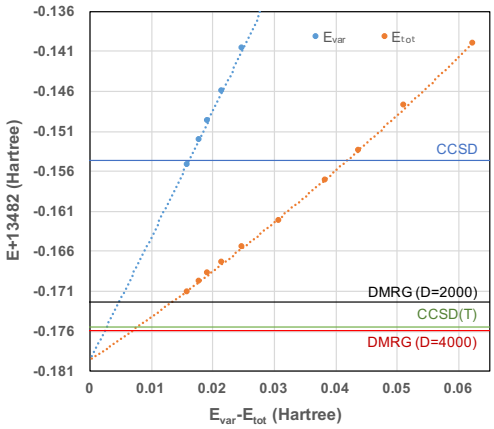

FIG. 1. SHCI variational and total energies for progressively decreasing cutoffs (dots) along with quadratic extrapolations (dotted curves) of the (54e,54o) model of FeMoco in Ref. 7 (the estimated error in the extrapolated energy is about 2 mHa); variational DMRG results at bond dimension $D = 2000$ and $D = 4000$; CCSD and CCSD(T) energies. All calculations are for the $S = 0$ state.

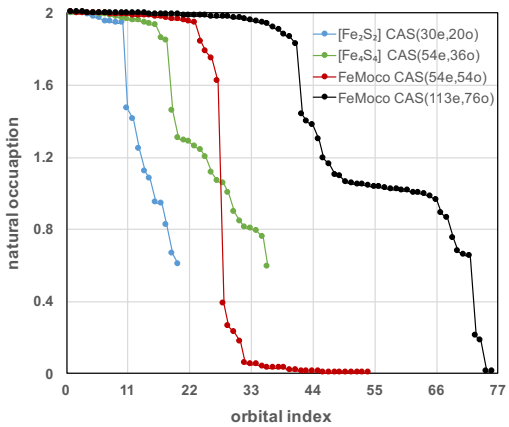

FIG. 2. Natural occupations obtained with DMRG for $S = 0$ state of a $[Fe_2S_2]$ complex with CAS(30e,20o) and $D = 8000$, $S = 0$ state of a $[Fe_4S_4]$ complex with CAS(54e,36o) and $D = 4000$, $S = 0$ state of FeMoco with CAS(54e,54o) reported in Ref. 7 and $D = 2000$, and the $S = 3/2$ state of FeMoco with CAS(113e,76o) constructed in this work and $D = 2000$. In contrast to the other models, the CAS(54e,54o) ground-state has no open shells.

clusters[23,24]. However, the one-body density matrix in the FeMo cofactor model of Ref. 7 has no open shells, as seen from the eigenvalues of the one-body density matrix (Figure 2). A related point is that the coefficient of the dominant (natural orbital) determinant in SHCI is very large (0.67) indicating that the wavefunction has mainly single or few determinantal character, which is not possible for a low-spin system with many open shells. A large determinant weight has also been observed in Ref. 25 (in fact they observed an even larger determinant weight, probably because of using a smaller number of variational determinants). As shown in Figure 1, the CCSD(T) energy is also within a few mE_h of the variational DMRG and extrapolated SHCI energies, confirming the single reference nature of this problem.

Although the electronic structure of the ground state within the active space of Ref. 7 is qualitatively incorrect, we nonetheless believe that the quantum resource estimates in Ref. 7, e.g. for a Trotter step, that are the primary focus of the paper, are probably reasonable and the main conclusions in that work are thus unaffected. This is because the cost of the Trotter step relies primarily on the magnitude and number of the Hamiltonian matrix elements which does not vary much with different choices of valence active space of similar size. The character of the ground-state affects the efficiency of adiabatic state preparation in the quantum algorithm, but this is left as an open problem in Ref. 7.

Nonetheless, it seems desirable to have a more qualitatively reasonable active space for future studies. For this purpose, we attach a valence active space Hamiltonian[26] of the FeMo cofactor constructed from all Fe 3d, S 3p, Mo 4d, and C 2s2p orbitals in the $[MoFe_7S_9C]$ core, as well as some bonding ligand orbitals. The active orbitals were obtained by first performing high-spin unrestricted Kohn-Sham calculations with the B3LYP functional[27–29] and the TZP-DKH[30] basis for Fe, S, and Mo, and the def2-SVP basis[31] for the other atoms (C, H, O, and N) using a structure in Ref. 22, and then split-localizing the unrestricted natural orbitals. This results in an active space model with 113 electrons in 76 orbitals. The detailed composition is shown in Table I and some selected localized orbitals are shown in Figure 3. The dimension of the full configuration interaction (FCI) space is on the order of $O(10^{35})$ for the spin $S = 3/2$ ground state[17,18] in this FeMoco active space. We have performed preliminary DMRG calculations to check the qualitative features of the active space. As shown in Figure 2, the natural occupation numbers obtained with a DMRG solution ($D = 2000$) for $S = 3/2$ show a large number of singly occupied orbitals, which demonstrates that this active space captures the open-shell character of FeMoco in sharp contrast with the previous model[7]. While we emphasize that a detailed and chemically meaningful study on FeMoco should consider many other factors, such as the convergence of the environment representation, different protonations, etc., we conclude that the active space Hamiltonian we provide contains at least a qualitative model of the open-shell character and low energy states of the cofactor. We hope this will be useful in future quantum (or classical) estimates of the complexity of FeMo cofactor electronic structure.

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