The Peculiar Case of Oxo-Mn(Salen)

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The oxo-Mn(Salen) molecule has been a subject of numerous computational studies motivated by its role in catalysis of the enantioselective epoxidation of unfunctional olefins. Its closely lying singlet and triplet states pose a considerable challenge due to its multireference character, which is the reason why the system has been used repeatedly to assess the performance of methods designed for treatment of strongly correlated systems. One of the frequently applied methods is density matrix renormalization group (DMRG), especially combined with the CASSCF approach [1-4]. More recently, even the effects of dynamic correlation has been examined [3,4], however, the underlying problem remains – the varying reports of different ground states at the DMRG-CASSCF level for calculations performed using active spaces of similar size and in the identical basis sets.

Our aim was to contribute to these efforts by exploring the impact the active space composition and basis set has on the character of the ground state. For this purpose, we selected two active spaces consisting of 22 and 27 orbitals for DMRG-CASSCF calculations. Afterwards, we studied the effect of dynamic correlation using our implementation of the DMRG-based tailored coupled clusters (DMRG-TCCSD) method [4], which newly employs the local pair natural orbital approach (LPNO). With the LPNO implementation we were able to investigate the effect of dynamic correlation up to the quadruple-ζ basis set, which amounts to 1178 basis functions.

References
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