

Accurate *ab initio* spin densities

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Supporting Information

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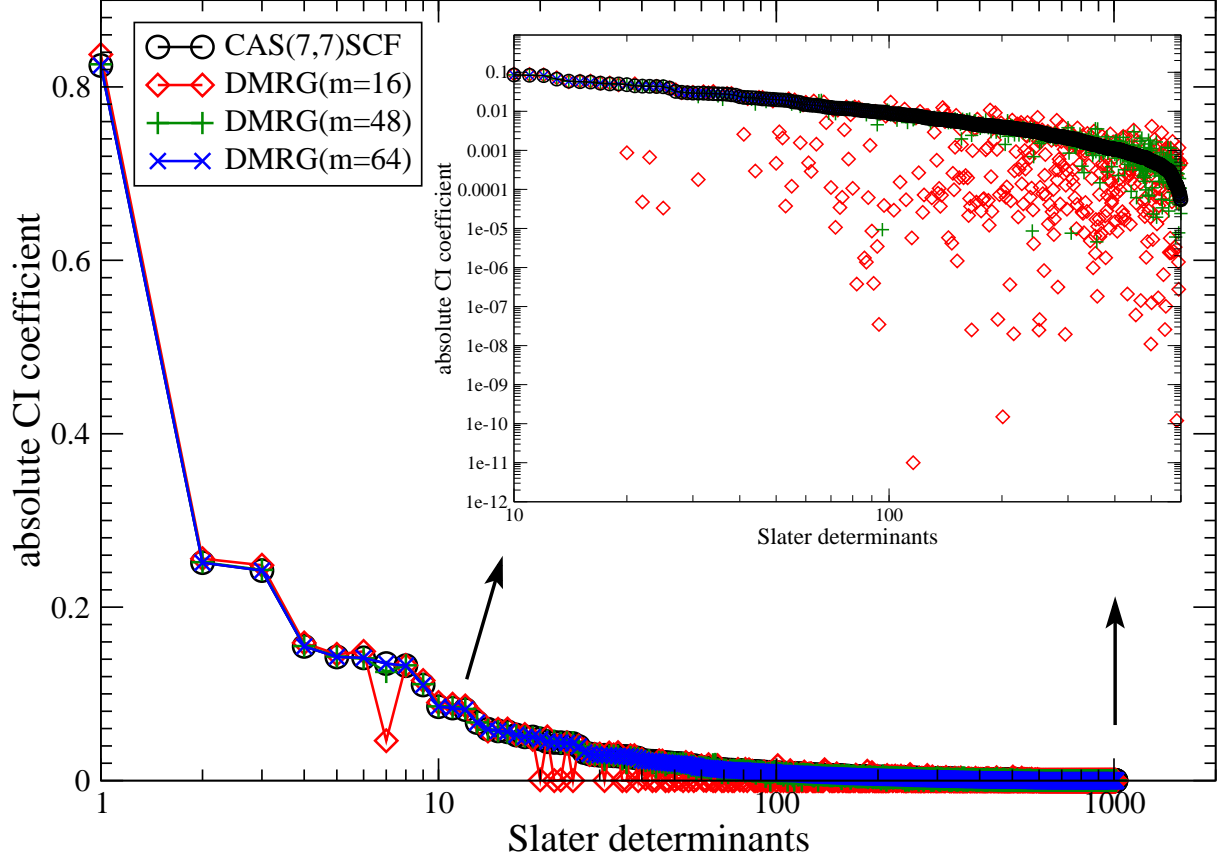


Figure 1: Distribution of the absolute value of the CI coefficients for the DMRG(7,7)[m] calculations employing different renormalized active-system states m and the CAS(7,7)SCF reference calculation for the $[\text{Fe}(\text{NO})]^{2+}$ molecule surrounded by four point charges located at a distance of 1.131 Å from the iron center. The CI coefficient obtained in the different calculations are always printed for the same Slater determinants. The determinants are ordered according to the CI weights of the CAS(7,7)SCF calculation.

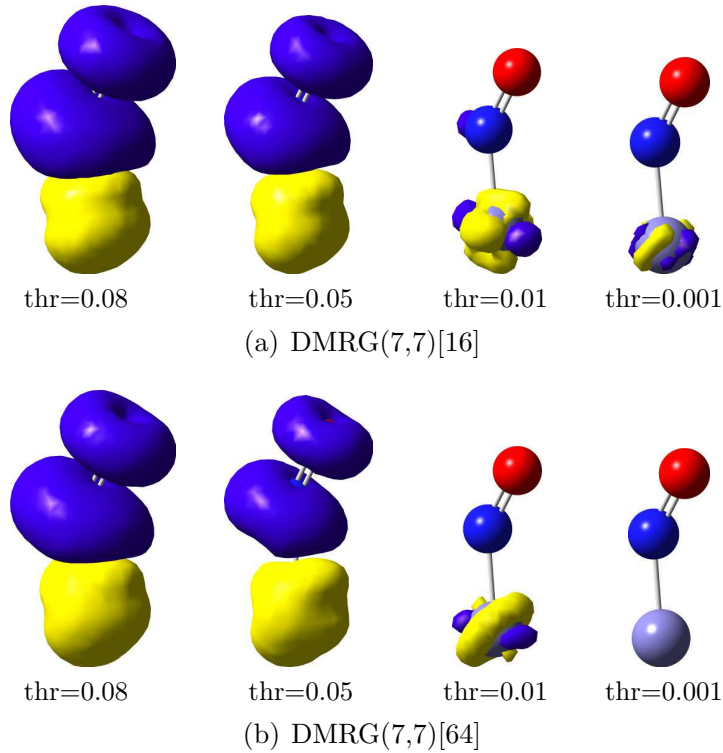


Figure 2: CAS(7,7)CI[m]-DMRG(7,7)[m] spin density difference plots determined for different sampled subspaces of the complete N -particle Hilbert space for the $[\text{Fe}(\text{NO})]^{2+}$ molecule surrounded by four point charges located at a distance of 1.131 Å from the iron center. The spin density differences are plotted for the reconstructed CAS(7,7)CI-type wave function with respect to the DMRG(7,7)[m] reference spin density for the same number of renormalized active-system states m . The threshold (thr) indicates the upper bound of the COM value in the sampling-reconstruction procedure for each CASCI-type wave function. An isosurface value of 0.0003 was chosen for all spin density difference plots.

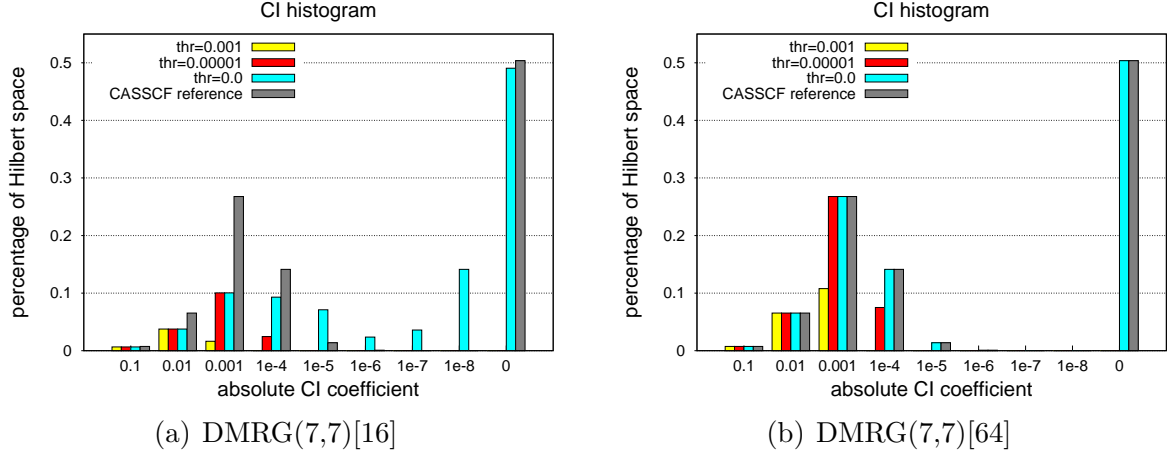


Figure 3: CI histogram of the absolute values of the CI coefficients for the Slater determinants for reconstructed CASCI-type wave function expansions from the DMRG(7,7)[m] calculations with different renormalized active-system states m for the $[\text{Fe}(\text{NO})]^{2+}$ molecule surrounded by four point charges at a distance of $d_{\text{pc}} = 1.131 \text{ \AA}$ from the iron atom. The CAS(7,7)SCF reference calculation is also shown for comparison. thr corresponds to the threshold value of COM in the sampling-reconstruction procedure and denotes the accuracy of the reconstructed CASCI-type wave function. All Slater determinants with CI coefficients in an interval as indicated on the abscissa are grouped together.

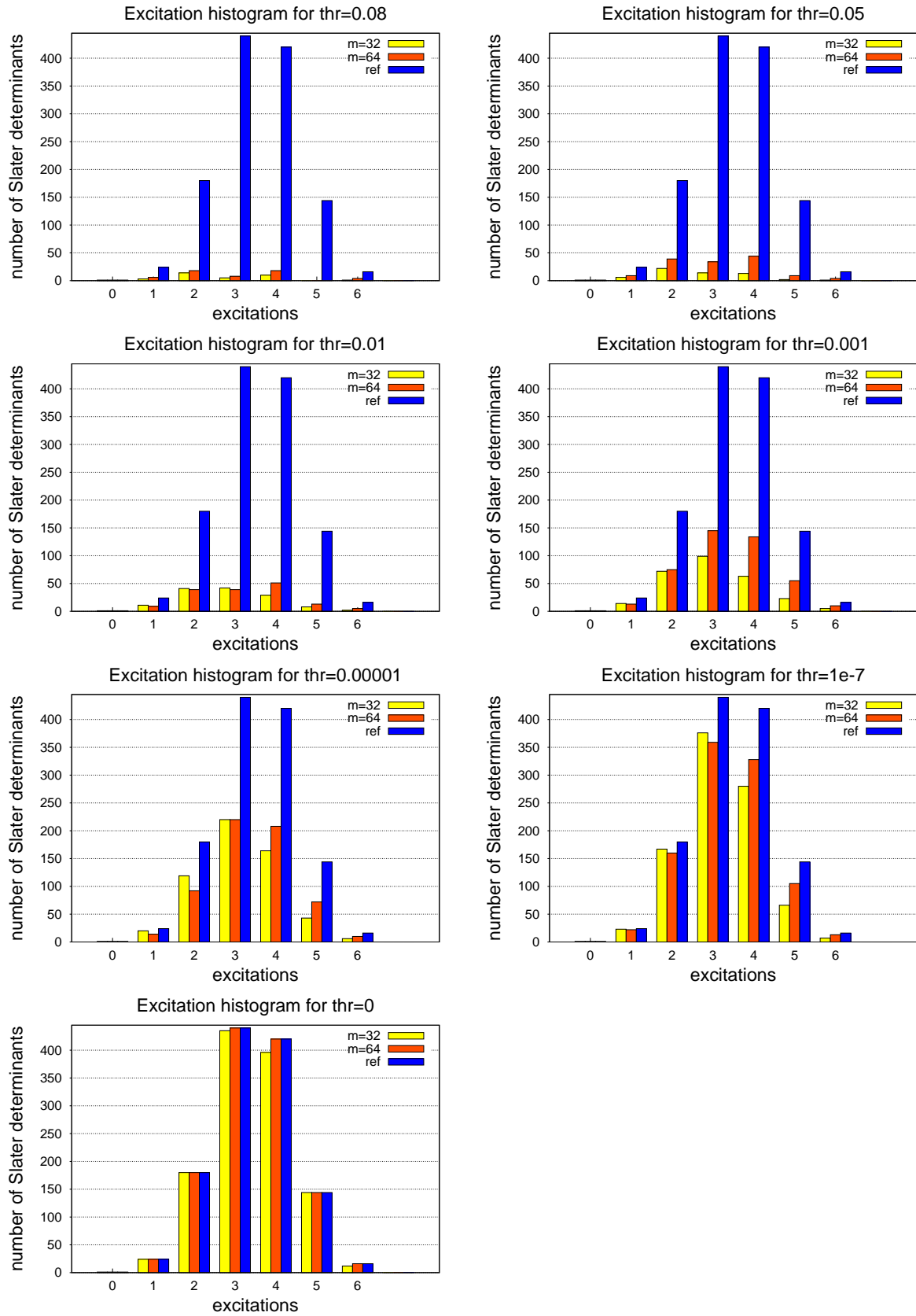


Figure 4: Excitation histogram for CAS(7,7)CI-type wave function expansion reconstructed for DMRG(7,7)[m] calculations with m renormalized active-system states and for different threshold (thr) values of COM for the $[\text{Fe}(\text{NO})]^{2+}$ molecule surrounded by four point charges located at a distance of 1.131 Å from the iron center. The CAS(7,7)SCF reference excitation pattern is also shown and marked as ref.

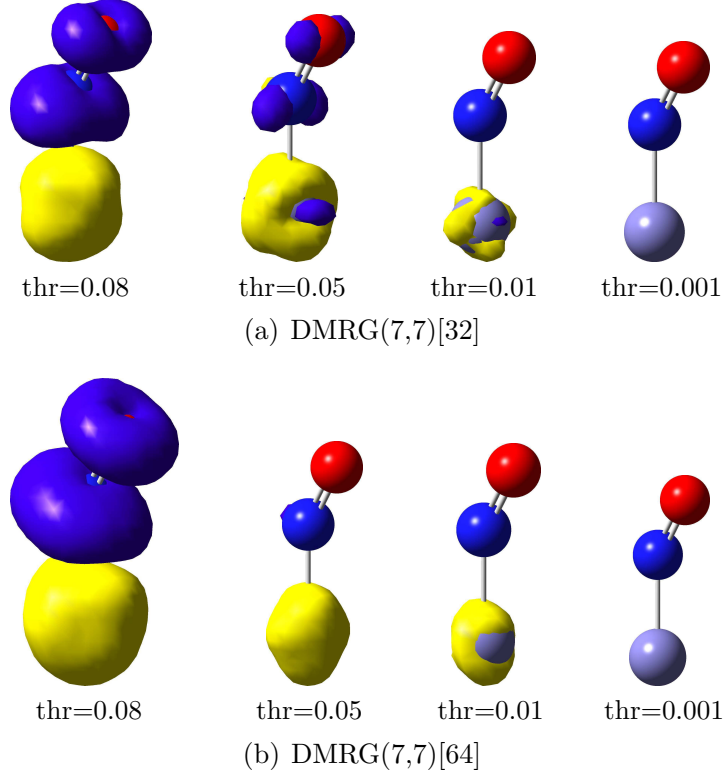


Figure 5: CAS(7,7)CI[m]-DMRG(7,7)[m] spin density difference plots determined for different sampled subspaces of the complete N -particle Hilbert space for the $[\text{Fe}(\text{NO})]^{2+}$ molecule surrounded by four point charges located at a distance of 0.598 Å from the iron center. The spin density differences are plotted for the reconstructed CAS(7,7)CI-type wave function with respect to the DMRG(7,7)[m] reference spin density for the same number of renormalized active-system states m . The threshold (thr) indicates the upper bound of the COM value in the sampling reconstruction procedure for each CASCI-type wave function. An isosurface value of 0.0003 was chosen for all spin density difference plots.

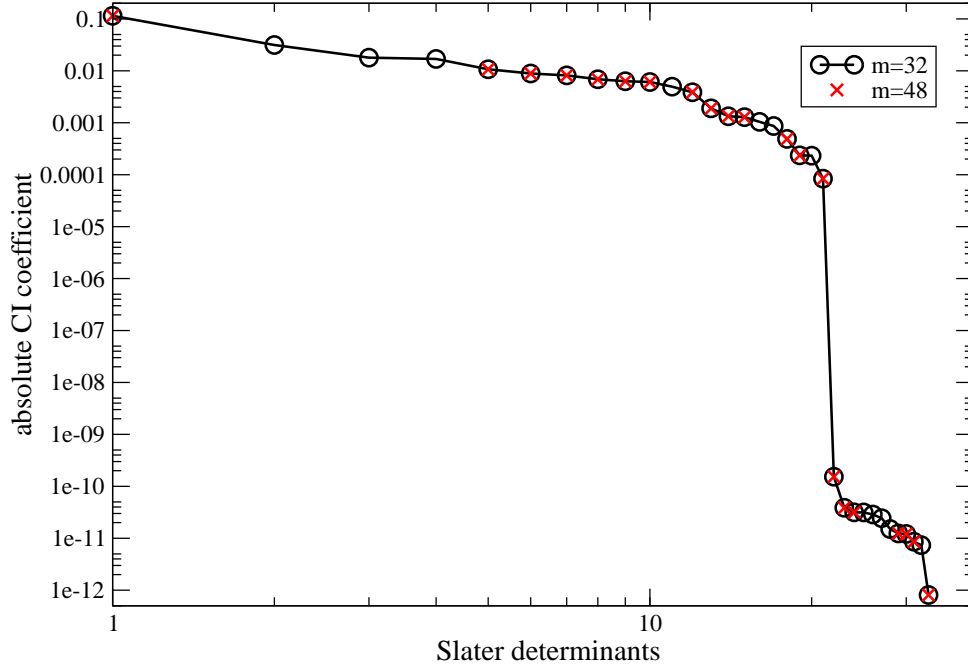


Figure 6: Slater determinants which are not incorporated by the DMRG algorithm for different renormalized active-system states m in the DMRG(7,7)[m] calculations for $[\text{Fe}(\text{NO})]^{2+}$ surrounded by four point charges in a distance of $d_{\text{pc}} = 0.598 \text{ \AA}$ from the iron atom. The missing Slater determinants are ordered according to their CI weight. Increasing m , embeds some of the previously missing configurations. The incorporated configurations for $m = 48$ are displayed as open circles in the $m = 32$ curve, while crossed circles correspond to missing Slater determinants for both $m = 32$ and $m = 48$. Note that important configurations which contain large CI weights could not be incorporated by the DMRG algorithm in small- m calculations.

CASSCF and DMRG spin density convergence for intermediate CAS

In Ref. [36], different medium-sized active orbital spaces are discussed ranging from 11 electrons correlated in 9 orbitals up to 13 electrons correlated in 16 active orbitals. In our DMRG study, we first focus on five different active orbital spaces, namely on a CAS(11,9), CAS(11,11), CAS(11,12), CAS(11,13), and a CAS(11,14). In the CAS(11,9), the active orbital space is composed of five Fe 3d-orbitals (d_{xy} , d_{xz} , d_{yz} , d_{z^2} , and $d_{x^2-y^2}$), both NO π - and π^* -orbitals. The latter four CASSCF calculations contain an additional shell of Fe d -orbitals: the Fe d_{xz} - and d_{xy} - (CAS(11,11)), d_{yz} - (CAS(11,12)) and d_{z^2} -double-shell orbitals (CAS(11,14) which contains also an additional empty ligand orbital). As orbital basis, natural orbitals from the corresponding CASSCF calculations are employed [68-70]. All CASSCF calculations as well as the calculation of the one-electron and two-electron integrals were performed with the MOLPRO program package [58] using Dunning’s cc-pVTZ basis set for all atoms [59,60]. As the convergence of DMRG calculations can crucially depend on the ordering of orbitals in the algorithm [Moritz, Hess, Reiher, *J. Chem. Phys.* **2005**, *122*, 024107], the DMRG orbital orderings were optimized by minimizing the entanglement among molecular orbitals following the ideas of Refs. [49,57,72]. Additionally, we applied the CI-DEAS procedure in the start up procedure in order to keep the system size small and accelerate convergence [57]. All DMRG calculations are performed with the Budapest DMRG program [71]. The number of DMRG active-system states m ranges from 220 for the smallest active orbital space CAS(11,9) up to 1680 for the CAS(11,14) calculation in order to reproduce the corresponding CASSCF reference energy, while for the intermediate active orbital spaces $m = 790$ (CAS(11,11)), $m = 960$ (CAS(11,12)) and $m = 1280$ (CAS(11,13)) active-system states, respectively, are required to reproduce the CAS(x,y)SCF energies and spin density distributions.

For all these DMRG calculations, the spin density distribution of the corresponding CASSCF reference calculation could be exactly reproduced and is therefore not displayed here. As an additional convergence criterion for the DMRG calculations, the reconstructed CASCI-type wave function of each DMRG calculation can be analyzed and compared to the exact CASSCF reference wave function. To perform such an analysis, we calculated the weighted quantum fidelity for a reconstructed CASCI-type wave function and the corresponding CASSCF reference wave function considering only the most important configurations ($CI > 10^{-6}$). The quantum fidelity was further normalized with respect to the norm of the truncated CASSCF reference wave function since all configurations with CI coefficients smaller than 10^{-6} were neglected. The set of quantum fidelity measures $F_{\text{DMRG,CASSCF}}$ for {CAS(11,9),CAS(11,11),CAS(11,12),CAS(11,13),CAS(11,14)} is {0.999999,0.999999,0.999999,0.999998,0.9999989}. Hence, the overlap of both wave functions is excellent, and similar spin density distributions are obtained.

Table I: The absolute error Δ_{abs} and the root-square error Δ_{rs} of DFT spin densities with respect to the converged DMRG(13,29)[2048] reference spin density for $[\text{FeNO}]^{2+}$ surrounded by four point charges at a distance of $d_{\text{pc}} = 1.131$ Å from the iron center.

Method	Δ_{abs}	Δ_{rs}
OLYP	0.360309	0.0826634
OPBE	0.395280	0.0891197
BP86	0.158527	0.0346259
BLYP	0.138796	0.0304860
TPSS	0.178942	0.0425946
TPSSh	0.718517	0.1634330
M06-L	0.446750	0.1048820
B3LYP	0.951955	0.2159410