两个典型氧桥三核铁(Ⅲ)配合物[$Fe_3O(O_2CCH_2OC_6H_5)_6(3H_2O)$]和[$Fe_3O(TIEO)_2(O_2CPh)_2Cl_3$]的局域自旋和磁性质的理论探讨

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摘要:用从头算波函数(UHF 或 UDFT 波函数)代替 ZILSH 方法中的半经验波函数得到了 ABLSH 方法,接着用该方法研究了两个典型氧桥三核铁(Ⅲ)配合物[$Fe_3O(O_2CCH_2OC_6H_5)_6(3H_2O)$]和[$Fe_3O(TIEO)_2(O_2CPh)_2Cl_3$]的局域自旋和磁性质。通过计算得到的局域自旋结果和前人的具有可比性,同时所得的磁交换耦合常数和实验值很吻合。该方法可作为研究海森堡型磁性系统(HM)的新工具。

关键词:局域自旋; Fe_3O; ZILSH; 对称性破缺
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A Theoretical Examination on the Local Spins and Magnetic Properties of Two Typical Oxo-bridged Trinuclear Iron(Ⅲ) Complexes [$Fe_3O(O_2CCH_2OC_6H_5)_6(3H_2O)$] and [$Fe_3O(TIEO)_2(O_2CPh)_2Cl_3$]

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Abstract: The local spin and magnetic properties of two typical oxo-bridged trinuclear iron(Ⅲ) complexes [$Fe_3O(O_2CCH_2OC_6H_5)_6(3H_2O)$] (complex **1**) and [$Fe_3O(TIEO)_2(O_2CPh)_2Cl_3$] (complex **2**) were examined based on the ABLSH method, which just replaces the semiempirical wave functions of the ZILSH method with ab initio ones (UHF or UDFT wave functions). The calculated local spin results are comparable to previous ones and the obtained pariwise exchange coupling constants are in well agreement with experiments. This method can be a new implement for the studies on the magnetic systems with Heisenberg model (HM).

Key words: local spin; Fe_3O; ZILSH; broken symmetry

0 Introduction

Magnetic materials have been extensively applied in a great diversity of fields, such as magnetic mechanism, electromagnetic shielding, and acoustic implements[1]. Recently, the molecule-based magnets of this kind of materials, which have shown potential use in molecule-level computing device, have attracted more

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and more attention from chemists, physicists and material scientists [2]. In the past several decades, a great number of polynuclear metal complexes have been prepared and characterized in the labs of universities and research institutes to obtain building blocks for molecule-based magnetic materials[3], representing a big stride towards great achievement in this field. These complexes generally contain several irons or manganeses which are bridged by oxygens and show ferromagnetic or antiferromagnetic behavior. Since this kind of complexes are plentiful, we can't concern all of them in this single study. Therefore, here we are only interested in those containing the Fe_3O building units[3a,3h].

For most trinuclear iron(Ⅲ) complexes containing the Fe_3O building units, three irons form either equilateral (Fig.1 (a)) or isosceles (Fig.1 (b)) triangle, and the pairwise magnetic exchange interactions obey $J_{12} \approx J_{13} \approx J_{23}$ and $J_{12} \neq J_{13} \approx J_{23}$, respectively. The clusters consisting of equilateral Fe_3O units are generally spin frustration systems and have a low spin ground state with S=1/2. But those consisting of isosceles Fe_3O units have either S=5/2 or S=3/2 ground state depending on the ratio of J_{12} to J_{13}[3a].

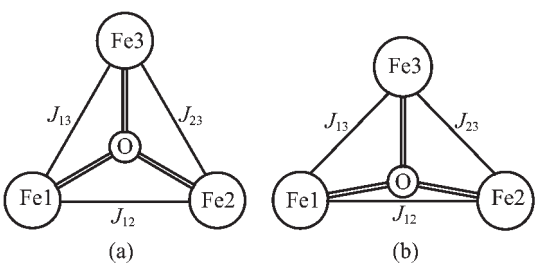


Fig.1 Possible structures of Fe_3O building units: (a) equilateral; (b) isosceles

The exchange constants of polynuclear transistion complexes can be experimentally determined by fitting to the variable-temperature susceptibility data. Alternatively, they also can be theoretically calculated by Noodleman broken symmetry approach[4] that have been extensively applied to a large number of magnetic systems[5]. However, while for larger polynuclear clusters with low symmetries Noodleman approach might not be quite as effective as for those with high symmetries.

Davidson and Clark have recently proposed the local spin theory[6] which can be applied to calculating the local spin expectation values and has been successfully applied to various magnetic systems [6,7]. Furthermore, the local spin quantity $\langle S_A \cdot S_B \rangle$ obtained by this method can be used for computing the exchange coupling constant [6d], which can scales the J obtained by Noodleman approach that uses ideal $\langle S_A \cdot S_B \rangle$. As the ab initio calculations are rather a time-consuming job for even larger complexes, O'Brien and Davidson then extended the local spin formalism to semiempirical single determinant wave functions and proposed the so-called ZILSH method [8], which is the combination of Zindo semiempirical method, Davidson's local spin formalism, and Heisenberg spin model (HSM). They have applied this new method to the complex containing from 2 to 6 high spin iron(Ⅲ) ions and the obtained exchange constants are in well agreement with experiments [8]. This method is promising since it involves less computational costs.

In this research, we replaced the semiempirical wave function of the ZILSH method with ab initio one for two reasons: One is that we can't perform the semiempirical calculations as O'Brien has done in ref.[8] while the ZINDO program is unavailable; The other is that although the ab inito calculations on large complexes like title ones are too difficult to perform, they become feasible if we use the reduced models to approximate them. This modified method is then named as ABLSH. It should be noted that it never be a fresh one for Davidson has mentioned it in ref.[6d]. However, since Davidson has not referred to it as any name, it is necessary to designate it to distinguish it from the ZILSH method. Davidson has used it for obtaining the magnetic coupling constants of the model magnets[6d]. To better understand this method, we would apply it to two typical experimental complexes $[Fe_3O(O_2CCH_2OC_6H_5)_6(3H_2O)]$[3h] (equilateral) and $[Fe_3O(TIEO)_2(O_2CPh)_2Cl_3]$[3a] (isosceles) below.

1 Computational methods

1.1 Davidson's local spin formalism

Davidson's local spin formalism can be summa-

rized as following matrices algebra (using Löwdin projector[9])

$$\rho^T = \rho^\alpha + \rho^\beta,\ \rho^\mu = \rho^\alpha - \rho^\beta \tag{1}$$

$$m_A = \langle S_{zA} \rangle = \frac{1}{2} \sum_{\mu \in A} (R^{1/2} \rho^\mu R^{1/2})_{\mu\mu} \tag{2}$$

$$B_{AB} = 2 \times \sum_{\mu \in A, \nu \in B} [(R^{1/2} \rho^\alpha R^{1/2})_{\mu\nu} (R^{1/2} \rho^\alpha R^{1/2})_{\nu\mu} + (R^{1/2} \rho^\beta R^{1/2})_{\mu\nu} (R^{1/2} \rho^\beta R^{1/2})_{\nu\mu}] \tag{3}$$

$$U_{AB} = \sum_{\mu \in A, \nu \in B} (R^{1/2} \rho^\mu R^{1/2})_{\mu\nu} (R^{1/2} \rho^\mu R^{1/2})_{\nu\mu} \tag{4}$$

$$F_A = \sum_{\mu,\nu \in A} [(R^{1/2} \rho^\mu R^{1/2})_{\mu\nu} (R^{1/2} \rho^\mu R^{1/2})_{\nu\mu}] \tag{5}$$

$$\langle S_A \cdot S_B \rangle = -\frac{3}{8} B_{AB} + m_A m_B + \frac{1}{2} U_{AB} \tag{6}$$

$$\langle S_A^2 \rangle = \frac{3}{8} \sum_{A \neq B} B_{AB} + m_A{}^2 + \frac{1}{2} F_A \tag{7}$$

Here, ρ^α, ρ^β, ρ^T, and ρ^μ is the α, β, total, and spin density matrices under orthogonal basis sets on each center, respectively. R is the block-diagonal overlap matrix and its square root $R^{1/2}$ can be calculated by

$$R^{1/2} = (1+R-1)^{1/2} = (1+X)^{1/2} = 1 + \frac{1}{2}X - \frac{1}{8}X^2 + \frac{1}{16}X^3 - \frac{1}{128}X^4 + \cdots + (-1)^{n+1} \cdot \frac{(2n-3)!!}{2^n \cdot n!} X^n \ (n \geqslant 2) \tag{8}$$

The m_A, F_A, and $\langle S_A^2 \rangle$ is the expected z-component of spin, free valence and S_A^2 localized to center A, respectively, B_{AB} is the bond order defined by Mayer[10], and $\langle S_A \cdot S_B \rangle$ is the expectation value of the operator $S_A \cdot S_B$, which is involved in the HSM and reflects the magnetic coupling between A and B. More details about these parameters can be seen from refs.[6].

1.2 ABLSH method and ZILSH method

The energies of the spin states of molecules with multiple radical centers or fragments have been described by the Heisenberg spin Hamiltonian (HSH).

$$\hat{H} = -\sum_{A<B} 2J_{AB} S_A \cdot S_B \tag{9}$$

or

$$\hat{H} = -\sum_{A<B} J'_{AB} S_A \cdot S_B \tag{10}$$

Here, A, B, ⋯ are radical centers, S_A is the spin assumed to be localized to the center (or fragment), and J_{AB} or J'_{AB} is the so-called Heisenberg coupling constant. Apparently, J_{AB} is a half of J'_{AB}. It should be noted that one can use J_{AB} or J'_{AB} at will. But, if one wants to make comparison between one′s results and others, it must be kept in mind that whether the same kind of coupling constant has been used. In this study, we use J_{AB} to describe all the pairwise magnetic exchange interactions.

Davidson have recently defined the energies of the spin states of multiple radical center systems for a given wave function as follows, based on the HSH and his local spin formalism[6d].

$$^M E_X = E_0 - 2 \sum_{A<B} J_{AB}^M \langle S_A \cdot S_B \rangle_X \tag{11}$$

Here, M and X represents the total spin z-component and the method respectively, E_0 is the zeroth-order energy, and $\langle S_A \cdot S_B \rangle$ is the expectation value which can be computed from eq.**6**.

A complex with N_m metals has $1/2N_m$ (N_m-1) exchange constants, plus the spin independent term E_0. There are thus $1/2N_m(N_m-1)+1$ parameters to be determined. Therefore, $1/2N_m(N_m-1)+1$ linear equations having the same form with eq.**11** are needed to solve these unknowns. For example, for the title complexes containing three iron ions, there are four parameters including three exchange constants (J_{12}, J_{13} and J_{23}) and E_0 to be determined. This kind of equations can be obtained by successively "flipping the spin" of the various metals in different ways. For a complex with N_m metals (assuming all the d electrons of each metal are unpaired and spin up or spin down simultaneously), there are 2^{N_m-1} unique ways of "flipping the spins", which is always larger or equal to $1/2N_m(N_m-1)+1$. Therefore, this method is always theoretically feasible independent of the number of the metals, and it is named as ZILSH if the semiempirical wave function is used, or ABLSH if ab initio one is used.

1.3 Basis sets and wave functions

Basis set LANL2DZ was used for all atoms and LANL2 pseudopotential was used for iron. The spin-unrestricted Hartree-Fock (UHF) wave functions and spin-polarized density functional (UB3LYP) to be used

to described various "spin flippings" were obtained by MELD program[(1)].

All local spin results were computed by eqs.**1**~**8** using our own program, and the pairwise exchange constants were obtained by ABLSH method.

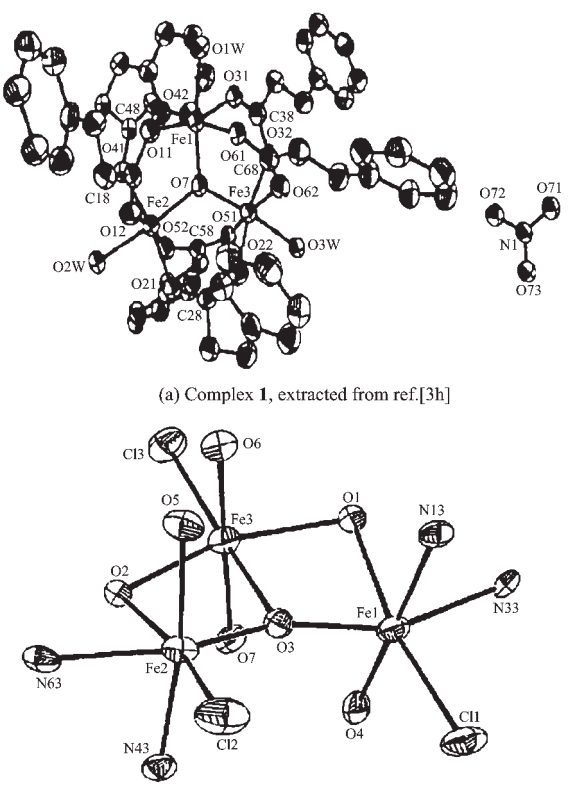
2 Results and discussion

2.1 Experimental magnetic properties of complexes 1 and 2 and their reduced models used in the calculations

The complex $[Fe_3O(O_2CCH_2OC_6H_5)_6(3H_2O)]$ (**1**) prepared by Yang et al.[3h] is a novel 2D supermolecular network formed by nearly equilateral Fe_3O building units through three hydrogen bonds (Fig.2 (a)). Each iron(Ⅲ) ion is octahedrally coordinated by six oxygen atoms of which there is a central one. The measured magnetic susceptibility data showed antiferromagnetic interactions between each pair of irons, and the fitting results gave $J_{12}\approx J_{13}\approx J_{23}\approx -59$ cm^{-1}. It is a spin frustration system and has the spin ground state with S=1/2.

The complex $[Fe_3O(TIEO)_2(O_2CPh)_2Cl_3]$ (**2**)[3a] consists of nearly isosceles Fe_3O building units (Fig.2(b)) and the iron(Ⅲ) ions are also octahedrally coordinated by ligands. $TIEO^-$ is the deprotonated anion of 1,1,2-tri(1-methylimidazole-2-yl) ethanol and severs as a tridentate ligand. This complex is somewhat unusual since most of complex of this family have equilateral Fe_3O units. The magnetic susceptibility studies showed $J_{12}\approx -55$ cm^{-1} and $J_{13}\approx J_{23}\approx -8$ cm^{-1} ($|J_{13}/J_{12}|\approx 6.875$). From the calculation of ground state energy as a function of the ratio J_{12}/J_{13} which predict the ground state to be S=5/2 for $|J_{12}/J_{13}|\geqslant 3.5$ indicates this complex should have a ground state with S=5/2[3a]. This was also confirmed by Mössbauer spectroscopy and this situation may be compared to the linear case: Fe1-Fe2-Fe3.

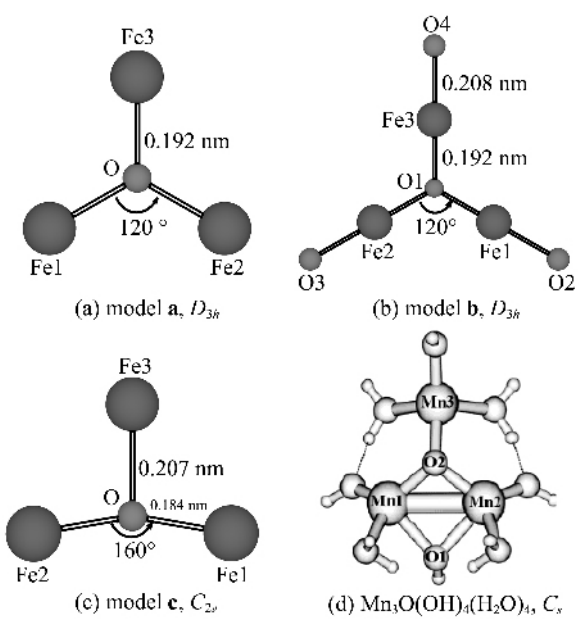
Since the *ab inito* calculations on the unit cells are difficult to perform, their reduced models are exceedingly desirable. This paper presented three reduced models **a**, **b**, and **c** (Fig.3) for approximation, of which **a** and **b** is for **1** and **c** is for **2**. **a** and **c** are the $[Fe_3O]^{7+}$ cations which are just directly extracted from respective crystal structure (Table 1) and were then averaged to D_{3h} and C_{2v} symmetry, respectively. **b** is the $[Fe_3O_4]^+$ cation with D_{3h} symmetry obtained by attaching a terminal oxygen to each iron of **a**. The Fe-O (terminal) bond lengths of b were chosen to be the ex-



(a) Complex **1**, extracted from ref.[3h]

(b) Complex **2**, extracted from ref.[3a]

Fig.2 Partial structures of complex **1** (a) and complex **2** (b)



(a) model **a**, D_{3h} (b) model **b**, D_{3h}

(c) model **c**, C_{2v} (d) $Mn_3O(OH)_4(H_2O)_4$, C_s

Fig.3 Geometrics and symmetries of models **a**, **b**, **c**, and model magnet $Mn_3O(OH)_4(H_2O)_4$

(1) MELD Codes were written by McMrchie L E, Elbert S T, Langhoff S R and Davidson E R, then were revised by Feller D and Rawlings D.

perimental value of 0.208 nm.

Table 1　Bond lengths (nm) and angles (°) of Fe_3O building units of complexes 1 and 2

1		2	
Fe1-O	0.198	Fe1-O	0.186
Fe2-O	0.191	Fe2-O	0.187
Fe3-O	0.188	Fe3-O	0.207
Fe1-O-Fe2	120.3	Fe1-O-Fe2	159.1
Fe1-O-Fe3	118.8	Fe1-O-Fe3	100.3
Fe2-O-Fe3	120.8	Fe2-O-Fe3	100.5

2.2　Local spin results of a~c

For a trinuclear high spin iron(Ⅲ) complex, there are one highest spin state (M=15/2, M is the total spin z-component. This state can be denoted by ↑↑↑ and every arrow represents five electrons spin up or spin down simultaneously) and three unique spin-broken states (M=5/2 and denoted by ↓↑↑, ↑↓↑ and ↑↑↓, respectively). The number of unique spin-broken states, however, will be reduced to one if the complex has D_{3h} symmetry, or two if C_{2v} symmetry. All these states can be approximately described by single determinant wave functions from which their local spin quantities m_A, $\langle S_A^2 \rangle$, $\langle S_A \cdot S_B \rangle$, and the total spin expectation value $\langle S^2 \rangle$ can also be calculated. These results were shown in Tables 2 and 3. In addition, the previous results of complex **1** and those of its analog $Mn_3O(OH)_4(H_2O)_4$[6d] (Fig.3(d)) were also given in Table 4 for comparison. It is noteworthy that some of the local spin results associated to the oxygen atoms have been omitted for clarity.

According to the idealized HSM, the nominal local spin values m_A, $\langle S_A^2 \rangle$, and $\langle S_A \cdot S_B \rangle$ for the com-

Table 2　Local spin expectation values and $\langle S^2 \rangle$ computed for various z-components of a and b by UB3LYP

	a		b	
z-components	M=15/2 (↑ ↑ ↑)	M=5/2 (↑ ↑ ↓)	M=15/2 (↑ ↑ ↑)	M=5/2 (↑ ↑ ↓)
$\langle S_{Fe1}^2 \rangle$, M_{Fe1}	8.42(8.96), 2.37(2.46)	8.34(8.95), 2.36(2.46)	6.23(6.80), 1.86(1.98)	6.30(6.75), 1.86(1.96)
$\langle S_{Fe2}^2 \rangle$, M_{Fe2}	8.42(8.96), 2.37(2.46)	8.34(8.95), 2.36(2.46)	6.23(6.80), 1.86(1.98)	6.07(6.75), 1.81(1.96)
$\langle S_{Fe3}^2 \rangle$, M_{Fe3}	8.42(8.96), 2.37(2.46)	8.29(8.93), −2.34(−2.46)	6.23(6.80), 1.86(1.98)	6.20(6.70), −1.83(−1.95)
$\langle S_{Fe1} \cdot S_{Fe2} \rangle$	5.58(6.03)	5.51(6.01)	3.37(3.86)	3.30(3.81)
$\langle S_{Fe1} \cdot S_{Fe3} \rangle$	5.58(6.03)	−5.57(−6.09)	3.37(3.86)	−3.46(−3.89)
$\langle S_{Fe2} \cdot S_{Fe3} \rangle$	5.58(6.03)	−5.57(−6.09)	3.37(3.86)	−3.38(−3.89)
$\langle S_{\mu 3\text{-}O}^2 \rangle$, $M_{\mu 3\text{-}O}$	1.48(1.12), 0.38(0.11)	1.32(1.10), 0.13(0.04)	1.23(1.13), 0.08(0.03)	1.23(1.13), 0.02(0.01)
$\langle S^2 \rangle$	63.76(63.76)	13.63(13.75)	63.79(63.79)	13.63(13.79)

Table 3　Local spin expectation values and $\langle S^2 \rangle$ computed for various z-components of c by UB3LYP

	c		
z-components	M=15/2 (↑ ↑ ↑)	M=5/2 (↑ ↓ ↑)	M=5/2 (↑ ↑ ↓)
$\langle S_{Fe1}^2 \rangle$, M_{Fe1}	8.48(8.96), 2.38(2.46)	8.34(8.93), 2.35(2.45)	8.41(8.96), 2.36(2.46)
$\langle S_{Fe2}^2 \rangle$, M_{Fe2}	8.48(8.96), 2.38(2.46)	8.31(8.93), −2.34(2.45)	8.41(8.96), 2.36(2.46)
$\langle S_{Fe3}^2 \rangle$, M_{Fe3}	8.05(8.88), 2.31(2.45)	8.01(8.89), 2.30(2.45)	8.00(8.90), −2.29(−2.45)
$\langle S_{Fe1} \cdot S_{Fe2} \rangle$	5.62(6.00)	−5.54(−6.04)	5.55(6.00)
$\langle S_{Fe1} \cdot S_{Fe3} \rangle$	5.42(5.96)	5.33(5.95)	−5.48(−6.08)
$\langle S_{Fe2} \cdot S_{Fe3} \rangle$	5.42(5.96)	−5.54(−6.06)	−5.48(−6.08)
$\langle S_{\mu 3\text{-}O}^2 \rangle$, $M_{\mu 3\text{-}O}$	1.57(1.16), 0.44(0.04)	1.38(1.14), 0.20(0.05)	1.33(1.14), 0.07(0.04)
$\langle S^2 \rangle$	63.76(63.76)	13.61(13.75)	13.60(13.75)

Values in parentheses are results by UHF.

Table 4 Local spin expectation values and $<S^2>$ for various *z*-components of complex 2 and $Mn_3O(OH)_4(H_2O)_4$ previously reported

	2[a]			
z-components	*M*=15/2 (↑ ↑ ↑)	*M*=5/2 (↓ ↑ ↑)	*M*=5/2 (↑ ↓ ↑)	M=5/2 (↑ ↑ ↓)
$<S^2_{Fe1}>$	8.27	8.16	8.16	8.26
$<S^2_{Fe2}>$	8.26	8.16	8.15	8.25
$<S^2_{Fe3}>$	8.30	8.27	8.27	8.25
$<S_{Fe1}\cdot S_{Fe2}>$	4.79	−4.70	−4.69	4.78
$<S_{Fe1}\cdot S_{Fe3}>$	4.79	−4.73	4.73	−4.77
$<S_{Fe2}\cdot S_{Fe3}>$	4.79	4.73	−4.73	−4.77
$<S^2_{\mu3\text{-}O}>$	0.97	0.96	0.96	0.96
$<S^2>$	65.37	15.32	15.31	15.33
	$Mn_3O(OH)_4(H_2O)_4$[b]			
z-components	*M*=15/2 (↑ ↑ ↑)	*M*=5/2 (↓ ↑ ↑)	*M*=5/2 (↑ ↑ ↓)	
$<S^2_{Fe1}>$, M_{Fe1}	8.25, 2.33	8.12, −2.30	8.20, 2.31	
$<S^2_{Fe2}>$, M_{Fe2}	8.25,2.32	8.19, 2.31	8.20, 2.31	
$<S^2_{Fe3}>$, M_{Fe3}	8.21, 2.31	8.18, 2.31	8.13, −2.31	
$<S_{Fe1}\cdot S_{Fe2}>$	5.37	−5.31	5.33	
$<S_{Fe1}\cdot S_{Fe3}>$	5.36	−5.30	−5.32	
$<S_{Fe2}\cdot S_{Fe3}>$	5.36	5.32	−5.32	
$M_{\mu3\text{-}O}$	0.17	0.04	0.07	
$M_{\mu2\text{-}OH}$	0.06	0.00	0.06	
$<S^2>$	63.8	13.7	13.7	

[a] ref.[8]; [b] ref.[6d].

plexes consisting of d^5 radical centers are +5/2 (spin up) or −5/2 (spin down), 8.75, +6.25 (ferromagnetic coupling) or −6.25 (antiferromagnetic coupling), respectively. Nevertheless, if the delocalizing LCAO-MOs are used, some spins of the radical centers will be thus delocalized to the ligands. Therefore, the local spin expectation values computed from *ab initio* wave function would be below the ideal values. This can be apparently seen from Tables 2~4. For example, for **a** these values for HS are 2.37, 8.42, and 5.58 respectively, which are 0.17, 0.33, and 0.65 below their respective ideal one. However, this is not always the case. For instance, all the $<S^2_{Fe}>$ values by UHF for **a** and **c** are exceptionally a little above the ideal value of 8.75. The reason, as has been suggested by Davidson[6b], is that the UHF calculations always yield excess free electrons on the metals, resulting in larger m_A and F_A.

The $<S^2>$ used to be an interesting quantity to be used for evaluating the deviation of approximate BS described by single determinant wave function from ideal BS. In our last study (submitted to Science in China), however, we have pointed out this quantity is less effective and intuitional than m_A, which are not available from Noodleman approach, for this evaluation. Therefore, in this sense, Davidson′s method may show advantage. From Table 2, we can see that the obtained $<S^2>$ by ZILSH are rather unreasonable. These values are about 1.6 above ideal values. Comparing them with those reasonable by ABLSH (just a difference of 0.15 at most) indicates the semiempirical single determinant wave function might be poor for describing magnetic behaviors though they are easily

available for the complexes with great number of radical centers. In addition, all the $<S^2>$ values at HS except those by ZILSH are nearly equal to the ideal 63.75, indicating that ab initio wave function better describe HS than BS.

Model **b** has three additional terminal oxygens and partial spins on the iron centers are delocalized to them through the Fe-O coordinating bonds, resulting in sharply decreasing of local spin expectation values of the radical centers. For example, the m_{Fe}, $<S_{Fe2}>$, and $<S_{Fe1}\cdot S_{Fe2}>$ for HS are just 1.86, 6.23, and 3.37, respectively. They are all much below the ideal values. Therefore, at this situation the assumption of Noodleman approach is less satisfied and might not be quite as valid as for **a** and **c**. Although Nooleman broken symmetry approach have been frequently adopted in recent literatures, whether the used wave functions can well satisfy the assumption of it has scarcely been mentioned therein. Hence, implementing Davidson local spin theory together with Noodleman approach may give more informing results. However, since there is some arbitrariness of partitioning the total spin onto atoms or fragments of molecules in Davidson′s theory, it would be unconvincing to say that Davidson′s local spin method have superiority over Noodlman approach.

2.3 Pairwise magnetic exchange constants of a~c

To obtain the exchange constants of **a~c**, two linear equation groups were constructed based on the ABLSH method as follows.

$$\begin{cases} {}^{15/2}E_{\mathrm{UHF,\ UDFT}}=E_0-2J_{12}(<S_{Fe1}\cdot S_{Fe2}>+<S_{Fe1}\cdot S_{Fe3}>+<S_{Fe2}\cdot S_{Fe3}>)(\uparrow\uparrow\uparrow) \\ {}^{5/2}E_{\mathrm{UHF,\ UDFT}}=E_0-2J_{12}(<S_{Fe1}\cdot S_{Fe2}>+<S_{Fe1}\cdot S_{Fe3}>+<S_{Fe2}\cdot S_{Fe3}>)(\uparrow\uparrow\downarrow) \end{cases} \quad (\mathbf{12})$$

$$\begin{cases} {}^{15/2}E_{\mathrm{UHF,\ UDFT}}=E_0-2J_{12}<S_{Fe1}\cdot S_{Fe2}>-2J_{13}(<S_{Fe1}\cdot S_{Fe3}>+<S_{Fe2}\cdot S_{Fe3}>)(\uparrow\uparrow\uparrow) \\ {}^{5/2}E_{\mathrm{UHF,\ UDFT}}=E_0-2J_{12}<S_{Fe1}\cdot S_{Fe2}>-2J_{13}(<S_{Fe1}\cdot S_{Fe3}>+<S_{Fe2}\cdot S_{Fe3}>)(\uparrow\downarrow\uparrow) \\ {}^{5/2}E_{\mathrm{UHF,\ UDFT}}=E_0-2J_{12}<S_{Fe1}\cdot S_{Fe2}>-2J_{13}(<S_{Fe1}\cdot S_{Fe3}>+<S_{Fe2}\cdot S_{Fe3}>)(\uparrow\uparrow\downarrow) \end{cases} \quad (\mathbf{13})$$

Here, eq. group **12** are for **a** and **b** and eq. group **13** is for **c**, and the arrows in parentheses stand for various "spin flippings". On solving these linear equations, both ideal and computed $<S_A\cdot S_B>$ were used. While the ideal $<S_{Fei}\cdot S_{Fej}>$ $(i\neq j)$ is used, eq. group **12** can be transformed into the following equation

$$J_{12}=\frac{{}^{5/2}E_{\mathrm{UHF,\ UDFT}}-{}^{15/2}E_{\mathrm{UHF,\ UDFT}}}{50} \quad (\mathbf{14})$$

Apparently, eq. **13** is just what can be derived from Noodleman broken symmetry approach for the trinuclear metal complexes with three equivalent pariwise exchange constants [5f]. Therefore, the ABLSH method is just a scaling of Noodleman approach.

Eq. groups **12** and **13** were solved using a simple mathematic program and the obtained results were given in Table 5. From Table 5, we can see all the results are comparable to those previously reported, experimentally or theoretically. For instance, the best J_{12} of **b**, −56 cm^{-1}, is in fairly well agreement with the experimental −59 cm^{-1} and the J_{12} of **c** by UB3LYP −53 cm^{-1} is also close to the experimental −55 cm^{-1} [3a] and O′Brien′s −52 cm^{-1} [8]. In addition, the J_{13} of **c** −17 cm^{-1}, though a little more than double of experimental −8 cm^{-1}, is almost no more than O′Brien′s −16 cm^{-1}. It should be noted, however, the theoretical and experimental results may essentially be different from each other since they are obtained using actual and ideal local spin values, respectively[11,12].

Unfortunately, both O′Brien′s results and ours predict the wrong ground state with S=3/2 for complex **2** since the ratios J_{12}/J_{13} are all below 3.5 except that those by UHF is narrowly larger than 3.5. O′Brien has attributed this inconsistence to the coarse accuracy of INDO method[8]. Nevertheless, in this study it may be due to the using of such reduced models. How to find

Table 5　Calculated exchange constants of a~c by UB3LYP

Systems	J_{12}	J_{13}	J_{12} / J_{13}
a	28(3), 28(3)*	—	—
b	56(12), 30(8)*	—	—
1expt.	59	—	—
c	53(4.9), 48(5.1)*, 52**	17(1.4), 15(1.4)*, 16**	3.1(3.5), 3.2(3.6)*, 3.2**
2expt.	55	8	6.9

* using ideal $<S_A\cdot S_B>$ values; ** ref.[8]; expt. experiments; values in parentheses are results by UHF.

the models from which the right ground state with S= 5/2 can be predicted is challenging. This work is in progress now. Moreover, we can find three inequations among these values that $J_{ij} > J_{ij}^{a}$, J_{ij} (UDFT) > J_{ij}(UHF), and J_{ij}(**b**) > J_{ij}(**a**), indicating the more spins delocalized from the irons to the ligands, the larger exchange constants are obtained. And all the J values by UHF underestimate the experiments, coinciding with our previous analysis for the complexes $[O(FeCl_3)_2]^{2-}$ [7a] and the reason for this has been well known[5d].

Table 5 also shows that the J is not much dependent on what kind of $<S_A \cdot S_B>$ is used at UHF level but is a little at UB3LYP level because of more spin delocalization arising from the latter. Although it seem more consistent, as Davidson has considered[4d], to use the exchange constants obtained by using the ideal $<S_A \cdot S_B>$ values, the J_{12} of **b** by UB3LYP can better predict the experiment when using calculated $<S_A \cdot S_B>$ than using ideal one. Therefore, the ABLSH method is empirically competitive.

3 Conclusions

This research has demonstrated the application of Davidson′s local spin theory to the reduced models of two typical trinuclear iron(Ⅲ) complexes **1** and **2** and the obtained local spin results are rational compared with those of the same complex or the analog previously reported. Furthermore, the local spin expectation values were found to be dependent on the wave functions used and the terminal ligand atoms. Generally, UDFT wave functions yield more spin delocalization than UHF wave functions and the terminal ligand atoms also results in great spin delocalization.

The obtained exchange constants for these reduced models are in well agreement with experiments, indicating it is not necessary to use the unit cells in this kind of calculations since their reduced models can work well, not to mention the ab initio calculations on these tremendous unit cells are so time-consuming that they may let one lose patience.

For complex **2**, the results by ABLSH have little difference from those by ZILSH, indicating these two methods might be nearly equivalent. However, less convergence failures arise from the ab inito calculations and the ZILSH method needs additional CAHF method[13] to overcome the convergence problems. Therefore, the ABLSH method is more straightforward.

Although using the calculated $<S_A \cdot S_B>$ values seems less consistent with idealized HSM, the J values computed from them are more reasonable, indicating the ABLSH method can be a good candidate other than the ZILSH method and Noodleman approach for predicting the exchange constants of magnetic systems.

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