

Density Functional Study of Exchange Coupling Constants in Single-Molecule Magnets: The Fe₈ Complex

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Abstract: Theoretical methods based on density functional theory have been employed to analyze the exchange interactions in a Fe₈ complex with single-molecule magnet behavior. The four exchange coupling constants, calculated by using a hybrid functional, provide an accurate description of the experimental magnetic susceptibility and excitation energies. This complex has been also employed to check the accuracy of classical and quantum Monte Carlo methods to obtain macroscopic properties by comparison with the results obtained via exact diagonalization of the Hamiltonian matrix.

Keywords: density functional calculations • exchange interactions • Fe₈ complex • magnetic properties • Monte Carlo simulations

Introduction

Some polynuclear complexes show the property that its magnetization relaxes slowly at low temperature and they have been named single-molecule magnets (SMM).^[1] Due to this appealing feature, such systems have been proposed as candidates for the storage of information at the molecular level. The first single-molecule magnet reported was the [Mn₁₂O₁₂(CH₃COO)₁₆(H₂O)₄] complex, usually known as Mn₁₂.^[2] The number of single-molecule magnets is still growing, but among them the more widely studied complex besides Mn₁₂ is the Fe₈ system,^[3] [Fe₈O₈(OH)₁₂-(tacn)₆]Br₈·9H₂O (tacn = 1,4,7-triazacyclononane).^[4] In the absence of magnetic field, these two complexes have S = 10 ground states, and cooling the sample slowly at low temperatures leaves the M_s = ± 10 levels as the only populated ones. In the presence of a magnetic field, only one of them will be populated. When the magnetic field is switched off, in order to attain thermodynamic equilibrium, the system must either climb the ladder of M_s states or undergo a tran-

sition through quantum tunneling between excited states with smaller M_s values. The crucial parameter that controls both processes, the thermal jump of the barrier and the thermally assisted quantum tunneling, is the height of the barrier. The energy barrier is equal to D·S², where D is the zero-field splitting parameter.^[1] Thus, in order to obtain a single-molecule magnet behavior at high temperatures, the requirements are a large spin ground state and a large negative anisotropy constant D.

The spin Hamiltonian for a general polynuclear complex can be expressed as:

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

where \hat{S}_i and \hat{S}_j are the spin operators of the paramagnetic centers *i* and *j* and \hat{S} and \hat{S}_z are the total spin operator of the molecule and its axial component, respectively.^[5] The *J_{ij}* values are the exchange coupling constants for the different pairwise interactions between the paramagnetic centers of the molecule, while *D* and *E* are the axial and rhombic components of the anisotropy, respectively. The spin-orbit coupling effects must be taken into account for the calculation of the zero field splitting parameters *D* and *E*.^[6] In this work, we will focus only on the calculations of exchange coupling constants that determine the S value of the ground state of the system. The *J* values can be obtained directly due to the non-inclusion of the spin-orbit coupling responsible of the zero-field splitting terms. Such contributions have

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been calculated by Pederson et al. by using DFT methods with a perturbative approach to include the spin-orbit coupling, obtaining excellent results for SMM systems. A more detailed description of the procedure to obtain the exchange coupling constants can be found elsewhere.^[7] In addition, we will perform a study of the accuracy of the different approximate Monte Carlo methods to calculate the magnetic susceptibility from the exchange coupling constants by comparison with the exact diagonalization method that is still feasible for the Fe₈ complex. The interest of such approaches is that they can be applied to obtain the magnetic susceptibility for larger systems for which an exact diagonalization cannot be carried out.

Computational Details

Electronic structure calculations have been performed with Gaussian98^[8] and SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms)^[9] codes. The calculations with the Gaussian98 code were performed with the hybrid B3LYP functional^[10] and a triple- ζ all electron basis set for the iron atoms and a double- ζ basis set for the other elements.^[11,12] In the case of the SIESTA code,^[13–15] the generalized-gradient approximation (GGA) functional proposed by Perdew, Burke and Ernzerhof^[16] was employed and pseudopotentials were generated according to the procedure of Trouiller and Martins.^[17] A more detailed description of the pseudopotentials employed can be found in the literature.^[18] We have used a numerical basis set of triple- ζ quality with polarization functions for the iron atoms and a double- ζ one with polarization functions for the main group elements.^[11,12] The values of 50 meV for the energy shift and 250 Ry for mesh cutoff, provide a good compromise between accuracy and computer time to estimate the exchange coupling constants according to a previous study.^[19] The use of the numerical code results in a considerable reduction of the computer time. Nevertheless, it is a well-known fact that GGA functionals, that are those available in the SIESTA code, overestimate the stability of low spin states in comparison with the more accurate results obtained with hybrid functionals.^[20,21] However, the use of pseudopotentials partially compensates these problems, and the sign and the relative strength of the interactions are well reproduced using GGA functionals.^[19]

Abstract in Spanish: *Se han empleado métodos teóricos basados en la teoría del funcional de la densidad para analizar las interacciones de intercambio del complejo Fe₈ con propiedades de imán unimolecular. Las cuatro constantes de intercambio, calculadas usando un funcional híbrido proporcionan una descripción precisa de la curva de susceptibilidad magnética experimental y de las energías de excitación. Este complejo ha sido también empleado para comprobar la precisión de los métodos de Monte Carlo clásico y cuántico en el cálculo de propiedades macroscópicas, por comparación con los resultados obtenidos mediante la diagonalización exacta de la matriz Hamiltoniana.*

Results and Discussion

Exchange coupling constants: The calculated exchange coupling constants are presented in Table 1. We have employed a set of four equations obtained as differences of the energies of five spin distributions (see Supporting Information, sd1, sd2, sd3, sd4 and sd5). In order to check the stability of the calculated J values with the choice of the spin distributions, we have calculated two additional spin distributions using the B3LYP functional (see Supporting Information, sd6 and sd7) and performing a least-squares fitting to the six equations system. The new values corresponding to the B3LYP functional are almost identical to those obtained previously, confirming their small dependence with the choice of the spin distributions. However, in the case of the PBE functional the changes are slightly larger probably due to the bigger variations of the atomic local spin values (see Table S1, Supporting Information) that would result in a larger deviation of the phenomenological Heisenberg Hamiltonian, in which such value is assumed as a constant.

Table 1. Description of the bridging ligands, average Fe...Fe distances, bond angles and calculated exchange coupling constants J [cm⁻¹] for the Fe₈ complex.^[a]

| | Bridging ligands | $d(\text{Fe}\cdots\text{Fe})$ [Å] | Fe-O-Fe [°] | J_{PBE} | J_{B3LYP} | J_{prop} |
|----------|---------------------------------|-----------------------------------|-------------|------------------|--------------------|-------------------|
| J_{12} | (O ²⁻) ₂ | 2.938 | 96.9 | +28.9 (+26.4) | +5.1 (+4.7) | -25, -20, -25 |
| J_{15} | (OH ⁻) ₂ | 3.448 | 99.9 | -9.2 (-11.3) | -10.4 (-10.7) | -18, -15, -15 |
| J_{37} | OH ⁻ | 3.534 | 126.5 | -14.4 (-13.1) | -34.1 (-34.1) | -41, -35, -40 |
| J_{13} | O ²⁻ | 3.046 | 128.8 | -55.8 (-56.3) | -66.5 (-66.4) | -120, -120, -140 |

[a] The results with the PBE functional and numerical functions were obtained with the SIESTA code whilst those with the B3LYP hybrid functional with the Gaussian98 code (values in parenthesis are those obtained with a least-squares fitting of six equations). Values proposed to reproduce the experimental magnetic susceptibility curve are also indicated (J_{prop}).^[22–24]

The large number of states ($6^8=1.6\cdot 10^6$ states) present in the Fe₈ complex makes it impossible to perform a fitting of the measured magnetic susceptibility to obtain the four different J values (see Figure 1) as usually done for smaller molecules. Thus, some authors have proposed sets of J values that approximately reproduce the experimental magnetic susceptibility curve using as reference the J values obtained for similar exchange pathways in dinuclear complexes.^[22–24] Comparison of such values with the calculated ones allows us to extract some conclusions: i) the J_{15} , J_{37} and J_{13} constants correspond to antiferromagnetic coupling in all cases, J_{15} and J_{13} being the weakest and strongest interactions, respectively; ii) the sign and the relative strength of such calculated interactions using either functionals agree well with those proposed earlier to reproduce the experimental magnetic susceptibility but the calculated values are smaller; and iii) the calculated J_{12} values indicates a weak ferromagnetic interaction between the two central iron atoms, in contrast with antiferromagnetic values previously proposed for such interaction.

Hendrickson et al. and Overgaard et al. have shown for Fe₄ butterfly complexes that the influence of the J_{12} constant on the shape of the magnetic susceptibility curve is very small, due to its weakness and the presence of four stronger J_{13} couplings.^[25,26] As a result, an accurate estimation of such

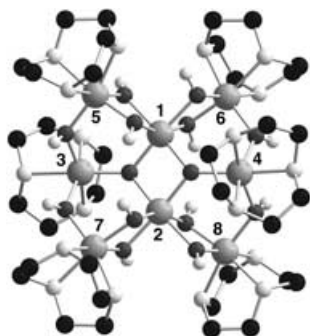


Figure 1. Representation of the molecular structure of the $[\text{Fe}_8\text{O}_8(\text{OH})_{12}(\text{tacn})_6]^{8+}$ complex (tacn = 1,4,7-triazacyclononane). The carbon, oxygen, iron, nitrogen, and hydrogen atoms are represented by spheres of different shades of gray, from dark to bright, respectively. The labels of the iron atom are employed to describe the four different exchange coupling constants (J_{12} , J_{15} , J_{37} and J_{13}). There is one J_{12} coupling constant between the two central iron atoms and four for each of the other three types of interaction.

interaction from the magnetic susceptibility is very difficult. Recently, ferromagnetic couplings have been obtained via interactions through a double oxo-bridge in Fe_6 complexes.^[27,28] From all these data, we can conclude that a relatively weak ferromagnetic or antiferromagnetic coupling should be expected for such kind of interactions depending on the geometry of the framework. The relative strength of the exchange interactions follows a trend previously noticed from theoretical and experimental data, that the single bridging ligand pathways show the strongest antiferromagnetic coupling (see Table 1), stronger for the oxo than for the hydroxo bridge.^[22,23]

Magnetic susceptibility and Monte Carlo simulations: In order to compare the calculated exchange coupling constants directly with the experimental data, we have undertaken the calculation of the magnetic susceptibility from calculated J values by exact diagonalization of the Hamiltonian matrix using the MAGPACK code.^[29] The calculated curves are represented together with the experimental one in Figure 2. The “experimental” curve corresponds to that obtained using the proposed J values,^[23] that fit correctly the experimental points and does not include the zero-field splitting contributions. Clearly, the curve generated with the J values obtained with the B3LYP functional shows an excellent agreement with the experimental values whilst the susceptibility curve obtained with the J values from the PBE functional and numerical functions are considerably different. It is worth noting how sensitive the shape of the susceptibility curve is relative to the J values. Thus, relatively similar sets of theoretical values, such as those obtained theoretically (see Table 1), give completely different curves. Likewise, the experimental value^[30] of the excitation energy between the ground state and the first excited $S=9$ state (24.5 cm^{-1}) is well reproduced by the eigenvalues obtained through exact diagonalization using the B3LYP J values (30.5 cm^{-1}), while a much smaller excitation energy is obtained with the PBE functional (4.5 cm^{-1}). Nevertheless,

both theoretical approaches reproduce correctly the spin values of the ground and the first excited state determined from inelastic neutron scattering.

The use of the exact diagonalization procedure to obtain magnetic susceptibilities is considerably limited by the size

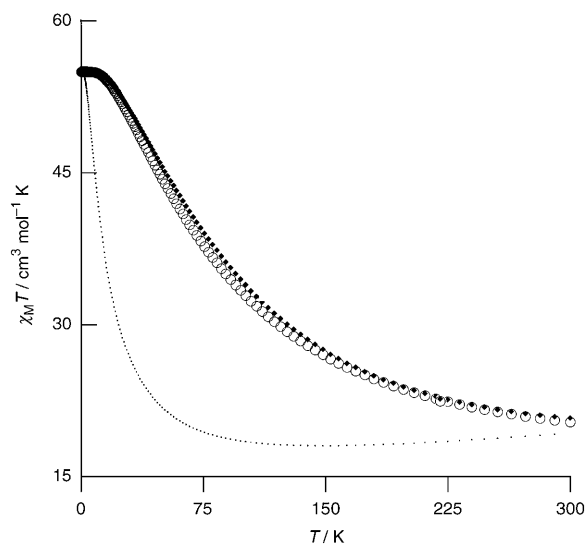


Figure 2. Calculated magnetic susceptibility curves for the Fe_8 complex obtained by exact diagonalization compared with the experimental data. The bold dotted line has been calculated with the B3LYP/Gaussian (\blacklozenge) coupling constants and the dotted line corresponds to the PBE values (\bullet) obtained with the SIESTA code. The experimental values (\circ) correspond to one of the proposed sets of J values that fit correctly the experimental points and does not include the zero-field splitting contributions to allow for comparison with the theoretical results.^[23]

of the systems. The Fe_8 complex is close to the limit of applicability of such an approach with state-of-the-art computational resources. Thus, it is an excellent benchmark to check the accuracy of approximate methods that could be employed with larger systems for which the exact diagonalization cannot be applied. Some of the approximate methods most commonly employed to obtain the magnetic susceptibility are those based on Monte Carlo simulations. We can classify them in two groups: The first one constituted by the methods commonly known as classical Monte Carlo based on a Metropolis algorithm that can be applied successfully only to systems with large local spin values, for instance $S = 5/2$ in Fe^{III} or Mn^{II} complexes.^[31,32] In such a method, the energy and probability of the spin flip is obtained as the interaction of two non-quantized spins. A sampling of states is thus generated to calculate the average magnetization M by using Equation (2), that preferentially includes the configurations that bring important contributions at temperature T .

$$\langle M \rangle = \frac{\sum_{i=1}^n M_i e^{-E_i/kt}}{\sum_{i=1}^n e^{-E_i/kt}} \quad (2)$$

The magnetic susceptibility, χ_m , can be obtained from the fluctuations in the magnetization by employing Equation (3), where $\langle M \rangle$ and $\langle M^2 \rangle$ are the mean values of M and M^2 .

$$\chi = (\langle M^2 \rangle - \langle M \rangle^2) / kT \quad (3)$$

The number of steps in the Monte Carlo simulation for each temperature is $5 \cdot 10^7 / T$ (T in K). Thus, we include more steps in the sampling at low temperature because it is more difficult to describe correctly the magnetic behavior at such temperatures. A 10% of the steps are employed for the thermalization of the system.

The second group of Monte Carlo methods are those extensions that allow to treat quantum spin systems including local spins of $S = 1/2$, usually called quantum Monte Carlo methods.^[33] Among them we have employed the Decoupled Cell Monte Carlo Method (DCM) proposed by Homma et al.^[34] and a modification of such approach proposed by Miyazawa et al.^[35] that improves the results at low temperature (mDCM). The basic idea of such methods is to perform the exact diagonalization only for a subsystem, the decoupled cell. The conditional probability of a spin placed in the center of the subsystem being up or down is obtained from these exact diagonalization procedures, then it is possible to construct a Markov chain of a quantum system by using the Metropolis algorithm as in the Classical Monte Carlo approach. Due to the incompleteness of these subsystems, there are truncated interactions between some paramagnetic centers, especially in the simplest subsystem that is formed by a central spin and its first neighbors. For such centers, the mDCM method includes also in the calculation of the probability of the spin flip, the results obtained using other subsystems built up with different central spins and where the spin candidate to flip is included. In general, the quality of such quantum methods depends on the size of the subsystem employed in the calculation of the probabilities, being hypothetically exact when the whole system is considered. It is known that the proper shape and size of a cell depend on the type of lattice,^[36] being especially difficult for the mDCM method when the second-neighbor interactions are considered, which is our case.

The results of the three Monte Carlo approaches described above for the calculation of magnetic susceptibility of the Fe_8 complex by using the exchange coupling constants obtained with the B3LYP method are shown in Figure 3. As expected, the classical Monte Carlo method provides reasonable values only down to 140 K, while the limit is extended to 80 K with quantum Monte Carlo methods using a DCM approach with a decoupled cell including only first neighbors (black triangles in Figure 3). However, the DCM quantum method fails at low temperature due to the small size of the cell considered for the outermost iron atoms (see Figure 1), where only subsystems of three Fe centers have been considered. Such results can be considerably improved by extending the decoupled cell for such external center to five centers (black squares in Figure 3). Finally, it is worth

noting that the mDCM method^[37] correctly describes the shape of the susceptibility curve at low temperature, at difference with other Monte Carlo methods. However, at high temperature it provides results closer to the classical Monte Carlo method than to the DCM method or the exact diagonalization.

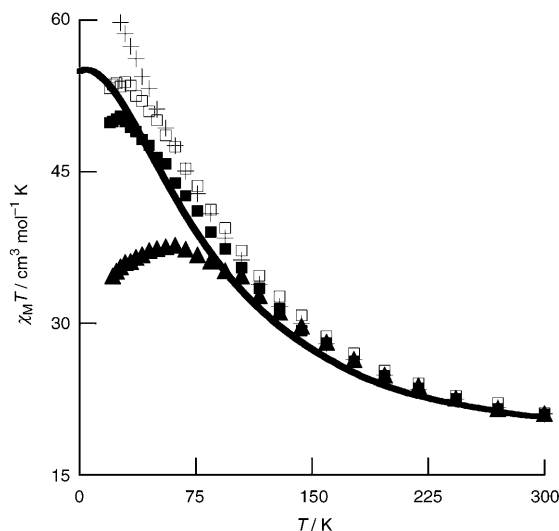


Figure 3. Magnetic susceptibility curves for the Fe_8 complex obtained by exact diagonalization with the B3LYP J values (—) and also shown are the results for Classical Monte Carlo (+) and quantum Monte Carlo methods (\blacktriangle) and DCM approach with two different cells (\blacksquare), mDCM method (\square).

Spin density distribution: Finally, we have analyzed the distribution of the spin density in the Fe_8 complex (Figure 4, detailed atomic spin populations are provided as Supporting Information). The spin density is mostly localized at the Fe^{III} cations, with local magnetic moments between 4.10 and 4.17 calculated with the natural bond orbital method^[38] (or between 4.18 and 4.25 using a Mulliken population analysis). Significant spin delocalization towards donor atoms is observed, mostly associated to the σ antibonding e_g electrons.^[39] The oxygen atoms of the central bridges have positive spin densities because they are each surrounded by two Fe^{III} cations with positive spin density and only one with negative spin. Pontillon et al., using polarized neutron diffraction, have obtained a non-symmetric spin distribution for the Fe_8 complex with small local moments for some Fe^{III} cations,^[40] between 1.94 and 4.91 e^- . They argue that the reason for such values is the existence of configuration interaction in the ground state. However, this fact cannot explain the asymmetry of the magnetic moments of for example, the Fe3 and Fe4 cations (see Figure 1 for labeling scheme), with calculated values of 1.94 and 4.91 e^- , respectively.

In conclusion, despite the computational difficulties associated to the small energy differences involved in the exchange coupling interactions, theoretical methods based on density functional theory provide excellent results when compared with the available experimental data. The combi-

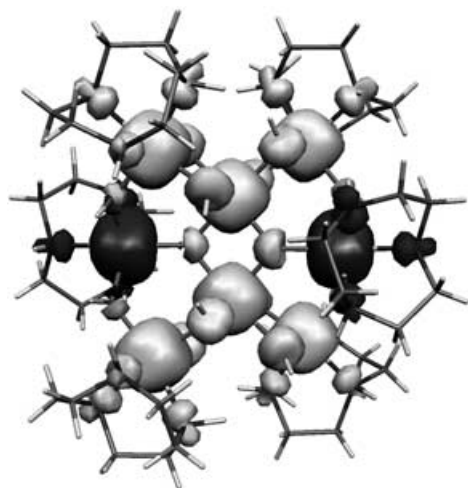


Figure 4. Representation of the spin density map calculated at the B3LYP level for the single-determinant ground state of the Fe_8 complex (clear and dark regions indicate positive and negative spin populations, respectively). The isodensity surface corresponds to a value of $0.01 \text{ e}^- / \text{bohr}^3$.

nation of density functional methods with Monte Carlo simulations opens up a wider range of applications to larger systems, allowing for a more detailed knowledge of the different exchange interactions involved than is possible from the experimental data. This knowledge will facilitate a better understanding of the correlation between magnetic properties and geometric structure in this kind of complex polynuclear systems that will ultimately permit a rationalization of the properties despite the traditionally serendipitous process used to obtain new single-molecule magnets.

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