Magnetic Exchange Couplings from Semilocal Functionals Evaluated Nonself-Consistently on Hybrid Densities: Insights on Relative Importance of Exchange, Correlation, and Delocalization

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Ⓢ Supporting Information

ABSTRACT: Semilocal functionals generally yield poor magnetic exchange couplings for transition-metal complexes, typically overpredicting in magnitude the experimental values. Here we show that semilocal functionals evaluated nonself-consistently on densities from hybrid functionals can yield magnetic exchange couplings that are greatly improved with respect to their self-consistent semilocal values. Furthermore, when semilocal functionals are evaluated nonself-consistently on densities from a "half-and-half" hybrid, their errors with respect to experimental values can actually be lower than those from self-consistent calculations with standard hybrid functionals such as PBEh or TPSSh. This illustrates that despite their notoriously poor performance for exchange couplings, for many systems semilocal functionals are capable of delivering accurate relative energies for magnetic states provided that their electron delocalization error is corrected. However, while self-consistent calculations with hybrids uniformly improve results for all complexes, evaluating nonself-consistently with semilocal functionals does not give a balanced improvement for both ferro- and antiferromagnetically coupled complexes, indicating that there is more at play with the overestimation problem than simply the delocalization error. Additionally, we show that for some systems the conventional wisdom of choice of exchange functional mattering more than correlation does not hold. This combined with results from the nonself-consistent calculations provide insight on clarifying the relative roles of exchange, correlation, and delocalization in calculating magnetic exchange coupling parameters in Kohn−Sham Density Functional Theory.

■ INTRODUCTION

Density functional theory in the Kohn−Sham realization[1] has become one of the most commonly used electronic-structure methods for solid-state physics and quantum chemistry. Kohn−Sham density functional theory (KS-DFT) achieves both appreciable accuracy and computational simplicity by invoking a noninteracting reference system of electrons. The non-interacting reference system allows one to calculate a large fraction of the total energy exactly, with the remaining contribution bundled into the exchange-correlation energy functional, $E_{xc}[\rho(\mathbf{r})]$, that in-principle accounts for all many-body effects.[2] The exact form of $E_{xc}[\rho(\mathbf{r})]$ remains elusive, and one must rely on approximations determined by principled and/or empirical means.

A frustrating feature endemic to many approximate functionals is the self-interaction error (SIE),[3−6] which manifests itself in problems such as unphysical fractional-charges on molecular fragments after dissociation,[7−10] unbound anions,[11−15] and generally excessive delocalization of the electron density.[5,16,17] The relative amount of SIE in a functional can be qualitatively shown by plotting the total energy with respect to fractional electron occupation, $E(N + \delta N)$, and one finds (in contrast to the linear relationship expected from the exact functional[18]) that all semilocal functionals yield concave-up curves while Hartree−Fock (HF) gives concave-down.[6,10,17,19−21] That a method gives nonlinear behavior for $E(N + \delta N)$ has physical relevance: if one imagined two identical molecular fragments separated by a

great distance and were to place one extra electron on this system, a semilocal functional would incorrectly predict a state with the extra electron delocalized across both fragments to be lower in energy, while HF would (also incorrectly) predict a state with the electron localized on one molecule to be lower in energy. Either state should be degenerate, and this illustrates the energetic basis for semilocal functionals to bias toward delocalization while HF biases toward localization. This fundamental bias results in failure for the quantitative (and even qualitative) description of chemical phenomena that sensitively depend on electron (de)localization. For example, semilocal functionals typically underestimate reaction barrier-heights while HF overestimates them.[9,22−29] This is because the delocalization error of semilocal functionals lowers the energy of the transition-state relative to the reactants, while the localization of HF errs in the opposite manner.

In a similar vein, the accurate *first-principles* study of the magnetic exchange coupling between metal atoms in transition-metal (TM) complexes and solids remains a difficulty, with HF and semilocal functionals typically displaying opposite incorrect extremes in the calculated results. Again, there is substantial reason to attribute a large part of this error to the tendency toward delocalization with approximate density-functionals and localization with HF. To give the reader some context, we briefly discuss relevant aspects of the magnetic coupling

between weakly interacting spins and how coupling parameters can be determined from electronic structure calculations. For the more inquisitive reader we suggest several nice articles and reviews.[30−35]

Determining Magnetic Coupling Parameters from Electronic-Structure Calculations. The magnetic exchange coupling parameter, J_{ij}, gives the strength and sign of the isotropic spin−spin interaction between two local spin-centers, $\{S_i, S_j\}$, in the phenomenological Heisenberg Hamiltonian[36]

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

With appropriately chosen parameters, J_{ij}, this simple model Hamiltonian (in conjunction with additional terms as needed) is routinely used to describe the behavior of magnetic materials. One technologically relevant application is polynuclear transition-metal complexes featuring unpaired d-electrons. These unpaired electrons reside in orbitals localized on the respective metal atoms, with some delocalization onto the surrounding coordinated ligands. This results in weak spin-dependent interactions between the metal centers that depend on the nature and geometry of the ligands, giving rise to a spectrum of low-lying magnetic states describable by eq 1. In the simple case of two spin-centers, $\{S_1, S_2\}$, there is one magnetic coupling parameter to determine, J. Neglecting spin−orbit coupling, for spin-centers of $S_1 \geq S_2$ addition of angular momenta yields spin eigenfunctions of total spin quantum number $S = \{S_1 + S_2, S_1 + S_2 - 1, ..., S_1 - S_2\}$ and magnetic quantum number $m = \{S, S - 1, ..., -S\}$. A magnetic coupling parameter of $J > 0$ would correspond to ferromagnetic coupling of the spins and a high-spin (HS) ground state of $S = S_1 + S_2$, while $J < 0$ would correspond to antiferromagnetic coupling and a low-spin (LS) ground state of $S = S_1 - S_2$. In the context of electronic structure calculations, the magnetic coupling is commonly determined by relating J to differences in total energies of reference spin-states. For example, provided that we can calculate the energy difference between the HS and LS states, J can be extracted by mapping the energies of the spin eigenstates onto the Heisenberg Hamiltonian

$$
\begin{aligned}
E_{LS} - E_{HS} &= \langle -J\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 \rangle_{LS} - \langle -J\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 \rangle_{HS} \\
&= -\frac{1}{2} J[\langle (\hat{S}^2 - \hat{S}_1^2 - \hat{S}_2^2) \rangle_{LS} \\
&\quad - \langle (\hat{S}^2 - \hat{S}_1^2 - \hat{S}_2^2) \rangle_{HS}] \\
&= -\frac{1}{2} J[((S_1 - S_2)(S_1 - S_2 + 1) - S_1(S_1 + 1) \\
&\quad - S_2(S_2 + 1)) - ((S_1 + S_2)(S_1 + S_2 + 1) \\
&\quad - S_1(S_1 + 1) - S_2(S_2 + 1))] \\
&= \frac{1}{2} J[4S_1 S_2 + 2S_2]
\end{aligned}
\tag{2}
$$

giving us

$$J = \frac{E_{LS} - E_{HS}}{2S_1 S_2 + S_2}, \quad S_1 \geq S_2 \tag{3}$$

Among wave function-based methods, the difference dedicated configuration interaction (DDCI) method[37] has proven to be one of the most accurate approaches for calculating magnetic couplings.[38−45] Complete active-space second-order perturbation theory (CASPT2)[46] has also been shown to yield good magnetic couplings,[47−50] with a computational demand significantly less than DDCI.[49] However there is often a systematic deviation between the two methods, as CASPT2 may fail to capture all the dynamic-correlation effects important for J that are successfully treated on the DDCI level.[32,33,35,51] This can be corrected by extending the complete active space (CAS) to include more orbitals, but the computational demand in terms of memory or time requirements may increase greatly.[49,50] A general observation is that increasing the sophistication of the wave function-based method often makes the calculated J more negative (more antiferromagnetic).[32,48,50,52−54] This is because J is the sum of two contributions, $J = J_{FM} + J_{AFM}$, and while typically the dominant interaction responsible for J_{FM} is the direct exchange between the magnetic orbitals, J_{AFM} is the result of correlation effects that are only progressively recovered at successively more sophisticated levels of calculation. This is worth noting, as later it will provide an interesting contrast to the observed dependence of J on correlation functionals of successive sophistication in KS-DFT calculations.

Despite the well-established accuracy of DDCI and CASPT2, the scaling of their computational demand limits widespread use with complicated magnetic systems. The size of the active space in large systems can overwhelm computer resources,[55] and the selection of the active space can be subtle and far from "black-box".[51] For the study of complex magnetic systems this motivates turning to an effective single-particle theory like KS-DFT, which has a gentle computational scaling of $O(N^2)$ to $O(N^3)$, depending on the system size-regime.[56] KS-DFT, when used with a quality density functional, has been found to accurately describe the magnetic anisotropy,[57] geometries,[58] and the general chemistry[59,60] of TM complexes. However a problem encountered with magnetic systems is that KS-DFT calculations struggle to properly describe multireference spin eigenstates, e.g. for $S_1 = S_2 = 1/2$ the two states of $m = 0$, given by $(1/\sqrt{2})(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$ and $(1/\sqrt{2})(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$. Fortunately a strategy suggested by Noodleman[61] rescues us from this dilemma, which is to converge to a broken-symmetry (BS) state, given by $|\uparrow\downarrow\rangle$. Here though one must be careful in the mapping and interpretation of the BS solution, as though $|\uparrow\downarrow\rangle$ is an eigenfunction of $\hat{S}_z$, it is not an eigenfunction of $\hat{S}^2$ nor the Heisenberg Hamiltonian.[62] For two spin-1/2 centers the BS state is formally an equal mixture of the two spin eigenfunctions of $m = 0$, i.e.

$$
\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) + \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)\right) \\
= |\uparrow\downarrow\rangle
\tag{4}
$$

For any two spins, $S_1 \geq S_2$, Dai and Whangbo showed[62] that the BS state is a linear combination of all $m = S_1 - S_2$ spin eigenfunctions spanning the range of total spin quantum numbers $S = \{S_1 + S_2, S_1 + S_2 - 1, ..., S_1 - S_2\}$. By analytically calculating $\langle \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 \rangle$ for this general BS state, Dai and Whangbo derived the following relation for mapping the energies of the BS and HS solutions onto the Heisenberg Hamiltonian

$$J = \frac{E_{BS} - E_{HS}}{2S_1 S_2} \tag{5}$$

This is a formal generalization of Noodleman's original relation for identical spins and is commonly referred to as the "spin-projected" (SP) approach.[61,63] Alternative mapping

procedures include the "non-projected" (NP) approach,[64,65] which argues that the BS energy can be a suitable approximation to the LS energy and eq 3 should be used for DFT calculations instead of eq 5, and the "approximate spin-projected" approach[66] given by

$$J = \frac{E_{BS} - E_{HS}}{\frac{1}{2}\left(\langle \hat{S}^2 \rangle_{HS} - \langle \hat{S}^2 \rangle_{BS}\right)} \tag{6}$$

Although there have been strong discussions on this[65,67,68] there are compelling arguments in the literature suggesting that the SP method has the most principled theoretical grounding.[67,69−72] Use of the SP approach is equivalent to assuming a weakly interacting limit,[73] where the overlap of the magnetic orbitals is approaching zero, $\langle a|b \rangle \approx 0$, and $\langle \hat{S}^2 \rangle$ is close to that of a pure BS state, i.e.

$$\langle \uparrow\downarrow |\hat{S}^2| \uparrow\downarrow \rangle = S_1(S_1 + 1) + S_2(S_2 + 1) - 2S_1 S_2 \tag{7}$$

Conversely the NP approach assumes a strongly interacting limit where the overlap is approaching unity, $\langle a|b \rangle \approx 1$. However the work of Caballol and co-workers[69] makes clear that, barring a few specific systems with LSDA, in most relevant cases the situation is much closer to $\langle a|b \rangle \approx 0$ than $\langle a|b \rangle \approx 1$. The approximate spin-projected method of Yamaguchi and co-workers[66] interpolates between SP and NP: in the limiting case that $\langle \hat{S}^2 \rangle_{BS}$ approaches eq 7 one recovers eq 5, and conversely when $\langle \hat{S}^2 \rangle_{BS} \approx \langle \hat{S}^2 \rangle_{LS}$ one recovers eq 3. In this work (see table of $\langle \hat{S}^2 \rangle$ values in the Supporting Information) for most systems the $\langle \hat{S}^2 \rangle$ values are close to eq 7, and hence magnetic couplings calculated with eq 6 and eq 5 will be practically the same.

Semilocal Functionals, Spin-Delocalization, and the Overestimation of J Parameters. When magnetic exchange couplings are calculated by energy differences with a SP mapping (eq 5) typically one finds that DFT employing semilocal functionals overpredicts experimental values while HF underpredicts.[30,34,65,69,74−84] The overprediction by semilocal functionals can often be substantial, and sometimes even the predicted sign of J can be incorrect. For example, in a recent study of 14 TM complexes on the LSDA to M-GGA level the predicted couplings could on average be a factor of 6 to even a factor of 11 times larger than the experimental values, while one ferromagnetic system in the set (a dinuclear Cu^{II} complex,[85] designated as $7Cu^{II}−Cu^{II}$ here) was incorrectly predicted to be antiferromagnetic by LSDA, PBE, and TPSS.[84] By admixing Hartree−Fock-like exchange (HFX) with DFT exchange hybrid functionals find a desirable balance between over- and underprediction, yielding significantly improved magnetic couplings whether one uses global[75,77,81,83,84,86,87] or range-separated[86−91] hybrids. Interestingly, range-separation of the exchange *per se* does not seem to be important for J, provided that there is "enough" HFX.[86] It is also worth noting that when magnetic couplings are calculated by Spin-Flip DFT, either in the constricted-variational[92] or time-dependent realization,[93] very similar trends with respect to the exchange-correlation functional are found, demonstrating that the overestimation problem is not just an artifact of broken-symmetry approaches. Calzado and co-workers provided an illuminating analysis of the overprediction problem, by demonstrating that the interactions responsible for J_{FM} and J_{AFM} monotonically reduce in magnitude as more HFX is admixed.[33] Similarly Rivero and co-workers,[94] and Grau-Crespo and co-workers,[95] have shown that LSDA+U and GGA+U[96] can counteract the tendency to

overpredict exchange couplings in both molecular systems and solids. Additionally, Ruiz and co-workers have shown that the Perdew−Zunger SIE correction[3] can yield SP J parameters remarkably close to the full CI results for the model H−He−H system.[65] These studies strongly suggest that excessive spin-delocalization is the cause of the overprediction of J, with the delocalization arising from SIE in the exchange functional.[31,75] However, achieving spin-localization *via* constrained-DFT (C-DFT)[97] has mixed effects on J that strongly depend on the particular system studied.[98,99] One could rationalize this discrepancy by suggesting that localization resulting from the exchange-correlation functional is more robust for describing J than localization from applied constraints in C-DFT, yet this would be contradicted by the observation that LSDA+U/GGA+U and Rung 3.5 functionals[100] do not correct the over-estimation of J for some ferromagnetic complexes despite the fact that they successfully correct the delocalization of unpaired *d* electrons.[84,94] From the above it appears that there is more at play in determining the accuracy which hybrid functionals display for both ferro- and antiferromagnetically coupled systems than simply that these methods find a balance between the localization of HF and the delocalization of semilocal functionals. In other words, for many systems it appears that the choice of exchange-correlation functional matters equally or more than the localization of the density on which that functional is evaluated.

A simple way to address these questions is to calculate J parameters by evaluating semilocal functionals nonself-consistently (NSC) on the more localized densities of their respective hybrid counterparts. Recently several workers have demonstrated that problems associated with SIE and delocalization can be remedied by evaluating functionals nonself-consistently on HF densities. For example, it was demonstrated by Janesko and Scuseria,[29] and Kim and co-workers,[15] that evaluating semilocal functionals nonself-consistently on HF densities could appreciably improve reaction barrier-heights and correct the problem of unbound anions, respectively. Motivated by this, we investigate magnetic exchange couplings in 14 TM complexes calculated by a variety of semilocal functionals (LSDA,[101] PBE,[102] TPSS[103]) by evaluating these functionals nonself-consistently on the converged densities of their hybrids. To systematically probe the effect of HFX and spin-localization we vary in fine intervals the exchange mixing parameter *a*, given by

$$E_{xc} = aE_x^{HF} + (1 - a)E_x^{DFT} + E_c^{DFT} \tag{8}$$

In this way we aim to discern to what extent the overestimation of J is attributable to spin-delocalization (and hence SIE in the exchange functional).

To avoid mixing exchange and correlation effects (in the density functional theory sense) we will use the same correlation functional for all NSC calculations, thereby allowing for a more clean analysis of the role of the exchange functional in these calculations. For completeness then, we will also calculate J self-consistently with different combinations of exchange and correlation functionals. While it has been shown on the LSDA to GGA level in ionic solids that the choice of correlation functional only marginally affects J,[75] we will show in these TM complexes the role of the correlation functional should not be underestimated. In the end this should provide a useful analysis of the relative roles of spin-delocalization, exchange, and correlation on the final computed J parameter.
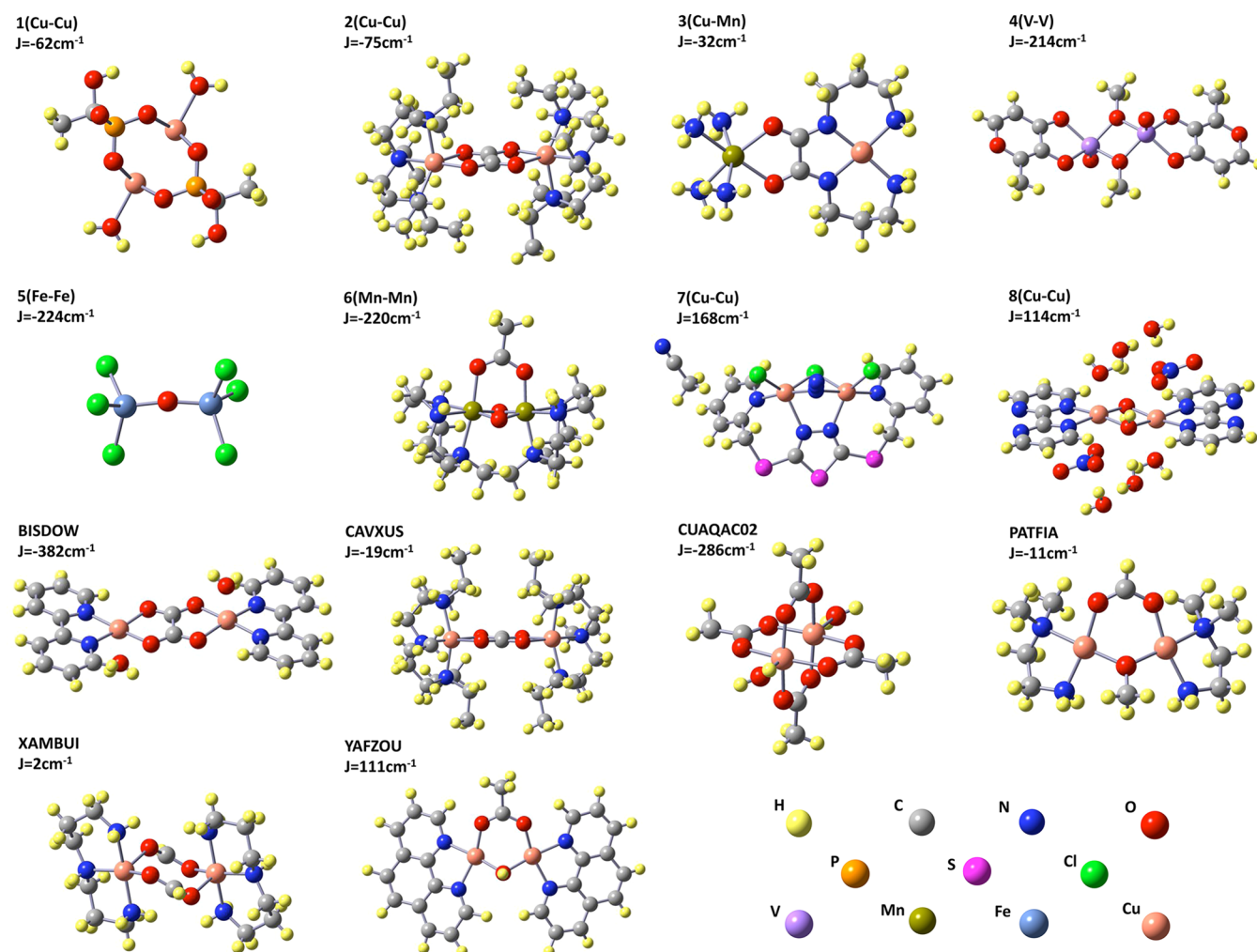
Figure 1. The 14 TM complexes used in this work, presented alongside experimental reference values. All quantities in units of cm^{-1}.

Here it is important to emphasize that SIE originates in the energy functional. Therefore, even if one had the *exact* ground state density of a given system, evaluating an approximate density functional nonself-consistently on this density would still yield an energy contaminated with SIE. However, because we are interested only in *relative energies* of magnetic states, to the extent that SIE is similar for the magnetic states we can expect cancellation of errors. Because in "Heisenberg-like" systems the electron density is approximately the same throughout the different spin-states, this is not an unreasonable expectation.

COMPUTATIONAL DETAILS

All calculations performed here are KS-DFT on the level of theory of LSDA (Slater exchange and Vosko, Wilk, Nusair correlation),[101] PBE (Perdew, Burke, Ernzerhof exchange, and correlation),[102] TPSS (Tao, Perdew, Staroverov, Scuseria exchange, and correlation)[103] and hybrids thereof,[104,105] on the Gaussian '09 suite of programs.[106] For all metal atoms we use the 6-3111+G basis with an additional *f*-type function of exponent 0.5283, while for all other atoms 6-31G(*d*) is used. For numerical integration a pruned-grid of 99 radial shells and 590 angular points per shell is used. All calculations are performed with convergence criteria of 10^{-8} rms variation in the density matrix, 10^{-6} maximum variation in any density matrix element, and 10^{-6} hartree ($\approx$0.2 cm^{-1}) variation in

energy. No symmetry constraints are imposed, and no relativistic effects are considered in the calculations. In all cases magnetic couplings parameters are calculated with the broken-symmetry (BS) spin-projection (SP) method.[61−63] The BS states were obtained with a locally modified C-DFT code by first imposing spin-constraints to force spin-symmetry-breaking and then releasing the constraints once it was clear that the system was properly converging to the target $|\uparrow\downarrow\rangle$ state.[107] The nature of the converged magnetic state was verified by minimum basis-set Mulliken (MBS) spin populations.[108,109]

Because the goal of the NSC calculations herein is to isolate the effect of the exchange functional on the final computed *J* value, the same correlation functional (VWN5) will be used to avoid mixing exchange and correlation effects. Therefore we use SVWN5 (Slater exchange and VWN5 correlation), PBEVWN5 (PBE exchange and VWN5 correlation), and TPSSVWN5 (TPSS exchange and VWN5 correlation). We choose VWN5, a correlation functional from the first-rung of Jacob's Ladder,[110] as presumably it will be the simplest and least accurate of the three correlation functionals and hence provide a good control. We note that this choice is somewhat arbitrary, and hence for completeness we also perform self-consistent calculations for different combinations of exchange and correlation functionals from the LSDA to M-GGA level, i.e. the nine possible combinations of S, PBE, and TPSS exchange with VWN5, PBE, and TPSS correlation.
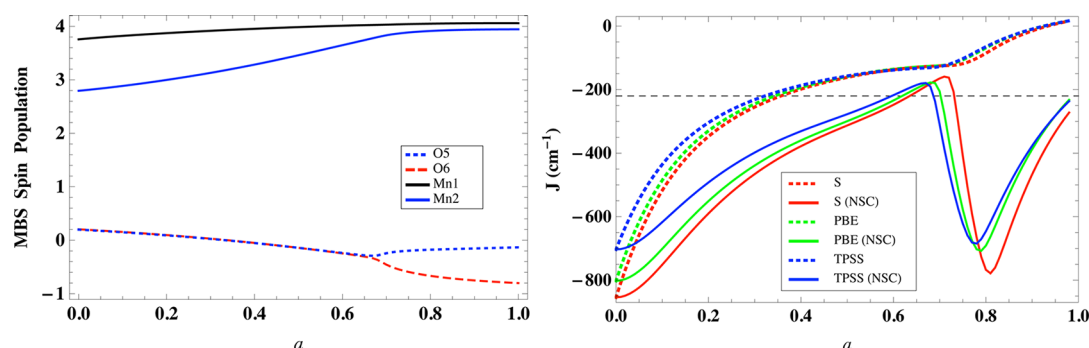
Figure 2. Hybrid DFT calculations with the trapped mixed valence complex, $6Mn^{III}-Mn^{IV}$.[122] Left: MBS spin populations with respect to exchange mixing parameter. Right: Calculated magnetic couplings with respect to exchange mixing parameter. The gray dashed-line indicates the experimental value.

All of the NSC calculations are done as follows: A calculation is converged with a hybrid functional of the form given by

$$E_{xc} = aE^{HFX} + (1-a)E^{DFTX} + E^{VWN5} \qquad (9)$$

and subsequently a semilocal functional of the form

$$E_{xc} = E^{DFTX} + E^{VWN5} \qquad (10)$$

is evaluated NSC on the density. This is repeated across a domain of exchange mixing given by $0.0 \leq a \leq 0.7$ in intervals of $a = 0.01$. In contrast to other workers[15,29] we do not evaluate NSC on HF densities (or HF + DFT correlation) as beyond about $a = 0.7$ the densities of some of these TM complexes become poor (this will be elaborated in subsequent sections). The above is done for DFTX = S, PBE, and TPSS exchange. To assess the relative accuracy of these methods, we define the relative mean error, δ_J, given by

$$\delta_J = \frac{1}{N} \sum_i^N \left| \frac{J_{calc}^i - J_{exp}^i}{J_{exp}^i} \right| \qquad (11)$$

where $N = 14$ (the number of TM complexes in this set), and J_{calc}^i and J_{exp}^i are the calculated and experimentally determined J values of the i'th complex. We find that a statistical measure of this nature is useful, as it accounts for the order of magnitude differences in J that can occur for different systems.

TM Complexes. The systems included in this study were chosen from the open-shell databases of Valero and co-workers[81] and Rudra and co-workers.[98] In all cases the geometries used are the crystallographic structures, and no further optimizations have been performed, as geometry-optimizations in "gas-phase" calculations can lead to conformations not possible in the crystal-phase.[111] From the test-set of Valero et al. we have selected six dinuclear Cu^{II} complexes, given by BISDOW,[112] CAVXUS,[113] CUA-QAC02,[114] PATFIA,[115] XAMBUI,[111] and YAFZOU.[116] YAFZOU and XAMBUI are ferromagnetic, while the other four complexes are antiferromagnetic. All of the above six complexes have $S_1 = S_2 = 1/2$ metal centers. From the set of Rudra et al. we have selected $1Cu^{II}-Cu^{II}$,[117] $2Cu^{II}-Cu^{II}$,[118] $3Cu^{II}-Mn^{II}$,[119] $4V^{IV}-V^{IV}$,[120] $5Fe^{III}-Fe^{III}$,[121] $6Mn^{III}-Mn^{IV}$,[122] $7Cu^{II}-Cu^{II}$,[85] and $8Cu^{II}-Cu^{II}$.[123] Of these, $7Cu^{II}-Cu^{II}$ and $8Cu^{II}-Cu^{II}$ are ferromagnetic, while $1Cu^{II}-Cu^{II}$, $2Cu^{II}-Cu^{II}$, $4V^{IV}-V^{IV}$, and $5Fe^{III}-Fe^{III}$ are antiferromagnetic, and $3Cu^{II}-Mn^{II}$ and $6Mn^{III}-Mn^{IV}$ are ferrimagnetic. The metal atoms of this set have the following spin: for Cu^{II} and V^{IV} $S = 1/2$, for Fe^{III} and Mn^{II} $S = 5/2$, while for Mn^{III} and Mn^{IV} $S = 2$ and $S = $

3/2, respectively. Altogether these comprise a set of 14 dinuclear and heteronuclear TM complexes, and they are shown in Figure 1 alongside their experimentally determined J parameters.

RESULTS

As mentioned before and elsewhere,[31,77,81,84,86,91,124] the presence of HFX has a pronounced effect on the localization of spin-density onto metal atoms, enough so that one can essentially tune spin-localization at will by dialing the parameter a in eq 9 between the two extremes of $a = 0$ and $a = 1$. Unfortunately this means by dialing a to high enough values in some cases one can obtain solutions so localized that their physical meaning is dubious. Hybrid DFT calculations with the complex $6Mn^{III}-Mn^{IV122}$ are a good example of such a case. This trapped mixed valence system features four unpaired electrons on Mn^{III} ($S = 2$) and three unpaired electrons on Mn^{IV} ($S = 3/2$), yet at high HFX admixture hybrid calculations can yield $S = 2$ for both metal atoms. To maintain the correct spin-multiplicity then an antialigned unpaired electron appears on one of the bridging oxygen atoms. This is shown in Figure 2, where on the left the MBS spin populations of the two Mn and their two O bridging ligands are plotted, and on the right the J couplings for SVWN5, PBEVWN5, and TPSSVWN5 evaluated self-consistently and NSC are plotted. Though the spin-population on Mn1 is only moderately affected, the spin-population on Mn2 clearly ramps-up greatly from about 2.8 at $a = 0$ to 3.8 at $a = 0.7$, at about which the spin of O6 sharply deviates from O5, producing essentially an entire unpaired electron on O6. Concomitant with the deviation between O5 and O6 is a sharp oscillation in J for the NSC calculations as well as a sudden bend for the self-consistent results. Though not all complexes displayed such unphysical behavior for $a \geq 0.7$, for several systems we were not able to obtain convergence for $a \geq 0.8$ with all the functionals. This suggests that at very high exchange admixtures these hybrids are not consistently yielding a meaningful description of these systems, and for these reasons we will focus our analysis on the regime of $0 \leq a \leq 0.7$ in this work. Nevertheless, as the right-hand plot in Figure 2 indicates, the magnetic couplings both for the NSC and self-consistent calculations were improved considerably as HFX was admixed in, and in the subsequent section this will be discussed in detail.

Nonself-Consistent vs Self-Consistent Calculations. In Figure 3 we show the relative mean error, δ_J, as calculated by eq 11, for SVWN5, PBEVWN5, and TPSSVWN5. The solid-line curves correspond to J values calculated by evaluating the
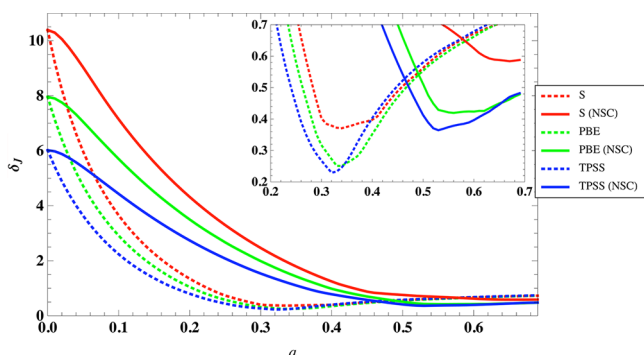
Figure 3. Relative mean error, δ_J, as calculated by eq 11, plotted with respect to the exchange mixing parameter, a, as defined by $E_x = (1 - a)E_x^{DFT} + aE_x^{HF}$, for SVWN5 (red), PBEVWN5 (green), and TPSSVWN5 (blue). The dotted lines correspond to hybrid calculations, while solid lines correspond to semilocal functionals evaluated nonself-consistently (NSC) on hybrid densities. The graph inset in the upper-right is a zoom-in of the relevant region where all curves reach their respective minima.

semilocal functional of eq 10 NSC on the densities converged by the hybrid of eq 9, while the dashed-line curves correspond to J values from self-consistent calculations with the hybrid of eq 9. Immediately evident from Figure 3 is the very large (approximately order of magnitude or greater) drop in δ_J both for NSC and self-consistent calculations as the exchange mixing parameter a is increased. Depending on the functional used, for the self-consistent calculations δ_J reaches a minimum between 32 and 34% HFX admixture, while for the NSC calculations the δ_J is minimized between 53 and 68%. That δ_J minimizes in the vicinity of 33% HFX for the hybrids investigated here reflects closely the previously reported results of other workers.[31,33,77,79,86,93] Comparing the δ_J minima for self-consistent calculations at $a \approx 0.33$ and NSC calculations at $a \approx 0.55$, the results indicate that semilocal functionals can on average be as accurate as their standard respective hybrids for calculating magnetic couplings provided that their delocalization-error is compensated for. Furthermore, as one climbs Jacob's Ladder the δ_J minima become successively lower and occur at smaller HFX admixtures, both for the NSC and self-consistent calculations. This strongly indicates that more sophisticated functionals (e.g., TPSS) are plagued with less SIE (both 1-electron and many) and hence require less HFX to minimize δ_J, with the SIE-induced spin-delocalization accounting for the majority of the large δ_J seen in semilocal functionals.

The above would seem to verify one of the earlier mentioned possibilities, i.e. the problem with overestimation of J lies in the too-delocalized density yielded by the semilocal functional, not in the relative energies given by the semilocal functional itself. However this simple explanation fails when one looks at the predicted couplings on a case-by-case basis. To demonstrate this, in Figure 4 and Figure 5 we plot $J_{calc} - J_{exp}$ with respect to the exchange mixing parameter a for TPSSVWN5 evaluated self-consistently and NSC, respectively (similar figures for SVWN5 and PBEVWN5 can be found in the Supporting Information). As the purpose of these graphs is to provide a "bird's-eye view" of the dependence of the computed magnetic coupling on the nature of the exchange functional for the group of antiferromagnetic/ferrimagnetic complexes as a whole vs individual ferromagnetic complexes, in Figure 4 and Figure 5 the antiferromagnetic/ferrimagnetic complexes are all indicated
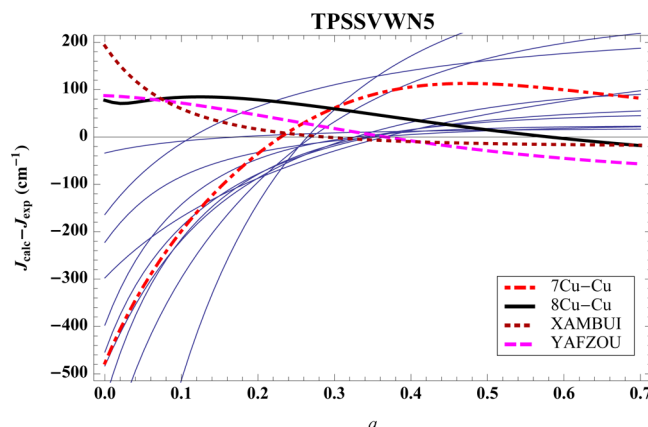

Figure 4. Difference between calculated and experimental magnetic couplings for self-consistent TPSSVWN5 with varying exchange weightings, a. The blue solid-lines indicate magnetic couplings of antiferromagnetic and ferrimagnetic complexes, while the remaining four lines represent magnetic couplings of the four ferromagnetic complexes, $7Cu^{II}-Cu^{II}$, $8Cu^{II}-Cu^{II}$, XAMBUI, and YAFZOU. Note that the curve of XAMBUI has been scaled by a factor of 10 in order to make its trend visible.
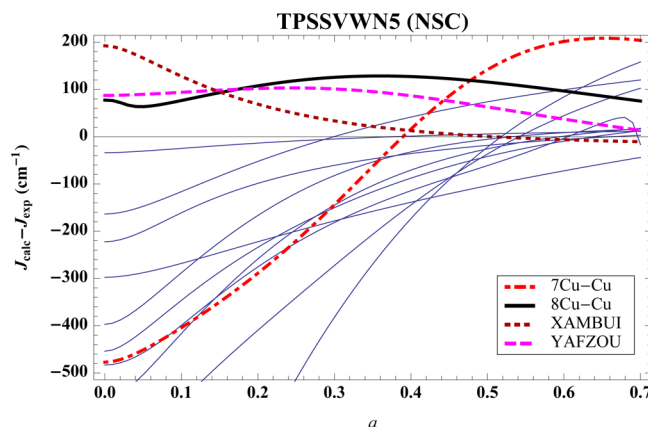

Figure 5. Difference between calculated and experimental magnetic couplings for NSC TPSSVWN5 with varying exchange weightings, a. The blue solid-lines indicate magnetic couplings of antiferromagnetic and ferrimagnetic complexes, while the remaining four lines represent magnetic couplings of the four ferromagnetic complexes, $7Cu^{II}-Cu^{II}$, $8Cu^{II}-Cu^{II}$, XAMBUI, and YAFZOU. Note that the curve of XAMBUI has been scaled by a factor of 10 in order to make its trend visible.

with a solid-blue line, while the four ferromagnetic complexes are individually marked.

Beginning with Figure 4, one can see that the computed magnetic couplings for antiferromagnetically coupled complexes as a whole have a remarkably uniform behavior with respect to exchange admixture parameter a: at small a the magnetic coupling is overestimated in magnitude (the calculated J is too antiferromagnetic), and as a is dialed-up the magnitudes of the predicted couplings decay rapidly. The tendency for semilocal functionals to predict J to be too antiferromagnetic in antiferromagnetically coupled systems is well-known and has been attributed to the exchange functional's underestimation of the on-site repulsion, U, leading to an exceedingly large J_{AFM} contribution.[33] The admixture of HFX leads to large increases in U and reductions in J_{AFM}.

Table 1. Magnetic Exchange Couplings As Calculated for Different Combinations of Exchange and Correlation Functionals[a]

	exchange									
	S			PBE			TPSS			
	correlation									
	VWN5	PBE	TPSS	VWN5	PBE	TPSS	VWN5	PBE	TPSS	J_{exp}
1(Cu–Cu)	−1195	−1178	−1179	−842	−832	−833	−619	−615	−615	−62
2(Cu–Cu)	−968	−974	−976	−713	−717	−719	−529	−534	−536	−75
3(Cu–Mn)	−365	−359	−359	−310	−304	−304	−254	−251	−251	−32
4(V–V)	−842	−902	−911	−547	−599	−607	−378	−422	−427	−214
5(Fe–Fe)	−591	−576	−572	−577	−562	−558	−522	−508	−505	−224
6(Mn–Mn)	−854	−814	−807	−802	−756	−749	−703	−662	−656	−220
7(Cu–Cu)	−379	−285	−278	−362	−280	−275	−309	−235	−231	168
8(Cu–Cu)	350	354	359	247	258	263	191	208	213	114
YAFZOU	367	390	394	241	260	264	198	213	216	111
XAMBUI	26	30	30	23	26	26	21	24	24	2
PATFIA	−673	−621	−614	−536	−497	−491	−408	−382	−375	−11
CAVXUS	−127	−114	−115	−93	−83	−84	−53	−46	−46	−19
CUAQAC02	−1511	−1485	−1477	−1145	−1139	−1133	−981	−984	−980	−286
BISDOW	−3243	−3278	−3282	−2335	−2373	−2377	−1788	−1826	−1829	−382
δ_J	10.39	10.09	10.05	7.96	7.74	7.71	6.02	5.90	5.87	

[a]All quantities in units of cm^{-1}.

In contrast, the ferromagnetic complexes in Figure 4 behave less uniformly: YAFZOU and 8Cu^{II}–Cu^{II} are overestimated at low a but decay comparatively slowly with increasing a; XAMBUI is also overestimated at low a but instead decays rapidly with increasing a similar to antiferromagnetically coupled complexes; 7Cu^{II}–Cu^{II} is predicted to be strongly antiferromagnetic at low a and rapidly becomes ferromagnetic with increasing a. For XAMBUI it is known that the magnetic orbitals have a parallel alignment which reduces the super-exchange contribution to J_{AFM},[81,111] thus leaving J to be determined by a weak J_{FM} contribution. Therefore, that the coupling of XAMBUI is strongly overestimated indicates the approximate semilocal functional is overestimating the direct exchange contribution to J_{FM}. For YAFZOU and 8Cu^{II}–Cu^{II} a similar overestimation of J_{FM} is likely the origin of the overestimation of J. At this point though, whether the overestimation of J_{FM} is due to the delocalization error or the actual energy expression of the semilocal functional is unclear. The prediction of 7Cu^{II}–Cu^{II} to be strongly antiferromagnetic at low exchange mixing is not necessarily surprising if one remembers that the DFT magnetic orbitals are typically too delocalized,[31] and delocalization can enhance the interactions contributing to both J_{FM} and J_{AFM}.

Turning now to Figure 5, the antiferromagnetically coupled complexes again as a whole behave uniformly with respect to a, and furthermore their trends are qualitatively similar to the self-consistent results of Figure 4: overprediction at low a accompanied by swift reductions in magnitude of the computed coupling with increasing a, albeit with a reduction that is not quite as rapid as the self-consistent calculations. Looking at the ferromagnetic complexes, the NSC results for 7Cu^{II}–Cu^{II} and XAMBUI are also qualitatively very similar to their self-consistent counterparts in Figure 4. For XAMBUI at least this shows that the overestimation of J_{FM} was due to the delocalization of the density, not the energy expression itself. However the NSC results for 8Cu^{II}–Cu^{II} and YAFZOU are markedly different: the coupling of YAFZOU remains essentially flat with respect to a and does not begin to reduce in magnitude until $a > 0.4$, while the coupling of 8Cu^{II}–Cu^{II} at

$a = 0.7$ is no lower in magnitude than at $a = 0$. Note that for both systems this is occurring despite quite large changes in their spin-densities from $a = 0$ to $a = 0.7$. For example, the MBS spin populations of 8Cu^{II}–Cu^{II} and YAFZOU at $a = 0$ are about 0.67 and 0.62, respectively, while at $a = 0.7$ they are 0.9 and 0.87, respectively. That the magnetic coupling of these complexes displays such a stubborn indifference to large changes in spin-density indicates that the delocalization-error is not responsible for the overestimation of J with YAFZOU and 8Cu^{II}–Cu^{II}, and the reduction in magnitude of the coupling for self-consistent calculations in Figure 4 for these two complexes must be due entirely to the incrementing presence of HFX in the energy functional. To return to the original question, for at least YAFZOU and 8Cu^{II}–Cu^{II} this indicates that the problem is not the density but the relative energies of the semilocal functional itself. Here we note that Rivero and co-workers[94] made a very similar observation pertaining to the failure of LDA+U and GGA+U to correct the overestimation of J for the two ferromagnetic complexes YAFZOU and JEJCIK.[125] The authors observed that for these two complexes the calculated coupling was almost independent of the U parameter, indicating a more fundamental failure in the exchange functional's capacity for correctly describing the direct exchange responsible for J_{FM}. Obviously then our NSC calculations are demonstrating a very similar point for YAFZOU and 8Cu^{II}–Cu^{II}, though we cautiously point out that the results for XAMBUI and 7Cu^{II}–Cu^{II} indicate that this is not general to ferromagnetic complexes.

A possible explanation for the overprediction of J for ferromagnetic systems is that the approximate exchange functional is overestimating the direct exchange contribution to J_{FM}. Admixture of HFX in the exchange functional then is needed not only for localization of the density but also to give an accurate (not overestimated) description of the direct exchange. However this view would have difficulty to explain why 7Cu^{II}–Cu^{II} is predicted to be strongly antiferromagnetic by semilocal functionals, and why both 7Cu^{II}–Cu^{II} and XAMBUI can be correctly described by semilocal functionals when the delocalization-error is compensated for. Furthermore,

Table 2. MBS Spin Populations As Calculated for Different Combinations of Exchange and Correlation Functionals[a]

	exchange								
	S			PBE			TPSS		
	correlation								
	VWN5	PBE	TPSS	VWN5	PBE	TPSS	VWN5	PBE	TPSS
1(Cu−Cu)	0.5965	0.6016	0.6021	0.6179	0.6232	0.6236	0.6418	0.6469	0.6474
2(Cu−Cu)	0.5631	0.5683	0.5686	0.5870	0.5923	0.5926	0.6103	0.6157	0.6161
3(Cu−Mn)	0.5461	0.5492	0.5499	0.5665	0.5693	0.5700	0.5860	0.5886	0.5894
	4.8494	4.8664	4.8635	4.8503	4.8677	4.8648	4.8639	4.8805	4.8775
4(V−V)	1.0915	1.0960	1.0931	1.0873	1.0979	1.0963	1.0999	1.1126	1.1111
5(Fe−Fe)	4.0655	4.0882	4.0891	4.0840	4.1072	4.1079	4.1145	4.1383	4.1391
6(Mn−Mn)	3.7158	3.7296	3.7288	3.7306	3.7484	3.7475	3.7561	3.7753	3.7745
	2.8568	2.8906	2.8925	2.8010	2.8395	2.8413	2.7948	2.8348	2.8368
7(Cu−Cu)	0.5079	0.5142	0.5146	0.5284	0.5349	0.5353	0.5523	0.5588	0.5593
8(Cu−Cu)	0.5934	0.5952	0.5955	0.6293	0.6311	0.6314	0.6678	0.6691	0.6693
YAFZOU	0.5752	0.5781	0.5785	0.5970	0.5998	0.6002	0.6187	0.6213	0.6219
XAMBUI	0.5879	0.5900	0.5904	0.6138	0.6157	0.6162	0.6362	0.6380	0.6386
PATFIA	0.5697	0.5736	0.5740	0.5906	0.5944	0.5948	0.6107	0.6145	0.6149
CAVXUS	0.5580	0.5634	0.5639	0.5798	0.5852	0.5857	0.6013	0.6069	0.6075
CUAQAC02	0.6141	0.6164	0.6169	0.6390	0.6411	0.6415	0.6612	0.6631	0.6636
BISDOW	0.6153	0.6177	0.6182	0.6383	0.6406	0.6410	0.6593	0.6614	0.6619

[a]For all systems (except for 3Cu−Mn and 6Mn−Mn) the population of only one metal center is given, as they are practically identical. For 3Cu−Mn and 6Mn−Mn two rows are listed for each complex, corresponding to the two spin-centers of each complex. All spin populations listed are for the HS state.

if the presence of HFX in the energy expression reduces J_{FM}, then one would expect the self-consistent curves of strong antiferromagnetically coupled complexes to be shifted more negative at low a than the respective NSC curves, but this is not what happens: Figure 5 and Figure 4 clearly show that NSC ferri/antiferromagnetic curves are more negative at low a. Evidently for a given fixed density, replacing some DFT exchange with HFX reduces not only J_{FM} but also J_{AFM} as well. We think the simplest explanation of this observation is that the approximate exchange functional must be responsible for some of the correlation effects contributing to J_{AFM}, and in the subsequent section we will argue that the results for different exchange and correlation functionals suggest both these correlation effects and the direct exchange are overestimated by approximate exchange functionals in a system dependent manner.

Exchange vs Correlation. In Table 1 and Table 2 we show calculated magnetic couplings and MBS spin populations, respectively, for the nine possible combinations of S, PBE, and TPSS exchange with VWN5, PBE, and TPSS correlation. Looking at the δ_J values in Table 1, one can see that the choice of correlation functional only marginally affects δ_J, the effect being a full order of magnitude smaller than choice of exchange. Similar observations have been made before by Illas and Martin.[75] However what is interesting to notice is that the error δ_J always reduces with increasing sophistication of exchange and correlation functionals (e.g., the largest and smallest δ_J are found with SVWN5 and TPSSTPSS, respectively, while PBEPBE yields the median δ_J). At first glance this is encouraging, as it implies that successively more sophisticated exchange and correlation functionals are yielding increasingly more accurate predictions of J. However when one looks closer, the small reduction in δ_J for correlation functionals of increasing sophistication is entirely a statistical bias resulting from our test-set having more antiferromagnetically than ferromagnetically coupled complexes. This is because for all

complexes (except $2Cu^{II}−Cu^{II}$, $4V^{IV}−V^{IV}$, and BISDOW) our results show that increasing the sophistication of the correlation functional almost always makes J more positive (more ferromagnetic). Therefore with a set where the calculated couplings for 11 out of 14 complexes are already too antiferromagnetic, this effect must invariably reduce δ_J.

Despite the negligible effect this has on δ_J, the tendency for more accurate correlation functionals to make J more positive should not be dismissed as unimportant compared to effects from the exchange functional. Indeed, for $7Cu^{II}−Cu^{II}$ the correlation functional actually has a larger effect on J than exchange, while for XAMBUI they are on roughly equal footing. For $1Cu^{II}−Cu^{II}$ though the effect of the correlation functional is miniscule ($\sim$5 to 20 cm^{-1}) compared to the dominant effect of the exchange functional ($\sim$500 cm^{-1}), so this is obviously a strongly system dependent. Nevertheless, this behavior is still frustrating as it implies that for most cases the problem of overestimation of J in ferromagnetic complexes will actually be exacerbated by improving the sophistication of the correlation functional. A consequence of this is that systems like XAMBUI experience little improvement from SVWN5 to TPSSTPSS, as whatever gains are made with the exchange functional are almost completely nullified by the correlation functional. More specifically, for YAFZOU, XAMBUI, and $8Cu^{II}−Cu^{II}$ the worst calculated couplings are found with STPSS, while the best are found with TPSSVWN5. What is the origin of higher rung correlation functionals yielding more ferromagnetic J couplings? A simple and intuitive answer is found with reference to the work of Calzado et al.,[33] wherein they analyzed the relevance of the on-site repulsion U to the magnetic coupling in dinuclear complexes. These authors demonstrated that approximate density functionals significantly underestimate U, which leads to the common overprediction of J for antiferromagnetic complexes. While the authors attributed the underestimation of U to the exchange functional,[33] the trends in Table 1 suggest that correlation functionals on higher rungs

of Jacob's Ladder are yielding increasingly more accurate (larger) on-site repulsions, resulting in J becoming more positive. Additionally, it is worth noting in Table 2 that increasing the sophistication of the correlation functional results in a small but consistent enhancement of the metal spin-populations for all complexes. This is not surprising if one remembers that SIE can originate not only from the exchange functional but also from unphysical one-electron self-correlation in the correlation functional. Because more delocalized magnetic orbitals result in smaller on-site repulsions[31] (which tend to make J more antiferromagnetic), it is possible that this enhancement of the spin-populations for all complexes is related to J becoming more positive with correlation functionals of increasing sophistication. As a final remark on the role of the correlation functional, the results here are contrasted with those of wave function-based methods, where often successively more sophisticated calculations make the final computed J more negative (more antiferromagnetic).[32,48,50,52−54] As mentioned previously, this is because J_{AFM} largely is the result of dynamic correlation effects which are only progressively recovered at higher levels of theory. What is more, properly recovering the necessary correlation effects in wave function methods can greatly impact the computed J value. For example, ascending from CASCI to the DDCI level of theory can alter J in some antiferromagnetic dinuclear Cu^{II} complexes by an order of magnitude.[32] While in this work we argue that the role of the correlation functional has been perhaps underestimated for TM complexes, clearly in Table 1 there are no variations with the correlation functional that approach remotely near even a factor of 2, much less an order magnitude change in J. To account for this discrepancy between KS-DFT and wave function methods, the correlation effects contributing to J_{AFM} must be overestimated at lower levels of theory (with higher levels revising this and making J more positive), and/or these correlation effects must be divided between the exchange and correlation functional in their treatment.

Turning now to the exchange functional, Table 1 shows that contrary to correlation, increasing the sophistication of the exchange functional *always improves J* for all complexes and for all possible pairings with different correlation functionals. Furthermore, increasing the sophistication of the exchange functional always reduces the magnitude of J, both for ferro- and antiferromagnetic couplings. For many systems this effect can be quite large: systems like $4V^{IV}−V^{IV}$ and CAVXUS decrease by over a factor of 2 from Slater to TPSS exchange, while systems like BISDOW, CUAQAC02, $1Cu^{II}−Cu^{II}$, and $2Cu^{II}−Cu^{II}$ still reduce in magnitude considerably. In contrast, the systems $7Cu^{II}−Cu^{II}$, XAMBUI, and $5Fe^{III}−Fe^{III}$ are only weakly affected by the exchange functional. While there does not appear to be a general trend to these results, it is somewhat perplexing that the systems most strongly affected by choice of exchange are strong antiferromagnetic complexes (e.g., BISDOW). If one operates from the vantage that the exchange functional is responsible for describing J_{FM} while the correlation functional describes J_{AFM}, then it would be intuitive to expect that systems dominated by J_{FM} (J_{AFM}) would be affected strongly (weakly) by the choice of exchange functional. Yet what one finds in Table 1 is that both ferro- and antiferromagnetically coupled systems can be affected strongly by the exchange functional, with antiferromagnetic complexes typically showing the greatest dependence.

One explanation of this is that in addition to describing the direct exchange largely responsible for J_{FM}, the exchange functional also indirectly modulates the magnitude of J_{FM} and J_{AFM} through spin-localization. This could make sense, as Table 2 shows the exchange functional has an order of magnitude greater effect on the metal spin-populations than correlation for many of the systems in this set (e.g., $1Cu^{II}−Cu^{II}$), and Figure 3 and Figure 5 in the prior section clearly establish that spin-localization is important for many systems. However this still does not explain the large reductions in magnitude of J for a system like $4V^{IV}−V^{IV}$: at the PBEVWN5 level the spin-density is actually slightly more delocalized than at SVWN5, and TPSSVWN5 yields a spin-density that is only marginally more localized than SVWN5, yet as one ascends each level of theory J is always considerably reduced in absolute value. More generally, there is not a very good correlation between the change in spin-localization and change in J with respect to different exchange functionals in Table 1 and Table 2. For example, the metal spin-populations of $7Cu^{II}−Cu^{II}$ change by ≈ 0.05 (which is one of the larger variations seen), yet its computed magnetic coupling shows one of the weakest responses to choice of exchange functional. BISDOW, in contrast, shows similar ≈ 0.05 variations in the metal spin-populations yet displays a strong variation in J with the exchange functional. Furthermore, we know from Figure 5 that correcting spin-delocalization has a pronounced effect on J for both of these systems. Clearly the exchange functional is capable of strongly determining J for systems dominated by J_{AFM} for reasons independent of spin-localization. Again, we think this demonstrates that the exchange functional must be accounting for some of the correlation effects responsible for J_{AFM}. Additionally, here we note that Rivero and co-workers have made similar observations.[88]

To recap the important results for this section, we have seen that both calculations with fixed exchange and varying correlation, and calculations with fixed correlation and varying exchange, consistently demonstrate that some of the correlation effects important to J must in actuality be coming from the approximate exchange functional. The notion that exchange and correlation in the Kohn−Sham density functional theory sense are not precisely the same as exchange and correlation in the conventional wave function theory sense is not a new one: differences exist in how they are defined in theory,[126] and in practice it has been often observed that exchange-only KS-DFT calculations contain aspects of correlation in their energies[127,128] and densities.[129,130] Particularly, Jankowski and co-workers have shown for Neon and Argon (systems where dynamic correlation effects dominate) that exchange-only KS-DFT calculations, both with and without SIE correction, display aspects of correlation.[130] In this light, it seems justifiable to speculate that some dynamic correlation contributions to J_{AFM} are in fact coming from the approximate exchange functional.

■ CONCLUSIONS

Calculations with semilocal functionals evaluated nonself-consistently on hybrid densities as well as self-consistent calculations with a variety of different exchange and correlation functionals from LSDA to M-GGA have been performed to explore the overprediction problem of magnetic exchange couplings in transition-metal complexes in Kohn−Sham density functional theory. This has led to a number of insights as well as provided complementary evidence and understanding to long-

standing issues with magnetic coupling parameters in density functional theory, with the most relevant being the following:

1. Nonself-consistent calculations demonstrate that semilocal functionals can yield magnetic couplings with accuracy on the level of hybrid functionals provided that the delocalization of the unpaired metal d electrons is corrected. However, while correcting delocalization can drastically improve J for some systems, it cannot generally be considered a panacea for TM complexes. For example, with some ferromagnetic complexes J can remain stubbornly overestimated, independent of spin-localization, while with some antiferromagnetic complexes the improvement in J with respect to increasing exchange mixing a is significantly slower with nonself-consistent semilocal calculations than with self-consistent hybrid. This shows that the presence of Hartree−Fock-like exchange is needed in the exchange functional not just to remove SIE and the resulting delocalization but also to yield more accurate relative energies of the magnetic states. Because of this, self-consistent evaluation of a hybrid functional remains the optimal choice for calculating magnetic couplings, and we are not advocating nonself-consistent calculations as a practical methodology for computing coupling parameters.

2. More sophisticated correlation functionals tend to make J more positive (more ferromagnetic), which ameliorates the overestimation problem in antiferromagnetically coupled complexes and exacerbates it in ferromagnetically coupled complexes. While this effect can often be small relative to the exchange functional, for some systems it can be larger and hence generally should not be underestimated. This is strongly contrasted with wave function methods, where more accurate treatments of correlation tend to make J more negative, and can often substantially alter the final computed value.

3. From Tables 1 and 2, more sophisticated exchange functionals in all 14 complexes reduce the magnitude of J, both for ferro- and antiferromagnetically coupled complexes, and in a manner that is apparently independent of spin-localization. Strong antiferromagnetic complexes tend to show the greatest response to variations in the exchange functional, whereas ferromagnetic complexes have a more moderate response.

4. Together, points 2 and 3 suggest that the role of the exchange functional is limited not just to describing the direct exchange contributions to J_{FM} but additionally some dynamic correlation contributions to J_{AFM}. This is in line with previously reported KS-DFT exchange-only calculations which yield densities with aspects of correlation for systems known to be dominated by dynamic correlation.[130]

Why do self-consistent calculations with hybrid functionals display good accuracy for both ferro- and antiferromagnetically coupled complexes? We think there is a confluence of three mechanisms at work. First, Hartree−Fock-like exchange has a pronounced effect on spin-localization, and the nonself-consistent results in this work clearly indicate that localization improves J substantially for most complexes. Second, approximate exchange functionals can overestimate the direct exchange contribution to J_{FM}; therefore, replacing some density functional theory exchange with HFX can ameliorate over-estimation of J in ferromagnetic complexes. Third, the approximate exchange functional is responsible for some of the dynamic correlation contributions to J_{AFM}, while HFX does not include these correlation effects. Hence, hybrid functionals which build HFX in place of DFTX lose some of these contributions to J_{AFM}, which mitigates overestimation in antiferromagnetically coupled complexes. Taken altogether,

this explains why hybrids can calculate J accurately, albeit sometimes in an empirical system-dependent manner.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A table of $\langle \hat{S}^2 \rangle$ values for the HS and BS states for all complexes and all combinations of exchange and correlations functionals is provided. Additionally, figures showing the calculated magnetic couplings for self-consistent and nonself-consistent SVWN5 and PBEVWN5 with respect to exchange admixture a can be found. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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