# Magnetic Exchange Couplings from Noncollinear Perturbation Theory: Dinuclear Cu^{II} Complexes

Jordan J. Phillips[†] and Juan E. Peralta*[†,‡]

[†]Science of Advanced Materials, Central Michigan University, Mt. Pleasant, Michigan 48859, United States
[‡]Department of Physics, Central Michigan University, Mt. Pleasant, Michigan 48859, United States

ABSTRACT: To benchmark the performance of a new method based on noncollinear coupled-perturbed density functional theory [J. Chem. Phys. 138, 174115 (2013)], we calculate the magnetic exchange couplings in a series of triply bridged ferromagnetic dinuclear Cu^{II} complexes that have been recently synthesized [Phys. Chem. Chem. Phys. 15, 1966 (2013)]. We find that for any basis-set the couplings from our noncollinear coupled-perturbed methodology are practically identical to those of spin-projected energy-differences when a hybrid density functional approximation is employed. This demonstrates that our methodology properly recovers a Heisenberg description for these systems, and is robust in its predictive power of magnetic couplings. Furthermore, this indicates that the failure of density functional theory to capture the subtle variation of the exchange couplings in these complexes is not simply an artifact of broken-symmetry methods, but rather a fundamental weakness of current approximate density functionals for the description of magnetic couplings.
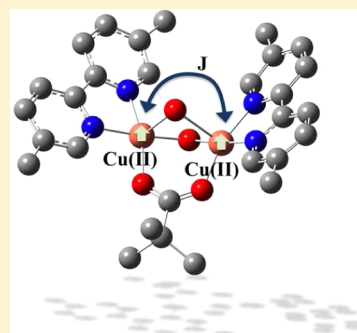
INTRODUCTION

Model spin Hamiltonians play an important role in the quantum mechanical description of magnetic systems, because they reduce the complicated electronic structure problem to a simplified description in terms of spin degrees of freedom only. This simplified description captures the low-lying energy spectrum for magnetic excitations, and it has the advantage of being both computationally more tractable and conceptually simpler. Probably one of the most well-known model spin Hamiltonians is the Heisenberg–Dirac Hamiltonian,[1,2] given by

$$\hat{H}_{HD} = -\sum_{i<j} J_{ij}\hat{S}_i \cdot \hat{S}_j \tag{1}$$

which describes the isotropic exchange-correlation (XC) interactions that couple the spin-moments of unpaired electrons residing on "spin-centers" S_i, S_j, in materials such as organic diradicals, ionic solids, and transition-metal (TM) complexes.[3] TM complexes have received a large amount of attention, as a number of applications have been proposed exploiting their unique properties,[4−6] and in this work we focus on the use of eq 1 in describing the magnetic properties of these systems.

As with any model Hamiltonian, its practical application requires that the parameters J_{ij}, termed magnetic couplings, are appropriately chosen. Magnetic coupling parameters are routinely determined *via* magnetochemistry studies, by fitting temperature-dependent magnetic susceptibility data. This methodology works well and is routinely applied to small TM complexes with few metals and/or high-symmetry. However, as complexes grow larger and more complicated, there quickly become more unique J_{ij}'s than can be rigorously

determined by fitting to susceptibility data. This difficulty can be summarized well by saying that analytical methods measure directly the magnetic properties of the system (e.g., magnetic susceptibility), and from that must *indirectly* infer the couplings J_{ij}. Here, theoretical methods can make a contribution, as their approach is essentially converse to that of magnetochemistry studies. In electronic structure calculations one is able to determine the couplings J_{ij} directly, and from those couplings indirectly infer the magnetic properties of the system. For example, once the J_{ij} parameters are calculated, then $\hat{H}_{HD}$ can, in principle, be diagonalized, thereby granting the magnetic ground-state of the system. Of course for large and complicated TM complexes the large dimension of $\hat{H}_{HD}$ may preclude direct diagonalization, but still, by knowing J_{ij}, it is possible to qualitatively rationalize the magnetic properties of the system. More importantly, by knowing the specific magnetic coupling pathways in a TM complex, researchers synthesizing these systems are able to make motivated structural perturbations, effectively allowing them to engineer novel molecular magnets.[7,8] Hence, magnetochemistry analysis and theoretical calculations may be considered complementary.

From this standpoint there is motivation to develop methods that allow for the practical and principled estimation of magnetic coupling parameters in TM complexes. Currently the standard method for determining J_{ij} in electronic structure calculations is by mapping differences in calculated total

energies onto the spin-states of $\hat{H}_{HD}$. For example, assuming the simple case of a dinuclear system with spin-centers S_a, S_b, one could, in principle, perform a calculation for a high-spin (HS) state with spin quantum number $S = S_a + S_b$ and low-spin (LS) state with $S = S_a - S_b$, and exploiting that $\hat{\mathbf{S}}_a \cdot \hat{\mathbf{S}}_b = 1/2 \, (\hat{S}^2 - \hat{S}_a^2 - \hat{S}_b^2)$ calculate the following energy-difference

$$
\begin{aligned}
E_{HS} - E_{LS} &= \langle \hat{H}_{HD} \rangle_{HS} - \langle \hat{H}_{HD} \rangle_{LS} \\
&= -\frac{1}{2} J (\langle \hat{S}^2 \rangle_{HS} - \langle \hat{S}^2 \rangle_{LS}) \\
&= -\frac{1}{2} J ((S_a + S_b)(S_a + S_b + 1) \\
&\quad - (S_a - S_b)(S_a - S_b + 1)) \\
&= -J(2S_a S_b + S_b)
\end{aligned}
\tag{2}
$$

yielding

$$
J = \frac{E_{LS} - E_{HS}}{2S_a S_b + S_b}, \quad S_a \geq S_b
\tag{3}
$$

Implicit to eq 3 is that the theoretical method used can obtain eigenstates of $\hat{S}^2$. This is not a trivial requirement, as excepting the HS state where all unpaired electrons are spin-aligned, LS eigenstates such as the open-shell singlet $(\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2}$ are intrinsically multideterminantal. While this presents no problem to methods founded on configuration interaction,[9] such methods are usually not amenable to the study of large polynuclear TM complexes. In contrast, a single Slater determinant formalism such as Kohn−Sham Density Functional Theory (KS-DFT)[10,11] offers a feasible methodology for the study of such systems because of its manageable computational scaling[12] and appreciable accuracy,[13] yet it is unable to rigorously describe multideterminantal states such as $(\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2}$. Noodleman's suggestion[14] was to consider in lieu of the LS state a broken-symmetry (BS) solution, given by $\uparrow\downarrow$, which Mouesca et al.[15] first and Dai and Whangbo[16,17] later independently showed for a general spin dimer affords the following relationship for J,

$$
J = \frac{E_{BS} - E_{HS}}{2S_a S_b}
\tag{4}
$$

The use of eq 4 in Hartree−Fock and KS-DFT has come to be called the spin-projected (SP) mapping. While the application of eq 4 to dinuclear systems is straightforward, there are many subtle issues involved when working in such a formalism. A solution such as $\uparrow\downarrow$ is a mixture of spin-states and is not an eigenstate of $\hat{S}^2$ or eq 1. For example, when $S_a = S_b = 1/2$ then $\uparrow\downarrow = [(\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2} + (\uparrow\downarrow + \downarrow\uparrow)/\sqrt{2}]/\sqrt{2}$, i.e. the BS solution is a mixture of singlet and triplet states. This has led some to argue[18] that, when approximate density functionals with self-interaction error are employed, the resulting BS wave function can have multideterminant character and hence include static correlation contributions to the total energy. In this line of reasoning, $E_{BS} \approx E_{LS}$, and eq 3 should be employed instead of eq 4. Such an approach has been termed "nonprojected" (NP). This led to strong discussions,[19,20] and the matter may fairly be characterized as unresolved since SP and NP mappings are both still commonly used in the literature.[21] Furthermore Neese, in a meticulous analysis,[22] observed that, due to the orthogonality of $\uparrow$ and $\downarrow$ spin−orbitals, the BS solution possesses more variational flexibility than the HS solution, and it is this artificial variational freedom that allows

unrestricted Hartree−Fock to predict antiferromagnetic coupling.

These issues have already been discussed extensively,[3,23,24] and we do not wish to contribute further to this debate. Our purpose in this work is to show that it is possible to accurately calculate magnetic coupling constants in dinuclear systems (and polynuclear) without recourse to BS solutions. Recently we introduced a new method for calculating J_{ij} based on noncollinear coupled-perturbed KS-DFT.[25] This method takes as input a standard collinear HS zeroth-order KS-DFT solution, then calculates the first-order noncollinear response of the spin density from a transversal spin-torque perturbation. From a principled standpoint, the advantage of this method is that the magnetic coupling is determined purely by the information contained in the rigorously describable HS state. From a practical standpoint, for polynuclear systems the benefit of this method is that the number of coupled-perturbed calculations needed to determine J_{ij} grows *linearly* with the number of spin-centers,[26] in contrast to BS energy-differences methods where it grows quadratically. In principle, our method introduces no new approximations beyond those implied by $\hat{H}_{HD}$, and thus recovers in an ideal Heisenberg system magnetic couplings identical to those determined by traditional energy differences. To validate this last point, in this work we apply our methodology to a set of dinuclear ferromagnetic Cu^{II} complexes that have been recently synthesized.[27] To complement the set of ferromagnetic complexes studied in this work, we also consider two antiferromagnetic complexes, BISDOW and PATFIA, which feature strong and weak antiferromagnetic interactions, respectively.

For completeness we briefly review the theory of this noncollinear methodology[25] for dinuclear systems. Beginning with the simple observation that

$$
\langle \hat{H}_{HD} \rangle = -J\mathbf{S}_a \cdot \mathbf{S}_b = -JS_a S_b \cos(\theta)
\tag{5}
$$

it is straightforward to show[28] that the magnetic coupling can be defined as the second-order change in the Kohn−Sham energy with respect to spin-rotations from the HS state as

$$
J = \frac{1}{S_a S_b} \frac{d^2 E_{KS}}{d\theta^2} \bigg|_{\theta=0°}
\tag{6}
$$

The simple idea of our method is to treat θ as a constraint as in Dederich's constrained-DFT (C-DFT),[29] but instead of actually performing C-DFT calculations we consider the constraint-potentials to be perturbations and thereby approach the C-DFT problem with the machinery of coupled-perturbed KS-DFT.[30−32] This allows us to calculate eq 6 analytically and affords a method of defining J purely on the basis of the physical information contained in the HS state. To constrain the relative angle of a pair of metal atoms, we introduce the constraint condition

$$
\frac{\mathbf{s}_a \times \mathbf{s}_b}{s_a s_b} = \theta \hat{\mathbf{y}}
\tag{7}
$$

where $\mathbf{s}_a$, $\mathbf{s}_b$ are the local-spin[33,34] vectors of the ath, b^{th} metal atoms, θ is a small angle, and $\hat{\mathbf{y}}$ is an axial-vector chosen for simplicity to lie along the Cartesian y-axis such that the local-spins are confined to the x−z plane. Finding the stationary points of the Kohn−Sham energy subject to this additional constraint yields a modified single-particle eigenfunction
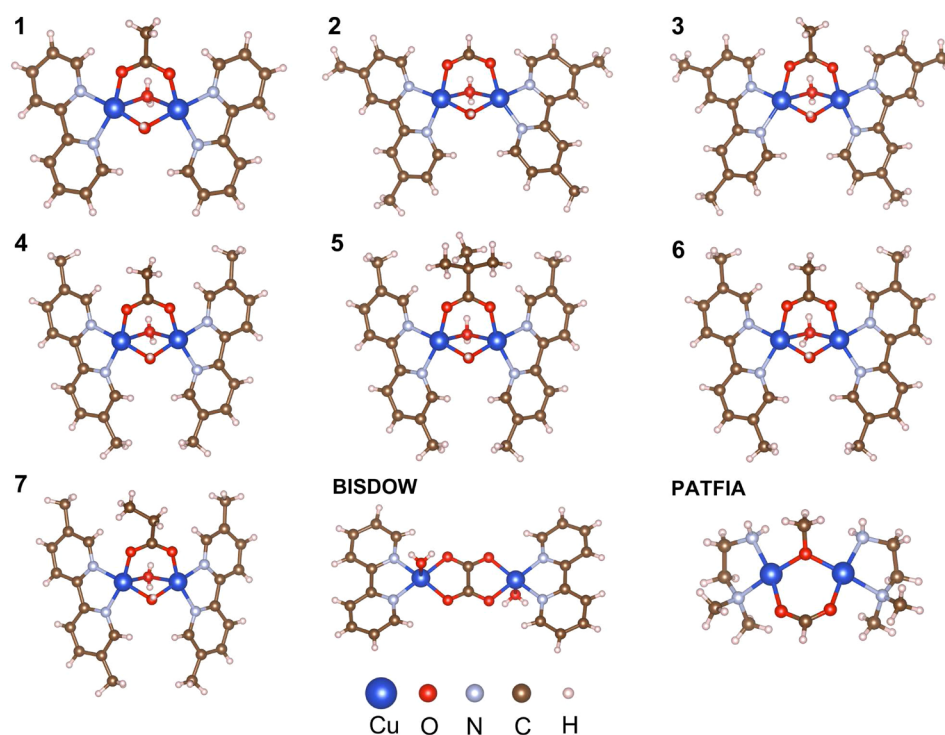
Figure 1. Molecular schemes for the nine dinuclear Cu^{II} complexes considered in this work. Complexes **1**−**7** are taken from Wannarit et al.,[27] while BISDOW and PATFIA are from Valero et al.[48] Images of the molecular structures were generated by VESTA.[49]

problem which, in the case of a collinear HS reference solution, simplifies to

$$(\hat{h} + \hat{J} + \hat{V}_{XC} - \lambda\hat{t})\psi_i = \varepsilon_i\psi_i$$

$$\hat{t} = -\frac{\hat{\sigma}_a^x}{s_a} + \frac{\hat{\sigma}_b^x}{s_b} \tag{8}$$

where $\hat{\sigma}_a^x$, $\hat{\sigma}_b^x$ are local-spin operators[33,34] acting on spin-centers a and b respectively, and λ is a Lagrange multiplier. By considering λ as "small" we may solve the coupled-perturbed equations thereby obtaining $d^2E_{KS}/d\lambda^2$, the reciprocal of which grants the magnetic coupling via

$$J = \frac{1}{S_aS_b}\frac{d^2E_{KS}}{d\theta^2}\bigg|_{\theta=0°} = \frac{1}{S_aS_b}\left(\frac{d^2E_{KS}}{d\lambda^2}\right)^{-1}\bigg|_{\lambda=0} \tag{9}$$

For a derivation of eqS 8 and 9 we refer the reader to ref 25. The simple and physically intuitive reasoning behind eq 9 is that for small relative angles from collinearity the energy will be quadratic in θ, $E(\theta) = 1/2\ k\theta^2$, while the constraint-torque required to maintain this rotation will grow linearly as $\lambda = k\theta$, where $k = JS_aS_b$ is the torsion constant. By substitution it is simple to show $d^2E/d\lambda^2 = 1/k = (d^2E/d\theta^2)^{-1}$. Therefore, in eq 9 the magnetic coupling is defined as the "stiffness" of the spin density against the torsional deflection arising from a torque constraint field. We think this definition is attractive from a principled standpoint, as it is free from the empirical and system-dependent rationalizations often present when calculating J using BS energy-differences in its various projected schemes.[18,35]

From eqs 7 and 8 it is obvious that the concept of a local-spin underpins much of our methodology. A pertinent question to ask then is the following: To what extent does the basis-set dependence of spin-populations[36] undercut the principled

nature of our methodology? Furthermore, because in a coupled-perturbed calculation the first-order occupied orbitals are constructed as a linear-combination of the zeroth-order virtual orbitals and since larger basis sets have larger virtual spaces, it is also relevant to ask if the accuracy of our methodology will intrinsically carry a greater basis set dependence than traditional BS energy differences. In answer to both of these questions, we will show in this work that, remarkably, the magnetic couplings predicted by our methodology are essentially identical to those of spin-projected BS energy differences for both large and small basis sets. This validates the principled nature of our method and also provides a unique justification for using the spin-projected approach over other projection schemes in an energy-differences calculation.

In closing this section it is worth noting that other methods have been proposed that allow one to calculate J while avoiding BS solutions. For example, spin-flip time-dependent[37] and constricted-variational[38] DFT begin with the ↑↑ state and by spin-flip (de)excitations construct $1/\sqrt{2}(↑↓ - ↓↑)$ and $1/\sqrt{2}(↑↓ + ↓↑)$, thereby calculating J by singlet−triplet energy differences.

■ COMPUTATIONAL DETAILS

All calculations reported here were carried out using an in-house modified Gaussian Development Version,[39] using a hybrid of LDA (Slater exchange and Vosko, Wilk, Nusair correlation)[40,41] given by $E_{XC} = aE_{HF}^X + (1 - a)E_{LDA}^X + E_{LDA}^C$, where $a = 0.3$. When calculating magnetic couplings, any type of functional (LDA, GGA, M-GGA) can show reasonable accuracy when admixed with around 30%HFX.[37,42−47] To investigate the basis-set dependence of our methodology for the Cu^{II} complexes, calculations are performed with a series of Pople basis sets given by: (i) 3-21G on all atoms; (ii) 6-31G on all atoms; (iii) 6-31G* on all atoms; and (iv) 6-311+G* on Cu,

Table 1. Magnetic Couplings Calculated with LDA+30%HFX for different basis-sets[a]

	3-21G			6-31G			6-31G*			6-311G*			
	J^{HS}	$J^{\Delta E}_{SP}$	$J^{\Delta E}_{NP}$	J^{HS}	$J^{\Delta E}_{SP}$	$J^{\Delta E}_{NP}$	J^{HS}	$J^{\Delta E}_{SP}$	$J^{\Delta E}_{NP}$	J^{HS}	$J^{\Delta E}_{SP}$	$J^{\Delta E}_{NP}$	J_{exp}
1	56.9	56.8	28.4	120.9	121.1	60.6	137.1	138.1	69.0	171.6	173.5	86.7	102
2	54.7	54.4	27.2	116.9	116.9	58.4	132.9	135.4	67.7	172.1	171.5	85.8	73
3	58.3	58.1	29.1	122.1	122.3	61.1	138.3	138.6	69.3	174.8	174.6	87.3	90
4	57.2	57.1	28.6	120.0	120.4	60.2	136.9	137.2	68.6	170.9	172.5	86.2	104
5	53.5	52.6	26.3	118.4	118.5	59.3	136.9	137.3	68.6	173.6	174.8	87.4	99
6	54.9	55.1	27.6	122.4	122.7	61.4	141.0	142.2	71.1	187.4	180.1	90.1	92
7	60.6	60.7	30.4	123.2	123.6	61.8	139.3	139.8	69.9	174.5	175.7	87.8	103
BISDOW	−218.9	−218.3	−109.1	−355.9	−350.4	−175.2	−402.8	−394.2	−197.1	−488.3	−475.6	−237.8	−382
PATFIA	−33.1	−33.0	−16.5	−14.5	−14.1	−7.0	−22.7	−22.2	−11.1	−8.8	−8.1	−4.0	−11

[a]Here J^{HS} is the coupling determined from eq 9, $J^{\Delta E}_{NP}$ is the coupling determined from eq 3, and $J^{\Delta E}_{SP}$ is the coupling determined from eq 4. All quantities are in units of cm^{-1}.

with 6-311G* on all other atoms (for brevity this will be denoted as 6-311G* elsewhere in this work). All calculations are performed employing pure d and f functions (Gaussian keyword "5d 7f"), without symmetry ("nosymm"), and the numerical integration is done with a pruned grid of 99 radial shells and 590 angular points per shell ("grid=ultrafine"). The convergence criteria employed are as follows: the reference zeroth-order calculations are converged to 10^{-10} Hartrees, 10^{-10} RMS variation in the density matrix, and 10^{-8} maximum allowed variation in any element of the density matrix, while the first-order calculations are converged to 10^{-8} RMS variation in the first-order commutator matrix, with max allowed variation in the analytic second derivatives of 1 Hartree/λ^2 (typical second derivatives values are of order 10^3 Hartrees/λ^2 for the systems considered in this work).

We consider nine dinuclear Cu^{II} complexes in this work. Complexes **1−7** are taken from Wannarit et al.,[27] while BISDOW and PATFIA are from Valero et al.[48] **1−7** are all ferromagnetic and feature subtle variations in their measured experimental couplings that are unable to be even qualitatively reproduced by BS DFT calculations.[27] BISDOW and PATFIA in contrast feature strong and weak antiferromagnetic interactions, respectively. These nine systems are shown in Figure 1 (images generated by VESTA software[49]).

■ RESULTS

In Tables 1 and 2 we show magnetic couplings and Löwdin spin populations, respectively, calculated with 3-21G, 6-31G, 6-31G*, and 6-311G* basis-sets, using LDA+30%HFX. We consider three types of calculated couplings: J^{HS}, being the

Table 2. Löwdin Spin-Populations Calculated at the LDA +30%HFX Level of Theory for Different Basis Sets[a]

	3-21G	6-31G	6-31G*	6-311G*
1	0.8375	0.7469	0.7298	0.6947
2	0.8415	0.7529	0.7347	0.7021
3	0.8385	0.7486	0.7308	0.6972
4	0.8358	0.7450	0.7269	0.6918
5	0.8378	0.7448	0.7273	0.6903
6	0.8381	0.7474	0.7289	0.6937
7	0.8343	0.7437	0.7254	0.6912
BISDOW	0.8429	0.7505	0.7380	0.7033
PATFIA	0.8213	0.7090	0.6927	0.6416

[a]For each system the spin of only one Cu^{II} is shown, as they are practically identical.

couplings determined from eq 9; $J^{\Delta E}_{NP}$, being the couplings determined from eq 3; and $J^{\Delta E}_{SP}$, being the couplings determined from eq 4.

First, looking at Table 2 it is interesting to observe the progressive delocalization of the spin density off of the metal centers as the size of the basis set is increased. The trend for each system is monotonic with respect to basis size, and quantitatively similar across systems. This trend is not merely an artifact of the Löwdin method, as a qualitatively identical delocalization is found with many other population methods as one increases the basis for these systems (e.g., see Figure 5 in ref 35.). We think the simplest explanation for this is that larger basis sets give more flexibility for the d electrons to delocalize onto the ligand structure, with the delocalization likely aided by the self-interaction error of approximate density functionals. In any case, Table 2 establishes that the local-spin quantity indeed changes significantly with basis set.

Turning now to Table 1, we examine the calculated magnetic couplings. We find that for each system, for any basis set, $J^{HS} \approx J^{\Delta E}_{SP}$, meaning that our methodology yields magnetic couplings that are practically identical to those from spin-projected energy differences. Unfortunately, though, this means that our methodology also fails to capture the subtle trends in the experimental values of complexes **1−7**. This demonstrates the deviation from experiment is not due to any approximations made in the BS energy differences calculation, but is due to the intrinsic accuracy of the density functional approximation employed. It is important to note that this failure to capture these subtle trends is not the fault of the simple LDA+30%HFX hybrid model, as the relatively much more sophisticated LC-ωPBE gave essentially the same results in the work of Wannarit et al.[27] It is worth stressing that from previous assessments,[46,48,50,51] current density functional approximations are not expected to yield magnetic exchange couplings accurate enough to capture the subtle differences in these dinuclear Cu^{II} complexes. We point out here that Onofrio et al. have presented a detailed analysis of the BS method in connection to the full-valence bond and configuration interaction approximations in Cu(II) dimers.[52,53]

Why is it that $J^{HS} \approx J^{\Delta E}_{SP}$ even though the local-spin quantity changes significantly with the basis-set? We think there are two reasons for this. The first is that it is not only the local-spin of the metals that responds to the torque. For example, in Figure 2 on the left we show the labeled core structure of BISDOW, and on the right we give the zeroth-order z-component spin population s^0_z, first-order x-component spin-population $s^{(1)}_x$, and the first-order rotation defined as $\theta^{(1)}_z = s^{(1)}_x / s^0_z$. Examining the

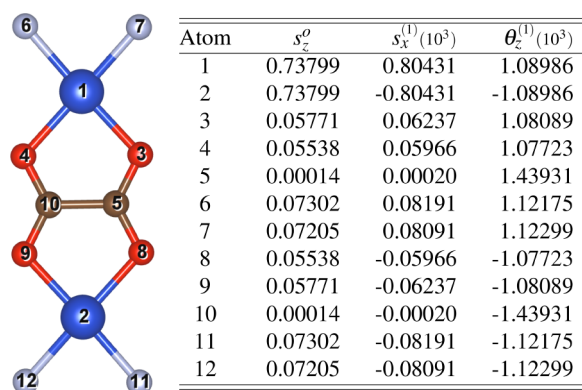| Atom	s_z^o	$s_x^{(1)}(10^3)$	$\theta_z^{(1)}(10^3)$
1	0.73799	0.80431	1.08986
2	0.73799	-0.80431	-1.08986
3	0.05771	0.06237	1.08089
4	0.05538	0.05966	1.07723
5	0.00014	0.00020	1.43931
6	0.07302	0.08191	1.12175
7	0.07205	0.08091	1.12299
8	0.05538	-0.05966	-1.07723
9	0.05771	-0.06237	-1.08089
10	0.00014	-0.00020	-1.43931
11	0.07302	-0.08191	-1.12175
12	0.07205	-0.08091	-1.12299

Figure 2. (Left) Core of BISDOW, where Cu, N, O, and C atoms are colored blue, light blue, red, and brown, respectively. (Right) Löwdin spin populations for the zeroth-order z-component s_z^0, first-order x-component $s_x^{(1)}$, and the first-order rotation defined as $\theta_z^{(1)} = s_x^{(1)}/s_z^0$. These results were obtained using LDA+30%HFX with the 6-31G* basis.

different values, it is clear that all atoms featuring spin density respond to the perturbation, even though the perturbation acts only on atoms 1 and 2 (the Cu^{II} spin centers). This is because when the first-order coupled-perturbed equations are iterated to convergence, the response of the *entire system* must be brought to self-consistency with the local response of the metal atoms.

The second reason is that it is more precise to say that this method depends on the local-rotation than the local-spin. To explain this, consider that the form of the spin-torque perturbation is $\hat{t} = -((\hat{\sigma}_a^x/s_a) + (\hat{\sigma}_b^x/s_b))$. Given a first-order density matrix $\mathbb{P}^{(1)}$, and where $[\mathbb{T}]_{\mu\nu} = \langle\mu|\hat{t}|\nu\rangle$ are the matrix elements of the perturbation, we have that

$$\frac{d^2 E_{KS}}{d\lambda^2}\Big|_{\lambda=0} = Tr[\mathbb{T}\mathbb{P}^{(1)}] = -\frac{s_a^{x(1)}}{s_a} + \frac{s_b^{x(1)}}{s_b}$$

$$= -\theta_a^{(1)} + \theta_b^{(1)} \quad (10)$$

Referencing Figure 2 we see that $\theta_a^{(1)} = -\theta_b^{(1)} = 1089.86$ for BISDOW. From this it is simple to show that

$$J = \frac{1}{S_a S_b}\left(\frac{d^2 E_{KS}}{d\lambda^2}\right)^{-1}\Big|_{\lambda=0} = \frac{2}{-\theta_a^{(1)}} = -402.758 \text{cm}^{-1} \quad (11)$$

which illustrates that this noncollinear methodology essentially defines and obtains J by probing the local torsional response of the spin density of the metals, with the local response being self-consistent at first-order with that of the rest of the system. Therefore, it is irrelevant how s_a and s_b change with the basis set *per se*, because what actually contributes to the coupling is the torsional response $\theta_a^{(1)}$, $\theta_b^{(1)}$.

Finally, it is worth emphasizing again that the derivation of this noncollinear approach[25] was based purely on the physics implied by the Heisenberg−Dirac Hamiltonian, with no recourse to different mapping procedures (i.e., spin-projected vs nonprojected). Therefore, *a priori* there was no reason to expect J^{HS} should coincide with $J_{SP}^{\Delta E}$ or $J_{NP}^{\Delta E}$. That J^{HS} does match $J_{SP}^{\Delta E}$ should be taken as an independent confirmation that if J is calculated by BS energy-differences with hybrid functionals, then a spin-projected mapping should be employed. That J_{NP} can be in remarkably close agreement with experimental values

in some cases should be considered as a fortuitous combination of the functional and basis set used.

CONCLUSIONS

We have used our novel methodology based on noncollinear coupled-perturbed density functional theory to determine the magnetic couplings in a series of triply bridged ferromagnetic dinuclear Cu^{II} complexes and two antiferromagnetic dinuclear Cu^{II} complexes. Our results show that the noncollinear coupled-perturbed approach yields magnetic exchange couplings that are effectively identical to to those from spin-projected broken-symmetry energy differences for any basis-set when a hybrid functional is used. This validates that the noncollinear methodology does not introduce any new approximations when calculating magnetic couplings and is robust in its predictive power. Additionally, the couplings calculated by this noncollinear method for the ferromagnetic complexes show very little variation across the series, which indicates that the failure of the broken-symmetry energy differences approach to capture the subtle variation of the exchange couplings in these Cu^{II} complexes is likely related to a weakness of current approximate density functionals, and not of the broken-symmetry or noncollinear coupled-perturbed approaches themselves. This underscores the need to develop more quantitatively accurate density functional approximations for describing the magnetic properties of large strongly correlated TM complexes.

AUTHOR INFORMATION

Corresponding Author
*E-mail: juan.peralta@cmich.edu. Telephone: +1(989)774-3375. Fax: +1(989)774-2697.

Notes
The authors declare no competing financial interest.

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