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Computational quantum chemistry for single Heisenberg spin couplings made simple: Just one spin flip required

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Abstract

We highlight a simple strategy for computing the magnetic coupling constants, J , for a complex containing two multiradical centers. On the assumption that the system follows Heisenberg Hamiltonian physics, J is obtained from a spin-flip electronic structure calculation where only a single electron is excited (and spin-flipped), from the single reference with maximum \hat{S}_z , M , to the $M - 1$ manifold, regardless of the number of unpaired electrons, $2M$, on the radical centers. In an active space picture involving $2M$ orbitals, only one β electron is required, together with only one α hole. While this observation is extremely simple, the reduction in the number of essential configurations from exponential in M to only linear provides dramatic computational benefits. This $(M, M - 1)$ strategy for evaluating J is an unambiguous, spin-pure, wave function theory counterpart of the various projected broken symmetry density functional theory schemes, and likewise gives explicit energies for each possible spin-state that enable evaluation of properties. The approach is illustrated on five complexes with varying numbers of unpaired electrons, for which one spin-flip calculations are used to compute J . Some implications for further development of spin-flip methods are discussed.

I. INTRODUCTION

Transition metal complexes often exhibit strongly correlated electronic states, particularly if there are multiple metals in the complex. A strongly correlated wave function contains contributions of roughly equal magnitude from multiple electron configurations, in contrast to the single configuration that is dominant in typical closed shell molecules or simple radicals.¹ In most cases, the electronic structure of strongly correlated states is challenging to model using computational methods, because standard density functional theory (DFT)^{2,3} and wave function electronic structure methods⁴ are based on a single reference configuration. On the other hand, multiconfigurational methods^{5,6} in general scale exponentially with the number of strongly correlated electrons, which precludes applications to systems where this number is large. Whilst it is an open research area, new methods are being actively pursued to prevent this exponential scaling. Examples include pairing theories based on coupled-cluster theory,⁷⁻¹⁴ density matrix renormalization group methods,¹⁵⁻¹⁸ reduced density matrix theory,¹⁹⁻²¹ improved antisymmetric geminal power wavefunctions,²² and Löwdin partitioning techniques.²³⁻²⁵

Given the electronic structure challenge, it is no surprise that strongly correlated states are usually difficult to understand in physical terms. However there are exceptions. Amongst the most important cases are molecules containing two weakly interacting radical centers, each with some number of well-localized unpaired electrons. The low-lying, strongly correlated states involve the recoupling or spin-pairing of the unpaired electrons into all the different possible total spin states, according to the Clebsch-Gordon series. To an excellent approximation, the resulting spectrum of low energy states can usually be mapped onto the phenomenological Heisenberg-Dirac-Van Vleck (HDVV) spin hamiltonian,²⁶⁻²⁸

$$\hat{H}^{\text{HDVV}} = -2J\hat{S}_a\hat{S}_b \tag{1}$$

where the only interaction, J , is the isotropic magnetic coupling constant between magnetic sites a and b , and \hat{S}_a is the spin operator for center a only. J completely determines the low energy spectrum, where the gap between any two adjacent states of spin, S , is given as,

$$E(S) - E(S - 1) = -2SJ, \tag{2}$$

which is known as the Landé interval rule.²⁹

The simplified HDVV description of the electronic structure makes it possible to obtain straightforward statistical mechanics expressions for bulk properties such as the paramagnetic susceptibility, χ . The Van Vleck equation defines χ as a function of both J and temperature (T).²⁸ By fitting the Van Vleck equation to an experimental χ vs. T plot, one can obtain an experimentally determined magnetic coupling constant, J .

Electronic structure calculations, on the other hand, are capable of providing explicit state energies for each spin multiplicity directly. The J values can then be determined directly via the Landé interval rule in Eq. 2. However, due to the multiconfigurational nature of the lower spin states, this remains a practical challenge. While multireference methods can be successful in computing, J ,³⁰⁻³³ the computational cost of such calculations increases exponentially with the number of unpaired electrons, as already discussed above. Therefore it is important to understand clearly the minimum extent to which strong correlations must be treated in order to correctly obtain J , which is the purpose of this paper.

The most important existing approach is due to Noodleman, who showed that it is, in fact, possible to obtain an approximate description of such systems using only a single-configuration method, such as Hartree-Fock (HF) or density functional theory (DFT).³⁴ In this approach, a broken symmetry DFT solution, (a configuration with excess α on one metal and excess β on the other and denoted as $|\mathbf{BS}\rangle$) is treated as a mixture of the spin-pure high spin state, $|\mathbf{HS}\rangle$, and low spin antiferromagnetic state, $|\mathbf{AF}\rangle$.

By mapping the electronic Hamiltonian, \hat{H} , onto the phenomenological HDVV Hamiltonian, and using a suitable spin projection of $|\mathbf{BS}\rangle$, the J values can be obtained from,

$$\begin{aligned} & \langle \mathbf{HS} | \hat{H} | \mathbf{HS} \rangle - \langle \mathbf{BS} | \hat{H} | \mathbf{BS} \rangle \\ & = \langle \mathbf{HS} | \hat{H}^{\text{HDVV}} | \mathbf{HS} \rangle - \langle \mathbf{BS} | \hat{H}^{\text{HDVV}} | \mathbf{BS} \rangle \end{aligned} \tag{3}$$

Because \hat{H}^{HDVV} returns the energy difference between the $|\mathbf{HS}\rangle$ and $|\mathbf{BS}\rangle$ states in units of J , the energy of the $|\mathbf{AF}\rangle$ state can be estimated. The effectiveness of BS-DFT relies on the fact that the $|\mathbf{BS}\rangle$ solution includes implicit coupling with ionic configurations via orbital relaxation, which results in non-orthogonal magnetic orbitals. Compared to multireference methods, BS-DFT presents an enormous advantage in terms of computational efficiency, which explains why BS-DFT has become the most popular strategy for modeling antiferromagnetically coupled complexes.

BS-DFT is, however, not fully satisfactory. In addition to the formal objections related

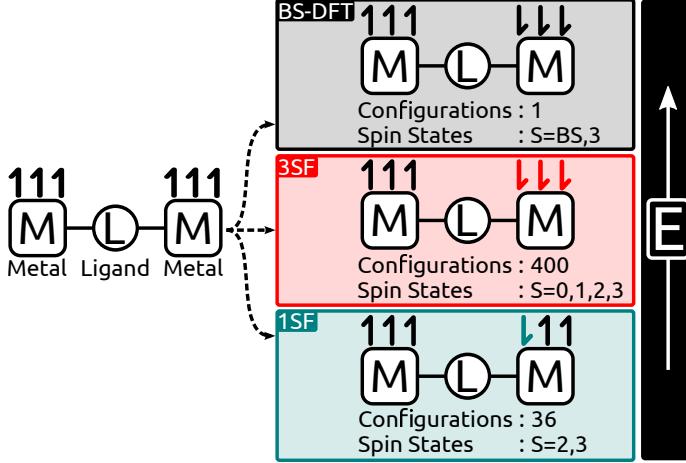


FIG. 1: Schematic representation of the comparison of computing J with a BS-DFT, 3SF, or 1SF calculations for a complex with 6 strongly correlated electrons (for instance the dichromium complex shown in Figure 2). The highest spin configuration is shown at the far left, with all spins aligned parallel. From this reference, three possibilities are shown, indicated the spin-contaminated BS-DFT solution, the 3SF-CI wavefunction consisting of 400 determinants, and the 1SF-CI wavefunction consisting of only 36 determinants. For the 3SF and 1SF illustrations, only a single representative configuration is shown. The far right illustrates the spin states accessible by each of the three strategies. The order of the states increase with increasing energy.

to the spin-contamination of the $|\mathbf{BS}\rangle$ state, the spin-projection is not unique, and multiple expressions have been put forth, all of which can (and do) provide different results.^{34–38} Furthermore, the fraction of exact exchange strongly affects the relative energies of the high-spin and broken-symmetry solutions, resulting in a strong dependence of J on the choice of DFT functional.^{39–41} In light of these ambiguities (and notwithstanding its successes), a well defined and systematically improvable alternative methodology is highly desirable.

II. PROCEDURE

As the focus of the current article, we suggest a simple and efficient strategy to obtain J constants from conventional ab initio wavefunction methods which is well-defined, and can be free from spin-contamination. We advocate using the $E^{\mathbf{HS}} - E^{\mathbf{HS-1}}$ energy gap for determining J , where $|\mathbf{HS-1}\rangle$ is taken to be the lower multiplicity spin state, adjacent to

$|\mathbf{HS}\rangle$ (i.e., $S^{\mathbf{HS}-1} = S^{\mathbf{HS}} - 1$). The expression for J is then given by,

$$J = -\frac{E^{\mathbf{HS}} - E^{\mathbf{HS}-1}}{2S^{\mathbf{HS}}}, \quad (4)$$

where $S^{\mathbf{HS}}$ is the total spin of the highest spin state, $|\mathbf{HS}\rangle$.

The choice of the $|\mathbf{HS}\rangle$ state is because one of its components is typically well described as a single configuration: the highest $M = S^{\mathbf{HS}}$ component is simply obtained by placing all the radical orbitals in the α space, while leaving the β space empty. There are $2S^{\mathbf{HS}}$ unpaired electrons. With a good single reference, the ferromagnetic $|\mathbf{HS}\rangle$ state can be calculated using standard electronic structure methods.

The choice of the $|\mathbf{HS}-1\rangle$ state is because its highest $M = S^{\mathbf{HS}} - 1$ component shows minimal strong correlations; a result of preserving as much ferromagnetic coupling as possible. We can see this in two complementary ways, which we discuss in turn. The first viewpoint is on the basis of an active space, where the natural active space is the set of orbitals defined by the half-occupied orbitals of the $|\mathbf{HS}\rangle$ state. To access the $M = S^{\mathbf{HS}} - 1$ component, $2S^{\mathbf{HS}} - 1$ α electrons are assigned to occupy the $2S^{\mathbf{HS}}$ α orbitals, while 1 β electron is assigned to the $2S^{\mathbf{HS}}$ β orbitals. Since there is only 1 hole in the α active space, and only 1 electron in the β active space, the number of essential configurations rises only linearly in the size of the active space, $2S^{\mathbf{HS}}$.⁴² This is a great contrast with the exponential dependence of the number of essential configurations on $2S^{\mathbf{HS}}$ in the lowest spin state, and is the essence of the advantage of our procedure.

The second viewpoint is in terms of the spin-flip approach,⁴³ which have been extensively developed for configuration interaction (CI) methods⁴³⁻⁴⁹, coupled cluster (CC) theory,^{50,51} and DFT.^{52,53} This approach provides a capable methodological framework which is well suited for describing energy differences between states of different multiplicity. Spin-flip methods begin from the single reference which is the highest multiplicity state of low energy. This reference is naturally $|\mathbf{HS}\rangle$ in our case. From the high-spin reference, spin-flipping excitations ($\alpha \rightarrow \beta$) are then performed to generate superpositions of lower spin determinants.

While the $|\mathbf{AF}\rangle$ state could be computed directly using SF if all possible spins are flipped, (and recent SF-CI methods, such as RAS-SF,^{48,49,54} SF-CAS(h,p),⁵⁵ and SF-CAS(S),⁵⁶ are, in fact, designed for flipping multiple spins), the computational cost of flipping all spins increases exponentially with number of unpaired electrons. However, if only the $M_s = S - 1$

TABLE I: Magnetic couplings, J , (cm^{-1}) for the dichromium complex, **A**, as computed with the SF-CAS method and different numbers of spin flips. The spin states used to compute a given J constant are specified in parentheses ($S \rightarrow S - 1$). The 6-31G* basis set was used for all SF-CAS calculations.

	Number of Configurations	Multiplicities Accessible	$J(3 \rightarrow 2)$	$J(2 \rightarrow 1)$	$J(1 \rightarrow 0)$
ROHF	1	7	–	–	–
1SF-CAS	36	5,7	-46.80	–	–
2SF-CAS	225	3,5,7	-46.80	-46.93	–
3SF-CAS	400	1,3,5,7	-46.80	-46.93	-46.97

component of the $|\mathbf{HS-1}\rangle$ state is sought, it suffices to perform a single excitation spin-flip (1SF) calculation, of which several realizations are already implemented.^{43–45,50,52,53,57} Single spin-flips describe the least entangled wave functions obtainable from $|\mathbf{HS}\rangle$ at vastly lower computational cost than accessing $|\mathbf{AF}\rangle$ by multiple spin flips.

The general result that a 1SF calculation might be used in place of an n -spin-flip calculation coincides with the strategy used within the multireference community in which only the two highest spin multiplets are used for computing J (when the HDVV Hamiltonian is valid).⁴² This reveals a slightly more general interpretation of the spin-flip methodology altogether. While the SF-CIS method (1SF) can be described as full CI for the “two electrons-in-two orbitals” problem, requiring only a single electron excitation as opposed to two excitations with non-spin-flip CI, the correspondence with multireference methods described above illustrates that SF-CIS might just as well be described as full CI for the $\langle S^2 \rangle = n(n - 2)/4$ state of the “ n electrons-in- n orbitals” problem.

To summarize, by properly exploiting the HDVV Hamiltonian for a bimetallic complex, one can use a single excitation spin-flip method to extract the J constant, regardless of the number of electrons on each metal. A schematic representation of this approach is depicted in Fig. 1, using an example with three unpaired electrons on each metal center.

FIG. 2: Bimetallic complex structures. **A** $[\text{Cr}_2(\text{NH}_3)_{10}(\text{O})]^{4+}$ has six unpaired electrons, with three on each metal. **B** $[\text{Fe}_2^{\text{II}}\text{OCl}_6]^{-2}$ has ten unpaired electrons, with five on each metal. **C** $[\text{Cr}_2(\text{NH}_3)_{10}(\text{OH})]^{5+}$ has six unpaired electrons, with three on each metal. **D** $[\text{GaCr}(\text{tren})_2(\text{CA}^{\text{sq,cat}})](\text{BPh}_4)_2(\text{BF}_4)$ has four unpaired electrons, three on Cr(III) and one on the oxidized ligand, L. **E** $[\text{Mn}(3\text{-MeOsalen})(\text{H}_2\text{O})(\mu\text{-NC})\text{Cr}(\text{bipy})(\text{CN})_3]\cdot\text{H}_2\text{O}$ has seven unpaired electrons, three on Cr(III) and four on Mn(III).

TABLE II: Magnetic couplings, J , (cm^{-1}) for the diiron complex, **B**, as computed with the SF-CAS method and different numbers of spin flips. The spin states used to compute a given J constant are specified in parentheses ($S \rightarrow S - 1$). Because the SF-CAS calculations grow very quickly in size for a (10,10) active space, calculations larger than 2SF-CAS were not done for this system. The 6-31G* basis set was used for all SF-CAS calculations.

	Configurations	Multiplicities Accessible	$J(5 \rightarrow 4)$	$J(4 \rightarrow 3)$	$J(3 \rightarrow 2)$	$J(2 \rightarrow 1)$	$J(1 \rightarrow 0)$
ROHF	1	11	–	–	–	–	–
1SF-CAS	100	9,11	-30.9	–	–	–	–
2SF-CAS	2025	7,9,11	-30.9	-31.1	–	–	–
3SF-CAS	14400	5,7,9,11	N/A	N/A	N/A	–	–
4SF-CAS	44100	3,5,7,9,11	N/A	N/A	N/A	N/A	–
5SF-CAS	63504	1,3,5,7,9,11	N/A	N/A	N/A	N/A	N/A

III. EXAMPLE CALCULATIONS

To illustrate the concepts put forth in this paper, we consider five bimetallic complexes. The experimental nuclear coordinates are used, and the structures are shown in Fig. 2. All calculations were performed with the Q-Chem program.^{64,65}

A. Configuration space size versus J value

In Tables I and II, we demonstrate how the number of spins flipped has a negligible effect on the resulting J couplings using the simplest spin-pure method, SF-CAS.

The first structure in Fig. 2, **A**, is a dichromium complex, which has two antiferromagnetically coupled oxo-bridged Cr(III) centers, each harboring three unpaired electrons. A direct calculation of the ground state requires one to move from the high spin heptet to the low spin singlet via three spin flips. In this way, the J value for this complex has previously been computed using several active-space 3SF-CI methods.^{49,56} However, as discussed above, if the HDVV Hamiltonian is a good model of the system, a simple 1SF calculation should be sufficient for extracting J . This is numerically demonstrated in Table I, where the 1SF-CAS, 2SF-CAS, and 3SF-CAS calculations are shown. Negligibly different J values are obtained from each pair of adjacent spin states. Given the dimensionality differences

TABLE III: Application of explicitly single spin flip methods to the five complexes shown in Fig. 2. Magnetic coupling constants, J , are given in cm^{-1} . SC indicates that results could not be obtained due to spin-contamination. The 6-31G* basis set was used for all but the DMRG results, which used customized basis sets as specified in Ref. 58

J	A: Cr-O-Cr B: Fe-O-Fe C: Cr-OH-Cr D: Cr-L E: Cr-CN-Mn				
	Spin-Complete				
SF-CAS	-46.8	-30.9	-2.6	-41.8	-0.2
SF-CAS(S)	-117.2	-145.2	-7.9	-160.8	-1.0
	Spin-Incomplete				
SF-CIS	-56.5	-33.2	-3.6	SC	SC
SF-CIS(D)	-111.6	-78.8	-6.7	SC	SC
EOM-SF-CCSD	-158.1	-118.4	-9.3	SC	SC
SF-DFT (50/50)	-165.5	-156.1	-10.0	SC	SC
DMRG	-165.9 ^a	-117.4 ^b	–	–	–
Experiment	-225 ^c	-112 ^d	-15.8 ^e	< -243 ^f	-2.8 ^g

^aActive space = (12,32) Reference 58.

^bActive space = (16,26) Reference 58.

^cReference 59.

^dReference 60.

^eReference 61.

^fReference 62.

^gReference 63.

between the different values of m_s (see Table I), it is clearly preferable to diagonalize the ab initio Hamiltonian in the $m_s = n - 1 = 2$ sub-block (1SF), rather than the $m_s = n - n = 0$ sub-block (3SF). The scheme in Fig. 1 illustrates the presented strategy for complex **A**.

The second molecule, **B**, is an antiferromagnetically coupled, oxo-bridged diiron complex.

Each iron center contains five unpaired electrons. Because the high spin reference has ten alpha electrons, accessing the singlet ground state requires five spin flips. This is a quintuple excitation operator, which, even if only performed within an active space as in SF-CAS, becomes a rather large number of configurations. The size of the configuration space for each number of spin flips is shown in Table II. This diiron complex provides an excellent example of the computational advantages afforded by being able to leverage the HDVV Hamiltonian assumption. Although the number of configurations required to directly compute the ground state in the 5SF-CAS method is 63504, the J constant can, alternatively, be obtained from a calculation comprised of only 100 determinants via a single spin flip from the 11-et reference.

B. Comparison of 1SF methods to experiment

To demonstrate the ability to obtain reasonably accurate results, we have used a variety of single spin-flip methods to compute the J -couplings for all the complexes shown in Fig. 2. In addition to complexes **A** and **B**, three additional complexes are included for the comparison to experiment. These are also shown in Fig. 2.

Complex **C** contains an antiferromagnetically coupled pair of Cr(III) centers. Compared to **A**, **C** has a weaker J -coupling due to the protonation of the oxo-bridge. The protonated oxygen disrupts the linearity of the bridge, resulting in decreased spin-coupling.

Complex **D** contains a Cr(III) center with three unpaired electrons, coupled to an oxidized ligand which contains a single unpaired electron. This example is different from the other systems in that one of the radical bearing units is neither a metal, nor a single atom. Nonetheless, the Heisenberg model can be used to understand the electronic structure of this complex.

The heterometallic complex **E** contains both a Cr(III) and a Mn(III), bridged by a cyano group. The extended separation between the metal centers reduces the spin-coupling.

In Table III, the J -couplings are given for the complexes in Fig. 2 using a variety of single spin-flip methods. The first two methods are based on ROHF orbitals and are completely spin-pure, while the remaining methods are based on UHF orbitals, and are not generally spin-pure. The spin-pure and non-spin pure methods will be discussed in turn.

The first two spin-pure methods, SF-CAS and SF-CAS(S),⁵⁶ are actually capable of performing multiple spin-flips. However, the results here only include calculations in which

one spin was flipped. Thus, the computational advantage of only flipping one spin made these calculations very efficient. For each of the complexes, SF-CAS significantly underestimated the J values. Containing only excitations within the unpaired orbitals, SF-CAS provides a poor description of the ionic configurations, a fact which is well documented.⁴² SF-CAS(S) is a perturbative extension of SF-CAS in which single excitations outside of the singly-occupied orbitals are allowed to couple to the determinants in the SF-CAS perturbatively.⁵⁶ For SF-CAS(S) calculations consisting of only a single spin-flip, this represents a second-order approximation to the SF-XCIS method. As seen in Table III, the perturbative singles correction has a significant effect, and enhances all the J -couplings considered. With the exception of **B**, the SF-CAS(S) still underestimates the experimental values, but to a much lesser degree than SF-CAS.

The remaining wavefunction methods, SF-CIS, SF-CIS(D), and EOM-SF-CCSD, have neither spin-pure orbitals, nor spin-complete determinant expansions. As a result, spin-contamination can become a problem, making it difficult or impossible to obtain J -couplings, since it can become impossible to label a given state as being to a single spin multiplicity.⁷³

For complexes **A-C**, the observed levels of spin-contamination happened to be negligible. This allowed the spin-incomplete methods to be used for computing J . For complexes **D** and **E**, spin-contamination was extensive and prevented J from being obtained.

The SF-CIS method is a purely one electron transition method, being comprised of single excitations from all occupied α orbitals, to all unoccupied β orbitals. This includes the subset of configurations that are present in the 1SF-CAS, in addition to excitations which move α electrons out of the magnetic orbitals, and β electrons into the magnetic orbitals. However, it is clear that these additional excitations should not contribute too significantly. As such, the SF-CIS results for **A-C** are quite similar to the SF-CAS results. Furthermore, inspection of the $\langle S^2 \rangle$ expectation values for the SF-CIS wavefunctions indicate minimal mixing of this non-spin-complemented excitations. For **A**, the J constant is determined from the energy gap between the heptet and the quintet. Proper spin eigenstates have $\langle S^2 \rangle$ values of 12 and 6, respectively. In comparison, the computed SF-CIS $\langle S^2 \rangle$ values are 12.07 and 6.04, indicating nearly zero spin contamination. Similarly, **C** has high spin and low spin $\langle S^2 \rangle$ values of 30.05 and 20.03, respectively, an almost perfect comparison with the expected values of 30 and 20. Unfortunately, the spin-incomplete models could not be used with **D** and **E** due to high levels of spin-contamination.

For systems capable of being qualitatively described by SF-CIS, the SF-CIS(D) method can be used to perturbatively include dynamical correlation energy to refine J . In **A-C**, dynamical correlation from SF-CIS(D), brings the experimental and theoretical J values into better agreement. A comparison of the SF-CIS(D) results with EOM-SF-CCSD,^{44,45,50} provides insight into the accuracy of the perturbative SF-CIS(D) correction. Table III reveals that while SF-CIS(D) recovers a fair amount of the electron correlation component of J , there is still a non-trivial difference between SF-CIS(D) and EOM-SF-CCSD. However, even at the EOM-SF-CCSD level, complex **A** is still underestimated, compared to the experimental values. This is likely due to the small, 6-31G* basis set used for these results.

Although this paper focuses primarily on the application of wavefunction methods for computing J constants, the spin-flip framework admits a DFT formulation as well.^{52,53,57} Because time-dependent DFT contains only single excitations, SF-DFT has been limited to computing only singlet/triplet or doublet/quartet energy gaps directly.⁶⁶⁻⁶⁹ However, as we have already demonstrated, with the help of a HDVV Hamiltonian, J constants can be computed from single spin-flip calculations. SF-DFT is no exception, and as a simple example, we also report SF-DFT results in Table III using the 50% exact exchange functional recommended in the original SF-DFT paper.⁵⁷ For the molecules which are not plagued by spin-contamination, SF-DFT offers similar accuracy to the more expensive SF-CIS(D). However, as with BS-DFT, the choice-of-functional degree of freedom is still present.

IV. DISCUSSION AND CONCLUSIONS

In this paper, we highlight a dramatic shortcut that can be taken when using spin-flip methods for computing magnetic coupling constants of bimetallic complexes. For cases where a Heisenberg Hamiltonian applies, the well known Landé interval rule allows J to be computed from any two adjacent spin-states. This enables one to compute J from the energy gap between the highest spin, S , state, and the $S - 1$ state. These are exactly the states described from a one spin-flip excitation, which are the simplest and least computationally demanding SF methods. Consequently, one spin-flip CI calculations can be used to compute J , regardless of the number of electrons on the spin-coupled metal sites, with no need to flip larger numbers of spins at exponentially increasing cost. This approach is a well defined analog of the popular BS-DFT approaches that is spin-pure (if the corresponding SF methods

are also spin-pure).

The results in this paper have the immediate consequence that currently developed spin-flip methods can be used for a broader range of problems, and provides a renewed motivation for the development of new spin-pure spin-flip methods, the most obvious of which would be an extension of the SF-XCIS method⁴⁷ for dealing with asymmetric spin determinants.⁷⁴ The need for spin-pure spin-flip methods is especially highlighted by the problems with spin-contamination in complexes **D** and **E**.

An additional benefit of this approach is that the extrapolated ground state $|\mathbf{AF}\rangle$ energy can be written as a linear combination of the reference $|\mathbf{HS}\rangle$ energy and the 1SF-CI energy, which makes geometry optimizations of the ground state $|\mathbf{AF}\rangle$ state immediately possible, provided that the 1SF-CI method has gradients available.

Of course, since the Heisenberg Hamiltonian is only a phenomenological model, there may be interactions missing in Eq. 1, but present in the ab initio Hamiltonian (low-lying non-Hund states, zero-field splitting), which create deviations from the Landé predicted energy gaps. Although, the ability of experimentalists to successfully obtain quality fits of the HDVV Hamiltonian to experimental data is supportive of the underlying model, if an adequate fit cannot be obtained, additional interactions (such as those with non-Hund states), which define a biquadratic Heisenberg Hamiltonian,⁷⁰⁻⁷² can be included into the HDVV Hamiltonian which depend quadratically on the local spin moments.

$$H = -2J\hat{S}_a\hat{S}_b + j(\hat{S}_a\hat{S}_b)^2 \tag{5}$$

This contains two parameters, and so one would minimally need to perform a 2SF-CI calculation, to have enough equations (three spin states) to fully parameterize the Hamiltonian. A 2SF-CI calculation is still computationally efficient compared to flipping all spins when large active spaces are needed, and multiple two spin-flip methods have been implemented.^{48,51} However, the motivation for the current paper draws on the ubiquity of the simple HDVV Hamiltonian. As such, we put off a detailed consideration of non-Landé behavior for future work. Another very interesting topic is the generalization to larger numbers of radical sites.

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