

Supporting information for: Analytic energy gradients for variational two-electron reduced-density-matrix-driven complete active space self-consistent field theory

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1 Errors in equilibrium bond lengths

Table S1 provides computed equilibrium molecular geometries for a set of twenty small molecules at the full-valence complete active space self-consistent field (CASSCF) level of theory. Both conventional configuration-interaction (CI)-based and variational two-electron reduced-density-matrix (v2RDM)-based CASSCF computations were performed. CASSCF computations employed the cc-pVXZ basis set (X = D, T, Q). The reduced-density matrices

in the v2RDM-CASSCF computations satisfied either two-particle¹ (PQG) or two-particle and partial three-particle^{2,3} (PQG+T2) N -representability conditions. The CASSCF equilibrium bond lengths were compared to those determined experimentally. All experimentally-obtained equilibrium bond lengths, with the exception of that for molecular hydrogen, were taken from Ref. 4 and the references therein. For H₂, the equilibrium bond length was taken from Ref. 5.

2 Redundant orbital rotations

The v2RDM-CASSCF energy is invariant to rotations among active, inactive, or external orbitals. Here, we provide numerical evidence for the invariance of the v2RDM-CASSCF energy and energy gradient to active-active orbital rotations. Table S2 provides full-valence v2RDM-CASSCF energies and magnitudes of the energy gradient for the same twenty small molecules considered in the Table S1 at experimental geometries obtained from the Computational Chemistry Comparison and Benchmark Database.⁶ The semidefinite optimization of the active-space two-electron reduced-density matrix was considered converged when the primal ($||\mathbf{Ax} - \mathbf{b}||$) and dual ($||\mathbf{A}^T\mathbf{y} - \mathbf{c} + \mathbf{z}||$) errors fell below 10^{-9} and the primal/dual energy gap ($|E_{\text{primal}} - E_{\text{dual}}|$) fell below $10^{-9} E_h$. The orbital optimization procedure was considered converged when the orbital gradient fell below $10^{-9} E_h$ and the energy change produced by orbital rotations fell below $10^{-12} E_h$. The v2RDM-CASSCF computations were performed within the cc-pVDZ basis set while enforcing the PQG N -representability conditions. Results are presented for computations that either include or ignore active-active orbital rotations. The largest deviation between energies computed with and without such rotations is only $1.4 \times 10^{-9} E_h$, which is comparable to the energy convergence criterion employed in this study. The largest deviation between magnitudes of energy gradients computed with and without active-active orbital rotations is only $4.1 \times 10^{-9} E_h a_0^{-1}$.

Table S1: Errors in computed equilibrium bond lengths (Δr_e , pm) from CI- and v2RDM-CASSCF in the cc-pVXZ (X = D, T, Q) basis sets.^a Computed bond lengths are compared to those obtained from experiment (r_e , Å). All values of r_e were taken from Ref. 4 and the references therein, with the exception of that for H₂, which was taken from Ref. 5.

Molecule	Bond	Δr_e				Δr_e				Δr_e			
		cc-pVDZ				cc-pVTZ				cc-pVQZ			
		PQG	PQG+T2	CI	r _e	PQG	PQG+T2	CI	r _e	PQG	PQG+T2	CI	r _e
C ₂ H ₂	C-H	3.0	2.3	2.3	1.2	1.9	1.2	1.2	1.2	1.9	1.2	1.2	1.062
C ₂ H ₂	C-C	3.3	2.6	2.5	1.4	2.0	1.4	1.3	1.3	2.0	1.3	1.2	1.203
C ₂ H ₄	C-H	3.3	2.7	2.6	1.6	2.3	1.6	1.6	1.5	2.3	1.5	1.5	1.081
C ₂ H ₄	C-C	2.4	2.1	2.1	1.4	1.6	1.4	1.3	1.3	1.6	1.3	1.3	1.334
CH ₂	C-H	3.6	3.2	3.2	1.8	2.3	1.8	1.8	1.7	2.1	1.7	1.7	1.107
CH ₂ O	C-O	1.5	0.7	0.6	0.3	1.0	0.3	0.2	0.1	0.8	0.1	0.1	1.203
CH ₂ O	C-H	3.6	2.9	2.9	1.7	2.6	1.7	1.7	1.6	2.5	1.6	1.6	1.099
CH ₄	C-H	3.3	2.6	2.6	1.6	2.3	1.6	1.5	1.5	2.3	1.5	1.5	1.086
CO ₂	C-O	1.8	1.2	1.1	0.6	1.3	0.6	0.6	0.4	1.1	0.5	0.4	1.160
CO	C-O	1.8	1.4	1.4	0.8	1.2	0.8	0.7	0.5	0.9	0.5	0.5	1.128
F ₂	F-F	10.5	10.5	10.5	4.9	4.9	4.9	4.9	4.8	4.8	4.8	4.8	1.412
H ₂	H-H	2.9	2.9	2.9	1.4	1.4	1.4	1.4	1.3	1.3	1.3	1.3	0.741
H ₂ O ₂	O-H	1.0	0.9	0.9	0.2	0.2	0.2	0.1	0.0	0.1	0.0	0.0	0.967
H ₂ O ₂	O-O	5.5	4.0	4.0	2.5	4.0	2.5	2.4	2.2	3.7	2.2	2.1	1.456
H ₂ O	O-H	1.5	1.4	1.4	0.8	0.8	0.7	0.7	0.6	0.7	0.6	0.5	0.957
HCN	C-H	2.9	2.3	2.3	-0.7	-0.7	-0.8	-0.8	-0.8	1.8	-0.8	-0.8	1.065
HCN	C-N	3.1	2.3	2.2	1.2	1.2	0.8	0.7	0.6	1.8	0.6	0.6	1.153
HF	H-F	0.5	0.5	0.5	0.0	0.0	0.0	0.0	-0.2	-0.2	-0.2	-0.2	0.917
HNC	C-N	2.9	2.1	2.0	1.7	1.7	0.9	0.8	0.7	1.5	0.7	0.6	1.169
HNC	N-H	2.5	1.7	1.7	1.6	1.6	0.9	0.8	0.8	1.6	0.9	0.8	0.994
HNO	N-H	2.7	2.6	2.5	1.6	1.6	1.5	1.5	1.4	1.5	1.4	1.3	1.063
HNO	N-O	1.1	0.3	0.3	0.7	0.7	0.0	-0.1	-0.3	0.5	-0.2	-0.3	1.212
HO ₂	O-H	1.6	1.4	1.4	0.8	0.8	0.6	0.6	0.5	0.7	0.5	0.5	0.966
HO ₂	F-O	6.1	5.6	5.6	3.2	3.2	2.8	2.8	2.6	3.1	2.6	2.6	1.435
N ₂	N-N	2.3	1.9	1.8	1.2	1.2	0.9	0.8	0.7	1.1	0.7	0.6	1.098
N ₂ H ₂	N-N	1.3	1.4	1.3	0.7	0.7	0.8	0.7	0.5	0.5	0.6	0.5	1.252
N ₂ H ₂	N-H	3.3	2.6	2.5	2.3	2.3	1.6	1.5	1.4	2.2	1.4	1.4	1.028
O ₃	O-O	4.2	2.6	2.0	3.2	3.2	1.7	1.3	0.9	2.8	1.4	0.9	1.272
NH ₃	N-H	2.5	2.2	2.2	1.5	1.5	1.1	1.1	1.0	1.4	1.0	1.0	1.012
MSE ^b		3.0	2.4	2.4	1.7	1.7	1.2	1.1	1.1	1.7	1.1	1.0	-
MUE ^c		3.0	2.4	2.4	1.7	1.7	1.3	1.2	1.1	1.7	1.1	1.1	-
Max ^d		10.5	10.5	10.5	4.9	4.9	4.9	4.9	4.8	4.8	4.8	4.8	-

^a $\Delta r_e = r_e^{\text{CASSCF}} - r_e$. ^b mean unsigned error. ^c mean signed error. ^d maximum unsigned error.

Table S2: Full-valence v2RDM-CASSCF energies (E_h) and magnitudes of the energy gradients ($E_{ha_0^{-1}}$) for twenty small molecules at experimental geometries obtained from the Computational Chemistry Comparison and Benchmark Database.⁶ The v2RDM-CASSCF orbital optimizations either did or did not include active-active orbital rotations.

Molecule	energy		gradient	
	active-active rotations?		active-active rotations?	
	yes	no	yes	no
C ₂ H ₂	-77.0005879659	-77.0005879659	0.0707616781	0.0707616787
C ₂ H ₄	-78.2278654946	-78.2278654946	0.0373411038	0.0373411041
CH ₂	-114.0364964079	-114.0364964081	0.0932386472	0.0932386484
CH ₂ O	-38.9237035145	-38.9237035145	0.0327917165	0.0327917160
CH ₄	-40.2940001093	-40.2940001091	0.0414512353	0.0414512344
CO ₂	-187.8506879157	-187.8506879152	0.0467292144	0.0467292151
CO	-112.8889003176	-112.8889003186	0.0594535374	0.0594535374
F ₂	-198.7657406549	-198.7657406555	0.0575191239	0.0575191239
H ₂	-1.1469295720	-1.1469295720	0.0287647997	0.0287647997
H ₂ O ₂	-150.8987800334	-150.8987800342	0.0494914313	0.0494914323
H ₂ O	-76.0814873694	76.0814873708	0.0294042832	0.0294042822
HCN	-93.0530070519	-93.0530070522	0.0758791629	0.0758791628
HF	-100.0439426124	-100.0439426120	0.0080527299	0.0080527297
HNC	-93.0262784072	-93.0262784073	0.0619382277	0.0619382293
HNO	-129.9506463130	-129.9506463131	0.0276487230	0.0276487271
HOF	-174.8374077773	-174.8374077778	0.0403951421	0.0403951416
N ₂	-109.1126670185	-109.1126670181	0.0955042450	0.0955042478
N ₂ H ₂	-110.1751499059	-110.1751499063	0.0461777019	0.0461777021
O ₃	-224.5353702162	-224.5353702162	0.0468856709	0.0468856706
NH ₃	-56.2751424265	-56.2751424260	0.0408123411	0.0408123423

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