

magnetism and Quantum Espresso

A default QE calculation is not spin-polarized (colloquially: 'non-magnetic'). It means that every Kohn-Sham orbital is occupied by two electrons, one with spin-up and one with spin-down. Therefore, the total spin moment for the crystal is necessarily zero. In this text, you'll learn how to do spin-polarized (a.k.a. 'magnetic') calculations.

ferromagnetism

The most straightforward magnetic situation is a crystal with ferromagnetic order. Take bcc-Fe as an example. Its primitive unit cell has one atom. In a non-spinpolarized calculation, that atom has as many spin-up as spin-down electrons. If we allow more spin-up than spin-down electrons for that atom, the atom has a spin magnetic moment. Due to periodicity, *all* atoms in the infinite crystal will have the same spin magnetic moment. That's ferromagnetic order.

Whatever is your unit cell, you can always attempt a ferromagnetic calculation. Add the following two lines to your input file :

```
&SYSTEM
  nspin = 2,
  starting_magnetization(1)=1,
```

The keyword `nspin` tells that a spin-polarized calculation needs to be done. The keyword `starting_magnetization (i)` determines for atom nr. `i` the initial spin moment at the start of the selfconsistent cycle. A value of `+1` means that the spin moment is maximally positive (=the number of spin-up electrons is as large as it can be, the number of spin-down electrons is as small as it can be). A value of `-1` means the opposite. The keyword `starting_magnetization` has to be specified for every atom separately (and can therefore be used to impose a particular type of magnetic order, see further).

Apply this to bcc Fe. Search an experimental cif file, and change the lattice parameter to 2.8342 Å (this is the optimized value for PBE – an alternative is to use an experimental value). Take [this](#) PBE pseudopotential, use `ecutwfc=90` and `ecutrho=360`, and a 21x21x21 k-mesh. After a static spin-polarized calculation (static = no geometry optimization, estimated calculation time about 5 minutes), you find in the output file this information:

```
total magnetization      =      2.13 Bohr mag/cell
absolute magnetization   =      2.25 Bohr mag/cell
```

The meaning of these quantities : <http://www.quantum-espresso.org/faq/self-consistency/#6.3>

This means that per unit cell (which in this case is identical to 'per atom') there are 2.13 electrons more with spin-up than with spin-down (every electron contributes 1 Bohr magneton of spin moment, with 'Bohr magneton' being the atomic unit for magnetic moment).

antiferromagnetism

bcc-Cr is an example of a crystal with antiferromagnetic order. In this crystal, half of the Cr-atoms have a spin magnetic moment pointing in one direction (called 'up' – as we do not consider spin-orbit coupling so far in our DFT calculations it cannot be specified which direction in space this 'up' is), while the other half have their spin magnetic moments pointing in the opposite direction (called 'down' – it is not specified which direction in space this is, but it is opposite to the direction we called 'up').

If we would take the same primitive bcc unit cell we took for iron, we would have a problem: there is only one atom in that cell, so how can we give one half of them a moment 'up', and the other half a moment 'down'? In order to solve that dilemma, we need to take a larger unit cell for bcc Cr, one that has two atoms. The conventional bcc cube is an example.

In order to construct that cell, start from the cif template with P1 symmetry. Look up the lattice parameter of Cr that you want to use (e.g. the experimental value 2.884 Å from COD 9008531), and put it in the cif file. Add two position lines for Cr-atoms, one at the corner of the bcc cube, and one at the center of the bcc cube. These will become the two kinds of atoms with opposite spin moments.

```
data_
_cell_length_a          2.884
_cell_length_b          2.884
_cell_length_c          2.884
_cell_angle_alpha       90.0
_cell_angle_beta        90.0
_cell_angle_gamma       90.0
_symmetry_space_group_name_H-M  'P 1'
_symmetry_Int_Tables_number  1
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
  1  'x, y, z'

loop_
_atom_site_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
Cr1 0.0 0.0 0.0
Cr2 0.5 0.5 0.5
```

As we want to benefit as much as possible from symmetry information, we'll pass this cif file through FINDSYM. However, FINDSYM will detect that these two Cr atoms are equivalent, and it will reduce the unit cell to one with only one Cr atom – not what we want. Therefore, temporarily replace 'Cr2' by 'Fe1', to make these two atoms inequivalent. We'll change this back later, once the symmetry information is generated. Pass this cif file now through FINDSYM, which will detect space group nr. 221 (this is not space group 229, the one you found for bcc-iron, where there was no

inequivalence between two types of atoms). Read that cif file in VNL, and export to a Quantum Espresso input file. Change the Fe atom back to Cr in that QE input file, and add a number to the Cr atoms to let QE know they are different (add the number as well in the ATOMIC_SPECIES as in the ATOMIC_POSITIONS):

```
ATOMIC_SPECIES
  Cr1 51.996100d0 Cr.pbe-sp-van.UPF
  Cr2 51.996100d0 Cr.pbe-sp-van.UPF

ATOMIC_POSITIONS {crystal}
  Cr1 0.0000000000d0 0.0000000000d0 0.0000000000d0
  Cr2 0.5000000000d0 0.5000000000d0 0.5000000000d0
```

Use [this](#) PBE pseudopotential, and the same basis set size and k-mesh as for the preceding Fe example. Give the two Cr-atoms an opposite initial magnetic moment by adding these lines:

```
&SYSTEM
  nspin = 2,
  starting_magnetization(1)=1,
  starting_magnetization(2)=-1,
```

Run a static calculation (estimated time is less than 1 minute), and inspect the output:

```
Magnetic moment per site:
  atom:    1    charge:  12.4187    magn:   -2.0473    constr:  0.0000
  atom:    2    charge:  12.4187    magn:    2.0473    constr:  0.0000
```

You see that the sign of the two magnetic moments is indeed opposite. Therefore, the total magnetization will be zero:

```
total magnetization      =   -0.00 Bohr mag/cell
absolute magnetization   =    4.35 Bohr mag/cell
```

You will notice that the stress tensor is quite far from zero – apparently DFT/PBE wants to have a somewhat more condensed lattice.

This was just one of the many possible antiferromagnetic configurations for bcc Cr. You might want to try to create the input for another configuration where two layers of ‘up’ moments are followed by two layers of ‘down’ moments.