ecutrho depend in general on the pseudopotential used and one needs to choose values that are good for all atomic species that are present in the calculation.

b) Convergence with respect to K point sampling

The k-point sampling is very important. However in the current case we are interested in describing an isolated molecule, hence periodic replicas should not interact and gamma point sampling ought to be sufficient. If periodic images do interact, as shown by a significant volume dependence of the results, we rather need to chose a larger super-cell to decouple them.

c) Is magnetism relevant in my system ?

Calculations performed so far have been made assuming a spin compensated system with no magnetism.

In order to check this we can repeat the calculation with spin polarization switched on

nspin=2 in &system namelist

In addition one needs to allow partial occupation of the electronic levels defining

occupations = 'smearing', smearing = 'gaussian', degauss=0.001 (&system namelist) and

break the up-down symmetry by defining starting_magnetization(1)=0.7 (&system namelist) .

Other smearing choices are possible and are more convenient when dealing with real metals.

In the case of the molecule it will be found that magnetization is not relevant.

Isolated C and O atoms however have open shells and in the calculation of their energy inclusion magnetization is relevant.

Energy for isolated atoms :

C (npsin=1) = _____Ry . O (nspin=1) = _____Ry
C (nspin=2) = _____Ry . O (nspin=2) = _____Ry

Howework. Chose another set of pseudopotentials, corresponding to a exchange-correlation functional and repeat the study.

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Structural optimization of a 3D crystal: fcc Pt

Platimun crystallize at ambient conditions in the face centered cubic (fcc) lattice (space group Fm3m n°225) . The lattice parameter is a = 3,924 A.

The input file pt.pw.in can be found in the directory $home/QE/Pt you can copy in your working directory.

% cp $home/QE/Pt/pt.pw.in .

The pseudopotential file is not present in the pseudodirectory but can be downloaded from the QE website with the command

```
wget -O ./Pt.pbe-nd-rrkjus.UPF \
  http://www.quantum-espresso.org/pseudo/1.3/UPF/Pt.pbe-nd-rrkjus.UPF
```

Remember to move the file in the directory used to store pseudopotentials (for instance $home/QE/espresso-4.3.1/pseudo)

The structure can be visualized using XcrysDen

% xcrysden --pwi pt.pw.in

Examining the input fill the following information

type and number of k-points used ? _____

how many atoms are optimized ?_____

What is the cutoff used ?_____

How to determine the equilibrium structure of fcc Pt crystal ?

In this system with one atom per unit cell and cubic symmetry only the cell volume needs to be optimized. The simples way to optimize the cell in this case is to perform a number (about 10) of single point calculations around an estimated lattice parameter and fit the results with an equation of state or a parabolic fit.

Typically about 10 calculations in a range of +/- 5-10 % around the equilibrium geometry are sufficient.

This can be done manually or via a script like the one that can be found in the directory Pt

copy it to your working directory and run it

% sh ./run_eos

In the script use is made of code ev.x that the fit an equation of state to an energy vs volume data set.

From the results of this script get and report

what is the equilibrium lattice parameter ? a_0 = _____

what is the electronic energy at the minimum E_0 ? E_0 = _____

what is the Bulk Modulus B_0 ? B_0 = _____

Convergence tests

As in the case of the CO molecule one needs to verify the convergence with respect to cutoff, k-point sampling, importance of magnetism.

a) convergence with respect the cutoff

In the script above a cutoff of 30 Ry (240 Ry for the charge) was used. Verify that the result does not change significantly when the cutoff is increased by 5-10 Ry.

b) convergence with respect to BZ sampling

The script calculated fcc Pt with set of k-points corresponding to a N x N x N regular grid with N=8, a "marzari-vanderbilt" smearing with a smearing width of 0.02 Ry.

Repeat the calculation with different sets of points corresponding to N=8,9,10,11, 12, ... report the sesults in the table below and determine what value provide a total energy convergence within 1.d-4 Ry.

GRID M&P	8x8x8	9x9x9	10x10x10	11x11x11	12x12x12
Total energy					
Number of K pts					

c) Importance of magnetic polarization ?

Repeat the calculation allowing the system to develop a magnetic polarization. (npsin=2, starting_magnetization(1)=0.7). Does the final self-consistent solution maintain a non vanishing magnetization ? Is magnetism relevant in the system ?

d) conclusion

The above convergence test should lead to the folowing results :

a = 3.998 A.

K-points: 10x10x10

E_{cut} : 30, 240

NoSpin

Homework. Repeat the same calculation for the bcc, sc, and hcp structures. Find the equilibrium parameters and the relative stability of the different structures.

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Build a repeated slab model for Pt (001) surface

In order to describe a 2D system like a surface using a 3D code like QE it is necessary to build a supercell where the desired 2D system, a slab containing a certain number of atomic planes, is repeated in the third direction interspacing a sufficient amount of vacuum so that the two surfaces do not interact significantly. In general a vacuum region of the order of 8-10 A is reasonable.

The in-plane lattice parameters are defined by the corresponding bulk calculation while in order to determine the atomic positions relaxation is necessary.

In a symmetric slab all atoms are allowed to relax and the number of layers needs to be large enough that the central layers recover the bulk properties.

Alternatively an asymmetric slab can be used where two or more layer on one side of the slab are frozen and only the opposite surface is allowed to relax. This usually allows to use a smaller number of layers to describe the surface.

In a fcc metal the (001) surface can be described by a tetragonal cell (ibrav=6) with celldm(1) equal to the bulk lattice parameter and celldm(3)=c/a large enough to account for the desired layers and the vacuum region.

For a five layer (10 atoms) slab of Pt with atoms in the ideal bulk positions the following coordinates (in celldm(1) units) apply

```
ATOMIC_POSITIONS alat
Pt 0.0 0.0  1.0
Pt 0.5 0.5  1.0
Pt 0.5 0.0  0.5
Pt 0.0 0.5  0.5
Pt 0.0 0.0  0.0
Pt 0.5 0.5  0.0
Pt 0.5 0.0 -0.5
Pt 0.0 0.5 -0.5
Pt 0.0 0.0 -1.0
Pt 0.5 0.5 -1.0
```

and a value of celldm(3) between 4 and 5 should be sufficient.

In addition to relaxation, surfaces can undergo reconstruction when the surface periodicity is modified with respect to the one that would be implied by the bulk symmetry.

Here we will start considering the effect of relaxation.

In the QE/Pt001 directory an input file can be found corresponding to a 5 layer slab with the two bottom layer frozen with the following parameters: celldm(1) = and a 8x8 2D sampling

K_POINTS automatic
8 8 1 1 1 0

NB: this is not the cell with the smallest surface periodicity that can be built !
Can you build an equivalent cell containing only one atom per layer ?

The structure can be visualized by XCrysDen
- Is this a (1x1), c(2x2) or a (2x2) surface ?
- is this a single-point or a relaxation input ?
- what is the value of vacuum used ?

run pw.x
```
% pw.x < pt001.pw.in > pt001.pw.out
```

Edit the pw001.pw.out file and analyze the forces

- Are forces oriented toward the vacuum (outward) of toward the center of the slab (inward) ?
- What is the total energy of the slab before relaxation ?

Calculate the unrelaxed surface energy by the formula
$\sigma_{unrelaxed} = 1/2(E_{surf} - N_{atoms}E_{bulk})$

Why the factor of ½ ?

Let's now relax the surface.
Modify the input as required for a structural relaxation using default thresholds.
Execute pw.x
% pw.x < pt001.rx.in > pt001.rx.out

verify that the forces on atoms are decreasing.
Did the relaxation converged ?
What is the relaxed energy ?
Analyze the displacement of each atom along z (dz = $z_{opt.}$ - z_{bulk}).

Reduce the convergence threshold on forces to forc_conv_thr = 1.d-4 and continue the relaxation.
How much does the relaxed geometry change ? And the relaxed energy ?

Calculate the relaxation energy and the relaxed surface energy.

$E_{relax.} = E_{surf. opt.} - E_{surf.}$

sigma = sigma unrelaxed + Erelax

Why the factor of ½ is missing here ?

To compare with experimental data surface energy should be expressed per unit surface area using the conversion factor $1 J/m^2 = 16.02 eV/A^2 = 0.3297 Ry/bohr^2$.

Homework. Convergence tests

Perform the convergence tests with respect to

- number of k points (10x10x1, 12x12x1 , …)

- number of layers in the cell (6, 7, 8,...)

- dimension of the vacuum layer (10 A, 12 A, ..)

Calculate how interlayer distances and surface energy converge as a function of these paramenets

Homework. Build a symmetric slab model

Repeat the calculation assuming a symmetric slab geometry where all atoms are relaxed.

As previously done for the asymmetric slab, study the convergence of the results with respect to slab thickness. Verify that the resulting relaxation patterns and surface energies are consistent with the results obtained for the asymmetric slab.

Surface reconstruction

We are not considering surface reconstruction here.

Interested readers can start looking at Ritz et al, Phys. Rev. B 56, 10518 (1996), Havu et al, Phys. Rev. B 82, 161418 (2010)

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Adsorption of CO on Pt (001) c(2x2) surface

Several possible adsorption geometry are possible for CO molecule.

Let's take our 5-layer asymmetric slab as model and let's study the vertical adsorption of CO on top of a Pt atom .

Build the imput staring from the relaxed slab geometry and taking as initial position such that distance d(Pt-C) = 2 A, d(CO) = 1.15 A, angle Pt-C-O = 180°.

Optimize the structure and report the parameter of the final geometry

d(Pt-C) : _____ , d(C-O) : _____

Compute the adsorption energy of CO@Pt(001) from the relaxed energies of the combined system and of Co and Pt(001) fragments.

$E_{ads.}$ = _____eV

Repeat the calculation considering other adsorption sites like the bridge position, the hollow site or a a top site with a molecule tilted off vertical.

In all cases relax the system and determine the optimized geometry and the adsorption energy.

What is the most favorable adsorption geometry ?

Density of state (DOS) and projected Density of States calculations.

Take CO@Pt(001) surface and after the self-consistent calculation perform a non-selfconsitent run with a denser grid of k-points in order to compute density of states.

Choose calculatin="nscf" in &control name list and, for instance,

```
K_POINTS automatic
12 12 12 0 0 0
```

Run pw.x with the resulting input, have a look at the output to find out what are good lower and upper bounds for the band energies and the value of the Fermi energy. Then run the post-processing code dos.x with the the following input


```
% cat > dos.in << EOF
 &inputpp
   outdir='$TMP_DIR/'
   prefix='co_at_pt001'
   fildos='co_at_pt001.dos',
   Emin=5.0, Emax=25.0, DeltaE=0.1
 /
EOF
```


% dos.x < dos.in > dos.out

This will produce a simple two column file containing the band energy (in eV) and the corresponding DOS (in #states/eV).

Running the projwfc.x post-processing code with the following input

```
% cat > pdos.in << EOF
 &inputpp
    outdir='$TMP_DIR/'
    prefix='co_at_pt001'
    Emin=5.0, Emax=25.0, DeltaE=0.1
    ngauss=0, degauss=0.02
 /
EOF

% projwfc.x < pdos.in > pdos.out
```

This will generate a number of files containing the density of states projected on the atomic wavefunctions associated to the various atoms in the cell.

Examining pDOS plot it is possible to identify common resonances in the density of states associated to neighboring atoms that are associated to the formation of covalent chemical bonds.

At the end of the output of the projwfc.x code information about integrated projected density of states for each atom and its angular momentum decomposition is displayed.

Band structure calculation for the clean Pt (001) surface

Run again the self consistent calculation for the Pt (001) surface in its equilibrium geometry.

Take note of the value of the Fermi energy at the end of the run.

Then modify the input defining calculation="bands" in &system namelist and defining a path connecting the G-X-M-G high symmetry points in the BZ.

[G = (0, 0,0) ; X= (0.5,0,0) ; M=(0.5,0.5,0) in unit of 2pi/a]

It is therefore practical to use the "tpiba_b" K_POINTS format for this purpose: in the card defined below four points are generated along each segment connecting two subsequent high symmetry points, for a total of 13 points, including the final one

```
K_POINTS tpiba_b
4
0.0 0.0 0.0 4
0.5 0.0 0.0 4
0.5 0.5 0.0 4
0.0 0.0 0.0 1
```

running pw.x with this input a non self consistent calculation will be performed for the desired k-points without running additional self-consitency.

These bands can be collected in file pt001.bands using code bands.x with the following input

% cat > pt001.bands.in << EOS

```
&inputpp
    prefix='pt001',
    outdir='/the/same/as/in/the scf/calculation/'
    filband='pt001.bands'
    lsym=.true.,
 /
```

A xmgr or postscript graph can be created by running plotbands.x with (hopefully self-evident interactive input)

Work-function calculations of the clean Pt (001) surface

The calculation of work-function can be done running the pp.x code.

In the QE examples directory there is a WorkFct_example where the workfunction of a 4-layer unrelaxed Al(100) slab is computed.

Run and understand that example and then set-up the simulation calculation for the Pt (001) surface.

Charge density analysis

A plot of the charge density of CO adsorbed on Pt (001) surface can be obtained saving a file containing the 3D charge density by the pp.x code with the following input

```
% cat >  co_at_pt001 << EOF
 &inputpp
    prefix  = 'co_at_pt001'
    outdir = '$TMP_DIR/'
    filplot = 'co_at_pt001_charge'
    plot_num= 0
 /
 &plot
    nfile = 1
    filepp(1) = 'co_at_pt001_charge'
    weight(1) = 1.0
    iflag = 3
    output_format = 5    ! xcrysden
    fileout = 'co_at_pt001_charge.xsf'
 /
EOF
```

and visualizing it with XcrysDen.

```
% xcrysden --xsf co_at_pt001_charge.xsf
```

Homework: bonding charge.

One can visualize the bonding charge by calculating the charge density of the two separate fragments , CO molecule and Pt(001) surface, keeping the same coordinate as in the combined system and then

create the combined 3D charge density file obtained by subtracting the charge density of the fragments from total charge.