

**Supplementary Material for
Numerical methods for computing ROHF ground states. Part I: SCF algorithms**

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Atomic coordinates (in Angstroms) :

Pyridine – Cu(2+) system (12 atoms, charge 2, multiplicity 2) :

C 6.0 -0.79417 1.15549 -0.73004
N 7.0 -0.77147 -0.00005 -1.40326
C 6.0 -0.75549 1.20942 0.68028
C 6.0 -0.77590 -0.00092 1.40164
C 6.0 -0.75376 -1.21083 0.67954
C 6.0 -0.79232 -1.15605 -0.73072
H 1.0 -0.81077 -2.05573 -1.32099
H 1.0 -0.76947 -2.16071 1.18522
H 1.0 -0.78710 -0.00126 2.47840
H 1.0 -0.77279 2.15896 1.18655
H 1.0 -0.81424 2.05551 -1.31973
Cu 29.0 1.12360 0.00072 -0.00658

Pyridine – Fe(2+) or Fe(3+) systems (12 atoms, charge 2 or 3, multiplicity 5 or 6 respectively) :

C 6.0 -2.1853 -1.50067 0.662721
N 7.0 -2.7965 -2.55019 1.26604
C 6.0 -2.4724 -1.10719 -0.670485
C 6.0 -3.42828 -1.85803 -1.39688
C 6.0 -4.05578 -2.9613 -0.774398
C 6.0 -3.70334 -3.26223 0.561698
H 1.0 -4.1526 -4.10453 1.0798
H 1.0 -4.77004 -3.58087 -1.30627
H 1.0 -3.66073 -1.59882 -2.42527
H 1.0 -1.99868 -0.215119 -1.09376
H 1.0 -1.4973 -0.929194 1.27798
Fe 26.0 -4.28268 -1.18964 0.365066

Porphyrin model – Fe(2+) (29 atoms, charge 2, multiplicity 5) :

FE 26.0 0.0 0.0 0.0
N 7.0 1.406727 1.406727 0.0
N 7.0 -1.406727 1.406727 0.0
N 7.0 1.406727 -1.406727 0.0
N 7.0 -1.406727 -1.406727 0.0
C 6.0 0.0 3.400142 0.0
C 6.0 0.0 -3.400142 0.0
C 6.0 3.400142 0.0 0.0
C 6.0 -3.400142 0.0 0.0
C 6.0 1.222770 2.760387 0.0
C 6.0 -1.222770 2.760387 0.0
C 6.0 1.222770 -2.760387 0.0
C 6.0 -1.222770 -2.760387 0.0
C 6.0 2.760387 1.222770 0.0
C 6.0 -2.760387 1.222770 0.0
C 6.0 2.760387 -1.222770 0.0
C 6.0 -2.760387 -1.222770 0.0
H 1.0 0.0 4.482672 0.0
H 1.0 0.0 -4.482672 0.0
H 1.0 4.482672 0.0 0.0
H 1.0 -4.482672 0.0 0.0
H 1.0 2.181081 3.277651 0.0
H 1.0 -2.181081 3.277651 0.0
H 1.0 2.181081 -3.277651 0.0
H 1.0 -2.181081 -3.277651 0.0
H 1.0 3.27765 2.181081 0.0
H 1.0 -3.27765 2.181081 0.0
H 1.0 3.27765 -2.181081 0.0
H 1.0 -3.27765 -2.181081 0.0

Porphyrin – Fe(2+) (37 atoms, charge 2, multiplicity 5) :

C 6.0 3.3131 -6.6931 0
C 6.0 4.4844 -6.0238 0
C 6.0 2.1753 -6.0238 0
N 7.0 4.6852 -4.7186 0
C 6.0 5.6557 -6.6262 0
C 6.0 6.6262 -5.6891 0
C 6.0 5.9903 -4.4844 0
C 6.0 6.6596 -3.3466 0
C 6.0 5.9903 -2.2087 0
N 7.0 4.6852 -1.9745 0
C 6.0 6.6262 -1.004 0
C 6.0 4.4844 -0.6693 0
C 6.0 5.6557 -0.0669 0
C 6.0 3.3131 0 0
C 6.0 2.1753 -0.6693 0
N 7.0 1.9745 -1.9745 0
C 6.0 0.6693 -2.2087 0
C 6.0 0.0669 -1.004 0
C 6.0 1.004 -0.0669 0
C 6.0 0 -3.3466 0
C 6.0 0.6693 -4.4844 0
N 7.0 1.9745 -4.7186 0
C 6.0 1.004 -6.6262 0
C 6.0 0.0669 -5.6891 0
Fe 26.0 3.33 -3.344 0.0
H 1.0 5.80745 0.96197 0
H 1.0 7.65315 -0.839733 0
H 1.0 7.6996 -3.34662 0
H 1.0 7.65315 -5.85337 0
H 1.0 5.80745 -7.65507 0
H 1.0 3.30655 -7.73308 0
H 1.0 0.843252 -7.6537 0
H 1.0 -0.959674 -5.85567 0
H 1.0 -1.04 -3.34662 0
H 1.0 -0.959674 -0.837428 0
H 1.0 0.843252 0.960602 0
H 1.0 3.30655 1.03998 0

	GAMESS			This work	
	$g_{A,B}$ - based methods			g_{new} - based methods	
A_{tt}, B_{tt}	$f_{A,B}$ -DIIS	SOSCF	f_{new} -DIIS	f_{new} -DIIS	ODA
Pyridine-Cu ²⁺					
Guest and Saunders	×	×	✓(-1884.512770)	~ (-1884.49)	✓(-1884.512770)
Roothan	×	×	✓(-1884.512770)		
McWeeny	×	×	✓(-1884.542232)		
Euler	×	×	✓(-1884.477241)		
Other coefficients	×	×	×		
Pyridine-Fe ²⁺					
Guest and Saunders	×	×	✓(-1507.965876)	✓(-1508.134654)	✓(-1508.134042)
Other coefficients	×	×	×		
Pyridine-Fe ³⁺					
Guest and Saunders	×	×	✓(-1507.349495)	✓(-1507.414474)	✓(-1507.414474)
Other coefficients	×	×	×		
Porphyrin model-Fe ²⁺					
Guest and Saunders	×	×	✓(-1940.357814)	~(-1940.46)	✓(-1940.513031)
Other coefficients	×	×	×		

Table 1: Energies at convergence starting from core initial guess (6-31G basis set). The color code is detailed in the introduction to Section 5 of the main article. The notation f -DIIS refers to a FD-DIIS method using f as residual function. The DIIS depth parameter m_{max} is fixed to 10 (default value in GAMESS). All energies are expressed in Hartrees.

	GAMESS			This work	
	$g_{A,B}$ - based methods			g_{new} - based methods	
A_{tt}, B_{tt}	SOSCF	$f_{A,B}$ -DIIS	f_{new} -DIIS	f_{new} -DIIS	ODA
Pyridine-Cu ²⁺					
Roothan	✓(-1884.512768)	✓(-1884.512768)	✓(-1884.512770)		
Guest and Saunders	✓(-1884.512768)	✓(-1884.512768)	✓(-1884.512770)		
Euler	✓(-1884.512768)	✓(-1884.512768)	✓(-1884.512770)		
McWeeny	✓(-1884.512768)	✓(-1884.512768)	✓(-1884.512770)		
Canonical II	✓(-1884.512768)	✓(-1884.512768)	✓(-1884.512770)		
Davidson	✓(-1884.542230)	×	×		
Other coefficients	×	×	×		
Pyridine-Fe ²⁺					
Guest and Saunders	×	✓(-1508.013967)	✓(-1507.965876)		
Euler	✓(-1508.134652)	✓(-1508.134652)	✓(-1508.134654)		
McWeeny	✓(-1508.134652)	✓(-1508.134652)	✓(-1508.134654)		
Canonical II	✓(-1508.134652)	×	×		
Other coefficients	×	×	×		
Pyridine-Fe ³⁺					
Guest and Saunders	×	×	✓(-1507.357500)		
Euler	×	×	✓(-1507.304589)		
Other coefficients	×	×	×		
Porphyrin model-Fe ²⁺					
Guest and Saunders	×	×	✓(-1940.513030)		
Euler	×	×	✓(-1940.512761)		
Mc Weeny	×	✓(-1940.513025)	×		
Other coefficients	×	×	×		

Table 2: Energies at convergence starting from GAMESS extended Hückel initial guess (6-31G basis set). The color code is detailed in the introduction to Section 5 of the main article. The notation f -DIIS refers to a FD-DIIS method using f as residual function. The DIIS depth parameter m_{max} is fixed to 10 (default value in GAMESS). All energies are expressed in Hartrees.