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Exchange Coupling Interactions from the Density
Matrix Renormalization Group and N -Electron Valence
Perturbation Theory: Application to a Biomimetic
Mixed Valence Manganese Complex

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ABSTRACT

The accurate description of magnetic level energetics in oligonuclear exchange-coupled transition metal complexes remains a formidable challenge for quantum chemistry. The density matrix renormalization group (DMRG) brings such systems for the first time easily within reach of multireference wave function methods by enabling the use of unprecedentedly large active spaces. But does this guarantee systematic improvement in predictive ability, and if so, under which conditions? We identify operational parameters in the use of DMRG using as a test system an experimentally characterized mixed valence bis- μ -oxo/ μ -acetato Mn(III,IV) dimer, a model for the oxygen-evolving complex of photosystem II. A complete active space of all metal 3d and bridge 2p orbitals proved to be the smallest meaningful starting point; this is readily accessible with DMRG and greatly improves on the unrealistic metal-only configuration interaction or complete active space self-consistent field (CASSCF) values. Orbital optimization is critical for stabilizing the antiferromagnetic state, while a state-averaged approach over all spin states involved is required to avoid artificial deviations from isotropic behavior that are associated with state-specific calculations. Selective inclusion of localized orbital subspaces enables probing the relative contributions of different ligands and distinct superexchange pathways. Overall, however, full-valence DMRG-CASSCF calculations fall short from providing a quantitative description of the exchange coupling owing to insufficient recovery of dynamic correlation. Quantitatively accurate results can be achieved through a DMRG implementation of second order N -electron valence perturbation theory (NEVPT2) in conjunction with a full-valence metal and ligand active space. Perspectives for future applications of DMRG-CASSCF/NEVPT2 to exchange coupling in oligonuclear clusters are discussed.

1. INTRODUCTION

Cluster complexes containing multiple magnetically coupled transition metal ions have received intense and sustained attention from experiment and theory alike.¹⁻⁵ For example, oligonuclear systems of magnetically interacting manganese ions feature prominently in fields as diverse as single-molecule magnetism⁶⁻⁹ and photosynthetic water oxidation.¹⁰⁻¹⁶ First-principles computational description of low-lying spin states in exchange-coupled transition metal systems has been so far dominated by density functional theory with the broken-symmetry approach (BS-DFT).^{3, 17-30} The broken-symmetry solutions are not spin eigenstates and cannot be used directly for any comparisons with experiment, but the BS-DFT energies can be used to extract pairwise exchange coupling constants J_{ij} to be substituted into an appropriate phenomenological Heisenberg–Dirac–van Vleck Hamiltonian (Eq. 1).³⁰⁻³²

$$\hat{H}_{\text{HDvV}} = -2 \sum_{i < j} J_{ij} \hat{S}_i \hat{S}_j \quad (1)$$

The exchange coupling constants J_{ij} parameterize the fictitious interactions between the different spin sites and hence determine the relative spin state energies of the coupled system. Appropriate spin projection techniques may enable the use of a specific BS-DFT solution for predicting various spin-dependent spectroscopic observables of the real system.³³

Although its practical utility is undeniable, the standard BS-DFT approach has weaknesses and shortcomings that relate to the formally deficient treatment of an intrinsically multireference problem, the dependence on the nature of the chemical system, and the sensitivity to the choice of density functional.^{27, 34-37} Other DFT-based approaches are being actively pursued.^{29, 38-44} Wave function based methods have been successfully employed only for a comparatively limited number of simple systems with few unpaired electrons. The use of multireference methods that address the static correlation problem,⁴⁵ such as the complete active space self-consistent field (CASSCF), to directly obtain the energies of spin levels in magnetically coupled systems would be the most desirable foundation for

tackling such problems, but their application is severely restricted by their computational cost. Methods that account for dynamic correlation on top of a minimal active space have been explored. Among them, difference dedicated configuration interaction (DDCI) has been shown to offer an elegant and systematic way towards accurate results,⁴⁶⁻⁵⁰ but the applicability of such methods is still strictly constrained by their explosive cost with increasing number of unpaired electrons and the fact that high-order excitations are indispensable in magnetic coupling problems.⁵¹⁻⁵²

The obstacle to the use of sufficiently extended active spaces can potentially be lifted with the density matrix renormalization group (DMRG).⁵³⁻⁵⁶ In the context of quantum chemistry, DMRG has emerged as a powerful algorithm that enables multireference calculations with significantly larger active spaces than ever before.⁵⁷⁻⁶¹ This is achieved by representing the wave function as a tensor network and constructing it from matrix products so that efficient mathematical formalisms can be exploited resulting in polynomial rather than exponential algorithmic scaling. The applicability of DMRG to transition metal chemistry has been explored in a number of recent studies.⁶²⁻⁶⁸ A few reports have described DMRG-based calculations on transition metal clusters containing up to four open-shell (Mn or Fe) ions,⁶⁹⁻⁷⁰ however without explicitly addressing the problem of exchange coupling. Pilot studies of binuclear and tetranuclear iron-sulfur model clusters⁷¹ as well as of two simple quasi-linear Fe and Cr dimers with a single oxo bridge⁷² showcased the feasibility of DMRG calculations for this problem, but the results highlighted uncertainties with respect to methodological requirements and the role of dynamic correlation. The performance of the approach and the necessary conditions for its successful application remain poorly defined.

In the present work we investigate how DMRG can be used to obtain exchange coupling constants in combination with complete active space configuration interaction (CASCI) and CASSCF approaches on large active spaces. We use an experimentally characterized manganese complex of known structure and

magnetic properties, an antiferromagnetically coupled mixed-valence bis- μ -oxo/ μ -acetato Mn(III,IV) dimer.⁷³ Magnetic properties of cluster complexes with magnetically interacting Mn ions bridged by multiple oxo and carboxylato bridges have long been studied,^{5, 14, 74-83} owing to their direct relevance to single molecule magnets and the water-oxidizing Mn₄CaO₅ cluster of biological photosynthesis, so the present complex can be considered an archetypal model for a wide variety of larger systems. We establish the dependence of exchange coupling on active space composition, orbital optimization, and number of renormalized states, determining the requirements for successful application of the method. DMRG allows us not only to simply include the orbitals of all bridging ligands in the active space, but also to selectively turn specific (super)exchange pathways on and off by choosing specific ligand-localized orbital subspaces. We demonstrate that this approach can be used to assess the role of each bridge in determining the sign and magnitude of the exchange coupling. Additionally, we evaluate the application of N -electron valence perturbation theory (NEVPT2)⁸⁴⁻⁸⁵ coupled to large active space DMRG as a way to converge towards reliable recovery of dynamic correlation in the description of exchange coupling.

2. MODELS AND METHODS

2.1. Reference Model. Complex **1** (Figure 1) was reported by Wieghardt and coworkers.⁷³ It is a mixed valence bis- μ -oxo/ μ -acetato Mn(III,IV) dimer with 1,4,7-trimethyl-1,4,7-triazacyclononane and acetates as terminal ligands. The metal oxidation states, bridging patterns, ligand types, and coordination geometries are relevant to manganese-based single-molecule magnets, but they also mimic those that occur in the OEC of photosystem II.^{9-10, 86} Specifically, the Mn₄CaO₅ cluster of the enzyme is known to cycle from Mn(III)₃Mn(IV) in the lowest oxidized state (S₀) up to an all-Mn(IV) form in the S₃ state that precedes the final, as yet unobserved, O₂-evolving transient state (S₄).⁸⁷⁻⁹² Mirroring the situation in the OEC, the Mn(III) ion of complex **1** features a strong axial pseudo-Jahn–Teller elongation that leads to an approximately square-pyramidal coordination geometry, precisely like the Mn(III) ions in the S₁ and S₂ states of the OEC.⁹³⁻⁹⁵ The Mn ions in the OEC are similarly bridged by oxo and carboxylato bridges, while the ancillary ligands on the Mn(III) center of **1** also mimic the first coordination sphere of the OEC, which is rich in Glu and Asp residues.⁹⁵⁻⁹⁷

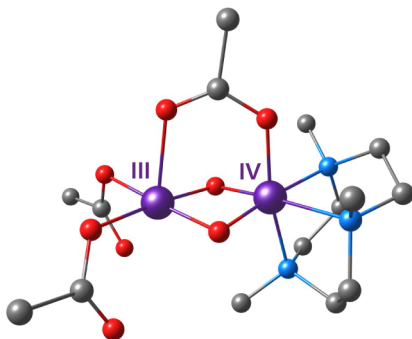


Figure 1. Structure of complex **1**. Mn purple, O red, N blue, C grey. Hydrogen atoms are omitted for clarity.

This is a rare example of a Mn dimer with crystallographically well-defined valence localization and Jahn–Teller distortion thanks to the asymmetric ligand environment of the two metal ions. Therefore, the crystallographic model (CSD access code KUVPEW) was employed directly after optimizing the hydrogen positions. Since **1** is neutral, there is no need to account for counterion effects. Additionally,

avoiding a charged system in the present case helps eliminate theoretical and computational complications that may manifest as convergence failures or negative ionization energies for anions. Magnetic susceptibility measurements showed that complex **1** is antiferromagnetically coupled and shows Heisenberg behavior with an exchange coupling constant $J = -90.0 \text{ cm}^{-1}$ (according to the Hamiltonian convention shown in Eq. 1).

2.2. Computational Details. All DFT and the majority of multireference (CASCI, CASSCF, and NEVPT2) calculations were performed with the ORCA program package⁹⁸ interfaced with the BLOCK code^{55, 99-102} of Chan and coworkers for DMRG. In the case of DMRG-NEVPT2 calculations with an active space of 19 electrons in 16 orbitals we used the MOLBLOCK code developed by one of us (M. R.) that is also interfaced with the BLOCK code. DFT calculations used the TPSS functional¹⁰³ with D3BJ corrections¹⁰⁴⁻¹⁰⁵ for geometry optimizations and the TPSSh,¹⁰⁶ BP86¹⁰⁷⁻¹⁰⁸ and M06-2X¹⁰⁹ density functionals for calculation of exchange coupling constants, with tight convergence criteria and extra fine integration grids (Grid6 and GridX8), setting the overall radial integration accuracy to 6.0 in ORCA nomenclature. The zeroth order scalar relativistic approximation (ZORA)¹¹⁰⁻¹¹⁴ was used in all calculations, in combination with the ZORA-adapted¹¹⁵ and partially decontracted polarized triple-zeta def2-TZVP and doubly polarized quadruple-zeta def2-QZVPP basis sets,¹¹⁶ and appropriate versions of corresponding auxiliary basis sets by Weigend¹¹⁷ and Hättig.¹¹⁸ Starting orbitals for DMRG calculations were obtained from Pipek–Mezey localization¹¹⁹ of canonical or quasi-restricted¹²⁰ DFT orbitals. Automatic ordering of orbitals was performed with the Fiedler vector algorithm.¹²¹⁻¹²⁴ In the following we use the common nomenclature ($N_{\text{el}}, N_{\text{orb}}$) to denote the number of active space electrons and orbitals.

Since the optimal selection of the various methodological parameters that enter a DMRG calculation is one of the targeted outcomes of the present work, most of these details will be presented and discussed as needed in the following. The distinct difference in applications of DMRG to magnetic

coupling compared with many other situations in chemistry is that the target energy differences need to be determined with a precision on the order of a few wavenumbers (cm^{-1}). Most relevant for the convergence of the energy of any DMRG calculation is the number of states M retained during the renormalization step and the associated discarded weight. The latter corresponds to the difference between the trace of the active space density obtained from the renormalized wave function and an ideal value of 1. A commonly chosen approach to approximate the true full-CI energies from DMRG calculations is to perform a number of calculations with a varying number of retained states and then extrapolate to zero discarded weight. However, in the current investigation of magnetic couplings such a procedure is not viable since the obtained discarded weights (and their differences) are negligible (on the order of 10^{-15}) for all reported calculations and no systematic correlation between the energy convergence in the wavenumber regime and the largest discarded weight could be observed. Therefore the number of retained states was increased until convergence of the magnetic coupling constants on the order of 1 cm^{-1} was achieved.

For some active spaces the calculated DMRG energies were refined by taking into account dynamic electron correlation within the framework of second order N -electron valence perturbation theory (NEVPT2).⁸⁴⁻⁸⁵ This widely used approach describes the influence of the first order interacting space¹²⁵ on the DMRG-CASSCF or DMRG-CASCI energy (and wave function) by means of second order perturbation theory. More precisely, we have used the strongly contracted variant of NEVPT2 as implemented for DMRG by Chan and coworkers.¹²⁶ As suggested previously the required active space reduced density matrices were generated using a compressed number of renormalized states.¹²⁶ This was achieved by carrying out a “reverse scheduled” set of sweeps, where the number of renormalized states is first increased to a maximum value of $M = 2000$ before it is reduced to a final value of M' .¹²⁷ A key ingredient of strongly contracted NEVPT2 is the orbital energies that enter the expressions for the

perturbed energy and wave function. In calculating multiple states with the largest active spaces reported in this work state-averaged orbitals were employed in NEVPT2 unless stated otherwise. Avoiding recanonicalization of the state-averaged CASSCF orbitals leads to practically identical results as the use of state-adapted orbitals in the present NEVPT2 calculations, because the states of different multiplicity arise from the same configuration. Note that although in the majority of the presented DMRG-CASSCF calculations the molecular orbitals are optimized in a state-averaged fashion, separate DMRG calculations were performed for each spin state.

3. RESULTS AND DISCUSSION

3.1. Exchange Coupling Constants from DFT. To have a measure of comparison of the DMRG values discussed in the following, we first describe some fundamental concepts and show what can be obtained with straightforward broken-symmetry DFT calculations. The two metal centers in complex **1** have local spins $S_A = 3/2$ and $S_B = 2$, for the d^3 and d^4 ions Mn(IV) and Mn(III). Coupling of the two spins yields total spin states $S = S_A + S_B, S_A + S_B - 1, \dots, |S_A - S_B|$ and hence the Heisenberg spin ladder for the dimer is composed of the spin states $S = 1/2, 3/2, 5/2,$ and $7/2$.¹²⁸⁻¹²⁹ If Eq. 1 applies then the energies follow a regular spacing provided by Eq. 2:

$$E(S) = -J[(S(S+1) - S_A(S_A+1) - S_B(S_B+1))] \quad (2)$$

and the sign of J determines whether $S = 1/2$ or $S = 7/2$ is the ground state. Thus, in the ideal isotropic case, the energy spacings between the four spin states for the present dimer are equal to $3J, 5J$ and $7J$, from lowest to highest spin.¹²⁸⁻¹²⁹ Multireference methods enable direct access to all these possible spin states. If these indeed conform to the Landé pattern of Eq. 2, then J can be determined by any energy difference between pairs of spin states. Alternatively, by solving Eq. 2 for J , a fitted exchange coupling constant can be obtained from the slope of a linear regression between $E(S)$ and $S(S+1)$. Departures from

isotropic behavior, for example due to double exchange, can also be determined by analyzing the complete energy spectrum obtained directly from multireference calculations.^{71, 130}

On the other hand, the DFT-based approach to exchange coupling relies on calculation of the high-spin $S = 7/2$ state (note that no other spin state of the ladder can be approximated by a single determinant) and of a broken-symmetry solution with $M_S = 1/2$, obtained by “flipping” the spin of one ion while maintaining the local high-spin configurations.^{3, 17-19, 25, 27, 32, 131-133} No other solution relevant to the magnetic coupling problem is possible. Convergence to the desired broken symmetry determinant is confirmed by the spin populations, close to 4 spin-up electrons for the Mn(III) site and 3 spin-down electrons for Mn(IV). This BS solution is not a spin eigenfunction and should not be confused with the $S = 1/2$ spin state mentioned above. Instead its computed energy can be used with an appropriate projection formula such as the Yamaguchi projection that weighs the energies of the high-spin and BS solutions by the spin expectation values to extract a J constant (Eq. 3),¹³⁴ which is subsequently used to reproduce the spin state ladder as described above. More complex treatments involving multiple BS solutions are used for higher nuclearity systems.^{26, 33, 70, 83, 135-139}

$$J = -\frac{E_{\text{HS}} - E_{\text{BS}}}{\langle S^2 \rangle_{\text{HS}} - \langle S^2 \rangle_{\text{BS}}} \quad (3)$$

In the present case this approach yields $J = -161.7 \text{ cm}^{-1}$ using the BP86 functional, $J = -18.2 \text{ cm}^{-1}$ with M06-2X, and $J = -95.1 \text{ cm}^{-1}$ with TPSSh, to be contrasted with the experimental value of -90.0 cm^{-1} .⁷³ These values highlight the strong dependence of exchange couplings on the choice of functional. In high-valent Mn systems it has been noted that the performance of the hybrid meta-GGA functional TPSSh is consistently reliable,^{14, 33, 76-77, 89} at least partly owing to the moderate amount of exact exchange (10%). However, this is not a universally applicable recipe for any exchange coupled system. The fundamental weakness remains that BS-DFT cannot be systematically improved and conclusions regarding the optimal functional and its error margins are not transferable.

3.2. Multireference Treatment with Metal-only Active Space. The smallest chemically reasonable active space that can be used for a multireference description of complex **1** is a space composed of all unpaired electrons of the Mn ions distributed over the Mn 3d orbitals, i.e. a (7,10) active space (see Figure 2). Calculations with this active space were performed with traditional CASSCF and with DMRG-CASSCF and the results are identical already with a number of renormalized states $M = 500$. As a first step in the use of multireference methods we investigated a straightforward configuration interaction approach using Pipek–Mezey localized quasi-restricted orbitals from a DFT calculation. The (7,10) CI calculation resulted in a very large ferromagnetic coupling of $J = +179 \text{ cm}^{-1}$ (the same value is obtained regardless of the specific energy difference between states used) in profound disagreement with experiment. Staying within the confines of this minimal active space, we examined whether the reason for this failure could be the origin of localized orbitals by comparing results obtained using different source orbitals and localized orbitals derived from the alternative Foster–Boys localization scheme.¹⁴⁰ As these different choices did not introduce any delocalization, they also did not affect the exchange coupling qualitatively and therefore we conclude that a (7,10) CI description of the system with metal-based orbitals is fundamentally deficient.

Orbital optimization changes the picture drastically. The energies of individually optimized spin states do not follow a regular Landé pattern: the ground state is correctly predicted to be the low-spin, $S = 1/2$ state, but this is followed by the $S = 7/2$ at 12.1 cm^{-1} , $S = 3/2$ at 16.2 cm^{-1} and $S = 5/2$ at 27.9 cm^{-1} . This suggests that these state-specific CASSCF(7,10) calculations are not appropriate for discussing exchange coupling. We note that using a *single* set of orbitals optimized for either the high-spin ($S = 7/2$) or the low-spin ($S = 1/2$) state and determining the relative energies of the remaining states from CI calculations does not lead to meaningful results, because the corresponding state for which the orbitals are optimized always lies two to three thousand wavenumbers below the others.

In contrast, state-averaged (7,10) CASSCF results lead to a normal Landé distribution of spin states with an antiferromagnetic exchange coupling constant of -1.6 cm^{-1} with a spread of 0.2 cm^{-1} ($J_{(7/2-5/2)} = -1.5 \text{ cm}^{-1}$, $J_{(5/2-3/2)} = -1.6 \text{ cm}^{-1}$, and $J_{(3/2-1/2)} = -1.7 \text{ cm}^{-1}$). Note that under the assumption of Landé spacing one can use any pair of spin state energies to derive an effective J value, or a linear regression as mentioned above. For the four spin states in the present case there are six possible energy differences (three linearly independent ones) that can be used. The relative energies of all states are provided explicitly in the present work. To facilitate the discussion, J values obtained from energy differences between successive pairs of spin states (that is, doublet–quartet, quartet–sextet, and sextet–octet) are mentioned and the average of these three values is used as an effective J for a given method, while “spread” refers to the difference between the largest and smallest of these three successive J values and is a measure of deviations from the Landé pattern. Values of J obtained from linear fits as described in the previous section are also reported in the Supporting Information, along with associated R^2 values; they are consistent with the averaged J values reported in the main text.

The result of the CASSCF(7,10) calculation described above is that it introduces small delocalization “tails” to the starting tightly localized orbitals, that is, the final state-averaged CASSCF orbitals have non-zero amplitudes on the bridging ligands. Still, the numerical result is of no practical value. The importance of orbital choice in multireference calculations with a minimal active space has been discussed with respect to the delocalization on the bridging ligands and in relation to the relative description of neutral and ionic components of the wave function.¹⁴¹⁻¹⁴⁴ In a view that attempts to distinguish between metal-based magnetic orbitals as the basis for static correlation and everything else added on top as contributor to dynamic correlation, a minimal metal-based active space is seen as the starting point for subsequent dynamic correlation treatments like DDCI, which enables clearly distinguishable classes of excitations.^{47, 49-52, 145} As an operational concept this is not applicable in the

present study, where we target active space expansion by virtue of the DMRG. Therefore in the following we extend the active space in a chemically motivated and systematic way that aims to directly incorporate the ligand contributions (ligand-to-metal charge transfer)^{49, 145-147} to the magnetic coupling.

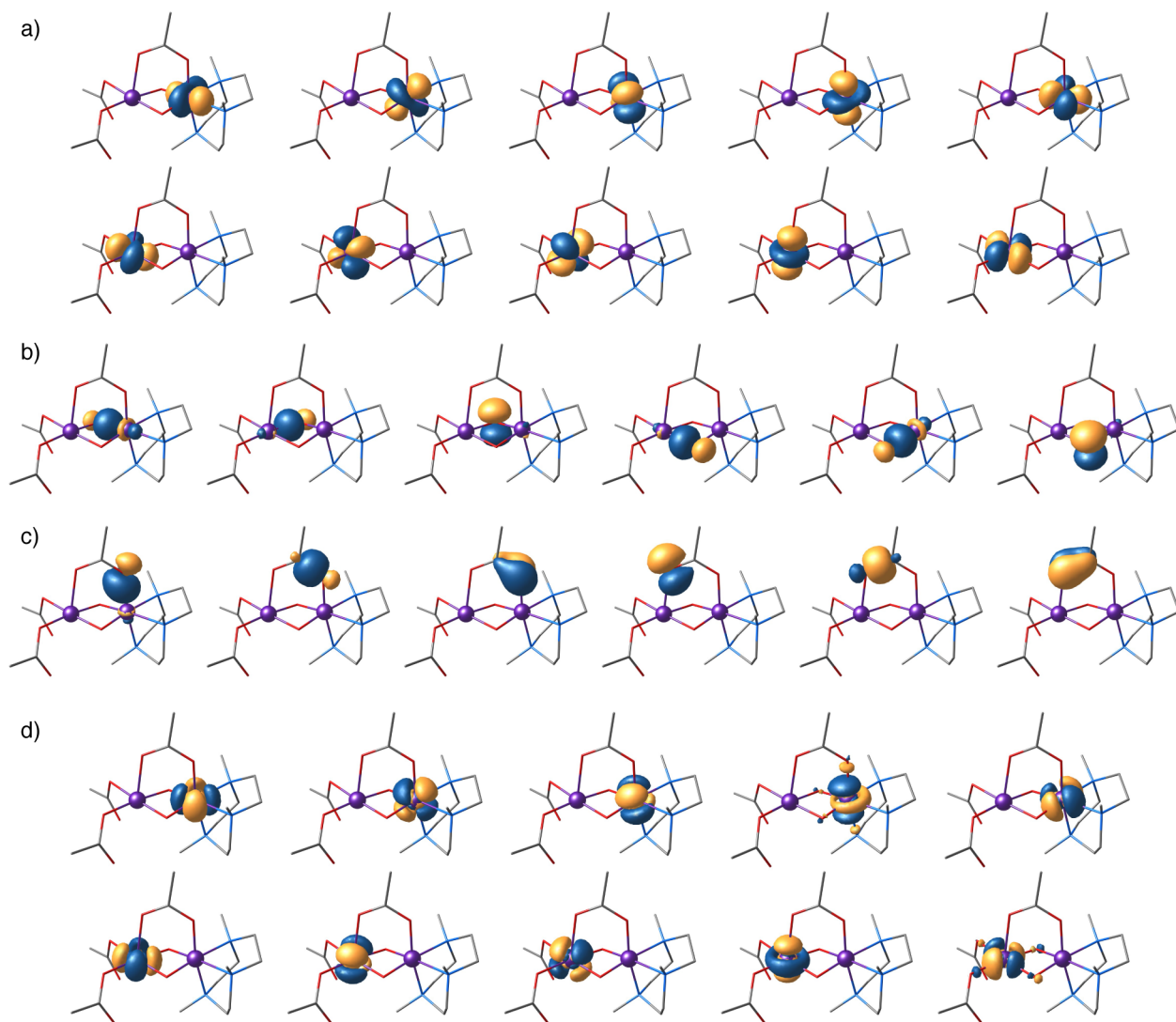


Figure 2. Main localized orbitals used for initial construction or extension of the active spaces described in the present work. a) Mn 3d orbitals, b) O 2p orbitals, c) OAc 2p orbitals, and d) Mn 4d orbitals.

3.3. Inclusion of Oxo Bridge Orbitals. Inclusion of the occupied 2p orbitals of the two oxo bridges (three orbitals for each O bridge) is expected to switch the superexchange mechanism on and thus enhance the antiferromagnetic coupling. This leads to a (19,16) active space. In the preceding section we showed that the direct use of metal 3d localized orbitals in a CI treatment resulted in a qualitatively

incorrect description of the system and an inverted spin ladder. It is useful to know whether orbital optimization might have a less profound effect if a more complete active space is used, so we first performed DMRG-CASCI calculations using the (19,16) active space consisting of localized Mn 3d orbitals and 2p oxo bridge orbitals. In this case all active space orbitals were derived simultaneously from the initial localization procedure. These DMRG-CASCI calculations still incorrectly predicted an inverted spin ladder with the high-spin $S = 7/2$ state as the ground state and yielded distinct deviations from Heisenberg behavior. The sextet, quartet and doublet states are located at 433 cm^{-1} , 897 cm^{-1} and 1324 cm^{-1} above the ground octet state (values identical to canonical CASCI at $M = 1500$). It is clear that the direct use of localized QROs in constructing the large active space and the lack of orbital optimization restrict the utility of this DMRG-CASCI approach for studying exchange coupling.

As a second step, we investigated the addition of localized O 2p orbitals on top of the previously optimized (7,10) Mn 3d orbitals, but without orbital reoptimization in the (19,16) active space. A DMRG-CASCI calculation with this type of active space yields a J of -28.8 cm^{-1} , drastically improving the (7,10) CASSCF result of $J = -1.6 \text{ cm}^{-1}$. This value is converged at $M = 1000$. Finally, proceeding with orbital optimization using spin-state-averaged DMRG-CASSCF(19,16) calculations more than doubles the strength of antiferromagnetic coupling, leading to a J value of -59.0 cm^{-1} . The natural orbital occupation numbers for the O 2p orbitals deviate non-negligibly from 2.0 and are reduced to ca. 1.85 electrons for the in-plane orbitals that interact in a σ -fashion with the Mn(IV) center and 1.95 electrons for the other two. Although the predicted coupling still underestimates the experimental value, the result appears to finally provide a physically sound description of the system as it enables the inclusion of ligand-to-metal charge transfer that contributes to superexchange.^{31, 52} Given that a convincing description of the system is obtained at this level, it is worth discussing a few methodological points in greater detail.

First of all, we note that DMRG-CASSCF requires a higher number of retained states than CASCI to achieve similar convergence, and this requirement increases with larger spaces. As a technical note, it proved most efficient to achieve convergence of DMRG-CASSCF by adding localized orbitals on top of pre-optimized orbital subspaces and directly starting with relatively high values for M , i.e. at least 1000. This avoids convergence problems observed in direct large-active-space use of localized orbitals, but also requires manual, chemically-driven construction of intermediate subspaces. Given the necessity for this type of manipulation and for orbital optimization, coupled to the fact that high starting M values may be required, it is not clear whether an automated orbital selection approach¹⁴⁸ that relies on analysis of preliminary orbitals at low M values would be of the same effectiveness here as in other applications.

Table 1 shows how the energy levels evolve with the number of renormalized states ranging from 250 to 3000. Smaller values of M either lead to scattered results or do not converge at all. The results obtained with $M = 250$ are unusable because there is no reasonable relationship between adjacent energy levels. In our opinion the results with $M = 500$ are also unusable, despite the fact that the average of the energy differences between adjacent levels does lead to the same value of J as the results with higher M values. From $M = 1000$ onwards the average J value is converged. The only differences are small improvements in the relative energy of the first excited state ($S = 3/2$), which result in restricting the differences between the three possible J values from 3.4 cm^{-1} ($M = 1000$) to 2.4 cm^{-1} ($M = 3000$).

Inclusion of the O 2s orbitals was also evaluated as an extension of the above results. The corresponding DMRG-CASCI calculations with an (23,18) active space showed no further effect on the exchange coupling ($J = -58.5 \text{ cm}^{-1}$). The (19,16) active site was deemed appropriate to test possible basis sets effects, so DMRG-CASSCF calculations were repeated (starting from the initial localization setup up to the construction of the final active space) using the more extensively polarized ZORA-recontracted def2-QZVPP basis sets for Mn and O. Similarly to the known weak basis set dependence of

classical CASSCF, the DMRG-CASSCF results also proved insensitive. Compared to the results reported in Table 1, the def2-QZVPP values deviated by ca. 1 cm^{-1} for equivalent M values.

Table 1. Energy level differences in cm^{-1} between spin states computed from state-averaged DMRG-CASSCF calculations on complex **1** with a (19,16) active space composed of Mn 3d and O 2p orbitals for different numbers of renormalized states M , corresponding exchange coupling constants derived from energy differences of adjacent spin levels, and average J value (cm^{-1}).

S	$M = 250$	$M = 500$	$M = 750$	$M = 1000$	$M = 1500$	$M = 2000$	$M = 2500$	$M = 3000$
$7/2$	775.3	868.2	876.7	878.7	879.6	879.9	879.9	879.9
$5/2$	694.8	486.3	477.6	476.3	475.9	475.9	475.9	475.9
$3/2$	490.1	215.0	186.0	182.6	181.0	180.6	180.5	180.4
$1/2$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$J_{(7/2-5/2)}$	-11.5	-54.6	-57.0	-57.5	-57.7	-57.7	-57.7	-57.7
$J_{(5/2-3/2)}$	-40.9	-54.3	-58.3	-58.7	-59.0	-59.1	-59.1	-59.1
$J_{(3/2-1/2)}$	-163.4	-71.7	-62.0	-60.9	-60.3	-60.2	-60.2	-60.1
J	-71.9	-60.2	-59.1	-59.0	-59.0	-59.0	-59.0	-59.0

The convergence of absolute energies (Table S1) shows that individual states are stabilized with increasing M as expected, but to different extents. Comparison of the $M = 1000$ total energies with those obtained with $M = 250$ show that the $S = 7/2$ state is lowered by 26.2 cm^{-1} , whereas the $S = 5/2$, $3/2$ and $1/2$ states are respectively stabilized by 348.0 cm^{-1} , 437.0 cm^{-1} and 129.5 cm^{-1} . Comparison of $M = 1000$ and $M = 2000$ results shows much smaller change in total energies by 0.4 cm^{-1} , 2.0 cm^{-1} , 3.7 cm^{-1} , and 1.6 cm^{-1} . Finally, at $M = 3000$ there is a further minute stabilization of the $S = 3/2$ state by 0.2 cm^{-1} , whereas the energies of all other states are affected by less than 0.1 cm^{-1} . The reported discarded weight is negligible for all states. It is important to note that since the highest and lowest spin states for dimer **1** converge faster than the intermediate ones, a rather converged J value could also be extracted directly from the expected total span of the spin ladder. We stress however that this conclusion might not be general and that the orbitals to be used in this case still derive from a fully spin-state-averaged approach.

3.4. State-Specific Calculations and Potential Deviations from Isotropic Behavior. For comparison to the above state-averaged results, we carried out DMRG-CASSCF calculations with the same (19,16) active space but optimizing the orbitals for each spin state individually. These calculations produce the correct ordering of states, i.e. $S = 1/2$ is the ground state, but the energy intervals deviate strongly from the regular Landé pattern observed in the state-averaged calculations. The spin ladder becomes progressively compressed at higher spin levels. This effect is exaggerated at low M values and reduced significantly at higher M , but deviations remain. Compared to the state-averaged results, the two intermediate $S = 3/2$ and $S = 5/2$ states are strongly destabilized, while the high-spin $S = 7/2$ state is too low in energy: the J values computed from energy differences between adjacent levels are -74.9 cm^{-1} , -64.1 cm^{-1} and -43.8 cm^{-1} . Note that the DMRG-CASSCF total energy of each state with $M = 2000$ is already converged to within 0.2 cm^{-1} of the exact CASSCF energy. In contrast to the state-specific results obtained with the (7,10) active space, the (19,16) state-specific results follow the expected spin progression but it is still impossible to use them predictively.

This effect could go unnoticed if only two states were computed and used to extract an exchange coupling constant. One might incorrectly predict a rather optimistic value for J with DMRG-CASSCF(19,16), remaining oblivious to the fact that the complete spin ladder is inconsistent. Alternatively, results like this—when not so obviously problematic—might be treated as valid and interpreted as deviations from the isotropic bilinear HDvV Hamiltonian. Such deviations can be modeled with additional isotropic and anisotropic terms. For mixed-valence systems double exchange (coupling through an itinerant electron) may be significant, but the present system has well-localized unpaired electrons owing to the asymmetric coordination sphere that is distinct for each Mn site and of the extremely strong Jahn–Teller distortion and stabilization energy of the Mn(III) ion. These factors result in the absence of an accessible valence-interchanged state. A relevant term might instead be an

isotropic biquadratic term¹⁴⁹⁻¹⁵⁰ of the form $-j(\mathbf{S}_1\mathbf{S}_2)^2$, which attempts to account for deviations arising from lower local M_S configurations.^{130, 151-152} A previous observation that the J derived from higher spin states is weaker than that derived from lower spin states in an antiferromagnetically coupled system has been discussed in connection with biquadratic exchange.⁷² In our opinion this type of analysis is in general seriously complicated by the lack of experimentally fitted j values for molecular systems, and in the present case is rendered moot by the observation that differences in J values are diminished with progressively increasing M values. Besides, the fact that J values computed even with the (19,16) active space are still far from experiment speaks against using them in deriving hypothetical extra terms. Spivak et al.¹⁴³ already described a situation where such deviations are produced as methodological artifacts (in that case of CASPT2) and additionally confirmed that previously reported deviations⁷² on a Cr dimer cannot be reproduced with a state-averaged approach. Therefore, we advise caution in the use of state-specific energies in predicting deviations from isotropic Heisenberg behavior.

The divergence observed with spin state specific energies presumably arises from imbalances in the appropriateness of a given active space in recovering part of dynamic correlation or balancing ionic contributions. The energetic effect may be insignificant for many applications, but it appears sufficiently large to confound studies of exchange coupling. Based on the present observations we conclude that instead of deducing exchange coupling constants from energy differences between a limited number of isolated states, the simultaneous calculation of the complete spin ladder using averaged orbitals is to be preferred as a more robust and numerically superior approach.

3.5. Effect of Acetato Orbitals and Evaluation of Discrete Exchange Pathways. A major benefit of being able to use large active spaces with DMRG is that it provides a new powerful tool to probe the role of each diamagnetic bridge in a multiply bridged dimer, or even in systems with several paramagnetic sites and exchange pathways. Specifically, by selective inclusion of localized orbital

subspaces it is possible to switch specific exchange pathways on and off, thus quantifying the relative contribution of each bridging ligand to superexchange. Here we show how this approach can be used to compare the contribution of the oxo bridges versus the acetato ligand. There are six localized occupied orbitals on the acetato bridge; adding them to the metal-only (7,10) active space leads again to a (19,16) active space. DMRG-CASSCF calculations with this active space lead to results essentially identical to the metal-only CASSCF(7,10), with natural orbital occupation numbers of the acetato ligands remaining essentially 2.0, showing that this ligand does not contribute to superexchange.

Using both the oxo and the acetato orbitals results in an active space (31,22). DMRG-CASCI calculations up to $M = 3000$ with the (31,22) active space in which acetato orbitals were added to the previously optimized Mn 3d + O 2p (19,16) active space showed no appreciable deviation from the (19,16) results ($J = -59.2 \text{ cm}^{-1}$). Orbital optimization with this larger active space was laborious but could also be completed up to $M = 3000$. The DMRG-CASSCF relative energies agree with the DMRG-CASCI results (Table 2), leading to an average J of -58.4 cm^{-1} . These results confirm that the acetato bridge is not mediating superexchange in this system.

The above observations are relevant for the treatment of similar systems bearing carboxylato bridges, such as the oxygen-evolving cluster of photosystem II or its many synthetic analogs. In that case the four Mn ions, which adopt combinations of oxidation states III and IV in different steps of the catalytic cycle, are connected by glutamate and aspartate residues in addition to oxo or hydroxo bridges (Figure S1). However, although the above observations in the case of dimer **1** do suggest that the acetato orbitals can be excluded, this conclusion should not be considered necessarily transferable to any system; this pathway may be deactivated in dimer **1** due to the mixed valence situation. Besides, acetato bridges are known to be magnetically active, as in the archetypal paddlewheel Cu(II) acetate dimers.^{145, 153-154} Therefore, the possible roles of carboxylato bridges and concepts related to acetato ligands such as the

counter-complementarity effect are worth investigating further with a DMRG-based approach for diverse systems and metal oxidation state combinations.

Table 2. Energy level differences in cm^{-1} between spin states computed from state-averaged DMRG-CASCI and DMRG-CASSCF calculations on complex **1** with a (31,22) active space composed of Mn 3d, O 2p, and acetato orbitals for different numbers of renormalized states M ; corresponding exchange coupling constants derived from energy differences of adjacent spin levels, and average J value (cm^{-1}).

S	DMRG-CASCI				DMRG-CASSCF		
	$M = 500$	$M = 1000$	$M = 2000$	$M = 3000$	$M = 1000$	$M = 2000$	$M = 3000$
$7/2$	791.5	862.2	880.0	882.5	841.5	869.3	870.5
$5/2$	469.4	474.7	476.9	477.4	467.8	470.8	471.2
$3/2$	249.6	200.1	184.7	182.2	202.2	180.0	179.0
$1/2$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$J_{(7/2-5/2)}$	-46.0	-55.4	-57.6	-57.9	-53.4	-56.9	-57.0
$J_{(5/2-3/2)}$	-44.0	-54.9	-58.4	-59.0	-53.1	-58.2	-58.4
$J_{(3/2-1/2)}$	-83.2	-66.7	-61.6	-60.7	-67.4	-60.0	-59.7
J	-57.7	-59.0	-59.2	-59.2	-58.0	-58.4	-58.4

Similarly to the above, the use of localized orbital subspaces can be used to selectively probe symmetry-distinct exchange pathways within the *same* bridging unit. For example, we performed DMRG-CASCI calculations with active spaces that included only the $2p_z$ orbitals of the O bridges in addition to the Mn 3d orbitals (π -pathway). These (11,12) active space calculations resulted in doubling the exchange coupling of the metal-only (7,10) CASSCF calculations, from -1.9 cm^{-1} to -3.9 cm^{-1} . Contrasting however this value with that of DMRG-CASCI calculations that included all O 2p orbitals in the (19,16) active space (-28.8 cm^{-1}) clearly demonstrates that the in-plane interactions between the O $2p_x/2p_y$ and the Mn $3d_{xy}$ orbitals are the dominant contributors to superexchange (σ -pathway).

Corresponding orbital transformation (COT) of broken-symmetry solutions has been used as a method to produce pairs of “magnetic orbitals” in order to visualize superexchange pathways and

quantify antiferromagnetic contributions through overlap integrals.¹³¹ An example of COT analysis for dimer **1** is provided in Figure S2 of the Supporting Information. This method has relevance to the selective orbital subspace approach described here, because it is also a tool for investigating or mapping the “magnetic topology” of a molecular system. However, the present approach is more generally applicable because it can extend beyond two-spin systems to clusters of arbitrary nuclearity and bridging motifs, as long as appropriate orbital subspaces can be constructed and evaluated.

3.6. Effect of Virtual Orbitals. In the preceding sections we established that a spin-state-averaged DMRG-CASSCF approach with an active space encompassing all metal 3d and all oxo 2p orbitals offers a qualitatively correct description of the exchange interaction, but the result is still not quantitatively accurate. Therefore we sought to determine the possibility of improvements by inclusion of virtual orbitals in the active space. Of these the most important are the Mn 4d orbitals, which are associated with the “double shell” effect. The reason for including virtual orbitals in the active space is seen as an attempt to recover dynamic correlation.³¹ We extended the previously obtained DMRG-CASSCF (19,16) optimized active orbitals with localized Mn 4d orbitals, leading to a (19,26) active space. DMRG-CASCI calculations were successful and converged at $M = 3000$ to a very slightly improved J value of 64.8 cm^{-1} (see Table S3) compared to the (19,16) active space. Subsequently we localized separately the oxygen 3p virtual orbitals and added them to the above (19,26) active space, leading to a final active space of 19 electrons in 32 orbitals. DMRG-CASCI(19,32) calculations with this complete set of metal 3d + 4d and oxygen 2p + 3p orbitals led to an average J value of -60.4 cm^{-1} . The maximum M that could be used for the (19,32) calculations was 1000 and still led to a spread of ca. 9 cm^{-1} ($J_{(7/2-5/2)} = -56.1 \text{ cm}^{-1}$, $J_{(5/2-3/2)} = -59.7 \text{ cm}^{-1}$, $J_{(3/2-1/2)} = -65.3 \text{ cm}^{-1}$) similar to the spread for the (19,26) results in Table S3. In analogy to the (19,26) results, we anticipate that the average would not

change significantly at higher M , so we conclude that there is no advantage in going beyond the DMRG-CASSCF(19,16) treatment within a DMRG-CASCI approach.

Orbital optimization is necessary to relax these types of excitation, but with such extended active spaces this represents a considerably more complex and computationally demanding task than calculations reported up to this point. State-averaged DMRG-CASSCF(19,26) calculations could be completed with $M = 1000$ and $M = 1500$. The results indicate that with this active space convergence of relative energies with M deteriorates dramatically. Pairwise J values evolve from $J_{(7/2-5/2)} = -39.4 \text{ cm}^{-1}$, $J_{(5/2-3/2)} = -73.5 \text{ cm}^{-1}$, $J_{(3/2-1/2)} = -142.3 \text{ cm}^{-1}$ at $M = 1000$ to $J_{(7/2-5/2)} = -61.3 \text{ cm}^{-1}$, $J_{(5/2-3/2)} = -75.2 \text{ cm}^{-1}$, $J_{(3/2-1/2)} = -97.1 \text{ cm}^{-1}$ at $M = 1500$. Obviously, even at $M = 1500$ the differences in pairwise J values are still too large. We note however that as shown above for the (19,16) active space (Table 1), the total span of the ladder is less sensitive to M than the relative energies of the intermediate spin levels. This is also the case for the present DMRG-CASSCF(19,26) calculations, where the relative energy of the $S = 7/2$ state with respect to the $S = 1/2$ ground state changes by less than 30 cm^{-1} , from 1070.3 cm^{-1} ($M = 1000$) to 1096.6 cm^{-1} ($M = 1500$). Using these energy differences one can derive J values of -71.4 cm^{-1} and -73.1 cm^{-1} , respectively. This implies that orbital optimization in the (19,26) active space is expected to contribute ca. 10 cm^{-1} to the magnitude of the antiferromagnetic exchange coupling compared to the CI result of Table S3. This would be an improvement over the average J obtained from the DMRG-CASSCF(19,16) calculations (Table 1). However, one is faced with the law of diminishing returns. The high cost of these calculations and the fact that quantitative accuracy is still not achieved suggests that at least in the case studied here this path is not the optimal strategy.

The approach followed up to this point treats metal and ligand orbitals as complete blocks (i.e. all metal 3d, all bridge 2p etc) and does not attempt to distinguish between more or less important ones. Attempts to select a limited number of orbitals with which to extend the minimal Anderson active space

of magnetic orbitals have been discussed in the past on a smaller scale.^{51, 144} In the present work we will not diverge into the question of active space customization for the specific complex. We do expect however that this will be important for applications on exchange coupled systems that require large active spaces like the present manganese dimer. This problem is likely to be most efficiently addressed through automated screening techniques¹⁴⁸ based on orbital entanglement information.¹⁵⁵

3.7. Perturbational Treatment of Dynamic Correlation. The importance of dynamic electron correlation for the quantitatively correct description of magnetic coupling in transition metal clusters is well established.³¹ The effect of the occupied bridging orbitals is difficult to capture using dynamic electron correlation methods such as perturbation theory on top of a minimal metal-based active space^{31, 156-157} and therefore is best included explicitly in the active space. On the other hand our results suggest that it might be futile to attempt to recover all dynamic electron correlation required for an accurate description of the magnetic coupling problem by aggressively extending the active space much beyond the metal d and bridge p orbitals due to the steep increase in computational cost. In contrast, dynamic electron correlation methods such as the multireference configuration interaction or canonical transformation theory for DMRG wave functions provide a computationally feasible option.^{59, 158-159} Herein, we use the strongly contracted (SC) variant of NEVPT2 for DMRG to tackle dynamic electron correlation because of its robustness and good accuracy at manageable computational cost.^{126, 160-162}

We examined the effect of this treatment on predicted exchange coupling constants with two of the easily accessible CAS spaces. First we applied NEVPT2 on the (7,10) active space, which had yielded an average J of -1.6 cm^{-1} by CASSCF. NEVPT2 energies lead to drastically increased antiferromagnetic coupling, with an average J of -24.8 cm^{-1} ($J_{(7/2-5/2)} = -22.3 \text{ cm}^{-1}$, $J_{(5/2-3/2)} = -25.2 \text{ cm}^{-1}$, $J_{(3/2-1/2)} = -26.8 \text{ cm}^{-1}$). Partially contracted NEVPT2 leads to a slightly better average J value of -33.6 cm^{-1} . Although NEVPT2 improves the results, quantitative agreement with experiment is not

achieved because the CASSCF reference is inadequate. The (19,16) active space that includes the Mn 3d and O 2p orbitals seems a more appropriate starting point, because it already yields a qualitatively correct description of the spin ladder at the CASSCF level.

DMRG-NEVPT2 calculations with this active space converge to an average J value of ca. -85 cm^{-1} at $M' = 1500$, which approaches the experimental value very well (Table 3). As expected, a slightly larger number of retained states is required to achieve satisfactory convergence as compared to the DMRG-CASSCF(19,16) calculations. This is due to the requirement to calculate reduced density matrices for more than two active electrons within NEVPT2.⁸⁵ With relatively small variations within the J values obtained from different steps of the spin ladder ($\pm 0.9 \text{ cm}^{-1}$) we conclude that the application of NEVPT2 retains the Heisenberg behavior as it was observed for DMRG-CASSCF and CASSCF. Importantly, this finding holds true only for large M' since the different spin state energies converge at different rates with increasing M' , as also described above for DMRG-CASSCF.

Table 3. Energy level differences, exchange coupling constants from adjacent spin levels and average J values (cm^{-1}) for complex **1** by DMRG-NEVPT2(19,16) calculations.

S	$M' = 500$	$M' = 1000$	$M' = 1500$
7/2	1232.2	1249.4	1268.4
5/2	668.6	674.5	676.3
3/2	262.8	259.4	256.9
1/2	0.0	0.0	0.0
$J_{(7/2-5/2)}$	-80.5	-82.1	-84.6
$J_{(5/2-3/2)}$	-81.2	-83.0	-83.9
$J_{(3/2-1/2)}$	-87.6	-86.5	-85.6
J	-83.1	-83.9	-84.7

Although the results obtained with an (19,16) active space already match the experimentally observed value within a few wavenumbers, which is on the order of the experimental accuracy, slight numerical improvement might be achieved by the inclusion of the Mn 4d orbitals in the active space thus explicitly

accounting for the “double shell effect”. Considering the tight energy convergence criteria required (see above) such calculations come at immensely increased computational cost and proved to be intractable with the computer setups available to us. The present calculations already require considerable resources as the NEVPT2 algorithm requires the active space density matrices for up to four electrons, whereas regular DMRG-CASCI or DMRG-CASSCF calculations only require two-electron density matrices.⁸⁵ The formal scaling of NEVPT2 or alternative methods such as CASPT2 can in principle be reduced by application of cumulant approximations.^{64, 67, 163-164} However, such approximations introduce non-negligible errors⁶⁷ and hence are inappropriate for applications to magnetic properties.

4. CONCLUSIONS AND PERSPECTIVES

DMRG holds the promise to extend the applicability of multireference methods into the field of oligonuclear magnetically coupled transition metal systems. Here we evaluated the application of DMRG to the prediction of the exchange coupling for an archetypal mixed valence manganese dimer that serves as a model for a range of materials, molecules, and bioinorganic systems. Two important conclusions of the present work are that antiferromagnetic coupling is reproduced by any choice of active space as long as orbital optimization is carried out but not otherwise, and that a spin-state-averaged approach is necessary to avoid unphysical deviations from the Landé spin ladder. Complete active space self-consistent field (CASSCF) calculations that employ a metal-only active space do not lead to reasonable values for exchange coupling constants. A physically more realistic picture of the coupled system is obtained upon inclusion of ligand-based orbitals, thus accounting for ligand-to-metal charge transfer configurations: an active space containing Mn 3d and O 2p orbitals yields an exchange coupling constant of the same order of magnitude as the experimental value, whereas the acetato bridge orbitals do not seem to have any effect. Quantitative agreement with experiment is nevertheless impossible to achieve at any readily accessible size of active space.

DMRG-NEVPT2 is used in the present study to further recover dynamic correlation. It has been suggested that perturbational treatments such as CASPT2¹⁶⁵ and NEVPT2 are less robust than variational methods for magnetic coupling problems.^{52, 166} This is however contingent upon the quality of the starting wave function and whether the active space used is a minimal metal-based active space or not.^{156-157, 167} Our results for the present dimer suggest that NEVPT2 is successful if applied to an active space comprising all metal 3d and ligand 2p orbitals. This active space represents the point where state-averaged DMRG-CASSCF already provides a qualitatively correct description of the system and pays off maximally with limited effort, whereas expanding into the virtual space entails a steep increase in complexity and cost without proportionately high returns.

At this point we would like to reflect on the applicability of the approach to larger and more complex systems. Taking the Mn_4CaO_5 cluster of the OEC as an example, the present study suggests that the smallest acceptable active space should comprise the manganese 3d and the oxo bridge 2p orbitals. This would lead to a total of 35 orbitals for the OEC,⁶⁹ which might still miss important contributions from other bridging ligands. The challenge is then how to perform a DMRG-CASSCF calculation in a state-averaged approach encompassing all necessary Heisenberg spin states. It is unclear whether such calculation is at all possible for an oligonuclear system or, alternatively, if there is a way to obtain physically realistic energy levels for a subset of the spin states without solving for the complete ladder. Most importantly, even if such calculations were possible the results are not expected to be of predictive value, while the applicability of NEVPT2 as a way to introduce meaningful corrections at such active spaces is improbable. One should also keep in mind the necessity for increasingly high M values that is exacerbated with increasing active spaces as CASSCF orbitals become progressively delocalized.

In conclusion, despite the enabling power of DMRG, quantitative results in exchange coupling constants by brute force increase of the active space are not to be expected in the near future. The

combination of full-valence DMRG-CASSCF and NEVPT2 that seems to work very well here is a pragmatic approach, but its applicability depends on the system-dependent balance of static and dynamic correlation within a given valence active space, as well as on the chemical nature of the constituent metal ions and bridging groups. In terms of defining the active space, automated orbital selection algorithms based on analysis of orbital entanglement may facilitate the selection of orbitals and help create more compact active spaces without significant loss of accuracy.¹⁴⁸ However we would like to caution that the orbitals eliminated in a DMRG-based prescreening are not necessarily insignificant for a subsequent NEVPT2 calculation. This topic is worth investigating more closely in the future. Instead of regarding DMRG calculations, even with very large active spaces, as a quantitative predictive tool for the analysis of exchange coupled systems it is perhaps more important and useful that one can obtain a high quality first-order description of the problem. Useful insights can be gained already at this point without quantitative accuracy, or this can form the basis for a dynamic correlation treatment. We demonstrated here one possibility, namely NEVPT2, but other approaches can be considered^{159, 168-171} and will be investigated in future work.

Supporting Information. Additional figures and results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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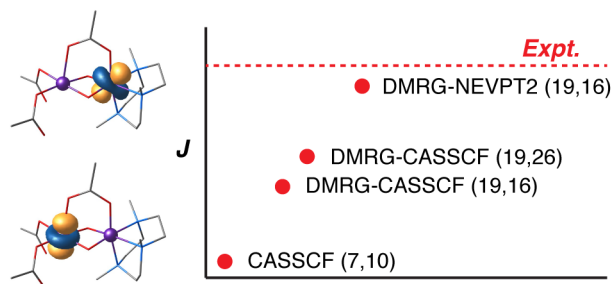
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The exchange coupling in a mixed-valence manganese(III,IV) dimer is studied using DMRG-CASSCF and DMRG-NEVPT2 approaches.