Polynuclear transition-metal (PNTM) clusters, ubiquitous in biological systems, owe their catalytic activity to the presence of a large manifold of low-lying spin states, and a number of stable oxidation states. The ab initio description of such systems - starting from the electronic Schrödinger equation - represents one of the greatest challenges of modern quantum chemistry, requiring highly multiconfigurational treatments. We propose a theoretical framework of simple and physically motivated molecular-orbital transformations that enable the resolution and characterization of targeted electronic wave functions with ease. This paradigm allows us to unravel the complicated electronic correlations in PNTM clusters. We apply it to two super-oxidized iron-sulfur cubane [Fe₄S₄] structures, and accurately characterize their singlet ground and low-lying excited states. Through direct access to their wave functions, we identify the important correlation mechanisms and their interplay with the geometrical distortions observed in these clusters. Our results unambiguously reveal a hidden magnetic order in the manifold of singlet states. Namely, that in all low-energy singlet states of the two compounds, well-defined spin structures are formed within two pairs of magnetic sites. For instance, in the ground state of one compound two iron sites of local $S = 5/2$ spins are strongly ferromagnetically correlated to form two $S = 5$ intermediate pair states; two such pairs are then anti-ferromagnetically coupled to yield an overall singlet. In the five excited singlets, the spin of these hidden pair-states is reduced in steps to zero. We find that the ab initio results for these compounds can be mapped with high fidelity onto a four-site Heisenberg–Dirac–van Vleck Hamiltonian with two anti-ferromagnetic coupling constants. Thus, the complexes are intrinsically frustrated anti-ferromagnets, and the obtained spin structures, together with the geometrical distortions represent two possible ways to release spin frustration. The geometrical distortions may be seen as the result of a spin-driven Jahn-Teller distortion, that lifts the electronic ground state degeneracies. Our paradigm provides a simple yet rigorous wave function-based route to uncover the electronic structure of PNTM clusters, and may be applied to a wide variety of such clusters.
Resolution of Low-Energy States in Spin-Exchange Transition-Metal Clusters:
Case Study of Singlet States in [Fe(III)\textsubscript{4}S\textsubscript{4}] Cubanes

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Polynuclear transition-metal (PNTM) clusters, ubiquitous in biological systems, owe their catalytic activity to the presence of a large manifold of low-lying spin states, and a number of stable oxidation states. The ab initio description of such systems - starting from the electronic Schrödinger equation - represents one of the greatest challenges of modern quantum chemistry, requiring highly multiconfigurational treatments. We propose a theoretical framework of simple and physically motivated molecular-orbital transformations that enable the resolution and characterization of targeted electronic wave functions with ease. This paradigm allows us to unravel the complicated electronic correlations in PNTM clusters. We apply it to two super-oxidized iron-sulfur cubane [Fe\textsubscript{4}S\textsubscript{4}] structures, and accurately characterize their singlet ground and low-lying excited states. Through direct access to their wave functions, we identify the important correlation mechanisms and their interplay with the geometrical distortions observed in these clusters. Our results unambiguously reveal a hidden magnetic order in the manifold of singlet states. Namely, that in all low-energy singlet states of the two compounds, well-defined spin structures are formed within two pairs of magnetic sites. For instance, in the ground state of one compound two iron sites of local $S = 5/2$ spins are strongly ferromagnetically correlated to form two $S = 5$ intermediate \textit{pair} states; two such pairs are then anti-ferromagnetically coupled to yield an overall singlet. In the five excited singlets, the spin of these hidden pair-states is reduced in steps to zero. We find that the \textit{ab initio} results for these compounds can be mapped with high fidelity onto a four-site Heisenberg–Dirac–van Vleck Hamiltonian with two anti-ferromagnetic coupling constants. Thus, the complexes are intrinsically frustrated anti-ferromagnets, and the obtained spin structures, together with the geometrical distortions represent two possible ways to release spin frustration. The geometrical distortions may be seen as the result of a spin-driven Jahn-Teller distortion, that lifts the electronic ground state degeneracies. Our paradigm provides a simple yet rigorous wave function-based route to uncover the electronic structure of PNTM clusters, and may be applied to a wide variety of such clusters.

I. INTRODUCTION

Polynuclear transition-metal (PNTM) clusters, such as iron-sulfur clusters and the manganese-oxygen cluster of photosystem II, play pivotal roles in bio-chemical processes, being crucially involved in electron transfer chains, as well as mediating spin-forbidden reactions such as oxygen evolution from splitting water.\textsuperscript{1–11} The catalytic activity of these compounds is to a large extent bound to the large manifold of energetically low-lying states that characterize their electronic structures, and a number of stable oxidation states. These energetically accessible electronic states allow electronic transitions – possibly varying in spin – with ease. Three different oxidation states are known for the biologically active Fe\textsubscript{4}S\textsubscript{4} clusters, as exemplified by ferredoxins ([Fe\textsubscript{4}S\textsubscript{4}]\textsuperscript{2+/1+}/[Fe\textsubscript{4}S\textsubscript{4}]\textsuperscript{1+}) and the high-potential ([Fe\textsubscript{4}S\textsubscript{4}]\textsuperscript{3+}/[Fe\textsubscript{4}S\textsubscript{4}]\textsuperscript{2+}) proteins.\textsuperscript{6} An all-ferrous [Fe\textsubscript{4}S\textsubscript{4}]\textsuperscript{0} has also been reported.\textsuperscript{12–14} Only very recently an all-ferric [Fe\textsuperscript{III}\textsubscript{4}S\textsubscript{4}]\textsuperscript{4+} cluster with terminal thiolates has been experimentally synthesized and characterized.\textsuperscript{15} Based on the experimental data the electronic ground state of the cluster has been assigned to be a singlet. Interestingly, this rare oxidation state is found to generate a larger [Fe\textsubscript{8}S\textsubscript{7}] P-cluster core,\textsuperscript{15} and it has been suggested to take place in hydrophobic and sterically hindered high-potential iron-sulfur protein pockets, where it is protected against attack by nucleophiles.\textsuperscript{16}

At the experimental level the ground- and excited-state electronic structures of PNTM clusters are difficult to resolve. Metal-based electronic transitions can be masked by intense ligand-based transitions, and they are part of the more complex system of vibronic excitations.\textsuperscript{5} Moreover, inter-cluster exchange interactions may exist in solid state and/or low-temperature measurements, affecting the magnetization measurements.\textsuperscript{16} Meanwhile, the theoretical characterization of these states by modern quantum chemical methods has been hindered by the computational complexity associated to the description of their ground- and excited-state wave functions. Mean-field approaches – with broken-symmetry density functional theory (BS-DFT)\textsuperscript{17–36} being most commonly used for these systems – fail to capture the fundamental electron correlation mechanisms involved. E.g., BS-DFT is incapable to correctly describe the non-local cor-

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relations and fluctuations between the localized spins at the magnetic centers.\textsuperscript{37} However, precisely these spin correlations are at the core of the chemical and physical properties of these compounds. Methodologies and schemes to partially circumvent the limitations in BS-DFT have been discussed extensively by Yamaguchi and co-workers,\textsuperscript{38,39} with \textit{noncollinear} schemes being closer to the accurate description of the non-local nature of spin correlations.\textsuperscript{40–44} Exact \textit{ab initio} wave functions, instead, allow for such correlations, but their applicability is hindered by the exponential scaling of the many-body wave function with respect to the number of unpaired electrons. Within \textit{ab initio} wave function based methods, low- and intermediate-spin states, consisting of a large number of open shell orbitals, exhibit a considerably strong multi-reference character, meaning that in the configuration interaction (CI) expansion of the wave function, there are multiple electronic configurations with large relative amplitudes. Among expensive \textit{ab initio} methods, the spin-adapted Density Matrix Renormalization Group (DMRG) approach has been widely utilized for studying exchange-coupled transition metal clusters,\textsuperscript{11,46–49} and \textit{ab initio} to [Fe$_2$S$_4$] complexes\textsuperscript{50,51} with similar active spaces considered in this paper, yielding accurate energies. The interpretation of many-body wave functions and their energetics, once available, represents another important challenge for the application of \textit{ab initio} quantum chemical methods to PNTM clusters. In this respect, \textit{ad hoc} model Hamiltonians have been implemented and demonstrated accurate.\textsuperscript{52,53} Our methodology yields comparable high accuracy to the DMRG studies, but crucially, provides a means to obtain extremely \textit{compact} forms of the many-electron wave functions, which enable immediate physical interpretation, something that is often difficult to do with other high-level \textit{ab initio} methods.

We propose a paradigm of chemically and physically motivated unitary transformations of molecular orbitals (MOs), that enables the selective targeting of energetically low-lying spin-states and the effortless optimization of their many-body wave functions, within a spin-adapted description of their wave functions. We show via theoretical and numerical arguments that the multireference character of the wave function of these systems can be greatly reduced via these unitary transformations, significantly reducing the associated computational costs. At the same time we show that these unitary transformations allow easy resolution of the manifold of low-lying excited states, even within the same spin symmetry sector, due to the resulting \textit{quasi} block-diagonal structure of the Hamiltonian matrix; thus, allowing the selective targeting of one or a few of these states.

Our paradigm represents a crucial milestone in the theoretical investigation of PNTM clusters within the first principle quantum chemical framework. The multireference nature of the electronic wave functions of these systems represents one of the greatest challenges in modern theoretical quantum chemistry, to date believed to only be solvable in a future era of quantum computing.\textsuperscript{54} We demonstrate that our paradigm challenges this assumption, offering a viable theoretical route to solve the problem on classical computers with modest computational resources. Our discovery is highly advantageous for methods that exploit the sparsity of the CI Hamiltonian matrix and its eigensolutions, such as the spin-adapted Full Configuration Interaction Quantum Monte Carlo (FCIQMC)\textsuperscript{55–57} within the Graphical Unitary Group Approach (GUGA)\textsuperscript{66–71}, used in this work. This paradigm provides a direct understanding of the fundamental mechanisms that govern the electron interactions and are responsible for the electronic structure of PNTM clusters.

The theoretical arguments are supported by computations on the six lowest singlet spin states of two [Fe(III)$_4$S$_4$(SCH$_3$)$_4$] cubanes in their highest oxidized form, Fe$_4$(III) and with thiolate terminal ligands, an exotic form that has been synthesized only very recently.\textsuperscript{15} We unambiguously show a hidden internal magnetic order for the low-energy singlet states of these compounds; namely, well-defined spin structures are formed within pairs of magnetic sites for all their low-energy singlet states.

We also show, for the first time via \textit{ab initio} computations, that these compounds can be mapped to the Heisenberg–Dirac–van Vleck Hamiltonian\textsuperscript{72} with two anti-ferromagnetic coupling constants, in good agreement with the experimentally determined ones,\textsuperscript{18} and that the observed spin structures and geometrical distortions are ways to release spin frustration, a phenomenon known as \textit{spin-driven Jahn–Teller distortion}\textsuperscript{73}.

\section{II. THEORETICAL ARGUMENTS}

\subsection{A. Spin-exchange coupled systems}

The low- and intermediate-spin wave functions of PNTM clusters, with multiple unpaired electrons at each site, are characterized by a very large number of similarly important electronic configurations. For MOs localized at the transition metal sites three leading classes of configurations can promptly be identified that concern the metal centers, namely effective spin-spin interactions mediated by spin-exchange, metal-to-metal charge-transfer, and excitations that violate on-site Hund’s rules (non-Hund configurations). Other important electronic configurations that contribute to the complicated electron correlation mechanisms, involve excitations from and to the bridging ligand atoms, such as ligand-to-metal charge-transfer excitations. A detailed analysis on the role of these terms within CI wave functions can be found in the literature.\textsuperscript{71,74,75}

In this work we adopt the GUGA formalism,\textsuperscript{66–71} which uses spin-adapted basis functions known as configuration state functions (CSFs), denoted here as $|\mu\rangle$. The total number of CSFs, $f(N, n, S)$, dependent on the
number of active electrons \((N)\), orbitals \((n)\), and spin \((S)\) of the wave function, combinatorially increases and is given by the Weyl-Paldus dimension formula:66

\[
f(N, n, S) = \frac{2S+1}{n+1} \binom{n+1}{\frac{N}{2}-S} \binom{n+1}{\frac{N}{2}+S}.
\]

(1)

The FCI wave function \(\Psi\) for a given \((N, n, S)\) set is written as

\[
\Psi = \sum_{\mu} c_{\mu} |\mu\rangle.
\]

(2)

The sum entails the entire Hilbert space, consisting of all possible configurations, with amplitudes \(c_{\mu}\) to be determined by solution of the Schrödinger equation \(\hat{H}\Psi = E\Psi\) via, for example, FCIQMC. Here \(\hat{H}\) is the quantum chemical Hamiltonian expressed in spin-free form:

\[
\hat{H} = \sum_{ij} t_{ij} \hat{E}_{ij} + \frac{1}{2} \sum_{ij,kl} V_{ij,kl} \hat{e}_{ij,kl},
\]

(3)

where \(t_{ij} = \langle i | \hat{h} | j \rangle\), \(V_{ij,kl} = \langle ik | r_{12}^{-1} | jl \rangle\) are the one- and two-electron integrals of the Schrödinger operator in the chosen basis of spatial orbitals, and

\[
\hat{E}_{ij} = \sum_{\sigma} a_{i\sigma}^{\dagger} a_{j\sigma}
\]

(4)

\[
\hat{e}_{ij,kl} = \hat{E}_{ij} \hat{E}_{kl} - \delta_{ik} \delta_{jl} \hat{E}_{il}
\]

(5)

are the spin-free excitation operators. The advantage of using this formulation in FCIQMC has been discussed in70,71, namely full spin symmetry is dynamically preserved in the QMC simulation, allowing to target specific spin states.

Out of this generally vast number of configurations \(f\), a smaller subset, discussed below, forms a reference space, which provide the leading coefficients in this expansion. If the reference space consists of only one configuration, the problem is said to be “single reference”, and the corresponding FCI wave function is generally fairly simple to approximate, for example, with standard perturbation theory. Multi-reference systems, with reference spaces often significantly exceeding one CSF, are much harder to handle and generally require complete-active-space (CAS)76,77 type methods, including FCIQMC and DMRG. Low-spin wave functions of non-mixed valence PNTM clusters, with many open-shell orbitals, fall into this category. In these systems, spin exchange is the most important form of electron interactions, given by terms of the form \(V_{ij,ji}\). The reference space then consist of all possible distributions of spins among the singly occupied orbitals, consistent with the total spin, \(S\), effectively defining a system of interacting spins, or short a spin system. If there are \(N_o\) open-shell orbitals, the size of this space is given by the van Vleck-Sherman formula:76

\[
g(N_o, S) = \binom{N_o}{N_o/2 - S} - \binom{N_o}{N_o/2 - S - 1}.
\]

(6)

Although much smaller than the FCI space, \(f\), the \(g\) space nevertheless grows rapidly with \(N_o\), making PNTM clusters extreme examples of multi-reference problems.
B. Genealogical branching diagrams

The spin-exchange electronic configurations of spin systems can be graphically represented via genealogical branching diagrams\(^8\) (see Figure 1). All paths below and including the blue path in Figure 1 constitute the genealogical branching diagram of a spin-exchange model of a cluster, for example the \([\text{Fe(III)}_2\text{S}_4(\text{SCH}_3)_4]\) system of Figure 2, with its twenty unpaired electrons explicitly correlated in the twenty valence \(3d\) orbitals (a \((20e,20o)\) active space), and coupled to a singlet spin state. The reference space of this wave function consists of \(g(20,0)=16796\) CSFs. This is the number of CSFs obtained from Equation 6. A much larger space, containing \(f(20,20,0) \approx 6 \times 10^9\) CSFs, is obtained when the full configuration interaction (FCI) expansion is built from the CAS(20e,20o), which also includes configurations with doubly-occupied orbitals (obtained from Equation 1). Configurations with doubly-occupied orbitals are not represented by genealogical branching diagrams.

While only spin-exchange interactions are assumed in the spin system, no assumptions on the actual nature of electron interactions are made in the FCI expansion, used in this work. Instead, as explained in the following, we apply MO transformations that quasi-block diagonalize the FCI Hamiltonian matrix within each spin sector. As a consequence the spin-system character of these systems directly emerges without any approximation, with the additional feature that the effective reference space for a given wave function is drastically reduced.

We observe a dramatic compression of the wave function – meaning far fewer CSFs populate the FCI wave functions of the targeted states – when using localized singly-occupied orbitals that are sorted by magnetic centers (ABCD in Figure 2), that is, first the five orbitals of site Fe\(_A\), followed by the five orbitals of each of the other sites, Fe\(_B\), Fe\(_C\) and Fe\(_D\). We refer to this as atom-separated ordering.\(^7\) In this ordering, CSFs corresponding to metal-to-metal charge-transfer and non-Hund configurations will either vanish because of symmetry, or contribute only marginally to the multi-configurational expansion. For systems characterized by non-covalent bondings among magnetic sites, these configurations contribute only marginally to the low-energy states of PNTM clusters. However, it is only via our paradigm that their negligible contribution is fully reflected into the multi-configurational wave functions of the low-energy spectrum of these clusters. These configurations are the ones that on-site Fe\(_A\) do not comply with local spin \(S_{\text{local}} = 5/2\) for that site. Similarly, configurations vanish that do not comply with the cumulative spin recoupling for site Fe\(_D\). These vanishingly small terms have been marked in gray in Figure 3. Thus, when the assumptions made when transforming the molecular orbitals are valid, FCI eigensolvers that can take advantage
of the sparsity will find these transformations very beneficial. In practice, the atom-separated ordering allows to easily transfer known physical concepts directly to the wave function description and consequently reduces the number of leading configurations compared to the one given by the van Vleck-Sherman formula (Equation 6). The localized and sorted magnetic orbitals define four domains in the genealogical branching diagram of Figure 3. The cumulative nature of the spin recouplings in the genealogical branching diagrams implies that orbital ordering contributes to the overall structure of the spin-adapted representation of the wave function, and ultimately to the physical interpretation of each configuration in the multi-configurational expansion. The possibility to connect physical concepts to the control of the sparsity of large multi-configurational expansions ultimately allows ab initio methods that exploit the sparsity of the CI Hamiltonian matrix and its eigensolutions, such as FCIQMC, to describe these complex electronic structure and quasi block-diagonal form of the CI matrix by MO localization and ordering in conjunction with a spin-adapted basis. Red and blue squares represent negative and positive Hamiltonian matrix elements, respectively. Non-drawn squares (white) are zeroes entries of the CI Hamiltonian matrix. On the right, the small 20 by 20 sub-block in the top-left corner (green background), corresponds to the CSFs depicted in Figure 3, while the remaining sub-blocks (bottom right) correspond to non-Hund spin-flip excitations.

C. PNTM clusters as spin-exchange systems

In their fully oxidized form, [FeIII4S4]4+ cubanes feature five unpaired valence electrons with parallel spin per iron center. Hence, considering these as spin-systems implies the coupling of four local spins \( S = 5/2 \), where non-Hund configurations are excluded. Combining two spin angular momenta with local spin \( S = 5/2 \) results in the direct product of the 6 possible intermediate spin states from \( S_{\text{interm}} = 0 \) to \( S_{\text{interm}} = 5 \):

\[
\Gamma^{(5/2)} \otimes \Gamma^{(5/2)} = \Gamma^{(5)} \oplus \Gamma^{(4)} \oplus \Gamma^{(3)} \oplus \Gamma^{(2)} \oplus \Gamma^{(1)} \oplus \Gamma^{(0)}. \tag{7}
\]

The two dimers couple further to give the complete wave function. In the following we only consider the case where the two dimers are coupled to singlet spin states for the tetramer \( S_{\text{total}} = 0 \). Spin couplings with \( S_{\text{total}} > 0 \) can be treated in a similar way. For the \( S_{\text{total}} = 0 \) case only the following direct coupleings are possible:

\[
\begin{align*}
\Gamma^{(5)} \otimes \Gamma^{(5)}, & \quad \Gamma^{(4)} \otimes \Gamma^{(4)}, & \quad \Gamma^{(3)} \otimes \Gamma^{(3)}, \\
\Gamma^{(2)} \otimes \Gamma^{(2)}, & \quad \Gamma^{(1)} \otimes \Gamma^{(1)}, & \quad \Gamma^{(0)} \otimes \Gamma^{(0)}.
\end{align*}
\]

These couplings are promptly identifiable in Figure 3. The highest blue and lowest brown paths represent the \( \Gamma^{(5)} \otimes \Gamma^{(5)} \) and \( \Gamma^{(0)} \otimes \Gamma^{(0)} \) states, respectively. The \( \Gamma^{(3)} \otimes \Gamma^{(3)} \) case is promptly described as the anti-ferromagnetic coupling of the two dimers, \( (AB) \) and \( (CD) \), with parallel spins within each dimer. In a spin-model space of only singly-occupied orbitals, the two \( \Gamma^{(5)} \otimes \Gamma^{(5)} \) and \( \Gamma^{(0)} \otimes \Gamma^{(0)} \) states are represented by a single CSF: thus, they are intrinsically single-reference (in terms of CSFs within GUGA). Of course, the expansion of the single CSF in a basis of Slater determinants leads to a multi-determinantal wave function, whose coefficients are completely determined by Clebsch-Gordan coupling terms. The single-reference nature of the wave function in CSF basis, clearly shows one of the practical advantages of working in a spin-adapted basis, in addition to the possibility to target spin-pure states. On the contrary, the four intermediate states, \( \Gamma^{(4)} \otimes \Gamma^{(4)}, \Gamma^{(3)} \otimes \Gamma^{(3)}, \Gamma^{(2)} \otimes \Gamma^{(2)}, \Gamma^{(1)} \otimes \Gamma^{(1)} \), are intrinsically multi-reference within GUGA. As an example we discuss the \( \Gamma^{(1)} \otimes \Gamma^{(1)} \) state in detail: There are five different paths to reach the intermediate spin, \( S_{\text{interm}} = 1 \) (magenta nodes, and all connecting arcs in between, in Figure 3). These five paths represent the five leading non-vanishing components in the corresponding CI expansion. Symmetrically, five paths exists for the second dimer, \( (CD) \), not drawn in Figure 3 for simplicity. Thus, the singlet spin state \( \Gamma^{(1)} \otimes \Gamma^{(1)} \) has a total of 25 leading CSFs. Similarly, the number of leading CSFs can be derived from Figure 3 for the \( \Gamma^{(4)} \otimes \Gamma^{(4)}, \Gamma^{(3)} \otimes \Gamma^{(3)}, \Gamma^{(2)} \otimes \Gamma^{(2)} \) states. States \( \Gamma^{(3)} \otimes \Gamma^{(3)} \) and \( \Gamma^{(2)} \otimes \Gamma^{(2)} \) are the most multi-reference with 100 leading CSFs dominating their spin-exchange-only wave functions.

In a system of non-interacting magnetic centers, or with perfect cubic symmetry (\( T_d \)), the six singlet states are degenerate. However, in more realistic systems, such as the \([Fe_4S_4]\) cubanes studied in this work, this degeneracy is lifted because of the lowered symmetry and

FIG. 4. Hamiltonian matrices of exclusively exchange-coupled open-shell CSFs (including non-Hund spin-flip excitations) of a (12e,12o) active space, for a \( N_4 \) model system in the same geometry as the iron atoms in Figure 2. The active space consists of the 12 2p orbitals of the nitrogens and their electrons. The Hamiltonian matrix of this simple model mimics well the one corresponding to the [Fe(III)4S4(SCH3)4] compounds, with the exception that each site features a local spin \( S = 3/2 \), and the intermediate pair states may only have spin \( S_{AB} \) ranging from 0 to 3. On the left the orbitals are ordered as \( 2p^x_A \otimes 2p^x_B \otimes 2p^y_C \otimes 2p^y_D \otimes 2p^z_A \), while on the right the localized orbitals are ordered in the atom-separated manner described in the text. There is a striking effect on the sparsity and quasi block-diagonal form of the CI matrix by MO localization and ordering in conjunction with a spin-adapted basis. Red and blue squares represent negative and positive Hamiltonian matrix elements, respectively. Non-drawn squares (white) are zeroes entries of the CI Hamiltonian matrix.
geometrical distortions of the molecule. In these cases the different paths of the genealogical branching diagrams identify the leading components of the six lowest non-degenerate singlet states. The precise quantitative splittings between these states is also affected by other forms of correlations, namely metal-to-metal and ligand-to-metal charge-transfer excitations, which are obtained by diagonalizing the CAS(2e0,20o) and CAS(44e,32o) problems respectively, and will be discussed in greater detail in the next section.

The localization of MOs and atom-separated ordering lead to more sparse and quasi-block-diagonal CI Hamiltonian matrices. For illustration purposes, we show the block-diagonal structure of the many-body Hamiltonian in Figure 4, for the exchange-only singlet configuration space of a N\textsubscript{4} model system. The block diagonal structure of the CI Hamiltonian matrix is evident. This block-diagonal structure ensures that in projective methods, such as FCIQMC, the choice of a specific CSF as the initial configuration allows us to uniquely target specific low-lying excited states within the same spin-symmetry sector. The extremely weak coupling of these initial states to the lower energy states effectively leads the projective method to converge to the lowest state matching the local spin coupling of the initial CSF, which is a particular property of the localized and ordered basis.

Thus, our proposed paradigm of MO localization and atom-separated ordering has a two-fold effect on the wave functions of spin-exchange coupled systems: (a) It provides a simple tool to compress the CI expansion of ground- and excited-states wave functions, greatly decreasing the number of leading configurations and thus computational costs. (b) It opens the route for inexpensive state-specific wave functions optimizations, thus giving us the possibility to study the electronic structure of the manifold of low-lying excited states of PNTM clusters.

### III. NUMERICAL ARGUMENTS

In this section numerical evidence will be given of the compression and resolution of states, by considering the six low-energy singlet spin states of two [Fe(III)\textsubscript{4}]S\textsubscript{4}(SCH\textsubscript{3})\textsubscript{4} model systems. One cubane is characterized by two long and four short Fe–Fe bonds, (1), the other is characterized by two short and four long Fe–Fe bonds, (2), as experimentally reported by Ibers and co-workers\textsuperscript{41} and Kazuyuki and co-workers\textsuperscript{42}, respectively. As will be evident from the discussion below, the choice of these two systems stems from their complementary geometrical distortions, which can be described as elongation and compression, for (1) and (2) respectively, along one of the S\textsubscript{4} axis of the D\textsubscript{4h} point group, which these structures belong to. From this deformation two (or four) long and four (or two) short Fe–Fe bonds are obtained for (1) (or (2)). Two CAS will be considered, the CAS(20e,20o) containing only the dominantly singly-occupied 3d orbitals of the four iron centers, and the larger CAS(44e,32o) where the additional 12 doubly-occupied 3p orbitals of the bridging S atoms are also correlated. The latter active space choice shows that the wave function compression and resolution of states are retained even when the FCI wave functions include forms of electron correlation (ligand-to-metal charge-transfer, superexchange) that go beyond the spin-exchange interactions already captured by the smaller CAS(20e,20o).

#### A. Resolution of the singlet states of compound (1)

**CAS(20e,20o) wave functions.** The CAS(20e,20o) spin-adapted FCIQMC trajectories for the six low-energy singlet spin states of (1) are reported in Figure 5, and the corresponding energy splittings are summarized in Table 1. FCIQMC solves the imaginary-time Schrödinger equation by stochastically sampling the ground- or excited-state wave function by a set of so-called walkers. The number of walkers, N\textsubscript{w}, is a critical input parameter, that determines the accuracy and the computational costs of a calculation. The trajectories are found to be rapidly convergent in imaginary-time and extremely stable, with stochastic fluctuations well below the energy separation among the states. Both aspects point to the fact that the wave functions are very compact with this choice of orbitals in the spin-adapted representation. Only 1 × 10\textsuperscript{6} walkers have been utilized for these dynamics, a tiny number in comparison to the (20e,20o) Hilbert space, and yet achieve high accuracy. Increasing the population to 1 × 10\textsuperscript{7} walkers has negligible effects on the lowest-to-highest spin gap. For comparison, in our experience for similar systems treated with a less optimal orbital choice, a much larger number of walkers (in the
From which the propagation of walkers is started. The FCIQMC dynamics, only criterion utilized to separate the states is the CSF bitals are localized and sorted by magnetic centers. The quasi block-diagonal structure of the Hamiltonian it is possible to target the lowest and the highest of the six singlet states directly, opposed to conventional procedures where all states in between must be optimized, with associated considerable computational costs. This feature has been used here for the CAS(44e,32o) calculations. The CAS(44e,32o) spin-state splittings for compound (2) are in preparation.

Table I. Energies [meV] of the lowest six singlet states and the $S = 10$ state for (1) and (2), relative to the corresponding ground states, as obtained from the ab initio calculations and the model Hamiltonian (Equation 8) using the extracted parameters from Table III. The states are labeled as $|(S_{AB}, S_{CD}, S_{tot}, S_{Fe})\rangle$, as explained in the main text. It is important to note that due to the quasi block-diagonal structure of the Hamiltonian it is possible to target the lowest and the highest of the six singlet states directly, opposed to conventional procedures where all states in between must be optimized, with associated considerable computational costs. This feature has been used here for the CAS(44e,32o) calculations. The CAS(44e,32o) spin-state splittings for compound (2) are in preparation.

| State   | CAS(20e,20o)  | $\hat{H}_{mod}$ | CAS(44e,32o)  | $\hat{H}_{mod}$ | CAS(20e,20o)  | $\hat{H}_{mod}$ |
|---------|---------------|-----------------|---------------|-----------------|---------------|-----------------|
| (5, 5), 0, 0 | 0.0           | 0.0             | 0.0           | 0.0             | 65.0          | 65.0            |
| (4, 4), 0, 0 | 27.8          | 29.2            | —             | 50.2            | 41.6          | 43.4            |
| (3, 3), 0, 0 | 51.8          | 52.6            | —             | 90.3            | 24.7          | 26.0            |
| (2, 2), 0, 0 | 70.1          | 70.1            | —             | 120.5           | 12.2          | 13.0            |
| (1, 1), 0, 0 | 82.9          | 81.8            | —             | 140.5           | 4.7           | 4.3             |
| (0, 0), 0, 0 | 87.6          | 87.6            | 150.6         | 150.6           | 0.0           | 0.0             |
| (5, 5), 10, 0 | 378.5         | 378.5           | 615.8         | 615.8           | 347.7         | 347.7           |

range of billions) is needed to achieve a similar energy resolution.\(^{71}\)

The lowest ($S_{intert} = 5$) and highest ($S_{intert} = 0$) states show the most stable dynamics, with their wave functions being dominated by the single CSFs drawn as the blue and brown paths in Figure 3, respectively, with a reference weight of 96% in both cases. In practice, this implies a striking operation count reduction by five orders of magnitude, from 16796 similarly important CSFs to a single dominating CSF. The four intermediate states, especially the ones with $S_{intert} = 3$ and $S_{intert} = 2$, show more stochastic noise, yet negligible, to be attributed to the inherently multi-reference nature of their wave functions. The gap between the lowest and the highest of the six singlet states, within the (20e,20o) active space is only 88 meV, and demonstrate the level of resolution that can be obtained by MO transformations and methods that can screen out "deadwood" configurations.

The FCIQMC trajectories of Figure 5 are well separated even though no orthogonalization procedure has been enforced, indicating the quasi block-diagonal structure of the Hamiltonian, that follows when molecular orbitals are localized and sorted by magnetic centers. The only criterion utilized to separate the states is the CSF chosen as an initial state for the FCIQMC dynamics, from which the propagation of walkers is started.

At the same level of theory the highest spin state, $S = 10$, is 378.5 meV above the ground state (Table I), thus suggesting that these systems are anti-ferromagnets, as already shown in Reference 15, and further discussed in Section III C of this work.

The ordering of the six singlet states and the highest $S = 10$ state can be understood by considering the geometrical distortions of the system. In (1) two long Fe–Fe bonds exist. In the ground state singlet, spins along these bonds are parallel aligned to allow an energetically favor-
TABLE II. $\langle \hat{S}_A^2 \rangle$, $\langle (\hat{S}_A + \hat{S}_B)^2 \rangle$ and $\langle (\hat{S}_A + \hat{S}_B + \hat{S}_C)^2 \rangle$ expectation values for the CAS(20e,20o) wave functions of the six singlet spin states of (1). In parenthesis the corresponding values from the CAS(44e,32o).

| State ($S_{\text{interm}}$) | $\langle \hat{S}_A^2 \rangle$ | $\langle (\hat{S}_A + \hat{S}_B)^2 \rangle$ | $\langle (\hat{S}_A + \hat{S}_B + \hat{S}_C)^2 \rangle$ |
|----------------------|-----------------|-----------------|-----------------|
| 5                    | 8.69 (8.34)     | 29.77 (28.52)   | 8.69 (8.36)     |
| 4                    | 8.69            | 19.84           | 8.69            |
| 3                    | 8.67            | 11.88           | 8.67            |
| 2                    | 8.68            | 5.95            | 8.65            |
| 1                    | 8.69            | 1.99            | 8.69            |
| 0                    | 8.69 (7.81)     | 0.02 (0.05)     | 8.69 (7.82)     |

The role of charge-transfer excitations has also been quantified by computing the eigenvalues of the $\hat{S}_A^2$, $(\hat{S}_A + \hat{S}_B)^2$ and $(\hat{S}_A + \hat{S}_B + \hat{S}_C)^2$ spin operators (see Table II). The CAS(20e,20o) $\hat{S}_A^2$, $(\hat{S}_A + \hat{S}_B)^2$ and $(\hat{S}_A + \hat{S}_B + \hat{S}_C)^2$ eigenvalues closely follow the formal $S_{\text{local}}(S_{\text{local}}+1)$ values to be expected from the coupling of four $S_{\text{local}} = 5/2$ spins, in line with the description of this system as a spin system. The small deviations are to be attributed to metal-to-metal charge-transfer excitations. On the contrary, the CAS(44e,32o) wave functions show substantial deviations from the formal values both for the ground and the highest singlet states. The observed reduction of these quantities is related to effective charge-transfer excitations, from the bridging sulfur atoms to the metal centers, a form of correlation that can only be captured explicitly by the larger active space. For the CAS(44e,32o) highest singlet state ($S_{\text{interm}} = 0$), the $\langle (\hat{S}_A + \hat{S}_B)^2 \rangle$ expectation value is in practice unchanged when compared to the smaller CAS(20e,20o) wave function. This is to be expected, considering that charge-transfer excitations happen symmetrically for site $A$ and $B$, leading to the symmetric reduction of local spin of anti-ferromagnetically aligned centers. Upon enlarging the active space, from (20e,20o) to (44e,32o), we find a larger reduction in the $\langle \hat{S}_A^2 \rangle$ and $\langle (\hat{S}_A + \hat{S}_B + \hat{S}_C)^2 \rangle$ for the $S_{\text{interm}} = 0$ state as compared to the ground $S_{\text{interm}} = 5$ state. $\langle \hat{S}_A^2 \rangle$ reduces from a value of 8.69 to 7.81 for $S_{\text{interm}} = 0$, while from 8.69 to 8.34 for $S_{\text{interm}} = 5$. This aspect indicates that ligand mediated charge-transfer effects are different for the lowest and highest singlet states, and that electron interactions in these system may be more complex than predicted by a simple spin model.

The enlarged CAS(44e,32o) lowest-to-highest singlet spin gap is a clear indication of a differential role of the ligand-mediated charge-transfer excitations in the relative stabilization of the two singlet states. In the ground state the ligand-to-metal charge-transfer excitations enhance the anti-ferromagnetic exchange interactions along the short bonds. On the contrary, in the highest singlet state the same excitations only enhance the exchange along the long bonds. The latter enhancement is weaker, therefore leading to an overall relative stabilization of the ground state.

B. Resolution of the singlet states of compound (2)

The six low-energy singlet states of (2) present inverted relative order as compared to the same states for (1) (see Table I). The ground state of (2) is characterized by anti-ferromagnetic alignment within each of the two short-bonded pairs, while the highest singlet state shows ferromagnetic alignment within each pair of short-bonded iron centers and anti-ferromagnetic alignment across the pairs. At the CAS(20,20) level of theory, the highest spin state, $S = 10$, of (2) is 347.7 meV above the ground state.

As for compound (1), the relative stability of the spin states of (2) is promptly explained by considering the geometrical distortions of the system and anti-ferromagnetic interactions among spins of neighboring sites. In the ground state of (2) two short and four long Fe–Fe bonds exist, and an anti-ferromagnetic alignment of spins is observed only within the short bonds, with spins along the long bonds left uncoupled. This effect can be interpreted as a way to lift spin frustration, and can be linked to a spin-driven Jahn-Teller distortion, which we will discuss in greater details below.

C. Exchange interactions via model Hamiltonian

In order to support and rationalize the ab initio results we utilize the isotropic Heisenberg–Dirac–van Vleck
model Hamiltonian with nearest-neighbor interactions\textsuperscript{72}

\[
\hat{H}_{\text{mod}} = J_{2B} (\vec{S}_A \cdot \vec{S}_B + \vec{S}_C \cdot \vec{S}_D) + J_{1B} (\vec{S}_A \cdot \vec{S}_D + \vec{S}_B \cdot \vec{S}_C + \vec{S}_A \cdot \vec{S}_C + \vec{S}_B \cdot \vec{S}_D),
\]

where \(J_{2B}\) and \(J_{1B}\) are two non-equivalent coupling constants, following the geometric distortions of the Fe\(_3\)S\(_4\) systems (Figure 2). \(\vec{S}_i\) (with \(i = A, B, C\) and D) are local spin 5/2 operators. This model Hamiltonian has also been chosen in Reference 15. For (1) \(J_{2B}\) and \(J_{1B}\) refer to the two long and the four short bond interactions, respectively. For (2) the two coupling constants refer to the two short and the four long bonds, respectively. The matrix elements of the Hamiltonian (Equation 8) can be computed in the uncoupled basis defined by local spin projections, \(|S_A S_B S_C S_D\rangle\), using the ladder-operator expansion for each \(S_i\). The corresponding Hilbert space consists of 1296 states. A unitary transformation, \(U\), to the total-spin-adapted coupled basis can be constructed using the relevant Clebsch-Gordan coefficients \(\langle j_1 m_1 j_2 m_2 | j m \rangle\). Its elements are given by

\[
(S_A S_B S_C S_D) U |(S_A S_B S_C) S_{c\text{tot}} S_{g\text{tot}}\rangle = \sum_{S_{AB} S_{AB} S_{CD} S_{CD}} \langle S_A S_B | S_{CD} S_{CD} \rangle \langle S_A S_B S_{AB} S_{AB} \rangle \langle S_{CD} S_{CD} S_{CD} S_{CD} \rangle \langle S_{CD} S_{CD} | S_{CD} S_{CD} \rangle,
\]

which \(S_{AB}\) and \(S_{CD}\) refer to spin operators over the \(AB\) and \(CD\) pairs of iron centers, and \(S_{c\text{tot}}\) and \(S_{g\text{tot}}\) the target total spin, in this case \(S_{c\text{tot}} = 0\), and its projection (indicated by the \(z\) superscript). The choice of the spin coupling scheme is important, because \(\hat{H}_{\text{mod}}\) takes a diagonal form in the \(|S_{C} S_{D} S_{CD} S_{CD}\rangle\) basis, while it only has a block-diagonal structure if other spin coupling schemes are used, such as \(|S_{A} S_{B} S_{C} S_{D}\rangle S_{c\text{tot}} S_{g\text{tot}}\rangle\) or \(|S_{A} S_{B} S_{A} S_{B}\rangle S_{c\text{tot}} S_{g\text{tot}}\rangle\). We want to emphasize that the diagonal structure in the coupled basis is a consequence of the symmetry of the system. The corresponding configurations dominate the low-energy eigenstates both of the model and the \textit{ab initio} Hamiltonian as discussed in the previous sections.

An analytical expression for the eigenvalues of the model Hamiltonian (Equation 8) was obtained by Griffith\textsuperscript{82}

\[
E(S_{AB}, S_{CD}, S_{\text{c\text{tot}}}) = 1/2 J_{2B} [S_{\text{c\text{tot}}} (S_{\text{c\text{tot}}} + 1) - S_{AB} (S_{AB} + 1) - S_{CD} (S_{CD} + 1)] + 1/2 J_{1B} [S_{AB} (S_{AB} + 1) - S_A (S_A + 1) - S_B (S_B + 1) + S_{CD} (S_{CD} + 1) - S_C (S_C + 1) - S_D (S_D + 1)],
\]

where the \(S_i\) on each metal site are kept to the constant value of 5/2 for the Fe(III) case. The energies of the six possible states of the \(S_{\text{c\text{tot}}} = 0\) spin sector, parameterized in the exchange coupling constants, are

| Compound (1) | Compound (2) |
|--------------|--------------|
| \(J_{4B}\) | 55.5 | 90.3 | 41.5 | 70 |
| \(J_{2B}\) | 32.0 | 49.8 | 58.9 | 82 |
| \(J_{4B} - J_{2B}\) | 23.5 | 40.5 | -17.5 | -12 |

\((J_{4B} - J_{2B}) \times \{0, 10, 18, 24, 28, 30\}\), for the states with intermediate spins \(S_{AB} = S_{CD} = \{3, 4, 5, 6\}\), relative to the \((5, 5, 0, 0)\) state. The splittings within each \(S_{\text{c\text{tot}}}\) manifold are completely defined by the difference of the exchange parameters, \((J_{4B} - J_{2B})\), whilst the high-spin \(S_{\text{c\text{tot}}} = 10\) \((5, 5, 0, 0)\) state is 55\(J_{4B}\) above the singlet \((5, 5, 0, 0)\) state.

We can evaluate the exchange parameters by mapping the model eigenvalues to the corresponding \textit{ab initio} excitation energies. Using the three \((5, 5, 0, 0)\), \((0, 0, 0, 0)\) and \((5, 5, 10, 0)\) states, the exchange parameters of Table III are obtained. The energy splittings of the six low-energy singlet states, obtained from the parameterized model are reported in Table I.

For (1) and (2), both coupling parameters are antiferromagnetic, demonstrating the intrinsic frustration in these systems. In compound (1) the larger \(J_{2B}\) interaction forces spins along the longer bonds to be ferromagnetically aligned (Figure 6). The elongation of the Fe\(_A\)–Fe\(_B\) and Fe\(_C\)–Fe\(_D\) bonds is a direct consequence of the unfavorable interaction of the frustrated spins. For (2) \((J_{4B} - J_{2B}) < 0\) confirming the inverted relative ordering of the six states. The agreement between the \textit{ab initio} and the model Hamiltonian results is exceptionally good, despite the simplicity of the latter. Moreover, the model Hamiltonian provides an estimate for states that are harder to obtain within the \textit{ab initio} framework.

The slight deviations between the model and \textit{ab initio} Hamiltonian (\(\approx 2\text{meV}\)) may be attributed to the absence of higher-order couplings in the model Hamiltonian, such as the biquadratic and ring exchange. Nevertheless, taking them into account would lead only to marginal changes in the extracted parameters. Similarly, further improvements on the \textit{ab initio} side, such as taking into account orbital relaxation and dynamical correlation effects may lead to quantitative changes in the energy splittings of the singlet states.

The coupling constants extracted from the CAS(44e,32o) \textit{ab initio} calculations are larger compared to the ones obtained from the CAS(20e,20o). However, as shown in Table III the increase is different for the two coupling constants, indicating that the ligand-to-metal charge-transfer excitations (explicitly included in the larger active space) have a differential
enhancing effect on the superexchange mechanism for the long and short bonds.

The agreement between the coupling constants extracted from our computations and the experimental ones for (2) are genuinely good, despite the computational simplicity of the former.

The observation that the \( J_{1B} = J_{2B} \) model, which corresponds to a model with perfect tetrahedral symmetry, gives rise to a six-fold degenerate singlet states has interesting consequences. Griffith\(^{32}\) has shown that in the case of \( S = 5/2 \) Heisenberg model, the six singlet states span \( A_1 + A_2 + 2E \) irreducible representations. The presence of states with \( E \) symmetry implies the possibility of a spin-driven Jahn-Teller distortion, where the degeneracy is lifted by distortions of \( E \) symmetry, contained by the symmetric square \((E \otimes E)_+ = A_1 \oplus E\). Similar considerations will apply to the higher spin states as well, where degeneracies of other types \((T_1 \text{ and } T_2)\) occur, and which may be lifted by distortions of \( T_2 \) symmetry. Thus vibronic effects on the spectra of such cubanes may be understood and predicted as the interplay between spin-frustration and Jahn-Teller distortions, a point we return to in a separate publication. Interestingly, these distortions already exist in homovalence all-ferric \([\text{Fe(III)}_4S_4(SCH}_3)_4]\) clusters, and are not to be related specifically to the mixed-valence species.

### IV. CONCLUSIONS

We propose a paradigm consisting of simple and physically motivated MO transformations (localization and reordering) that, in realistic spin-exchange coupled PNTM clusters, lead to FCI molecular Hamiltonian matrices within the GUGA formalism with an extraordinary quasi block diagonal structure. The spin-system nature of these systems directly emerges from this structure of the Hamiltonian, without any simplifying approximation. A large compression of the multi-configurational wave functions results, which can be understood via simple genealogical branching diagrams. Moreover, the quasi block diagonal structure of the Hamiltonian opens the route to direct state-specific wave function optimizations of ground and excited states, thereby removing the often undesired overhead of computing all intermediate states. Methods such as FCIQMC greatly benefit from these features, enabling accurate calculation of the wave functions with modest computational effort.

This paradigm allows us to unravel the complicated electronic correlations in PNTM clusters, and to provide straightforward physical interpretations of the magnetic interactions within. This is demonstrated in the case of two fully oxidized \([\text{Fe(III)}_4S_4(SCH}_3)_4]\) clusters, by investigating the magnetic interactions in their six energetically low-lying singlet states. Highly compressed, or even single-reference wave functions are obtained, that allow a simple physical interpretation of the magnetic interactions characterizing these systems. Our results show that a hidden magnetic order exists in this manifold of states, namely, that well-defined spin structures are formed within two pairs of magnetic centers.

More generally, this methodology can be applied to a wide range of PNTM clusters, including \([\text{MnO}]\) and \([\text{CoO}]\) cubanes, to partially reduced systems, and different spin states, and will be of great value in uncovering the chemical activity of these systems in electron transport, oxygen evolution, and potentially other spin-forbidden reactions.

### CONFLICTS OF INTEREST

There are no conflicts of interest to declare.

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### ADDITIONAL INFORMATION

Supplementary information is available in the online version of the paper.

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