Hands on Session IV

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Overview

- fcc Ni, an elementary ferromagnetic metal
- NiO, antiferromagnetic coupling
- LSDA+U (Dudarev's approach)
- SOI: freestanding fcc Fe and Ni (100) monolayers
- Constraining magnetic moments
- What to do about convergence problems?

fcc Ni

```
fcc:
 -10.93
 0.5 0.5 0.0
 0.0 0.5 0.5
 0.5 0.0 0.5
   1
Cartesian
0 0 0


k-points
0
Gamma
 11 11 11
  0  0  0
```

POSCAR

- Volume set to 10.93 Å
- fcc primitive cell

KPOINTS

- $11 \times 11 \times 11$ Γ-centered Monkhorst-Pack grid

POTCAR

`makepaw_GGA Ni`

(a PAW-GGA PW91 potential)

```
SYSTEM  = Ni fcc bulk
ISTART  = 0
ISPIN   = 2
MAGMOM  = 1.0
ISMEAR  = -5
VOSKOWN = 1
LORBIT  = 11
```

Or copy the files from:

`~vw/4_1_Ni`

INCAR

- Spin polarized calculation (collinear)
- Initial magnetic moment: 1 μ_B
- Interpolation of the correlation part of the exchange-correlation functional according to:
  S. H. Vosko, L. Wilk and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
- k-mesh integration:
  tetrahedron method with Blöchl's corrections
- Orbital resolved DOS
  and calculation of local magnetic moment

The magnetic moment

In OSZICAR (total magnetic moment):

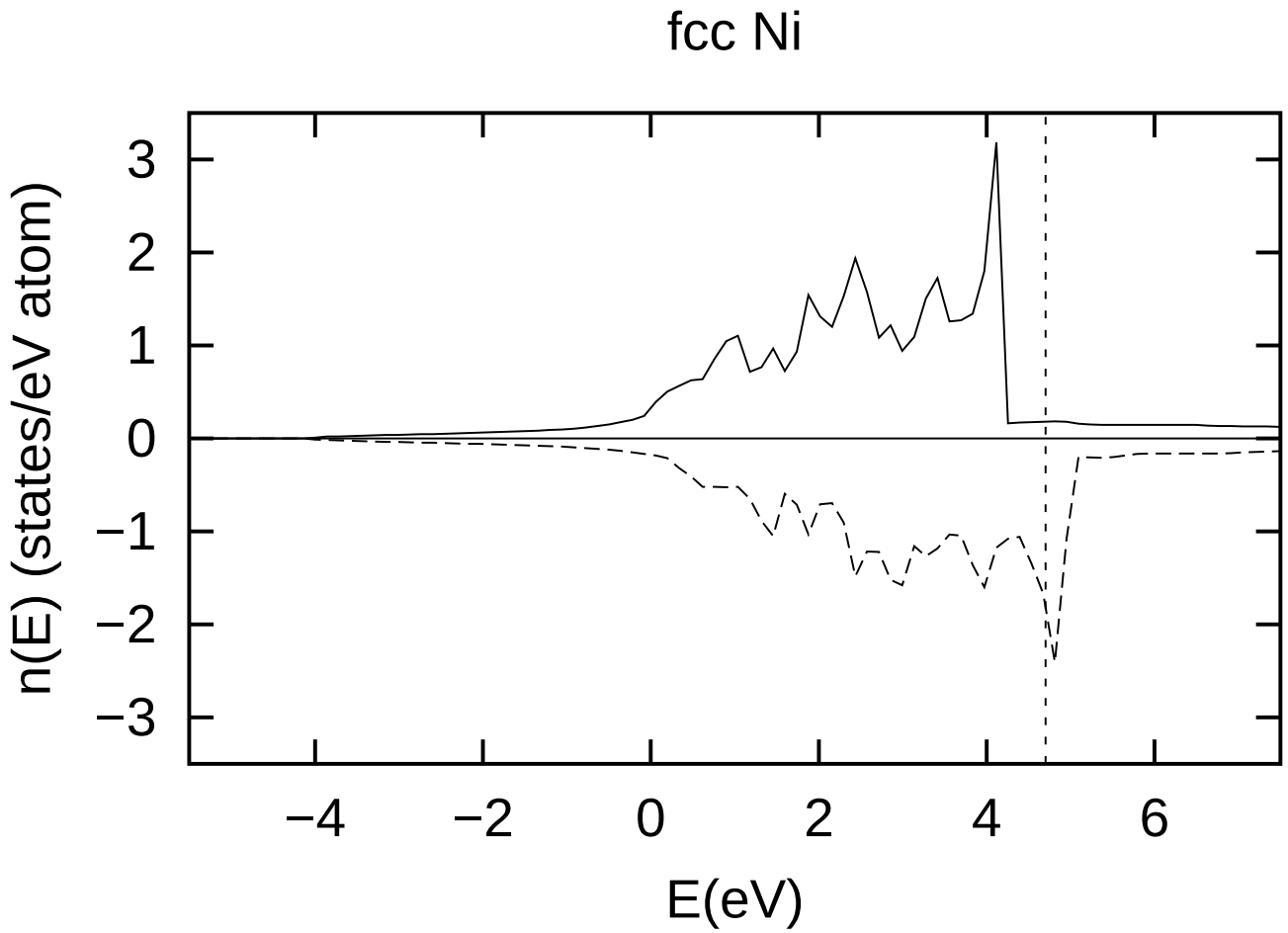
```
       N       E                     dE             d eps       ncg     rms          rms(c)
DAV:   1     0.139935173959E+02    0.13994E+02   -0.35801E+03  2338   0.828E+02
DAV:   2    -0.623612680591E+01   -0.20230E+02   -0.19281E+02  2282   0.123E+02
DAV:   3    -0.643764005251E+01   -0.20151E+00   -0.19906E+00  2536   0.140E+01
DAV:   4    -0.643786482872E+01   -0.22478E-03   -0.22442E-03  2344   0.459E-01
DAV:   5    -0.643786514671E+01   -0.31798E-06   -0.31687E-06  1832   0.173E-02    0.793E+00
...
DAV:   9    -0.545953126374E+01    0.48409E-02   -0.96206E-03  2946   0.839E-01    0.847E-02
DAV:  10    -0.545946513577E+01    0.66128E-04   -0.77007E-05  1364   0.126E-01
   1 F= -.54594651E+01 E0= -.54594651E+01  d E =0.000000E+00  mag=     0.5781
```

in OUTCAR (integration of magnetic moment in the PAW sphere):

```
 magnetization (x)

# of ion     s       p       d       tot
------------------------------------------
  1       -0.007  -0.026   0.625   0.591
```

DOS



Exchange splitting ≈ 0.5 eV

Proper initialization of magnetic moment

- Too small initial moment will/may lead to a nonmagnetic solution (the previous example with `MAGMOM = 0.0`)

```
...
DAV:   9    -0.540773198300E+01    0.31931E-03   -0.39421E-04  2091   0.339E-01    0.300E-02
DAV:  10    -0.540780668590E+01   -0.74703E-04   -0.46454E-05  1059   0.106E-01
   1 F= -.54078067E+01 E0= -.54078067E+01  d E =0.000000E+00  mag=     0.0020
```

- Badly initialized calculations take longer to converge
- Coexistence of low- and high spin solutions

Noncollinear magnetism

Replace `ISPIN = 2` and `MAGMOM = 1.0` by:

```
LNONCOLLINEAR = .TRUE.
MAGMOM        = 0.0  0.0  1.0
```

leads to

```
DAV:   9    -0.546480633680E+01    0.41628E-02   -0.49402E-04  7532   0.330E-01    0.695E-02
DAV:  10    -0.546475032360E+01    0.56013E-04   -0.52286E-05  4328   0.446E-02
   1 F= -.54647503E+01 E0= -.54647503E+01  d E =0.000000E+00  mag= 0.0000   0.0000   0.5792
```

or with `MAGMOM = 1.0 0.0 0.0`

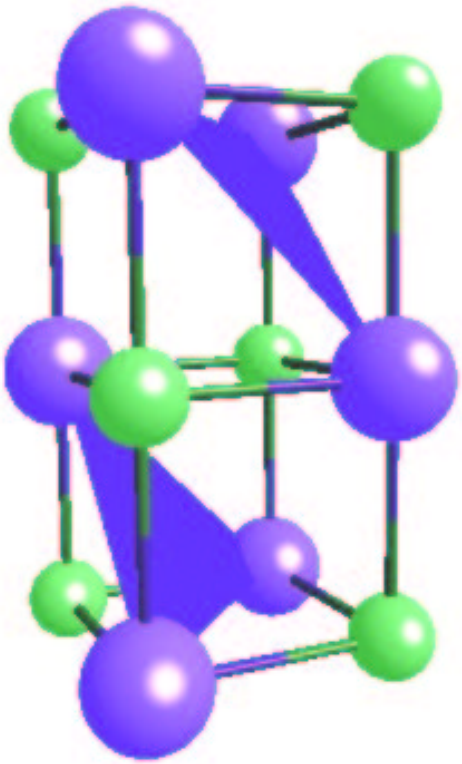
```
DAV:   9    -0.546481348871E+01    0.41496E-02   -0.50294E-04  7548   0.330E-01    0.692E-02
DAV:  10    -0.546474438319E+01    0.69106E-04   -0.51451E-05  4288   0.432E-02
   1 F= -.54647444E+01 E0= -.54647444E+01  d E =0.000000E+00  mag= 0.5792   0.0000   0.0000
```

idem for `MAGMOM = 0.0 1.0 0.0`

```
DAV:   9    -0.546481179459E+01    0.41515E-02   -0.50430E-04  7552   0.330E-01    0.692E-02
DAV:  10    -0.546474640011E+01    0.65394E-04   -0.51658E-05  4292   0.434E-02
   1 F= -.54647464E+01 E0= -.54647464E+01  d E =0.000000E+00  mag= 0.0000   0.5792   0.0000
```

NiO

- Rocksalt structure
- AFM ordering of Ni (111) planes



```
NiO AFM
 4.17
 1.0 0.5 0.5
 0.5 1.0 0.5
 0.5 0.5 1.0
 2 2
Cartesian
 0.0 0.0 0.0
 1.0 1.0 1.0
 0.5 0.5 0.5
 1.5 1.5 1.5

k-points
0
Gamma
  4  4  4
  0  0  0
```

POSCAR

- AFM coupling:
  4 atoms in the basis (instead of 2)

KPOINTS

- 4×4×4 Γ-centered
  Monkhorst-Pack grid

POTCAR

`makepaw Ni O_s`

(PAW-LDA potentials)

```
SYSTEM    = NiO

ISPIN     = 2
MAGMOM    = 2.0 -2.0 2*0

ENMAX     = 250
EDIFF     = 1E-3

ISMEAR    = -5

AMIX      = 0.2
BMIX      = 0.00001
AMIX_MAG  = 0.8
BMIX_MAG  = 0.00001

LORBIT    = 11
```

INCAR

- Initial magnetic moment:
  $\pm 2\ \mu_B$ (Ni), $0\ \mu_B$ (O)
- `AMIX=0.2` and `AMIX_MAG=0.8` (default)
  `BMIX` and `BMIX_MAG` practically zero,
  i.e. linear mixing

Or copy the files from:

`~vw/4_2_NiO`

The magnetic moment

In OSZICAR (total magnetic moment = **0!**):

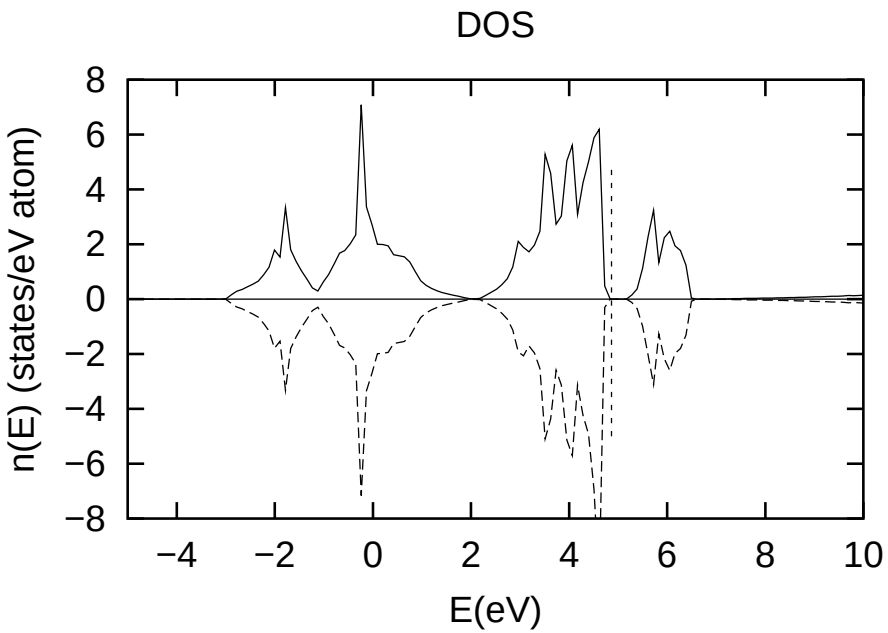
```
       N       E                     dE             d eps       ncg     rms          rms(c)
...
DAV:  13    -0.267936242334E+02    0.12794E-03   -0.12638E-04   552   0.298E-01    0.169E-02
DAV:  14    -0.267936352231E+02   -0.10990E-04   -0.21775E-05   520   0.107E-01
   1 F= -.26793635E+02 E0= -.26793635E+02  d E =0.000000E+00  mag=     0.0000
```

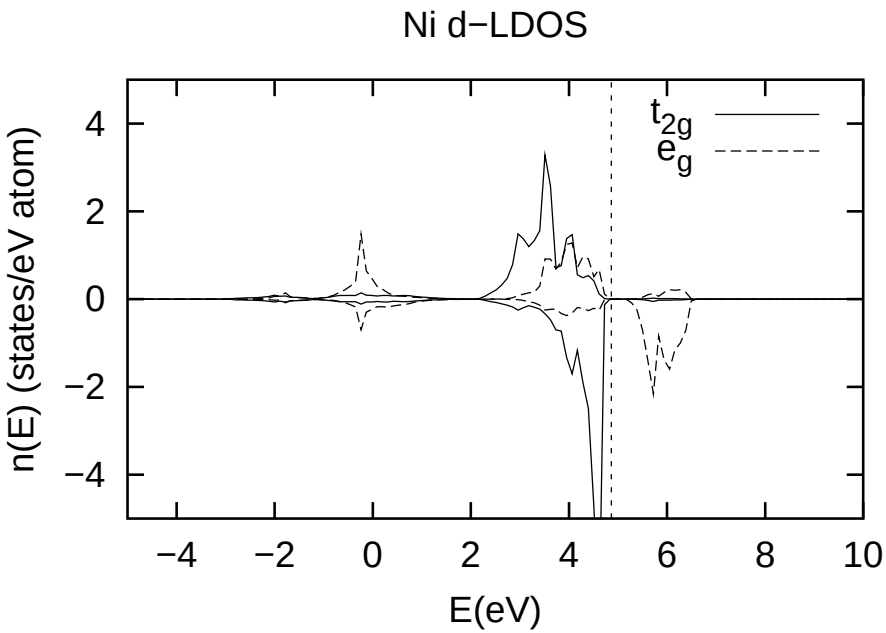
in OUTCAR (integration of magnetic moment in the PAW sphere):

```
 magnetization (x)

# of ion     s       p       d       tot
------------------------------------------
  1       -0.012  -0.014   1.245   1.219
  2        0.012   0.014  -1.242  -1.216
  3        0.000  -0.001   0.000  -0.001
  4        0.000  -0.001   0.000  -0.001
-----------------------------------------------
tot        0.000  -0.003   0.003   0.000
```

Total DOS, and LDOS Ni d-orbitals





$|m_{\mathrm{Ni}}| = 1.21\ \mu_{\mathrm{B}}$ (exp. 1.70 μ_{B}) $E_{\mathrm{gap}} = 0.44$ eV (exp. 4.0 eV)

LSDA+U; Dudarev's approach

```
...
LDAU       = .TRUE.
LDAUTYPE   = 2
LDAUL      = 2 -1
LDAUU      = 8 00  0.00
LDAUJ      = 0.95  0.00
LDAUPRINT = 2
```

Or copy the files from:

`~vw/4_3_NiO_LSDA+U`

addition to INCAR of NiO calc.

- Switch on L(S)DA+U
- Select Dudarev's approach
  (LSDA+U Type 2)
- L quantum number for which on site interaction is added
  (-1 = no on site interaction)
- U parameter
- J parameter
- Print occupation matrices in OUTCAR

L,U, and J must be specified for all atomic types!

On site occupancies (see OUTCAR)

```
atom =   1  type =  1  l = 2

 onsite density matrix
...
...
 occupancies and eigenvectors

o = 0.1696 v =  0.0000  0.0000  0.0000  0.0000  0.0000  0.0013 -0.0006 -0.9999 -0.0007 -0.0104
o = 0.1696 v =  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000 -0.0011 -0.0104  0.0011  0.9999
o = 0.9770 v =  0.0000  0.0000  0.0000  0.0000  0.0000  0.7787 -0.1766  0.0015 -0.6020  0.0005
o = 0.9770 v =  0.0000  0.0000  0.0000  0.0000  0.0000  0.2456 -0.7972  0.0005  0.5516 -0.0015
o = 0.9770 v =  0.0000  0.0000  0.0000  0.0000  0.0000  0.5774  0.5774  0.0000  0.5774  0.0000
o = 0.9803 v = -0.0193  0.7166  0.0001 -0.6972 -0.0039  0.0000  0.0000  0.0000  0.0000  0.0000
o = 0.9803 v =  0.8163 -0.3914 -0.0039 -0.4249 -0.0001  0.0000  0.0000  0.0000  0.0000  0.0000
o = 0.9803 v =  0.5774  0.5774  0.0000  0.5774  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
o = 1.0248 v = -0.0032  0.0016 -1.0000  0.0016  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
o = 1.0248 v =  0.0000  0.0027  0.0000 -0.0027  1.0000  0.0000  0.0000  0.0000  0.0000  0.0000
```

$d^{\uparrow}_{xy}$ $d^{\uparrow}_{yz}$ $d^{\uparrow}_{z^2-r^2}$ $d^{\uparrow}_{xz}$ $d^{\uparrow}_{x^2-y^2}$ $d^{\downarrow}_{xy}$ $d^{\downarrow}_{yz}$ $d^{\downarrow}_{z^2-r^2}$ $d^{\downarrow}_{xz}$ $d^{\downarrow}_{x^2-y^2}$

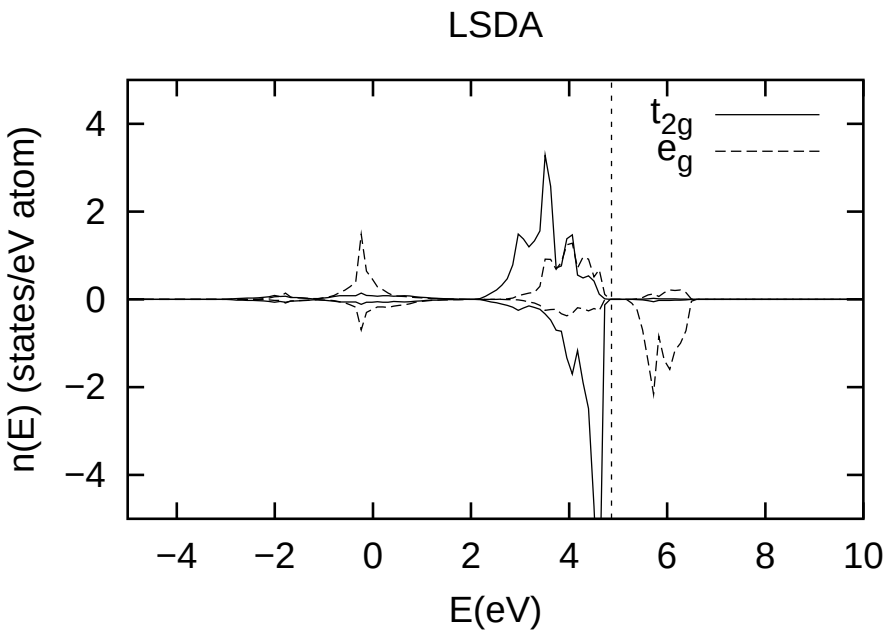
For comparison:

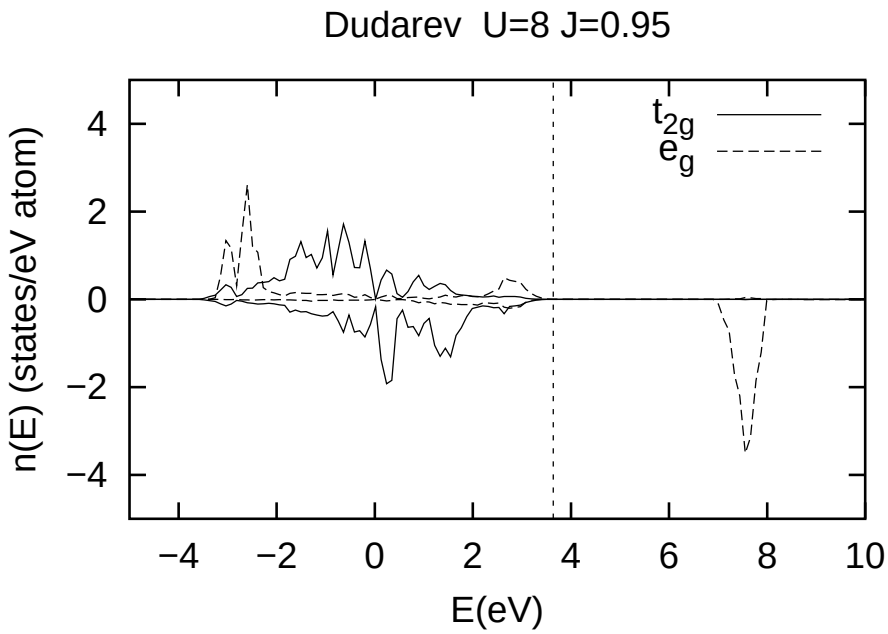
when `U=0` and `J=0` (i.e. just LSDA) the on site occupancies are as follows:

```
o = 0.3462 v =  0.0000  0.0000  0.0000  0.0000  0.0000 -0.0048  0.0028  0.9951  0.0020 -0.0986
o = 0.3462 v =  0.0000  0.0000  0.0000  0.0000  0.0000  0.0005  0.0039 -0.0986 -0.0044 -0.9951
o = 0.9491 v =  0.0000  0.0000  0.0000  0.0000  0.0000  0.5774  0.5774  0.0000  0.5774  0.0000
o = 0.9495 v =  0.0000  0.0000  0.0000  0.0000  0.0000 -0.0588  0.7347 -0.0004 -0.6759  0.0059
o = 0.9495 v =  0.0000  0.0000  0.0000  0.0000  0.0000  0.8144 -0.3563  0.0059 -0.4581  0.0004
o = 0.9527 v =  0.0477 -0.0256  0.9974 -0.0221 -0.0420  0.0000  0.0000  0.0000  0.0000  0.0000
o = 0.9527 v =  0.0020  0.0403  0.0420 -0.0423  0.9974  0.0000  0.0000  0.0000  0.0000  0.0000
o = 0.9598 v =  0.5774  0.5774  0.0000  0.5774  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
o = 0.9599 v = -0.1186  0.7577  0.0085 -0.6391 -0.0579  0.0000  0.0000  0.0000  0.0000  0.0000
o = 0.9599 v =  0.8064 -0.3005 -0.0579 -0.5059 -0.0085  0.0000  0.0000  0.0000  0.0000  0.0000
```

$$d^{\uparrow}_{xy} \quad d^{\uparrow}_{yz} \quad d^{\uparrow}_{z^2-r^2} \quad d^{\uparrow}_{xz} \quad d^{\uparrow}_{x^2-y^2} \quad d^{\downarrow}_{xy} \quad d^{\downarrow}_{yz} \quad d^{\downarrow}_{z^2-r^2} \quad d^{\downarrow}_{xz} \quad d^{\downarrow}_{x^2-y^2}$$

The Ni d-LDOS and local magnetic moment





magnetization (x)

# of ion	s	p	d	tot
1	-0.003	-0.006	1.721	1.711
2	0.003	0.006	-1.719	-1.710
3	0.000	-0.001	0.000	-0.001
4	0.000	-0.001	0.000	-0.001
tot	0.000	-0.002	0.002	0.000

Total Energy

On site occupancy matrix is NOT idempotent $\rightarrow$

Total energy contains penalty contribution!

```
...
DAV:  15    -0.229633055256E+02   -0.11057E-03   -0.50020E-05   520   0.104E-01    0.118E-02
DAV:  16    -0.229633263321E+02   -0.20806E-04   -0.16650E-05   520   0.492E-02
   1 F= -.22963326E+02 E0= -.22963326E+02  d E =0.000000E+00  mag=     0.0000
```

The total energy for $(U-J) > 0$ is in that case always higher than for $(U-J) = 0$ (just LSDA, see below):

```
...
DAV:  13    -0.267936242334E+02    0.12794E-03   -0.12638E-04   552   0.298E-01    0.169E-02
DAV:  14    -0.267936352231E+02   -0.10990E-04   -0.21775E-05   520   0.107E-01
   1 F= -.26793635E+02 E0= -.26793635E+02  d E =0.000000E+00  mag=     0.0000
```

Comparing the total energies from calculations with different $(U-J)$ is meaningless!

SOI: freestanding fcc Fe and Ni (100) monolayers

```
fcc Ni (100) monolayer
 3.53
   .50000   .50000   .00000
  -.50000   .50000   .00000
   .00000   .00000  5.00000
  1
Cartesian
   .00000   .00000   .00000


K-Points
 0
Monkhorst-Pack
9 9 1
0 0 0
```

POSCAR

- Lattice constant for bulk fcc Ni (for Fe take $a_0 = 3.45$ Å)

POTCAR

- `makepaw_GGA Ni`

  or

  `makepaw_GGA Fe`

```
ISTART         = 0
ENCUT          = 270.00
LNONCOLLINEAR = .TRUE.
MAGMOM         = 0.0 0.0 1.0
VOSKOWN        = 1
LSORBIT        = .TRUE.
```

INCAR

- Initialize moment along z-direction (out of plane)
  For Fe: `MAGMOM = 0.0 0.0 3.0`
- Switch on Spin-Orbit Interaction

For the second calculation, switch to in-plane magnetization, setting
`MAGMOM = 1.0 0.0 0.0` (for Fe: `MAGMOM = 3.0 0.0 0.0`)

Input files can be found in:

`~vw/4_4_SOI_Ni` and `~vw/4_4_SOI_Fe`

Results

fcc Ni (100) monolayer (out of plane magnetization)

```
...
DAV:  20    -0.371322930070E+01    0.15852E-03   -0.11632E-03   636   0.235E-01    0.225E-02
DAV:  21    -0.371323204989E+01   -0.27492E-05   -0.13047E-05   500   0.184E-02
   1 F= -.37132320E+01 E0= -.37139803E+01  d E =0.224478E-02  mag=  0.0000  0.0000  0.9035
```

fcc Ni (100) monolayer (in plane magnetization)

```
...
DAV:  19    -0.371443443024E+01   -0.80757E-04   -0.35822E-03  1084   0.323E-01    0.119E-02
DAV:  20    -0.371446032472E+01   -0.25894E-04   -0.42423E-05   916   0.263E-02
   1 F= -.37144603E+01 E0= -.37150300E+01  d E =0.170900E-02  mag=  0.9049  0.0000  0.0000
```

$E_{\mathrm{MAE}} = E(m_{\perp}) - E(m_{||}) = 1.2\ \mathrm{meV}$ (easy axis lies in plane)

For Fe the same procedure yields

$E_{\mathrm{MAE}} = E(m_{\perp}) - E(m_{||}) = -0.2\ \mathrm{meV}$ (easy axis lies out of plane)

Constraining the direction of magnetic moments

```
Fe dimer
 1.0
 8.0 0.0 0.0
 0.0 8.0 0.0
 0.0 0.0 8.0
   2
Cartesian
 3.0 0.0 0.0
 5.0 0.0 0.0

k-points
0
Gamma
 1  1  1
 0  0  0
```

POSCAR

- An iron dimer in a box

KPOINTS

- We only take the Γ point

POTCAR

- `makepaw_GGA Fe`

Or copy the files from:

`~vw/4_5_Fe_dimer`

```
 ISTART         = 0
 ISYM           = 0
 LNONCOLLINEAR  = .TRUE.
 MAGMOM         = 0 0 3  0 0 3
 VOSKOWN        = 1
 LORBIT         = 11
```

INCAR

- Switch of symmetry
- Initialize moments for ferromagnetic coupling

```
...
DAV:  20    -0.929676054634E+01   -0.26101E-03   -0.16780E-03    60   0.102E-01    0.537E-02
DAV:  21    -0.929679955346E+01   -0.39007E-04   -0.30319E-04    60   0.590E-02
   1 F= -.92967996E+01 E0= -.93047629E+01  d E =0.238900E-01  mag= -0.0006 -0.0003  6.0537
```

Now take `MAGMOM = 0 0 3  0 2 2`

```
 magnetization (y)                                 magnetization (z)
# of ion     s       p       d       tot    # of ion     s       p       d       tot
------------------------------------------   ------------------------------------------
  1        0.018  -0.001   1.071   1.087      1        0.045  -0.003   2.587   2.628
  2        0.019  -0.001   1.069   1.087      2        0.045  -0.003   2.588   2.629
------------------------------------------   ------------------------------------------
tot        0.037  -0.003   2.140   2.174    tot        0.089  -0.007   5.175   5.257
```

System converges to FM solution

However when we add the following lines to the INCAR

```
I_CONSTRAINED_M = 1
RWIGS           = 1.0
LAMBDA          = 10
M_CONSTR        = 0 0 1  0 1 1
```

- Switch on constraints on magnetic moments
- Integration radius to determine local moments
- Weight in penalty functional
- Target directions

a penalty functional is added to the system which drives the integrated local moments into the desired directions.

Beware: The penalty functional contributes to the total energy

The necessary information is found in the OSZICAR:

```
 E_p =  0.35424E-02  lambda =  0.100E+02
 ion        MW_int                  M_int
  1  0.000  0.013  1.557    0.000  0.014  2.674
  2  0.000  1.092  1.110    0.000  1.880  1.901
DAV:  35    -0.905322335169E+01    0.58398E-04   -0.60872E-04    60   0.734E-02
   1 F= -.90532234E+01 E0= -.90355617E+01  d E =-.529849E-01  mag= -0.0005  2.1161  5.1088
```

E_p is the energy arising from the penalty functional

It decreases with increasing LAMBDA!

By increasing LAMBDA stepwise one can bring E_p down
(slowly so the solution remains stable from one run to another)

```
 E_p =  0.22591E-03  lambda =  0.500E+02
 ion        MW_int                  M_int
  1  0.000  0.002  1.545    0.001 -0.005  2.654
  2  0.000  1.086  1.087    0.001  1.871  1.862
DAV:  33    -0.907152551238E+01    0.48186E-04   -0.33125E-04    60   0.163E-01
   1 F= -.90715255E+01 E0= -.90541505E+01  d E =-.521251E-01  mag=  0.0042  2.0902  5.0659
```

This way one approaches the LSDA total energy for a given magnetic configuration

What can one do when convergence is bad?

- Start from charge density of non-spin-polarized calculation, using

  `ISTART = 0` (or remove WAVECAR)

  `ICHARG = 1`

- Linear mixing

  `BMIX = 0.0001 ; BMIX_MAG = 0.0001`

- Mix slowly, i.e., reduce `AMIX` and `AMIX_MAG`

- Reduce `MAXMIX`, the number of steps stored in the Broyden mixer (default = 45)

- Restart from partly converged results
  (stop a calculation after say 20 steps and restart from the WAVECAR)

- Use constraints to stabilize the magetic configuration

- Pray