CIPSI Algorithm on 3 electrons

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In the CIPSI algorithm, the determinant space (generated by ijkl/fock) is partitioned into 3 subspaces. The subspace S is the reference space chosen by the user. The obtained submatrix is then diagonalized to get netat energies corresponding to the lowest states. The contribution of the determinants outside of space S is evaluated with a second order perturbative algorithm. The subspace M is formed by the determinants with a contribution superior to a given threshold. The matrix formed by the association S+M contained all determinants deemed important and is the one which will be diagonalized at the end of the procedure. The subspace P is formed by the leftovers determinants, they can be taken into account by including their second order perturbative contribution to the energy.

In the current implementation, the *cip* binary generate the subspace S and compute the perturbation of other determinants, the *moy* binary construct the matrix of S+M and the *bd* binary diagonalize said matrix and add various corrections (perturbation, Davidson correction, ...) to the final energies.

Note that cip only generate mono- and di-excited determinants of each determinants of the reference space. The active space will be smaller than the total space.

1 Benchmark

Several computations were done on RbCa at $R = 9.0$ $a.u.$ and $R = 32.0$ $a.u.$ with differents input parameters. Results are compiled in tables 1,2,3 and show the importance of a description as accurate as possible of the reference space. Recommandation is to use the spin symmetrized algorithm (replace last call of *moy* and *bd* by *moysym* and *bdsym*) with a starting reference space containing all monoexcited determinants and to do more than one iteration. The final S space should contains 1000-2000 determinants.

Note that the rigorous algorithm is to iterate until the perturbative correction (computed by *cip*) is lower than the threshold. However with the current implementation it is not time efficient (or even possible) to use *cip* with an active space greater than a few thousands of determinants. This means we have to work with a rather small reference space S and a comparatively big subspace M. We also can't compute an accurate perturbative correction after the final call to *bd* (too many determinants). We thus have no garranty that our results have correctly converged (outside of directly comparing to the FCI results).

1.1 Determinaton of the Spin

The use of *moysym* and *bdsym* at the last step of the CIPSI algorithm is found to be more precise and more efficient than the use of *moy*, though not by much. The gain is greater in Full CI mode (all determinants taken means no addition from YSPIPRO).

1. Using *moysym* (generation of a spin symmetrized matrix prior to the diagonalisation) increase the number of determinants used because we need to use the option YSPIPRO=T. For a given set of occupied spatial orbitals one can generate several determinants each with a different combinaison of spin up/spin down. Due to the CIPSI selection some combinaison can be missing (not generated by *cip* or generated but below threshold). With the option the routine will generate all the missing determinants, this is required by *moysym* to compute a correctly symmetrized matrix.

2. *moysym* is usually slower than *moy*

3. *bdsym* will be faster than *bd* : each spin block is diagonalized independently.

4. *moysym* use the old routine to order the determinant (space S first, then the rest), *moy* use the one from *cip* (monoexcited first, then second exc, etc...). Using the same than *cip* is needed by the iterative algorithm, however it make *bd* slower. Because the initial diagonalization step ncper*ncper give less acurate results, the convergence will be slower.

5. The spin of each state is imposed : avoid numerical mistake and no need to run a sorting routine afterwards.

1.2 Initial reference space

Starting from the smallest space possible is more time efficient as we know that only important determinant will be included. *bd* also converge faster because the initial ncper*ncper block doesn't contain any "non-important" elements. The total active space is however smaller increasing the possibility that we "missed" an important determinant. This is the case for all parasite Delta state which are not accuratly computed. But more importantly this is the case, at long-range, even for the ground state. Starting from a bigger initial space reduce the possibility of having an issue, however it slow down the computation as the reference space now include "non-important deterinant".

Spin		with Spin symmetry					
Starting space	FCI	All monoexcited			2 active orbitals		
Ref. space		min. size	1000	2000	1000	2000	5000
n. det	214887	69908	65905	62005	56691	61506	58408
n. det S		262	1020	3205	1698	2076	6035
active space	214887	190512	203956	212507	168521	192083	209671
total time (s)		366.1	402.4	357.9	234.0	248.8	292.1
time bd+moy (s)		295.4	326.0	248.1	175.	164.	140.
$E_{CIPSI} - E_{FCI}$ (10^{-6} *a.u.*)							
ΔE_1		107.7	1.93	2.37	2.15	2.07	2.86
ΔE_2		144.1	2.39	2.93	2.34	2.35	3.59
ΔE_3		79.1	1.99	2.49	1.96	2.03	3.08
ΔE_4		110.3	2.66	3.17	2.56	2.76	4.02
ΔE_5		14.1	1.24	1.73	1.30	1.34	2.13
ΔE_6		777.4	3.21	3.58	501.1	3.85	4.63
ΔE_7		76.9	2.55	3.01	2.64	2.52	3.86
ΔE_8		113.6	3.41	3.77	888.1	16.60	5.09
ΔE_9		81.8	3.22	3.77	3.36	3.49	4.68
ΔE_{10}		24.9	1.83	2.30	2.19	1.59	2.91
ΔE_{11}		100.6	3.35	4.07	3.26	3.78	5.11
ΔE_{12}		132.1	2.27	2.65	962.7	2.23	3.21
ΔE_{13}		281.5	2.65	3.26	934.8	4.42	3.83
ΔE_{14}		39.5	2.21	2.72	2.47	2.28	3.48
ΔE_{15}		109.1	2.70	3.27	2.57	2.73	4.22
ΔE_{16}		115.4	3.54	3.88	3.32	3.69	5.01
ΔE_{17}		48.7	5.04	5.91	1604	328.8	7.47
ΔE_{18}		87.7	3.30	3.66	3.36	3.45	4.90
ΔE_{19}		21.5	4.18	4.71	4.76	4.49	5.96
ΔE_{20}		1272.3	3.92	6.78	2029	21.5	5.55
$\Delta PDM(\%)$		2.76	0.01	0.008	0.006	0.004	0.01

Table 1: Computation of RbCa PECs at $R = 9.0$ *a.u.*. All tests were done for 20 Σ with a value of $ENVP\_max = 10^{-5}$ *a.u.*

Spin		Spin computed afterwards				
Starting space	FCI	All monoexcited			2 active orbitals	
Ref. space		min. size	1000	2000	1000	2000
n. det	214887	55713	54249	52155	50499	53766
n. det S		262	1020	3205	1698	2076
total time (s)		499.5	373.6	419.3	286.4	320.2
time bd+moy (s)		367.6	242.0	258.5	174.9	176.81
$E_{CIPSI} - E_{FCI}$ (10^{-6} *a.u.*)						
ΔE_1		114.4	2.49	2.95	2.64	2.39
ΔE_2		158.2	3.26	3.75	2.91	2.81
ΔE_3		89.9	2.88	3.39	2.58	2.62
ΔE_4		132.8	3.68	4.20	3.24	3.36
ΔE_5		21.6	1.96	2.46	1.65	1.84
ΔE_6		799.2	4.44	4.43	540.3	5.16
ΔE_7		87.2	3.50	3.87	3.37	3.10
ΔE_8		157.1	4.45	4.51	955.8	18.6
ΔE_9		94.1	4.13	4.45	3.95	3.92
ΔE_{10}		29.4	2.90	3.17	2.84	2.14
ΔE_{11}		123.2	4.41	4.97	3.86	4.31
ΔE_{12}		865.5	8.56	3.70	999.4	4.86
ΔE_{13}		2468.	18.6	5.65	952.3	9.92
ΔE_{14}		815.1	3.31	3.72	3.17	2.92
ΔE_{15}		118.1	3.88	4.41	3.16	3.39
ΔE_{16}		127.0	4.65	4.83	3.87	4.26
ΔE_{17}		58.6	6.24	6.46	1661.	1965.
ΔE_{18}		105.4	4.68	4.96	3.98	1646.
ΔE_{19}		25.8	6.91	7.24	5.31	5.01
ΔE_{20}		1405.	41.3	32.7	2059.	83.1
$\Delta PDM(\%)$		2.94	0.018	0.017	0.013	0.008

Table 2: Computation of RbCa PECs at $R = 9.0$ *a.u.*. All tests were done for 20 Σ with a value of $ENVP\_max = 10^{-5}$ *a.u.*

Starting space	FCI	All monoexcited		2 active orbitals	
Ref. space		1000	2000	2000	5000
n. det	214887	32921	31206	32430	26987
n. det S		1845	2949	2635	6256
active space	214887	212317	213223	168460	209987
total time (s)		102.5	148.9	90.9	217.9
time bd+moy (s)		46.4	69.4	54.4	35.6
$E_{CIPSI} - E_{FCI}$ (10^{-6} *a.u.*)					
ΔE_1		1.61	1.75	1973.	1.90
ΔE_2		2.49	2.81	36.1	2.94
ΔE_3		0.70	0.83	529.7	0.90
ΔE_4		0.71	0.84	529.7	0.91
ΔE_5		2.73	3.03	3.97	3.19
ΔE_6		3.25	3.06	3.17	3.20
ΔE_7		0.91	1.13	1187.6	1.21
ΔE_8		0.96	1.14	1187.7	1.22
ΔE_9		1.38	1.22	2686.0	1.32
ΔE_{10}		2.35	0.66	1033.5	0.80
ΔE_{11}		7.91	3.56	3.40	3.82
$\Delta TDM(\%)$		0.0002	0.0002	0.38	0.0002

Table 3: Computation of RbCa PECs at $R = 32.0$ *a.u.*. All tests were done for 20 Σ states with a value of $ENVP\_max = 10^{-5}$ *a.u.*