https://github.com/chrisahart/cp2k/tree/nelectron-specify_outer-scf

CP2K code changes

Major:

1. New keywords (float) for number of electrons NELEC_ALPHA, NELEC_BETA
2. New keyword (float) EPS_SCF_ARRAY to decrease EPS_SCF through OUTER_SCF

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

```
MUST_CONVERGE TRUE
EPS_SCF 5E-3
EPS_SCF_ARRAY 5E-3 5E-4
```

Minor:

1. New keyword (logical) MUST_CONVERGE aborts CP2K if inner SCF does not converge
2. New keyword (float) EPS_SCF_MULTIPLIER as an alternative to EPS_SCF_ARRAY
3. New keywords (integer) MAGNETIZATION_N and MAGNETIZATION_L
4. &BS section NEL integer is now a float

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

Bug fixes:

1. OUTER_SCF now works for BROYDEN_MIXING (buffer reset each OUTER_SCF)
2. OUTER_SCF now works for DIRECT_P_MIXING (RMS gradient is now calculated correctly)

https://github.com/chrisahart/cp2k/tree/nelectron-specify_outer-scf

Decreasing EPS_SCF through OUTER_SCF

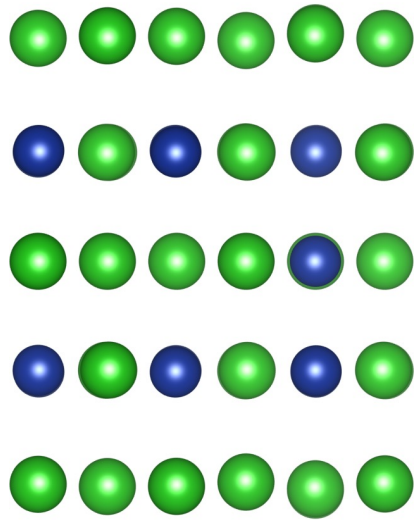
- EPS_SCF_ARRAY is used to specify EPS_SCF for each OUTER_SCF

```
&OUTER_SCF
  MAX_SCF 12
  EPS_SCF 5E-6

&SCF
  MAX_SCF  60
  MUST_CONVERGE TRUE
  EPS_SCF 5E-3
  EPS_SCF_ARRAY 5E-3 5E-4 4E-4 3E-4 2E-4 1E-4 5E-5 4E-5 3E-5 2E-5 1E-5 5E-6
```

```
max_scf:                                                60
max_scf_history:                                         0
max_diis:                                                4
---------------------------------------------------------
eps_scf:                                          5.00E-03
eps_scf_history:                                  0.00E+00
eps_diis:                                         1.00E-01
eps_eigval:                                       1.00E-05
---------------------------------------------------------
level_shift [a.u.]:                               0.000000
added MOs                                         100  100
eps_scf_array( 1)                                5.00E-03
eps_scf_array( 2)                                5.00E-04
eps_scf_array( 3)                                4.00E-04
eps_scf_array( 4)                                3.00E-04
eps_scf_array( 5)                                2.00E-04
eps_scf_array( 6)                                1.00E-04
eps_scf_array( 7)                                5.00E-05
eps_scf_array( 8)                                4.00E-05
eps_scf_array( 9)                                3.00E-05
eps_scf_array(10)                                2.00E-05
eps_scf_array(11)                                1.00E-05
eps_scf_array(12)                                5.00E-06
---------------------------------------------------------
Mixing method:                          BROYDEN_MIXING
                        charge density mixing in g-space
---------------------------------------------------------
Smear method:                              FERMI_DIRAC
Electronic temperature [K]:                     2000.0
Electronic temperature [a.u.]:                6.33E-03
Accuracy threshold:                           1.00E-10
---------------------------------------------------------
Outer loop SCF in use
No variables optimised in outer loop
eps_scf                                          5.00E-06
max_scf                                                12
```

$Pt_3Ni(111)$ Yike structure ENERGY

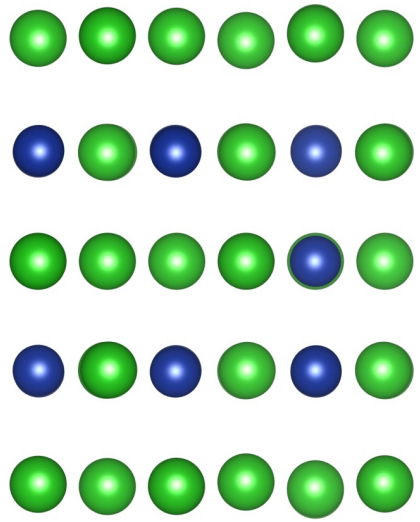


- /rds/general/user/cahart/projects/archive/live/CX1/YIKE/ORR/water/Pt3Ni/water_bilayer
- Pt-segregated $Pt_3Ni(111)$ structure with 45 Pt atoms, 15 Ni atoms (water removed)
- ~ 20A total vacuum (cell size: 9.378 0.0 0.0, -4.689 8.122 0.0, 0.0 0.0 29.0618991852)

Folder	Kpoints	Multiplicity	Energy / Ha	IASD	EPS_SCF	SCF steps	SCF loops *
(1)	1x1x1	(0*15)+1=1	-7948.9024	0.00	5e-6	44	1
(2)	1x1x1	(2*15)+1=31	-7948.9273	22.4	1e-2 -> 5e-6	176	16
(3)	8x8x1	(1*15)+1=16	-7949.3226	19.8	5e-3 -> 5e-6	130	12
(4)	8x8x1	(1*15)+1=16	-7949.3226	19.8	5e-3 -> 5e-6	128	8

* Equal to 1 for no OUTER_SCF, else equal to len(EPS_SCF_ARRAY)
(1) Gitlab pt3ni/slab_yike/scarf/convergence/testing/Ni-0_Pt-0_yike_4e-2_4e-3_16_100_2000_1-1-1_pbe-d3_dzvp_eps-5e-6
(2) Gitlab pt3ni/slab_yike/scarf/convergence/testing/Ni-2_Pt-0_yike_4e-2_4e-3_16_100_2000_1-1-1_pbe-d3_dzvp_eps-1e-2-5e-6-16
(3) Gitlab pt3ni/slab_yike/scarf/convergence/outer_scf/eps_scf_array/Ni-1_Pt-0_yike_4e-2_4e-3_16_100_2000_8-8-1_pbe-d3_tzvp/MUST_CONVERGE_eps-5E-3_1E-3_5E-4_3E-4_2E-4_1E-4_5E-5_4E-5_3E-5_2E-5_1E-5_5E-6
(4) Gitlab pt3ni/slab_yike/scarf/convergence/outer_scf/eps_scf_array/Ni-1_Pt-0_yike_4e-2_4e-3_16_100_2000_8-8-1_pbe-d3_tzvp/MUST_CONVERGE_eps-5E-3_5E-4_4E-4_3E-4_2E-4_1E-4_5E-5_5E-6

$Pt_3Ni(111)$ Yike structure GEO_OPT



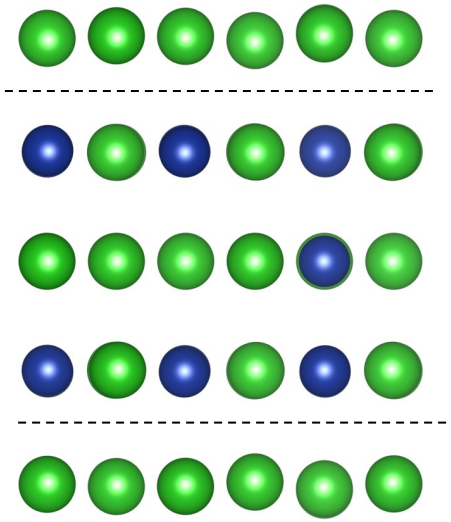
- Geometry optimisation can be run using OUTER_SCF and EPS_ARRAY
- SCF_GUESS ATOMIC
- 12 SCF loops is more reliable than 8 and adds negligible additional SCF steps

Step	Energy / Ha	IASD	EPS_SCF	SCF steps	SCF loops *
0	-7949.3226	19.8	5e-3 -> 5e-6	134	12
1	-7949.3287	20.04	5e-3 -> 5e-6	105	12
2	-7949.3301	20.07	5e-3 -> 5e-6	95	12
3	-7949.3303	20.08	5e-3 -> 5e-6	87	12
10	-7949.3306	20.14	5e-3 -> 5e-6	71	12

* Equal to 1 for no OUTER_SCF, else equal to len(EPS_SCF_ARRAY)

(1) Gitlab pt3ni/slab_yike/scarf/geo_opt/guess/Ni-1_Pt-0_yike_4e-2_4e-3_16_100_2000_8-8-1_pbe-d3_tzvp/MUST_CONVERGE_eps-5E-3_5E-4_4E-4_3E-4_2E-4_1E-4_5E-5_4E-5_3E-5_2E-5_1E-5_5E-6

$Pt_3Ni(111)$ Yike structure GEO_OPT constrained



- Geometry optimisation can be run using OUTER_SCF and EPS_ARRAY
- SCF_GUESS RESTART
- GEO_OPT with geometry constraints (surface reconstruction only)

Step	Energy / Ha	IASD	EPS_SCF	SCF steps	SCF loops *
0	-7949.3226	19.8	(5e-3 -> 5e-6)	(128)	(8)
1	-7949.3260	19.8	5e-3 -> 5e-6	83	8
2	-7949.3263	19.8	5e-3 -> 5e-6	79	8
3	-7949.3263	19.8	5e-3 -> 5e-6	83	8
8	-7949.3263	19.9	5e-3 -> 5e-6	53	8

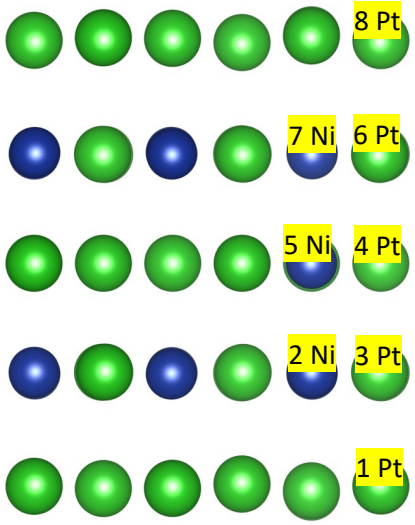
* Equal to 1 for no OUTER_SCF, else equal to len(EPS_SCF_ARRAY)

(1) Gitlab pt3ni/slab_yike/scarf/geo_opt_constrained/restart/Ni-1_Pt-0_yike_4e-2_4e-3_16_100_2000_8-8-1_pbe-d3_tzvp/MUST_CONVERGE_eps-5E-3_5E-4_4E-4_3E-4_2E-4_1E-4_5E-5_5E-6

Supporting Information

Spin moments

Source	Bulk spin moment Ni, Pt
This work	0.61, 0.20
[1] VASP PBE	0.67, 0.16
[2] DFTB	0.65, 0.16
[3] DFTB	0.58, 0.10



Numbering corresponds to CP2K atomic kind

Hirshfeld Charges

#Atom	Element	Kind	Ref Charge	Population		Spin moment	Net charge
1	Pt	1	18.000	9.049	8.957	0.092	-0.007
2	Pt	1	18.000	9.036	8.961	0.075	0.003
3	Pt	1	18.000	9.055	8.929	0.126	0.015
4	Pt	1	18.000	9.055	8.930	0.126	0.015
5	Pt	1	18.000	9.049	8.952	0.097	-0.001
6	Pt	1	18.000	9.036	8.958	0.078	0.007
7	Pt	1	18.000	9.048	8.950	0.098	0.002
8	Pt	1	18.000	9.035	8.955	0.080	0.010
9	Pt	1	18.000	9.058	8.923	0.135	0.019
10	Pt	1	18.000	9.058	8.923	0.135	0.019
11	Pt	1	18.000	9.059	8.919	0.140	0.022
12	Pt	1	18.000	9.059	8.920	0.139	0.022
13	Ni	2	18.000	9.493	8.675	0.818	-0.168
14	Ni	2	18.000	9.491	8.678	0.813	-0.168
15	Ni	2	18.000	9.489	8.680	0.809	-0.169
16	Ni	2	18.000	9.503	8.651	0.852	-0.154
17	Pt	3	18.000	9.041	8.857	0.185	0.102
18	Pt	3	18.000	9.041	8.856	0.186	0.103
19	Ni	2	18.000	9.502	8.652	0.850	-0.154
20	Ni	2	18.000	9.500	8.654	0.846	-0.154
21	Pt	3	18.000	9.041	8.857	0.184	0.102
22	Pt	3	18.000	9.041	8.854	0.187	0.105
23	Pt	3	18.000	9.041	8.855	0.186	0.104
24	Pt	3	18.000	9.041	8.854	0.188	0.105
25	Pt	4	18.000	9.050	8.836	0.214	0.114
26	Pt	4	18.000	9.022	8.877	0.145	0.101
27	Ni	5	18.000	9.398	8.784	0.613	-0.182
28	Pt	4	18.000	9.051	8.837	0.214	0.112
29	Pt	4	18.000	9.050	8.835	0.215	0.115
30	Pt	4	18.000	9.050	8.836	0.215	0.114
31	Ni	5	18.000	9.401	8.781	0.620	-0.182
32	Pt	4	18.000	9.022	8.876	0.145	0.102
33	Ni	5	18.000	9.394	8.790	0.604	-0.183
34	Pt	4	18.000	9.051	8.837	0.214	0.112
35	Pt	4	18.000	9.050	8.835	0.215	0.115
36	Pt	4	18.000	9.021	8.876	0.146	0.103
37	Pt	6	18.000	9.041	8.854	0.188	0.105
38	Pt	6	18.000	9.041	8.855	0.186	0.104
39	Pt	6	18.000	9.041	8.854	0.187	0.105
40	Pt	6	18.000	9.041	8.857	0.184	0.102
41	Ni	7	18.000	9.501	8.652	0.849	-0.154
42	Pt	6	18.000	9.041	8.856	0.186	0.103
43	Ni	7	18.000	9.500	8.654	0.847	-0.154
44	Pt	6	18.000	9.041	8.857	0.184	0.102
45	Ni	7	18.000	9.503	8.652	0.851	-0.154
46	Ni	7	18.000	9.489	8.680	0.809	-0.168
47	Ni	7	18.000	9.493	8.675	0.818	-0.168
48	Ni	7	18.000	9.491	8.677	0.813	-0.168
49	Pt	8	18.000	9.059	8.920	0.139	0.021
50	Pt	8	18.000	9.059	8.920	0.139	0.021
51	Pt	8	18.000	9.057	8.924	0.134	0.019
52	Pt	8	18.000	9.057	8.924	0.134	0.019
53	Pt	8	18.000	9.036	8.955	0.081	0.010
54	Pt	8	18.000	9.049	8.949	0.100	0.002
55	Pt	8	18.000	9.036	8.957	0.079	0.007
56	Pt	8	18.000	9.049	8.951	0.098	-0.001
57	Pt	8	18.000	9.055	8.930	0.125	0.015
58	Pt	8	18.000	9.055	8.930	0.124	0.015
59	Pt	8	18.000	9.036	8.961	0.075	0.003
60	Pt	8	18.000	9.049	8.957	0.093	-0.006

[1] Sharma, B. K., Kwon, O., Odkhuu, D. & Hong, S. C.. *Journal of Magnetism and Magnetic Materials* 339, 89–93 (2013).
[2] Paudyal, D., Saha-Dasgupta, T. & Mookerjee, A. *J. Phys.: Condens. Matter* **16**, 2317–2334 (2004).
[3] Singh, P. P. *Journal of Magnetism and Magnetic Materials* **261**, 347–352 (2003).

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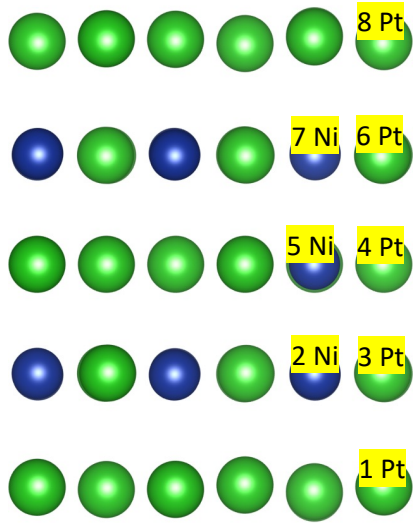

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31	Ni	5	18.000	9.401	8.781	0.620	-0.182
32	Pt	4	18.000	9.022	8.876	0.145	0.102
33	Ni	5	18.000	9.394	8.790	0.604	-0.183
34	Pt	4	18.000	9.051	8.837	0.214	0.112
35	Pt	4	18.000	9.050	8.835	0.215	0.115
36	Pt	4	18.000	9.021	8.876	0.146	0.103

[1] Sharma, B. K., Kwon, O., Odkhuu, D. & Hong, S. C.. *Journal of Magnetism and Magnetic Materials* 339, 89–93 (2013).
[2] Paudyal, D., Saha-Dasgupta, T. & Mookerjee, A. *J. Phys.: Condens. Matter* **16**, 2317–2334 (2004).
[3] Singh, P. P. *Journal of Magnetism and Magnetic Materials* **261**, 347–352 (2003).

Methodology

Initial settings:

Ni MAGNETIZATION (2.0), Pt MAGNETIZATION (0.0) from Hund's rule

PBE, DZVP-MOLOPT, 1x1x1, ADDED_MOS (100), ELECTRONIC_TEMPERATURE (2000), ALPHA (4e-2), CUTOFF (600)

1. Using multiple restarts/OUTER_SCF: initial validation of lower energy ferromagnetic structure
2. Using multiple restarts/OUTER_SCF: initial screening for all parameters
3. Using coarse EPS_SCF 5e-4 and MAX_SCF 300: perform convergence grid searches for all parameters

Optimised settings:

Ni MAGNETIZATION (1.0), Pt MAGNETIZATION (0.0)

PBE, TZVP-MOLOPT, 8x8x1, ADDED_MOS (100), ELECTRONIC_TEMPERATURE (2000), ALPHA (4e-2), CUTOFF (500)