

About the Calculation of Exchange Coupling Constants in Polynuclear Transition Metal Complexes

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Abstract: The application of theoretical methods based on the density functional theory with hybrid functionals provides good estimates of the exchange coupling constants for polynuclear transition metal complexes. The accuracy is similar to that previously obtained for dinuclear compounds. We present test calculations on simple model systems based on $\text{H} \cdots \text{He}$ and $\text{CH}_2 \cdots \text{He}$ units to compare with Hartree–Fock and multiconfigurational results. Calculations for complete, nonmodeled polynuclear transition metal complexes yield coupling constants in very good agreement with available experimental data.

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Introduction

Molecular magnetism is one of the most active areas in modern transition metal chemistry. Early on, research in this field focused mainly on the magnetic properties of dinuclear complexes with the aim of gaining some understanding of the key structural and electronic factors that control the exchange coupling between two metal centers.¹ During the last decade, however, interest in molecular magnetism has shifted towards the preparation of new materials with predetermined magnetic properties. To achieve this, two different strategies have been adopted by different researchers. In the first one new magnetic properties have been sought for by extending the exchange interaction from dinuclear to chain, to two-dimensional or even to three-dimensional structures based on molecular building blocks.² The second approach consists of increasing the complexity of these building blocks by synthesizing polynuclear complexes with more than two interacting paramagnetic centers.^{3,4} The magnetic properties of these compounds are expected to be intermediate between those of simple dinuclear complexes and those of bulk materials. Among these, the so-called Mn_{12} and Fe_8 compounds have attracted the interest of many researchers, especially due to their new magnetic properties associated to the quantum magnetic quantum tunneling effect.⁵ The

search for new polynuclear complexes showing single-molecule magnet character is today one of the most active subjects of research in molecular magnetism.

Theoretical studies of the magnetic behavior of polynuclear complexes have been limited usually to dinuclear complexes.⁶ The need for the inclusion of electron correlation effects to reach a proper description of the electronic structure of exchange-coupled polynuclear transition metal complexes has limited the applications of the most popular semiempirical methods in this field.⁷ Sophisticated post-Hartree–Fock methods have been shown to provide good approximations to coupling constants, but the huge demand of computational resources associated to these methods severely limits their applicability to most of the complexes of actual experimental interest.^{8–11} Methods based on density functional theory (DFT)¹² have been shown in the last years to provide a reasonable compromise between the size of the compounds that can be studied and the accuracy of the calculated coupling con-

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stants.^{13–17} Among the few DFT theoretical studies devoted to magnetic properties of open shell complexes of transition metals with higher nuclearity, we should mention the pioneering work of Noodleman et al. on the biologically relevant iron–sulphur clusters.^{18–21}

The present article has two goals. First, to present a general strategy to calculate exchange coupling constants for transition metal compounds of high nuclearity using computational methods based on DFT and, second, to test the performance of such methods by comparing the calculated coupling constants for small benchmark systems with those obtained by *ab initio* methods. The applicability of the proposed methods to polynuclear transition metal complexes will be, on the other hand, gauged by comparing the calculated coupling constants with the corresponding experimental data for a set of selected compounds. Such a comparison must be performed carefully because experimental data are in most cases obtained from a fitting of the magnetic susceptibility data to the expression obtained using a model Hamiltonian that includes several fitting parameters. One of the problems associated with this technique is the existence of several independent sets of parameters that provide fair fittings of the susceptibility curve. Another difficulty arises from some simplifying hypothesis, such as the neglect of next nearest neighbor interactions or the assumption of identical parameters for interactions that are not equivalent by symmetry, often adopted to reduce the number of fitting parameters. Good sources of experimental data would be inelastic neutron scattering experiments, but these are not commonly employed, mainly due to the technical requirements involved.²² Thus, the use of theoretical methods to estimate the exchange coupling constants can be foreseen as a valuable tool for the experimental chemist to rule out those sets of experimental fitted constants that are deemed unrealistic according to calculations.

Phenomenological Hamiltonians to Describe Exchange Interactions

If we neglect the zero field splitting terms, the main parameter used to quantify the magnetic properties of dinuclear complexes is the exchange coupling constant J between the two paramagnetic centers with total spins S_1 and S_2 , respectively,¹ which is defined through the phenomenological Heisenberg Hamiltonian:

$$\hat{H} = -J\hat{S}_1\hat{S}_2 \quad (1a)$$

We have shown in previous works that methods based on DFT using hybrid functionals constitute a powerful tool to calculate exchange coupling constants, and hence magnetic properties, of dinuclear systems.^{14,17,23} If we turn to complexes of higher nuclearity, the Hamiltonian usually employed is considerably more complex due to the presence of several exchange pathways with different J values and to the inclusion of anisotropic zero field splitting terms. The Hamiltonian for a general polynuclear complex is indicated in eq. (1b),

$$\hat{H} = - \sum_{i>j} J_{ij}\hat{S}_i\hat{S}_j + D(\hat{S}_z^2 - \frac{1}{3}\hat{S}^2) + E(\hat{S}_x^2 - \hat{S}_y^2) \quad (1b)$$

where \hat{S}_i and \hat{S}_j are the spin operators of the different paramagnetic centers and \hat{S} and \hat{S}_z are the total spin moment of the molecule and its axial component, respectively. The J_{ij} values are the coupling constants between all the paramagnetic centers of the molecule, while D and E are the axial and rhombic components of the anisotropy, respectively. For the estimation of these two parameters it is unavoidable to include spin-orbit coupling corrections in the electronic structure calculations and in this work, we will focus only on the calculation of J_{ij} values in isotropic systems. It is interesting to point out, however, that Pederson et al. have recently presented an approach based on a perturbative method to include the spin-orbit coupling that allows the calculation of the zero field splitting for different polynuclear complexes.²⁴ It is important to clarify that the noninclusion of the spin-orbit coupling in the usual density functional calculations allows, however, the direct determination of the exchange coupling constants independently of D and E if only the first term of the Hamiltonian in eq. (1b) is considered.

At this point it is worth discussing about the comparability of the calculated and experimental exchange coupling constants in some detail. From the experimental point of view, the Heisenberg Hamiltonian is employed to estimate the energies of the states that are used in the fitting of the magnetic susceptibility. In the calculation of coupling constants by quantum chemical methods, the Heisenberg Hamiltonian is also adopted. The eigenvalues and eigenvectors of the related Hamiltonian matrix, that contains non-zero off-diagonal elements, correspond to the states of the system. These functions and energies can be straightforwardly calculated by using a multiconfigurational approach. However, when using single-determinant methods, such as DFT or HF, the calculated energies are related to the diagonal matrix elements of the Heisenberg Hamiltonian and not with its eigenvalues as in the multiconfigurational methods. An alternative way to describe the system is by considering an Ising Hamiltonian as a special case of a Heisenberg Hamiltonian in which only the diagonal terms are kept. Thus, we can consider that the wave functions obtained with the single-determinant methods (sometimes called microstates) are eigenfunctions of an Ising Hamiltonian that is formulated with the same J values than the original Heisenberg Hamiltonian because their diagonal terms are identical. For that reason, the J values obtained with single-determinant methods are directly comparable to those obtained with multiconfigurational methods or from experimental data.

To conclude this discussion, it is important to bear in mind the differences of the use of an Ising Hamiltonian in theoretical and experimental work. From the theoretical point of view, some authors usually indicate that they are using an Ising Hamiltonian when using single-determinant methods, for the reasons that we have previously indicated. However, the use of the Ising Hamiltonian to fit experimental data is restricted only to cases where there is a strong anisotropy in the magnetic properties.²⁵ In such cases the energies derived from the Ising Hamiltonian are employed as those corresponding to the states instead of those of the microstates as done in single-determinant calculations. Thus, the experimental coupling constants obtained using an Ising Hamiltonian cannot be directly compared with the theoretical results using the usual approaches.

Computational Details

The Gaussian98 program²⁶ has been used for all the Hartree–Fock and DFT calculations presented in this work. To compare the performance of different computational approaches, we have carried out Hartree–Fock, generalized gradient DFT (BLYP),^{27,28} and hybrid DFT (B3LYP) calculations.²⁹ In previous work, after evaluating the use of several functionals, we found that the hybrid method provides the best results for the calculation of exchange coupling constants in dinuclear complexes.^{14,30} Accurate post-Hartree–Fock methods have been employed as benchmark calculations for simple systems, notably CASSCF and CASPT2 calculations, using the MOLCAS 5.0 code.³¹

For the $\text{H} \cdots \text{He} \cdots \text{H}$ and $\text{CH}_2 \cdots \text{He} \cdots \text{CH}_2$ systems, the 6-311G** basis set was employed. To analyze the basis set dependence of the CASSCF and CASPT2 results we performed some test calculations with an ANO (7s, 3p) basis set contracted to [4s, 3p] for hydrogen and helium atoms, and (10s, 6p, 3d) contracted to [7s, 6p, 3d] for the carbon atoms.³² For the calculations on transition metal complexes, a triple- ζ basis set proposed by Ahlrichs et al. was employed for the transition metal atoms³³ and the double- ζ basis set proposed by the same authors for the other atoms.³⁴

Evaluation of Coupling Constants in Polynuclear Systems

As discussed in previous works,^{14,30} the estimation of the exchange coupling constants in dinuclear complexes using methods based on density functional theory involves the calculation of the energy difference between the high-spin state and a low-spin solution, which corresponds to a broken symmetry wave function in the case of symmetric homodinuclear complexes. From the experimental point of view, the exchange coupling constant is introduced by using phenomenological spin Hamiltonians and for the simplest case of two unpaired electrons on two centers, its value corresponds to the energy difference between the triplet and the singlet states. In DFT calculations the energy of the singlet state can be approximated using that of the single-determinant broken-symmetry solution,

$$E_{\text{BS}} - E_{\text{HS}} = (2S_1S_2 + S_2)J_{12} \quad (2a)$$

where $S_2 = S_1$.³⁰ On the other hand, for Hartree–Fock calculations a spin-projected formula must be used and the relationship between the calculated energies and the exchange coupling constant that results is:

$$E_{\text{BS}} - E_{\text{HS}} = 2S_1S_2J_{12} \quad (2b)$$

The use of the nonspin projected energy of the broken symmetry solution as the energy of the low spin state within the DFT framework has been the source of controversy between different authors. Recently, Polo et al.³⁵ have shown that the self-interaction error of commonly used exchange functionals mimics long-range (nondynamic) pair correlation effects in an unspecified way. On the contrary, if system-specific nondynamic correlation effects are

introduced via the form of the wave function as in BS-UDFT calculations through spin projection, these effects will be suppressed if the exchange functional already covers a considerable number of nondynamic correlation effects. Thus, the application of spin projection techniques to DFT calculations results then probably in the suppression (or double counting) of such long-range correlation effects. This fact has been noticed by other authors previously. Wittbrodt and Schlegel discussed the influence of the spin projection on the DFT study of potential energy surfaces, concluding that the best results are obtained with nonprojected energies.³⁶ An alternative point of view to explain these results was proposed by Perdew et al.^{37,38} These authors propose that the broken-symmetry single determinant wave function is the correct solution for the Kohn–Sham equations, and the energy of this solution corresponds to the energy of the singlet state in spite of its wrong description of the spin density.

The procedure proposed by us here for the theoretical estimation of the exchange coupling constants in a polynuclear complex with n different J_{ij} values consists in the calculation of $n + 1$ single-determinant energies corresponding to different spin distributions. Such energies, as indicated above, are related to the eigenvalues of the Ising Hamiltonian (identical to the diagonal matrix elements of the Heisenberg Hamiltonian) and we can use them to obtain a system of n equations with n unknowns, the J_{ij} values. We propose two alternative approaches to obtain this set of equations. The first one would be the construction of the Hamiltonian matrix as we have indicated, but an alternative simpler approach to obtain the same equations consists in just analyzing the changes in sign of the local spin moments between spin distributions i and j and to employ the pairwise expression of the Ising (or Heisenberg) Hamiltonians.

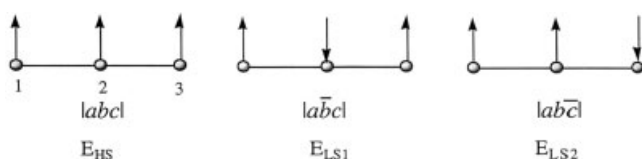
Because we have found for dinuclear complexes that the energy difference between the ferromagnetic and the antiferromagnetic spin configurations is given by eq. (2a),³⁰ we can extend that approach to polynuclear compounds by just expressing the difference in energy between different spin configurations as a sum of pairwise interactions. Hence, for a linear trinuclear system two exchange coupling constants can be defined, J_{12} between nearest neighbors and J_{13} between next nearest neighbors. The relative energies of the spin configurations shown in Scheme I are therefore given by eqs. (3a) and (3b).

$$E_{\text{HS}} - E_{\text{LS1}} = -2J_{12} \quad (3a)$$

$$E_{\text{HS}} - E_{\text{LS2}} = -J_{12} - J_{13} \quad (3b)$$

As an example of how these relations are obtained, consider the HS and LS1 configurations (Scheme I). They differ in the two nearest-neighbor interactions (1–2 and 2–3), whereas the next nearest neighbor interaction (1–3) is identical in both cases. Hence, the energy difference between those two configurations is given by $-(2S_1S_2 + S_2)J_{12} - (2S_2S_3 + S_3)J_{23} = -2(2S_1S_2 + S_2)J_{12}$ (which gives $-2J_{12}$ for the $S_1 = S_2 = S_3 = 1/2$ case). The differences between HS and LS2, on the other hand, appear in the 2–3 first neighbor interaction and in the 1–3 next-nearest-neighbor interaction, and the resulting expression is given by eq. (3b).

For the case of Hartree–Fock calculations, each interaction term has the form $(2S_iS_j)J_{ij}$ and the expressions for the energy differences, obtained in a similar way, are those given in eqs. (4).



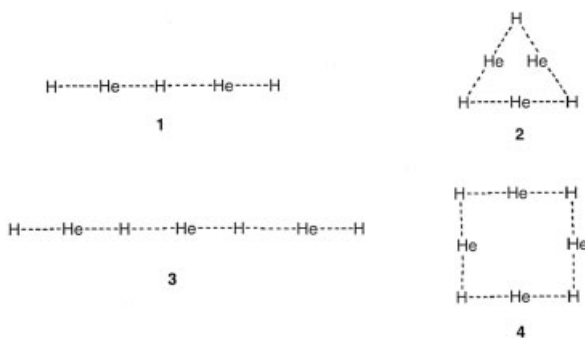
Scheme I

The procedure indicated can be applied to calculate the exchange coupling constants of any polynuclear complex. Kortus et al. have employed a similar approach using a fitting procedure to obtain the J_{ij} values for a V_{15} complex by calculating more spin configurations than those needed to build up the set of equations.³⁹

Application to Benchmark Systems

To check the accuracy of single-determinant methods to calculate the exchange coupling constants in systems with multiple paramagnetic centers, we have selected a series of test systems (**1–4**) related to the $H \cdots He \cdots H$ biradical complex that has been commonly employed as a model for exchange coupling between two paramagnetic centers. In such cases, we have only one unpaired electron per center. The $He \cdots H$ distance has been fixed to 1.625 Å in all cases. Although there is no experimental information for such hypothetical compounds, we can employ highly accurate post-HF calculations to obtain reference values for comparison.

The J_{ij} values obtained for such compounds using several methods are presented in Table 1. As main features we can note that the calculated values for these four systems show the same trends found earlier for the $H \cdots He \cdots H$ dinuclear model:³⁰ (1) the spin-projected Hartree–Fock method underestimates the J values, while the UBLYP method, based on a pure GGA functional overestimates them; (2) the UB3LYP method provides values intermediate between those obtained in CASSCF and CASPT2 calculations; (3) the J values for next-nearest neighbor interactions obtained in CASPT2 and UB3LYP calculations are in good agreement, while those obtained with the CASSCF method seem to overestimate the ferromagnetic contributions, compared to the more accurate CASPT2 results, a problem that can be ascribed to the non inclusion of dynamic correlation effects in the CASSCF calculations. As previously found for two-center interactions, the



$$E_{HS} - E_{LS1} = -J_{12} \quad (4a)$$

$$E_{HS} - E_{LS2} = -J_{12}/2 - J_{13}/2 \quad (4b)$$

The same result would be obtained if the diagonal terms of the Heisenberg Hamiltonian are taken as the energies of the spin configurations in Scheme I:

$$E_{HS} = -J_{12}/2 - J_{13}/4 \quad (5a)$$

$$E_{LS1} = J_{12}/2 - J_{13}/4 \quad (5b)$$

$$E_{LS2} = J_{13}/4 \quad (5c)$$

Table 1. Calculated Exchange Coupling Constants J (cm^{-1}) for Different $H \cdots He$ Multicenter Complexes Represented in **1–4** with $H \cdots He$ Distances Equal to 1.625 Å.

Model	UHF	UB3LYP	UBLYP	CASSCF small ^a	CASPT2 small ^a	CASSCF large ^b	CASPT2 large ^b
1							
J_{12}	−453	−552	−677	−504	−586	−526	−595
J_{13}	−1.3	−4.7	−8.0	+20	−4.0	+21	−5.8
2							
J_{12}	−151	−184	−220	−174	−197	−166	−195
3							
J_{12}	−454	−554	−681	−525	−587	−546	−594
J_{23}	−488	−585	−720	−514	−629	−515	−639
J_{13}	−1.3	−4.4	−6.7	+39	−3.4	+42	−8.0
4							
J_{12}	−410	−490	−599	−444	−516	−463	−521
J_{13}	−1.2	−3.2	−0.6	+13	−8.8	+28	−5.2

The UHF values have been obtained by using spin projection while the DFT ones are nonprojected.

^aActive space (electrons, orbitals): **1**, (7, 5); **2**, (9, 6); **3**, (10, 7); **4**, (12, 8).

^bActive space (electrons, orbitals): **1**, (7, 8); **2**, (9, 9); **3**, (10, 11); **4**, (12, 12).

Table 2. Calculated Exchange Coupling Constants J (cm^{-1}) for the Model Compounds Containing CH_2 as Paramagnetic Center (**5** and **6**).

Model	UHF	UB3LYP	UBLYP	CASSCF small ^a	CASPT2 small ^a	CASSCF large ^b	CASPT2 large ^b
5							
J_{12}	−107	−197	−292	−115	−155	−116	−153
6							
J_{12}	−112	−204	−306	−115	−158	−115	−163
J_{13}	−0.3	−2.6	−9.6	+4.0	+1.9	+4.8	+2.9

The C...He and C—H distances used are 2.0 and 1.08 Å, respectively, while the H—C—H angle is 135°. The UHF values have been obtained by using spin projection while the DFT ones are nonprojected.

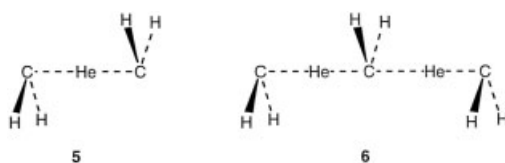
^aActive space (electrons, orbitals): **5**, (4, 4); **6**, (6, 6).

^bActive space (electrons, orbitals): **5**, (14, 11); **6**, (6, 6) + ANO basis set.

use of eq. (2a) (without spin projection) for HF calculations gives a much poorer agreement with the CASPT2 results than the same calculations including spin projection [eq. (2b)]. Conversely, DFT calculations with eq. (2a) are in much better agreement with CASPT2 results than those obtained using eq. (2b). This finding is related to the lack of nondynamic correlation in the HF method. Because such effects are introduced by the spin projection via eq. (2b), much better agreement is obtained using this equation with the HF method. In contrast, nondynamic correlation effects are already included in the single-determinant energy in DFT methods and the use of nonprojected energies [eq. (2a)] provides more accurate J values.

As a second benchmark for our computational approach, we have selected model compounds with carbenes as paramagnetic centers. In this case each center bears two unpaired electrons, again connected via He atoms that play the role of diamagnetic bridges. This type of compounds should allow us to test the influence of the number of unpaired electrons on the accuracy of the calculated J values. Table 2 presents the calculated exchange coupling constants obtained employing different methods for hypothetical dinuclear (**5**) and trinuclear complexes (**6**).

The analysis of the results presented in Table 2 shows that: (1) the calculated J_{ij} values follow the same trends observed above for the H—He systems, i.e., the projected UHF method gives smaller absolute values than the nonprojected UB3LYP or UBLYP calculations, while the CASPT2 method gives intermediate values which are close to the UB3LYP ones; (2) the substitution of the 6-311G** by the larger ANO basis set does not substantially change the CASSCF and CASPT2 results, (3) the sign for the J_{13} values calculated with single-determinant methods is opposite to that found using CAS methods. Surprisingly, the positive value obtained in CASSCF and CASPT2 calculations is in disagreement with the usual antiferromagnetic coupling found for next-nearest neighbor interactions.



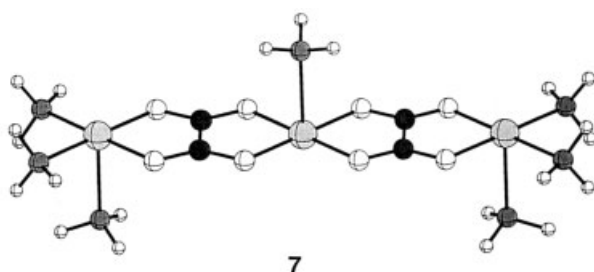
Now that we have seen that UB3LYP calculations are a good choice for the estimation of the exchange coupling constants in hypothetical benchmark systems with several paramagnetic centers, we turn our attention to polynuclear transition metal complexes, much closer to what can be experimentally verified.

Application to Polynuclear Transition Metal Complexes

For the purpose of the calculation of exchange coupling constants in polynuclear transition metal complexes we selected two types of systems: (a) some model complexes with idealized structures and simple terminal ligands, and (b) real compounds considering their whole unmodeled molecular structure: an oxamato-bridged Cu(II) trinuclear complex⁴⁰ and a dimethylglyoximate-bridged Mn(III)Cu(II)Mn(III) heterotrinuclear complex.⁴¹

For the analysis of the exchange coupling constants in model compounds we selected the oxalato-bridged Cu(II) complexes. Because we have previously studied⁴² the magnetostructural correlations and the influence of the ligands on the exchange coupling of oxalato-bridged Cu(II) dinuclear complexes using the same computational approach, we wish to find out if new unenvisioned features appear in the case of polynuclear analogues. We have calculated the exchange coupling constants for the trinuclear model shown in **7** and for the analogous tetranuclear complex and the results are reported in Table 3. As an alternative way of estimating coupling constants in these compounds we have also obtained the exchange coupling constants for the trinuclear complex by replacing one of the Cu(II) ions by a diamagnetic Zn(II) ion. The resulting Cu_2Zn complexes are equivalent to a dinuclear Cu(II) complex from the magnetic point of view and we can obtain the two exchange coupling constants (J_{12} and J_{13}), depending on which of the copper atoms is replaced by zinc.

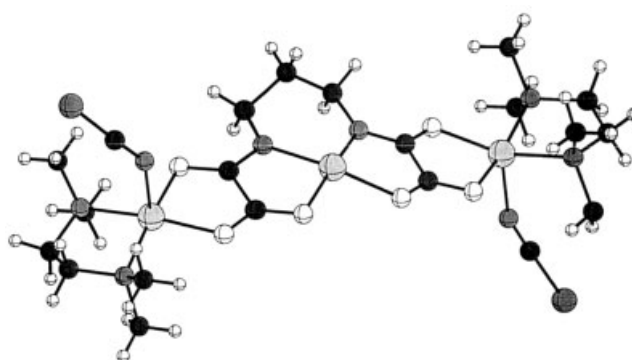
The following conclusions can be extracted from the results of our calculations on oxalato-bridged Cu(II) model complexes: (1) the influence of the number of paramagnetic centers on the calculated nearest neighbor coupling constant J_{12} is small; (2) the values of the calculated J_{12} constants are within the range of the experimental values for oxalato-bridged dinuclear complexes (−284 to −402 cm^{-1});⁴² (3) the calculated J values obtained by



substituting a Cu(II) by a Zn(II) cation are in very good agreement with those obtained directly for the trinuclear complex. Thus, the strategy of substituting paramagnetic atoms by diamagnetic ones to reduce the evaluation of coupling constants to calculations for magnetically dinuclear complexes seems highly promising and might be extended to more time demanding methods such as the DDCI ones; (4) the next-nearest neighbor (J_{13}) and next-next-nearest neighbor (J_{14}) coupling constants are much smaller than the nearest neighbor one; (5) the J_{23} value for the tetranuclear complex is slightly larger than that corresponding to the interaction involving a terminal copper ion (J_{12}) as found above for the $\text{H} \cdots \text{He}$ systems. If we extrapolate

Table 3. Exchange Coupling Constants J (cm^{-1}) Calculated at B3LYP Level for Polynuclear Oxalato-Bridged Cu(II) Complexes 7.

	J_{12}	J_{13}	J_{23}	J_{14}
Dinuclear Cu_2	-369			
Trinuclear	-387	-5.4		
Trinuclear Cu_2Zn	-381			
Trinuclear CuZnCu		-2.8		
Tetranuclear	-375	-5.8	-421	-0.1

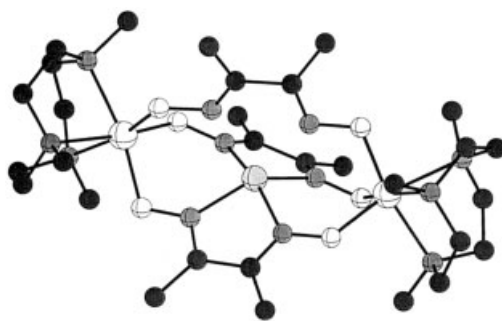


this last result to a compound with a chain structure, the nearest-neighbor exchange coupling constant at the chain ends should be somewhat more antiferromagnetic than in the corresponding dinuclear or trinuclear complexes.

The last calculation using model structures that we present in this section corresponds to a trinuclear complex with two external Fe(III) and a central Cr(III) cations, bridged by mercaptobenzyl ligands and having triazacyclononane as terminal ligands (see 8).⁴³ Due to the large number of atoms in that complex, we have modeled it by just retaining the atoms represented by spheres in 8 and introducing hydrogen atoms to saturate the dangling bonds. In such a model we keep just one atom corresponding to the bridging or terminal ligands. The magnetic susceptibility data was fitted by Glaser et al.⁴³ using two coupling constants, corresponding to the exchange interaction between Cr(III) and Fe(III) centers (J_{12}) and between the terminal Fe(III) cations (J_{13}). The experimental fitted values are -260 and -100 cm^{-1} for J_{12} and J_{13} , respectively, indicating two relatively strong antiferromagnetic interactions, in excellent agreement with our calculated values for the modeled structure (-250 and -103 cm^{-1} , respectively).

We turn now to the calculation of the exchange coupling constants for the full structure of an oxamato-bridged trinuclear Cu(II) complex, [bis(μ^2 - N,N' -propane-1,3-diyl-bis(oxamato))-bis(N,N,N',N' -tetramethylethane-1,2-diamine)-bis(selenocyanato)-tri-copper(II) dihydrate], shown in 9, including counterions and solvent molecules that are close to the molecule of the complex.⁴⁰ The experimental magnetic susceptibility data has been fitted with just one exchange coupling constant, $J_{12} = -355.7 \text{ cm}^{-1}$. Our calculations using the UB3LYP method confirm that the interaction between the terminal Cu(II) ions is rather weak, -2.2 cm^{-1} , while the coupling constant between two adjacent Cu(II) ions is -277 cm^{-1} , thus reproducing the sign and magnitude of the experimental value.

The second full structure analyzed is that of a heterotrinuclear Mn(III) complex with tris(dimethylglyoximate)copper(II) tetranions as bridging ligands (10).⁴¹ We have chosen this compound to consider a case with different paramagnetic centers having more than one unpaired electron in two of the paramagnetic centers. The calculated coupling constants are -141.3 cm^{-1} for the Mn(III)Cu(II) interaction and -6.2 cm^{-1} for the Mn(III)Mn(III) one, that com-



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pare very well with the experimental values of -126.2 and -5.6 cm^{-1} , respectively.

Conclusions

The exchange coupling constants in polynuclear complexes can be calculated using an extension of the computational strategy employed previously for dinuclear complexes. Good estimates of the coupling constants can be obtained using the hybrid B3LYP functional and taking the energy of the low spin configurations without spin projection. The independent estimation of each exchange coupling constant by using models with only two paramagnetic centers while replacing the others by similar diamagnetic centers also seems to be a promising approach. The proposed approach gives good results compared with *ab initio* CASPT2 calculations for small benchmark systems and excellent estimates compared with experimental data for polynuclear transition metal complexes considering the complexity of such systems. The use of this methodology opens up a wide range of applications to the study of the electronic structure and the magnetic properties of inorganic and bioinorganic compounds as well in organic radical compounds with multiple paramagnetic centers.

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