The electronic complexity of the ground-state of the FeMo cofactor of nitrogenase as relevant to quantum simulations

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We report that a recent active space model of the nitrogenase FeMo cofactor, proposed in the context of quantum simulations, is not representative of the electronic structure of the FeMo cofactor ground-state. Although quantum resource estimates, outside of the cost of adiabatic state preparation, will not be much affected, conclusions should not be drawn from the complexity of classical simulations of the electronic structure of this system in this active space. We provide a different model active space for the FeMo cofactor that contains the basic open-shell qualitative character, which may be useful as a benchmark system for making classical and quantum resource estimates.

The process of nitrogen fixation, namely that of converting atmospheric dinitrogen to a reduced form, such as ammonia, which can then be metabolized by biological species, is essential to life on this planet[1–4]. The industrial Haber-Bosch process to produce fertilizer from the endothermic reaction $N_2 + 3H_2 \rightarrow 2NH_3$ is very energy intensive, requiring a careful balance of high temperatures and high pressures to achieve efficient catalysis. In contrast, natural bacteria and archaea carry out nitrogen fixation under ambient conditions through nitrogenases. At the molecular level, the nitrogenase enzyme, an agglomeration of a homodimer Fe protein and the MoFe protein (in its most common Mo containing form), catalyzes the nitrogen bond-breaking process via a family of 3 metallic cofactors: the $[Fe_4S_4]$ iron cubane, the $[Fe_8S_7]$ P cluster, and the $[MoFe_7S_9C]$ FeMo cofactor (FeMoco), with FeMoco serving as the site of nitrogen reduction. The contrast between the conditions of biological nitrogen fixation and the Haber-Bosch process is an enduring source of fascination for chemists.

In the search to unravel the secrets of biological nitrogen fixation, the first stage is to understand the structure of the enzyme itself. After many decades, we now possess atomic scale resolution structures of nitrogenase, including all cofactors[5,6]. However, the electronic structure of the cofactors, and in particular the large P cluster and FeMo cofactor, remains poorly understood. This is due to the complexity of tackling the multiple transition metal ions with their multiple charge states and complicated spin-couplings. Even though the qualitative electronic structure is believed to be captured using only the valence active space of the metals and bridging S ligands which provides a great reduction of the problem size (to, for example, 103 electrons in 71 orbitals in the case of FeMoco considering the Fe 3d, S 3p, Mo 4d, and the interstitial C 2s2p for the $[MoFe_7S_9C]$ core assuming a total charge -1), no satisfactory classical many-electron simulation within this valence active space has yet been performed. Because of the need for tangible objectives for quantum simulations of electronic structure, these metallic cofactors have thus been suggested as an interesting target for future quantum simulators. Ref. 7 provides a pedagogical discussion of

the chemical questions that must be considered when elucidating a complex reaction such as nitrogen fixation, as well as concrete resource estimates resulting from 54 electron in 54 orbital (54e,54o), and 65 electron in 57 orbital (65e,57o) models of the FeMoco cluster.

Although the focus of Ref. 7 was the quantum resource estimates for this problem, it is natural to ask whether a classical calculation of the electronic structure of FeMoco at the level described in Ref. 7 is feasible. For this reason, we report that the active space in Ref. 7 does not actually contain the representative features of the electronic structure of the FeMoco ground-state that make its classical simulation difficult. Consequently, if taken out of context, it provides a misleading characterization of the classical complexity of obtaining the low-energy states. In fact, as shown in Fig. 1 for the (54e,54o) model of Ref. 7, we can obtain accurate ground-state energies ($S = 0$) using standard classical algorithms such as coupled cluster theory[8], variational density matrix renormalization group[9–13], and the semistochastic heatbath configuration interaction (SHCI) method[14–16] (a recent variant of selected configuration interaction plus perturbation theory methods). The lowest DMRG variational energy and the extrapolated SHCI energy agree to within 5 mE_h or about 0.6 mE_h per metal center (comparable to the 1 mE_h accuracy in relative energies usually considered to be chemical accuracy). Note that only modest resources were required for these calculations and higher accuracy, e.g. more variational determinants in selected CI or larger bond dimensions in DMRG, is very feasible.

As we have mentioned, the reason for the simplicity of the classical simulations is not from the intrinsic electronic structure of the FeMo cofactor but due to the active space in Ref. 7. In FeMoco, the Fe and Mo ions are expected to be in the (II), (III), or (IV) formal oxidation states[17–22], which leads to approximately 35 open shells (singly filled orbitals) depending on the charge state of the cluster. The prevalence of Fe(II) and Fe(III) oxidation states is supported experimentally by the Fe Mössbauer spectrum[17–19], and can be seen in direct theoretical calculations of smaller pieces of the FeMo cofactor, such as the $[Fe_2S_2]$ or $[Fe_4S_4]$