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Ab initio correlation approach to a ferric wheel-like molecular cluster

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Abstract. We present an ab initio study of electronic correlation effects in a molecular cluster derived from the hexanuclear ferric wheel $[LiFe_6(OCH_3)_{12}\text{-}(dbm)_6]PF_6$. The electronic and magnetic properties of this cluster have been studied with all-electron Hartree-Fock, full-potential density functional calculations and multi-reference second-order perturbation theory. For different levels of correlation, a detailed study of the impact of the electronic correlation on the exchange parameter was feasible. As the main result, we found that the influence of the bridge oxygen atoms on the exchange parameter is less intense than the influence of the apical ligand groups, which is due to the geometry of the cluster. With respect to the cluster model approach, the experimental value of the exchange parameter was affirmed.

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1 Introduction

In contemporary condensed-matter physics, the role of molecular magnetism is steadily growing and receives attention from both experimental and theoretical physicists and chemists [1–4]. The most studied and therefore best known molecule in this field is the Mn-12-acetate [5], but the class of the ferric wheels (wheel-shaped iron rings) is becoming an important subject of various studies [6–8].

In the past few years, molecular magnets and some ferric wheels have been treated with ab initio quantum chemical methods like the Hartree-Fock approximation and density functional approaches using several functionals like the local density approximation or hybrid functionals. The usually observed results are that Hartree-Fock theory often strongly underestimates physical properties like the exchange parameter [9–12], while the DFT methods overestimate those values [9,13–15].

This paper will deal with a molecular cluster derived from the hexanuclear ferric wheel $[LiFe_6(OCH_3)_{12}\text{-}(dbm)_6]PF_6$ [9,16]. The previous analysis based on the full molecule [9] showed that one-determinantal Hartree-Fock theory failed to reproduce the observed exchange parameter $J = -21$ K [16]. Density functional calculations, on the other hand, indicated that there is an enormous dependence of the computed exchange parameter on the functional chosen. This problem was already observed earlier for other systems, e.g. [15,17,18]. A possible solution to this discrepancy is to consider the electronic correlation, which is strongly influencing the exchange parameter, by wave function-based methods. This should lead to a more controlled description of the magnetic behavior of the complex, as it was demonstrated for various systems (e.g. [19–27]).

For antiferromagnetic systems like the ferric wheels, the magnetic exchange can be qualitatively described considering the electronic charge transfer between the magnetic centers over a bridging atom or between the magnetic centers and various ligand groups. Within a cluster approach, the electronic charge transfer can be analyzed within a multi-reference second-order perturbation theory scheme (MRPT2) [28]. MRPT2 is very similar to the complete active space second-order perturbation theory (CASPT2) that has been found to give very accurate results for the exchange parameter (see, e.g. [15,23,24]). The MRPT2 method is based on a reference ground state wave function which can be chosen as a multiconfiguration self-consistent field (MCSCF) wave function. This reference wave function is the initial point for treating the electronic correlation perturbationally. In some cases, the occurrence of intruder states can cause convergence problems [23,29], and the level-shift technique proposed by Roos et al. [30] has to be applied.

In this paper, we analyze the electronic properties of the simplified complex displayed in Figure 1. The model

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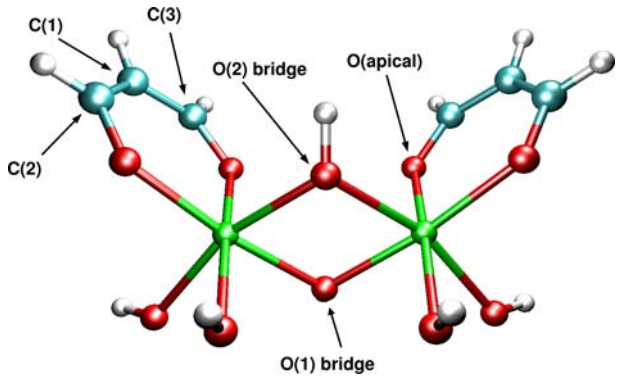

Fig. 1. Geometry of the molecular cluster. The model complex was derived from the full molecule $[LiFe_6(OCH_3)_{12}$-$(dbm)_6]PF_6$ and was slightly modified to achieve $C_s(x)$-symmetry.

is derived from the molecule $[LiFe_6(OCH_3)_{12}$-$(dbm)_6]PF_6$ whose structure has been determined by Abbati et al. [16]. We first apply the Hartree-Fock and a hybrid functional (B3LYP) approach, in order to verify the cluster model which is used to represent a fragment of the full molecule. Then the effect of electronic correlations is studied more detailed, with second order perturbation theory at the MRPT2 level. The influence of the level shift on the MRPT2 results is determined in detail.

2 Method

The geometry of the molecular cluster is based on the measurements of the primal ferric wheel $[LiFe_6(OCH_3)_{12}$-$(dbm)_6]PF_6$ by Abbati et al [16]. From these data, a complex consisting of two iron atoms and some ligands was modeled (see Fig. 1), as this is the maximum what can be treated by MRPT2. The iron atoms are six-fold coordinated and thus have the proper coordination of the Fe ions like in the full molecule. Two point charges of +1 were added at the position of the neighboring iron atoms in order to restore the charge neutrality of the cluster. The C_6H_5 rings were replaced with hydrogen atoms (bonding length 0.93 Å) as well as the methyl groups at the bridge oxygen atoms (0.95 Å). To achieve $C_s(x)$-symmetry which is necessary to keep the MRPT2 calculations tractable, the positions of the atoms were slightly modified. The full geometry is given in Table 1.

For a proper description of the physical properties of the molecular cluster, calculations with the codes CRYSTAL2003 [31,32] and MOLPRO2002 [33] were carried out. Within the scope of the CRYSTAL calculations, we employed the unrestricted Hartree-Fock (UHF) method and the hybrid functional B3LYP (a functional with admixtures, amongst others, of functionals by Becke, Lee, Yang and Parr). Note that the CRYSTAL code can treat systems of any periodicity, so that the molecular cluster was treated as a single molecule, i.e. not as a periodic system. These calculations are of broken symmetry type [34–37], as the space symmetry is lowered. The state is not an eigenfunction of $\mathbf{S^2}$, but only of S_z.

Table 1. Geometrical parameters of the molecular cluster, in Å. The mirror plane is the yz plane.

	x	y	z
Fe	–1.568236	2.716264	0.000000
O(1)	0.000000	1.952334	–1.010690
O(2)	0.000000	3.375149	1.066879
H	0.000000	2.019278	–1.966749
H	0.000000	4.227152	1.505766
O	–1.660933	4.316006	–1.146858
O	–2.906901	3.596739	1.146858
C(3)	–2.381312	5.371681	–1.023420
C(1)	–3.232182	5.601224	0.000000
C(2)	–3.460321	4.748871	1.023420
H	–4.021835	4.973378	1.723433
H	–3.551594	6.475448	0.000000
H	–2.293279	5.970805	–1.723433
O	–2.815456	1.465882	–0.940540
O	–1.442379	1.009753	1.120700
H	–3.525746	1.728168	–1.530737
H	–1.465828	1.108581	2.107450
+1	–2.774296	–0.177610	0.182920

For the needs of a molecular system, we first chose the same basis set as used in reference [9] for the full molecule, which was found to be reliable. Henceforth this basis set is referred as basis set A. In contrast to the code MOLPRO, the possibility of adding point charges is not implemented in the CRYSTAL code. A point charge of +1 can however be achieved by a H atom with a basis function with a very high exponent (100 000 a.u.), which does not allow charge transfer to the H atom and thus acts like a point charge. The idea of the CRYSTAL calculations was to verify that the results did not significantly change when the geometry was modified from the full ferric wheel with six iron atoms to the cluster with two iron atoms. This was first done with basis set A, so that an identical basis set was applied for the full molecule and the fragment.

With the code MOLPRO, calculations at the level of MCSCF and MRPT2 were performed. For these methods, a modified basis set (from now on labeled as basis set B) was used. For iron, a $[8s5p3d]$ [38] basis set was chosen, where a f-exponent of 2.48 was added which was optimized in a preceding calculation. For oxygen, a $[4s3p]$ [39] basis set was chosen where a d-exponent of 0.8 was added. The basis sets for carbon and hydrogen were chosen accordingly to basis set A. Thus, the final basis set B was of the size $[8s5p3d1f]$ (iron), $[3s2p]$ (carbon), $[4s3p1d]$ (oxygen) and $[2s]$ (hydrogen). The enlargement of the basis set for iron and oxygen in basis set B compared to basis set A is a necessary procedure to properly account for the needs of *post* Hartree-Fock calculations, which in contrast to the calculations at the UHF and B3LYP level include electronic excitations and thus require a larger virtual orbital space. To investigate the impact of the enlargement of the basis set on the results, calculations were carried out with MOLPRO using either basis set A or basis set B at the MCSCF level. Despite the slightly different basis sets, no significant changes in the results were observable, and basis set B can be considered as an extension of

Table 2. Total energies ($E_h \equiv$ hartree), the differences in total energies of the ferromagnetic (FM) and the antiferromagnetic (AF) state and exchange parameters J. At the MRPT2 level, all orbitals except the core orbitals were correlated and a level shift of $0.3E_h$ was applied. The core orbitals include the iron 1*s*-, 2*sp*-, 3*sp*-, the oxygen 1*s*- and the carbon 1*s*-orbitals. For comparison, the results for the full molecule obtained from reference [9] are given in the first section of this table.

Basis set	Molecule	Method	FM total energy (E_h)	AF total energy (E_h)	Difference of total energy (mE_h)	J (K)
A	full molecule [9]	UHF	–13295.73287	–13295.73125	–1.62	+7
A	full molecule [9]	B3LYP	–13334.50676	–13334.51409	7.33	–31
A	cluster	UHF	–3507.80720	–3507.80693	–0.27	+7
A	cluster	B3LYP	–3514.95130	–3514.95209	0.79	–20
A	cluster	MCSCF	–3507.90171	–3507.90175	+0.04	–1
B	cluster	MCSCF	–3508.31083	–3508.31085	+0.02	–0.5
B	cluster	MRPT2	–3511.04152	–3511.04209	0.57	–14.4

basis set A for wave function based correlation calculations. Subsequently all MRPT2 calculations were performed with the enlarged basis set B.

The properties of the ferromagnetic (FM) state (all spins parallel, total spin 10 μ_B) and of the antiferromagnetic (AF) state (spins alternating up and down, total spin 0) were computed with each method. To obtain the net charge, a Mulliken population analysis was performed at all levels of theory.

3 Results

Table 2 summarizes the results for the total energies of the ferromagnetic and the antiferromagnetic ground states, their differences and the magnetic exchange parameter J for the molecular cluster.

Depending on the ansatz for the ground state wave functions the magnetic coupling in the molecular cluster is derived from fits to an Ising or Heisenberg model.

The analysis in terms of a Heisenberg model

$$H_H = -J \cdot \mathbf{S}_1 \cdot \mathbf{S}_2$$

with

$$\mathbf{S}_1 \cdot \mathbf{S}_2 = \frac{(\mathbf{S}_1 + \mathbf{S}_2)^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2}{2}$$

is appropriate when the approximate ground state is an eigenfunction of $(\mathbf{S}_1 + \mathbf{S}_2) = \mathbf{S}^2$. This is the case for MCSCF and MRPT2. The exchange parameter is obtained from the difference between the ferromagnetic ($S = 5$) and the antiferromagnetic alignments which is given by

$$\begin{aligned} E_{H,tot}^{FM} - E_{H,tot}^{AF} &= -J(\mathbf{S}_1 \cdot \mathbf{S}_2{}^{FM} - \mathbf{S}_1 \cdot \mathbf{S}_2{}^{AF}) \\ &= -15 \cdot J \end{aligned}$$

for quantum spins. The trial wave functions used for UHF and B3LYP calculations usually lack invariance under spin rotation. Since they are constructed as eigenfunctions of the spin projection S_z the energy gain from magnetic correlations is analyzed in terms of the Ising model:

$$H_I = -J \cdot S_{1z} \cdot S_{2z}.$$

The corresponding energy difference between ferromagnetic ($S_{1z} = S_{2z}$) and antiferromagnetic ($S_{1z} = -S_{2z}$) alignment is given by

$$E_{I,tot}^{FM} - E_{I,tot}^{AF} = -2 \cdot J \cdot S_{1z}^2 = -12.5 \cdot J$$

which agrees with the Heisenberg value in the classical limit $S_i \to \infty$.

The experimental value for the exchange parameter of the primal ferric wheel was found to be $J = -21$ K [16]. Thus for all results in this dimension the difference in the exchange parameter between the Ising and the Heisenberg model is about a few Kelvin; with respect to this actuality we consider the Ising model approach as a valid description of the magnetic coupling in the cluster.

We first compare the results of one-determinantal methods for the model cluster and the full molecule. In a second step, we focus on the influence of correlations. In our previous studies of the full molecule [9], we determined an exchange parameter of $J = +7$ K at the UHF level and $J = -31$ K at the B3LYP level.

The UHF result for the full molecule is perfectly reproduced by the cluster yielding $J = +7$ K. A good agreement between cluster and periodic system at the Hartree-Fock level was already observed in earlier studies, e.g. NiO [15], $KNiF_3$ and K_2NiF_4 [26] or Ca_2CuO_3 and Sr_2CuO_3 [27]. At the B3LYP level, the computed exchange parameter is $J = -20$ K. The agreement with the value for the full molecule is thus not as perfect as at the UHF level, but still reasonable (a similar deviation was found, for example, when comparing B3LYP exchange couplings for K_2CuF_4 from cluster [40] and periodic systems [18]; it should be mentioned that there seem to be fewer comparisons between cluster and periodic calculations at the B3LYP level). In addition, the Mulliken population analysis (Tabs. 3 and 4) demonstrates that the charge is practically identical at the various levels: B3LYP populations for the cluster and the full molecule [9] are virtually identical, and similarly UHF populations agree very well. In addition, the MCSCF charge agrees with the UHF charge. As a whole, we feel that the cluster model can be considered to be physically valid.

Table 3. Charge at various sites, in $|e|$. Note that the charge is virtually identical for the ferromagnetic and the antiferromagnetic state. For comparison, the results for the full molecule obtained from reference [9] are given in the first section of this table.

Basis set	Molecule	Method	O (apical)	O (bridge)	C(1)	C(2)/C(3)
A	full molecule [9]	UHF	–1.10	–1.18	–0.22	0.82
A	full molecule [9]	B3LYP	–0.86	–0.88	–0.11	0.62
A	cluster	UHF	–1.03	–1.13	–0.17	0.77
A	cluster	B3LYP	–0.80	–0.89	+0.01	0.60
A	cluster	MCSCF	–1.03	–1.14	–0.17	0.77
B	cluster	MCSCF	–1.15	–1.22	–0.13	0.85

Table 4. Mulliken charge of Fe, in $|e|$. Note that the charge is virtually identical for the ferromagnetic and the antiferromagnetic state. The f-population of the iron atoms is negligible. The core orbitals include the iron 1s-, 2sp-, 3sp-, the oxygen 1s- and the carbon 1s-orbitals. For comparison, the results for the full molecule obtained from reference [9] are given in the first section of this table.

Basis set	Molecule	Method	net charge	s	p	d
A	full molecule [9]	UHF	2.16	6.28	12.28	5.29
A	full molecule [9]	B3LYP	1.56	6.38	12.37	5.69
A	cluster	UHF	2.13	6.29	12.30	5.28
A	cluster	B3LYP	1.55	6.39	12.40	5.66
A	cluster	MCSCF	2.14	6.29	12.30	5.27
B	cluster	MCSCF	2.26	6.37	12.07	5.31

Concerning the individual charge, we note that as a confirmation of the former findings [9], the net charge of iron is between 1.55 (B3LYP) and 2.26 (MCSCF) and thus far away from the formal charge of +3 of the primal ferric wheel [16]. The charge is thus more delocalized at the B3LYP level, which can also be seen in the spin-density plot in Figure 2. At the B3LYP level the local magnetic moment is distributed over the cluster to a certain extent, while the level of delocalization is apparently smaller at the UHF level.

To serve as a starting point for the MRPT2 calculations, a MCSCF calculation was performed. The active space is made of the iron d-orbitals. The obtained value for the exchange parameter is $J = -0.5$ K. Compared to UHF, a MCSCF wave function is a better approximation to the ground state than a single determinant, which is the reason for the slight change of the exchange parameter from UHF to MCSCF towards the experimental value. A direct comparison between the calculations with the code CRYSTAL and MOLPRO is only approximatively possible, and only in case of high spin. First, the MOLPRO energy must be corrected for the fact that MOLPRO does not take the interaction of point charges into account when computing the total energy: when this is done, then the MCSCF energy with MOLPRO is –3507.90171+1/(2·2.774296/0.5291772) E_h = −3507.80634 E_h. The remaining difference to the energy computed with CRYSTAL (–3507.80720 E_h) is because the MOLPRO MCSCF wave function has identical orbitals for up and down spin, whereas the CRYSTAL UHF wave function has not; and because the codes use different screening parameters for the selection of the integrals.

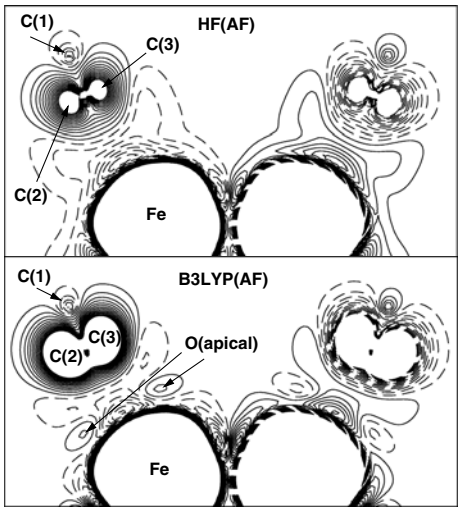

Fig. 2. Spin densities of the molecular cluster for the antiferromagnetic (AF) state at the UHF level (upper panel) and the B3LYP level (lower panel). Both graphs show the spin density in the plane given by the planar arrangement of the six iron atoms of the primal ferric wheel. For all figures, the contour lines range from –0.0004 to 0.0005 in steps of 0.000035 electrons/(a.u.)^3. Full lines indicate positive spin density and dashed lines indicate negative spin density.

Within the MCSCF scheme, the wave function is built from all Slater determinants representing charge transfer configurations between the orbitals in the active space, and the orbitals are optimized. The MRPT2 calculation is based on the MCSCF orbitals. The reference configurations are made of all determinants in the active space

Table 5. Total energies ($E_h \equiv$ hartree), the differences in total energies for the ferromagnetic (FM) and the antiferromagnetic (AF) state and exchange parameters J for different level shifts at the MRPT2 level for the molecular cluster. All orbitals except the core orbitals were correlated. The energies were corrected for the level shift. The core orbitals include the iron 1*s*-, 2*sp*-, 3*sp*-, the oxygen 1*s*- and the carbon 1*s*-orbitals. Basis set B was used.

level shift	FM total energy (E_h)	AF total energy (E_h)	difference of total energy (mE_h)	J (K)
0.20	–3511.05498	–3511.05563	0.65	–16.4
0.21	–3511.05375	–3511.05439	0.64	–16.1
0.22	–3511.05251	–3511.05314	0.63	–15.9
0.23	–3511.05124	–3511.05185	0.62	–15.6
0.24	–3511.04993	–3511.05054	0.61	–15.4
0.25	–3511.04860	–3511.04921	0.60	–15.2
0.26	–3511.04724	–3511.04784	0.59	–15.0
0.27	–3511.04586	–3511.04644	0.59	–14.8
0.28	–3511.04444	–3511.04502	0.58	–14.6
0.30	–3511.04152	–3511.04209	0.57	–14.4

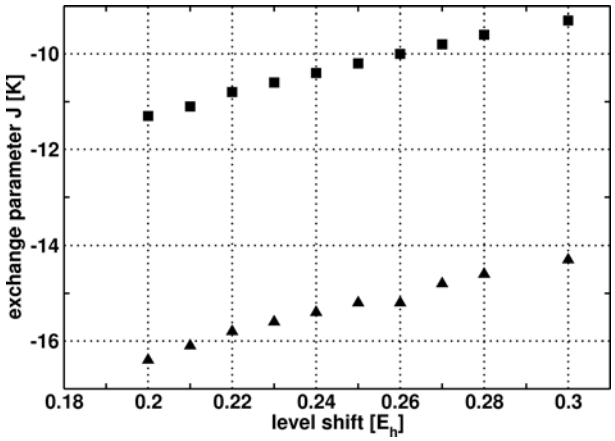

Fig. 3. Magnetic exchange parameter of the molecular cluster for different values of the level shift. The upper graph (squares) represents the uncorrected values, the lower graph (triangles) the corrected values (correction performed according to Roos et al. [30]).

(i.e. the iron *d*-orbitals), and subsequently second-order perturbation theory is applied. The level of correlation can additionally be varied by keeping different sets of core orbitals frozen, as described later on in this section.

While performing the MRPT2 calculations, intruder state problems appeared which are due to a near degeneracy of the ground state. One possibility to remedy those intruder states is to increase the active space, which is definitely not possible for the considered molecular cluster, or, following the proposal by Roos et al. [30], to implement a level shift to the MRPT2 calculations. By means of this technique, a level shift parameter is added to the zeroth order Hamiltonian to avoid those intruder states. Thus, the resulting exchange parameters are influenced by the level shift (c.f. upper graph (squares) in Fig. 3, corresponding to Eq. (6) in [30]). To approximatively correct for this effect, a correction to the second order energies can be applied afterwards, as was suggested in [30], equation (7). The corresponding data are displayed in the lower graph (triangles) in Figure 3. The quantitative dependence of the exchange parameter on the level shift is shown in Table 5. For level shift values smaller than 0.17 E_h ($E_h \equiv$ hartree), the MRPT2 results became unstable. The level shift interval (for the corrected values of the exchange parameter) from $0.20E_h$ to $0.30E_h$ leads to an exchange parameter of $J = 15 \pm 2$ K, which is a reasonably stable result. For other systems, similar results were obtained, see e.g. de Graaf et al. [23] and Hozoi et al. [29].

The results for the MRPT2 calculations are given in Table 6. Considering the magnetic iron *d*-orbitals as the only orbitals to be correlated led to an exchange parameter of $J = -6.4$ K. The included configurations are thus the charge transfer configurations between the occupied iron *d*-orbitals and the excitations to the virtual orbitals (for the high-spin state, only excitations to the virtual orbitals are possible). Therefore, accounting for those charge transfer configurations explains the change of the exchange parameter from the MCSCF level to the MRPT2 level (–0.5 K (MCSCF) → –6.4 K (MRPT2)). Adding the 2*sp*-orbitals of one of the bridging oxygens to the orbitals to be correlated gave rise to an exchange parameter of $J = -4.9$ K (O(1)) and $J = -7.4$ K (O(2)). Taking both these 2*sp*-orbitals into account caused only an exchange parameter of $J = -5.8$ K, i.e. the effect of correlating both orbital groups is approximatively additive.

Correlating all oxygen atoms results in a value of –13.7 K. A further increase of the orbitals to be correlated (up to a maximum where only the iron 1*s*-, 2*sp*-, 3*sp*-, the oxygen 1*s*- and the carbon 1*s*-orbitals are kept frozen) led to a exchange parameter of $J = -14.4$ K, which is in the range of the experimental value. With respect to the geometry of the cluster, the influence of those apical ligand groups to the exchange parameter is the dominant one, whereas the oxygen bridge atoms have only little impact on the exchange parameter. As a conclusion, for this particular ferric wheel under consideration the metal ↔ ligand charge transfer configurations dominate the metal ↔ metal charge transfer configurations over the bridging oxygen atoms, which is basically the result of the ordering of the magnetic orbitals according to the Goodenough-Kanamori rules [41]: essentially, the Fe–O–Fe angle is nearly right-angled and thus the coupling is small.

Table 6. Total energies ($E_h \equiv$ hartree), the differences in total energies for the ferromagnetic (FM) and the antiferromagnetic (AF) state and exchange parameters J for different levels of correlation at the MRPT2 level for the molecular cluster. A level shift of $0.3E_h$ was applied. The energies were corrected for the level shift. The core orbitals include the iron 1*s*-, 2*sp*-, 3*sp*-, the oxygen 1*s*- and the carbon 1*s*-orbitals. Basis set B was used.

	Level of correlation	FM total energy (E_h)	AF total energy (E_h)	Difference of total energy (mE_h)	J (K)
(I)	iron *d*-orbitals	–3508.43623	–3508.43649	0.26	–6.4
(II)	(I)+2*sp*-orbitals of O(1)	–3508.63134	–3508.63154	0.19	–4.9
(III)	(I)+2*sp*-orbitals of O(2)	–3508.64415	–3508.64444	0.29	–7.4
(IV)	(I)+2*sp*-orbitals of O(1),O(2)	–3508.84371	–3508.84394	0.23	–5.8
(V)	(I)+all oxygen orbitals	–3510.58726	–3510.58781	0.54	–13.7
(VI)	all orbitals except core	–3511.04152	–3511.04209	0.57	–14.4

In the experiments, when comparing various ferric wheels, an approximatively linear relationship between the Fe–O–Fe angle and the value of the exchange coupling was observed [8] and confirmed [42]. This indicates that this angle is crucial for the strength of the coupling (as long as the Fe–Fe distance is approximatively constant, otherwise this distance may also have an impact). This is not in contradiction to the findings here: essentially, the strength and the nature of the coupling (ferro- or antiferromagnetic) is strongly influenced by this angle, but still, to compute the interaction properly, the ligands must be included in the correlation treatment. This was demonstrated, for example, in [24] (Fig. 2): when the correlation treatment is not sufficient, the exchange couplings come out too small; but still, the dependence on the angle is correct. Even more striking were earlier calculations where the ligands were crucial to obtain reasonable values for the exchange couplings, e.g. for $KNiF_3$ and K_2NiF_4 [26] or NiO [43].

4 Conclusion

Wave function-based correlation methods were applied to a molecular cluster derived from the hexanuclear ferric wheel $[LiFe_6(OCH_3)_{12}\text{-}(dbm)_6]PF_6$ [16]. The validity of the molecular cluster containing two iron atoms was tested by means of a one-determinantal approach with respect to the formerly calculated results for the full molecule [9] for the exchange parameter of the primal ferric wheel. In addition, at the UHF and B3LYP level, the spin densities and the electronic population, at the MCSCF level the electronic population were calculated. The population analysis supported the validity of the cluster model approach.

The best result for the exchange coupling parameter J was obtained at the MRPT2 level ($J = 15 \pm 2$ K). The influence of intruder state problems on the exchange parameter was explicitly investigated, and applying the level shift technique [30] was found to lead to stable results. MRPT2 thus gives a more controlled approach to the importance of electronic correlations for exchange couplings, whereas the density functional results depend strongly on the functional chosen. Also, the impact of certain atom groups on the exchange parameter was determined at the MRPT2 level. Correlation of the electrons of the bridging oxygen atoms was of minor importance for the coupling strength. A strong enhancement of the computed exchange coupling was however observed by additionally correlating the electrons of the apical oxygen atoms.

Most of the calculations were performed at the compute-server *cfgauss* (Compaq ES 45) of the data processing center of the TU Braunschweig. The geometry plot of the molecular cluster was performed with VMD [44].

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