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Metals
Magnetic systems

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Metallic systems: k-points and smearing:

Let us consider iron, in the bcc phase.

In the first part of this exercise, we neglect magnetism and perform non-spin polarized calculations.

Task 1: Create a pwscf input file for scf total energy calculations in this system with the following features:

- Use the Fe.pz-nd-rrkjus.UPF pseudopotential
- Cutoffs: 30 Ry (wavefunctions), 250 Ry (charge density)
- Lattice constant: 5.38 (a.u.)
- K-point mesh: 7×7×7 with shift 1×1×1
- Marzari-Vanderbilt smearing with degauss=0.03 Ry

Solution 1:

```
&control
   calculation = 'scf',
   prefix = 'Fe_bcc',
   pseudo_dir = './',
   outdir = './'
/
&system
   ibrav =  3,
   celldm(1) = 5.38,
   nat =  1,
   ntyp = 1,
   nbnd = 10
   ecutwfc = 30.,
   ecutrho = 250.,
   occupations='smearing'
   smearing='marzari-vanderbilt'
   degauss=0.03
/
&electrons
   mixing_beta = 0.7
/
ATOMIC_SPECIES
 Fe 55.845  Fe.pz-nd-rrkjus.UPF
ATOMIC_POSITIONS (alat)
 Fe 0.0 0.0 0.0
K_POINTS (automatic)
  7 7 7  1 1 1
```

bcc-lattice
lattice constant

increased number of bands
cutoffs

metallic smearing

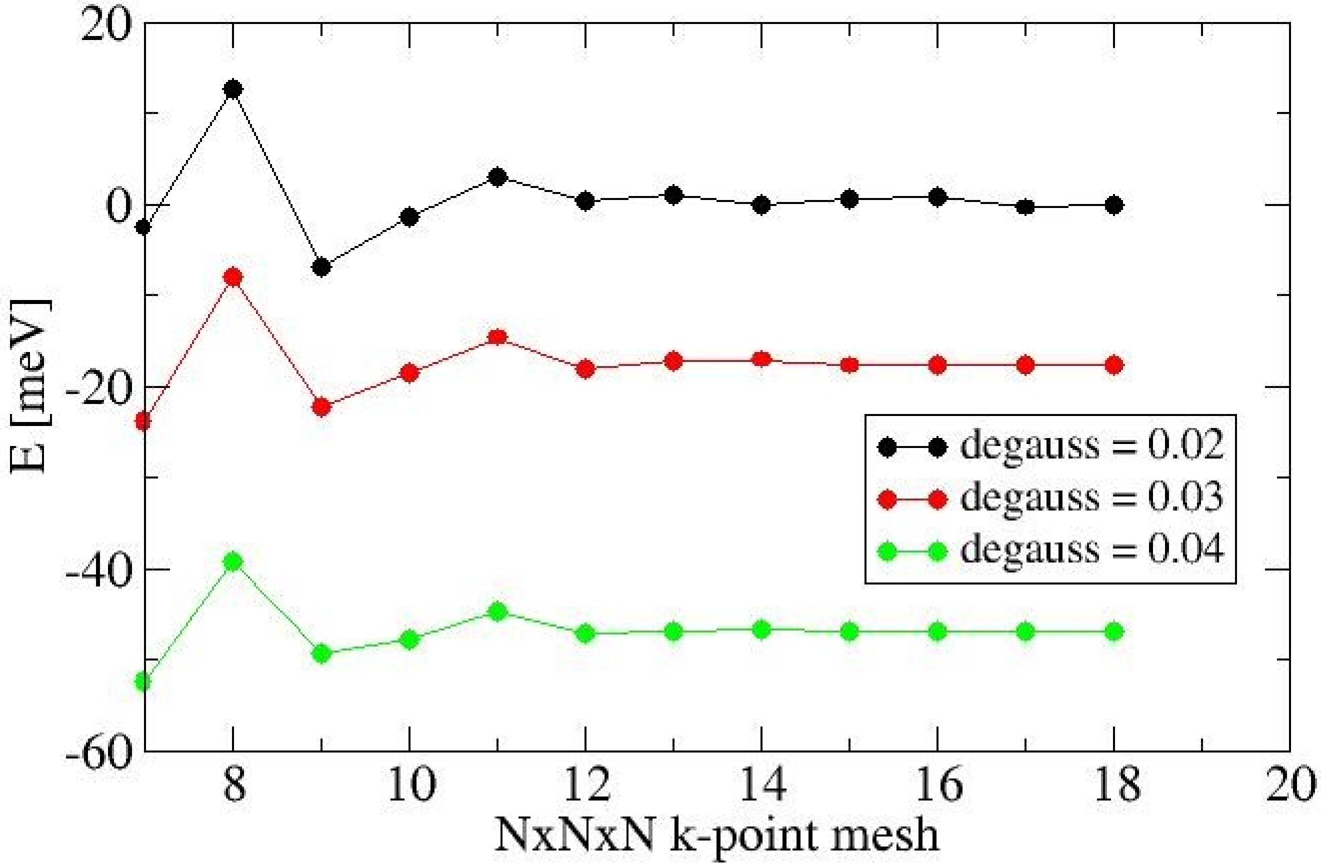
Metallic systems: k-points and smearing:

Task 2: Compute the total energy for this system with the following values for degauss and k-point meshes:

degauss = 0.02, 0.03, 0.04
k-points: N×N×N (1×1×1) with N=7,8,9, ..., 18

Plot the convergence of the total energy with respect to the number of k-points for the different smearing values.

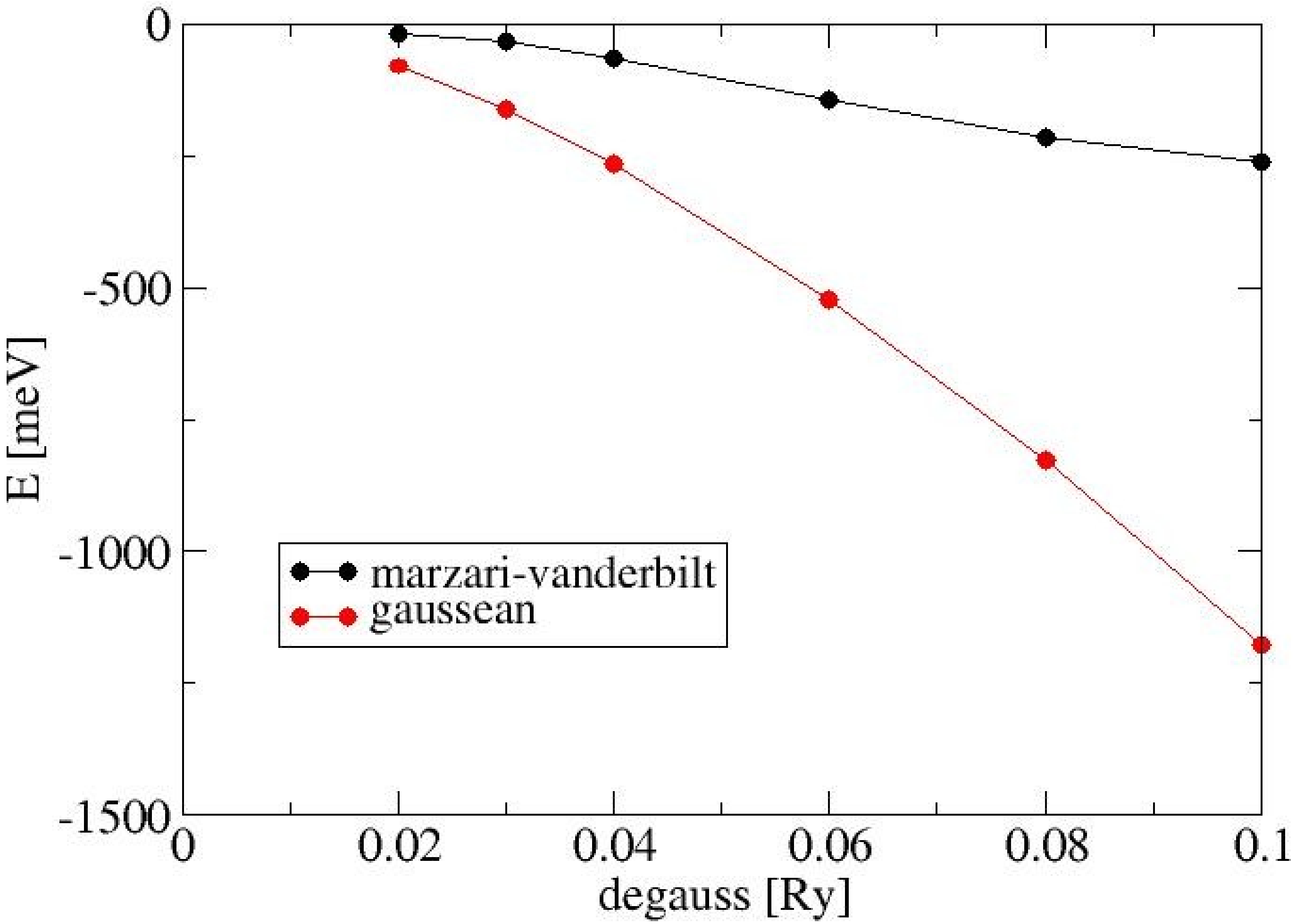
Solution2:


20
0
-20
-40
-60
E [meV]
8
10
12
14
16
18
20
NxNxN k-point mesh
degauss = 0.02
degauss = 0.03
degauss = 0.04

Metallic systems: k-points and smearing:

Task 3: Choose a 14×14×14 (1×1×1) k-point mesh and plot the total energy as a function of degauss for Marzari-Vanderbilt and Gaussean smearing

Solution3:


0
-500
-1000
-1500
E [meV]
0
0.02
0.04
0.06
0.08
0.1
degauss [Ry]
marzari-vanderbilt
gaussean

Magnetism and spin polarized systems

So far in this course: we “neglected” spin of the electrons:

$$n(\boldsymbol{r}) = \enclose{circle}{2} \sum_{i=1}^{N_{el}/2} |\psi_i(\boldsymbol{r})|^2$$

Implicitly, we have assumed that spin-up and spin-down wavefunctions are the same:

$$\psi_i^{\uparrow}(\boldsymbol{r}) = \psi_i^{\downarrow}(\boldsymbol{r})$$

Advantage: we need only N_{el} /2 orbitals

Spin polarized systems

For the case of spin-polarized systems, we drop this constraint and Use N orbitals:

$$\left\{\psi_i^{\uparrow}\right\}, \quad i = 1, \frac{N}{2} \qquad \left\{\psi_i^{\downarrow}\right\}, \quad i = 1, \frac{N}{2}$$

$$n^{\uparrow}(\boldsymbol{r}) = \sum_i \left|\psi_i^{\uparrow}(\boldsymbol{r})\right|^2 \qquad n^{\downarrow}(\boldsymbol{r}) = \sum_i \left|\psi_i^{\downarrow}(\boldsymbol{r})\right|^2$$

$$n(\boldsymbol{r}) = n^{\uparrow} + n^{\downarrow}$$

$$m(\boldsymbol{r}) = n^{\uparrow} - n^{\downarrow}$$

Spin polarized systems

Look at how the total energy depends on the two charge densities:

$$E[n^\uparrow,n^\downarrow] = E_{kin}+E_{ext}\boxed{[n^\uparrow+n^\downarrow]}+E_{Har}\boxed{[n^\uparrow+n^\downarrow]}+E_{xc}\boxed{[n^\uparrow,n^\downarrow]}$$

Calculate the functional derivative in order to obtain the Hamiltonian:

$$\frac{\delta E}{\delta n^\uparrow(\boldsymbol{r})} \neq \frac{\delta E}{\delta n^\downarrow(\boldsymbol{r})}$$

Spin polarized systems

We can also write the exchange-correlation energy as $E_{xc}[n, m]$.

Since we have:

$$\frac{\delta n}{\delta n^{\uparrow}(\boldsymbol{r})} = \frac{\delta n}{\delta n^{\downarrow}(\boldsymbol{r})} = 1$$

$$\frac{\delta m}{\delta n^{\uparrow}(\boldsymbol{r})} = 1$$

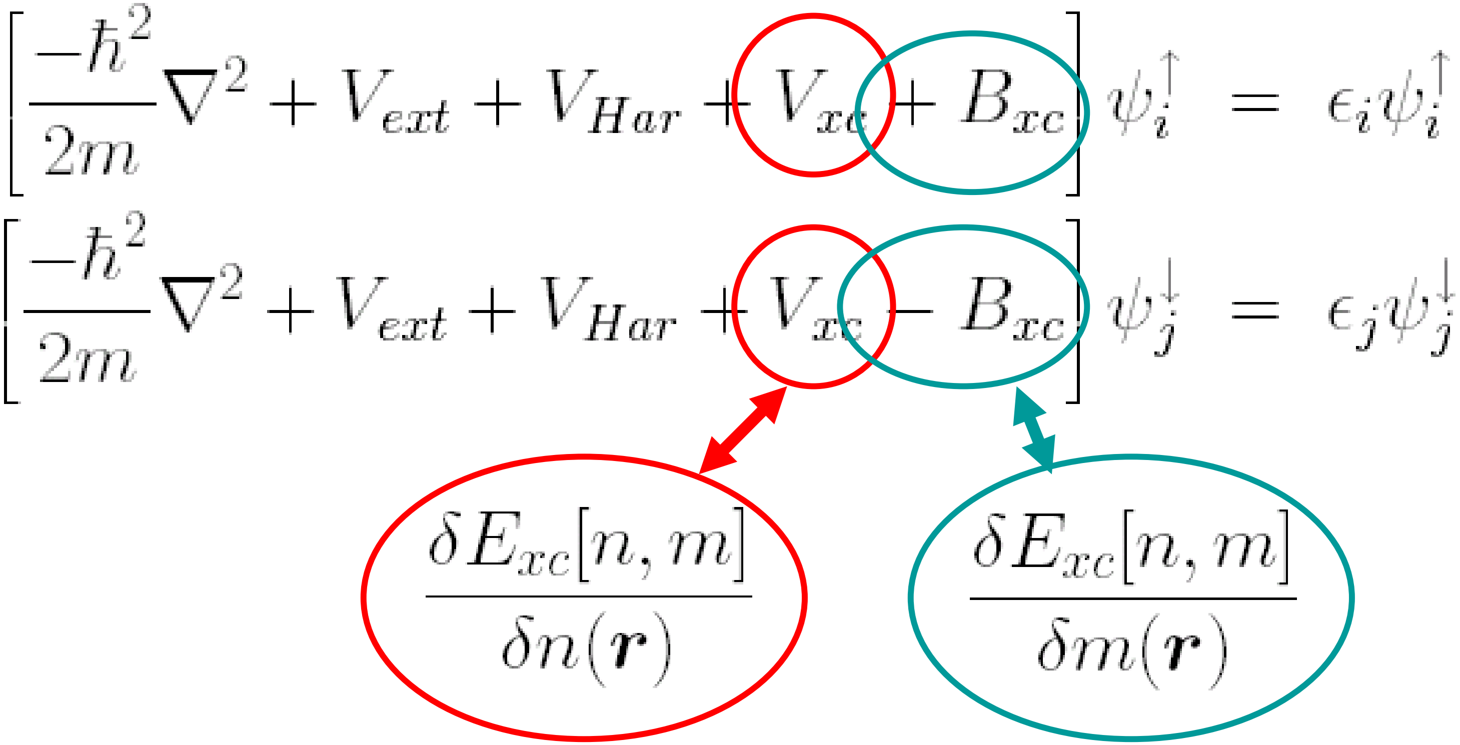
$$\frac{\delta m}{\delta n^{\downarrow}(\boldsymbol{r})} = -1$$

The Hamiltonian looks like:

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V_{ext} + V_{Har} + V_{xc} + B_{xc}\right]\psi_i^{\uparrow} = \epsilon_i \psi_i^{\uparrow}$$

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V_{ext} + V_{Har} + V_{xc} - B_{xc}\right]\psi_j^{\downarrow} = \epsilon_j \psi_j^{\downarrow}$$

Spin polarized systems



$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V_{ext} + V_{Har} + V_{xc} + B_{xc}\right]\psi_i^{\uparrow} = \epsilon_i\psi_i^{\uparrow}$$

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V_{ext} + V_{Har} + V_{xc} - B_{xc}\right]\psi_j^{\downarrow} = \epsilon_j\psi_j^{\downarrow}$$

$$\frac{\delta E_{xc}[n,m]}{\delta n(\boldsymbol{r})} \qquad \frac{\delta E_{xc}[n,m]}{\delta m(\boldsymbol{r})}$$

Magnetic systems:

We now come back to iron, in the bcc phase.

We now take into account magnetism and perform spin polarized calculations.

Task 4: Create a pwscf input file for scf total energy calculations in this system with the following features:

- Use the Fe.pz-nd-rrkjus.UPF pseudopotential
- Cutoffs: 30 Ry (wavefunctions), 250 Ry (charge density)
- Lattice constant: 5.38 (a.u.)
- K-point mesh: 14×14×14 with shift 1×1×1
- Marzari-Vanderbilt smearing with degauss=0.03 Ry
- spin polarized

Solution 4:

```
&control
   calculation = 'scf',
   prefix = 'Fe_bcc',
   pseudo_dir = './',
   outdir = './'
/
&system
   ibrav =  3,
   celldm(1) = 5.38,
   nat =  1,
   ntyp = 1,
   nbnd = 20
   ecutwfc = 30.,
   ecutrho = 250.,
   occupations='smearing'
   smearing='gauss'
   degauss=0.03
   nspin=2
   starting_magnetization(1)=0.2
/
&electrons
   mixing_beta = 0.7
/
ATOMIC_SPECIES
 Fe 55.845  Fe.pz-nd-rrkjus.UPF
ATOMIC_POSITIONS (alat)
 Fe 0.0 0.0 0.0
K_POINTS (automatic)
  14 14 14 1 1 1
```

increased number of bands

set nspin=2

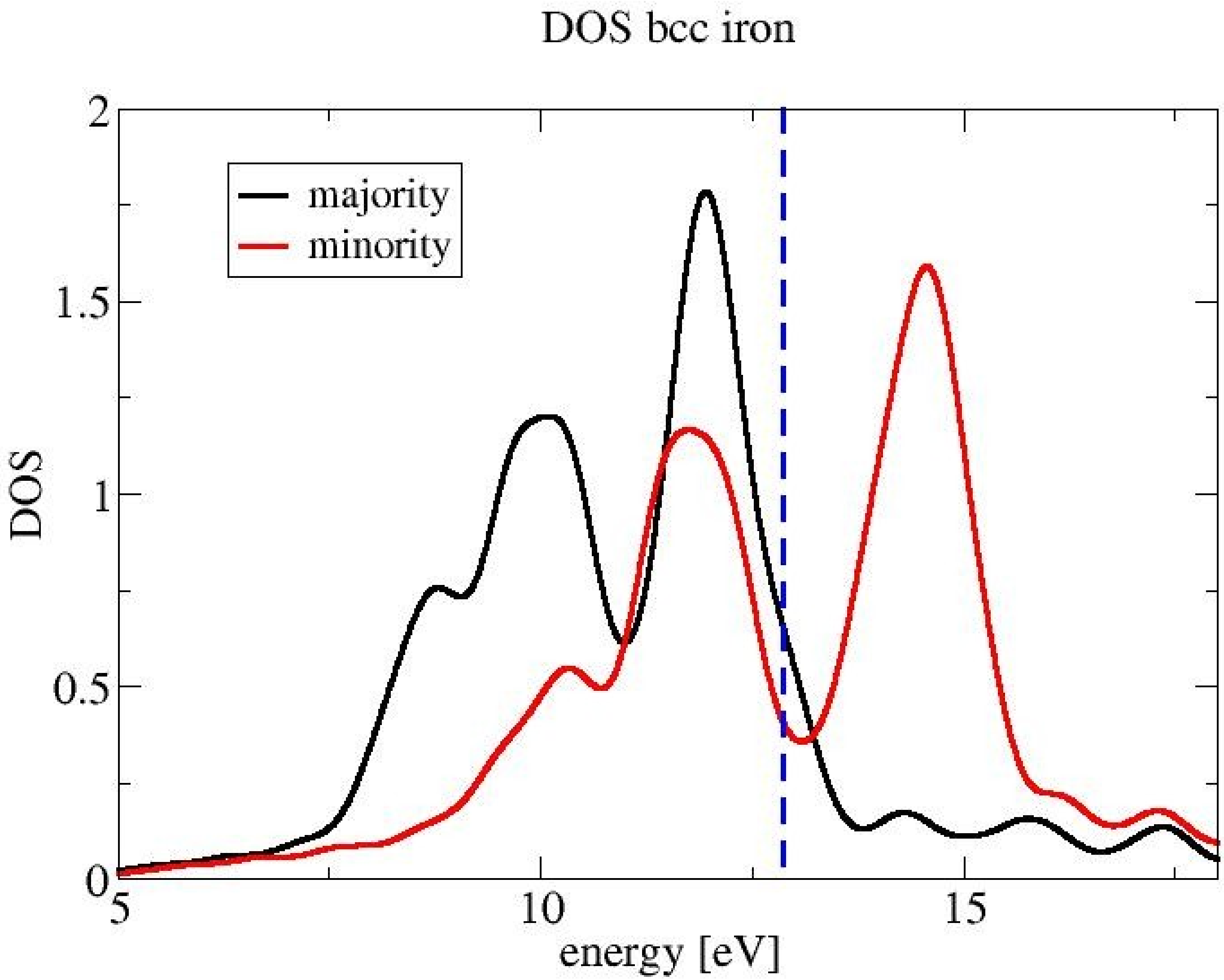
don't forget: starting_magnetization

Magnetic systems: Density of states

Task 5: Using the input file from task 4, calculate the total energy of magnetic bcc iron. Then, use the input file below for the postprocessing program dos.x. Plot the DOS of magnetic iron.

```
&inputpp
outdir='./'
prefix='Fe_bcc'
fildos='Fe.dos'
Emin=5., Emax=18., DeltaE=0.005
/
```

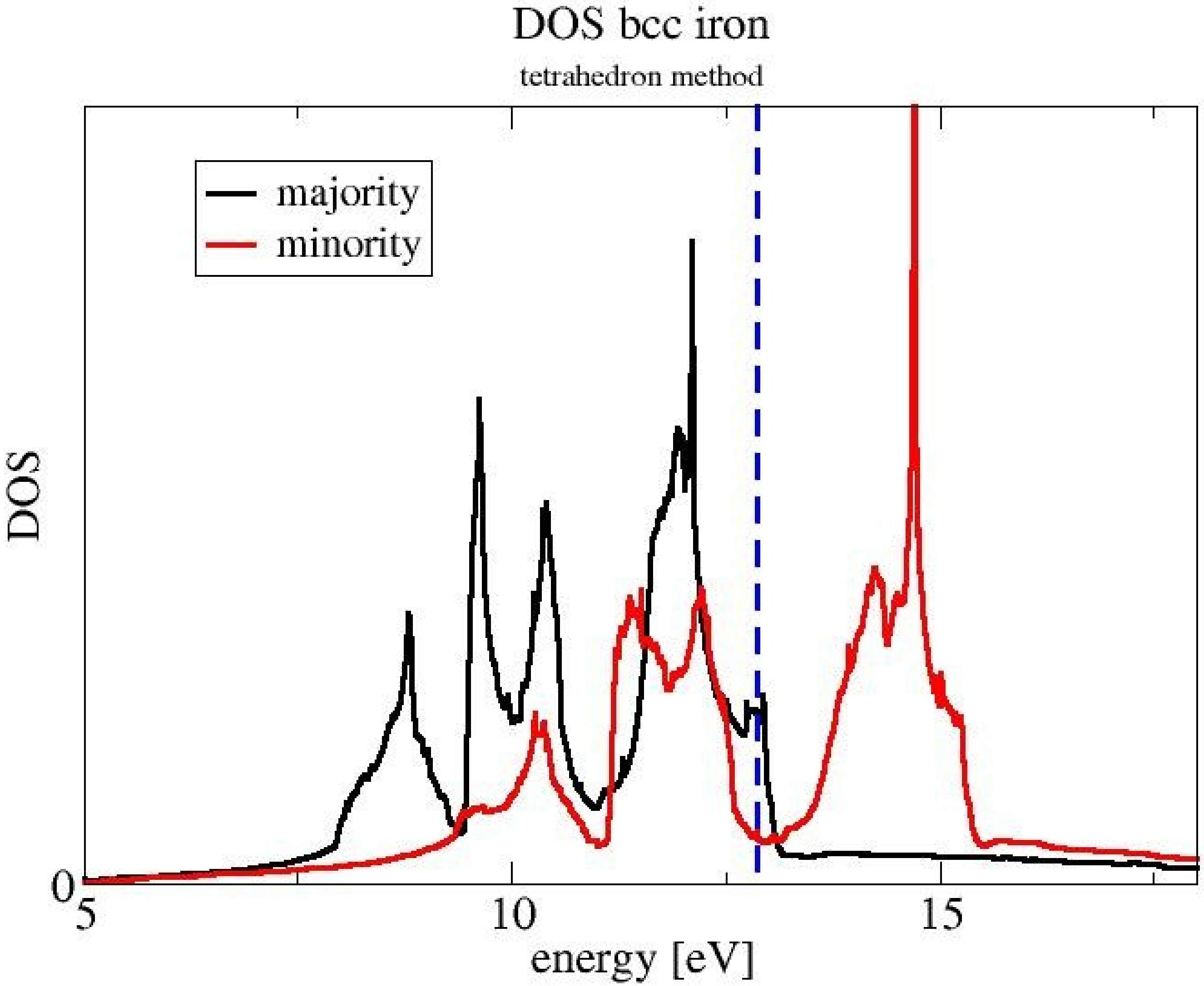
Solution 5:



Magnetic systems: Density of states

Task 6: Do a non-selfconsistent calculation of magnetic bcc iron using the “tetrahedron method” for determining the occupations. Then calculate the DOS again (using dos.x). Plot the DOS.

Solution 6:


DOS bcc iron
tetrahedron method
majority
minority
DOS
0
5
10
15
energy [eV]