

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)

Decreasing EPS_SCF through OUTER_SCF

- EPS_SCF_ARRAY is used to specify EPS_SCF for each OUTER_SCF

```

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

```

&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

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 576.0000000000000000
```

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
```

Supporting Information

Decreasing EPS_SCF through OUTER_SCF

Step	Update method	Time	Convergence	Total energy	Change
1	NoMix./Diag. 0.40E-01	6.1	1.51802062	-7965.6865412497	-7.97E+03
2	Broy./Diag. 0.40E-01	9.3	0.30600462	-7918.7846870823	4.69E+01
3	Broy./Diag. 0.40E-01	9.3	0.36936802	-7944.3798539088	-2.56E+01
4	Broy./Diag. 0.40E-01	9.3	0.60252877	-7945.2039021751	-8.24E-01
5	Broy./Diag. 0.40E-01	9.3	0.34821317	-8087.2150660060	-1.42E+02
6	Broy./Diag. 0.40E-01	9.4	0.13200263	-8015.1456996628	7.21E+01
7	Broy./Diag. 0.40E-01	9.5	0.24114766	-7982.3137703190	3.28E+01
8	Broy./Diag. 0.40E-01	9.4	0.20840555	-8017.1547958741	-3.48E+01
9	Broy./Diag. 0.40E-01	9.5	0.24079286	-7999.1693193037	1.80E+01
10	Broy./Diag. 0.40E-01	9.5	0.05625844	-7960.4254271744	3.87E+01
11	Broy./Diag. 0.40E-01	9.6	0.06641341	-7956.8879064619	3.54E+00
12	Broy./Diag. 0.40E-01	9.6	0.07176897	-7949.5019691276	7.39E+00
13	Broy./Diag. 0.40E-01	9.7	0.03976312	-7940.1586829323	9.34E+00
14	Broy./Diag. 0.40E-01	9.8	0.01441953	-7935.4531969146	4.71E+00
15	Broy./Diag. 0.40E-01	9.9	0.05207589	-7936.4705573957	-1.02E+00
16	Broy./Diag. 0.40E-01	9.9	0.03138270	-7933.5406285320	2.93E+00
17	Broy./Diag. 0.40E-01	10.1	0.03379357	-7934.7090109904	-1.17E+00
18	Broy./Diag. 0.40E-01	10.1	0.01709458	-7940.8909091014	-6.18E+00
19	Broy./Diag. 0.40E-01	10.1	0.02138230	-7943.7375635652	-2.85E+00
20	Broy./Diag. 0.40E-01	10.3	0.00634488	-7948.0376888692	-4.30E+00
21	Broy./Diag. 0.40E-01	11.0	0.01188758	-7948.0492514599	-1.16E-02
22	Broy./Diag. 0.40E-01	10.1	0.01025771	-7947.5008197877	5.48E-01
23	Broy./Diag. 0.40E-01	10.1	0.00649499	-7946.9981766734	5.03E-01
24	Broy./Diag. 0.40E-01	10.1	0.00494034	-7947.6378252186	-6.40E-01
25	Broy./Diag. 0.40E-01	10.1	0.00462543	-7948.2009106343	-5.63E-01
26	Broy./Diag. 0.40E-01	10.1	0.00743254	-7947.9074830826	2.93E-01
27	Broy./Diag. 0.40E-01	10.1	0.00207730	-7947.7597508969	1.48E-01
28	Broy./Diag. 0.40E-01	10.2	0.00396035	-7947.6188954468	1.41E-01
29	Broy./Diag. 0.40E-01	10.1	0.00129147	-7947.4743796719	1.45E-01
30	Broy./Diag. 0.40E-01	10.2	0.00543622	-7947.6008382376	-1.26E-01
31	Broy./Diag. 0.40E-01	10.1	0.00410161	-7947.5695608539	3.13E-02
32	Broy./Diag. 0.40E-01	10.2	0.01845561	-7947.4833548767	8.62E-02
33	Broy./Diag. 0.40E-01	10.2	0.00454560	-7946.7966591186	6.87E-01
34	Broy./Diag. 0.40E-01	10.2	0.00349466	-7946.9657105351	-1.69E-01
35	Broy./Diag. 0.40E-01	10.2	0.01361047	-7946.9091439109	5.66E-02
36	Broy./Diag. 0.40E-01	10.2	0.00185611	-7947.2351795108	-3.26E-01
37	Broy./Diag. 0.40E-01	10.2	0.00367467	-7947.2479315254	-1.28E-02
38	Broy./Diag. 0.40E-01	10.2	0.01151304	-7947.4248842992	-1.77E-01
39	Broy./Diag. 0.40E-01	10.2	0.00372606	-7947.7476933952	-3.23E-01
40	Broy./Diag. 0.40E-01	10.2	0.00786135	-7947.9569796519	-2.09E-01
41	Broy./Diag. 0.40E-01	10.1	0.01003709	-7947.8220058571	1.35E-01
42	Broy./Diag. 0.40E-01	10.2	0.00923127	-7947.5975981228	2.24E-01
43	Broy./Diag. 0.40E-01	10.1	0.00372510	-7947.8952257884	-2.98E-01
44	Broy./Diag. 0.40E-01	10.2	0.01510619	-7947.9300824638	-3.49E-02
45	Broy./Diag. 0.40E-01	10.2	0.00483338	-7949.0289802826	-1.10E+00
46	Broy./Diag. 0.40E-01	10.2	0.00979778	-7949.3241137297	-2.95E-01
47	Broy./Diag. 0.40E-01	10.2	0.00245529	-7949.4154028590	-9.13E-02
48	Broy./Diag. 0.40E-01	10.2	0.01350208	-7949.4838077052	-6.84E-02
49	Broy./Diag. 0.40E-01	10.2	0.00911029	-7949.2587795067	2.25E-01
50	Broy./Diag. 0.40E-01	10.3	0.00712300	-7949.2638207782	-5.04E-03

50	Broy./Diag. 0.40E-01	10.3	0.00712300	-7949.2638207782	-5.04E-03
51	Broy./Diag. 0.40E-01	10.3	0.00464948	-7949.2996871537	-3.59E-02
52	Broy./Diag. 0.40E-01	10.2	0.00838276	-7949.1104741153	1.89E-01
53	Broy./Diag. 0.40E-01	10.2	0.00897999	-7948.6582116400	4.52E-01
54	Broy./Diag. 0.40E-01	10.2	0.00425566	-7948.8931235651	-2.35E-01
55	Broy./Diag. 0.40E-01	10.2	0.01990650	-7949.1509157179	-2.58E-01
56	Broy./Diag. 0.40E-01	10.3	0.00745009	-7949.0684620128	8.25E-02
57	Broy./Diag. 0.40E-01	10.3	0.02216853	-7949.0871336774	-1.87E-02
58	Broy./Diag. 0.40E-01	10.3	0.01548114	-7948.5376708141	5.49E-01
59	Broy./Diag. 0.40E-01	10.3	0.00454727	-7948.1101884463	4.27E-01
60	Broy./Diag. 0.40E-01	10.3	0.02056864	-7948.2947376922	-1.85E-01
61	Broy./Diag. 0.40E-01	10.2	0.02053541	-7947.9387664327	3.56E-01
62	Broy./Diag. 0.40E-01	10.3	0.01125674	-7948.3803588065	-4.42E-01
63	Broy./Diag. 0.40E-01	10.3	0.01313202	-7948.0850984941	2.95E-01
64	Broy./Diag. 0.40E-01	10.2	0.00260087	-7947.8490616796	2.36E-01
65	Broy./Diag. 0.40E-01	10.2	0.01177046	-7948.0285477664	-1.79E-01
66	Broy./Diag. 0.40E-01	10.3	0.01010776	-7948.3622626670	-3.34E-01
67	Broy./Diag. 0.40E-01	10.3	0.01199503	-7948.2901788796	7.21E-02
68	Broy./Diag. 0.40E-01	10.2	0.00374991	-7948.4371035638	-1.47E-01
69	Broy./Diag. 0.40E-01	10.4	0.00304936	-7948.5555377331	-1.18E-01
70	Broy./Diag. 0.40E-01	10.3	0.01256317	-7948.4894298081	6.61E-02
71	Broy./Diag. 0.40E-01	10.3	0.01927694	-7948.7277816830	-2.38E-01
72	Broy./Diag. 0.40E-01	10.3	0.02250994	-7948.1515497007	5.76E-01
73	Broy./Diag. 0.40E-01	10.3	0.03226402	-7948.3889666939	-2.37E-01
74	Broy./Diag. 0.40E-01	10.3	0.02531005	-7948.6432218646	-2.54E-01
75	Broy./Diag. 0.40E-01	10.3	0.00781089	-7948.5333639443	1.10E-01
76	Broy./Diag. 0.40E-01	10.3	0.00786747	-7948.3823075743	1.51E-01
77	Broy./Diag. 0.40E-01	10.4	0.01417011	-7948.2897273724	9.26E-02
78	Broy./Diag. 0.40E-01	10.4	0.00353312	-7948.1259697342	1.64E-01
79	Broy./Diag. 0.40E-01	10.3	0.00963183	-7948.2605530905	-1.35E-01
80	Broy./Diag. 0.40E-01	10.4	0.00350842	-7948.2052944506	5.53E-02
81	Broy./Diag. 0.40E-01	10.4	0.03362614	-7948.0583902766	1.47E-01
82	Broy./Diag. 0.40E-01	10.5	0.00401678	-7946.9329831135	1.13E+00
83	Broy./Diag. 0.40E-01	10.3	0.01487937	-7947.1030498026	-1.70E-01
84	Broy./Diag. 0.40E-01	10.4	0.00423199	-7947.1187624241	-1.57E-02
85	Broy./Diag. 0.40E-01	10.4	0.00644501	-7947.1227566634	-3.99E-03
86	Broy./Diag. 0.40E-01	10.3	0.01739201	-7947.2650636095	-1.42E-01
87	Broy./Diag. 0.40E-01	10.4	0.00864119	-7946.8463925957	4.19E-01
88	Broy./Diag. 0.40E-01	10.4	0.01052623	-7946.9778240614	-1.31E-01
89	Broy./Diag. 0.40E-01	10.4	0.01126983	-7946.7374723094	2.40E-01
90	Broy./Diag. 0.40E-01	10.4	0.01197348	-7946.4717315330	2.66E-01
91	Broy./Diag. 0.40E-01	10.4	0.01413830	-7946.5250427891	-5.33E-02
92	Broy./Diag. 0.40E-01	10.4	0.01216388	-7946.6270727793	-1.02E-01
93	Broy./Diag. 0.40E-01	10.5	0.00636582	-7946.6273766022	-3.04E-04
94	Broy./Diag. 0.40E-01	10.5	0.00347778	-7946.3656571682	2.62E-01
95	Broy./Diag. 0.40E-01	10.5	0.03878581	-7946.2856650689	8.00E-02
96	Broy./Diag. 0.40E-01	10.6	0.01059835	-7946.8117294680	-5.26E-01
97	Broy./Diag. 0.40E-01	10.4	0.02370343	-7946.5422746866	2.69E-01
98	Broy./Diag. 0.40E-01	10.4	0.01056889	-7947.1777705618	-6.35E-01
99	Broy./Diag. 0.40E-01	10.5	0.02064579	-7946.7909821241	3.87E-01
100	Broy./Diag. 0.40E-01	10.4	0.01753950	-7946.8984508985	-1.07E-01

Decreasing EPS_SCF through OUTER_SCF

Step	Update method	Time	Convergence	Total energy	Change
1	NoMix/Diag. 0.40E-01	6.1	1.51802062	-7965.6865412497	-7.97E+03
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3	Broy./Diag. 0.40E-01	9.3	0.36936802	-7944.3798539088	-2.56E+01
4	Broy./Diag. 0.40E-01	9.3	0.60252877	-7945.2039021751	-8.24E-01
5	Broy./Diag. 0.40E-01	9.3	0.34821317	-8087.2150660060	-1.42E+02
6	Broy./Diag. 0.40E-01	9.4	0.13200263	-8015.1456996629	7.21E+01
7	Broy./Diag. 0.40E-01	9.5	0.24114766	-7982.3137703190	3.28E+01
8	Broy./Diag. 0.40E-01	9.4	0.20840555	-8017.1547958741	-3.48E+01
9	Broy./Diag. 0.40E-01	9.5	0.24079286	-7999.1693193037	1.80E+01
10	Broy./Diag. 0.40E-01	9.5	0.05625844	-7960.4254271744	3.87E+01
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15	Broy./Diag. 0.40E-01	9.9	0.05207589	-7936.4705573957	-1.02E+00
16	Broy./Diag. 0.40E-01	9.9	0.03138270	-7933.5406285320	2.93E+00
17	Broy./Diag. 0.40E-01	10.1	0.03379357	-7934.7090109904	-1.17E+00
18	Broy./Diag. 0.40E-01	10.1	0.01709458	-7940.8909091014	-6.18E+00
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22	Broy./Diag. 0.40E-01	10.1	0.01025771	-7947.5008197877	5.48E-01
23	Broy./Diag. 0.40E-01	10.1	0.00649499	-7946.9981766734	5.03E-01
24	Broy./Diag. 0.40E-01	10.1	0.00494034	-7947.6378252186	-6.40E-01
25	Broy./Diag. 0.40E-01	10.1	0.00462543	-7948.2009106343	-5.63E-01
26	Broy./Diag. 0.40E-01	10.1	0.00743254	-7947.9074830826	2.93E-01
27	Broy./Diag. 0.40E-01	10.1	0.00207730	-7947.7597508969	1.48E-01
28	Broy./Diag. 0.40E-01	10.2	0.00396035	-7947.6188954468	1.41E-01
29	Broy./Diag. 0.40E-01	10.1	0.00129147	-7947.4743796719	1.45E-01
30	Broy./Diag. 0.40E-01	10.2	0.00543622	-7947.6008382376	-1.26E-01
31	Broy./Diag. 0.40E-01	10.1	0.00410161	-7947.5695608539	3.13E-02
32	Broy./Diag. 0.40E-01	10.2	0.01845561	-7947.4833548767	8.62E-02
33	Broy./Diag. 0.40E-01	10.2	0.00454560	-7946.7966591186	6.87E-01
34	Broy./Diag. 0.40E-01	10.2	0.00349466	-7946.9657105351	-1.69E-01
35	Broy./Diag. 0.40E-01	10.2	0.01361047	-7946.9091439109	5.66E-02
36	Broy./Diag. 0.40E-01	10.2	0.00185611	-7947.2351795108	-3.26E-01
37	Broy./Diag. 0.40E-01	10.2	0.00367467	-7947.2479315254	-1.28E-02
38	Broy./Diag. 0.40E-01	10.2	0.01151304	-7947.4248842992	-1.77E-01
39	Broy./Diag. 0.40E-01	10.2	0.00372606	-7947.7476933952	-3.23E-01
40	Broy./Diag. 0.40E-01	10.2	0.00786135	-7947.9569796519	-2.09E-01
41	Broy./Diag. 0.40E-01	10.1	0.01003709	-7947.8220058571	1.35E-01
42	Broy./Diag. 0.40E-01	10.2	0.00923127	-7947.5975981228	2.24E-01
43	Broy./Diag. 0.40E-01	10.1	0.00372510	-7947.8952257884	-2.98E-01
44	Broy./Diag. 0.40E-01	10.2	0.01510619	-7947.9300824638	-3.49E-02
45	Broy./Diag. 0.40E-01	10.2	0.00483338	-7949.0289802826	-1.10E+00
46	Broy./Diag. 0.40E-01	10.2	0.00979778	-7949.3241137297	-2.95E-01
47	Broy./Diag. 0.40E-01	10.2	0.00245529	-7949.4154028590	-9.13E-02
48	Broy./Diag. 0.40E-01	10.2	0.01350208	-7949.4838077052	-6.84E-02
49	Broy./Diag. 0.40E-01	10.2	0.00911029	-7949.2587795067	2.25E-01
50	Broy./Diag. 0.40E-01	10.3	0.00712300	-7949.2638207782	-5.04E-03

&SCF

MAX_SCF 2000

EPS_SCF 1E-2

EPS_SCF_ARRAY 1E-2 5E-3

Step	Update method	Time	Convergence	Total energy	Change
1	NoMix/Diag. 0.40E-01	6.1	1.51802062	-7965.6865412497	-7.97E+03
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3	Broy./Diag. 0.40E-01	9.3	0.36936802	-7944.3798539088	-2.56E+01
4	Broy./Diag. 0.40E-01	9.3	0.60252877	-7945.2039021751	-8.24E-01
5	Broy./Diag. 0.40E-01	9.3	0.34821317	-8087.2150660061	-1.42E+02
6	Broy./Diag. 0.40E-01	9.4	0.13200263	-8015.1456996629	7.21E+01
7	Broy./Diag. 0.40E-01	9.4	0.24114766	-7982.3137703191	3.28E+01
8	Broy./Diag. 0.40E-01	9.5	0.20840554	-8017.1547958746	-3.48E+01
9	Broy./Diag. 0.40E-01	9.5	0.24079286	-7999.1693193090	1.80E+01
10	Broy./Diag. 0.40E-01	9.5	0.05625844	-7960.4254271737	3.87E+01
11	Broy./Diag. 0.40E-01	9.5	0.06641341	-7956.8879064624	3.54E+00
12	Broy./Diag. 0.40E-01	9.6	0.07176897	-7949.5019691257	7.39E+00
13	Broy./Diag. 0.40E-01	9.7	0.03976312	-7940.1586829300	9.34E+00
14	Broy./Diag. 0.40E-01	9.7	0.01441953	-7935.4531969161	4.71E+00
15	Broy./Diag. 0.40E-01	9.8	0.05207589	-7936.4705573937	-1.02E+00
16	Broy./Diag. 0.40E-01	9.9	0.03138270	-7933.5406285388	2.93E+00
17	Broy./Diag. 0.40E-01	10.0	0.03379357	-7934.7090109889	-1.17E+00
18	Broy./Diag. 0.40E-01	10.0	0.01709458	-7940.8909091001	-6.18E+00
19	Broy./Diag. 0.40E-01	10.1	0.02138230	-7943.7375635666	-2.85E+00
20	Broy./Diag. 0.40E-01	10.1	0.00634488	-7948.0376888713	-4.30E+00

*** SCF run converged in 20 steps ***

Electronic density on regular grids: -1080.0000000001 -0.0000000001
 Core density on regular grids: 1080.0000000000 -0.0000000000
 Total charge density on r-space grids: -0.0000000001
 Total charge density g-space grids: -0.0000000001

Overlap energy of the core charge distribution: 0.00000000599456
 Self energy of the core charge distribution: -12142.97180818642482
 Core Hamiltonian energy: 2928.71915368190821
 Hartree energy: 2049.39723225692751
 Exchange-correlation energy: -781.64386625310658
 Dispersion energy: -1.20318238291638
 Electronic entropic energy: -0.33465920432903
 Fermi energy: 0.09116496204116

Total energy: -7948.03768887125261

outer SCF iter = 1 RMS gradient = 0.63E-02 energy = -7948.0376888713
 1 NoMix/Diag. 0.40E-01 24.9 0.17328582 -7948.9220173178 -8.84E-01
 2 Broy./Diag. 0.40E-01 9.8 0.32152326 -7969.2492414467 -2.03E+01
 3 Broy./Diag. 0.40E-01 9.3 0.28081506 -7939.8156695952 2.94E+01
 4 Broy./Diag. 0.40E-01 9.3 0.19021826 -7946.7611351885 -6.95E+00
 5 Broy./Diag. 0.40E-01 9.4 0.06687941 -7952.6300658914 -5.87E+00
 6 Broy./Diag. 0.40E-01 9.4 0.01586540 -7949.4931859050 3.14E+00
 7 Broy./Diag. 0.40E-01 9.4 0.00468512 -7948.5616570264 9.32E-01

*** SCF run converged in 7 steps ***

Manual restarts

Folder	Energy	SCF	Time	IASD
1E-2	-7939.772753	21	171.077000	18.594150
5E-3	-7949.208426	19	160.068000	20.111828
4E-3	-7948.566685	8	76.655000	20.923427
3E-3	-7948.813170	10	93.779000	21.448586
2E-3	-7948.713399	11	100.221000	21.768366
1E-3	-7948.943405	14	122.720000	21.926384
5E-4	-7949.113206	15	131.289000	22.300353
4E-4	-7948.899659	10	92.138000	22.263735
3E-4	-7948.930371	9	85.211000	22.295090
2E-4	-7948.902940	7	70.316000	22.324563
1E-4	-7948.927166	8	79.416000	22.343675
5E-5	-7948.922704	8	78.702000	22.352922
4E-5	-7948.928868	7	71.108000	22.357608
3E-5	-7948.924406	6	65.180000	22.360157
2E-5	-7948.928108	9	88.323000	22.361741
1E-5	-7948.926755	6	62.679000	22.362524
5E-6	-7948.927575	8	78.408000	22.362995
4E-6	-7948.927082	6	61.930000	22.363207
3E-6	-7948.927401	8	80.900000	22.363364
2E-6	-7948.927093	7	71.084000	22.363443
1E-6	-7948.927301	9	86.513000	22.363478

```
restarts=("1E-2" "5E-3" "4E-3" "3E-3" "2E-3" "1E-3" "5E-4" "4E-4" "3E-4" "2E-4" "1E-4" "5E-5" "4E-5" "3E-5" "2E-5" "1E-5" "5E-6" "4E-6" "3E-6" "2E-6" "1E-6")

length=${#restarts[@]}
loops=length-1
echo "Number of runs" $length

for (( i=0; i<loops; i++ )); do
    if [[ "$result" == "${restarts[$i]}" ]]; then

        echo "Submitting job" ${restarts[$i+1]}
        cd ..

        cp -r scf-${restarts[i]} scf-${restarts[i+1]}
        cd scf-${restarts[i+1]}
        sed -i -e "s/EPS_SCF ${restarts[i]}/EPS_SCF ${restarts[i+1]}/g" input/input.inp
        rm log.out; rm Pt3Ni*; rm slurm-*
        cp ../scf-${restarts[i]}/Pt3Ni-RESTART.kp input/
        sbatch submit.slurm

    fi
done
```

Mixing: DIRECT_P_MIXING

$$\rho_{n+1}^{\text{in}} = (1 - \alpha)\rho_n^{\text{in}} + \alpha\rho_n^{\text{out}}, \quad 0 < \alpha \leq 1$$

src/qs_scf_methods.F SUBROUTINE scf_env_density_mixing

- As a mixing scheme will likely never converge
- First SCF step does not perform any mixing, evaluates energy of input density only
- Second step performs standard density mixing (ALPHA)

1	P_Mix/Diag.	0.50E+00	6.1	1.51839432	-7966.1196078017	-7.97E+03
2	P_Mix/Diag.	0.50E+00	9.1	2.99797384	-7951.8657395742	1.43E+01

```
SUBROUTINE scf_env_density_mixing(p_mix_new, mixing_store, rho_ao, para_env, &
| | | | | | | | | | iter_delta, iter_count, diis, invert)
```

```
CALL cp_sm_mix(m1=p_mix_new(ispin, ic)%matrix, &  
               m2=rho_ao(ispin, ic)%matrix, &  
               p_mix=my_p_mix, &  
               delta=tmp, &  
               para_env=para_env)
```

```
SUBROUTINE cp_sm_mix(m1, m2, p_mix, delta, para_env, m3)
```


Mixing: BROYDEN_MIXING

$$\rho_{n+1}^{\text{in}} = \rho_n^{\text{out}} - J_n^{-1} R_n$$

src/qs_gspace_mixing.F SUBROUTINE broyden_mixing

- Appears to be the most common mixing scheme
- First SCF step does not perform any mixing, evaluates energy of input density only
- Second step onwards performs Broyden mixing with Kerker preconditioning of the density (ALPHA, BETA, NBUFFER)

```
1 NoMix/Diag. 0.40E-01    6.2    1.51808391    -7966.1196078017 -7.97E+03
2 Broy./Diag. 0.40E-01    9.3    0.29929503    -7921.5726582353  4.45E+01
```

```
SUBROUTINE broyden_mixing(qs_env, mixing_store, rho, para_env)
```

```
! *****
!> \brief Broyden Mixing using as metrics for the residual the Kerer damping factor
!>      The mixing is applied directly on the density expansion in reciprocal space
```

Mixing: other schemes

- BROYDEN_MIXING_NEW, PULAY_MIXING, MULTISECANT_MIXING and KERKER_MIXING are also implemented
- BROYDEN_MIXING_NEW immediately crashes with segmentation fault, as reported on Google group in 2021 [1]
- PULAY_MIXING does not appear to ever converge
- MULTISECANT_MIXING does not appear to ever converge
- KERKER_MIXING does not appear to ever converge

[1] <https://groups.google.com/g/cp2k/c/LgIHVLeReck/m/vebZVnpuBgAJ>

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
0.33541395522983858	0.33541395520909806
0.21813725336214776	0.21813725319575078
0.21813721860272914	0.21813721859516533
0.21451999753753381	0.21451999735887881

SUM(occ_a)
300.35421073021865

0.99961523541004316	0.99961523541004249
0.33541395513933492	0.21813725338589141
0.21813721865361865	0.21813721863148941
0.21813721858464186	0.21452003167550554
0.21451999735861882	3.2653117149019535E-003

SUM(occ_b)
275.64578926978157