CP2K changes

https://github.com/chrisahart/cp2k/tree/nelectron-specify

CP2K code changes

1. &BS section NEL integer is now a float
2. New keywords (integer) MAGNETIZATION_N and MAGNETIZATION_L
3. New keywords (float) for number of electrons NELEC_ALPHA, NELEC_BETA

```
  &BS
  &ALPHA
   N  4  3
   L  0  2
   NEL 0  2.0
  &END
  &BETA
   N 4  3
   L 0  2
   NEL  0  -2.0
  &END
&END
```

55 files modified, most features likely will not support non-integer number of electrons

Known incompatibilities:

OT: number of orbitals must be equal to the number of electrons

```
&KIND Ni
  BASIS_SET DZVP-MOLOPT-SR-GTH
  POTENTIAL GTH-PBE-q18
  MAGNETIZATION 2.0
  MAGNETIZATION_N 3
  MAGNETIZATION_L 2
&END KIND
```

Possible issues:

Kpoints: subroutines previously always would override molecular orbital occupations, I have restored original molecular orbital occupations for T=0. This seems to work.

```
CHARGE 0
NELEC_ALPHA 316.8
NELEC_BETA  259.2
```

https://github.com/chrisahart/cp2k/tree/nelectron-specify

Manual allocation of electrons

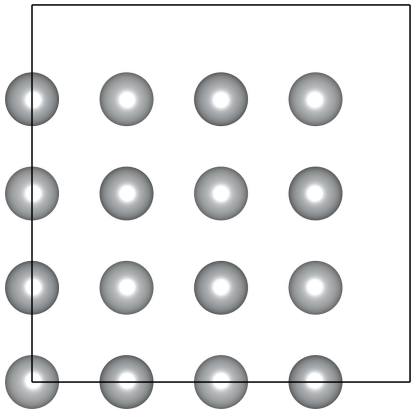
```
CHARGE 0
NELEC_ALPHA 316.8
NELEC_BETA  259.2
```

- Number of alpha electrons NELEC_ALPHA - CHARGE and beta electrons NELEC_BETA
- Sum of NELEC_ALPHA and NELEC_BETA must be an integer
- Number of alpha, beta molecular orbitals = CEILING(number of alpha, beta electrons) + ADDED_MOS

```
*** WARNING in qs_environment.F:1457 :: Number of electrons will be ***
*** overwritten by NELEC_ALPHA and NELEC_BETA, multiplicity will be ***
*** ignored.                                                        ***

Number of electrons should be         576
Sum of NELEC_ALPHA and NELEC_BETA is   576.00000000000000

 Spin 1

 Number of electrons:                                                316.800
 Number of occupied orbitals:                                        317

 Spin 2

 Number of electrons:                                                259.200
 Number of occupied orbitals:                                        260


Integrated absolute spin density  :                          57.5999999999

Total charge and spin      316.800000   259.200000    -0.000000    57.600000
```

Ni

Manual allocation of electrons: bulk Ni



Ferromagnetic bulk Ni 2x2x2 supercell. Converged spin moment 0.687. Kpoints 1x1x1

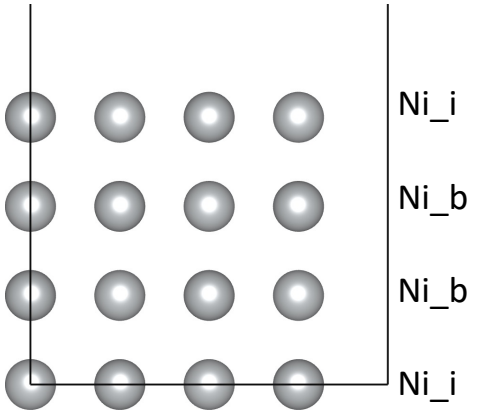
SCF shown for EPS_SCF 5E-7. IASD, spin and energy shown for MAX_SCF 1 and DIRECT_P_MIXING

Right hand side table for ADDED_MOS=0 and T=0, as smearing changes guess density

Ni	Multiplicity	Electrons	IASD/32	Spin	Energy	SCF
2	(32*2*)+1=65		0.961	0.957	-5430.5035	29
1.8		316.8, 259.2	0.796	0.772	-5430.2732	43
1.5	(32*1.5)+1=49		0.684	0.680	-5429.9727	39
1	(32*1)+1=33		0.544	0.446	-5429.5932	28
0.5	(32*0.5)+1=17		0.480	0.437	-5429.3654	

Spin	IASD/32
2	2.000
1.8	1.800
1.5	1.500
1	1.000
0.5	0.500

Manual allocation of electrons: Ni slab



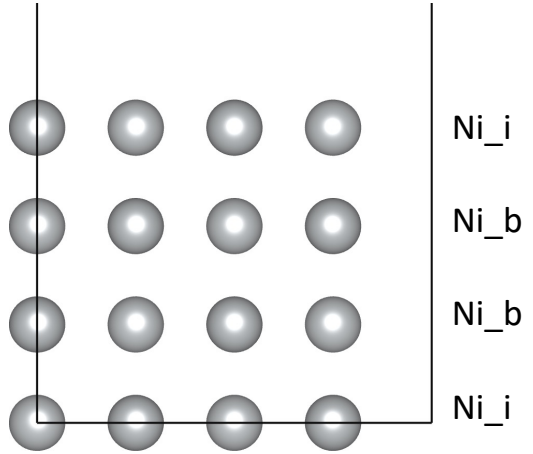
Ferromagnetic Ni 2x2x2 slab. Converged spin moment 0.70, 0.61. Kpoints 4x4x1

SCF shown for EPS_SCF 1E-3. IASD, spin and energy shown for MAX_SCF 1 and DIRECT_P_MIXING

Right hand side table for ADDED_MOS=0, no smearing. IASD and total Mulliken spin

Ni	Multiplicity	Electrons	IASD/32	Spin	Energy	SCF	Mulliken	IASD
1	(32*1)+1=33		0.660	0.642, 0.560	-5426.6352	95	32.00	32.00
0.75	(32*0.75)+1=25		0.579	0.578, 0.500	-5426.5023	17	24.00	24.13
0.7, 0.8	(16*0.7+16*0.8)+1=25		0.580	0.614, 0.466	-5426.5031	13	24.00	24.12
0.625	(32*0.625)+1=21		0.526	0.530, 0.457	-5426.4501	11	20.00	20.56
0.5, 0.7		297.6, 278.4	0.516	0.591, 0.391	-5426.4438	9	19.20	19.76

Manual allocation of electrons: Ni slab



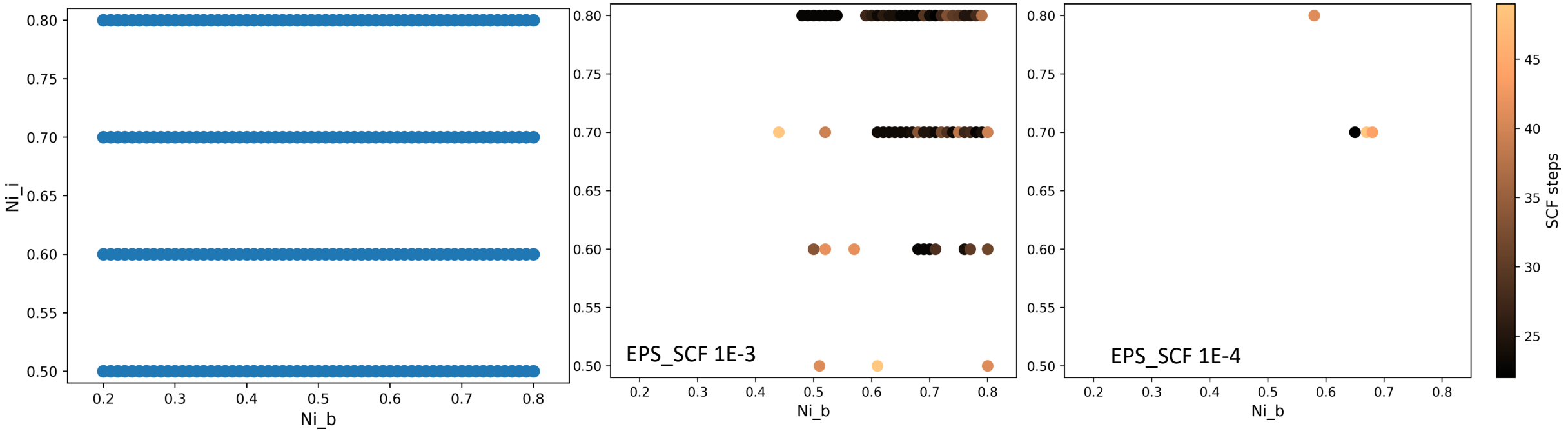
Ferromagnetic Ni 2x2x2 slab. Converged spin moment Ni_b=0.61, Ni_i=0.70. IASD 23.65

1D grid search for KPOINTS (4x4x1), ADDED_MOS (-1), ELECTRONIC_TEMPERATURE (2000)

8x8=64 2D grid search for ALPHA (0.08), BETA (1.5)

4x60=240 2D grid search for Ni_b, Ni_i MAGNETIZATION shown for SCF < 50 and IASD > 20

Ni_b (0.65), Ni_i (0.70) converges in 63 steps for EPS_SCF 1E-5 with 1 restart, with further refinement should be faster



Supporting Information

Smearing

```
Spin 1

Number of electrons:                                    316.800
Number of occupied orbitals:                            317
Number of molecular orbitals:                           832

Spin 2

Number of electrons:                                    259.200
Number of occupied orbitals:                            260
Number of molecular orbitals:                           832
```

```
1.0000000000000000   1.0000000000000000   1.0000000000000000   1.0000000000000000
1.0000000000000000   1.0000000000000000   1.0000000000000000   0.19999999999998863
0.0000000000000000   0.0000000000000000   0.0000000000000000   0.0000000000000000
0.0000000000000000   0.0000000000000000   0.0000000000000000   0.0000000000000000
0.0000000000000000   0.0000000000000000   0.0000000000000000   0.0000000000000000
```

```
SUM(mo_set%occupation_numbers)
  316.80000000000001
```

```
SUM(mo_set%occupation_numbers)
  259.19999999999999
```

```
0.99961525679507690   0.99961523541008257   0.99961523541004316   0.99961523541004249
0.33541395522983858   0.33541395520909806   0.33541395513933492   0.21813725338589141
0.21813725336214776   0.21813725319575078   0.21813721865361865   0.21813721863148941
0.21813721860272914   0.21813721859516533   0.21813721858464186   0.21452003167550554
0.21451999753753381   0.21451999735887881   0.21451999735861882    3.2653117149019535E-003
```

```
SUM(occ_a)
  300.35421073021865
```

```
SUM(occ_b)
  275.64578926978157
```