A trust-region augmented Hessian implementation for restricted and unrestricted Hartree–Fock and Kohn–Sham methods

Supplementary Material

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I. COMPARISON WITH THE QC-SCF IMPLEMENTATION IN DALTON

In the DALTON program package,[1] there is a restricted-step second-order SCF implementation for restricted closed-shell Hartree–Fock wavefunctions that is based on the initial MCSCF implementation of Ref. 2. In this section, we compare the convergence of our second-order SCF implementations in ORCA (TRAH-SCF) and with that in DALTON. Here, the number of iterations are compared for the closed-shell Hartree–Fock calculations of Cr_2 with 2.0 $\mathring{A}$ inter-nuclear distance using the TZVPP basis set.[3] The results are shown in Tab. I for calculations that either exploit (D_{2h}) or neglect (C_1) Abelian point-group symmetry.

In case of the D_{2h} calculations, both second-order SCF implementations in ORCA and DALTON converge to the same total energy, -2085.683248587351 a.u., within 26 iterations. However, our new TRAH-SCF calculation takes less macro iteration but more micro iterations and has a lower residual norm with our default convergence threshold. This convergence comparison though must be taken with cation because different starting molecular orbitals (MO) were taken. By default, ORCA generates initial MOs by diagonalizing an approximate Kohn-Sham matrix built from atomic densities (`PModel`) while DALTON takes and extended Hückel guess.

A major difference in the SCF convergence is observed for the C_1 calculation. Without imposing point-group symmetry constraints, the symmetry gets broken for both ORCA and DALTON calculations. But our new TRAH-SCF implementation converges to a solution with a much lower energy (-2086.145610513081 a.u.) than the DALTON implementation (-2085.797496061530 a.u.) at the expense of much more iterations. For these C_1 calculations, DALTON takes 30 iterations while our new implementation in ORCA needs 247. The different convergence behavior for the unconstrained second-order SCF calculation can be attributed to the way we choose the second start vectors for the Davidson algorithm. For those we add random numbers in the range of $[-0.01; 0.01]$ on top of the lowest eigenvectors of the diagonal Hessian. This white noise initiates symmetry breaking and helps to find the lowest energy solution though there is no guarantee that global minima can be found with any of the methods presented in the current work.

II. CARTESIAN COORDINATES

TABLE I: Gradient norm $||\mathbf{g}||$ and number of micro iterations.

	DALTON		ORCA	
Macro	# Micro	$\|\|\mathbf{g}\|\|$	# Micro	$\|\|\mathbf{g}\|\|$
		D_{2h}[a]		
1	4	$2.4 \times 10^{+0}$	6	$2.1 \times 10^{+0}$
2	4	8.5×10^{-1}	5	1.1×10^{-1}
3	3	1.5×10^{-1}	4	4.8×10^{-3}
4	6	1.4×10^{-2}	6	3.2×10^{-4}
5	3	5.6×10^{-5}	0	3.2×10^{-7}
6	0	2.5×10^{-6}	/	/
		C_1		
1	3	$4.7 \times 10^{+00}$	13	$2.1 \times 10^{+00}$
2	4	$2.4 \times 10^{+00}$	7	3.3×10^{-01}
3	3	5.1×10^{-01}	7	1.2×10^{-01}
4	3	1.8×10^{-01}	8	1.2×10^{-01}
5	5	2.3×10^{-02}	10	4.7×10^{-01}
6	5	5.2×10^{-04}	10	1.7×10^{-01}
7	0	6.9×10^{-06}	14	9.3×10^{-02}
8	/	/	14	$1.2 \times 10^{+00}$
9	/	/	14	7.7×10^{-01}
10	/	/	14	8.9×10^{-02}
11	/	/	14	3.3×10^{-02}
12	/	/	14	7.0×10^{-03}
13	/	/	14	3.0×10^{-03}
14	/	/	15	9.3×10^{-04}
15	/	/	15	6.1×10^{-05}
16	/	/	15	1.8×10^{-05}
17	/	/	15	4.0×10^{-06}
18	/	/	15	1.1×10^{-06}
19	/	/	0	2.7×10^{-07}

[a] $a_g = 8$, $b_{1g} = 1$, $b_{2g} = 2$, $b_{3g} = 2$,$a_u = 0$, $b_{1u} = 5$, $b_{2u} = 3$, $b_{3u} = 3$

A. $UO_2(OH)_4$

```
11

U     0.000000    0.000000    0.000000
O     1.840000    0.000000    0.000000
O    -1.840000    0.000000    0.000000
O    -0.000000    0.000000   -2.330000
H    -0.000000    0.931956   -2.598995
O    -0.000000   -2.330000   -0.000000
H    -0.000000   -2.598995   -0.931956
O     0.000000   -0.000000    2.330000
H     0.000000   -0.931956    2.598995
O     0.000000    2.330000   -0.000000
H     0.000000    2.598995    0.931956
```

B. Roussin's red dianion $[Fe_2S_2(NO)_4]^{2-}$

```
12

Fe   0.000000  -0.000000   1.379006
N   -0.000000   1.591670   2.308963
N    0.000000  -1.591670   2.308963
S   -1.716557  -0.000000   0.000000
S    1.716557  -0.000000   0.000000
Fe   0.000000  -0.000000  -1.379006
N    0.000000  -1.591670  -2.308963
N    0.000000   1.591670  -2.308963
O   -0.000000   2.808854   2.404356
O   -0.000000  -2.808854   2.404356
O   -0.000000   2.808854  -2.404356
O   -0.000000  -2.808854  -2.404356
```

C. hemocyanin model complex

164

O	10.43974010597315	15.99945510207685	13.55772467988408
O	10.92851662604793	17.22757498718534	13.05756090305485
Cu	11.63615824155408	15.70757999499295	12.10972557806300
Cu	9.73210748911415	17.51945109329867	14.50557000658749
N	12.08251919145782	13.75763076780016	12.09132466667064
N	9.28574753704861	19.46939932133450	14.52397092040944
N	10.61907550521983	15.43112849066839	10.11056168951854
N	10.74918122524586	17.79590159685953	16.50473289360477
N	13.28772695914548	16.18710555728147	11.10132243315006
N	8.08053977099405	17.03992452820486	15.51396315214455
N	12.60184470130807	13.22134528246111	11.02480396866392
N	8.76642203231607	20.00568480516313	15.59049162032059
N	11.39408035120663	14.64991992584598	9.26188366086504
N	9.97417638054523	18.57711016083695	17.35341092297935
N	13.73307507054094	15.32790695704666	10.06389802651017
N	7.63519165834219	17.89912312864806	16.55139755852334
B	12.76730535593193	14.13816518894987	9.69911310737490
B	8.60096037450289	19.08886489712029	16.91618147662774
C	10.46354263014904	11.96089137671055	14.65649601136104
C	10.90471314004386	21.26613872055853	11.95879860721116
C	12.80438547963604	12.76119239468118	15.41067385145896
C	8.56388130735795	20.46584771391541	11.20461070832791
C	11.58758882508313	12.94774979784298	14.41896593258862
C	9.78067793337963	20.27928030990337	12.19632866585598
C	12.09970348851030	12.75467848937489	13.00654005221535
C	9.26856223788403	20.47235160498661	13.60874453742600
C	12.64742206317117	11.61720170158627	12.43480273283595
C	8.72084467231608	21.60982839865908	14.18048286474876

C	12.98811261553706	11.93714919288300	11.13495221120651
C	8.38014412623954	21.28988089663151	15.48033338628188
C	13.57368596771660	11.05393033993714	10.08400709549539
C	7.79458075733176	22.17309973847080	16.53128850009246
C	12.50224778369863	10.35910571522563	9.25639566822104
C	8.86600879341008	22.86792437324623	17.35889810145190
C	14.50904417127523	10.03062146011115	10.74501595622534
C	6.85922345046950	23.19640861955442	15.87026879409110
C	7.73152380957549	17.50487559136226	8.98959086191142
C	13.63673192209058	15.72215449203711	17.62569470299923
C	7.31097605210632	15.69488349326883	10.60773566561986
C	14.05729066408940	17.53214761112748	16.00754891538854
C	8.50198495044928	16.63944138708137	10.06646064017255
C	12.86628177670302	16.58758869528921	16.54883492775093
C	9.58156081937333	15.79935183313864	9.41708939039570
C	11.78670591198887	17.42767825145350	17.19819618648615
C	9.58560142620026	15.19852796008992	8.13277105622210
C	11.78266430902265	18.02850212457304	18.48252352179086
C	10.71520131549614	14.50003068435552	8.07474188227089
C	10.65306442130095	18.72699940311604	18.54055270187059
C	11.30999810980948	13.73388670604466	6.89604645787113
C	10.05825863141307	19.49314238041828	19.71924813005869
C	12.16629901752721	14.64312623123754	6.03023222994310
C	9.20196772324895	18.58390285531025	20.58506335863138
C	10.16784800662118	13.10292290269271	6.04728791301330
C	11.20041773943057	20.12410617772612	20.56800867290142
C	14.26483135026823	19.59362915072675	11.44689962581313
C	7.10343437959780	13.63340093451757	15.16839695044459
C	15.49739216221850	18.16382829584002	13.08194666922507
C	5.87087356504739	15.06320180405014	13.53334990909003
C	14.22230692424068	18.22939936381453	12.18340782850233
C	7.14594980918443	14.99763072024586	14.43188774701930

C	14.28676021845945	17.10200179077851	11.16218314987471
C	7.08150651444078	16.12502829169954	15.45310243140305
C	15.29024690056489	16.86829340210452	10.19122589221812
C	6.07801882879615	16.35873668040102	16.42407068906068
C	14.78264943333676	15.76223264540695	9.52763647963636
C	6.58560629640837	17.46479743701740	17.08765810077962
C	15.64672723665426	14.98251196334962	8.44446626128101
C	5.72153849638321	18.24451811738867	18.17081832630134
C	16.37943851011147	15.99421224027399	7.53628603465477
C	4.98882723029888	17.23281783582835	19.07899955259277
C	16.54234487185179	13.92737471218426	9.06022689979927
C	4.82591186038750	19.29965537935966	17.55505870422008
H	13.26654704936273	13.46687583521402	8.82120456719921
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H	12.78455623722381	10.65386792082408	12.93726972278858
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H	11.83269268798296	11.09414524442790	8.76373122947796
H	11.86677020058874	9.71056405167629	9.89542461256941
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H	16.40121546183188	18.31554259562453	12.45711757212982
H	15.59596859470455	17.18372462649665	13.58471050690067
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H	5.88689860472831	14.27157720941473	12.75804557408810
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H	15.67118896890659	16.72663011793900	7.10159421649156
H	4.20845246011433	16.67126462905754	18.52461675690677

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H	5.69663388383567	16.49905718385244	19.51209362554053
H	17.07365171968614	13.35553821503435	8.27132280705248
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H	5.41287555285009	20.01936549365554	16.94891548982246
H	4.29356062355450	19.87048893488526	18.34397826246482
H	4.06161386546297	18.85001426273960	16.88574155578319

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