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Computational Quantum Chemistry for Multiple Site Heisenberg Spin Couplings Made Simple: Still Only One Spin Flip Required

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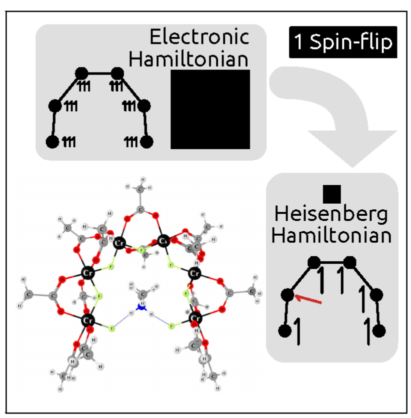
Abstract

We provide a simple procedure for using inexpensive ab initio calculations to compute exchange coupling constants, J_{AB}, for multiradical molecules containing both an arbitrary number of radical sites and an arbitrary number of unpaired electrons. For a system comprised of $2M$ unpaired electrons, one needs only to compute states having the $\hat{S}_z$ quantum number $M-1$. Conveniently, these are precisely the states that are accessed by the family of single spin-flip methods. Building an effective Hamiltonian with these states allows one to extract all the J_{AB} constants in the molecule. Unlike approaches based on density functional theory, this procedure relies on neither spin-contaminated states, nor non-unique spin-projection formulas. A key benefit is that it is possible to obtain completely spin-pure exchange coupling constants with inexpensive ab initio calculations. A couple of examples are provided to illustrate the approach, including a 4-nickel cubane complex, and a 6-chromium horseshoe complex with 18 entangled electrons.

Graphical TOC Entry



Keywords

Organometallic chemistry, Heisenberg Hamiltonian, Exchange coupling constant, Spin-flip, ab initio, DFT

Molecules and complexes containing multiple radical sites are important for a variety of current and future applications, including molecular magnetism,[1,2] redox non-innocent ligand chemistry,[3–5] and artificial photosynthesis.[6–9] Multiradical molecules are often characterized by electronic structures involving spatially separated regions of localized spin-density. Because the exchange interactions coupling the distant unpaired electrons decays exponentially with distance, different alignments of the local spins gives rise to many low-energy and quasidegenerate electronic configurations. Computationally, this renders conventional (or single reference) electronic structure methods generally unsuitable for modeling such systems, and thus multireference methods are often needed to obtain meaningful results.[10] However, multireference methods are typically too computationally demanding for application to multiradical complexes due to the relatively large size. Formally, multireference methods scale exponentially with the number of strongly correlated electrons. As a result, broken symmetry density functional theory (BS-DFT) has become the most widely used approach for studying this class of strongly correlated molecules.[11]

In BS-DFT, a shortcut is taken by mapping the ab initio Hamiltonian to the phenomenological Heisenberg-Dirac-Van Vleck (HDvV) spin hamiltonian,[12–14]

$$\hat{H}^{\mathrm{HDvV}} = -2\sum_{\mathrm{AB}} J_{\mathrm{AB}}\hat{S}_{\mathrm{A}}\hat{S}_{\mathrm{B}}, \tag{1}$$

where J_{AB} is the effective exchange coupling constant between radical sites A and B, and $\hat{S}_{\mathrm{A}}$ ($\hat{S}_{\mathrm{B}}$) is the local spin operator acting on site A (B). The sign of J_{AB} determines the nature of the coupling; $J_{\mathrm{AB}} > 0$ indicates high-spin or ferromagnetic coupling, and $J_{\mathrm{AB}} < 0$ indicates low-spin or antiferromagnetic coupling. It is thus J_{AB} which usually acts as the point-of-contact between theory and experiment.

By assuming that the energies of the broken-symmetry DFT solutions[1] correspond to the diagonal elements of the Heisenberg Hamiltonian matrix, the exchange coupling constants between all pairs of radical sites can be obtained by solving a generally over-determined set of linear equations.[15] While BS-DFT is arguably the most effective computational tool currently available, it has several deficiencies. Not only are approximate spin projections needed to partially remove the spin-contamination of the broken-symmetry solutions,[16–21] but also the projection formula needed to obtain J_{AB} is not unique, and multiple expressions have been put forth, all leading to different results.[11,22–25] Furthermore, there is a strong dependence on the density functional used. The fraction of exact exchange strongly affects the relative energies of the high-spin and broken-symmetry solutions, and different functionals can give qualitatively different results.[26–28]

Another source of ambiguity that is directly relevant to the topic of this paper can arise when large multiradical systems are studied. Because the number of unique broken-symmetry solutions (2^{N-1}) grows quickly with the number of radical sites (N), computing all BS-DFT solutions quickly becomes intractable. Thus, only a subset of the possible solutions are used, with the resulting J_{AB} values depending on the composition of the subset.[15,19,29]

In light of the computational complexities of multireference electronic structure methods and the stated deficiencies of BS-DFT, an alternative ab initio approach is desirable. In a recent paper,[30] we demonstrated how the spin-flip family of single reference electronic structure methods can be used in a very simple way to obtain exchange coupling constants for **bimetallic complexes** which follow Heisenberg Hamiltonian physics.

Spin-flip methods are single-reference electronic structure methods designed for describing strongly-correlated systems, and which have been extensively developed in the context of configuration interaction (CI) methods,[31–37] coupled cluster (CC) theory,[38,39] spin-pure active-space approaches,[34,36,37,40–44] and DFT.[45,46] The spin-flip strategy operates under the

[1] The broken-symmetry DFT solutions are obtained by allowing α and β spin-densities to localize independently on different regions of the molecule. These solutions correspond to the neutral configuration space which in which $\hat{H}^{\mathrm{HDvV}}$ represented, with the ionic configurations being treated implicitly by the delocalization of the magnetic orbitals in the BS-DFT solutions.

assumption that for many multiconfigurational (or strongly correlated) electronic states there exists a higher spin state which may be higher in energy, but which is well described with a single electronic configuration. By taking this high-spin configuration as a reference determinant, spin-flipping excitations can be applied to simultaneously excite and flip the spin of the electrons, providing a suitable configuration basis for describing the strongly correlated low-spin states of interest.

In our recent paper which focused on bimetallic complexes,[30] we highlighted the simple realization that since spin-flip configuration interaction methods are well suited for studying intermediate (or partially spin-flipped) spin states, one can focus exclusively on the two highest M_s manifolds, which have much smaller Hilbert spaces than the lower M_s manifolds. By using a single spin-flip (1SF) method, the energies of the highest spin state, $E(S)$, and second-highest spin state, $E(S-1)$, can be obtained directly, and in a much smaller configuration space than that of the lower spin (or fully spin-flipped) configuration space. Thus, for antiferromagnetically coupled molecules, this means that the ground state is never explicitly computed. The J_{AB} value is simply taken from the Landé interval rule,[47]

$$E(S) - E(S-1) = -2SJ_{\mathrm{AB}}, \tag{2}$$

using only the highest two spin states. Because only one spin-flip is needed, any of the already implemented (1SF) methods can be used. This is an extremely efficient alternative to the straightforward approach taken previously in which the maximum number of spin-flips are performed to obtain the ground state and the complete low-energy spectrum.[37,40,42,48] However, as the Landé interval rule only relates to a 2-site Heisenberg model, the described strategy only relates to bimetallic complexes.

In this work, we extend this 1SF approach to **multiradical systems** (molecules with more than two metals or radical sites). Instead of obtaining J_{AB} from only the eigenvalues of the 1SF calculation, we use both the 1SF eigenvalues and the eigenvectors to construct an effective Hamiltonian which maps directly to the Heisenberg Hamiltonian. From this effective Hamiltonian, the exchange coupling constants can be pulled directly from the off-diagonal elements.

The procedure for obtaining the effective Hamiltonian was first established by Bloch,[49,50] and has since been used extensively by Malrieu and coworkers for extracting effective Hamiltonian parameters from multireference CI calculations (see Ref. 10 and references therein). The detailed procedure is described below for a generic system comprised of M radical sites with N_x unpaired electrons on site x:

1. Converge the M lowest energy eigenvalues, $\mathbf{E}$, and eigenvectors, $\mathbf{b}$, using any 1SF method (i.e., SF-CIS, SF-DFT, EOM-SF-CCSD, 1SF-CAS, etc). Thus, the number of 1SF states required equals the number of radical sites.

2. Localize the molecular orbitals so that fractionally occupied orbitals are now assigned to specific radical sites. In this paper we have used Boys localization, although any localization scheme should work well for spin-coupled molecules for which the Heisenberg Hamiltonian is relevant. For spin-pure methods based on high-spin restricted open-shell Hartree-Fock (ROHF) references, only the singly occupied orbitals need to be localized. For methods based on unrestricted Hartree-Fock orbitals (UHF), a transformation to the corresponding orbital basis is first performed to identify a subset of "primarily singly-occupied orbitals".[2] It is then only these "primarily singly-occupied" orbitals which need to be localized.

3. Transform the 1SF eigenvectors, $\mathbf{b}$, into the localized orbital basis, and project onto the neutral determinant basis. In the localized orbital basis, the 1SF configurations

[2]These orbitals can be obtained by performing occupied-occupied and virtual-virtual rotations of the α and β orbitals, respectively. The transformation matrices used are the singular vectors of the matrix: $P_{ia}^{\alpha\beta} = \sum_{\mu\nu} C_{i\mu}^{\alpha} S_{\mu\nu} C_{a\nu}^{\beta}$, where $C^{\alpha/\beta}$ are the molecular orbital coefficient matrices and S is the atomic orbital overlap matrix.

can be partitioned into distinct neutral, $\mathbf{b_N}$, and ionic, $\mathbf{b_I}$, configurations:

$$\mathbf{b}^\intercal = \mathbf{b}_\mathbf{N}^\intercal || \mathbf{b}_\mathbf{I}^\intercal. \tag{3}$$

This projection simply amounts to deleting the ionic wavefunction components coming from spin-flipping excitations between different radical sites (i.e., $b_{i\bar{a},s}$ where i and $\bar{a}$ are localized on different radical sites). These ionic contributions must be small for validity of the $\hat{H}^{\text{HDvV}}$ model.

4. Orthogonalize the projected 1SF eigenvectors. The 1SF eigenvectors projected onto the neutral determinant basis, $\mathbf{b_N}$, are not generally orthogonal. Thus, to ensure a Hermitian effective Hamiltonian, we symmetrically orthogonalize the projected vectors.[50]

$$\tilde{\mathbf{b}}_\mathbf{N} = \mathbf{b_N} \left(\mathbf{b_N}^\intercal \mathbf{b_N}\right)^{-\frac{1}{2}} \tag{4}$$

5. Build an effective Hamiltonian in the symmetrically-orthogonalized neutral determinant basis, using the ab initio 1SF excitation energies.

$$\mathbf{H}^{\text{eff}} = \tilde{\mathbf{b}}_\mathbf{N} \mathbf{E} \tilde{\mathbf{b}}_\mathbf{N}^\intercal \tag{5}$$

6. Block diagonalize $\mathbf{H}^{\text{eff}}$ site-by-site, and project $\tilde{\mathbf{b}}_\mathbf{N}$ onto local high-spin ground state. If any of the M radical sites have more than one unpaired electron, then $\mathbf{H}^{\text{eff}}$ is rank-deficient. This is because $\mathbf{H}^{\text{eff}}$ has a rank of M (only M energies were used in Eq. 5), but a dimension equal to the total number of unpaired electrons ($\sum_x N_x$).

7. Form a new effective Hamiltonian, $\tilde{\mathbf{H}}^{\text{eff}}$, in this local ground state basis and obtain the exchange coupling constants via:

$$J_{\text{AB}} = -\frac{\tilde{H}^{\text{eff}}_{\text{AB}}}{2\sqrt{S_\text{A} S_\text{B}}} \tag{6}$$

where S_{A} is the total spin (half the number of unpaired electrons) on site A.

Note that since each J_{AB} parameter is obtained from a distinct effective Hamiltonian matrix element, the sign can be either positive or negative, permitting application to ferromagnetic, antiferromagnetic, or mixed ferro/antiferromagnetic systems. In Fig. 1, a schematic representation is provided for the steps described above. An Octave[51] script which takes the raw data provided by the ab initio calculations to extract the J_{AB} values is provided in the supplementary information (along with two sets of data files). All ab initio spin-flip calculations have been performed using a development version of QChem.[52] BS-DFT calculations have been performed starting from the molecular orbital guesses provided by the "Fragmo" guess in QChem.[53] As the goal of this paper is to demonstrate the efficient description of static correlation, and not dynamical correlation which is known to converge slowly with one electron basis set size, we have used the relatively small Ahlrich's VDZ basis set for the results in this paper.[54]

In a recent experimental study investigating the synthesis and characterization of molecular examples of finite one-dimensional spin-segments, Baker et al.[55] measured the exchange coupling constants of a family of molecular chains. These systems involve a quasi-one dimensional curved chain of Cr(III) atoms, taking the shape of a "horseshoe".

As depicted in Fig. 2, there are six Cr(III) atoms, each with three unpaired electrons. Thus a direct ab initio calculation of the ground state would be extremely expensive, requiring nine spin-flips to treat 18 strongly correlated electrons. Alternatively, following the procedure demonstrated above and in Fig. 1, we can obtained J_{AB} values from only a simple 1SF calculation, and starting from the single configurational high spin (19-et) Hartree-Fock reference.

As mentioned above, the strategy being described is general for any 1SF method. For demonstrative purposes, we will use our recently developed active-space based spin-flip methods, SF-CAS, SF-CAS(h,p), and SF-CAS(S).[41,42] The first method, spin-flip complete active-space (SF-CAS), is simply an nSF-CI method (where n is the number of spin-flips) for which

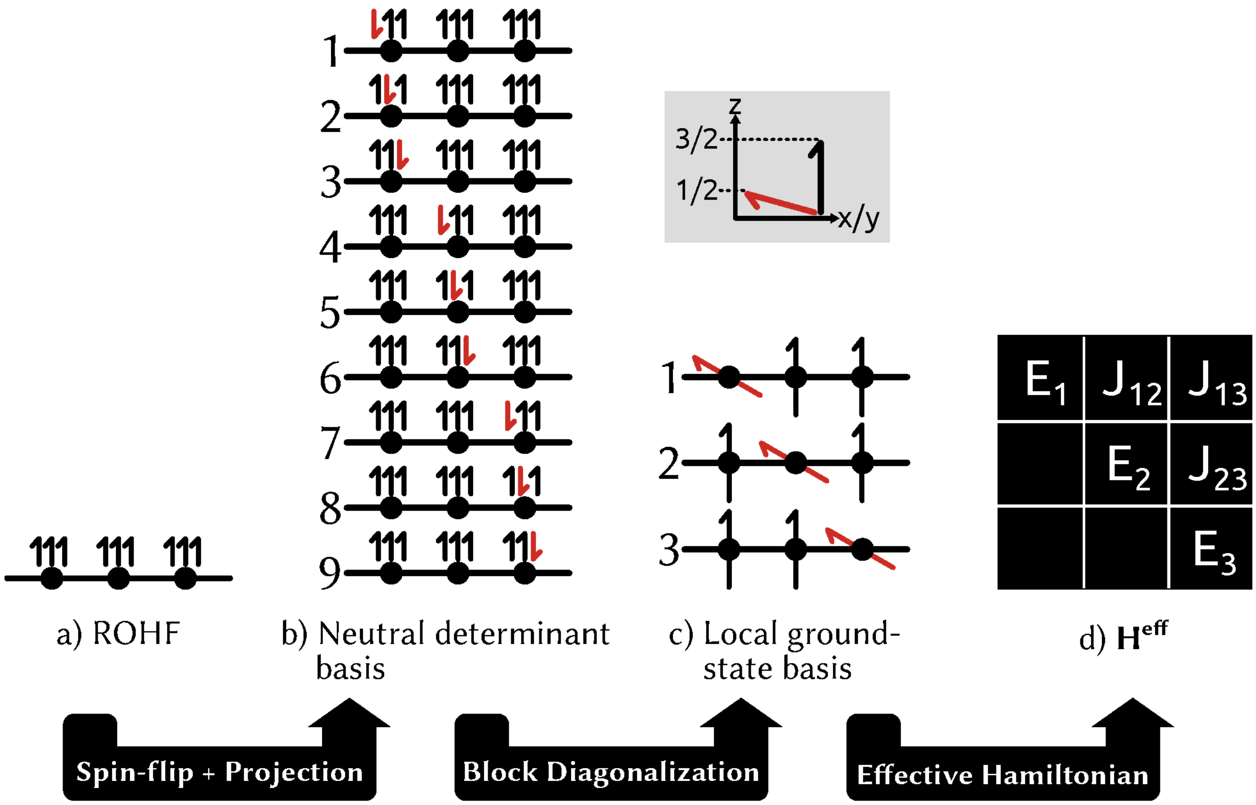


Figure 1: Schematic representation of the procedure for extracting exchange coupling constants from 1SF calculations for a molecule. a) Start with the Boys localized ROHF orbitals. b) After projection onto $\tilde{\mathbf{b}}_{\mathbf{N}}$ the three original 1SF eigenstates are now linear combinations of nine electronic configurations. c) After block-diagonalization, the three original 1SF eigenstates are now linear combinations of three M_s configurations of local quartet states: $\left|\frac{1}{2},\frac{3}{2},\frac{3}{2}\right\rangle$, $\left|\frac{3}{2},\frac{1}{2},\frac{3}{2}\right\rangle$, and $\left|\frac{3}{2},\frac{3}{2},\frac{1}{2}\right\rangle$. The tilted red arrows indicate the $M_s = 1/2$ microstate of the local quartet spin states. d) In the local eigenstate basis, the effective Hamiltonian is now full rank, and contains the exchange coupling constants, J_{AB}, as off-diagonal elements divided by $-2\sqrt{S_{\mathrm{A}}S_{\mathrm{B}}} = -3$.

all excitations occur only in an orbital active-space (i.e., the singly occupied ROHF orbitals). The second and third methods, SF-CAS(h,p) and SF-CAS(S), are methods which include perturbative corrections to SF-CAS. SF-CAS(h,p) includes single excitations into (*hole* excitations), and out-of (*particle* excitations), the active-space.[41] SF-CAS(S) includes these, as well as, all possible single excitations including the direct promotions from doubly occupied orbitals to virtual orbitals.[42] Although the SF-CAS based methods are capable of performing n spin flips, our present implementation would not be tractable for nine spin flips. Therefore, the 1SF strategy introduced here is vital to permit this application.

One benefit of using these methods is that, by construction, they are free from any spin-contamination. By using ROHF orbitals, there is no orbital spin-contamination. By restricting the spin-flipping excitations to occur within the singly-occupied orbitals, there is no "configurational spin-contamination" (or spin-contamination arising from the neglect of spin-complementing configurations).

We have also performed SF-TDDFT calculations using the non-collinear kernel of Ziegler and coworkers (NC-SF-TDDFT).[46,56,57] These methods are based on unrestricted Kohn-Sham (UKS) orbitals, and do not restrict spin-flipping excitations to an active-space. Thus, the NC-SF-TDDFT results suffer from both orbital and configurational spin-contamination, in addition to the deficiencies inherent in the underlying density functional. Nonetheless, the effective Hamiltonian strategy described in this paper still admits input from a NC-SF-TDDFT calculation. The results are tabulated in Table 1.

From Table 1, one immediately can recognize the well documented underestimation of the antiferromagnetic contributions to the SF-CAS exchange coupling constants.[42,43] Here, SF-CAS incorrectly predicts the Cr(III) atoms to be coupled ferromagnetically ($J_{\text{AB}} > 0$). By including state-specific orbital relaxation effects perturbatively via *hole* and *particle* excitations, SF-CAS(h,p) corrects the SF-CAS results and yields antiferromagnetic coupling constants ($J_{\text{AB}} < 0$). By adding the complete set of single excitations, SF-CAS(S) further improves the J_{AB} values, bringing them closer to the experimental values, although a more

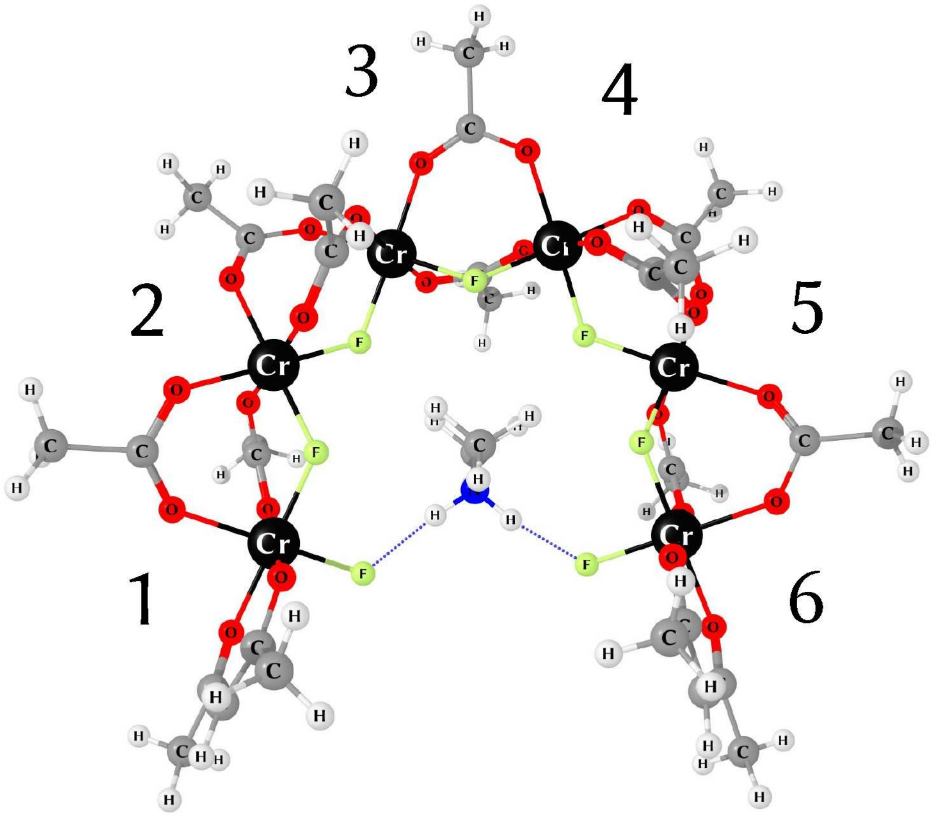


Figure 2: Molecular structure for the Cr(III) "Horseshoe complex". Chromium atoms are numbered clockwise starting from the bottom left.

Table 1: Exchange coupling constants for the "Horseshoe complex" shown in Fig. 2. Experimental values reported are -5.65 cm^{-1} for J_{Outside} (J_{12}, J_{56}) and -5.89 cm^{-1} for J_{Inside} (J_{23}, J_{34}, J_{45}). While the effective Hamiltonian provides all J_{AB} values, the quasi-one dimensional structure ensures that the coupling between non-nearest neighbor Cr(III) atoms are negligible. Thus, only the nearest neighbor coupling constants are reported below. For the BS-DFT results, seven (nine) solutions were used, as described in the supplementary information.

		Spin-Pure		NC-SF-TDDF			BS-DFT			
	SF-CAS	SF-CAS(h,p)	SF-CAS(S)	PBE0	5050	B3LYP	PBE0	5050	B3LYP	Exp.
J_{12}	0.51	-0.64	-2.30	-4.43	-2.28	-8.74	-5.74(-5.76)	-2.56(-2.57)	-7.99(-8.01)	–
J_{23}	0.52	-0.59	-2.20	-4.38	-2.35	-8.17	-5.82(-5.80)	-2.69(-2.68)	-7.88(-7.86)	–
J_{34}	0.57	-0.64	-2.37	-4.17	-2.39	-8.33	-5.69(-5.72)	-2.63(-2.64)	-7.93(-7.96)	–
J_{45}	0.42	-0.53	-1.90	-5.02	-2.71	-9.27	-6.48(-6.47)	-8.27(-8.26)	-8.73(-8.72)	–
J_{56}	0.43	-0.54	-1.94	-4.33	-2.27	-8.19	-5.67(-5.68)	-3.62(-3.62)	-7.68(-7.69)	–
J_{Outside}	0.47	-0.59	-2.12	-4.38	-2.28	-8.47	-5.87(-5.81)*	-4.12(-3.83)*	-7.97(-7.96)*	-5.65
J_{Inside}	0.50	-0.59	-2.15	-4.52	-2.48	-8.59	-5.98(-5.99)*	-4.44(-4.47)*	-8.17(-8.18)*	-5.89

*Values are not the average of the individual couplings, but rather solutions obtained by directly fitting the BS-DFT energies to a 2J model.

complete treatment of dynamical correlation would be needed to obtain more quantitative agreement.

Looking at the NC-SF-TDDFT results in Table 1, one quickly recognizes one of the most problematic aspects of using DFT; different functionals can provide very different results. However, even with this variance, the results for the three tested functionals[3] don't fall too far from the experimental values. Comparing the NC-SF-TDDFT results to the values obtained from BS-DFT,[4] one finds that the spin-flip approach provides similar results as the BS-DFT method, but without the previously described probilems of arbitrary projection formulas and configuration selection. We note that although we have used Ziegler's non-collinear kernel for the NC-SF-DFT here, the effective Hamiltonian procedure describe in this paper should also be possible for other types of SF-DFT, some of which are designed with general spin-flip excitation operators.[58,59]

Qualitatively, it is interesting to note that while Baker et al. obtained a good fit using only two J_{AB} values (J_{Outside} for the couplings on the tips and J_{Outside} for the couplings inside), our calculations indicate that the coupling between the tips (J_{12} and J_{56}) may differ by 10-15%. Even though NC-SF-DFT and BS-DFT seems to accurately reproduce the gap between the two model parameters, J_{Inside} and J_{Outside}, the variance among the individual parameters suggests that none of the theoretical methods actually support a two J_{AB} model. Furthermore, although we are only reporting the five nearest neighbor J_{AB} values, the single spin-flip results provide us with all possible (including non-nearest neighbor) pairwise couplings. The J_{AB} values for non-nearest neighbor couplings were all near zero, thus suggesting the intuitive five J_{AB} model. Many more BS-DFT configurations would need to be obtained to yield this same information.

[3] These three density functionals are not chosen to be broadly representative or even necessarily recommended. They simply act as demonstration that the effective Hamiltonian strategy can extract J_{AB} constants from DFT calculations as well, without relying on the broken-symmetry approach.

[4] In the table, the BS-DFT results have two values reported. The first value is obtained using only seven configurations: the high spin state, $\left|\frac{3}{2}\frac{3}{2}\frac{3}{2}\frac{3}{2}\frac{3}{2}\frac{3}{2}\right\rangle$, and all six single site flipped configurations, i.e., $\left|\frac{3}{2}\frac{-3}{2}\frac{3}{2}\frac{3}{2}\frac{3}{2}\frac{3}{2}\right\rangle$. The second value in parenthesis was obtained by adding two more double site-flipped configurations, namely $\left|\frac{-3}{2}\frac{-3}{2}\frac{3}{2}\frac{3}{2}\frac{3}{2}\frac{3}{2}\right\rangle$ and $\left|\frac{-3}{2}\frac{3}{2}\frac{3}{2}\frac{3}{2}\frac{3}{2}\frac{-3}{2}\right\rangle$.

Overall, SF-CAS(h,p), SF-CAS(S), and all the density functionals provide the correct sign of the exchange coupling constants for this molecule.

Obtaining J_{AB} constants from 1SF calculations provides a dramatic simplification compared to the direct ab initio calculation where the maximum number of spins are flipped. Of course, this strategy is only useful insofar as the extracted J_{AB} constants are reliable. While the best way to test this is to simply compare against experimentally obtained J_{AB} constants, this comparison is actually quite difficult to make. The reason is that most of the currently implemented spin-flip methods are not yet capable of reliably providing quantitative accuracy. Although SF-EOM-CCSD might well be sufficiently accurate, it is too computationally demanding to treat the large molecules in this letter. This means that any observed error in J_{AB} could be due to either the J_{AB} extraction procedure, or the underlying ab initio spin-flip method. Thus, in order to test the reliability of the extracted J_{AB} constants, one should make a comparison between the fully spin-flipped ab initio results and the 1SF parametrized Heisenberg Hamiltonian results. In other words, if we diagonalize $\hat{H}^{\mathrm{HDvV}}$ do we obtain a spectrum similar to the low-energy spectrum of the fully spin-flipped ab initio Hamiltonian?

To answer this question, we consider a relatively simple system for which the full ab initio calculation can be performed. In Fig. 3(a), an organometallic complex is shown which has a nickel-cubane core consisting of four Ni(II) centers, each with two unpaired electrons (3(b)). Since there are eight unpaired electrons, the high spin ROHF reference state is the single configuration nonet state. In order to access the full ab initio low-energy spectrum, a four spin-flip calculation (4SF-CI) is necessary. To diagonalize the 1SF parameterized $\hat{H}^{\mathrm{HDvV}}$ Hamiltonian, we used the open-source Fit-Mart software which was downloaded from Ref. 60.

In Fig. 3(c) a comparison is made between the state energies of the fully ab initio 4SF-CAS(S) calculation, and the diagonalization of the 1SF-CAS(S) parameterized $\hat{H}^{\mathrm{HDvV}}$ Hamiltonian. No discernible difference can be seen between the two data sets. This tells us two things:

1. The procedure for extracting the J_{AB} constants is reliable.

2. This particular complex is well-described by a $\hat{H}^{\mathrm{HDvV}}$ Hamiltonian.

While the approach outlined in this paper has been demonstrated to provide an extremely efficient alternative to the direct multiple spin-flip calculation, a number of limitations exist. First and foremost, the current approach is clearly only applicable for systems that are well described by a Heisenberg Hamiltonian. As a result, only molecules containing well-defined oxidation states and highly localized spin-densities can be studied. Furthermore, because the Heisenberg model assumes that each site has only a single electronic configuration which contributes to the complete electronic structure, (each radical site is in its local ground state), if any radical site has low-lying local excited states the simple Heisenberg model becomes suspect, and a biquadratic form must be considered.[61–63] Finally, as with any model Hamiltonian, any physical processes lying outside of the model will not be described and could lead to qualitative failures. A detailed analysis of many-body effects in magnetic systems has been conducted by Malrieu and coworkers and nicely summarized in Ref. 10. However, as the effective Hamiltonians are constructed by projecting ab initio wavefunctions onto a model space, one can monitor the relevance of the Heisenberg Hamiltonian by ensuring that the norms of the projected wavefunctions are close to one. Small norms act as a useful diagnostic, indicating that the model space is insufficient.

A second limitation is not related to the J_{AB} extraction procedure, but rather to the underlying ab initio method. First, for any 1SF method to be useful, the high-spin reference state must be well described. While this is very often true, Hartree-Fock sometimes does not provide a suitable set of orbitals for performing the subsequent SF-CI calculations.[5] DFT can be used to improve the situation, since the dynamical correlation provides a better set of high-spin orbitals. However, SF-DFT (both in the original[45] and non-collinear[46,57] variants) are sensitive to the chosen functional.

[5] Because the essence of the spin-flip approach assumes that a high-spin reference exists which is well described by a single configuration, a heavily spin-contaminated high-spin reference, or the presence of low-energy higher spin states are both harbingers of a poor reference state.

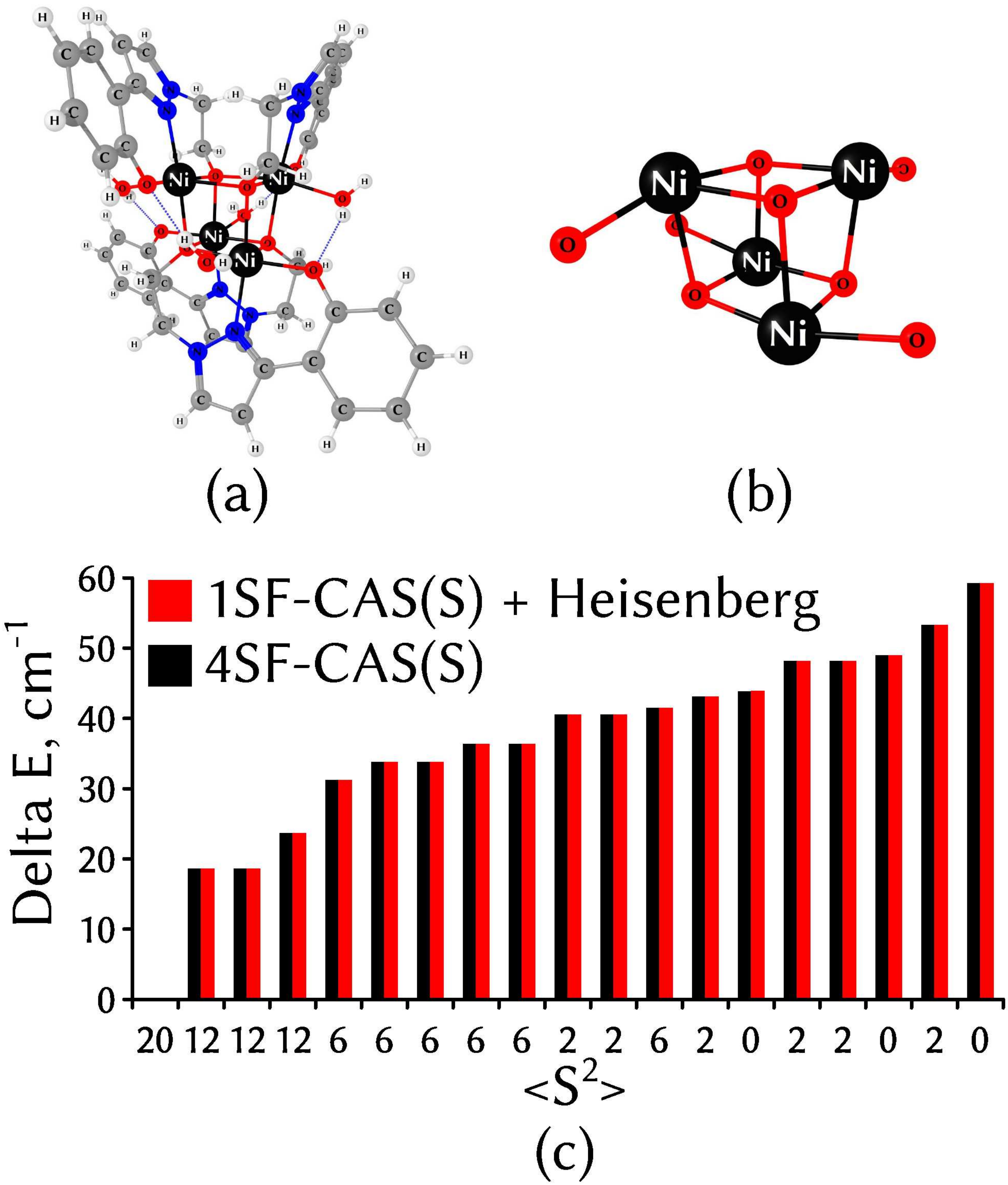


Figure 3: (a) Structure of Nickel complex. (b) Nickel-cubane core. (c) Comparison of the low energy spectrum taken from direct ab initio 4SF-CAS(S) calculations (gray) and the 1SF-CAS(S) + Heisenberg diagonalization (black). y-axis is Δ energy from ground state in cm^{-1}. x-axis is the $\langle S^2 \rangle$ for each state.

In conclusion, this letter serves to illustrate a very simple procedure for calculating exchange coupling constants for complexes containing several metal centers (or, more generally, several radical sites). It is shown that even with only single spin-flipping excitations, 1SF methods can be used to compute all exchange coupling constants in a molecule, regardless of both the total number of radical sites and total number of unpaired electrons per radical site. Thus, using rather inexpensive ab initio calcultions, it is possible to obtain completely spin-pure exchange coupling constants for molecules following Heisenberg physics. Diagonalizing the resulting Heisenberg hamiltonian gives explicit expressions for the energy levels (and their properties) of all lower spin states. The results obtained in this paper, provide fresh motivation for a new class of spin flip methods which are spin-pure, permit arbitrary numbers of unpaired electrons, and include dynamical correlation. Work in this direction is currently underway.

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Supporting Information Available

A simple Octave[51] script is provided which extracts the exchange coupling constants from the ab initio 1SF data (eigenvectors represented in a boys localized orbital basis, and the state energies). Also, cartesian coordinates are provided for both complexes in this letter. As BS-DFT calculations on multiradical complexes requires some choice about the configurations used, we have included (in a second Octave script) the data used for computing the BS-DFT exchange coupling constants in this paper. This material is available free of charge via the Internet at `http://pubs.acs.org/`.

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