

## Heisenberg Exchange in Dinuclear Manganese Complexes: A Density Functional Theory Study

Elias Rudberg,\* Paweł Sałek, Zilvinas Rinkevicius, and Hans Ågren

*Department of Theoretical Chemistry, Royal Institute of Technology,  
SE-10691 Stockholm, Sweden*

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**Abstract:** This work presents a systematic investigation of the performance of broken symmetry density functional theory for the evaluation of Heisenberg exchange constants. We study dinuclear  $\text{Mn}^{\text{IV}}\text{--Mn}^{\text{IV}}$  complexes with bis( $\mu$ -oxo), bis( $\mu$ -oxo)( $\mu$ -carboxylato), and tris( $\mu$ -oxo) cores for this purpose, as these are of fundamental biological interest as well as being potential precursors for molecular magnets based on manganese complexes, the so-called  $\text{Mn}_{12}$  magnets. The obtained results indicate that quantitative agreement with available experimental data for the Heisenberg exchange constants can be achieved for most of the investigated complexes but also that there are significant failures for some compounds. We evaluate factors influencing the accuracy of obtained results and examine effects of different mappings between broken symmetry and Heisenberg Hamiltonian states in an attempt to formulate a reliable recipe for the evaluation of magnetic coupling in these complexes. An assessment of the bonding situation in the molecular system under investigation is found crucial in choosing the appropriate scheme for evaluation of the Heisenberg exchange constants.

### I. Introduction

Contemporary research in magnetic properties of chemical compounds and solid-state materials often addresses the coupling between localized spins in terms of an empirical Heisenberg Hamiltonian.<sup>1</sup> In this description the magnetic spin coupling is parametrized in a pairwise manner via so-called Heisenberg exchange constants. These constants find applications primarily in mutually related fields of science devoted to paramagnetic compounds, such as (i) theory of magnetism, where the Heisenberg exchange constants are one of the key magneto-structural parameters of solid or molecular magnets required for characterization of their magnetization,<sup>2</sup> and (ii) electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR) spectroscopies of compounds with multiple localized electronic spins, where the Heisenberg exchange constants enter the spin Hamiltonian and are determined along with other parameters unique for EPR or NMR spectra.<sup>3–5</sup> The dependence of magnetic coupling on the electronic structure of molecular fragments carrying a localized spin and on localized spins arrangements in general has thus been of considerable interest in the field of theory of magnetism. This interest has also been greatly

spurred by the search for spin arrangements of single molecular magnets in which the magnetic coupling occurs between transition-metal ions in a complex with their ligand environments.<sup>2,6</sup> Another factor stimulating research in this direction refers to attempts to synthesize organic magnets suitable for practical applications, as these require microscopic understanding of the mechanisms for the magnetic coupling between organic radicals in polymer hosts in order to guide synthesis efforts.<sup>7</sup>

In the field of EPR and NMR spectroscopies the interest in magnetic couplings in molecular systems with multiple localized spins is mainly motivated by the aid they may provide in interpretation of measurements and in determination of geometrical and electronic structure through the measurements.<sup>3–5</sup> The need for microscopic understanding of magnetic coupling is particularly evident in applications of high field EPR spectroscopy on active sites of enzymes, where the interpretation of EPR spectra otherwise becomes more of an art than science. One notorious example of this kind is the oxygen evolving center in photosystem II, where different oxidation states have been assigned to manganese ions by various interpretations of EPR spectra (see for

example discussion in ref 8). The advances in these fields of research clearly make computational methods for the evaluation of the Heisenberg exchange constants highly desirable.

Computations of magnetic coupling as represented by Heisenberg exchange constants in molecular systems have posed a long standing problem in quantum chemistry, as calculations of this kind require an accurate description of electron correlation, both static and dynamic, as well as a reliable mapping between computed electronic states and states featured in the Heisenberg Hamiltonian.<sup>9–11</sup> These requirements actually quite severely limit the choice of methodology that can be suitable for calculations. In the domain of ab initio methods various configuration interaction as well as multireference perturbation theory methods can be successfully applied to compute Heisenberg exchange constants in small molecules.<sup>9,10</sup> For larger molecular systems, the broken symmetry density functional theory (BS-DFT) approach<sup>12</sup> has mostly been used for this purpose.<sup>6,9–11,13–15</sup> However, the mapping between broken symmetry states and Heisenberg Hamiltonian states is nonobvious, especially if localized spin centers have more than one unpaired electron, as pointed out, for example, by L. Noodleman<sup>12</sup> and F. Neese.<sup>10</sup> Despite this disadvantage of the BS-DFT approach, it is currently the only option for investigations of magnetic coupling in large molecular systems of experimental interest, and it has therefore been applied to a quite wide set of problems, ranging from investigations of molecular magnets to interpretation of EPR spectral parameters in paramagnetic transition-metal systems (see e.g. refs 14 and 16).

In the present paper we investigate the Heisenberg exchange constants in dinuclear manganese ( $\text{Mn}^{\text{IV}}\text{--Mn}^{\text{IV}}$ ) complexes with bis( $\mu$ -oxo), bis( $\mu$ -oxo)( $\mu$ -carboxylato), and tris( $\mu$ -oxo) cores. The main focus is to assess the performance of the broken symmetry DFT formalism for evaluation of magnetic coupling, using for the purpose a system that is of fundamental biological interest, and to evaluate factors influencing the accuracy of obtained results. Apart from this, we also examine effects of different mappings between broken symmetry and Heisenberg Hamiltonian states in an aim to formulate a reliable recipe for evaluation of magnetic coupling in manganese complexes. The latter effort is a preparatory step for a future investigation of molecular magnets based on manganese complexes, the so-called  $\text{Mn}_{12}$  magnets.

## II. Computational Details

Magnetic coupling between localized spins in the Heisenberg Hamiltonian is described via empirical parameters; the Heisenberg exchange constants  $J_{\text{AB}}$ <sup>1</sup>

$$H = -2J_{\text{AB}}\mathbf{S}_{\text{A}} \cdot \mathbf{S}_{\text{B}} \quad (1)$$

where  $\mathbf{S}_{\text{A}}$  and  $\mathbf{S}_{\text{B}}$  are spins localized on centers A and B, respectively. A key to a successful computation of  $J_{\text{AB}}$  with BS-DFT is an appropriate mapping between broken symmetry, high spin, and Heisenberg Hamiltonian states. A theoretically well justified mapping scheme has been pro-

posed by L. Noodleman,<sup>12</sup> in which  $J_{\text{AB}}$  is defined as

$$J_{\text{AB}} = \frac{E_{\text{BS}} - E_{\text{HS}}}{S_{\text{max}}^2}, \quad (2)$$

where  $E_{\text{BS}}$  and  $E_{\text{HS}}$  are the energies of the broken symmetry and high spin states obtained with the unrestricted DFT formalism, and where  $S_{\text{max}}$  is the number of the unpaired electrons in the molecular fragment carrying spin  $\mathbf{S}_{\text{A}}$  (assuming that the  $\mathbf{S}_{\text{B}}$  spin related fragment has the same number of unpaired electrons as the  $\mathbf{S}_{\text{A}}$  fragment). This evaluation scheme for  $J_{\text{AB}}$  is applicable for weakly bonded molecular fragments between which the magnetic orbital overlap is small.<sup>9,10,12</sup> An alternative mapping scheme in the BS-DFT approach has been used by E. Ruiz and co-workers,<sup>17</sup> following the work of Noodleman.<sup>12,18</sup> In this scheme,  $J_{\text{AB}}$  is computed as

$$J_{\text{AB}} = \frac{E_{\text{BS}} - E_{\text{HS}}}{S_{\text{max}}(S_{\text{max}} + 1)} \quad (3)$$

This scheme assumes strong bonding between molecular fragments with localized spins i.e., when the overlap between magnetic orbitals of the spins is non-negligible. Consequently, this mapping scheme should probably be more acceptable for treating dinuclear manganese complexes than the one proposed by L. Noodleman (see eq 2). The above-described schemes for computation of Heisenberg exchange constants correspond in fact to two limiting cases of bonding situations between localized spins, namely weak and strong bonding between molecular fragments carrying localized  $\mathbf{S}_{\text{A}}$  and  $\mathbf{S}_{\text{B}}$  spins. Therefore, an assessment of the bonding situation in the molecular system under investigation is helpful in choosing between the  $J_{\text{AB}}$  evaluation schemes. Another way to compute  $J_{\text{AB}}$  with the BS-DFT approach, which is independent of the bonding situation in the molecule, has been proposed by M. Nishino et. al. as<sup>19</sup>

$$J_{\text{AB}} = \frac{E_{\text{BS}} - E_{\text{HS}}}{\langle S^2 \rangle_{\text{HS}} - \langle S^2 \rangle_{\text{BS}}} \quad (4)$$

Here  $\langle S^2 \rangle_{\text{HS}}$  and  $\langle S^2 \rangle_{\text{BS}}$  are the total spin angular momentum expectation values for high spin and broken symmetry states obtained with the unrestricted DFT formalism. This evaluation scheme indirectly accounts for the overlap between magnetic orbitals of localized spins by employing expectation values of the total spin angular momentum,  $\langle S^2 \rangle_{\text{HS}}$  and  $\langle S^2 \rangle_{\text{BS}}$ . Here it is appropriate to mention that the  $S^2$  operator expectation values are well defined for the unrestricted Hartree–Fock method, while in the context of unrestricted density functional theory the  $S^2$  operator expectation values obtained from Kohn–Sham orbitals is not a well-defined procedure.<sup>20</sup> Despite this drawback, this approach is at the first glance most suitable for complexes such as the various dinuclear manganese complexes investigated in the present work. We nevertheless employ all three above-described  $J_{\text{AB}}$  evaluation schemes in order to assess their performance and suitability for computation of  $J_{\text{AB}}$  in general  $\text{Mn}^{\text{IV}}\text{--Mn}^{\text{IV}}$  complexes with different core arrangements. Previous theo-

**Table 1:** Results of Evaluation of Heisenberg Exchange Constants between Mn<sup>IV</sup> Centers in Various Manganese Compounds (cm<sup>-1</sup>) Using B3LYP and CAMB3LYP Exchange-Correlation Functionals<sup>a</sup>

complex	B3LYP			CAMB3LYP			exp
	$J_{AB}^b$	$J_{AB}^c$	$J_{AB}^d$	$J_{AB}^b$	$J_{AB}^c$	$J_{AB}^d$	
Mn <sub>2</sub> O <sub>2</sub> (pic) <sub>4</sub>	-112.5	-84.4	-111.2	-99.1	-74.3	-98.2	-86.5 <sup>e</sup>
[Mn <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub> (bpea) <sub>4</sub> ] <sup>2+</sup>	-144.2	-108.1	-159.6	-130.3	-97.8	-129.1	-144 <sup>f</sup>
[Mn <sub>2</sub> O <sub>2</sub> (phen) <sub>4</sub> ] <sup>4+</sup>	-131.9	-98.9	-130.4	-124.3	-93.3	-123.4	-147 <sup>g</sup>
[Mn <sub>2</sub> O <sub>2</sub> (OAc)(bpea) <sub>2</sub> ] <sup>3+</sup>	-36.0	-27.0	-35.7	-23.8	-17.8	-23.7	-124 <sup>h</sup>
[Mn <sub>2</sub> O <sub>2</sub> (OAc)(Me <sub>4</sub> dtne)] <sup>3+</sup>	-37.5	-28.1	-37.2	-30.7	-23.0	-30.5	-100 <sup>i</sup>
[Mn <sub>2</sub> O <sub>3</sub> (Me <sub>3</sub> tacn) <sub>2</sub> ] <sup>2+</sup>	-382.7	-287.0	-376.4	-370.7	-278.0	-367.9	-390 <sup>j</sup>

<sup>a</sup> Ahlrich's VTZ basis set employed in all calculations. <sup>b</sup>  $J_{AB}$  evaluated using eq 2. <sup>c</sup>  $J_{AB}$  evaluated using eq 3. <sup>d</sup>  $J_{AB}$  evaluated using eq 4. <sup>e</sup>  $J_{AB}$  experimental data taken from ref 23. <sup>f</sup>  $J_{AB}$  experimental data taken from ref 24. <sup>g</sup>  $J_{AB}$  experimental data taken from ref 25. <sup>h</sup>  $J_{AB}$  experimental data taken from ref 26. <sup>i</sup>  $J_{AB}$  experimental data taken from ref 27. <sup>j</sup>  $J_{AB}$  experimental data taken from ref 28.

retical investigations of dinuclear manganese complexes can be found in the literature.<sup>9,21,22</sup>

The selected test set of dinuclear manganese (Mn<sup>IV</sup>–Mn<sup>IV</sup>) compounds includes three molecules with bis( $\mu$ -oxo) core (Mn<sub>2</sub>O<sub>2</sub>(pic)<sub>4</sub>, [Mn<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub>(bpea)<sub>4</sub>]<sup>2+</sup>, [Mn<sub>2</sub>O<sub>2</sub>(phen)<sub>4</sub>]<sup>4+</sup>), two molecules with bis( $\mu$ -oxo)( $\mu$ -carboxylato) core ([Mn<sub>2</sub>O<sub>2</sub>(OAc)(bpea)<sub>2</sub>]<sup>3+</sup>, [Mn<sub>2</sub>O<sub>2</sub>(OAc)(Me<sub>4</sub>dtne)]<sup>3+</sup>), and one molecule with tris( $\mu$ -oxo) core ([Mn<sub>2</sub>O<sub>3</sub>(Me<sub>3</sub>tacn)<sub>2</sub>]<sup>2+</sup>). We use the following notation for the ligands: bpea – *N,N*-bis(2-pyridylmethyl)ethyldiamine, Me<sub>4</sub>dtne – 1,2-bis(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane, Me<sub>3</sub>tacn – 1,4,7-trimethyl-1,4,7-triazacyclonane, OAcH – methanecarboxylic acid, phen – 1,10-phenanthroline, and picH – picolinic acid. The geometries of the enlisted compounds, employed in all calculations, have been obtained combining crystallographic data<sup>23–28</sup> and molecular force field geometry optimization, where the positions of the heavy element atoms (C, N, O, Mn) have been taken from crystal structures and where the positions of the hydrogen atoms have been optimized (keeping heavy atoms positions fixed) using the MMFF94 force field<sup>29</sup> implemented in the Spartan program.<sup>30</sup> The only exception from this procedure is the Mn<sub>2</sub>O<sub>2</sub>(pic)<sub>4</sub> molecule for which the positions of the hydrogen atoms are available in the crystal structure data. Apart from building full size geometries for the above enumerated compounds, we also created reduced models of them in order to investigate the possibility to employ only rudiment ligand structures instead of full size ligands in the calculations of Heisenberg exchange constants as this would allow for a significant reduction of the computational cost. The reduced models were designed by substituting the ligands encountered in the manganese complexes by similar smaller ligands as bpea with (CHCH<sub>2</sub>-NH)<sub>2</sub>NH, Me<sub>4</sub>dtne with 1,2-bis(1,4,7-triazacyclonon-1-yl)ethane, Me<sub>3</sub>tacn with 1,4,7-triazacyclonane, phen with (CHNH)<sub>2</sub>, and pic with NHCHCO<sub>2</sub>. The position for heavy atoms (C, N, O, Mn) in the reduced ligands have been selected to be the same as in the nonreduced ligands, and the positions of the hydrogen atoms have been optimized employing an analogous procedure as in the case of optimizing the nonreduced compounds geometries.

The evaluation of  $J_{AB}$  constants for all compounds have been carried out employing the B3LYP exchange-correlation functional.<sup>31–34</sup> This functional is found to perform relatively well in our calculations of the Heisenberg exchange constants for cases in which the BS-DFT approach is applicable. However, for large molecular systems such as Mn<sub>12</sub>-type

single molecular magnets, the incorrect asymptotic behavior of the exchange part of this functional can become a potential problem. To sort out this problem, which in principle can hamper efforts of accurate evaluation of  $J_{AB}$  in large molecules, we investigated the suitability of the Coulomb attenuated model of the B3LYP functional (CAMB3LYP)<sup>36</sup> for computation of Heisenberg exchange constants. Results of this investigation are tabulated in Table 1 along with B3LYP and experimental results. CAMB3LYP predicts  $J_{AB}$  values to be on average 15 cm<sup>-1</sup> smaller (in terms of absolute values) compared to B3LYP calculation results. Consequently, the current CAMB3LYP exchange-correlation functional parametrization does not allow for the reproduction of the good performance of the ordinary B3LYP functional. Despite this deficiency of the CAMB3LYP functional in its current form, the in principle “more” asymptotically correct behavior of the exchange part of this functional might be advantageous in evaluation of  $J_{AB}$  in extended systems. To achieve better accuracy in these calculations one thus needs to make additional efforts to parametrize the CAMB3LYP functional.

The calculations reported in this work were carried out using our recently developed quantum chemistry program ErgoSCF,<sup>35</sup> in which we have implemented functionality for generating starting guesses and monitoring the electron spin density in unrestricted DFT calculations. The ErgoSCF program also includes an implementation of the CAMB3LYP functional.<sup>36</sup> We employed four different basis sets: 3-21G,<sup>37</sup> 6-31G,<sup>38</sup> 6-31G\*,<sup>38</sup> and AhlrichsVTZ.<sup>39</sup> This selection is motivated mainly by the attempt to find the smallest possible basis set which still provides reliable  $J_{AB}$  constants for further large scale computations of the Heisenberg exchange constants in molecular magnets.

Before concluding the computational section we want briefly to discuss two technical details related to the evaluation of broken symmetry states in the unrestricted Kohn–Sham formalism. First, a reasonable starting guess for the broken symmetry state is crucial to achieve convergence in the unrestricted calculations. In our case the starting density for the broken symmetry state has been constructed in the following way: The alpha- and beta-densities of a converged HS solution are combined to form a total density matrix and a spin density matrix. The spin density matrix is then modified by changing the sign of the matrix elements that correspond to one of the Mn centers. Starting guesses for the alpha- and beta- density matrices for the BS state

**Table 2:** Heisenberg Exchange Constants between  $\text{Mn}^{\text{IV}}$  Centers in  $\text{Mn}_2\text{O}_2(\text{pic})_4$  in  $\text{cm}^{-1}$ <sup>a</sup>

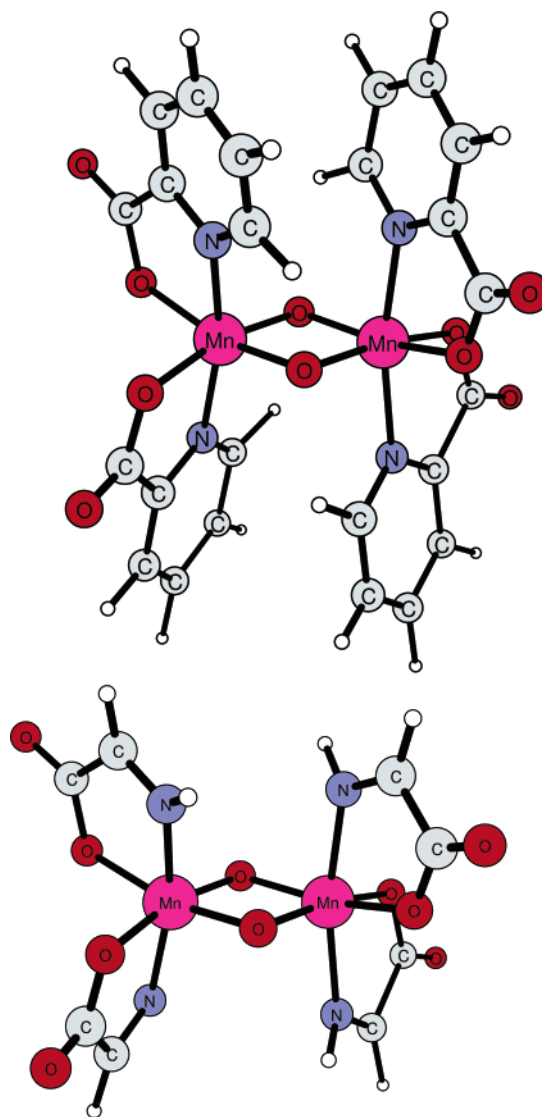
basis set	model <sup>a</sup>	$J_{\text{AB}}^b$	$J_{\text{AB}}^c$	$J_{\text{AB}}^d$	$\langle S^2 \rangle_{\text{BS}}$	$\langle S^2 \rangle_{\text{HS}}$
3-21G	full	-101.7	-76.3	-100.7	3.032	12.119
6-31G	full	-114.0	-85.5	-112.7	3.013	12.114
6-31G*	full	-110.3	-82.7	-109.1	3.009	12.109
AhlrichsVTZ	full	-112.5	-84.4	-111.2	3.005	12.111
3-21G	reduced	-104.5	-78.4	-103.3	3.026	12.130
6-31G	reduced	-117.9	-88.4	-116.4	3.007	12.123
6-31G*	reduced	-112.5	-84.4	-111.1	3.003	12.116
AhlrichsVTZ	reduced	-116.5	-87.4	-115.0	2.998	12.118
MIDI <sup>e</sup>	reduced	-126.0	-94.7	-124.0		
MIDI+pol(pdf) <sup>e</sup>	reduced	-117.0	-87.6	-115.0		
exp <sup>f</sup>			-86.5			

<sup>a</sup>  $J_{\text{AB}}$  model defines geometry of compound used in calculations, where "full" denotes whole compound and "reduced" denotes the smaller size model of it. <sup>b</sup>  $J_{\text{AB}}$  evaluated using eq 2. <sup>c</sup>  $J_{\text{AB}}$  evaluated using eq 3. <sup>d</sup>  $J_{\text{AB}}$  evaluated using eq 4. <sup>e</sup>  $J_{\text{AB}}$  B3LYP calculations results taken from T. Soda et. al.<sup>9</sup> <sup>f</sup>  $J_{\text{AB}}$  Experimental data taken from ref 23. <sup>g</sup> All calculations performed with B3LYP exchange-correlation functional.

are then formed using the total density matrix and the modified spin density matrix. Second, since broken symmetry calculations are notorious for their poor convergence, sometimes even with well designed starting guesses, one should always carefully examine the obtained state. One way of checking the validity of the result is to look at the spin density of the system; we here monitored the spin density on each Mn atom by means of numerical integration over a spherical region (radius 2.0 au) around each Mn atom. This procedure allowed us to ensure reliable control over the convergence of the broken-symmetry state in these unrestricted Kohn–Sham calculations.

### III. Results and Discussion

**A. Basis Set Dependence of Heisenberg Exchange Constants.** The  $\text{Mn}_2\text{O}_2(\text{pic})_4$  compound with bis( $\mu$ -oxo) core that is a part of our selected test set was a subject of an earlier BS-DFT investigation by T. Soda et al.<sup>9</sup> We therefore picked this complex for testing the suitability of various basis sets for evaluation of  $J_{\text{AB}}$  between the manganese centers. The Heisenberg exchange constants in the  $\text{Mn}_2\text{O}_2(\text{pic})_4$  compound computed using the B3LYP exchange-correlation functional and the various basis sets are presented in Table 2. The selection of the B3LYP functional for investigating the basis set dependence is motivated by the results of T. Soda et. al.,<sup>9</sup> showing that this functional led to the best agreement between computational and experimental results. In the present investigation we employ two models of the  $\text{Mn}_2\text{O}_2(\text{pic})_4$  complex, denoted as "full" and "reduced" in Table 2, where the "full" model (see Figure 1) corresponds to the entire  $\text{Mn}_2\text{O}_2(\text{pic})_4$  molecule and the "reduced" model (see Figure 1) corresponds to a smaller molecule mimicking  $\text{Mn}_2\text{O}_2(\text{pic})_4$  in which the picolinic acid cation ligands are substituted by  $\text{NHCHCO}_2$  ligands as proposed by T. Soda et. al.<sup>9</sup> For both models the basis set dependence shows the pattern of a moderate change going from one tested basis set to another. The Heisenberg exchange constants obtained with the 6-31G, 6-31G\* and Ahlrich's VTZ basis sets are in agreement within a  $5 \text{ cm}^{-1}$  range. An exception from this



**Figure 1.**  $\text{Mn}_2\text{O}_2(\text{pic})_4$  compound and the reduced model of this compound.

trend is the small 3-21G basis set, which leads to a noticeable underestimation in terms of absolute values of the  $J_{\text{AB}}$  constants compared to results obtained with other basis sets. This behavior of the Heisenberg exchange constants with respect to various basis sets indicates that the basis sets suitable for magnetic coupling calculations should be flexible to capture essential features of the electron density distribution, especially around the  $\text{Mn}^{\text{IV}}$  centers in the broken symmetry and high spin states. At the same time, in our opinion, the use of large basis sets in calculations of this kind is unnecessary, since in the BS-DFT approach the  $J_{\text{AB}}$  constants are evaluated using energies differences between two states of the same molecule, thus canceling basis set incompleteness to a large extent. For example, improving from 6-31G to 6-31G\* by adding polarization functions leads to a decrease of absolute values of the Heisenberg exchange constants only up to about 7%, depending on the  $J_{\text{AB}}$  evaluation scheme. At a first glance, this looks like a large effect, but in the context of the BS-DFT approach this effect is considerably smaller than the differences between the  $J_{\text{AB}}$  values computed using different mapping schemes between



**Table 3:** Heisenberg Exchange Constants between Mn<sup>IV</sup> Centers in Various Manganese Compounds (cm<sup>-1</sup>)<sup>k</sup>

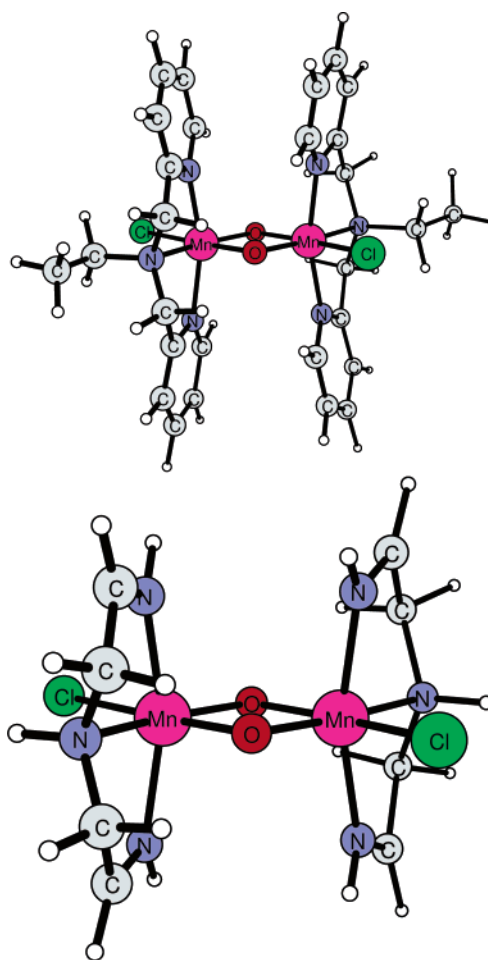
complex	model <sup>a</sup>	$J_{AB}^b$	$J_{AB}^c$	$J_{AB}^d$	$\langle S^2 \rangle_{BS}$	$\langle S^2 \rangle_{HS}$	exp
Mn <sub>2</sub> O <sub>2</sub> (pic) <sub>4</sub>	reduced	-116.5	-87.4	-115.0	2.998	12.118	
	full	-112.5	-84.4	-111.2	3.005	12.111	-86.5 <sup>e</sup>
[Mn <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub> (bpea) <sub>4</sub> ] <sup>2+</sup>	reduced	-148.5	-111.4	-146.3	2.989	12.122	
	full	-144.2	-108.1	-142.1	2.988	12.120	-144 <sup>f</sup>
[Mn <sub>2</sub> O <sub>2</sub> (phen) <sub>4</sub> ] <sup>4+</sup>	reduced	-141.7	-106.2	-139.9	3.006	12.116	
	full	-131.9	-98.9	-130.4	3.017	12.119	-147 <sup>g</sup>
[Mn <sub>2</sub> O <sub>2</sub> (OAc)(bpea) <sub>2</sub> ] <sup>3+</sup>	reduced	-24.5	-18.4	-24.3	3.028	12.098	
	full	-36.0	-27.0	-35.7	3.022	12.099	-124 <sup>h</sup>
[Mn <sub>2</sub> O <sub>2</sub> (OAc)(Me <sub>4</sub> dtne)] <sup>3+</sup>	reduced	-33.5	-25.1	-33.2	3.035	12.118	
	full	-37.5	-28.1	-37.2	3.032	12.117	-100 <sup>i</sup>
[Mn <sub>2</sub> O <sub>3</sub> (Me <sub>3</sub> tacn) <sub>2</sub> ] <sup>2+</sup>	reduced	-381.7	-286.2	-375.5	2.963	12.110	
	full	-382.7	-287.0	-376.4	2.958	12.109	-390 <sup>j</sup>

<sup>a</sup>  $J_{AB}$  model defines geometry of compound used in calculations, where "full" denotes whole compound and "reduced" denotes the smaller size model of it. <sup>b</sup>  $J_{AB}$  evaluated using eq 2. <sup>c</sup>  $J_{AB}$  evaluated using eq 3. <sup>d</sup>  $J_{AB}$  evaluated using eq 4. <sup>e</sup>  $J_{AB}$  experimental data taken from ref 23. <sup>f</sup>  $J_{AB}$  experimental data taken from ref 24. <sup>g</sup>  $J_{AB}$  experimental data taken from ref 25. <sup>h</sup>  $J_{AB}$  experimental data taken from ref 26. <sup>i</sup>  $J_{AB}$  experimental data taken from ref 27. <sup>j</sup>  $J_{AB}$  experimental data taken from ref 28. <sup>k</sup> Calculations carried out using B3LYP exchange-correlation functional and Ahlrich's VTZ basis set.

BS-DFT and Heisenberg Hamiltonian states and is thus of minor importance. With this reasoning we advocate the use of medium size basis sets, like Ahlrich's VTZ, in the investigation of magnetic coupling in larger molecular systems. Another practical argument for resorting to basis sets of this kind is that they are more suited for efficient calculations of large molecular systems with linear scaling methods than large basis sets with polarization and diffuse functions with small exponents which often lead to numerical problems in that context. Therefore, based on the discussion above we selected Ahlrich's VTZ basis set for all remaining calculations of the Heisenberg exchange constants in the dinuclear manganese complexes investigated in this paper.

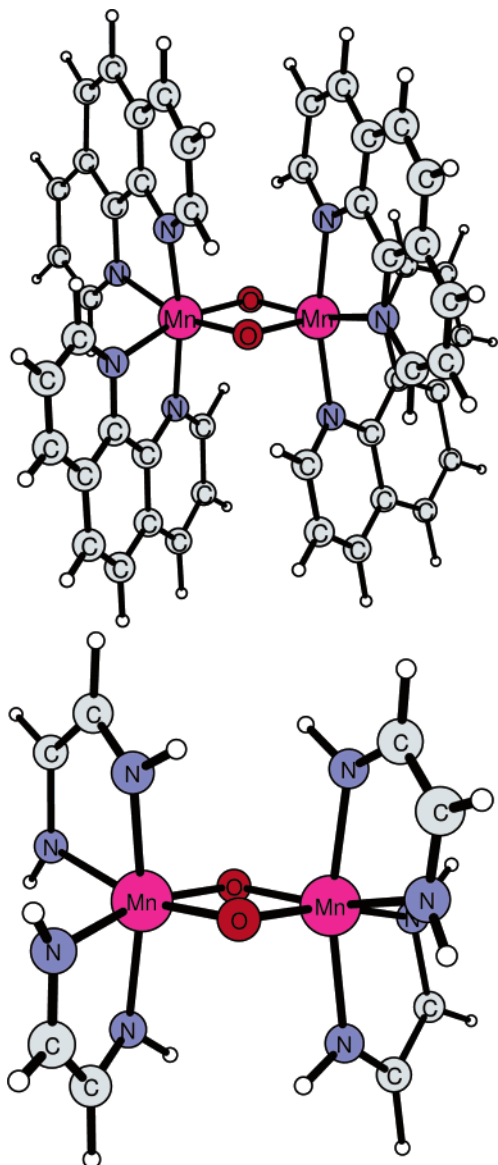
### B. General Trends in Heisenberg Exchange Constants.

The results of the calculations of the Heisenberg exchange constants between Mn<sup>IV</sup> centers in dinuclear manganese complexes along with available experimental data are summarized in Table 3. Comparison of these results indicates that the  $J_{AB}$  computation schemes proposed by L. Noodleman (eq 2) and M. Nishino et. al. (see eq 4) allow for obtaining a good agreement between calculated and experimental  $J_{AB}$  values for [Mn<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub>(bpea)<sub>4</sub>]<sup>2+</sup> (Figure 2), [Mn<sub>2</sub>O<sub>2</sub>(phen)<sub>4</sub>]<sup>4+</sup> (Figure 3), and [Mn<sub>2</sub>O<sub>3</sub>(Me<sub>3</sub>tacn)<sub>2</sub>]<sup>2+</sup> (Figure 6) compounds. The opposite situation is encountered for Mn<sub>2</sub>O<sub>2</sub>(pic)<sub>4</sub> (Figure 1), where the best agreement between calculations and experiment is obtained by employing the  $J_{AB}$  evaluation scheme given by eq 3. For the remaining two compounds with a bis( $\mu$ -oxo)( $\mu$ -carboxylato) core, namely [Mn<sub>2</sub>O<sub>2</sub>(OAc)(bpea)<sub>2</sub>]<sup>3+</sup> (see Figure 4) and [Mn<sub>2</sub>O<sub>2</sub>(OAc)(Me<sub>4</sub>dtne)]<sup>3+</sup> (see Figure 5), all three schemes for calculations of Heisenberg exchange constants perform poorly and severely underestimate the experimental  $J_{AB}$  numbers (in terms of absolute values). In line with previous observations, for positively charged complexes with bis( $\mu$ -oxo) and tris( $\mu$ -oxo) cores we observed a good performance of the  $J_{AB}$  evaluation scheme proposed by L. Noodleman (eq 2) as these compounds feature well localized unpaired electron orbitals on the Mn<sup>IV</sup> centers in these complexes, which is a necessary condition for good performance of this computational scheme. For investigated neutral complexes with bis( $\mu$ -oxo) core, the localization of the unpaired electrons on manganese



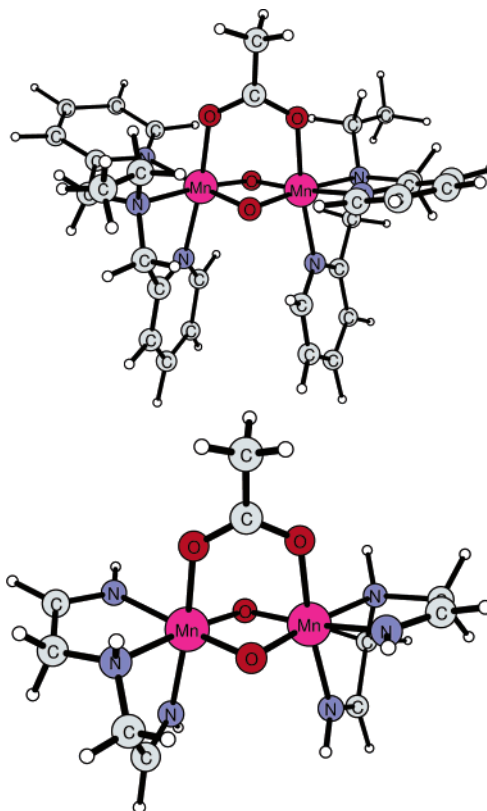
**Figure 2.** [Mn<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub>(bpea)<sub>4</sub>]<sup>2+</sup> compound and the reduced model of this compound.

centers are less pronounced, and consequently the overlap between magnetic orbitals of the Mn<sup>IV</sup> centers is stronger. This in turn leads to good performance of the Heisenberg exchange computation scheme given by eq 3, which has been designed for this particular bonding situation between localized spins. The breakdown of all three  $J_{AB}$  constant schemes observed for manganese complexes with bis( $\mu$ -oxo)-( $\mu$ -carboxylato) core can probably be attributed to delocal-

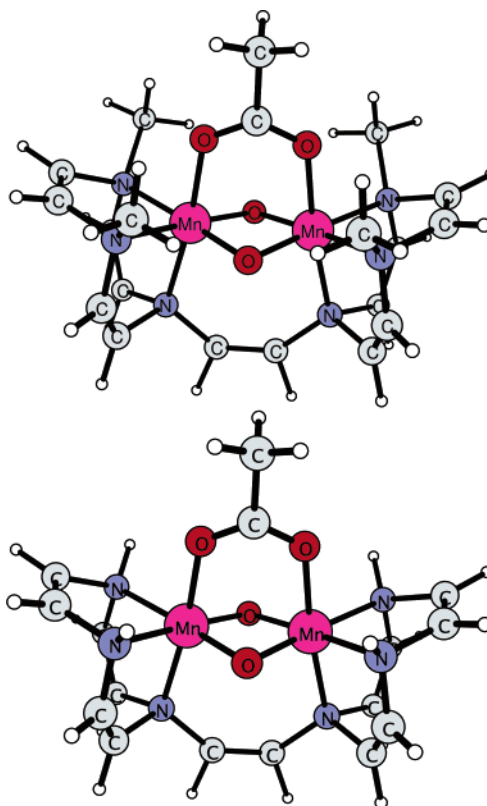


**Figure 3.**  $[\text{Mn}_2\text{O}_2\text{Cl}_2(\text{phen})_4]^{4+}$  compound and the reduced model of this compound.

ization of the unpaired electrons over both  $\text{Mn}^{\text{IV}}$  centers in the high spin state, which is caused by the OAc ligand binding to the manganese centers. Limitations of  $J_{\text{AB}}$  evaluation schemes employed in our calculations are well-known for compounds with a delocalized high spin state, and detailed discussion of this problem can be for example found in ref 14. Finally, we note that the Heisenberg exchange constants evaluated using the scheme of state mapping proposed by M. Nishino et. al. closely follow the results obtained by the Noodleman scheme in agreement with the behavior witnessed in other investigations of  $J_{\text{AB}}$ . Here it is worthwhile also to note that this scheme, according to their authors, should be able to take into account the specifics of the bonding character in the molecule under investigation and therefore hypothetically should lead to results similar to the ones obtained with the third scheme (eq 3) for  $\text{Mn}_2\text{O}_2(\text{pic})_4$ . However, our calculation results presented in Tables 2 and 3 as well as the results of previous calculations by Soda et al. do not support this claim. This discrepancy can most likely be explained by the fact that the total spin angular

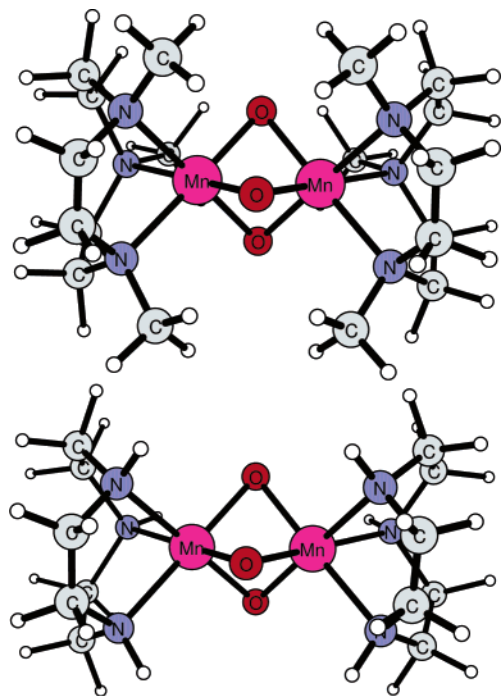


**Figure 4.**  $[\text{Mn}_2\text{O}_2(\text{OAc})(\text{bpea})_2]^{3+}$  compound and the reduced model of this compound.



**Figure 5.**  $[\text{Mn}_2\text{O}_2(\text{OAc})(\text{Me}_4\text{dtne})]^{3+}$  compound and the reduced model of this compound.

momentum value evaluated using Kohn–Sham orbitals is rather inaccurate (a detailed discussion of this topic can be found in ref 20). Therefore, based on these arguments, and



**Figure 6.**  $[\text{Mn}_2\text{O}_3(\text{Me}_3\text{tacn})_2]^{2+}$  compound and the reduced model of this compound.

in our opinion, the use of mapping schemes proposed by Noodleman and by Ruiz are more justified than the one of M. Nishino et al. in connection with BS-DFT calculations. From a quantitative point of view, our numerical results for  $\text{Mn}_2\text{O}_2(\text{pic})_4$ ,  $[\text{Mn}_2\text{O}_2\text{Cl}_2(\text{bpea})_4]^{2+}$ ,  $[\text{Mn}_2\text{O}_2(\text{phen})_4]^{4+}$ , and  $[\text{Mn}_2\text{O}_2(\text{phen})_4]^{4+}$  are in good agreement with experimental data, where the largest deviation is less than  $10\text{ cm}^{-1}$  if one employs the most suitable  $J_{\text{AB}}$  computation scheme for each compound, i.e., eq 2 or eq 3. In the above-described results thus evidence that a reliable mapping scheme between the states obtained with the BS-DFT approach and the Heisenberg Hamiltonian states is a key required for accurate evaluations of  $J_{\text{AB}}$  constants. On the other hand, a selection of suitable mapping schemes for particular molecular systems can by no means be done automatically. It requires detailed information on electron density and orbital localization in order to deduct which of the schemes for the Heisenberg exchange constants will give accurate results and will be in line with the correct picture of the physical interaction in the molecular system.

Apart from the results of the calculations of the Heisenberg exchange constants for full size dinuclear manganese complexes, we also present in Table 3 calculation results for reduced model systems of these compounds. The model systems, which mimic the full size dinuclear manganese compounds, have been designed according to the recipe described in the Computational Details section and are in Table 3 marked as “reduced”. For the  $\text{Mn}^{\text{IV}}-\text{Mn}^{\text{IV}}$  complexes with bis( $\mu$ -oxo) and tris( $\mu$ -oxo) cores, the differences between the Heisenberg exchange constant computed employing the full size compound (denoted in Table 3 as “full”) and its reduced model geometries are small, with the largest deviation not exceeding  $5\text{ cm}^{-1}$ . Furthermore, the effect on  $J_{\text{AB}}$  going from the full scale compound to its model is more pronounced in the  $J_{\text{AB}}$  evaluation schemes proposed by

Noodleman and Nishino et al. This is expected as the denominator in these schemes is smaller than the one in the third case (see eqs 2–4). The differences between the Heisenberg exchange constants obtained using the full scale compound and its model geometries are severely pronounced for the complexes with a bis( $\mu$ -oxo)( $\mu$ -carboxylato) core. The use of the reduced compound model then leads to underestimation of the absolute  $J_{\text{AB}}$  values up to 40%. A behavior of this kind is consistent with the assumed delocalization of the unpaired electron orbitals over both  $\text{Mn}^{\text{IV}}$  centers, since in this case our procedure to build the reduced models leads to larger deviations between electronic structures of the real and the model compounds. Therefore, this finding indirectly supports our claim that the BS-DFT approach fails to predict the Heisenberg exchange constant related to the delocalization of unpaired electron orbitals over both manganese centers. It also follows that for dinuclear manganese complexes with well localized spins the use of smaller model compounds, which mimic the bonding situation of the manganese centers by replacing large ligands with suitable smaller ones, leads to only slight changes in the values of Heisenberg exchange constants. Consequently, one can recommend to employ such model compounds in order to reduce computational cost and to gain insight.

#### IV. Conclusion

This work presents a systematic investigation of the performance of broken symmetry density functional theory for evaluation of Heisenberg exchange constants in dinuclear  $\text{Mn}^{\text{IV}}-\text{Mn}^{\text{IV}}$  compounds. We selected for exploration a number of complexes with three different arrangements of the  $\text{Mn}^{\text{IV}}$  centers, namely bis( $\mu$ -oxo), bis( $\mu$ -oxo)( $\mu$ -carboxylato), and tris( $\mu$ -oxo) cores, to cover different bonding characteristics occurring between these centers and in this way assess the performance of the BS-DFT approach with respect to these characteristics. Apart from investigating the suitability and accuracy of the BS-DFT approach for these manganese complexes we also aimed to design recipes for reliable calculations of Heisenberg exchange constants on molecular systems of this kind.

The results of our investigation emphasize the importance of the mapping between broken symmetry, high spin, states obtained with the unrestricted DFT formalism and states of the Heisenberg exchange constants, which has been observed in earlier works devoted to the evaluation of  $J_{\text{AB}}$  constants with the BS-DFT approach. A selection of an appropriate mapping scheme is found crucial for a reliable evaluation of Heisenberg exchange constants, where the scheme proposed by L. Noodleman<sup>12</sup> is well suited for weak bonding between the  $\text{Mn}^{\text{IV}}$  centers, while the scheme advocated by E. Ruiz<sup>17</sup> based on Noodleman’s work is more acceptable for the opposite situation. However, as we witnessed in the case of compounds with a bis( $\mu$ -oxo)( $\mu$ -carboxylato) core none of the tested  $J_{\text{AB}}$  evaluation schemes is adequate, probably due to delocalization of the unpaired electrons over the two manganese centers. This example indicates that the BS-DFT approach cannot straightforwardly be applied in investigations of magnetic coupling if the unique features of electronic structure of each molecule under investigation



is not carefully considered. Based on the calculation results presented in this paper, we recommend using the Noodleman or Ruiz/Noodleman schemes for computations of Heisenberg exchange constants, while the scheme of Nishino does not seem to be well suited for unrestricted DFT due the general inability of the Kohn–Sham method to evaluate expectation values of the total spin angular momentum operator. Furthermore, we advocate the use of the B3LYP exchange–correlation functional in combination with Ahlrich’s VTZ basis set; this combination indeed allowed an accurate reproduction of experimental  $J_{AB}$  values for most of the investigated compounds.

Another important issue addressed in this paper is the effect of long-range interactions for evaluation of Heisenberg exchange constants. On one hand we showed that it is possible to build reduced model compounds of manganese complexes by substituting large ligands with suitable smaller ones without affecting the magnetic coupling between the  $Mn^{IV}$  centers. The success of this methodology indicates that only the closest environment of the  $Mn^{IV}$  centers have significant effects on their electronic structure due to a localized nature of the unpaired electron orbitals. However, in the case of extended molecular systems the electronic structure of the ligands can be significantly dependent on their surrounding, that also leads to changes in electronic structure of the manganese centers. The design of reliable reduced model compounds is evidently not straightforward in such cases, and one can recommend reduced model compounds only for molecular systems in which each localized spin center has a well distinguished set of ligands. Another aspect related to the evaluation of  $J_{AB}$  constants in large molecular systems is the improper asymptotic behavior of our recommended B3LYP exchange–correlation. To tackle this issue we investigated the performance of the CAMB3LYP functional, which has improved asymptotic behavior of the exchange part, in the evaluation of  $J_{AB}$  constants. The obtained results indicate that before this functional can be used for routine calculations of Heisenberg exchange constants it should be reparametrized in order to reproduce the performance of the B3LYP functional. In the future we plan to investigate new sets of parameters for CAMB3LYP functionals oriented for accurate prediction of  $J_{AB}$  constants as part of our efforts in the theoretical design of single molecular magnets.

**Supporting Information Available:** Computed total energies and spin populations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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