

# Performance of the M06 family of exchange-correlation functionals for predicting magnetic coupling in organic and inorganic molecules

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The performance of the M06 family of exchange-correlation potentials for describing the electronic structure and the Heisenberg magnetic coupling constant ( $J$ ) is investigated using a set of representative open-shell systems involving two unpaired electrons. The set of molecular systems studied has well defined structures, and their magnetic coupling values are known experimentally. As a general trend, the M06 functional is about equally as accurate as B3LYP or PBE0. The performance of local functionals is important because of their economy and convenience for large-scale calculations; we find that M06-L local functional of the M06 family largely improves over the local spin density approximation and the generalized gradient approximation.

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## INTRODUCTION

The seminal work of Becke introducing the concept of hybrid density functional theory<sup>1</sup> constituted a large step forward in the quantitative description of main-group thermochemistry. The popular B3LYP (Refs. 1 and 2) functional has 20% nonlocal Hartree–Fock exchange, and other hybrid functionals such as PBE0 (Ref. 3) [also called PBE1PBE (Ref. 4) and PBEh] have been introduced that follow the spirit of B3LYP and exhibit similar performance. The success of these functionals is intrinsically linked to the introduction of an amount of Hartree–Fock exchange close to that proposed by Becke in his original work.<sup>1–5</sup> Progress in making density functional theory accurate for other properties has been slower. Recently a new suite of hybrid meta functionals (also called hybrid meta GGA functionals), including also one local meta functional (also called a meta GGA functional), generically called the M06-family, the M06 suite, or the set of M06-class functionals, has been introduced, which performs substantially better than B3LYP for a broad and meaningful set of molecular systems and properties.<sup>6–8</sup> The fraction of Hartree–Fock exchange in these functions ranges from 0% to 100%. Even the local functional of the M06 family (i.e., the functional with 0% Hartree–Fock exchange, which is called M06-L) provides results for thermochemistry that are competitive with those predicted by the B3LYP functional.<sup>6,8</sup> In addition, the hybrid functionals of the M06 family represent an overall improvement over B3LYP for a large number of applications including thermochemistry, reactive energy barriers, and weak interactions.<sup>8</sup> The M06 family has been tested for both closed-shell systems and open-

shell systems with the ground-state spin quantum number and for selected excited states of atoms<sup>8</sup> and Fe-containing diatomics.<sup>9</sup> Here we further investigate the performance of the M06-class functionals in describing electronic structure and properties of open-shell systems in various spin states.

A particularly interesting property involving open shells is the magnetic coupling in organic diradicals<sup>10–31</sup> and transition metal complexes.<sup>25–83</sup> Magnetic coupling is an observable strongly dominated by electron exchange and correlation effects.<sup>33</sup> Both nondynamical and dynamical correlation effects are important for this property.<sup>26,49,51,55,56</sup> The magnetic coupling constant can be extracted from a variety of experimental observables, such as magnetic susceptibility versus temperature measurements or polarized neutron diffraction experiments, if a model spin Hamiltonian is assumed. For typical magnetic systems in which the magnetism arises from transition metal centers, a nearest-neighbor Heisenberg spin Hamiltonian provides a sufficiently accurate description of the low-energy spectrum. This is given by

$$H = - \sum_{i>j} J_{ij} S_i \cdot S_j, \quad (1)$$

where  $J_{ij}$  is a phenomenological coupling constant, and  $S_i$  and  $S_j$  are atomic electron spin operators.  $J_{ij}$  is called the magnetic coupling constant, but it is not the result of a magnetic dipole interaction, which would be much too small to account for the spin splitting. Rather it arises from the fact that electronic kinetic and Coulomb energies depend on the spin state. For a system with two magnetic centers (atoms or groups of atoms),  $A$  and  $B$ , Eq. (1) reduces to

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$$H = -JS_A \cdot S_B. \quad (2)$$

When centers *A* and *B* correspond to particles with effective spin  $S = \frac{1}{2}$ , this Hamiltonian has two eigenstates, a triplet and a singlet with energies  $-J/4$  and  $+3J/4$ , respectively. Therefore, it is possible to map the Heisenberg eigenstates to the lowest triplet and singlet electronic states, and the magnetic coupling constant is simply given by the singlet-triplet energy difference. In a Hartree-Fock, independent-particle description, *J* may be equated to twice the exchange integral in this case of two spin- $\frac{1}{2}$  centers. This is precisely the reason why many authors define the Heisenberg Hamiltonian in Eq. (2) using  $2J$  instead of *J*. Therefore, one must be very careful when comparing experimental and theoretical results and ensure that the same definition of the Heisenberg Hamiltonian is used. For more complicated systems one can use similar mapping techniques<sup>25,30,45</sup> or make use of effective Hamiltonian theory.<sup>59</sup>

The objective of the present study is to explore the performance of the M06 family of exchange-correlation potentials in a set of representative systems, each involving two unpaired electrons. To this end, we first present a database of molecular compounds with well defined crystal structure and experimentally known magnetic coupling. Next, we discuss the different methods used and how to obtain the suitable energy difference and thus analyze the *J* values predicted by the different functionals.

## OPEN-SHELL DATABASE

In this section, we describe a broad family of molecular magnetic systems which are used to systematically investigate the performance of the M06-class exchange-correlation functionals to predict magnetic coupling constants. This set of molecules can also be used to test the performance of other exchange-correlation potentials or of wave function methods. The database includes the widely used H-He-H model system, two organic diradicals, and a representative set of molecular binuclear Cu complexes covering a broad range of *J* values, ranging from strong ferromagnetic coupling to strong antiferromagnetic coupling, and a wide diversity of bridging ligands. The linear H-He-H model system has been studied at three different He-H distances as in previous work.<sup>84</sup> The two organic diradicals considered are  $\alpha$ -4-dehydrotoluene and 1,1',5,5'-tetramethyl-6,6'-dioxo-3,3'-biverdazyl. The Cu complexes have been selected due to the simplicity of their magnetic spectra which minimizes additional zero field splitting effects and because their molecular structural parameters are known with good accuracy. In the following, we provide a short description of the key features of the compounds in the database. Experimental data for structures and magnetic coupling constants have been taken from the literature.<sup>10,11,32,39,40,50,67,85-91</sup> In order to avoid mixing structural and electronic effects, crystallographic structures have been used in all calculations without theoretical geometry optimization.

The compound  $\alpha$ -4-dehydrotoluene has an orthogonal  $\pi$ - $\sigma$  spin system that leads to strong ferromagnetic coupling between the unpaired electrons, with an experimental *J* value estimated to be somewhere in the range from

1050 to 1749  $\text{cm}^{-1}$ .<sup>11</sup> The biverdazyl diradical has one unpaired electron on the  $\pi$  system of each aromatic ring, with an antiferromagnetic coupling of 769  $\text{cm}^{-1}$ .<sup>10</sup> The geometry of  $\alpha$ -4-dehydrotoluene has been taken from the theoretical study of Cabrero *et al.*<sup>11</sup> and that of the biverdazyl radical has been taken from x-ray data by Brook *et al.*<sup>10</sup>

The  $\text{Cu}_2\text{Cl}_6^{2-}$  anion is a copper(II) complex with a very simple structure consisting of two edge-sharing  $\text{CuCl}_4^{2-}$  planar units found in solid  $\text{KCuCl}_3$ .<sup>32</sup> These  $\text{CuCl}_4^{2-}$  units can be more or less distorted depending on the size of the counterion in the crystal structure. This distortion provides an excellent test magnetic system since it has well characterized experimental magnetostructural correlations<sup>35</sup> that have been used as a reference for very accurate *ab initio* calculations.<sup>41-43</sup> The systems in the planar conformation show a weak antiferromagnetic interaction between the copper ions in the  $[-40, 0] \text{cm}^{-1}$  range.<sup>35</sup>

$\{[\text{Cu}(\text{H}_2\text{O})_2(\mu\text{-AcO})_4]\}$  (to be called CUAQAC02)<sup>85</sup> is the well known copper(II) acetate which consists of two copper ions bridged by four acetato groups in a paddle-wheel core. The coordination environment of the metals is square pyramid, with a water molecule in the apical position. This system has been studied by many groups either experimentally or theoretically and is one of the best-known models for fundamental magnetic studies.<sup>33</sup>

$\{[\text{Cu}(\text{phen})_2(\mu\text{-AcO})(\mu\text{-OH})](\text{NO}_3)_2 \cdot \text{H}_2\text{O}\}$  (to be called YAFZOU)<sup>40</sup> contains a cation that has a triplet ground state, and its structure contains a dimeric Cu(II) cation which metals are bridged by a hydroxo and a carboxylato ligands. These two bridging ligands and two terminal 1,10-phenanthroline ligands lead to an essentially square planar coordination geometry for each copper. The resulting core geometry leads to a strong ferromagnetic coupling that agrees with the well-studied magnetostructural correlation for this kind of heterobridged complexes.<sup>36-38,61,67</sup>

$\{[\text{Cu}(\text{petdien})_2(\mu\text{-C}_2\text{O}_4)](\text{PF}_6)_2\}$  (to be called CAVXUS)<sup>34,86</sup> contains a binuclear cation where the copper atoms are bridged through an oxalato bis-chelating ligand. The coordination environment is completed by a tridentate *NNN'N''N'''*-pentaethyldiethylenetriamine (petdien) ligand resulting in a pronounced trigonal bipyramidal (pentacoordinated) character. The deviation from the square planar to the trigonal bipyramidal geometry results in a reduction of the antiferromagnetic coupling.<sup>34</sup>

The  $\{[\text{Cu}(\text{dpt})_2\{\mu\text{-O}_2\text{C}-(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}_2](\text{ClO}_4)_2\}$  system<sup>50</sup> (to be called XAMBU) contains a centrosymmetric dicopper(II) cation which consists of two  $[\text{Cu}(\text{dpt})]$  fragments (dpt=dimethylpropilenetriamine) bridged by two ferrocenecarboxylato ligands in *syn-anti binding*, which form a core consisting of a six-membered ring in a chair conformation. The copper atoms are in a square-pyramidal coordination, with parallel basal planes, where each carboxylate group is bonded to a basal position of one copper and one apical position of the other. This disposition makes the magnetic orbitals parallel, which is unfavorable to the superexchange pathways, thus resulting in a very weak ferromagnetic coupling.

The  $\{[\text{Cu}(\text{dmen})_2(\mu\text{-OMe})\{\mu\text{-O}_2\text{C}-(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}_2](\text{ClO}_4)_2\}$  solid<sup>67</sup> (to be called PATFIA) consists

of two Cu(II) ions bridged by one methoxy and one ferrocenecarboxylato group. The coordination sphere of each copper ion is completed by one bidentate chelating ligand (dmen=*NN*-dimethylethylenediamine), resulting in a slightly distorted square planar environment. In this compound the methyl group of the bridge is close to the Cu–O(CH<sub>3</sub>)–Cu core plane, leading to an antiferromagnetic coupling.

Finally, the  $[\{\text{Cu}(\text{bpy})(\text{H}_2\text{O})(\text{NO}_3)\}_2(\mu\text{-C}_2\text{O}_4)]$  complex<sup>90</sup> (to be called BISDOW) consists of a centrosymmetric binuclear neutral molecule where the two copper ions are bridged by an oxalato bis-chelating anion. Coplanar to the bridge there are two terminal 2,2'-bipyridine chelating ligands, creating a square planar environment for the copper atoms. In addition, a nitrate anion and a water molecule coordinate each metal center at longer distances, completing a 4+1+1 coordination mode. The influence of these groups on the magnetic coupling is negligible, especially for the weak nitrate ligand, at a bond distance of 2.75 Å.

## M06 EXCHANGE-CORRELATION POTENTIALS

One may classify density functionals as local and hybrid. Local functionals include the local spin density approximation (LSDA), the generalized gradient approximations (GGAs), and meta functionals. The LSDA functional depends only on spin densities  $\rho_\sigma$ , where  $\sigma$  is  $\alpha$  for spin up and  $\beta$  for spin down. GGA functionals depend on the  $\rho_\sigma$  and their gradients  $\nabla\rho_\sigma$ . Meta functionals depend on  $\rho_\sigma$ ,  $\nabla\rho_\sigma$ , and either kinetic energy density or  $\nabla^2\rho_\sigma$ . Hybrid functionals include hybrid GGAs such as B3LYP and PBE0 (see the Introduction) and also hybrid meta functionals. The M06 suite includes one local meta functional M06-L, and three hybrid meta functionals, M06, M06-2X, and M06-HF. The local functionals are sometimes called “pure,” but that is unfortunate language since nonlocality is required to satisfy some of the exact constraints on the unknown exact functional.<sup>92</sup> Nevertheless it is worthwhile to search for accurate local functionals for two reasons, one practical and one fundamental. From a practical point of view, local functionals are prized because they are easier and much less expensive to employ for large systems. From a fundamental point of view, for analyzing the ultimate determinants of observable molecular properties, it is important to learn what features are *required* to produce an accurate functional for accurately predicting various kinds of properties, that is, how well one can do with restricted functionality.

The strategies used for the design and optimization of the M06 suite of local and hybrid meta GGA density functionals and their performance for a broad range of properties of main-group and transition metal compounds have been reported elsewhere,<sup>6–8</sup> and only a brief description of the functionals is given here. The M06-L functional is a local functional that was parametrized to satisfy the uniform-electron-gas limit and have good performance for both main-group and transition metal chemistry.<sup>6</sup> The M06-HF functional was constructed as a variant of M06-L that includes 100% HF exchange and is especially suited to the description of charge-transfer electronic states. The M06 exchange-correlation potential has the same functional form (with dif-

ferent parameters) as M06-L except that it includes Hartree–Fock exchange. It is recommended for organometallic and inorganometallic chemistry and for noncovalent interactions. Finally, the M06-2X functional has double the amount of Hartree–Fock exchange as M06 and is recommended for main-group thermochemistry, kinetics, noncovalent interactions, and excitation energies to valence and Rydberg states. The percentages of Hartree–Fock exchange in the M06 family of functionals are 0%, 27%, 54%, and 100% for M06-L, M06, M06-2X, and M06-HF, respectively. In the present study, the four density functionals of the M06 suite (M06-L, M06, M06-2X, and M06-HF) have been employed for all the systems. However, we note that the M06-2X and M06-HF functionals have been specifically designed to give the best possible results for main-group chemistry with the explicit consequence that these functionals have not been and are not recommended for transition metals.

Previous work has shown that the amount of Hartree–Fock exchange plays a crucial role in the final computed value of the magnetic coupling constant in transition metal-containing compounds.<sup>9,46,48,53,58,63–66,74–77</sup> Thus it is theoretically interesting to include the whole series of M06-class functionals in the present study. For comparison, B3LYP (Refs. 1 and 2) and PBE0 (Refs. 3 and 4) results are also presented for the magnetic coupling on the set of molecular systems described in the previous section.

## COMPUTATIONAL DETAILS

The basis sets used in the calculations are as follows. The 6-31++G(*d,p*) basis set was used for H–He–H. For  $\alpha$ -4-dehydrotoluene, the 6-31+G(*d*) basis set was used for both H and C, whereas for 1,1',5,5'-tetramethyl-6,6'-dioxo-3,3'-biverdazyl, 6-31G(*d*) was used for C, N, and O, and 6-31++G(*d,p*) was used for H. The basis sets used for the Cu<sup>II</sup> dimers are built on 6-3111+G for Cu and are 6-31G(*d*) for the remaining atoms. The basis set for Cu was supplemented with an *f*-type function with an exponent of 0.5283 for all the dimers except  $[\text{Cu}_2\text{Cl}_6]^{2-}$ . Here, we note that the dependence of the calculated *J* values on the size of the basis set is small for standard all-electron basis sets ranging from moderate to extended sets (see Ref. 93 for a discussion).

All calculations were performed with a locally modified version of GAUSSIAN03 Revision D.01,<sup>94</sup> employing the MN-GFM module.<sup>95</sup>

## ESTIMATING THE SINGLET-TRIPLET ENERGY GAP IN DENSITY FUNCTIONAL CALCULATIONS

Equation (2) shows that for the systems of interest in the present work, the calculation of *J* reduces to the calculation of the lowest singlet and triplet energies or their difference. For wave function methods, this can be accomplished by a configuration interaction expansion with spin-adapted configurational basis functions. For density functional theory there is no consensus on the best way to calculate *J*. For example, one can use the unrestricted Kohn–Sham formalism, which makes use of a single Slater determinant to represent the density of the noninteracting-electron reference

system, or one can make use of the ensemble Kohn–Sham formalisms.<sup>27,31,81</sup> In the first case one cannot guarantee that solutions obtained for the high-spin (total  $S_z=1$ ) and low spin (total  $S_z=0$ ) Kohn–Sham determinants adequately describe the lowest triplet and singlet states; in particular, for the singlet state one has to rely on a broken-symmetry approach, which localizes the unpaired electrons, and one has to decide how to relate the calculated broken-symmetry energy to that of the relevant singlet state. This problem has been discussed in a previous paper where two possible arguments, one based on expectation values of the Heisenberg Hamiltonian and one based on the Ising model led to the approximate relation,

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

where  $E(\text{BS})$  is the energy of the state with a broken-symmetry  $S_z=0$  Slater determinant, and  $E(T)$  is the energy of the spin unrestricted approximation to the triplet state with a single  $S_z=1$  Slater determinant. Interestingly enough, the same result is obtained by making use of the spin projection technique which makes use of the fact that, when almost all polarization occurs only in the singly occupied orbitals and the overlap between occupied alpha orbitals and their beta counterparts is almost unity, the broken-symmetry solution can be viewed as an almost 50% mixture of singlet and triplet states as suggested by the  $\langle S^2 \rangle \sim 1$  value.<sup>84</sup>

For comparison we also consider  $J$  values calculated by

$$J = E(\text{BS}) - E(T), \quad (4)$$

which assumes that the BS state with  $S_z=0$  is the best approximation to the singlet state. Unless specified, the discussion about  $J$  values corresponds to those obtained through Eq. (3). The density functional theory (DFT) values are compared to magnetic coupling constants calculated by complete configuration interaction (CCI) calculations and experiment by

$$J = E(S) - E(T), \quad (5)$$

where  $E(S)$  is the energy of the singlet state.

## RESULTS AND DISCUSSION

We start the analysis of results by inspecting the behavior of the H–He–H model system. For the H–He short (1.25 Å) and intermediate (1.625 Å) distances, the CCI singlet-triplet gap is large. Here, all functionals overestimate  $J$  as if uses Eq. (3) but five of the six functionals underestimate it with Eq. (4). For the H–He large (2.0 Å) distance, the model system is a better model of a binuclear transition metal complex. Here, M06 and M06-2X provide satisfactory estimates of the coupling constant. Within the M06 family the coupling constant increases when increasing the amount of Hartree–Fock exchange, in agreement with earlier analyses; however, in the sequence B3LYP, PBE0, M06-2X, the percentage of Hartree–Fock exchange increases from 20 to 25 to 54, but the coupling constant decreases, so Hartree–Fock exchange is not the whole story. In fact, it is pleasantly surprising that the M06-L functional performs much better

than might have been expected. For example, the LSDA predicts an exceedingly large value<sup>84</sup> whereas M06-L predicts a much more reasonable one.

To gain further insight we consider the atomic spin densities computed by Mulliken analysis. Table II shows that for  $R=1.625$  and  $2.0$  Å, all four M06-class functionals predict similar spin densities.

Next, consider the performance of the M06 family for the two organic diradicals. For the didehydrotoluene diradicals, experiments indicate a triplet ground state (ferromagnetic behavior) and a rather large singlet-triplet gap, in the 1050–1749  $\text{cm}^{-1}$  range, and Table I shows that this is properly reproduced by all six functionals. Surprisingly small variations are observed when going from M06-L (0% Hartree–Fock exchange) to M06-HF (100% Hartree–Fock exchange). In the case of the biverdazyl diradical, the experimental ground state is an open-shell singlet (antiferromagnetic behavior) with a magnetic coupling constant of  $\sim 800$   $\text{cm}^{-1}$ , and again this is well reproduced by all six functionals. Again the dependence of  $J$  on the amount of Hartree–Fock exchange is much smaller than what could be anticipated from previous studies.<sup>46,48,58,84</sup> Therefore, for both organic diradicals the overall behavior of the M06 family of functionals is very similar to the B3LYP and PBE0 descriptions. The small dependence of the magnetic coupling constant of these two diradicals on the amount of Hartree–Fock exchange is astonishing. Table II shows that the most localized spin densities correspond to M06-HF with 100% of Hartree–Fock exchange whereas the least localized ones correspond to M06-L with 0% Hartree–Fock exchange. The fact that M06-L leads to a semiquantitatively correct description indicates that it is now possible to study magnetic interactions in organic molecular crystals by periodic methods (see below) without needing to rely on simplified models using dimers. This is reinforced by the evidence<sup>8</sup> that the M06 family seems to be able to take weak interactions into account.

Next we consider the set of Cu binuclear complexes, which all involve localized open-shell  $3d$  orbitals. All the compounds examined correspond to Cu(II) and hence involve a local  $3d^9$  electronic configuration. The systems examined cover a broad range of bridging ligands that result in a rich variety of magnetic interactions.

For the simplest compound,  $[\text{Cu}_2\text{Cl}_6]^{2-}$ , which is known from experiment to be weakly antiferromagnetic, the predictions from the entire M06 family of functionals and from PBE0 are qualitatively correct in the sense that all of them predict a very small  $J$  value. However, M06 and M06-2X predict  $[\text{Cu}_2\text{Cl}_6]^{2-}$  to be weakly ferromagnetic whereas the potentials with 0% and 100% of Hartree–Fock exchange predict an antiferromagnetic interaction with a magnitude similar to one of the experimental estimates. For the M06-L functional this is really remarkable since previous local functionals largely overestimate the  $J$  value (by almost one order of magnitude). Notice that the accuracy of M06-L competes with PBE0 and B3LYP.

TABLE I. Magnetic coupling constants ( $J$ , in  $\text{cm}^{-1}$ )<sup>a</sup> predicted by six density functionals, compared to accurate values.

System	M06-L	M06	M06-2X	M06-HF	PBE0	B3LYP	Acc <sup>b</sup>
H–He–H, 1.25 Å	–9202	–7834	–7520	–5341	–6971	–8393	–4860
	<i>–4601</i>	<i>–3917</i>	<i>–3760</i>	<i>–2670</i>	<i>–3485</i>	<i>–4196</i>	
H–He–H, 1.625 Å	–557	–741	–893	–1405	–762	–994	–544
	<i>–279</i>	<i>–370</i>	<i>–446</i>	<i>–703</i>	<i>–381</i>	<i>–447</i>	
H–He–H, 2.0 Å	–19	–41	–58	–441	–77	–109	–50
	<i>–9</i>	<i>–20</i>	<i>–29</i>	<i>–220</i>	<i>–38</i>	<i>–55</i>	
$\alpha$ -4-dehydrotoluene	2346	2632	2599	2641	2339	1924	1050–1749
	<i>1173</i>	<i>1316</i>	<i>1300</i>	<i>1321</i>	<i>1170</i>	<i>962</i>	
Biverdazyl	–1307	–1184	–1185	–1326	–1313	–1224	–769
	<i>–654</i>	<i>–592</i>	<i>–593</i>	<i>–663</i>	<i>–656</i>	<i>–612</i>	
[Cu <sub>2</sub> Cl <sub>6</sub> ] <sup>2–</sup>	–53	5	0.1	–18	–49	–91	0 to –40
	<i>–26</i>	<i>2</i>	<i>0.05</i>	<i>–9</i>	<i>–24</i>	<i>–46</i>	
YAFZOU	334	294	75	11	170	194	111
	<i>167</i>	<i>147</i>	<i>37</i>	<i>6</i>	<i>85</i>	<i>97</i>	
XAMBUI	23	3	0.8	0.2	3	4	2
	<i>12</i>	<i>1</i>	<i>0.4</i>	<i>0.1</i>	<i>2</i>	<i>2</i>	
PATFIA	–169	–15	–19	–39	–35	–61	–11
	<i>–85</i>	<i>–8</i>	<i>–9</i>	<i>–19</i>	<i>–18</i>	<i>–32</i>	
CAVXUS	–25	–28	–6	–1	–16	–21	–19
	<i>–12</i>	<i>–14</i>	<i>–3</i>	<i>–0.7</i>	<i>–8</i>	<i>–12</i>	
CUAQAC02	–752	–436	–143	–44	–346	–429	–286
	<i>–376</i>	<i>–218</i>	<i>–72</i>	<i>–22</i>	<i>–173</i>	<i>–214</i>	
BISDOW	–1316	–632	–177	–64	–492	–634	–382
	<i>–658</i>	<i>–316</i>	<i>–88</i>	<i>–32</i>	<i>–246</i>	<i>–317</i>	

<sup>a</sup> $J$  positive corresponds to a triplet ground state, and  $J$  negative corresponds to a singlet ground state. For DFT calculations the upper value is calculated by Eq. (3), and the lower value (in italics) is calculated by Eq. (4).

<sup>b</sup>Complete configuration interaction calculations for H–He–H are from Ref. 44; other values are from experimental references given in text.

Next, we turn our attention to the rest of the Cu binuclear complexes; these are more representative of molecular magnetic systems of interest for applications. Results in Table I for this series are ordered by decreasing  $J$  values. All M06-class functionals correctly predict the ferromagnetic character of YAFZOU and XAMBUI and the antiferromagnetic behavior of PATFIA, CAVXUS, CUAQAC02, and BISDOW.

The spin densities in Table II show a clear tendency to localize unpaired electrons on the magnetic centers when the amount of Hartree–Fock exchange is increased. In all cases the spin densities obtained from the triplet and broken-symmetry solutions are almost identical, and the spatial electron density of both states is nearly the same.<sup>52</sup> The M06-class functionals provide an overall description that is similar to or better than that obtained with other hybrid functionals. The good performance of the M06-L functional is particularly noteworthy because it represents a significant improvement over the previous local functionals. The superiority of M06-L over LSDA and GGA has to be attributed, at least partially, to the inclusion of kinetic energy density. This is consistent with the results of Ciofini *et al.*,<sup>62</sup> which show that meta GGA functionals lead to a description that is roughly halfway between LSDA or GGA and hybrid schemes. The trends predicted by M06-L are qualitatively correct for all Cu binuclear complexes. The fact that a local functional is able to properly describe these systems opens a way for the correct description of magnetic coupling in a large number of

strongly correlated systems such as organic and inorganic molecular based magnets, in which weak interactions are responsible for their crystal structure, and also of other magnetic solids such as transition metal oxides and fluorides.

## CONCLUSIONS

In this work we used a set of magnetic open-shell systems to explore the performance of the M06 family of exchange-correlation potentials in describing the magnetic coupling constants. The test systems include the HeH<sub>2</sub> model system, two organic diradicals, and seven Cu binuclear complexes covering a broad range of magnetic interaction strengths. A general conclusion is that results obtained from this set of functionals are very close to those obtained with the best hybrid density functionals such as as B3LYP or PBE0.

We can make the following general observations:

- The M06-L, M06, and B3LYP functionals systematically provide numerical values closer to experiment with Eq. (4) than Eq. (3), and M06-HF is also more accurate, on average with Eq. (4) than Eq. (3); M06-2X is slightly more accurate with Eq. (3); and PBE0 is about equally accurate with either equation. Nevertheless, one must recall that Eq. (3) takes into account spin symmetry requirements and provides a consistent treatment of molecular and periodic systems.

TABLE II. Mulliken spin densities on relevant centers of selected systems as predicted by the M06 suite of density functionals.

System	M06-L		M06		M06-2X		M06-HF	
	BS	<i>T</i>	BS	<i>T</i>	BS	<i>T</i>	BS	<i>T</i>
H-He-H, 1.25 Å								
$\mu$ H	0.84	1.08	0.87	1.06	0.94	1.06	1.00	1.06
$\mu$ He	0.00	-0.15	0.00	-0.13	0.00	-0.12	0.00	-0.12
H-He-H, 1.625 Å								
$\mu$ H	1.02	1.03	1.01	1.02	1.00	1.02	1.00	1.02
$\mu$ He	0.00	-0.06	0.00	-0.04	0.00	-0.04	0.00	-0.03
H-He-H, 2.0 Å								
$\mu$ H	1.01	1.01	1.01	1.01	1.01	1.01	1.00	1.01
$\mu$ He	0.00	-0.02	0.00	-0.02	0.00	-0.02	0.00	-0.01
$\alpha$ -4-dehydrotoluene								
C <sub>1</sub>	0.36	-0.39	0.22	-0.33	0.28	-0.33	0.22	-0.37
C <sub>2</sub>	-0.24	0.30	-0.16	0.32	-0.18	0.26	-0.14	0.27
C <sub>4</sub>	0.69	1.17	0.90	1.36	0.81	1.23	0.96	1.43
C <sub>6</sub>	-0.24	0.30	-0.16	0.32	-0.18	0.26	-0.14	0.27
C <sub>7</sub>	-1.00	0.96	-0.94	0.90	-0.98	0.96	-1.03	1.00
Biverdazyl								
$\mu$ N9,12	0.37	0.36	0.41	0.39	0.42	0.39	0.43	0.40
$\mu$ N10,11	-0.37	0.36	-0.41	0.39	-0.42	0.39	-0.43	0.40
$\mu$ N13,16	0.20	0.21	0.19	0.19	0.20	0.21	0.20	0.20
$\mu$ N14,15	-0.20	0.21	-0.19	0.19	-0.20	0.21	-0.20	0.20
$\mu$ C1	0.13	-0.11	0.18	-0.15	0.19	-0.16	0.22	-0.18
$\mu$ C2	-0.13	-0.11	-0.18	-0.15	-0.19	-0.16	-0.22	-0.18
[Cu <sub>2</sub> Cl <sub>6</sub> ] <sup>2-</sup>								
$\mu$ Cu	0.57	0.56	0.57	0.57	0.72	0.72	0.82	0.82
$\mu$ Cl	0.00	0.16	0.00	0.16	0.00	0.11	0.00	0.07
YAFZOU								
$\mu$ Cu	0.62	0.62	0.65	0.65	0.79	0.80	0.86	0.86
$\mu$ O (OH)	0.00	0.21	0.00	0.19	0.00	0.11	0.00	0.07
$\mu$ O (AcO)	0.10	0.10	0.08	0.08	0.05	0.05	0.03	0.03
XAMBUI								
$\mu$ Cu	0.64	0.64	0.67	0.67	0.81	0.81	0.87	0.87
$\mu$ O (O <sub>2</sub> C)	0.08	0.08	0.07	0.07	0.04	0.04	0.03	0.03
PATFIA								
$\mu$ Cu	0.64	0.64	0.60	0.61	0.78	0.78	0.85	0.85
$\mu$ O (O <sub>2</sub> C)	0.08	0.08	0.09	0.09	0.05	0.04	0.03	0.03
$\mu$ O (OMe)	0.00	0.16	0.01	0.17	0.00	0.10	0.00	0.07
CAVXUS								
$\mu$ Cu	0.61	0.61	0.65	0.65	0.80	0.80	0.87	0.87
$\mu$ O (C <sub>2</sub> O <sub>4</sub> )	0.08	0.08	0.07	0.07	0.04	0.04	0.03	0.03
CUAQAC02								
$\mu$ Cu	0.67	0.67	0.72	0.72	0.84	0.84	0.89	0.89
$\mu$ O (AcO)	0.07	0.08	0.07	0.07	0.04	0.04	0.03	0.03
BISDOW								
$\mu$ Cu	0.63	0.66	0.68	0.69	0.81	0.82	0.87	0.87
$\mu$ O (C <sub>2</sub> O <sub>4</sub> )	0.06	0.08	0.06	0.07	0.04	0.04	0.03	0.03

- The most accurate functional, on average, of the six tested here is M06, followed very closely by both PBE0 and B3LYP, with M06-L and M06-2X slightly less accurate. (M06-2X and M06-HF are explicitly designed only for main-group chemistry, and they are included

here for transition metals only to show trends.)

- The four M06-class functionals are much less sensitive to the percentage of Hartree-Fock exchange than were previous functionals.

- The M06-L functional is the first qualitatively correct local functional for magnetic splittings in transition metal complexes. The good performance of this local functional opens the door for a more accurate treatment of periodic systems without needing to rely on hybrid approaches which are very difficult to implement in solid state codes using plane wave basis sets and are extremely computational demanding.

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