Imperial College London

Converging magnetic systems in CP2K: from bulk Ni to a Ni slab in vacuum

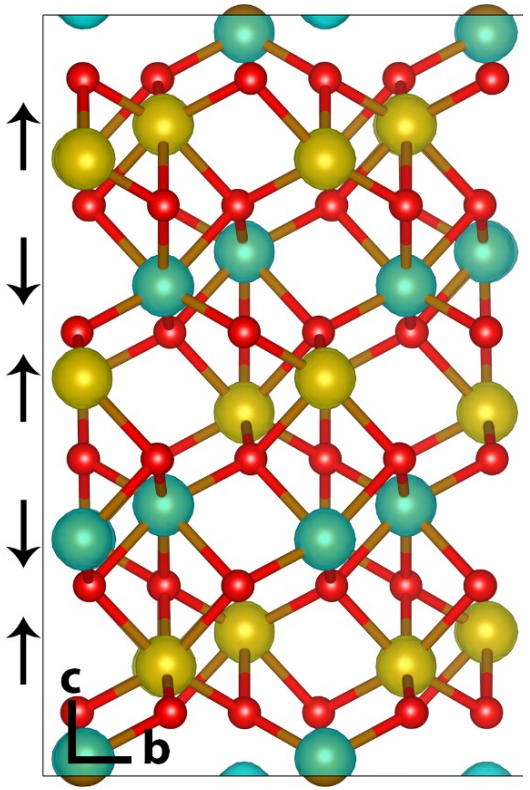
Christian Ahart

Motivation

- Magnetic systems are common in nature (Fe, Ni, Co etc.)
- Magnetic systems are typically more challenging and expensive to study

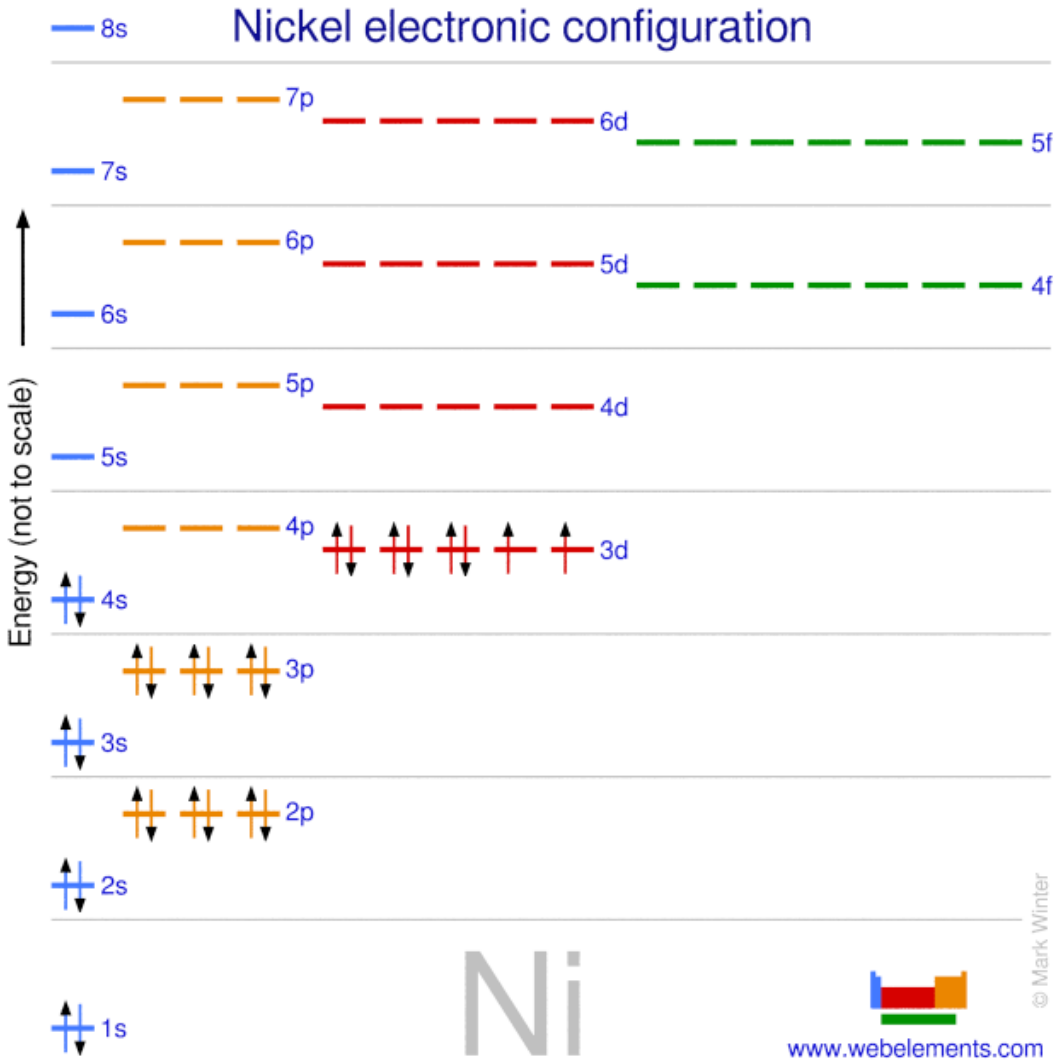
Conversations ▾ magnetic ✕ ▾

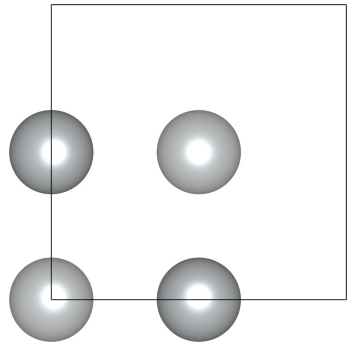
sun789...@gmail.com		**How to set MAGNETIZATION correctly to make the SCF calculation of NdFeO3 crystal converge** — . The **magnetic** structu...
leopold...@gmail.com, yakut...@gmail.com 3		**magnetic systems in cp2k / AiiDA common workflows** — cp2k to **magnetic** systems (both >> periodic and clusters). >> >> ...
krieger...@googlemail.com		**Heme in the excited state** — Dear all, I have already asked about a QM calculation of an isolated heme group some weeks ...
sun789...@gmail.com		**SCF calculation of NdFeO3 crystal does not converge** — . The **magnetic** moment of NdFeO3 shown on the Materials Proje...
lenardc...@gmail.com		**Fixing a spin help** — had a **magnetic** moment of ~1 magneton Bohr corresponding to a superoxide form, (O2)-. That means...
mdsimula...@gmail.com, uca...@ucl.ac.uk 3		**Ferromagnetic bulk nickel supercell optimization - multiplicity?** — Hi Frank, I attach files where I have converged a spin m...
izad...@gmail.com		**Cholesky decomposition failed** — Dear CP2K developers, I am going to use *aug-TZV2P-GTH *basis set along with "PRECO...
gengxi...@gmail.com, ... 10091...@qq.com 6		**SIRIUS run-time error** — is not **magnetic**, so non-spin polarized calculation should be enough. With kind regards, Anton. On ...
mdsimula...@gmail.com, Matthias Krack 2		**local magnetic moment - how to get?** — local atomic **magnetic** moments. HTH Matthias From: "cp2k@googlegroups.com" ...
Lucas Lodeiro		**Problems with BSSE calculation.** — Hello all, I am trying to compute the BSSE correction for a molecule adsorption on a m...
Salvatore Labonia, Matthias Krack 4		**CP2K freeze** — Hello, cp2k 8.2 was compiled using EasyBuild I attach some output from regression test Regards Salvatore ...
ma455...@gmail.com, jgh 4		**How to add MOS independently for spin up and spin down** — Hi, I'm a newbie using cp2k/9.1.0. I tried to use LSD and ADD...
antunh...@gmail.com, Marcella Iannuzzi 2		**Geometry doesn't converge** — Dear all, I'm trying to run some MD, but the geometry of my system doesn't converge. I get th...
pierre.an...@gmail.com		**transport calculations** — Dear CP2K users, I am trying to perform transport calculations. CP2K+OMEN were compiled with ...



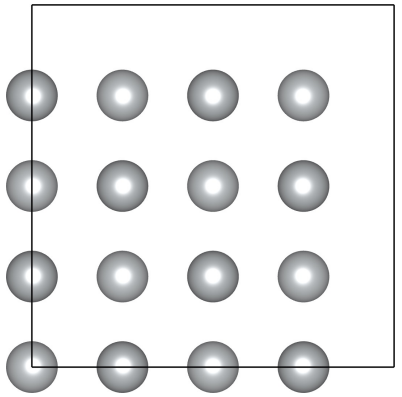
Bulk Ni

From electronic configuration [Ar] $3d^8$ $4s^2$ Ni should be ferromagnetic





FCC unit cell



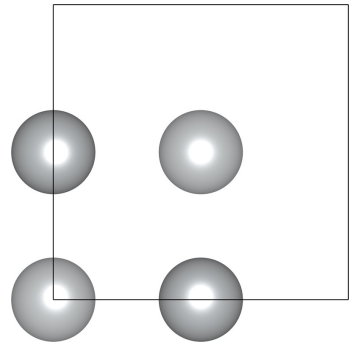
2x2x2 supercell

Bulk Ni

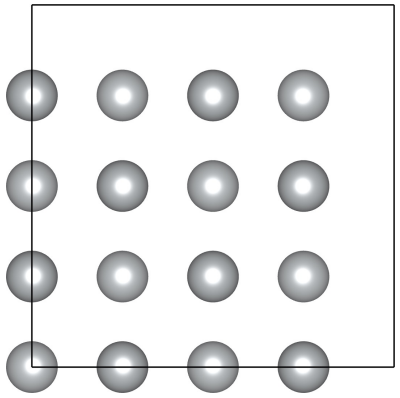
From electronic configuration [Ar] $3d^8$ $4s^2$ Ni should be ferromagnetic

Consider a 2x2x2 supercell of Ni with 32 atoms and 576 electrons (32*18=576):

```
&FORCE_EVAL
        METHOD Quickstep
        STRESS_TENSOR ANALYTICAL

        &DFT
                BASIS_SET_FILE_NAME BASIS_MOLOPT
                POTENTIAL_FILE_NAME GTH_POTENTIALS
                CHARGE 0
                MULTIPLICITY 1
                UKS .TRUE.

                &QS
                        EPS_DEFAULT 1.0E-12
                        EXTRAPOLATION ASPC
            &END QS

                &MGRID
                        NGRIDS 5
                        CUTOFF 600.0
                        REL_CUTOFF 60.0
                &END MGRID

                &SCF
                        SCF_GUESS ATOMIC
                        EPS_SCF 1.0E-8
                        MAX_SCF 500
                        ADDED_MOS 1000
                        &DIAGONALIZATION
                                ALGORITHM STANDARD
                        &END DIAGONALIZATION
                        &MIXING
                                METHOD BROYDEN_MIXING
                                ALPHA 0.1
                                NBUFFER 10
                        &END MIXING
                        &SMEAR
                                ELECTRONIC_TEMPERATURE [K] 500.0
                                METHOD FERMI_DIRAC
                        &END SMEAR
                &END SCF

                &XC
                        &XC_FUNCTIONAL PBE
                        &END XC_FUNCTIONAL
                &END XC
                &PRINT
                  &E_DENSITY_CUBE  ON
                  &END E_DENSITY_CUBE
                  &HIRSHFELD
                     SHAPE_FUNCTION  DENSITY
                  &END HIRSHFELD
                &END PRINT
            &END DFT

        &SUBSYS
                &CELL
                        ABC 3.50579800 3.50579800 3.50579800
                        ALPHA_BETA_GAMMA 90.000 90.000 90.000
                        MULTIPLE_UNIT_CELL 2 2 2
                &END CELL

                &TOPOLOGY
                        COORD_FILE_FORMAT XYZ
                        COORD_FILE_NAME ${INPUT_COORD_FILE_NAME}
                        MULTIPLE_UNIT_CELL 2 2 2
                &END TOPOLOGY

                &KIND Ni
                        ELEMENT Ni
                        BASIS_SET DZVP-MOLOPT-SR-GTH
                        POTENTIAL GTH-PBE
                &END KIND
        &END SUBSYS
&END FORCE_EVAL
```



FCC unit cell



2x2x2 supercell

Bulk Ni: multiplicity 1

From electronic configuration [Ar] $3d^8$ $4s^2$ Ni should be ferromagnetic

Consider a 2x2x2 supercell of Ni with 32 atoms and 576 electrons (32*18=576):

```
Electronic structure
   Total number of core electrons                              10.00
   Total number of valence electrons                           18.00
   Total number of electrons                                   28.00
   Multiplicity                                          not specified
   S    [  2.00  2.00] 2.00  2.00
   P    [  6.00] 6.00
   D       8.00


  Spin 1
  Re-scaling the density matrix to get the right number of electrons for spin 1
                  # Electrons             Trace(P)              Scaling factor
                          288              288.033                       1.000

  Spin 2
  Re-scaling the density matrix to get the right number of electrons for spin 2
                  # Electrons             Trace(P)              Scaling factor
                          288              288.033                       1.000
```

Bulk Ni: multiplicity 1

```
Spin 1
Re-scaling the density matrix to get the right number of electrons for spin 1
                # Electrons             Trace(P)               Scaling factor
                        288              288.033                       1.000

Spin 2
Re-scaling the density matrix to get the right number of electrons for spin 2
                # Electrons             Trace(P)               Scaling factor
                        288              288.033                       1.000


SCF WAVEFUNCTION OPTIMIZATION

 Step     Update method      Time    Convergence         Total energy    Change
 ------------------------------------------------------------------------------
    1 NoMix/Diag. 0.10E+00    0.4     0.80171411     -5429.7560153866 -5.43E+03
    2 Broy./Diag. 0.10E+00    0.6     0.02588730     -5335.8096605085  9.39E+01
    3 Broy./Diag. 0.10E+00    0.6     0.04784139     -5376.5137410802 -4.07E+01
    4 Broy./Diag. 0.10E+00    0.6     0.00924909     -5457.1568627918 -8.06E+01
    5 Broy./Diag. 0.10E+00    0.6     0.02124621     -5458.3145504847 -1.16E+00
    6 Broy./Diag. 0.10E+00    0.6     0.01756844     -5434.4301411166  2.39E+01
    7 Broy./Diag. 0.10E+00    0.6     0.00206891     -5415.3312463523  1.91E+01
    8 Broy./Diag. 0.10E+00    0.6     0.00044585     -5418.7667399029 -3.44E+00
    9 Broy./Diag. 0.10E+00    0.6     0.00013968     -5418.0821093648  6.85E-01
   10 Broy./Diag. 0.10E+00    0.7     0.00006977     -5418.2285997701 -1.46E-01
   11 Broy./Diag. 0.10E+00    0.7     0.00003185     -5418.2033048944  2.53E-02
   12 Broy./Diag. 0.10E+00    0.6     0.00000965     -5418.2400190922 -3.67E-02
   13 Broy./Diag. 0.10E+00    0.7     0.00002667     -5418.2281566399  1.19E-02
   14 Broy./Diag. 0.10E+00    0.7     0.00002834     -5418.2101435214  1.80E-02
   15 Broy./Diag. 0.10E+00    0.6     0.00000462     -5418.1881007901  2.20E-02
   16 Broy./Diag. 0.10E+00    0.6     0.00000071     -5418.1824488938  5.65E-03
   17 Broy./Diag. 0.10E+00    0.7     0.00000122     -5418.1824658980 -1.70E-05
   18 Broy./Diag. 0.10E+00    0.6     0.00000135     -5418.1824690107 -3.11E-06
   19 Broy./Diag. 0.10E+00    0.6     0.00000113     -5418.1824976251 -2.86E-05
   20 Broy./Diag. 0.10E+00    0.6     0.00000014     -5418.1824933141  4.31E-06
   21 Broy./Diag. 0.10E+00    0.6     0.00000008     -5418.1824664816  2.68E-05
   22 Broy./Diag. 0.10E+00    0.6     0.00000009     -5418.1824768989 -1.04E-05
   23 Broy./Diag. 0.10E+00    0.6     0.00000005     -5418.1824777986 -9.00E-07
   24 Broy./Diag. 0.10E+00    0.6     0.00000002     -5418.1824779812 -1.83E-07
   25 Broy./Diag. 0.10E+00    0.6     3.7035E-09     -5418.1824782140 -2.33E-07

*** SCF run converged in    25 steps ***
```

Hirshfeld Charges

#Atom	Element	Kind	Ref Charge	Population		Spin moment	Net charge
1	Ni	1	18.000	9.000	9.000	-0.000	-0.000
2	Ni	1	18.000	9.000	9.000	-0.000	-0.000
3	Ni	1	18.000	9.000	9.000	0.000	-0.000
4	Ni	1	18.000	9.000	9.000	-0.000	-0.000
5	Ni	1	18.000	9.000	9.000	-0.000	0.000
6	Ni	1	18.000	9.000	9.000	-0.000	-0.000
7	Ni	1	18.000	9.000	9.000	-0.000	0.000
8	Ni	1	18.000	9.000	9.000	-0.000	0.000
9	Ni	1	18.000	9.000	9.000	-0.000	0.000
10	Ni	1	18.000	9.000	9.000	-0.000	-0.000
11	Ni	1	18.000	9.000	9.000	0.000	-0.000
12	Ni	1	18.000	9.000	9.000	0.000	-0.000
13	Ni	1	18.000	9.000	9.000	-0.000	-0.000
14	Ni	1	18.000	9.000	9.000	-0.000	-0.000
15	Ni	1	18.000	9.000	9.000	0.000	-0.000
16	Ni	1	18.000	9.000	9.000	-0.000	0.000
17	Ni	1	18.000	9.000	9.000	-0.000	0.000
18	Ni	1	18.000	9.000	9.000	-0.000	0.000
19	Ni	1	18.000	9.000	9.000	0.000	-0.000
20	Ni	1	18.000	9.000	9.000	0.000	-0.000
21	Ni	1	18.000	9.000	9.000	-0.000	0.000
22	Ni	1	18.000	9.000	9.000	-0.000	-0.000
23	Ni	1	18.000	9.000	9.000	0.000	0.000
24	Ni	1	18.000	9.000	9.000	-0.000	-0.000
25	Ni	1	18.000	9.000	9.000	0.000	0.000
26	Ni	1	18.000	9.000	9.000	-0.000	0.000
27	Ni	1	18.000	9.000	9.000	0.000	0.000
28	Ni	1	18.000	9.000	9.000	0.000	0.000
29	Ni	1	18.000	9.000	9.000	-0.000	-0.000
30	Ni	1	18.000	9.000	9.000	-0.000	0.000
31	Ni	1	18.000	9.000	9.000	0.000	-0.000
32	Ni	1	18.000	9.000	9.000	-0.000	-0.000

DFT SCF converges in 25 SCF steps and Hirshfeld analysis shows Ni spin moment of 0.00

Bulk Ni: multiplicity 65

From electronic configuration [Ar] $3d^8$ $4s^2$ Ni should be ferromagnetic

2 unpaired electrons per atom -> total multiplicity 2S+1: 2*2*1/2*32+1=65

```
Electronic structure
   Total number of core electrons                          10.00
   Total number of valence electrons                       18.00
   Total number of electrons                               28.00
   Multiplicity                                       not specified
   S   [  2.00  2.00] 2.00  2.00
   P   [  6.00] 6.00
   D      8.00


   Spin 1
   Re-scaling the density matrix to get the right number of electrons for spin 1
                  # Electrons             Trace(P)              Scaling factor
                          320              288.033                      1.111

   Spin 2
   Re-scaling the density matrix to get the right number of electrons for spin 2
                  # Electrons             Trace(P)              Scaling factor
                          256              288.033                      0.889
```

Bulk Ni: multiplicity 65

```
Spin 1
Re-scaling the density matrix to get the right number of electrons for spin 1
                # Electrons             Trace(P)              Scaling factor
                       320              288.033                       1.111

Spin 2
Re-scaling the density matrix to get the right number of electrons for spin 2
                # Electrons             Trace(P)              Scaling factor
                       256              288.033                       0.889


SCF WAVEFUNCTION OPTIMIZATION

 Step     Update method       Time    Convergence         Total energy    Change
 ----------------------------------------------------------------------------
    1 NoMix/Diag. 0.10E+00    0.4     0.90450672     -5430.9290286363 -5.43E+03
    2 Broy./Diag. 0.10E+00    0.6     0.01963244     -5360.9174089422  7.00E+01
    3 Broy./Diag. 0.10E+00    0.6     0.03786641     -5391.3474411346 -3.04E+01
    4 Broy./Diag. 0.10E+00    0.6     0.01643672     -5405.2813195731 -1.39E+01
    5 Broy./Diag. 0.10E+00    0.6     0.01057503     -5388.1651812634  1.71E+01
    6 Broy./Diag. 0.10E+00    0.6     0.02784068     -5399.2606535744 -1.11E+01
    7 Broy./Diag. 0.10E+00    0.6     0.00097126     -5420.3160555134 -2.11E+01
    8 Broy./Diag. 0.10E+00    0.6     0.00691562     -5420.5626988254 -2.47E-01
    9 Broy./Diag. 0.10E+00    0.6     0.00073849     -5420.3611606832  2.02E-01
   10 Broy./Diag. 0.10E+00    0.6     0.00082272     -5419.8704837172  4.91E-01
   11 Broy./Diag. 0.10E+00    0.6     0.00103204     -5419.1493765569  7.21E-01
   12 Broy./Diag. 0.10E+00    0.6     0.00015473     -5418.4205397216  7.29E-01
   13 Broy./Diag. 0.10E+00    0.6     0.00020785     -5418.2998409068  1.21E-01
   14 Broy./Diag. 0.10E+00    0.6     0.00000517     -5418.2842484945  1.56E-02
   15 Broy./Diag. 0.10E+00    0.6     0.00004969     -5418.2863691706 -2.12E-03
   16 Broy./Diag. 0.10E+00    0.6     0.00023052     -5418.2951055282 -8.74E-03
   17 Broy./Diag. 0.10E+00    0.6     0.00078318     -5418.3069846198 -1.19E-02
   18 Broy./Diag. 0.10E+00    0.6     0.00002694     -5418.3257565653 -1.88E-02
   19 Broy./Diag. 0.10E+00    0.6     0.00007294     -5418.3160793514  9.68E-03
   20 Broy./Diag. 0.10E+00    0.6     0.00000274     -5418.3208987916 -4.82E-03
   21 Broy./Diag. 0.10E+00    0.6     0.00001096     -5418.3174419640  3.46E-03
   22 Broy./Diag. 0.10E+00    0.6     0.00001005     -5418.3093980076  8.04E-03
   23 Broy./Diag. 0.10E+00    0.6     0.00000298     -5418.3033214071  6.08E-03
   24 Broy./Diag. 0.10E+00    0.6     0.00000164     -5418.3010164987  2.30E-03
   25 Broy./Diag. 0.10E+00    0.7     0.00000062     -5418.2998759471  1.14E-03
   26 Broy./Diag. 0.10E+00    0.7     0.00000054     -5418.2993002624  5.76E-04
   27 Broy./Diag. 0.10E+00    0.6     0.00000031     -5418.2989713234  3.29E-04
   28 Broy./Diag. 0.10E+00    0.6     0.00000007     -5418.2987449650  2.26E-04
   29 Broy./Diag. 0.10E+00    0.6     0.00000004     -5418.2988038120 -5.88E-05
   30 Broy./Diag. 0.10E+00    0.7     0.00000004     -5418.2988106371 -6.83E-06
   31 Broy./Diag. 0.10E+00    0.7     0.00000006     -5418.2988164482 -5.81E-06
   32 Broy./Diag. 0.10E+00    0.8     0.00000010     -5418.2988162648  1.83E-07
   33 Broy./Diag. 0.10E+00    0.6     0.00000003     -5418.2988136581  2.61E-06
   34 Broy./Diag. 0.10E+00    0.6     0.00000002     -5418.2988129024  7.56E-07
   35 Broy./Diag. 0.10E+00    0.6     0.00000002     -5418.2988128930  9.37E-09
   36 Broy./Diag. 0.10E+00    0.6     5.3291E-09     -5418.2988130264 -1.33E-07

 *** SCF run converged in    36 steps ***
```

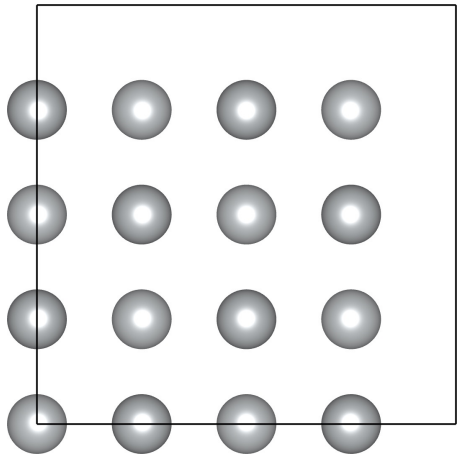
#Atom	Element	Kind	Ref Charge	Population		Spin moment	Net charge
1	Ni	1	18.000	9.344	8.656	0.687	0.000
2	Ni	1	18.000	9.344	8.656	0.687	0.000
3	Ni	1	18.000	9.344	8.656	0.687	-0.000
4	Ni	1	18.000	9.344	8.656	0.687	0.000
5	Ni	1	18.000	9.344	8.656	0.687	0.000
6	Ni	1	18.000	9.344	8.656	0.687	0.000
7	Ni	1	18.000	9.344	8.656	0.687	-0.000
8	Ni	1	18.000	9.344	8.656	0.687	-0.000
9	Ni	1	18.000	9.344	8.656	0.687	-0.000
10	Ni	1	18.000	9.344	8.656	0.687	-0.000
11	Ni	1	18.000	9.344	8.656	0.687	-0.000
12	Ni	1	18.000	9.344	8.656	0.687	-0.000
13	Ni	1	18.000	9.344	8.656	0.687	-0.000
14	Ni	1	18.000	9.344	8.656	0.687	-0.000
15	Ni	1	18.000	9.344	8.656	0.687	-0.000
16	Ni	1	18.000	9.344	8.656	0.687	-0.000
17	Ni	1	18.000	9.344	8.656	0.687	-0.000
18	Ni	1	18.000	9.344	8.656	0.687	0.000
19	Ni	1	18.000	9.344	8.656	0.687	-0.000
20	Ni	1	18.000	9.344	8.656	0.687	0.000
21	Ni	1	18.000	9.344	8.656	0.687	-0.000
22	Ni	1	18.000	9.344	8.656	0.687	-0.000
23	Ni	1	18.000	9.344	8.656	0.687	-0.000
24	Ni	1	18.000	9.344	8.656	0.687	-0.000
25	Ni	1	18.000	9.344	8.656	0.687	-0.000
26	Ni	1	18.000	9.344	8.656	0.687	-0.000
27	Ni	1	18.000	9.344	8.656	0.687	-0.000
28	Ni	1	18.000	9.344	8.656	0.687	0.000
29	Ni	1	18.000	9.344	8.656	0.687	-0.000
30	Ni	1	18.000	9.344	8.656	0.687	-0.000
31	Ni	1	18.000	9.344	8.656	0.687	-0.000
32	Ni	1	18.000	9.344	8.656	0.687	-0.000

DFT SCF converges in 36 SCF steps and Hirshfeld analysis shows Ni spin moment of 0.69

Bulk Ni summary

- Energy for bulk Ni is 3 eV lower with a ferromagnetic solution
- Correct choice of multiplicity is essential to converge magnetic solution

Multiplicity	Energy / Ha	SCF steps	Spin moment
1	-5418.1825	25	0.00
65	-5418.2988	36	0.69



2x2x2 Ni supercell

Improving the initial guess

&BS section defines the atomic orbital occupation assigned in initialization of the density matrix

N: Principal quantum number

L: Angular momentum quantum number

NEL: Orbital occupation number

```
&KIND Ni
        ELEMENT Ni
        BASIS_SET DZVP-MOLOPT-SR-GTH
        POTENTIAL GTH-PBE
        &BS
         &ALPHA
           N    4  3
           L    0  2
           NEL  0  2
         &END
         &BETA
           N    4  3
           L    0  2
           NEL  0 -2
         &END
 &END
&END KIND
```

```
Electronic structure
   Total number of core electrons                    10.00
   Total number of valence electrons                 18.00
   Total number of electrons                         28.00
   Multiplicity                                not specified
   S    [  2.00  2.00] 2.00  2.00
   P    [  6.00] 6.00
   D       8.00
```

```
Electronic structure
   Total number of core electrons                    10.00
   Total number of valence electrons                 18.00
   Total number of electrons                         28.00
   Multiplicity                                     triplet
   Alpha Electrons
   S    [  1.00  1.00] 1.00  1.00                          2*2*0.5+1=3
   P    [  3.00] 3.00
   D       5.00
   Beta Electrons
   S    [  1.00  1.00] 1.00  1.00
   P    [  3.00] 3.00
   D       3.00
```

Improving the initial guess

Alternative to &BS section is MAGNETIZATION keyword

```
&KIND Ni
        ELEMENT Ni
        BASIS_SET DZVP-MOLOPT-SR-GTH
        POTENTIAL GTH-PBE
        &BS
         &ALPHA
           N    4  3
           L    0  2
           NEL  0  2
         &END
         &BETA
           N    4  3
           L    0  2
           NEL  0 -2
         &END
 &END
&END KIND
```

```
Electronic structure
   Total number of core electrons                    10.00
   Total number of valence electrons                 18.00
   Total number of electrons                         28.00
   Multiplicity                                not specified
   S    [  2.00  2.00] 2.00  2.00
   P    [  6.00] 6.00
   D       8.00
```

```
&KIND Ni
        ELEMENT Ni
        BASIS_SET DZVP-MOLOPT-SR-GTH
        POTENTIAL GTH-PBE
        MAGNETIZATION 2.0
&END KIND
```

```
Electronic structure
   Total number of core electrons                    10.00
   Total number of valence electrons                 18.00
   Total number of electrons                         28.00
   Multiplicity                                     triplet
   Alpha Electrons
   S    [  1.00  1.00] 1.00  1.00
   P    [  3.00] 3.00
   D       5.00
   Beta Electrons
   S    [  1.00  1.00] 1.00  1.00
   P    [  3.00] 3.00
   D       3.00
```

Improving the initial guess

Alternative to &BS section is MAGNETIZATION keyword

```
&KIND Ni
        ELEMENT Ni
        BASIS_SET DZVP-MOLOPT-SR-GTH
        POTENTIAL GTH-PBE
        &BS
         &ALPHA
           N    4  3
           L    0  2
           NEL  0  2
         &END
         &BETA
           N    4  3
           L    0  2
           NEL  0 -2
         &END
 &END
&END KIND
```

```
Spin 1
Re-scaling the density matrix to get the right number of electrons for spin 1
                 # Electrons                Trace(P)                Scaling factor
                         320                 288.033                         1.111

Spin 2
Re-scaling the density matrix to get the right number of electrons for spin 2
                 # Electrons                Trace(P)                Scaling factor
                         256                 288.033                         0.889
```

```
Spin 1
Re-scaling the density matrix to get the right number of electrons for spin 1
                 # Electrons                Trace(P)                Scaling factor
                         320                 320.021                         1.000
```

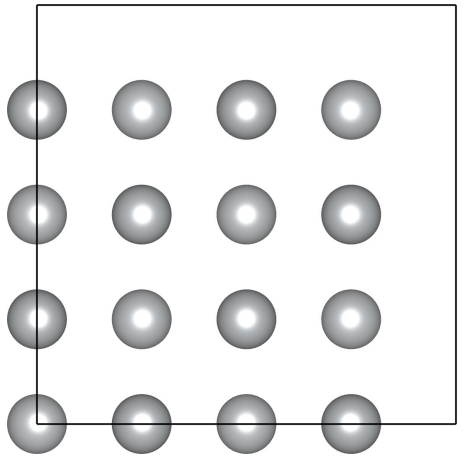
```
&KIND Ni
        ELEMENT Ni
        BASIS_SET DZVP-MOLOPT-SR-GTH
        POTENTIAL GTH-PBE
        MAGNETIZATION 2.0
&END KIND
```

```
Spin 2
Re-scaling the density matrix to get the right number of electrons for spin 2
                 # Electrons                Trace(P)                Scaling factor
                         256                 256.024                         1.000
```

Bulk Ni summary

- Energy for bulk Ni is 3 eV lower with a ferromagnetic solution
- Multiplicity can be optimised with knowledge of calculated spin moment (starting guess s=0.5 is faster than s=1)

Multiplicity	Energy / Ha	SCF steps	Spin moment
1	-5418.1825	25	0.00
65 (MAGNETIZATION 2)	-5418.2988	46	0.69
33 (MAGNETIZATION 1)	-5418.2988	23	0.69

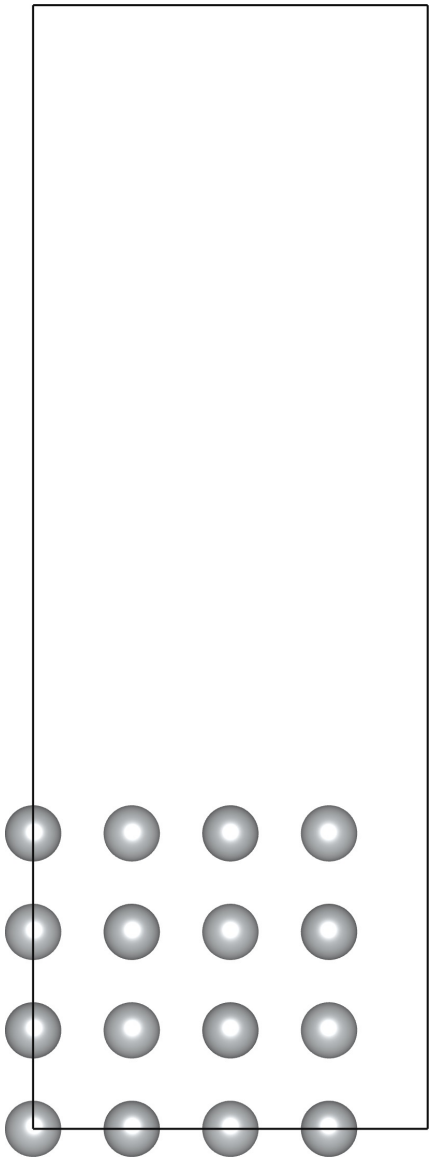


2x2x2 Ni supercell

Ni slab in vacuum

- Energy for Ni slab in vacuum is 2 eV lower with a ferromagnetic solution
- SCF convergence is very slow (SCF steps shown for EPS_SCF: 1e-5, 1e-7)

Multiplicity	Energy / Ha	SCF steps	Spin moment
1	-5417.5516	45, 73	0.00
65 (MAGNETIZATION 2)	-5414.6756	285, 374	0.68 bulk 0.74 interfacial
33 (MAGNETIZATION 1)	-5417.6242	564, 616	0.68 bulk 0.75 interfacial



2x2x2 Ni slab in vacuum

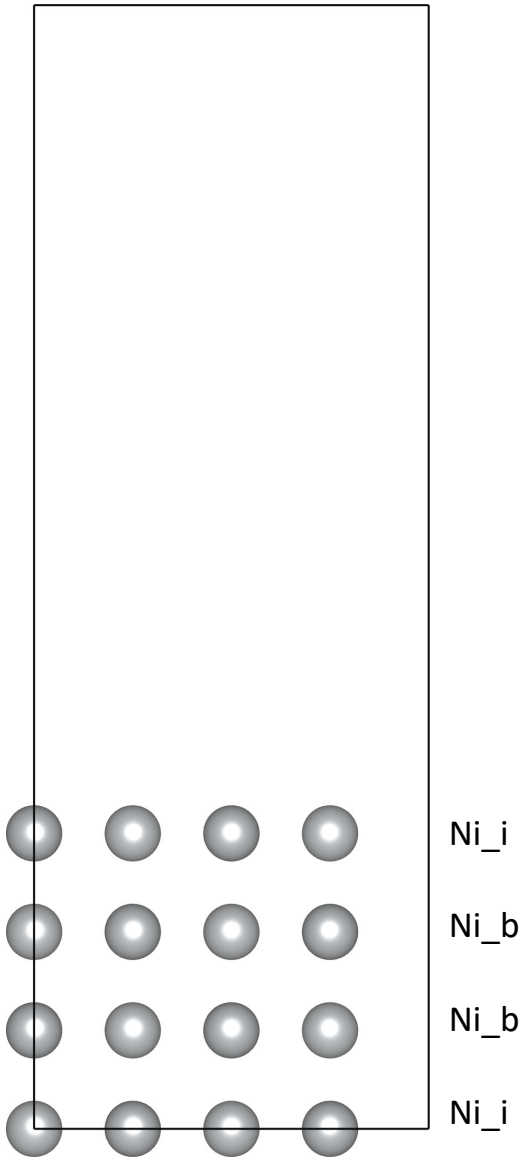
Improving the initial guess

1. Define MAGNETIZATION for each unique atomic environment
2. Choose non-integer magnetizations which sum to integer multiplicity (16*0.7+16*0.8)+1=25

```
&KIND Ni_b
        ELEMENT Ni
        BASIS_SET DZVP-MOLOPT-SR-GTH
        POTENTIAL GTH-PADE-q18
        MAGNETIZATION 0.7
&END KIND
```

```
&KIND Ni_i
        ELEMENT Ni
        BASIS_SET DZVP-MOLOPT-SR-GTH
        POTENTIAL GTH-PADE-q18
        MAGNETIZATION 0.8
&END KIND
```

Multiplicity	Energy / Ha	SCF steps	Spin moment
1	-5417.5516	45, 73	0.00
65 (MAGNETIZATION 2)	-5414.6756	285, 374	0.68 bulk 0.74 interfacial
25 (MAGNETIZATION 0.7, 0.8)	-5414.6756	57, 139	0.68 bulk 0.74 interfacial

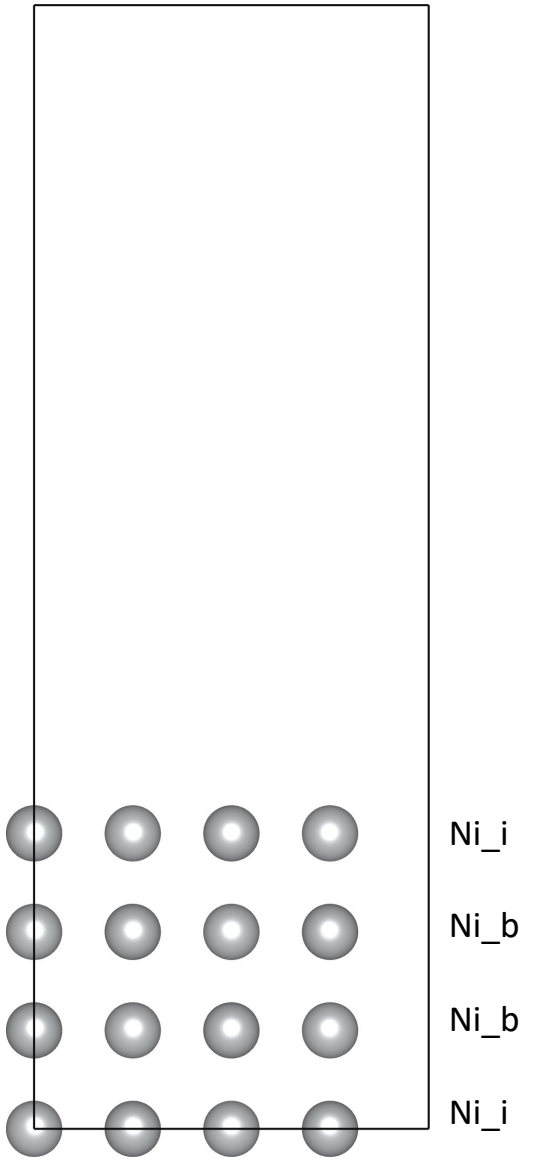


2x2x2 Ni slab in vacuum

General workflow

1. Converge bulk crystal with multiplicity according to Hund's rule
2. Converge interface with multiplicity according to Hund's rule
3. Define MAGNETIZATION for each unique atomic environment
4. Optimise MAGNETIZATION (float) consistently with MULTIPLICITY (integer)

Multiplicity	Energy / Ha	SCF steps	Spin moment
1	-5417.5516	45, 73	0.00
65 (MAGNETIZATION 2)	-5414.6756	285, 374	0.68 bulk 0.74 interfacial
25 (MAGNETIZATION 0.7, 0.8)	-5414.6756	57, 139	0.68 bulk 0.74 interfacial



2x2x2 Ni slab in vacuum

Thank you for listening

Supporting Information

Bulk Ni

Defining MAGNETIZATION increases number of SCF steps for bulk Ni

Multiplicity 65, MAX_SCF 1

```
1 NoMix/Diag. 0.10E+00    0.5      0.90450672     -5430.9290286363 -5.43E+03
1       Ni      1      18.000    9.482   8.518           0.964     -0.000
```

Multiplicity 65, MAX_SCF 1, MAGNETIZATION 2

```
1 NoMix/Diag. 0.10E+00    0.4      0.80945817     -5430.9700952423 -5.43E+03
1       Ni      1      18.000    9.479   8.521           0.957     -0.000
```

Multiplicity 65, MAX_SCF 1

```
1 NoMix/Diag. 0.10E+00    0.4      0.87189090     -5430.0490174185 -5.43E+03
1       Ni      1      18.000    9.227   8.773           0.453     -0.000
```

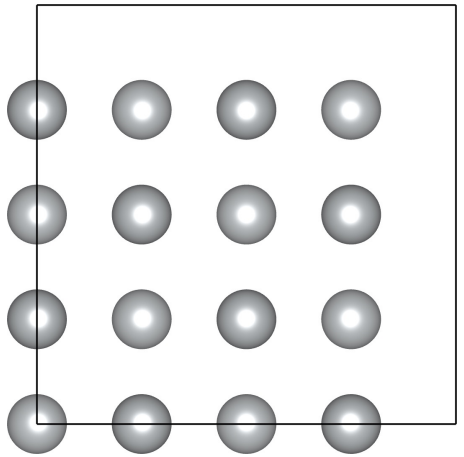
Multiplicity 65, MAX_SCF 1, MAGNETIZATION 1

```
1 NoMix/Diag. 0.10E+00    0.4      0.82500894     -5430.0597589981 -5.43E+03
1       Ni      1      18.000    9.223   8.777           0.446     -0.000
```

Bulk Ni

- Energy for bulk Ni is 3 eV lower with a ferromagnetic solution
- Correct choice of multiplicity is essential to converge magnetic solution
- &BS section or MAGNETIZATION lowers energy of first SCF step, however leads to slower convergence

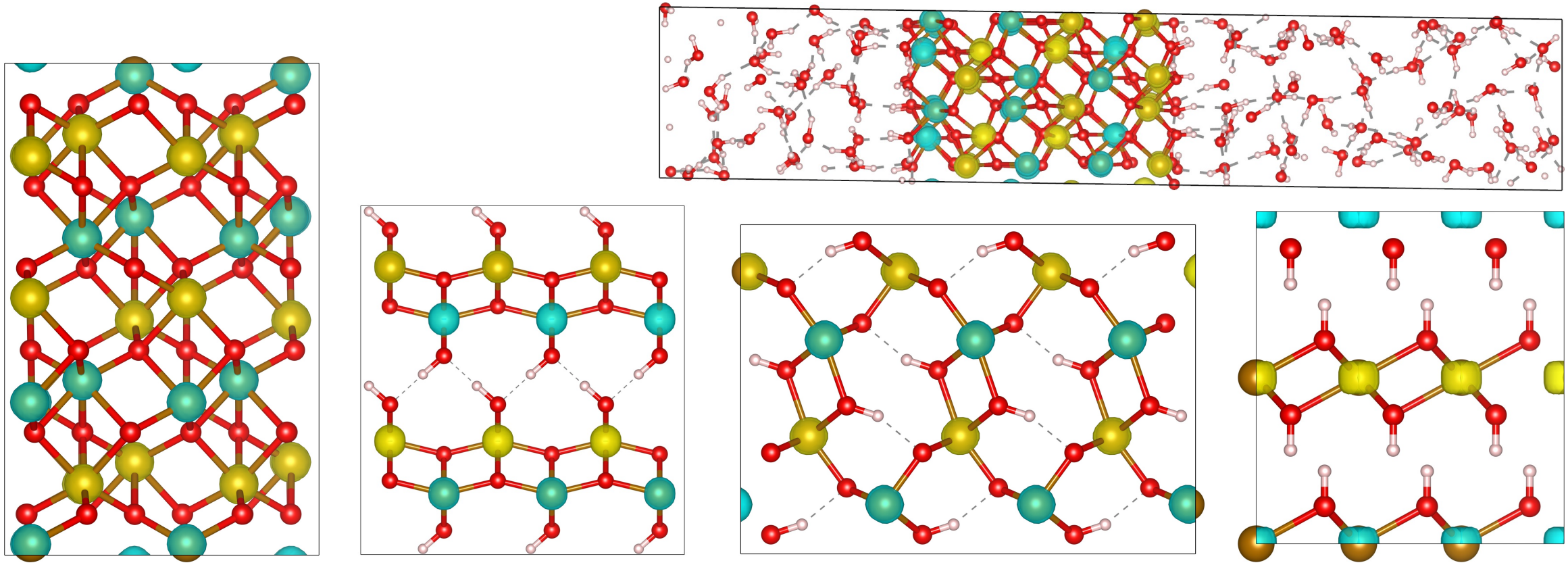
Multiplicity	Energy / Ha	SCF steps	Spin moment
1	-5418.1825	25	0.00
65	-5418.2988	36	0.69
65 (MAGNETIZATION 2)	-5418.2988	46	0.69
33	-5418.2988	19	0.69
33 (MAGNETIZATION 1)	-5418.2988	23	0.69



2x2x2 Ni supercell

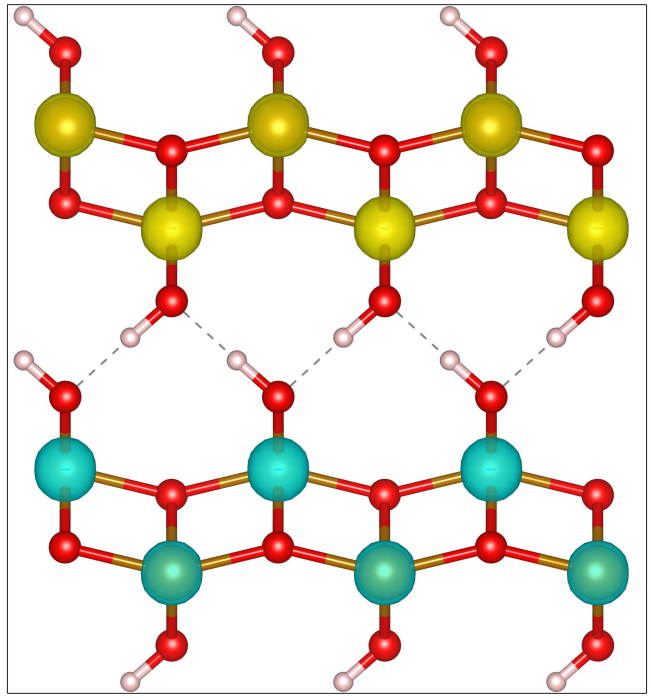
My background

- PhD research involved converging antiferromagnetic iron oxides
- No previous experience with Ni or pure metals

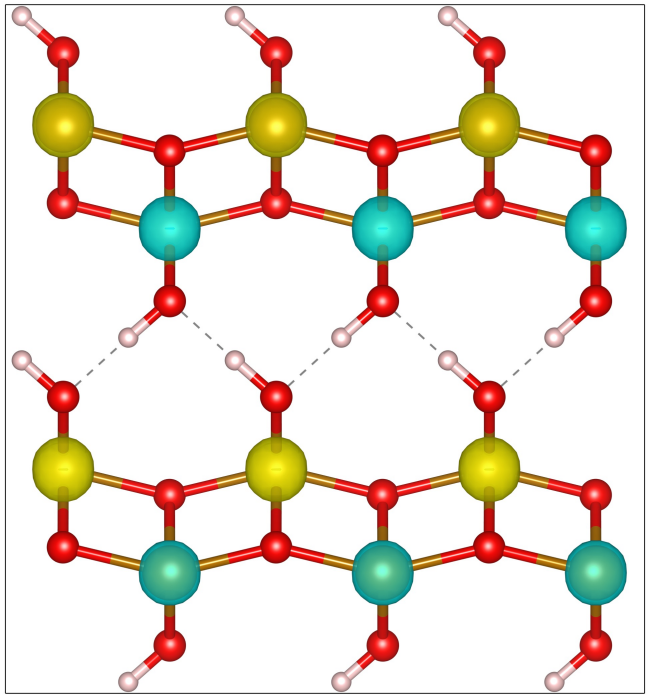


Lepidocrocite

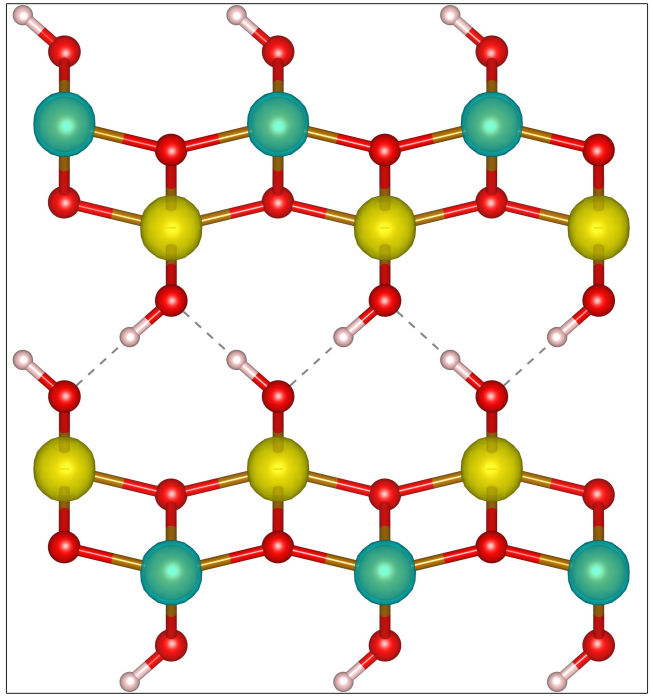
- Multiple magnetic solutions may exist for the same multiplicity, these must be checked manually



uudd -5623.8244 Ha
Spin moment 4.37 μ_B



udud -5623.8403 Ha
Spin moment 4.29 μ_B



uddu -5623.8383 Ha
Spin moment 4.29 μ_B