Density matrix renormalization group method for prediction of hyperfine structure

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Despite all recent progress, the accuracy of hyperfine coupling constants (HFCCs) is still challenging for quantum chemistry. In this work, we have performed the density matrix renormalization group (DMRG) calculations to predict the HFCCs of several π–radicals: BO, CO^+, CN, and AlO. The DMRG algorithm used herein was considered as a near full configuration interaction (FCI) method and the electron correlation effects were systematically investigated using the complete active space (CAS) procedures, i.e CASSCF and CASCI. The geometry of radicals has been adapted from experiments. The EPR-III basis set was used for C, O, and N elements, while the IGLO-III basis set was used for Al element.

Although the HFCCs of BO and CO^+ calculated by conventional methods, i.e. density functional theory (DFT) and coupled cluster (CC), were already in the acceptable agreements with experimental values, our DMRG calculations have pushed the accuracy of HFCCs further. For CN radical, our DMRG calculation has captured the high-order effect of correlation treatment. Regarding AlO radical, our DMRG calculation properly described the multi-reference problem resulting from the balance between ionic states. Therefore, the HFCCs of C center in CN and Al center in AlO are in the good agreements with experimental values.

Concerning the CAS-type procedure, most CASCI calculations provided the poor agreements with experimental values, while the quite accurate HFCCs of less electronegative centers can be found when the orbital optimization procedure was employed with the same CAS. These situations can be attributed to the nature of one-particle bases in which the DMRG calculations were performed. The canonical Hatree-Fock (HF) orbitals were used as the orbital bases for the DMRG-CASCI calculation. Whereas, the DMRG calculation in conjunction with CASSCF procedure was performed on much more compact orbitals which were obtained through orbital optimization procedure.

In summary, our results have confirmed that it is critical to correlate the core electrons to correctly obtain the spin density at the nucleus. Additionally, the inclusion of polarization shells is necessary for describing the dynamical correlation, which makes the proper spin-polarized effects. Finally, the assessment for the convergence of HFCCs with respect to the number of renormalized states M indicates that the acceptable result can be obtained even if total energy is not converged with respect to M.

Methods	^{27}Al				^{17}O			
	$A^{(K;c)}$	$A_{11}^{(K;d)}$	$A_{22}^{(K;d)}$	$A_{33}^{(K;d)}$	$A^{(K;c)}$	$A_{11}^{(K;d)}$	$A_{22}^{(K;d)}$	$A_{33}^{(K;d)}$
DMRG-CASCI(21e,36o)	710.91	−46.45	−46.62	93.06	1.82	44.98	44.89	−89.87
DMRG-CASSCF(21e,36o)	722.73	−54.19	−54.09	109.28	15.06	50.73	50.43	−101.16
B3LYP	512.21	−59.97	−59.97	119.93	8.17	66.22	66.22	−132.43
TPSS	656.79	−56.10	−56.10	112.21	9.52	59.91	59.91	−119.83
BP	653.71	−56.86	−56.86	113.72	14.21	59.60	59.60	−119.20
CCSD	482.40	−57.20	−57.20	114.30	18.10	63.80	63.80	−127.70
CCSD(T)	565.30	−56.20	−56.20	112.40	19.30	58.90	58.90	−117.80
Exp − gas-phase	738	−56	−56	112	n/a			
Exp − Ne-matrix	766	−52	−52	104	2	50	50	−100

HFCCs (in MHz) for AlO radical. The IGLO-III and EPR-III basis sets were used for Al and O, respectively. The total number of AOs is of 84.

M	Energy (E_h)	$A^{(K;c)}$ (MHz)	$A_{11}^{(K;d)}$ (MHz)
128	−92.570835	576.80	−53.18
256	−92.575539	563.79	−52.97
512	−92.577510	561.95	−52.92
1024	−92.578114	559.44	−52.86

The convergence of total energy, Fermi contact term, and spin-dipole term at C center (CN) with respect to number of renormalized states M. The active space is CAS(13e,30o). The EPR-III basis set was used.
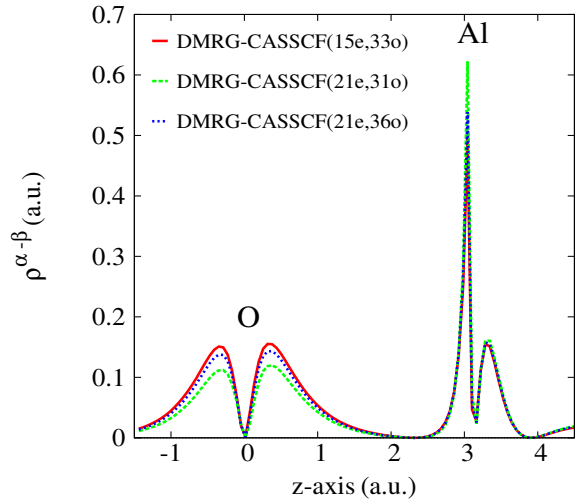
Spin density distribution of spin natural orbital (SNO) with largest spin occupation number of AlO radical. The geometry of AlO radical (in Bohr) are: O(0.000, 0.000, 0.000) and Al(0.000, 0.000, 3.057)