

## Comparison of Semiempirical ZILSH and DFT Calculations of Exchange Constants in Fe<sub>4</sub> Butterfly Complexes

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**Abstract:** Magnetic interactions in a series of tetranuclear Fe<sup>3+</sup> complexes with the butterfly core structure have been studied with semiempirical ZILSH and density functional theory (DFT) calculations (B3LYP functional). A theoretical analysis of a previously used method of estimating exchange constants from a restricted number of spin configurations reveals systematic errors arising from asymmetry in the complexes, which cause large variations in results with different choices of spin configurations. Correction factors are derived that yield the correct results obtained from full configuration space (FCS) calculations. Exchange constants obtained from DFT FCS calculations for the “body-body” interaction were large and ferromagnetic, in disagreement with values obtained from empirical fits of magnetic susceptibility data for the complexes, established magnetostructural correlations in polynuclear Fe<sup>3+</sup> complexes, and ZILSH calculations. DFT calculations also gave unreasonably large antiferromagnetic exchange constants for interaction between “wingtip” ions that are not directly bridged, again in disagreement with ZILSH calculations. Estimates of exchange constants for interaction of body and wingtip ions obtained with ZILSH and DFT were similar, with the ZILSH values in slightly better agreement with empirical fits. Considering all interactions, the ZILSH method provides results in better accord with experiment than DFT for these complexes. Additional comparisons of exchange constants obtained with different spin coupling schemes showed that values appropriate for two-center spin eigenfunctions gave consistently better results than values calculated with the local spin operator. The effect of basis set was found to be very small. A brief analysis of these findings is given.

### Introduction

Compounds containing multiple, magnetically coupled open shell transition metal ions have been intensively studied because they can display single molecule magnetism.<sup>1–9</sup> These so-called “single molecule magnets” (SMMs) have potential for applications in digital memory storage<sup>10</sup> and quantum computing.<sup>11,12</sup> One property crucial for single molecule magnetism is a large ground-state spin quantum number, which arises from magnetic interactions between transition metal ions with unpaired spins. It is thus vitally

important to understand these interactions and the factors that contribute to them, both to describe them in known SMMs and (eventually) to facilitate rational design of SMMs with tailored magnetic properties. Magnetic interactions are usually characterized with the Heisenberg spin model, in which the exchange constant  $J_{AB}$  describes the strength and direction of coupling between the spin moments of metal ions labeled “A” and “B”. From an experimental perspective, exchange constants are typically found by empirical fitting of the temperature response of the magnetic susceptibility of the complex. This becomes difficult as the number of metal ions (and, hence, number of exchange interactions) increases, leading to problems with obtaining a unique set

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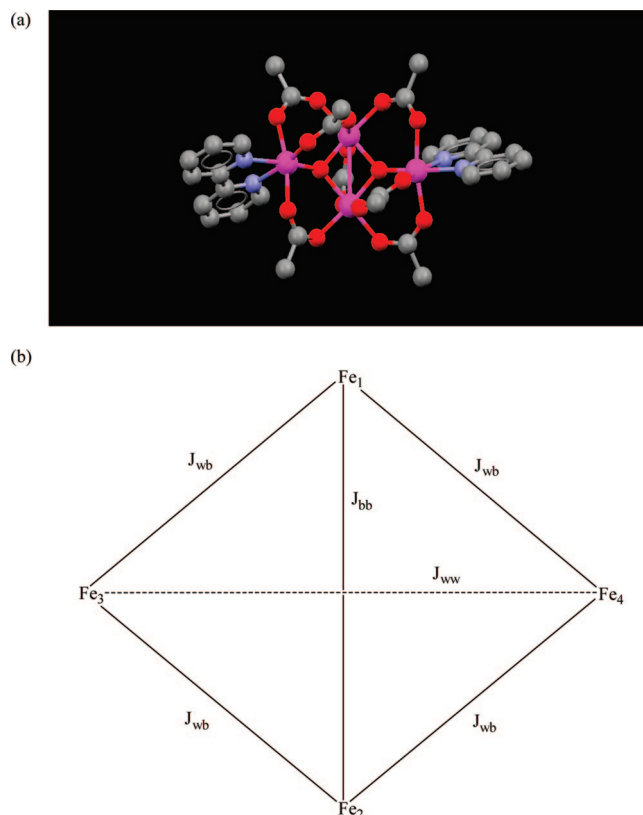
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of fitting parameters and heavy dependence on the initial parameter values assumed in the fit. There is thus no direct link between experiment and the underlying conceptual model for larger complexes.

Quantum chemistry could in principle be used to assess magnetic interactions between transition metal ions, either to provide corroboration for empirical fits or to independently provide estimates of exchange constants in large, asymmetric complexes. Following early work by Yamaguchi<sup>13,14</sup> and Noodleman,<sup>15–17</sup> exchange constants are typically obtained from theoretical methods by computing the energies of various spin components of the complex defined by different relative orientations of the unpaired spins on the metal centers. These energies are assumed to follow an effective Heisenberg Hamiltonian, and the exchange constants can be solved for simultaneously given energies for an appropriate number of spin components. A number of recent calculations of this sort have been reported, using either density functional theory (DFT; refs 18–29) or the ZILSH method of O'Brien and Davidson.<sup>24,30–36</sup> Both methods have shown some success in these applications but have been systematically compared for only two complexes.<sup>32</sup> Further comparisons are needed to judge the relative merits of the two methods. In this paper we present and compare results obtained for a series of tetranuclear iron compounds with ZILSH and DFT calculations.

There are two important issues to consider when comparing methods. The first of these is accuracy—how well do the methods reproduce exchange constants obtained from fits of magnetic data? Very few direct comparisons of this sort have been made between ZILSH and DFT calculations. ZILSH appeared to be more accurate than DFT for the complex  $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]^{8+}$ ,<sup>32</sup> while the opposite was found for the complex  $[\text{Mn}_{12}(\text{OAc})_{14}(\text{mda})_8]$ .<sup>24,29</sup> Cauchy et al. recently reported results of DFT calculations on the complexes  $[\text{Fe}_4\text{O}_2(\text{OAc})_7(\text{bpy})_2]^+$  (**1**),  $[\text{Fe}_4\text{O}_2(\text{O}_2\text{CPh})_7(\text{phen})_2]^+$  (**2**), and  $[\text{Fe}_4\text{O}_2(\text{O}_2\text{CPh})_8(\text{phen})_2]$  (**3**).<sup>27</sup> These complexes all have the well-known “butterfly” structure (Figure 1), and their magnetic interactions have been experimentally characterized.<sup>37,38</sup> They all have “wingtip-body” interactions with  $J_{wb}$  ca.  $-100\text{ cm}^{-1}$  (see Figure 1) and central, “body-body” interactions with  $J_{bb}$  ca.  $-10\text{ cm}^{-1}$ . Each also has a second-neighbor interaction between wingtip ions that are not directly bridged. The exchange constant for this interaction,  $J_{ww}$ , was assumed to be zero in fitting experimental magnetic susceptibility data,<sup>37,38</sup> but DFT calculations indicated these interactions might be significantly antiferromagnetic ( $J_{ww}$  ca.  $-5$  to  $-10\text{ cm}^{-1}$ ).<sup>27</sup> Together, complexes **1–3** provide a sufficient number of independent exchange constants to allow a thorough comparison of methods.

The second issue to consider in comparing computational methods is the size of complex that can be treated. As size increases calculations become more expensive, both on a per-calculation basis and in terms of the number of calculations that must be carried out; the number of exchange constants increases quadratically with the number of metal ions in the complex. The ZILSH method is based on the efficient semiempirical INDO/S method of



**Figure 1.** (a) Structure of  $\text{Fe}_4$  butterfly complexes: structural diagram of  $[\text{Fe}_4\text{O}_2(\text{OAc})_7(\text{bpy})_2]^+$  (**1**). Hydrogen atoms omitted for clarity. Structure obtained from ref 37. Fe - magenta; O - red; C - gray; N - blue. (b) Schematic representation of core structure with labeling scheme for iron ions and exchange constants. Solid lines represent exchange pathways mediated by bridging ligands. The broken line represents nonbridged second-neighbor interaction between wingtip ions.

Zerner,<sup>39–46</sup> so it can be applied to very large complexes. DFT calculations are much less efficient and become prohibitive for complexes with greater than ten or so transition metal ions present. Recourse is often made in such cases to what could be termed “restricted configuration space” (RCS) calculations, in which exchange constants assumed to have similar values are made equivalent and others neglected. This can greatly reduce the number of exchange constants to be solved for, and hence the number of spin configurations that must be considered compared to the standard “full configuration space” (FCS) approach, but if not done carefully can lead to systematic errors. Cauchy et al. used an RCS formulation for **1–3** in which all  $J_{wb}$  interactions were assumed to be equivalent.<sup>27</sup> These complexes are small enough that FCS calculations are readily feasible with DFT, allowing a comparison between RCS and FCS methods. The results show that the RCS calculations have systematic errors due to asymmetry in the  $J_{wb}$  pathways. Results are also presented for  $[\text{Fe}_4\text{O}_2\text{Cl}_2(\text{OAc})_6(\text{bpy})_2]$  (**4**), which is less symmetric than **1–3**, and also has been experimentally

characterized.<sup>47</sup> These calculations further illustrate the potential pitfalls of using the RCS method.

## Methods of Calculation

**A. Full Configuration Space (FCS) and Restricted Configuration Space (RCS) Calculations.** The FCS and RCS methods of obtaining exchange constants from quantum chemical calculations both use wave functions (or Kohn–Sham single determinants in the case of DFT calculations) for spin components in which the unpaired spins on certain metal centers are arranged either “spin-up” or “spin-down” with respect to those on other metal centers. For wave function methods (e.g., ZILSH) the electronic Hamiltonian,  $\hat{H}$ , is assumed to map onto an effective Hamiltonian of the Heisenberg spin form

$$\hat{H} = \hat{H}_0 - \sum_{A < B} J_{AB} \hat{S}_A \cdot \hat{S}_B \quad (1)$$

where A and B label metal centers with nonzero spins, and  $\hat{H}_0$  contains all spin-independent terms in the electronic Hamiltonian. Taking expectation values of this effective Hamiltonian for the appropriate number of spin component wave functions provides a set of equations that can be solved simultaneously for the unknown parameters  $E_0$  and the set  $\{J_{AB}\}$

$$E^i = E_0 - \sum_{A < B} J_{AB} \langle \hat{S}_A \cdot \hat{S}_B \rangle^i \quad (2)$$

where  $E^i$  is the energy of the  $i$ th component. In the case of DFT calculations, energies of unrestricted Kohn–Sham determinants are assumed to also follow eq 2.

The spin coupling expectation values  $\langle \hat{S}_A \cdot \hat{S}_B \rangle$  in eq 2 might be evaluated with an operator such as Davidson's local spin operator<sup>26,33,48</sup> but often are assigned values assuming formal local spin quantum numbers of the metal centers (e.g., high spin  $\text{Fe}^{3+}$  ions with five unpaired electrons have  $S_A = 5/2$ ) and that pairs of local spins A and B couple to form two-center spin eigenfunctions. For high spin  $d^5 \text{Fe}^{3+}$  ions,  $\langle \hat{S}_A \cdot \hat{S}_B \rangle$  is then +6.25 for parallel spins A and B or −8.75 for antiparallel spins. These values are assumed even when the complex has more than two spin centers and single determinant wave functions are used in the calculations rather than spin eigenfunctions. The effect of this approximation is discussed in the next section (*vide infra*).

The FCS method uses a number of spin components equal to the number of unknown parameters obtained by allowing A and B to run over all metal centers. It involves no assumptions based on either symmetry (grouping pairwise exchange constants together into equivalent parameters) or magnetic interaction strength (neglecting interactions for metal centers not directly bridged by ligands). The RCS method does make the preceding assumptions—groups of exchange parameters are treated as equivalent parameters, and/or other exchange constants are assumed to be zero. It is often used for larger complexes, because the number of parameters is proportional to the square of the number of metal centers. The set of calculations required for the FCS method thus quickly becomes intractable as the number of metals in the complex increases.

The RCS approach reduces the computational effort required to treat larger complexes, but this is accomplished at the risk of neglecting exchange interactions that might be significant (e.g., second-neighbor interactions). Another more serious problem that can be encountered is that the exchange constants might not be invariant to the choice of spin configurations chosen for the restricted configuration space, and truncation of the configuration space itself might affect the parameters that are obtained. The recent DFT study of tetranuclear  $\text{Fe}^{3+}$  complexes by Cauchy et al.<sup>37</sup> provides a good illustration of both the RCS approach itself and its associated problems. Its development for complexes **1–4** is summarized here.

Given the exchange constants and numbering scheme of Figure 1 for  $\text{Fe}_4$  butterfly complexes, the effective Hamiltonian of eq 1 becomes

$$\hat{H}_{\text{eff}} = \hat{H}_0 - J_{bb} \hat{S}_1 \cdot \hat{S}_2 - J_{ww} \hat{S}_3 \cdot \hat{S}_4 - J_{wb} (\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_1 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_4) \quad (3)$$

under the assumption that all  $J_{wb}$  interactions are equivalent. This leads to the energy expression

$$E^i = E_0 - J_{bb} \langle \hat{S}_1 \cdot \hat{S}_2 \rangle - J_{ww} \langle \hat{S}_3 \cdot \hat{S}_4 \rangle - J_{wb} (\langle \hat{S}_1 \cdot \hat{S}_3 \rangle + \langle \hat{S}_1 \cdot \hat{S}_4 \rangle + \langle \hat{S}_2 \cdot \hat{S}_3 \rangle + \langle \hat{S}_2 \cdot \hat{S}_4 \rangle) \quad (4)$$

There are thus four unknowns to be solved for, requiring wave functions or densities of four spin components.

Cauchy et al.<sup>37</sup> used the component with all unpaired spins aligned (“high spin”, HS), that with the unpaired spins on Fe4 (see Figure 1) reversed relative to all others, and those with unpaired spins on Fe2 and Fe4 or Fe3 and Fe4 reversed. They assumed spin couplings appropriate for two-center spin eigenfunctions, leading to

$$E^{\text{HS}} = E_0 - 6.25J_{bb} - 6.25J_{ww} - 25J_{wb} \quad (5)$$

$$E^4 = E_0 - 6.25J_{bb} + 8.75J_{ww} + 5J_{wb} \quad (6)$$

$$E^{24} = E_0 + 8.75J_{bb} + 8.75J_{ww} + 5J_{wb} \quad (7)$$

The three exchange constants are then found by making appropriate subtractions of these equations and rearranging the resulting expressions. For example, subtracting eq 8 from eq 5 leads to an expression involving only  $J_{wb}$  and the known energies  $E^{\text{HS}}$  and  $E$ .<sup>34</sup> Proceeding similarly for the other exchange constants, the following equations are obtained:

$$E^{34} = E_0 - 6.25J_{bb} - 6.25J_{ww} + 35J_{wb} \quad (8)$$

$$J_{wb} = \frac{E^{34} - E^{\text{HS}}}{60} \quad (9)$$

$$J_{bb} = \frac{E^{24} - E^4}{15} \quad (10)$$

(These expressions were derived with the subtractions (5)–(8), (6)–(7), and (5)–(6), respectively).

The following development shows that if the wingtip-body exchange couplings are inequivalent,  $J_{wb}$  obtained from eq 9 is actually the average of the four distinct wingtip-body couplings  $J_{13}$ ,  $J_{14}$ ,  $J_{23}$ , and  $J_{24}$  ( $J_{wb}$ ). Similarly,  $J_{bb}$  and  $J_{ww}$  obtained from eqs 10 and 11 contain errors arising from

artificially setting all wingtip-body couplings equal. To proceed, eqs 5–8 are recast assuming nonequivalent values for the four wingtip-body interactions, leading to

$$J_{ww} = \frac{E^4 - E^{HS}}{15} - 2J_{wb} = \frac{2E^4 - E^{34} - E^{HS}}{30} \quad (11)$$

$$E^{HS} = E_0 - 6.25J'_{bb} - 6.25J'_{ww} - 6.25(J_{13} + J_{14} + J_{23} + J_{24}) \quad (12)$$

$$E^4 = E_0 - 6.25J'_{bb} + 8.75J'_{ww} - 6.25(J_{13} + J_{23}) + 8.75(J_{14} + J_{24}) \quad (13)$$

$$E^{24} = E_0 + 8.75J'_{bb} + 8.75J'_{ww} - 6.25(J_{13} + J_{24}) + 8.75(J_{14} + J_{23}) \quad (14)$$

Making the same subtractions used above to obtain eqs 5–7 leads to

$$E^{34} = E_0 - 6.25J'_{bb} - 6.25J'_{ww} + 8.75(J_{13} + J_{14} + J_{23} + J_{24}) \quad (15)$$

$$\overline{J}_{wb} = \frac{J_{13} + J_{14} + J_{23} + J_{24}}{4} = \frac{E^{34} - E^{HS}}{60} = J_{wb} \quad (16)$$

$$J'_{bb} = \frac{E^{24} - E^4}{15} + (J_{24} - J_{23}) \quad (17)$$

$$J'_{ww} = \frac{E^4 - E^{HS}}{15} - (J_{14} + J_{24}) \quad (18)$$

Combining eq 17 with eq 10 and eq 18 with eq 11 gives

$$J'_{bb} = J_{bb} + (J_{24} - J_{23}) \quad (19)$$

$$J'_{ww} = J_{ww} + \frac{J_{13} + J_{23} - J_{14} - J_{24}}{2} \quad (20)$$

These equations clearly show that  $J_{bb}$  and  $J_{ww}$  as proposed by Cauchy et al.<sup>37</sup> provide correct estimates of the body-body and wingtip-wingtip exchange interactions only if the wingtip-body exchange interactions are equivalent. This is not the case for complexes 1–4. It should also be pointed out that experimental determinations of  $J_{bb}$  and  $J_{wb}$  in butterfly complexes by means of fitting magnetic susceptibility data have also assumed that all  $J_{wb}$  interactions are equivalent<sup>37,38,47</sup> and thus involve the same approximations expressed in eqs 16–18.

An additional problem with the RCS method just developed is that the exchange constants are not invariant to the choice of spin components used. This is easily illustrated by considering the component with the spins of Fe2 and Fe3 reversed relative to the others. The energy of this component assuming equivalent  $J_{wb}$  interactions is

$$E^{23} = E_0 + 8.75J_{bb} + 8.75J_{ww} + 5J_{wb} \quad (21)$$

which is equal to  $E^{24}$  (eq 7) within the RCS model with all  $J_{wb}$  assumed to be equivalent. Subtracting eq 21 from eq 6 leads to

$$J_{bb} = \frac{E^{23} - E^4}{15} \quad (22)$$

Clearly, eqs 22 and 10 will lead to different values of  $J_{bb}$  unless  $E^{23} = E^{24}$ , which does not occur in complexes 1–4.

Taking complex 3 as an example, values of  $J_{bb}$  of  $-15 \text{ cm}^{-1}$  and  $+7 \text{ cm}^{-1}$  can be obtained from eqs 10 and 22, respectively (*vide infra*). Similar variance is easily demonstrated for  $J_{ww}$  and  $J_{wb}$  as well. This problem with variance is discussed further in the next section.

**B. Computational Methods.** ZILSH calculations on compounds 1–4 were performed as described in ref 33. The INDO/S method of Zerner<sup>39–46</sup> was used to obtain unrestricted Hartree–Fock wave functions for the various spin configurations, and expectation values  $\langle \hat{S}_A \cdot \hat{S}_B \rangle$  were computed from the wave functions with Davidson’s local spin operator.<sup>26,33,48</sup> DFT calculations were performed with the Gaussian03 program,<sup>49</sup> using the B3 exchange functional<sup>50</sup> together with the correlation functional of Lee, Yang, and Parr<sup>51</sup> (B3LYP). Two basis sets were employed, either the all-electron Dunning–Huzinaga double- $\zeta$  basis set for light atoms<sup>52</sup> with the Los Alamos effective core potential plus double- $\zeta$  valence basis set for iron atoms<sup>53</sup> (LANL2DZ; basis set I) or the all-electron double- $\zeta$  DZVP basis set of Alrichs for light atoms<sup>54</sup> and the all-electron triple- $\zeta$  TZVP basis set of Alrichs<sup>55</sup> for iron atoms (basis set II). Basis set II was used in ref 27. Spin couplings computed with the ZILSH method are generally similar to those obtained from DFT densities<sup>25,26,33,48</sup> and were used with DFT energies to obtain DFT estimates of the exchange constants. Exchange constants were also computed with all methods assuming spin couplings appropriate for two-center spin eigenfunctions.

## Results and Discussion

The goal of this work was to compare FCS and RCS methods for 1–4 as well as the performance of the ZILSH and DFT methods with (in the latter case) different basis sets. Calculations were performed with ZILSH and the B3LYP functional with basis sets I and II for seven spin components for all complexes. This allowed for FCS calculations for each complex and RCS calculations with various choices of spin components. The spin components used were the component with all unpaired spins aligned (“high spin”), three components with the unpaired spins on Fe1, Fe2, or Fe4 (see Figure 1) reversed relative to all others,<sup>56</sup> and three components each with unpaired spins on two iron ions reversed relative to all others. The ions with reversed spins in the three cases were Fe2 and Fe3, Fe2 and Fe4, or Fe3 and Fe4. The ZILSH calculations followed the procedure described previously<sup>32,33</sup> and provided energies, spin densities, and spin couplings  $\langle \hat{S}_A \cdot \hat{S}_B \rangle^{\text{UHF}}$ . The latter were calculated with the semiempirical implementation<sup>33</sup> of Davidson’s local spin operator.<sup>26,48</sup> The DFT calculations also used a previously described procedure<sup>25</sup> and provided energies and spin densities.

The results of all calculations are presented in Table 1a. Relative energies for each spin component computed with each method are given for each complex in  $\text{cm}^{-1}$ , along with the absolute energy in atomic units found for the high spin component with each method. The latter were provided to facilitate direct comparisons if other workers seek to repeat these calculations. Raw data (i.e., absolute energies, spin couplings) have not often been presented in the literature on computational studies of exchange interactions in polynuclear complexes, which makes comparative studies like



**Table 1.** Computational Results for Compounds **1–4**<sup>a</sup>

spin component <sup>b</sup>							
quantity	HS	1	2	4	2,3	2,4	3,4
A. [Fe <sub>4</sub> O <sub>2</sub> (OAc) <sub>7</sub> (bpy) <sub>2</sub> ] <sup>+</sup> (Compound 1)							
E (ZILSH)	4532.2 <sup>c</sup> (−576.33840654) <sup>d</sup>	2137.0	2135.2	2231.9	2153.0	2043.7	0.0
E (B3LYP/I)	4971.8(−3234.36437118)	2675.5	2670.8	2387.5	2527.3	2548.5	0.0
E (B3LYP/II)	5040.0 (−7794.00462476)	2652.8	2646.9	2426.4	2493.0	2560.8	0.0
M <sub>1</sub> <sup>e</sup>	4.40 (4.27)	−4.34(−4.22)	4.41(4.27)	4.37(4.24)	4.37(4.25)	4.37(4.25)	4.34(4.22)
M <sub>2</sub>	4.40 (4.27)	4.41(4.28)	−4.34(−4.22)	4.37(4.24)	−4.37(−4.25)	−4.37(−4.25)	4.34(4.22)
M <sub>3</sub>	4.42 (4.25)	4.39(4.22)	4.39(4.22)	4.42(4.25)	−4.39(−4.21)	4.38(4.21)	−4.35(−4.19)
M <sub>4</sub>	4.42(4.25)	4.39(4.22)	4.39(4.22)	−4.35(−4.19)	4.39(4.21)	−4.38(−4.21)	−4.35(−4.19)
⟨Ŝ <sub>1</sub> •Ŝ <sub>2</sub> ⟩ <sup>f</sup>	4.862	−4.769	−4.781	4.781	−4.778	−4.779	4.706
⟨Ŝ <sub>1</sub> •Ŝ <sub>3</sub> ⟩	4.855	−4.742	4.815	4.811	−4.779	4.769	−4.710
⟨Ŝ <sub>1</sub> •Ŝ <sub>4</sub> ⟩	4.855	−4.741	4.817	−4.741	4.770	−4.777	−4.709
⟨Ŝ <sub>2</sub> •Ŝ <sub>3</sub> ⟩	4.855	4.811	−4.744	4.811	4.770	−4.777	−4.709
⟨Ŝ <sub>2</sub> •Ŝ <sub>4</sub> ⟩	4.854	4.810	−4.746	−4.741	−4.778	4.769	−4.710
⟨Ŝ <sub>3</sub> •Ŝ <sub>4</sub> ⟩	4.846	4.781	4.770	−4.769	−4.769	−4.767	4.696
B. [Fe <sub>4</sub> O <sub>2</sub> (O <sub>2</sub> CPh) <sub>7</sub> (phen) <sub>2</sub> ] <sup>+</sup> (Compound 2)							
E (ZILSH)	4846.0 <sup>c</sup> (−824.53737107) <sup>d</sup>	2208.1	2244.4	2323.0	2168.0	2217.0	0.0
E (B3LYP/I)	5229.4(−4727.58896405)	2686.5	2828.4	2495.9	2674.4	2534.3	0.0
E (B3LYP/II)	5291.4(−9286.34739508)	2665.4	2807.6	2530.5	2688.7	2502.7	0.0
M <sub>1</sub> <sup>e</sup>	4.41(4.27)	−4.33(−4.21)	4.41(4.27)	4.37(4.24)	4.37(4.24)	4.37(4.24)	4.34(4.21)
M <sub>2</sub>	4.40(4.27)	4.40(4.27)	−4.33(−4.21)	4.37(4.24)	−4.36(−4.24)	−4.37(−4.24)	4.34(4.21)
M <sub>3</sub>	4.41(4.24)	4.37(4.21)	4.37(4.21)	4.41(4.24)	−4.37(−4.21)	4.37(4.20)	−4.34(−4.18)
M <sub>4</sub>	4.41(4.24)	4.37(4.21)	4.37(4.21)	−4.33(−4.18)	4.37(4.21)	−4.37(−4.21)	−4.33(−4.18)
⟨Ŝ <sub>1</sub> •Ŝ <sub>2</sub> ⟩ <sup>f</sup>	4.833	−4.726	−4.714	4.788	−4.759	−4.688	4.744
⟨Ŝ <sub>1</sub> •Ŝ <sub>3</sub> ⟩	4.835	−4.743	4.791	4.742	−4.741	4.668	−4.739
⟨Ŝ <sub>1</sub> •Ŝ <sub>4</sub> ⟩	4.825	−4.725	4.746	−4.718	4.752	−4.687	−4.758
⟨Ŝ <sub>2</sub> •Ŝ <sub>3</sub> ⟩	4.846	4.795	−4.763	4.786	4.745	−4.683	−4.750
⟨Ŝ <sub>2</sub> •Ŝ <sub>4</sub> ⟩	4.836	4.768	−4.720	−4.760	−4.761	4.687	−4.760
⟨Ŝ <sub>3</sub> •Ŝ <sub>4</sub> ⟩	4.840	4.794	4.797	−4.716	−4.755	−4.684	4.748
C. [Fe <sub>4</sub> O <sub>2</sub> (O <sub>2</sub> CPh) <sub>8</sub> (phen) <sub>2</sub> ] (Compound 3)							
E (ZILSH)	4461.1 <sup>c</sup> (−894.32489930) <sup>d</sup>	2007.0	2006.9	2192.6	1830.0	2097.2	0.0
E (B3LYP/I)	5177.0 (−5148.94449971)	2586.8	2586.8	2482.1	2608.8	2276.1	0.0
E (B3LYP/II)	5163.2(−9707.54851198)	2553.0	2553.0	2481.0	2591.8	2252.3	0.0
M <sub>1</sub> <sup>e</sup>	4.43(4.28)	−4.36(−4.22)	4.43(4.28)	4.40(4.25)	4.39(4.25)	4.40(4.25)	4.37(4.22)
M <sub>2</sub>	4.43(4.28)	4.43(4.28)	−4.36(−4.22)	4.40(4.25)	−4.39(−4.25)	−4.40(−4.25)	4.37(4.22)
M <sub>3</sub>	4.45(4.25)	4.41(4.22)	4.41(4.22)	4.45(4.25)	−4.41(−4.21)	4.41(4.21)	−4.37(−4.19)
M <sub>4</sub>	4.45(4.25)	4.41(4.22)	4.41(4.22)	−4.37(−4.19)	4.41(4.21)	−4.41(−4.21)	−4.37(−4.19)
⟨Ŝ <sub>1</sub> •Ŝ <sub>2</sub> ⟩ <sup>f</sup>	4.904	−4.788	−4.787	4.866	−4.754	−4.823	4.819
⟨Ŝ <sub>1</sub> •Ŝ <sub>3</sub> ⟩	4.903	−4.792	4.857	4.862	−4.755	4.815	−4.827
⟨Ŝ <sub>1</sub> •Ŝ <sub>4</sub> ⟩	4.910	−4.827	4.827	−4.827	4.750	−4.823	−4.825
⟨Ŝ <sub>2</sub> •Ŝ <sub>3</sub> ⟩	4.896	4.819	−4.816	4.819	4.744	−4.813	−4.818
⟨Ŝ <sub>2</sub> •Ŝ <sub>4</sub> ⟩	4.903	4.862	−4.789	−4.792	−4.755	4.815	−4.827
⟨Ŝ <sub>3</sub> •Ŝ <sub>4</sub> ⟩	4.904	4.866	4.859	−4.788	−4.754	−4.823	4.819
spin component <sup>b</sup>							
quantity	HS	2	3 <sup>g</sup>	4	2,3	2,4	3,4
[Fe <sub>4</sub> O <sub>2</sub> Cl <sub>2</sub> (OAc) <sub>6</sub> (bpy) <sub>2</sub> ] (Compound 4)							
E (ZILSH)	3815.2 <sup>c</sup> (−559.84589131) <sup>d</sup>	1401.5	1665.3	2104.6	1557.6	1842.3	0.0
E (B3LYP/I)	4898.3(−3035.99026836)	2271.5	2216.0	2467.7	2309.2	2511.2	0.0
E (B3LYP/II)	4934.4(−8485.97744006)	2221.8	2215.7	2515.9	2296.8	2465.3	0.0
M <sub>1</sub> <sup>e</sup>	4.43(4.24)	4.43(4.24)	4.39(4.21)	4.40(4.21)	4.38(4.24)	4.38(4.24)	4.36(4.19)
M <sub>2</sub>	4.41(4.27)	−4.34(−4.21)	4.38(4.24)	4.38(4.24)	−4.40(−4.21)	−4.39(−4.21)	4.34(4.21)
M <sub>3</sub>	4.42(4.23)	4.38(4.19)	−4.35(−4.16)	4.42(4.22)	−4.38(−4.19)	4.39(4.19)	−4.35(−4.17)
M <sub>4</sub>	4.37(4.19)	4.34(4.16)	4.37(4.19)	−4.32(−4.14)	4.35(4.17)	−4.34(−4.16)	4.32(−4.14)
⟨Ŝ <sub>1</sub> •Ŝ <sub>2</sub> ⟩ <sup>f</sup>	4.882	−4.770	4.833	4.848	−4.807	−4.739	4.799
⟨Ŝ <sub>1</sub> •Ŝ <sub>3</sub> ⟩	4.884	4.801	−4.800	4.812	−4.802	4.730	−4.807
⟨Ŝ <sub>1</sub> •Ŝ <sub>4</sub> ⟩	4.844	4.802	4.804	−4.758	4.762	−4.718	−4.789
⟨Ŝ <sub>2</sub> •Ŝ <sub>3</sub> ⟩	4.856	−4.749	−4.737	4.816	4.777	−4.712	−4.774
⟨Ŝ <sub>2</sub> •Ŝ <sub>4</sub> ⟩	4.816	−4.740	4.737	−4.758	−4.745	4.685	−4.749
⟨Ŝ <sub>3</sub> •Ŝ <sub>4</sub> ⟩	4.820	4.778	−4.707	−4.730	−4.747	−4.691	4.750

<sup>a</sup> See text for descriptions of methods and basis sets. <sup>b</sup> Indices indicate metals with unpaired spins reversed to all other unpaired spins. See Figure 1 for numbering scheme. "HS" indicates component with all unpaired spins aligned. <sup>c</sup> Relative energy (cm<sup>−1</sup>). <sup>d</sup> Absolute energy of HS component (a.u.). <sup>e</sup> z component of spin for Fe1 computed from ZILSH component wave function. Values in parentheses obtained from B3LYP/II component density. <sup>f</sup> Spin coupling between Fe1 and Fe2 computed from ZILSH component wave function. <sup>g</sup> This choice of spin components (i.e., using that with spin of Fe3 reversed instead of that with Fe1 reversed) was adopted for **4** for consistent atom labeling with ref 33. The exchange constants obtained with FCS calculations and RCS eqs 9–11 are invariant to this choice.

the one reported here difficult. The high spin component was found to have the highest energy with all methods and basis

sets, indicating that exchange interactions in **1–4** are predominantly antiferromagnetic. This is discussed further

**Table 2.** Exchange Constants Obtained for **1–4** with RCS Calculations<sup>a</sup> Using B3LYP/II Energies and Spin Couplings for Two-Center Spin Eigenfunctions<sup>b,c</sup>

complex	interaction <sup>d</sup>	FCS	RCS <sup>e</sup>	RCS, corrected <sup>f</sup>
[Fe <sub>4</sub> O <sub>2</sub> (OAc) <sub>7</sub> (bpy) <sub>2</sub> ] <sup>+</sup> ( <b>1</b> )	$J_{bb} = J_{12}$	+8.7	+9.0 (+8.3)	+8.7
	$\overline{J_{ww}} = J_{34}$	−8.2	−6.2 (−5.8)	−8.2
	$\overline{J_{wb}}$	−84.0	−84.0 (−80.0)	−84.0
[Fe <sub>4</sub> O <sub>2</sub> (O <sub>2</sub> CPh) <sub>7</sub> (phen) <sub>2</sub> ] <sup>+</sup> ( <b>2</b> )	$J_{bb} = J_{12}$	+6.1	−1.9 (−0.9)	+6.1
	$\overline{J_{ww}} = J_{34}$	−9.4	−7.7 (−7.2)	−9.4
	$\overline{J_{wb}}$	−88.2	−88.2 (−84.2)	−88.2
[Fe <sub>4</sub> O <sub>2</sub> (O <sub>2</sub> CPh) <sub>8</sub> (phen) <sub>2</sub> ] ( <b>3</b> )	$J_{bb} = J_{12}$	−1.9	−15.2 (−15.2)	−1.9
	$\overline{J_{ww}} = J_{34}$	−8.7	−6.7 (−6.3)	−8.7
	$\overline{J_{wb}}$	−86.1	−86.1 (−82.8)	−86.1
[Fe <sub>4</sub> O <sub>2</sub> Cl <sub>2</sub> (OAc) <sub>6</sub> (bpy) <sub>2</sub> ] ( <b>4</b> )	$J_{bb} = J_{12}$	+1.0	−3.4	+1.0
	$\overline{J_{ww}} = J_{34}$	−6.8	+3.2	−6.8
	$\overline{J_{wb}}$	−82.2	−82.2	−82.2

<sup>a</sup> Equations 9–11. <sup>b</sup> The appropriate value for each spin coupling can be obtained from Table 1 by replacing all positive spin couplings with +6.25 and all negative spin couplings with −8.75. <sup>c</sup> All values in cm<sup>−1</sup>. <sup>d</sup> See Figure 1 for labeling scheme. <sup>e</sup> Values in parentheses from ref 27. <sup>f</sup> Equations 16, 19, and 20.

below in reference to exchange constants obtained from FCS and RCS calculations. The component with unpaired spins on Fe3 and Fe4 reversed relative to the unpaired spins on Fe1 and Fe2 (see Figure 1) was found to have the lowest energy with all methods and basis sets, in accord with previous experimental<sup>37,38,47</sup> and theoretical<sup>27,33</sup> studies of these Fe<sub>4</sub> butterfly complexes.

Local spin densities computed for the iron ions from ZILSH wave functions with the Löwdin scheme<sup>57</sup> are given in Table 1a, along with those found from DFT Kohn–Sham determinants (basis set II) with the Mulliken scheme.<sup>58</sup> The local spin density of an ion is approximately equal to the number of unpaired electrons associated with that ion.<sup>33</sup> All values found with ZILSH are ca. 4.40 in magnitude, close to the formal value of five expected for high spin d<sup>5</sup> Fe<sup>3+</sup> ions. The values given in Table 1b are reduced below five by spin delocalization and are similar to values obtained with ZILSH for other complexes of Fe<sup>3+</sup> ions.<sup>32,33,35,36</sup> Values obtained with DFT calculations are similar to the ZILSH values and resemble those reported for similar calculations.<sup>20,27</sup> The signs of the local spin densities indicate the relative directions of spin moments of the iron ions and demonstrate that correct spin distributions were obtained for each spin component with all methods and basis sets.

Spin couplings  $\langle \hat{S}_A \cdot \hat{S}_B \rangle^{\text{UHF}}$  found from ZILSH wave functions with the local spin operator<sup>26,33,48</sup> (Table 1c) took on values close to  $\pm 5$ , similar to those obtained from ZILSH calculations on other polynuclear Fe<sup>3+</sup> complexes.<sup>32,33,35,36</sup> One goal of this work is to compare exchange constants obtained in two ways, using spin couplings properly calculated as expectation values of the local spin operator or using spin couplings appropriate for two-center spin eigenfunctions. Values for the latter case for each spin component are given by replacing positive values of  $\langle \hat{S}_A \cdot \hat{S}_B \rangle^{\text{UHF}}$  in Table 1a with +6.25 and negative values with −8.75. Both choices of spin couplings are used with the energies in Table 1d to compute exchange constants with the FCS method and the RCS method with various sets of spin components. The results are presented and discussed in the following subsections.

**A. Comparison of FCS and RCS Methods.** Exchange constants obtained with FCS calculations and the RCS method of ref 27 (eqs 9–11) are compared in this subsection.

Discussion is limited to results found with energies from B3LYP/II calculations and  $\langle \hat{S}_A \cdot \hat{S}_B \rangle$  appropriate for two-center spin eigenfunctions. This allows direct comparison with previously reported results for compounds **1–3**.<sup>27</sup> Analogous conclusions would be reached based on results obtained from ZILSH or B3LYP/I calculations and either choice of spin couplings. Exchange constants  $J_{bb}$ ,  $J_{ww}$ , and  $\overline{J_{wb}}$  obtained from the data of Table 1a with eqs 9–11 are given in Table 2 for compounds **1–4**, along with those reported previously for **1–3**.<sup>27</sup> Values obtained with the correction factors of eqs 19 and 20 are also given as well as those found from FCS calculations with the same choice of method, basis set, and spin couplings.

A comparison of exchange constants obtained in this work with those reported previously for compounds **1–3**<sup>27</sup> shows very similar results:  $J_{bb}$  and  $J_{ww}$  agree within 1 cm<sup>−1</sup>, and  $\overline{J_{wb}}$ , which is much larger in magnitude, agrees within 4 cm<sup>−1</sup> (ca. 5%) for every complex. Though direct comparisons are difficult because no raw data were given in ref 27, the small discrepancies likely arise from different methods used for obtaining starting orbitals. We used the procedure described in ref 25, which uses standard starting guesses from the G03 program,<sup>49</sup> while Cauchy et al.<sup>27</sup> used starting guesses from the Jaguar 6.0 program.<sup>59</sup> Additionally, we used the standard G03 SCF algorithm, while they used the quadratically convergent algorithm. The SCF convergence threshold might also play a role. We assumed a threshold of 10<sup>−8</sup> a.u., compared to the standard threshold of 10<sup>−4</sup> a.u. employed by the G03 program. The latter threshold corresponds to ca. 20 cm<sup>−1</sup>, which is on the same order of magnitude as the exchange constants themselves. Again it is difficult to judge whether convergence criteria play a role in the discrepancies in computed exchange constants, as Cauchy et al. did not state the threshold they used in ref 27. Regardless of specific causes for the discrepancies, it is clear that the results found in the present work are substantially the same as those reported by Cauchy et al.

A comparison of exchange constants obtained for compounds **1–4** with RCS and FCS calculations (Table 2) shows that there are discrepancies in the values obtained for  $J_{bb}$  and  $J_{ww}$ , as anticipated from eqs 19 and 20. These discrepancies are small for **1**, which is the least asymmetric complex

**Table 3.** Limiting Values of Exchange Constants Obtained with RCS Calculations (B3LYP/II) on All Possible Choices of Spin Configurations for Compounds **1–4**<sup>a</sup>

compound	1	2	3	4
$J_{bb}$ (max)	+9.0	+10.8	+7.4	+16.6
$J_{bb}$ (min)	+4.4	−1.9	−15.2	−16.4
$J_{bb}$ (FCS)	+8.7	+6.1	−1.9	+1.0
$J_{ww}$ (max)	−5.7	+1.6	+2.6	+16.2
$J_{ww}$ (min)	−10.7	−20.3	−20.1	−16.8
$J_{ww}$ (FCS)	−8.2	−9.4	−8.7	−6.8
$J_{wb}$ (max)	−81.8	−81.9	−79.4	−65.7
$J_{wb}$ (min)	−86.2	−94.5	−92.7	−98.7
$J_{wb}$ (FCS)	−84.0	−88.2	−86.1	−82.2

<sup>a</sup> All values in  $\text{cm}^{-1}$ . See Figure 1 for labeling scheme for exchange constants.

and thus most closely reflects the approximation that all body-wingtip exchange couplings are equal. The discrepancies are larger for the less symmetric compounds, as large as  $13.2 \text{ cm}^{-1}$  in magnitude for  $J_{bb}$  of **3**. The sign of  $J_{bb}$  obtained for **2** from the RCS calculations is opposite that found with FCS calculations. The trend in  $J_{bb}$  and  $J_{ww}$  found with RCS calculations is reversed compared to that found with FCS calculations for **3**. In the case of **4**, the least symmetric compound in the set, the signs of both  $J_{bb}$  and  $J_{ww}$  found with RCS calculations are reversed relative to those found with FCS calculations, again leading to opposite trends. It is important to note that applying the correction factors of eqs 19 and 20 to  $J_{bb}$  and  $J_{ww}$  obtained from the RCS calculations leads to the FCS values in every case.<sup>60</sup> This is a clear demonstration that the RCS method does a poor job of recovering the FCS results for the less symmetric compounds.

An additional problem with the RCS method is that the exchange constants obtained are not invariant to the choice of spin components used, as discussed above. Seven spin components are needed for FCS calculations, while only four are needed for RCS calculations. Given energies and spin couplings for seven spin components in Table 1b, thirty-five different choices of four components can be made for RCS calculations. In some of these cases, the result of simultaneous solution of equations similar to eqs 9–11 is indeterminate. This is easily seen when the equations are cast into matrix form to occur when two rows in the square matrix containing the spin couplings are identical. In other cases this does not occur, and a solution for  $J_{bb}$ ,  $J_{ww}$ , and  $J_{wb}$  is obtained. The crucial point is that these solutions are not the same for different choices of spin components. This is shown in Table 3, which reports limiting values of the exchange constants found for each complex with RCS calculations on all possible choices of four spin components from Table 1a. The results in Table 3 were found using B3LYP/II energies and spin couplings appropriate for two-center spin eigenfunctions; again, similar conclusions would be reached with other choices of method, basis set, and spin coupling scheme. Large variations were found with different choices of spin components used in the RCS calculations, as large as  $\sim 32 \text{ cm}^{-1}$  for  $J_{bb}$  and  $J_{ww}$  of compound **4**, compared to FCS values of  $+1 \text{ cm}^{-1}$  and  $-7 \text{ cm}^{-1}$ , respectively. Again the variations are smallest for **1**, the most symmetric of the four compounds, but even in this case are

of substantial size compared to the FCS parameters (e.g., a variation of  $5.0 \text{ cm}^{-1}$  in magnitude for  $J_{ww}$ , compared to the FCS magnitude of  $8.2 \text{ cm}^{-1}$ ). From these results it is clear that exchange constants obtained from one particular choice of spin components are of limited validity.

A very important point in this regard is that despite the large variations in the RCS exchange constants found with different choices of spin components, the FCS values are obtained for *all* sets of spin components when correction terms analogous to those given in eqs 19 and 20 are applied. This is shown in Table 4, which presents RCS equations and correction factors for four different choices of spin components for compound **3**. Exchange constants obtained using B3LYP/II energies and spin couplings appropriate for two-center spin eigenfunctions are given as well, along with corrected values and values obtained from FCS calculations. From the RCS calculations  $J_{bb}$  ranges from  $-15.2 \text{ cm}^{-1}$  to  $+7.4 \text{ cm}^{-1}$ ,  $J_{ww}$  ranges from  $-20.0 \text{ cm}^{-1}$  to  $+2.6 \text{ cm}^{-1}$ , and  $J_{wb}$  ranges from  $-92.7 \text{ cm}^{-1}$  to  $-81.4 \text{ cm}^{-1}$ . Even so, applying the correction factors leads exactly to the FCS result in every case. This is a convincing demonstration that FCS calculations must be used to obtain a true measure of the performance of a particular method of calculation. In other words, comparisons between various computational methods, and between computational results and experiment, must be made on the basis of FCS calculations if they are to have any validity. This is done for compounds **1–4** in the following subsection.

**B. Comparisons between Methods and Experiment (FCS Calculations).** Exchange constants obtained for **1–4** with FCS calculations using different methods, basis sets, and spin coupling schemes are presented in Table 5. They are compared with exchange constants fit to reproduce experimental magnetic susceptibility data<sup>37,38,47</sup> in this section, with the goal of judging which method provides the most accurate picture of magnetic interactions in the complexes. Two general trends that are independent of basis set of spin coupling scheme are immediately apparent in Table 5. First, the body-body interactions  $J_{bb}$  found with DFT are uniformly ferromagnetic, while those found with ZILSH are antiferromagnetic. Fits of magnetic susceptibility data for each complex found  $J_{bb}$  to be antiferromagnetic,<sup>37,38,47</sup> in better agreement with the ZILSH calculations. It is, however, important to consider that the quality of the fits is relatively insensitive to the value of  $J_{bb}$ . In the case of **1**, for example, it was found that  $J_{bb}$  was “more positive than  $-15 \text{ cm}^{-1}$ ” and likely antiferromagnetic.<sup>37</sup> The experimental results are thus not definitive for these complexes regarding the sign of  $J_{bb}$ . Even so, the  $J_{bb}$  values from DFT calculations for **1–4** are very ferromagnetic, with magnitudes as large as  $+22 \text{ cm}^{-1}$  for **1** found with B3LYP/I energies and  $\langle \hat{S}_A \cdot \hat{S}_B \rangle^{\text{UHF}}$  values from Table 1a. Such large ferromagnetic interactions are at odds with virtually all salient interpretations of experimental magnetic data for polynuclear  $\text{Fe}^{3+}$  complexes, including correlations between exchange constants and geometric parameters in bridging pathways and exchange constants extracted from experimental data for diferric complexes. These are discussed in turn below.

**Table 4.** RCS Equations and Exchange Constants Found for Compound **3** (B3LYP/II) for Several Choices of Spin Configurations<sup>a</sup>

configurations <sup>b</sup>	RCS	correction	$J^{\text{RCS}}$	$J^{\text{RCS}}$ , corrected
HS, 4, 24, 34	$J_{bb} = (E^{24} - E^4)/15$	$J_{bb} = J_{bb} + J_{24} - J_{23}$	-15.2	-1.9 (-1.9) <sup>c</sup>
	$J_{ww} = (2E^4 - E^{\text{HS}} - E^{34})/30$	$J_{ww} = J_{ww} + 1/2(J_{13} + J_{23} - J_{14} - J_{24})$	-6.7	-8.7 (-8.7)
	$J_{wb} = (E^{34} - E^{\text{HS}})/60$	$J_{wb} = J_{wb}$	-86.1	-86.1 (-86.1)
HS, 2, 4, 23	$J_{bb} = (E^{23} - E^4)/15$	$J_{bb} = J_{bb} + J_{14} - J_{13}$	+7.4	-1.9
	$J_{ww} = (E^{23} - E^2)/15$	$J_{ww} = J_{ww} + J_{23} - J_{13}$	+2.6	-8.7
	$J_{wb} = (E^2 + E^4 - E^{23} - E^{\text{HS}})/30$	$J_{wb} = 1/2(J_{wb} + J_{13})$	-90.7	-86.1
2, 4, 24, 34	$J_{bb} = (E^{24} - E^4)/15$	$J_{bb} = J_{bb} + J_{24} - J_{23}$	-15.2	-1.9
	$J_{ww} = (E^{24} - E^2)/15$	$J_{ww} = J_{ww} + J_{24} - J_{14}$	-20.0	-8.7
	$J_{wb} = (E^{24} + E^{34} - E^2 - E^4)/30$	$J_{wb} = 1/2(J_{wb} + J_{24})$	-92.7	-86.1
1, 4, 23, 34	$J_{bb} = (E^{23} - E^4)/15$	$J_{bb} = J_{bb} + J_{14} - J_{13}$	+7.4	-1.9
	$J_{ww} = (E^{23} - E^1)/15$	$J_{ww} = J_{ww} + J_{14} - J_{24}$	+2.6	-8.7
	$J_{wb} = (E^{23} + E^{34} - E^1 - E^4)/30$	$J_{wb} = 1/2(J_{wb} + J_{14})$	-81.4	-86.1

<sup>a</sup> All values are given in cm<sup>-1</sup> and were obtained assuming spin couplings appropriate for two-center spin eigenfunctions. The appropriate value for each spin coupling can be obtained from Table 1 by replacing all positive spin couplings with +6.25 and all negative spin couplings with -8.75. <sup>b</sup> Indices indicate metals with unpaired spins reversed to all other unpaired spins. See Figure 1 for numbering scheme. "HS" indicates component with all unpaired spins aligned. <sup>c</sup> Values obtained from FCS calculations.

**Table 5.** Exchange Constants Obtained for **1–4** with FCS Calculations Using Energies and Spin Couplings Given in Table 1a<sup>a</sup>

complex	interaction <sup>b</sup>	ZILSH	B3LYP/I	B3LYP/II	exp <sup>c</sup>
[Fe <sub>4</sub> O <sub>2</sub> (OAc) <sub>7</sub> (bpy) <sub>2</sub> ] <sup>+</sup> ( <b>1</b> )	$J_{bb} = J_{12}$	-11.7 (-8.7) <sup>d</sup>	+21.6 (+12.5)	+15.6 (+8.7)	-17.8
	$J_{ww} = J_{34}$	-2.0 (-2.5)	-12.0 (-9.0)	-10.7 (-8.2)	-
	$J_{wb} = J_{13}$	-115.6 (-73.8)	-132.3 (-84.4)	-134.9 (-86.0)	-
	$J_{14}$	-121.1 (-77.2)	-127.4 (-81.2)	-128.3 (-81.8)	-
	$J_{23}$	-121.5 (-73.6)	-131.5 (-83.8)	-131.6 (-83.9)	-
	$J_{24}$	-115.5 (-73.6)	-128.8 (-82.1)	-132.2 (-84.3)	-
	$J_{wb}$	-118.4 (-75.5)	-130.0 (-82.9)	-131.8 (-84.0)	-91.0
	$J_{bb} = J_{12}$	-19.5 (-13.1)	+16.4 (+9.5)	+10.9 (+6.1)	-2.4
	$J_{ww} = J_{34}$	-2.4 (-2.2)	-14.9 (-10.2)	-13.7 (-9.4)	-
[Fe <sub>4</sub> O <sub>2</sub> (O <sub>2</sub> CPh) <sub>7</sub> (phen) <sub>2</sub> ] <sup>+</sup> ( <b>2</b> )	$J_{wb} = J_{13}$	-125.4 (-80.0)	-138.6 (-88.3)	-138.6 (-88.3)	-
	$J_{14}$	-129.4 (-82.8)	-141.9 (-90.7)	-145.2 (-92.8)	-
	$J_{23}$	-120.7 (-77.1)	-138.2 (-88.3)	-140.6 (-89.8)	-
	$J_{24}$	-129.8 (-83.2)	-126.8 (-81.3)	-127.6 (-81.9)	-
	$J_{wb}$	-126.3 (-80.8)	-136.4 (-87.2)	-138.0 (-88.2)	-77.6
	$J_{bb} = J_{12}$	-22.2 (-14.9)	+1.1 (-0.1)	-1.7 (-1.9)	-15.6
	$J_{ww} = J_{34}$	-3.6 (-2.9)	-13.8 (-9.6)	-12.4 (-8.7)	-
	$J_{wb} = J_{13}$	-121.9 (-79.0)	-126.3 (-82.0)	-125.4 (-81.4)	-
	$J_{14}$	-107.2 (-69.7)	-139.6 (-90.6)	-139.8 (-90.7)	-
[Fe <sub>4</sub> O <sub>2</sub> (O <sub>2</sub> CPh) <sub>8</sub> (phen) <sub>2</sub> ] ( <b>3</b> )	$J_{23}$	-108.0 (-70.1)	-143.9 (-93.1)	-143.3 (-92.7)	-
	$J_{24}$	-121.3 (-78.6)	-122.3 (-79.5)	-122.2 (-79.4)	-
	$J_{wb}$	-114.6 (-74.4)	-133.0 (-86.3)	-132.7 (-86.1)	-65.7
	$J_{bb} = J_{12}$	-18.5 (-12.3)	+8.1 (+4.6)	+2.5 (+1.0)	-22
	$J_{ww} = J_{34}$	-1.5 (-1.5)	-10.1 (-7.2)	-9.5 (-6.8)	-
	$J_{wb} = J_{13}$	-100.7 (-64.9)	-125.6 (-81.0)	-126.1 (-81.4)	-
	$J_{14}$	-63.3 (-40.8)	-102.4 (-65.9)	-102.2 (-65.7)	-
	$J_{23}$	-119.7 (-76.9)	-141.2 (-90.7)	-145.0 (-93.1)	-
	$J_{24}$	-112.4 (-71.7)	-139.5 (-89.0)	-139.1 (-88.7)	-
[Fe <sub>4</sub> O <sub>2</sub> Cl <sub>2</sub> (OAc) <sub>6</sub> (bpy) <sub>2</sub> ] ( <b>4</b> )	$J_{wb}$	-99.0 (-63.6)	-127.2 (-81.6)	-128.1 (-82.2)	-82

<sup>a</sup> All values in cm<sup>-1</sup>. <sup>b</sup> See Figure 1 for atom labeling scheme. <sup>c</sup> References 37 (**1**), 38 (**2**, **3**), and 47 (**4**). <sup>d</sup> Values in parentheses obtained assuming spin couplings appropriate for two-center spin eigenfunctions. The appropriate value for each spin coupling can be obtained from Table 1 by replacing all positive spin couplings with +6.25 and all negative spin couplings with -8.75.

Considering first correlations between structural parameters and exchange constants, empirical magnetostructural correlations have been found for both diferric and higher nuclearity Fe<sup>3+</sup> complexes with substituted and unsubstituted oxo bridging ligands.<sup>36,61–63</sup> The number of distinct bridging pathways considered in these works is quite large, on the order of 85. In all cases, the exchange constant was found to become more antiferromagnetic with decreasing average Fe–O bond distance in the coupling pathway. A dependence on Fe–O–Fe bridging angle was also found,<sup>36,61,62</sup> with the exchange constant becoming more antiferromagnetic with increasing angle. This dependence was especially marked

for higher nuclearity complexes<sup>36</sup> but was weaker than the dependence on bond distance in all cases. Although different fitting parameters for the magnetostructural correlation equations were found depending on the complexes considered (i.e., dinuclear or higher nuclearity, substituted vs unsubstituted oxo bridged or both considered together), all of these models predict antiferromagnetic  $J_{bb}$  values given the geometric parameters of the body-body pathways in **1–4**. The correlation of Cañada-Vilalta et al.<sup>36</sup> is perhaps most applicable for **1–4** since it was based on interactions in polynuclear complexes with O<sup>2-</sup>-mediated exchange interactions as small as -8 cm<sup>-1</sup>, and it gives estimates of  $J_{bb}$  in



the range  $-13\text{ cm}^{-1}$  to  $-16\text{ cm}^{-1}$  for **1–4**. The other magnetostructural correlations mentioned above<sup>61–63</sup> give even more antiferromagnetic estimates. The large ferromagnetic  $J_{bb}$  values found with DFT thus appear to disagree with trends extracted from a great deal of experimental data on dinuclear and higher nuclearity  $\text{Fe}^{3+}$  complexes.

Turning now to exchange constants extracted from magnetic susceptibilities of diferric complexes, the exchange constant in these cases is directly related to the experimental data since there is only one fitting parameter. A survey of the literature on 65 diferric complexes with substituted and/or unsubstituted oxo bridging ligands with available magnetic susceptibility data showed a very wide range of exchange constants, from  $-284\text{ cm}^{-1}$  ( $[(\text{TPP})_2\text{Fe}_2\text{O}]$ , TPP = 7,8-dihydro-5,10,15,20-tetraphenylporphyrinate; ref 64) to  $+2.4\text{ cm}^{-1}$  ( $[(\text{salmp})_2\text{Fe}_2]$ , salmp = 2-bis(salicylidenoamino)methylphenolate; ref 65). It is interesting to note that only one of the observed exchange constants is ferromagnetic, that for  $[(\text{salmp})_2\text{Fe}_2]$  with  $J = +2.4\text{ cm}^{-1}$ . This complex has substituted oxo bridging ligands rather than unsubstituted oxo ligands as in **1–4**; the latter are known to have interactions that are more antiferromagnetic.<sup>63</sup> The diferric complex also has significantly longer Fe–O bond distances in the bridging pathway ( $\sim 2.02\text{ \AA}$  vs  $\sim 1.95\text{ \AA}$  in **1–4**). Given that  $J$  becomes more antiferromagnetic with decreasing bond distance,<sup>36,61–63</sup> both factors indicate that  $J_{bb}$  in **1–4** would be substantially more antiferromagnetic than the value of  $+2.4\text{ cm}^{-1}$  observed for  $[(\text{salmp})_2\text{Fe}_2]$  and hence likely have negative signs. Again, the indication is that the  $J_{bb}$  values found with DFT are considerably too ferromagnetic. This might be a general tendency, as analogous behavior was found for a similar exchange pathway in the complex  $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]^{8+}$  (ref 20; see also discussion in ref 32). Additional testing is needed to further investigate this tendency.

Another trend apparent in the exchange constants of Table 5 is that the DFT calculations give strongly antiferromagnetic estimates for the wingtip-wingtip interactions  $J_{ww}$  for all four complexes. Again this does not depend heavily on basis set or choice of spin coupling scheme. The ZILSH calculations give estimates that are very weakly antiferromagnetic. Direct comparison with experiment is not possible for this interaction since fits of the magnetic data neglected this interaction.<sup>37,38,47</sup> This was done because the wingtip ions do not interact directly by means of a single-atom bridging mode and were thus assumed to have a negligibly small exchange constant. This is a standard assumption. While there is some experimental evidence that such “second neighbor” interactions might have nonzero exchange interactions (see, e.g., refs 66 and 67), the proposed exchange constants have magnitudes less than  $2\text{ cm}^{-1}$ . It seems unlikely that exchange interactions between metal ions that are not directly bridged would be as large in magnitude as the DFT estimates for  $J_{ww}$  in **1–4**. This is especially true given that  $J_{ww}$  is larger in magnitude than  $J_{bb}$  for **3** and **4** and of comparable magnitude for **1** and **2**, and the body-body interactions are mediated by single atom bridging ligands. It thus appears that the DFT calculations are overestimating the magnitudes of  $J_{ww}$  in **1–4**,

in contrast to the ZILSH calculations which give much smaller magnitudes for these interactions.

Estimates of  $\overline{J_{wb}}$  from the various methods of calculation are more similar than the estimates of  $J_{bb}$  and  $J_{ww}$ . When comparing computed values to those found from fits of experimental magnetic data, it is important to note that the fits assumed equivalent  $J_{wb}$  interactions, so the empirical values should be compared to average values obtained from the FCS calculations. Two factors must be considered in making these comparisons, including choice of method (ZILSH or DFT) and choice of spin coupling scheme. The role of basis set must also be considered for the DFT calculations; this is discussed below. Starting with the choice of method, the ZILSH calculations give better estimates of  $\overline{J_{wb}}$  (i.e., closer to the empirical values) than DFT for all four complexes with spin couplings computed from the ZILSH component wave functions and for compounds **2** and **3** with spin couplings appropriate for two-center spin eigenfunctions. Taken together with the results found for  $J_{bb}$  and  $J_{ww}$  given above, this is a strong indication that the ZILSH calculations provide a picture of magnetic interactions in these complexes that is more consistent with experiment. This was also found to be the case with the complex  $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]^{8+}$  (ref 32) but not for the complex  $[\text{Fe}_{14}\text{O}_6(\text{bta})_6(\text{OMe})_{18}\text{Cl}_6]$ , in which DFT calculations gave the correct ground-state spin while ZILSH calculations did not.<sup>68</sup> Clearly comparisons for additional complexes are needed to clarify if one method is consistently more reliable than the other for estimating exchange constants in polynuclear transition metal complexes.

Turning now to choice of spin coupling scheme, in comparisons within the same method DFT calculations give much more accurate estimates of  $\overline{J_{wb}}$  with spin couplings appropriate for two-center spin eigenfunctions (Table 5). The ZILSH calculations behave likewise for compounds **1–3**, while very similar errors in  $\overline{J_{wb}}$  are found with the two coupling schemes for **4**. From a practical standpoint, then, it appears that spin couplings appropriate for two-center spin eigenfunctions give consistently better results. It is unclear why this is the case. O'Brien and Davidson<sup>33</sup> and particularly Clark and Davidson,<sup>25,69,70</sup> among others,<sup>21,71,72</sup> have recently considered this question from a theoretical perspective rather than on the basis of a systematic comparison of calculated and experimental results. While it is not our intention to repeat or extend these theoretical analyses here, some remarks can be made based on the results found for **1–4**.

Conceptually, if spin component wave functions are assumed to follow the effective Hamiltonian of eq 1, then spin couplings should properly be evaluated as expectation values of the operator  $\hat{S}_A \cdot \hat{S}_B$ . O'Brien and Davidson<sup>33</sup> showed that in the formal case of single determinant component wave functions with open-shell MOs centered entirely on the radical centers and identical closed shell ligand MOs for  $\alpha$  and  $\beta$  electrons (i.e., no spin delocalization or spin polarization), the same exchange constants describing the true spin states of the system are obtained if the spin couplings are evaluated as expectation values of the local spin operator. Again in the formal case, these expectation values are smaller

in magnitude for single determinant wave functions than for two-center spin eigenfunctions (e.g.,  $\pm 6.25$  vs  $+6.25/-8.75$  for single determinant wave functions and spin eigenfunctions describing two coupled high spin  $d^5$   $\text{Fe}^{3+}$  ions, respectively). Exchange constants obtained with the method of simultaneous solution of equations similar to eq 2 above are inversely proportional to the magnitudes of the spin couplings used, since the exchange constants are formally obtained by multiplying a column matrix containing the component energies by the inverse of a square matrix containing the spin couplings. In the formal case, then, use of spin couplings appropriate for two-center spin eigenfunctions should lead to artificially small estimates of the magnitudes of the exchange constants.

The obvious problem with this analysis is that the smaller estimates obtained with two-center spin eigenfunction spin couplings are more consistent with experimental results for  $\overline{J_{wb}}$  for **1–4**. This could arise from cancelation of errors, as component wave functions for real complexes do not generally meet the formal conditions given above, i.e., unrestricted spin component wave functions do display spin polarization and delocalization. Exchange constants obtained from such wave functions are thus only approximations of the exchange constants describing the true spin eigenstates of a complex. Even if the component wave functions did behave formally, the methods themselves still have intrinsic error; i.e., neither ZILSH nor DFT calculations can be expected to perfectly reproduce magnetic interaction energies. The effect of these various considerations has not been thoroughly elucidated theoretically or on the basis of comparisons between calculated and empirical exchange constants. It is also very important to note that in other cases we have observed that the larger exchange constants found with spin couplings obtained from the local spin operator are more consistent with experiment.<sup>33,68</sup> Further study from both theoretical and practical perspectives is needed to clarify these issues.

A final point to consider is the effect of basis set in the DFT calculations. The larger exchange constants  $\overline{J_{wb}}$  found with the two basis sets are very similar (Table 5), with differences on the order of  $1\text{ cm}^{-1}$ . The pairwise wingtip-body interactions  $J_{13}$ ,  $J_{14}$ , etc. share this similarity, differing by no more than  $\sim 3\%$  ( $J_{14}$  of **2**;  $J_{23}$  of **4**) and by about  $1\text{ cm}^{-1}$  in all other cases. This level of agreement seems remarkable, given that basis set II is almost twice as large as basis set I (e.g., 1038 vs 622 basis functions for **4**), but it should be recalled that exchange constants are based on differences in energies of spin components with similar local electronic structure (i.e., all open shell metal ions are locally in high spin configurations, though they may be reversed relative to the unpaired spin on another metal ion). It is thus likely that any basis set error—which is itself a somewhat nebulous concept in DFT (e.g., ref 73)—approximately cancels in subtracting to obtain energy differences contributing to  $\overline{J_{wb}}$ . A clear basis set effect can be seen in the interactions that are not well-described by the DFT calculations, particularly in the  $J_{bb}$  interactions. For those the larger basis set consistently provides less ferromagnetic estimates, though the values obtained are still in qualitative disagree-

ment with values obtained from empirical fitting of magnetic susceptibility data.

## Conclusions

Exchange constants describing magnetic interactions in tetranuclear  $\text{Fe}^{3+}$  butterfly complexes **1–4** were estimated with semiempirical ZILSH calculations and DFT calculations using the B3LYP functional and two basis sets. Theoretical analysis of a restricted configuration space (RCS) method developed by Cauchy et al.<sup>37</sup> for these complexes showed that systematic errors in the exchange constants were incurred by assuming equivalent wingtip-body interactions  $J_{wb}$ . Correction factors were derived and found to exactly reproduce results from full configuration space (FCS) calculations. Additionally it was shown that exchange constants obtained from RCS calculations with different choices of spin configurations had large variances. Again, derived correction factors led exactly to FCS results in all cases. These results indicate that RCS calculations must be handled carefully to prevent significant errors if used in place of FCS calculations.

Comparisons of exchange constants obtained from ZILSH and DFT FCS calculations with those obtained from empirical fits of experimental magnetic susceptibility data were made. It was found that DFT calculations with both basis sets gave strongly ferromagnetic estimates of exchange constants describing interaction of the “body” iron ions ( $J_{bb}$ ), while ZILSH calculations gave antiferromagnetic estimates. The latter are in much better agreement with empirical values for these complexes as well as estimates from well-known magnetostructural correlations in dinuclear and higher nuclearity  $\text{Fe}^{3+}$  clusters and empirical values found for diferric complexes. DFT calculations with both basis sets also gave unreasonably strong, antiferromagnetic exchange constants for nonbridged, second-neighbor interactions between wingtip ions ( $J_{ww}$ ), while ZILSH calculations gave uniformly small estimates. ZILSH and DFT performed similarly for wingtip-body interactions  $J_{wb}$ , with the former giving slightly more accurate estimates. Together with the results found for  $J_{bb}$  and  $J_{ww}$ , these results indicate that the ZILSH method provides exchange constants that are more consistent with experiment for these complexes. Additional comparisons of the two methods are needed to judge their relative abilities to estimate exchange constants in polynuclear transition metal complexes. With further calibration and (perhaps) improvement, these computational methods could make important contributions to ongoing study and development of single molecule magnets.

Comparisons were also made between exchange constants obtained with different spin coupling schemes. Consistently better results were obtained with spin couplings appropriate for two-center spin eigenfunctions rather than couplings obtained as expectation values of the local spin operator evaluated with ZILSH spin component wave functions. A brief conceptual analysis of why this might occur was given. This question needs to be investigated further from both theoretical and practical (i.e., by comparing results against experiment for known complexes) perspectives.

Very small differences were observed when comparing exchange constants obtained from DFT calculations with

basis sets of distinctly different sizes. This likely occurs because basis set errors cancel in subtracting to obtain energy differences in evaluating exchange constants. DFT calculation of exchange constants in larger complexes would be facilitated by using smaller basis sets if the lack of basis set effect observed here is substantiated with additional comparisons.

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