

# Magnetic Coupling in Transition-Metal Binuclear Complexes by Spin-Flip Time-Dependent Density Functional Theory

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**ABSTRACT:** Spin-flip time-dependent density functional theory (SF-TDDFT) has been applied to predict magnetic coupling constants for a database of 12 spin-1/2 homobinuclear transition-metal complexes previously studied by Phillips and Peralta employing spin-projected broken-symmetry density functional theory (Phillips, J. J.; Peralta, J. E. *J. Chem. Phys.* **2011**, *134*, 034108). Several global hybrid density functionals with a range of percentages of Hartree–Fock exchange from 20% to 100% have been employed within the collinear-spin formalism, and we find that both the high-spin reference state and low-spin state produced by SF-TDDFT are generally well adapted to spin symmetry. The magnetic coupling constants are calculated from singlet–triplet energy differences and compared to values arising from the popular broken-symmetry approach. On average, for the density functionals that provide the best comparison with experiment, the SF-TDDFT approach performs as well as or better than the spin-projected broken-symmetry strategy. The constrained density functional approach also performs quite well. The SF-TDDFT magnetic coupling constants show a much larger dependence on the percentage of Hartree–Fock exchange than on the other details of the exchange functionals or the nature of the correlation functionals. In general, SF-TDDFT calculations not only avoid the ambiguities associated with the broken-symmetry approach, but also show a considerably reduced systematic deviation with respect to experiment and a larger antiferromagnetic character. We recommend MPW1K as a well-validated hybrid density functional to calculate magnetic couplings with SF-TDDFT.

## 1. INTRODUCTION

The synthesis and study of bi- and polynuclear transition-metal complexes has been motivated in part by the remarkable magnetic properties they often exhibit, ultimately leading to what has been called single-molecule magnets.<sup>1–10</sup> Magnetic molecules have a nonzero total spin and other properties that make them suitable for potential technological applications such as high-density information storage and quantum computing.<sup>11–13</sup> In transition-metal complexes, the metal atoms may act as paramagnetic centers with effective localized spin moments,  $S_i$ , where  $i$  identifies the atom on which the spin is localized, that interact with each other ferro-, ferri-, or antiferromagnetically. Experimental measurements of magnetic susceptibilities versus temperature or neutron diffraction, among other techniques, permit one to study the lower lying electronic states of magnetic systems. In many cases, the experimental data can be interpreted by describing the magnetic interactions with the isotropic Heisenberg–Dirac–Van Vleck (HDV) Hamiltonian, which for a binuclear complex takes the form<sup>14,15</sup>

$$\hat{H} = -J \mathbf{S}_1 \cdot \mathbf{S}_2 \quad (1)$$

where  $J$  represents the phenomenological magnetic exchange coupling between the two magnetic centers. A positive sign for  $J$  corresponds to ferromagnetic coupling and a negative sign to antiferromagnetic coupling. The HDV Hamiltonian is appropriate for the physical description of magnetic coupling in a wide variety of systems, including some organic biradicals, transition-metal complexes, and ionic solids.<sup>15</sup>

The prediction of magnetic couplings from first principles is a very important albeit difficult task, since this property depends strongly on a balanced treatment of electron exchange and electron correlation effects. Furthermore, both nondynamical and dynamical correlation have to be described accurately, as evidenced in a number of studies<sup>16–21</sup> that have employed high-level wave function methods such as difference-dedicated configuration interaction (DDCI)<sup>22</sup> and multiconfigurational second-order perturbation theory (e.g., CASPT2<sup>23,24</sup>). However, the size and complexity of transition-metal clusters of chemical interest preclude in most cases the use of these potentially accurate but computationally demanding electronic structure methods. In recent years, density functional theory (DFT) has emerged as a robust and practical electronic structure method in quantum chemistry and solid-state physics. DFT is formally a theory designed for the ground electronic state, which in the Kohn–Sham formulation is represented by a single Slater determinant formed by orbitals of a fictitious noninteracting system obtained by solving pseudoeigenvalue equations.

For two spin-1/2 centers, the HDV Hamiltonian in eq 1 has one triplet and one singlet eigenstate, with eigenvalues (energies) equal to  $-J/4$  and  $+3J/4$ , respectively. In this case, the magnetic coupling can be obtained by simply mapping the lowest triplet and singlet electronic states to the HDV eigenstates, and it is given by the difference between the energies of these states. For wave function methods, this mapping can be carried out by

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expressing the electronic state functions as expansions in configuration state functions having a well-defined spin symmetry.<sup>15</sup> In DFT, one way to calculate the splitting of two levels is to take the difference in energy of separate self-consistent-field (SCF) calculations on the two spin states, which is called the  $\Delta$ SCF approach. In the unrestricted Kohn–Sham formalism, the lowest triplet state, with energy  $E(\text{HS})$ , is in most cases approximately well represented by a single Slater determinant, but if we make an analogy with wave function theory, the lowest singlet state would require a spin-adapted linear combination of at least two determinants.<sup>25</sup> Noodleman<sup>26–28</sup> advocated a workaround to this problem that involves converging to a broken-symmetry (BS) solution of the Kohn–Sham equations such that the two spins are localized at the two centers. The BS determinant has neither singlet nor triplet spin symmetry, and a strategy must be adopted to relate its energy,  $E(\text{BS})$ , to that of the relevant singlet state. At this point there are two extreme approaches that can be called spin-unprojected and spin-projected. In the spin-unprojected approach,<sup>29,30</sup> one assumes that the energy of the BS state is an approximation of the energy of the open-shell singlet state, in which case the magnetic coupling would be obtained as

$$J = E(\text{BS}) - E(\text{HS}) \quad (2)$$

whereas in the spin-projected approach,<sup>26–28</sup> one assumes that the BS state is a weighted average of spin states; in this case that would be an equal mixture of singlet and triplet, which yields

$$J = 2(E(\text{BS}) - E(\text{HS})) \quad (3)$$

These two equations can be seen as limiting cases of the weighted-average formula proposed by Yamaguchi and co-workers,<sup>31–33</sup> in particular

$$J = \frac{2[E(\text{BS}) - E(\text{HS})]}{\langle S^2 \rangle_{\text{HS}} - \langle S^2 \rangle_{\text{BS}}} \quad (4)$$

where  $\langle S^2 \rangle_{\text{HS}}$  and  $\langle S^2 \rangle_{\text{BS}}$  are the expectations of the square of the spin angular momentum for the HS and BS solutions, respectively. If we assume that the high-spin unrestricted DFT determinant is a good approximation of the triplet, then  $\langle S^2 \rangle_{\text{HS}} = 2$ , and if the BS determinant is a good approximation of the singlet state, as assumed in the spin-unprojected approach, then  $\langle S^2 \rangle_{\text{BS}} \approx 0$ , and eq 4 reduces to eq 2. In practice, this would be achieved if the two centers were strongly coupled, so that the  $\alpha$  and  $\beta$  spins are covalently shared (not localized on the two centers at all); hence, this may be called the strong interaction limit. Conversely, in the weak interaction limit in which the two spin orbitals are completely localized, the BS determinant is a 50:50 mixture of pure singlet and triplet states,  $\langle S^2 \rangle_{\text{BS}} \approx 1$ , and eq 4 reduces to eq 3.<sup>34</sup> For unrestricted Hartree–Fock wave functions, this argument is straightforward, but in the case of DFT,  $\langle S^2 \rangle$  is not rigorously defined, and one can argue that spin symmetry does not have to be respected, although this argument presents conceptual complications.<sup>35</sup> In the present study we will compare the weighted-average BS approach to spin-flip time-dependent density functional theory<sup>36–39</sup> (SF-TDDFT), where the spin symmetry is less ambiguous. To anticipate the results, we will find that spin projection is required for consistency between the BS approach and the SF-TDDFT approach.

In section 2 we introduce the computational methods and motivate their use for the calculation of magnetic couplings. In section 3 we present the details of the database of transition-metal complexes employed. Section 4 contains the main results of the study and their relation to previous work. Finally, section 5 draws conclusions.

## 2. COMPUTATIONAL METHODOLOGY

Note that only singlet–triplet and doublet–quartet pairs of states can be studied in the present implementation of SF-TDDFT, and here we restrict our attention to the case of singlet–triplet splittings of systems with two spin-1/2 centers, each of which is an identical transition-metal atom, but with its own set of nonmagnetic ligands. Symmetry-adapting localized states leads to a spatially symmetric state and a spatially anti-symmetric state,  $\phi^+$  and  $\phi^-$ , respectively, and these are simply the sum and difference of singly occupied particle or hole states centered on the transition-metal atoms. These states can be used to form three singlet states and three triplet states:<sup>25,40</sup>

$$^1\Gamma_1 \propto (\lambda\phi^+\bar{\phi}^+ - \sqrt{1-\lambda^2}\phi^-\bar{\phi}^-) \quad (5)$$

$$^1\Gamma_2 \propto (\lambda\phi^+\bar{\phi}^+ + \sqrt{1-\lambda^2}\phi^-\bar{\phi}^-) \quad (6)$$

$$^1\Gamma_3 \propto (\phi^+\bar{\phi}^- - \phi^-\bar{\phi}^+) \quad (7)$$

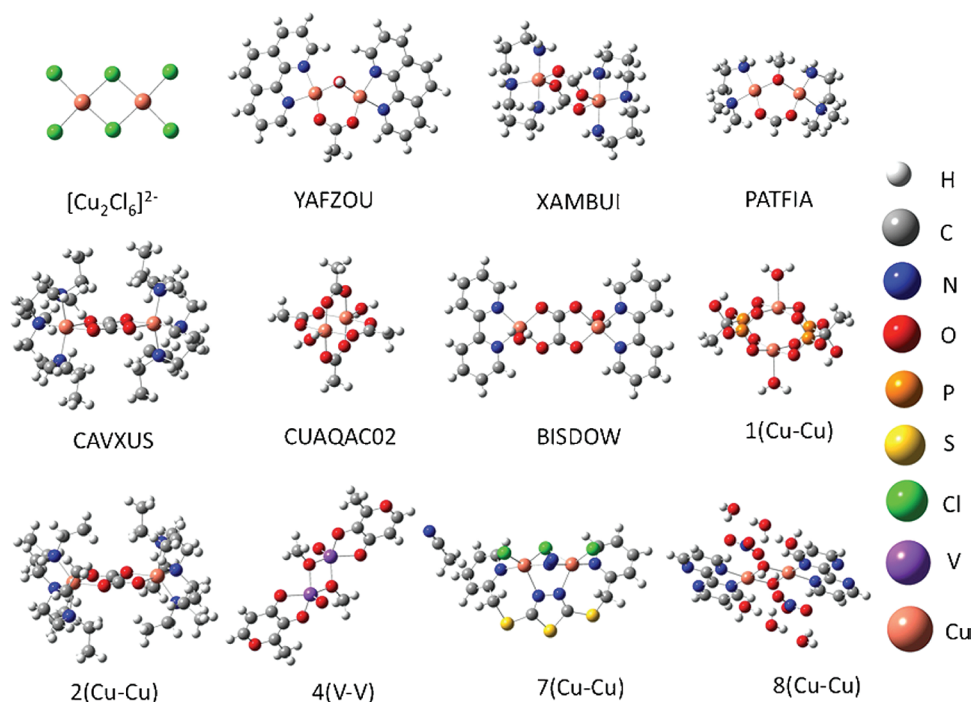
$$^3\Gamma_1 \propto (\phi^+\phi^-) \quad (8)$$

$$^3\Gamma_2 \propto (\bar{\phi}^+\bar{\phi}^-) \quad (9)$$

$$^3\Gamma_3 \propto (\phi^+\bar{\phi}^- + \phi^-\bar{\phi}^+) \quad (10)$$

where a spin orbital without or with an overbar has  $\alpha$  or  $\beta$  spin, respectively, and each product of spin orbitals should be interpreted as shorthand for a determinant. The three singlet spin states are each composed of two determinants; the first two triplet wave functions, eqs 8 and 9, which have  $M_S = 1$  and  $-1$ , respectively, are singly determinantal, and the third triplet spin state, eq 10 with  $M_S = 0$ , consists of two determinants. The lowest singlet state of two weakly coupled centers is eq 5, and the 3-fold-degenerate lowest triplet state is given by eq 8, 9, or 10.

In time-dependent DFT (TDDFT),<sup>41–47</sup> a time-dependent perturbation is added to the ground-state Hamiltonian and the poles of the response function are the frequencies of the allowed excitations (here “excitations” include both excitations and de-excitations, if any), thereby yielding the energies of the excited states. The perturbation is assumed small enough for the response function to be in the linear regime; furthermore, the dependence of the exchange–correlation potential on the frequency of the excitation is ignored—which is called the adiabatic approximation and entails using the ground-state exchange–correlation potentials. In the conventional formulation of TDDFT, which may be called the low-spin formulation or LS-TDDFT, the state before the perturbation is a closed-shell singlet. With these approximations, only single excitations from the closed-shell reference state can be captured by the formalism, and in particular the state of eq 5 cannot be obtained in LS-TDDFT.<sup>41</sup> However, in SF-TDDFT,<sup>36–39</sup> which may also be called high-spin TDDFT, the triplet wave function in eq 8 is taken as a reference, and both an excitation and a spin flip are applied to obtain both determinants in eq 5. The same kind of process also yields the triplet state with  $M_S = 0$  in eq 10. Thus, to represent the triplet state, there would be, in principle, two options, namely, to take the reference state with  $M_S = 1$  or to take the  $M_S = 0$  component of the triplet state generated in the spin-flip excitation process; this is a choice that also shows up when



**Figure 1.** Binuclear complexes studied in this investigation.

using configuration interaction (CI) wave functions. In principle, these two states should be exactly degenerate (i.e., the excitation energy would be zero). In practical calculations, there is an energy difference between these two components of the triplet state, and this energy difference has been called the self-splitting test.<sup>48</sup> It is supposed to be a measure of the consistency of the SF-TDDFT method. We follow here the usual procedure of calculating the singlet–triplet splitting from the  $M_S = 0$  component of the triplet because eq 10 generated by the response is more consistent than the reference (eq 8) for comparing with the generated eq 5.<sup>49,50</sup> In general, one expects more accurate energy splittings when one compares parallel calculations than when one compares disparate ones. In fact, we find that computing magnetic couplings using the  $M_S = 1$  results for the triplet leads to meaningless values. Because the use of the  $M_S = 0$  state is the standard approach in the literature, results obtained by this method are labeled SF-TDDFT, as usual.

Applications of the spin-flip strategy in the literature include the study of the singlet–triplet splitting and diradical character of organic systems,<sup>51–55</sup> bioinorganic chemistry,<sup>56–59</sup> conical intersections,<sup>60,61</sup> and electron transfer couplings.<sup>62–64</sup> To our knowledge, there are only two previous studies of magnetic splittings like those considered here with a formalism equivalent to SF-TDDFT, namely, the recent work of Ziegler and co-workers,<sup>50</sup> where they apply their spin-flip constricted variational DFT formalism to the study of trinuclear copper complexes, and the even more recent work of Yang et al.<sup>49</sup> on low-spin–high-spin splittings in p-block atoms.

The calculations in this study have been carried out with a collinear formulation<sup>36</sup> of SF-TDDFT and within the Tamm–Dancoff<sup>61,65,66</sup> approximation, as implemented in the Q-Chem program.<sup>67</sup> Within the collinear approach, only the Hartree–Fock exchange part of the exchange–correlation functional contributes to the SF coupling.<sup>36</sup> Therefore, only hybrid functionals can be employed in this formulation. For the triplet reference

state, the calculations were performed with a grid composed of 120 radial points and 302 Lebedev angular points.

The density functionals used in the present calculations and in those included in the tabular comparisons made in section 4) are all global hybrids (in a global hybrid, the percentage  $X$  of Hartree–Fock exchange is the same for all interelectronic distances) of the hybrid generalized gradient approximation (GGA) type and of the hybrid meta-GGA type. In particular, the functionals studied, in order of increasing  $X$ , are as follows:

- the popular B3LYP<sup>68–70</sup> hybrid GGA functional (20%)
- the Minnesota M06<sup>71,72</sup> hybrid meta-GGA (27%)
- PBE35 (a modification, with  $X = 35$ , of the PBE0<sup>73,74</sup> functional, which itself is a hybrid version ( $X = 25$ ) of the Perdew–Burke–Ernzerhof (PBE)<sup>75</sup> GGA)
- B3LYP40 (B3LYP with  $X = 40$ )
- B1LYP40 (the B1LYP<sup>76</sup> one-parameter hybrid GGA with the percentage of Hartree–Fock exchange raised from 25% to 40%)
- B1PW40 (the B1PW91<sup>76</sup> one-parameter hybrid GGA with the percentage of Hartree–Fock exchange raised from 25% to 40%)
- BMK<sup>77</sup> (the Boese–Martin model for kinetics hybrid meta-GGA with 42% Hartree–Fock exchange)
- MPW1K<sup>78</sup> (the modified Perdew–Wang one-parameter model for kinetics hybrid GGA with  $X = 42.8$ )
- B3LYP54 (B3LYP with 54% Hartree–Fock exchange)
- the Minnesota M06-2X<sup>71,72</sup> (54%) and M06-HF<sup>72,79</sup> (100%) hybrid meta-GGA functionals

In addition, a few functionals to which we compare will be explained in section 4.

### 3. TRANSITION-METAL COMPLEX DATABASE

We have chosen a database of 12 bimolecular transition-metal complexes, each containing two spin-1/2 metal centers,



**Table 1.** Magnetic Couplings ( $\text{cm}^{-1}$ ) for the 12 Transition-Metal Complexes Studied at the SF-TDDFT Level

system	B3LYP ( $X = 20$ )	M06 ( $X = 27$ )	B3LYP40 <sup>a</sup> ( $X = 40$ )	B1LYP40 ( $X = 40$ )	B1PW40 ( $X = 40$ )	BMK ( $X = 42$ )	MPW1K ( $X = 42.8$ )	B3LYP54 ( $X = 54$ )	M06-2X ( $X = 54$ )	M06-HF ( $X = 100$ )	exptl
$\text{Cu}_2\text{Cl}_6^{2-}$	−342	−210	−94 (−44)	−94	−88	−59	−69	−15	−13	35	0 to −94
YAFZOU	96	91	76 (73)	75	76	78	73	60	65	90	111
XAMBUI	−1	1	1 (−1)	1	2	1	1	1	0	3	2
PATFIA <sup>b</sup>	−399 [−420]	−198 [−140]	−98 (−98) [−100]	−98 [−101]	−98 [−105]	−71 [−86]	−81 [−86]	−35 [−37]	−22 [−24]	32 [26]	−11
CAVXUS	−65	−37	−15 (−19)	−15	−15	−14	−12	−7	−8	−2	−19
CUAQAC02	−721	−523	−245 (−245)	−244	−249	−214	−215	−123	−129	−31	−286
BISDOW	−1126	−743	−349 (−343)	−347	−354	−306	−306	−173	−181	−40	−382
1(Cu—Cu)	−426	−226	−74 (−57)	−74	−74	−59	−60	−27	−29	−8	−62
2(Cu—Cu)	−397	−280	−115 (−100)	−114	−115	−105	−98	−53	−56	−8	−75
4(V—V)	−444	−290	−159 (−154)	−159	−166	−156	−147	−85	−81	−3	−214
7(Cu—Cu)	−421	−145	177 (164)	183	181	159	198	198	194	143	168
8(Cu—Cu)	35	79	111 (102)	110	112	108	112	103	104	72	114
MSE <sup>c</sup>	−292	−147	−3 (−2)	−3	−4	7	11	47	46	82	
MUE <sup>c</sup>	292	147	29 (29)	30	28	32	35	62	59	98	
RMSE <sup>c</sup>	374	190	39 (39)	39	37	43	46	93	89	147	
MURE <sup>c</sup>	5.3	2.6	0.9 (1.0)	0.9	0.9	0.7	0.8	0.6	0.5	1.0	

<sup>a</sup> The values in parentheses are the results obtained with the def2-QZVPPD basis set for the metallic centers. <sup>b</sup> The values in brackets are the results obtained with the full PATFIA model. <sup>c</sup> The mean errors are calculated over rows YAFZOU through 8(Cu—Cu), as explained in the second paragraph of section 4.

to study the performance of SF-TDDFT in the calculation of magnetic couplings. The motivations for choosing this database are twofold: First, since this database was used by Phillips and Peralta<sup>80</sup> for a study of the performance of range-separated hybrid functionals by the spin-projected broken-symmetry approach, it allows us to make a precise comparison to that approach for a relatively extended set of complexes. Second, this database provides a particularly straightforward way to examine magnetic exchange constants because only singlet–triplet energy differences need to be calculated to obtain  $J$  for this database.

The 12 complexes are illustrated in Figure 1. Eleven of them have Cu(II)  $d^9$  atoms as metal centers, and one has a V(IV)  $d^1$  metal center. The first seven complexes are Cu(II) complexes, to be called here  $\text{Cu}_2\text{Cl}_6^{2-}$ , YAFZOU, XAMBUI, PATFIA, CAVXUS, CUAQAC02, and BISDOW, where the names of the latter six complexes correspond to their Cambridge Structural Database reference codes. Note that these seven cases have been used before to test various approaches to the calculation of magnetic couplings.<sup>81–85</sup> As in previous work, the XAMBUI and PATFIA systems are simplified as compared to the systems for which the spin splittings were measured experimentally; in particular, the ferrocenecarboxylate groups were replaced by formate groups. To test the accuracy of this approximation, the full PATFIA complex has also been used to compute magnetic couplings using the crystallographic data from López et al.<sup>86</sup> The last five complexes studied are four Cu(II) complexes and one V(IV) complex, to be called 1(Cu—Cu), 2(Cu—Cu), 4(V—V), 7(Cu—Cu), and 8(Cu—Cu), as in the work of Phillips and Peralta.<sup>80</sup> These complexes are the complexes of spin-1/2 centers from a larger database used by Rudra et al.<sup>35</sup> and later by Peralta and Melo<sup>87</sup> in their magnetic coupling studies (their database also included complexes with higher spin states). The geometries of all the complexes are taken from their crystallographic structures. The counterions are neglected in all cases.

The Gaussian basis sets employed for the first seven complexes are the same as in ref 83, and those for the last five complexes are taken from ref 87. For the full PATFIA complex, the Los Alamos ECP double- $\zeta$ -type basis set LANL2DZ<sup>88</sup> was employed for the Fe atoms. Additional SF-TDDFT calculations were carried out for the B3LYP40 functional using the larger def2-QZVPPD<sup>89,90</sup> basis set for the transition-metal atoms and the same basis sets as before for the rest of the atoms.

## 4. RESULTS AND DISCUSSION

The main results of the present work are presented in Table 1, where the calculated magnetic couplings for the 12 transition-metal complexes with each of the 10 density functionals are compared with experiment. The magnetic couplings are calculated simply as the difference between the singlet and triplet energies, as one would do in wave function theory. This is justified by the values of the spin-squared operator  $\langle S^2 \rangle$  of the two spin-flip states, eqs 5 and 10, which are presented in Table 2. It can be seen that the values of  $\langle S^2 \rangle$  are in most cases close to the theoretical values of 0.0 and 2.0 for the singlet and the triplet, respectively. The exceptions are the XAMBUI and the 7(Cu—Cu) complexes and for the M06-HF density functional also YAFZOU and PATFIA. In these cases we have taken a pragmatic approach and considered the singlet and triplet to be the states with the lower and higher values of  $\langle S^2 \rangle$ , respectively. The  $\langle S^2 \rangle$  values that show significant deviations from the nominally correct values may be an indication of the inadequacy of some presently available functionals for particular systems, but they might also indicate that  $\langle S^2 \rangle$  cannot always be used as a reliable indicator of the success of a given calculation. A more fundamental reason for this behavior might be a larger multiconfigurational character of a given complex with the Kohn–Sham orbitals differing from the magnetic orbitals.

We have computed four statistical measures of accuracy, namely, the mean signed error (MSE), the mean unsigned error (MUE), the root mean squared error (RMSE), and—following

Table 2. Values of  $\langle S^2 \rangle$  for the Magnetic States Obtained at the SF-TDDFT Level for the 12 Complexes Studied<sup>a</sup>

system	B3LYP	M06	B3LYP40	B1LYP40	B1PW40	MPW1K	BMK	B3LYP54	M06-2X	M06-HF
Cu <sub>2</sub> Cl <sub>6</sub> <sup>2-</sup>	0.03	0.01	0.02	0.02	0.02	0.02	0.01	0.02	0.01	2.01
	1.99	2.01	2.00	2.00	2.00	2.01	2.01	2.01	2.02	0.02
YAFZOU	1.71	2.00	2.00	2.00	2.01	2.01	1.92	2.01	2.00	1.45
	0.30	0.02	0.02	0.02	0.02	0.02	0.10	0.02	0.02	0.58
XAMBUI	0.98	1.73	1.52	1.51	1.49	1.47	1.50	1.52	1.85	1.05
	1.03	0.29	0.50	0.51	0.53	0.55	0.52	0.50	0.17	0.97
PATFIA	0.02	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.04	1.69
	1.99	2.01	2.01	2.01	2.01	2.01	2.00	2.01	1.98	0.34
CAVXUS	0.03	0.01	0.03	0.03	0.03	0.03	0.02	0.02	0.01	0.45
	1.99	2.01	2.00	2.00	2.00	2.00	2.00	2.01	2.01	1.58
CUAQAC02	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
	1.98	2.00	2.00	2.00	2.00	2.00	2.01	2.01	2.01	2.01
BISDOW	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
	1.99	2.01	2.01	2.01	2.01	2.01	2.01	2.01	2.01	2.01
1(Cu–Cu)	0.04	0.01	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.01
	1.98	2.01	2.00	2.00	2.00	2.01	2.01	2.01	2.01	2.01
2(Cu–Cu)	0.03	0.01	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.02
	1.98	2.01	2.01	2.00	2.00	2.01	2.01	2.01	2.02	2.02
4(V–V)	0.03	0.05	0.05	0.05	0.05	0.06	0.02	0.06	0.05	0.08
	2.03	2.06	2.07	2.07	2.07	2.08	2.03	2.10	2.08	2.13
7(Cu–Cu)	0.09	0.21	1.62	1.60	1.62	1.73	1.95	1.97	2.02	1.62
	1.94	1.83	0.45	0.46	0.44	0.34	0.10	0.20	0.04	0.43
8(Cu–Cu)	1.99	2.01	2.01	2.01	2.01	2.01	2.01	2.01	2.01	2.01
	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01

<sup>a</sup> The first and second values correspond to the lower and higher energy states, respectively.

Phillips and Peralta<sup>80</sup>—also the mean unsigned relative error (MURE). The definitions of these quantities are as follows:

$$\text{MSE} = \frac{1}{N} \sum_{i=1}^N [J_{\text{calcd},i} - J_{\text{exptl},i}] \quad (11)$$

$$\text{MUE} = \frac{1}{N} \sum_{i=1}^N \text{Abs}[J_{\text{calcd},i} - J_{\text{exptl},i}] \quad (12)$$

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^N [J_{\text{calcd},i} - J_{\text{exptl},i}]^2}{N}} \quad (13)$$

$$\text{MURE} = \frac{1}{N} \sum_{i=1}^N \text{Abs} \left[ \frac{J_{\text{calcd},i} - J_{\text{exptl},i}}{J_{\text{exptl},i}} \right] \quad (14)$$

First, note that there is some uncertainty as to the experimental value of  $J$  for the Cu<sub>2</sub>Cl<sub>6</sub><sup>2-</sup> complex. One experimental reference quotes an antiferromagnetic coupling of between 0 and –40 cm<sup>–1</sup>,<sup>91</sup> whereas another experiment suggests a significantly larger value of –94 cm<sup>–1</sup>.<sup>92</sup> There is also a spread in high-level ab initio results for this splitting. Thus, studies carried out with the DDCI approach<sup>21,93,94</sup> have found a magnetic coupling for the experimental structure in agreement with the first experimental interval and with more recent CASPT2 calculations.<sup>17</sup> In contrast, a recent application of state-specific multireference coupled cluster theory with single and double excitations yielded<sup>95</sup> values between –66 and –84 cm<sup>–1</sup>, in better agreement with the

second experimental value (–94 cm<sup>–1</sup>). The B3LYP40 result in Table 1 shows that the magnetic coupling for Cu<sub>2</sub>Cl<sub>6</sub><sup>2-</sup> depends strongly on the basis set used for the Cu atoms. Because of the larger experimental and theoretical uncertainties in this case, we omitted the magnetic couplings of Cu<sub>2</sub>Cl<sub>6</sub><sup>2-</sup> from all calculations of mean errors.

The most conspicuous trend in Table 1 is the strong dependence of the magnetic coupling on the percentage of Hartree–Fock exchange. In general, local functionals (i.e., those without Hartree–Fock exchange) tend to favor the low-spin states, and high- $X$  hybrid functionals tend to favor the high-spin states, probably because Hartree–Fock exchange correlates electrons with the same spin by enforcing the Fermi hole, but this does not apply to electrons with opposing spins. We find, for example, that B3LYP and M06 with  $X = 20$  and 27, respectively, are in most cases strongly antiferromagnetic, and they show a large systematic deviation from experiment. The optimal value of  $X$  is found to be about 40, as in B3LYP40, B1LYP40, and B1PW40, or a little higher, as in MPW1K and BMK. The MSE for all these functionals is very small, on the order of only a few wavenumbers. The best results are found with the B1PW40 density functional, and we will use this as a reference for subsequent comparisons. However, note that the MURE is still relatively large, mainly due to the large deviations (in terms of MURE) found for the PATFIA complex. The MURE becomes less appropriate in cases like this where some of the couplings are very small because these small quantities appear in the denominator of the relative error.

Table 1 also shows that the dependence of  $J$  on  $X$  is stronger for the antiferromagnetic than for the ferromagnetic complexes. Another interesting feature of the results is the small dependence

**Table 3.** Comparison of the Optimal Results of the Present Study with Those of Other Methods To Obtain Magnetic Couplings ( $\text{cm}^{-1}$ )

	SF-TDDFT, <sup>a</sup> B1PW40	BS- $\Delta$ SCF, <sup>b</sup> PBE35	BS- $\Delta$ SCF, <sup>c</sup> M06	BS- $\Delta$ SCF, <sup>c</sup> M06-2X	BS- $\Delta$ SCF, <sup>d</sup> B2-PLYP	BS- $\Delta$ SCF, <sup>d</sup> B2GP-PLYP	SF-TDDFT, <sup>a</sup> B1PW40	REKS, <sup>e</sup> B3LYP	REKS, <sup>e</sup> BH&HLYP	C-DFT, <sup>f</sup> B3LYP	exptl
$\text{Cu}_2\text{Cl}_6^{2-}$	−88	−9	5	0.1	−121	−61					0 to −94
YAFZOU	76	132	294	75	164	123	76	264	87		111
XAMBUI	2	1.5	3	0.8	−15	−11	2	6.2	0.75		2
PATFIA	−98	−7.5	−15	−19	15	19	−98	139	32		−11
CAVXUS	−15	−10.5	−28	−6	−17	−14	−15	3.3	−3.4		−19
CUAQAC02	−249	−233	−436	−143	−262	−177	−249	−285	−91		−286
BISDOW	−354	−308	−632	−177	−336	−122	−354	−429	−135		−382
MSE <sup>g</sup>	−9	27	−38	53	22	51	−9	47	79		
MUE <sup>g</sup>	32	27	100	68	28	55	32	63	88		
RMSE <sup>g</sup>	43	38	141	103	33	80	43	90	130		
MURE <sup>g</sup>	1.4	0.3	0.7	0.6	1.9	1.7	1.4	3.1	1.1		
1(Cu–Cu)	−74	−71								−32	−62
2(Cu–Cu)	−115	−89								−88	−75
4(V–V)	−166	−129								−166	−214
7(Cu–Cu)	181	277								224	168
8(Cu–Cu)	112	179								114	114
MSE <sup>h</sup>	1.5	47								24	
MUE <sup>h</sup>	23	56								29	
RMSE <sup>h</sup>	29	69								36	
MURE <sup>h</sup>	0.2	0.4								0.2	

<sup>a</sup> Present work. <sup>b</sup> Reference 80. <sup>c</sup> Reference 83. <sup>d</sup> Reference 85. <sup>e</sup> Reference 81. The results included here correspond to those computed using eq 14 of that work. <sup>f</sup> Reference 35. <sup>g</sup> Mean errors for rows YAFZOU though BISDOW. <sup>h</sup> Mean errors for rows 1(Cu–Cu) though 8(Cu–Cu).

found on the pure exchange and correlation functionals employed, as evidenced by the set of five density functionals mentioned above that have nearly the same accuracy for the prediction of magnetic couplings, despite significant differences in the functional forms and/or parameters of the exchange and correlation functionals.

The observation that magnetic couplings and, more generally, spin-state energy differences, depend strongly on  $X$  has been discussed at length in the literature for transition-metal-containing compounds<sup>96–110</sup> and p-block atoms.<sup>49</sup> In general,  $X$  in the range of 40–60 is often necessary to obtain good agreement with experiment for spin energy differences<sup>36,49,52,53,60,64</sup> (note, however, that B3LYP was found to perform well for bioinorganic copper complexes).<sup>56–59</sup> The optimum  $X$  value of about 40 found here is roughly in agreement with the observation made many years ago that  $X = 35$  is optimal for strongly correlated solids such as  $\text{NiO}$ <sup>96–98</sup> and others.<sup>111</sup> However,  $X$  of about 15 was found to be optimum for single-center  $\text{Fe(II)}$  complexes,<sup>99</sup> and local functionals ( $X = 0$ ) such as OPBE<sup>75,112</sup> and OLYP<sup>112,113</sup> were also found to perform well in several cases.<sup>100,108,110</sup> Thus, the calculation of magnetic couplings in transition-metal complexes could be seen in the wider context of the study of multiplicity-changing transitions in transition-metal chemistry, crucial to the understanding of, e.g., reaction mechanisms<sup>114</sup> and spin-crossover complexes.<sup>115–117</sup>

An important consideration to keep in mind in seeking generalizations is that the HDV model was designed for when the magnetic coupling is due to a pure spin flip without changes in the spatial orbitals, as is most likely to occur for weakly coupled centers, whereas many of the cases just mentioned involve spin states of different orbital parentage or orbitals on the same center that are not weakly coupled. The recent study of single-center

splittings in p-block atoms<sup>49</sup> showed that splittings depend strongly on  $X$  but also that the dependence on  $X$  and the optimum value of  $X$  depend on the system studied and on the method, being different for  $\Delta$ SCF, LS-TDDFT, and SF-TDDFT. In this context, it is interesting to compare the present SF-TDDFT results with previous studies, and we have prepared Table 3 to facilitate such a comparison. In this table, we will compare the present results with weighted-average BS- $\Delta$ SCF results based on spin projection (eq 3) and with those of two further strategies to obtaining magnetic couplings: the constrained DFT (C-DFT) method<sup>118</sup> as implemented by Wu and Van Voorhis<sup>119</sup> and the spin-restricted ensemble-referenced Kohn–Sham (REKS) method of Filatov and Shaik.<sup>120,121</sup>

The first set of results in Table 3 is the optimal set of results of the present study, which—on the basis of the values of MSE, MUE, and RMSE—are the B1PW40 results. The next column has the optimal spin-projected weighted-average BS- $\Delta$ SCF results of Phillips and Peralta,<sup>80</sup> namely, their PBE35 results. Note that these authors employed three density functionals in their study: PBEX, HSE $\Omega$ , and LC- $\omega$ PBE $\Omega$ , where  $X$  denotes a variable percentage of Hartree–Fock exchange and  $\Omega$  represents a variable range parameter  $\omega$  for the range-separated HSE and LC- $\omega$ PBE density functionals. The rest of their parameters were taken from the standard PBE0,<sup>73,74</sup> HSE,<sup>122</sup> and LC- $\omega$ PBE<sup>123</sup> functionals. Their results showed that one obtained the best results with HSE0 (HSE $\Omega$  with  $\Omega = 0.0 a_0^{-1}$ ) but that one obtains similar results for any  $\Omega$  between 0.0 and  $0.2 a_0^{-1}$ . (Note that HSE0 is the same as PBE0). However, Phillips and Peralta also pointed out that since one could expect results with the original HSE value of  $\Omega$  very similar to the best results with  $\Omega = 0.0$ , the standard HSE method with the value of  $\Omega = 0.11 a_0^{-1}$  would be advantageous

for extended systems because of its more favorable computational cost as compared to that using  $\Omega = 0.0$ . The mean errors in Table 3 are for two subsets. If we compute the mean errors of the results from weighted-average BS- $\Delta$ SCF calculations with PBE35 over the 11 complexes used for averages in Table 1, we obtain MSE, MUE, and RMSE values of 36, 40, and 54  $\text{cm}^{-1}$ , all larger than the corresponding values in Table 1 for SF-TDDFT with B1PW40; the MURE is smaller though (0.3 vs 0.9) because of the large relative error of SF-TDDFT with B1PW40 for PATFIA.

For the seven complexes  $\text{Cu}_2\text{Cl}_6^{2-}$ , YAFZOU, XAMBUI, PATFIA, CAVXUS, CUAQAC02, and BISDOW, we also compare the present results with two other sets of spin-projected weighted-average BS- $\Delta$ SCF results, the ones from our previous study<sup>83</sup> using the Minnesota M06 and M06-2X functionals<sup>71,72</sup> and those reported with the double-hybrid B2-PLYP<sup>124</sup> and B2GP-PLYP<sup>125</sup> functionals by Schwabe and Grimme.<sup>85</sup> The B2-PLYP and B2GP-PLYP density functionals are doubly hybrid functionals,<sup>126</sup> in which an SCF step is followed by a post-SCF perturbative calculation of the correlation energy; both the density functional correlation energy and the perturbative contribution are empirically scaled. For the six complexes YAFZOU, XAMBUI, PATFIA, CAVXUS, CUAQAC02, and BISDOW, we report the best results of two implementations of the REKS method as described in eqs 13 and 14 of the work in which the couplings are calculated.<sup>81</sup> Finally, for the five complexes 1(Cu–Cu), 2(Cu–Cu), 4(V–V), 7(Cu–Cu), and 8(Cu–Cu), we compare the present results with the C-DFT results of Rudra et al.<sup>35</sup>

The results in Table 3 show several interesting features. First, note that only SF-TDDFT with the present  $X = 40$  functional (or any other functional in Table 1 with  $X \cong 40$  since they all give similar results), PBE35 with the spin-projected weighted-average BS- $\Delta$ SCF approach, and C-DFT predict the correct sign (ferromagnetic or antiferromagnetic) for all the complexes for which they have been tested. (The only two methods for which it is certain that they predict all 12 signs correctly are the first two.) If we look at the MSEs as a measure of systematic deviations from experiment, it is clear that the best method is SF-TDDFT with  $X \cong 40$ . Furthermore, the only three methods with MUE and RMSE comparable to those of SF-TDDFT with  $X \cong 40$  are spin-projected weighted-average BS- $\Delta$ SCF with PBE35, doubly hybrid B2-PLYP, which was applied<sup>85</sup> using the spin-projected eq 3, and C-DFT. Note that, for the last two, results have been reported for only the second subset of magnetic complexes. If instead of the MSE, MUE, and RMSE we would take the MURE as a measure of accuracy, it is clear that PBE35 with the spin-projected broken-symmetry approach would be the best method overall (i.e., for the 12 complexes). The MURE obtained with SF-TDDFT is large because of the large relative error of the PATFIA complex, which has a very small splitting. The REKS method is systematically too ferromagnetic and does not provide results competitive with those of SF-TDDFT or the best spin-projected weighted-average BS ones. One can conclude that, to the extent that the database of 12 complexes studied is representative of homobinuclear transition-metal complexes with spin-1/2 centers, SF-TDDFT with  $X \cong 40$  makes more accurate predictions, on average, than any other method studied. Since all the SF-TDDFT functionals with  $X \cong 40$  make similar predictions, we recommend using MPW1K or BMK since they are standard functionals that have been well validated for a great variety of chemical properties; for example, MPW1K has been shown to

provide relatively accurate predictions for hydrogen-bonding and charge-transfer interactions.<sup>127</sup> Of the two, MPW1K is simpler (being a hybrid GGA, whereas BMK is a hybrid meta-GGA) and is therefore easiest to implement in a wide variety of programs.

The discussion above regarding the accuracy of the different approaches has focused on the comparison to experiment. From a fundamental point of view it is also interesting to compare SF-TDDFT and BS energy splitting values obtained with two different formalisms. We found that, in all cases studied, the results obtained from the BS approach compare to those arising from SF-TDDFT if and only if spin projections (eq 3) are taken into account; this is another indication that spin symmetry has to be taken into account in DFT calculations as is usually done when wave functions are used.

## 5. CONCLUSIONS

Magnetic exchange coupling constants have been computed for a database of 12 spin-1/2 homobinuclear transition-metal complexes previously studied by Phillips and Peralta<sup>80</sup> and others. In the present work, several global hybrid density functionals, with the percentage of Hartree–Fock exchange ranging from 20% to 100%, have been employed with collinear, Tamm–Dancoff spin-flip time-dependent density functional theory. The magnetic coupling constants are calculated from singlet–triplet energy differences, as one would do in wave function theory, with both spin states generally well adapted to spin symmetry.

For a given functional, the spin-state energy splitting values predicted by the SF-TDDFT formalism are consistent with those obtained from the broken-symmetry approach if and only if spin projection is taken into account in the latter. Considering all 12 complexes, we find that 40% Hartree–Fock exchange provides the best agreement with experiment and—in terms of mean signed error, mean unsigned error, and root-mean-square error—the SF-TDDFT approach performs systematically better than the spin-projected weighted-average broken-symmetry strategy, although the optimal percentage is slightly different in each case (about 40% for SF-TDDFT and 35% for spin-projected weighted-average broken symmetry). If one considers subsets of the database for which previous results are available, one finds that the spin-projected weighted-average broken-symmetry doubly hybrid functional B2-PLYP and the constrained density functional theory based on B3LYP also perform quite well.

For SF-TDDFT, the magnetic couplings show a much larger dependence on the percentage of Hartree–Fock exchange than on other aspects of the exchange and correlation density functionals employed. Given that hybrid meta-GGAs do not seem to improve the results with respect to hybrid GGAs, one can use a less computationally demanding hybrid GGA such as MPW1K for SF-TDDFT on this kind of system. Further studies on a greater variety of systems would be welcome.

In conclusion, we find that the SF-TDDFT approach provides more accurate spin-state energy splittings than the spin-projected weighted-average broken-symmetry scheme for binuclear spin-1/2 transition-metal complexes, with the added advantage of avoiding the ambiguities associated with the weighted-average broken-symmetry approach. We recommend MPW1K as a well-known, standard hybrid density functional to calculate magnetic couplings in the context of SF-TDDFT.



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