

Energy Spectrum of the Fe₄ Molecular Magnet

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We present a theoretical analysis of the energy spectrum of the magnetic molecular cluster Fe₄(OCH₃)(dpm)₆. Using a Heisenberg exchange model we obtain an expression for the energy levels and investigate how these are affected by asymmetry of the cluster. An analytical expression for the tunnel splitting is derived and we establish the existence of diabolical points in the magnetic field spectrum and their dependence on high order anisotropy.

Magnetic molecular clusters have been extensively researched in recent years, primarily because they exhibit interesting phenomena such as quantum spin tunneling, topological interference effects and exact degeneracies at so-called “diabolical points” in magnetic field space [1,2]. In the past decade, the majority of research has been conducted on the Mn₁₂ and Fe₈ clusters, both of which have a $S = 10$ ground state. The more recently synthesised Fe₄ cluster, with an $S = 5$ ground state, has been the subject of some experimental work but as far as we know there has been no published theoretical analysis. In this paper we discuss various aspects of its energy spectrum which are of importance to the aforementioned quantum phenomena.

As illustrated in Fig. 1(a), the Fe₄ cluster consists of four $S = 5/2$ Fe ions lying in a plane forming an (almost) equilateral triangle. The observed $S = 5$ ground state can be understood as arising from ferromagnetically aligned corner spins coupled antiferromagnetically to the central spin, with the associated exchange constants J_1 and J_2 as shown in Fig. 1(b). The parameters e and μ are used to account for the fact that in reality the system is not perfectly equilateral.

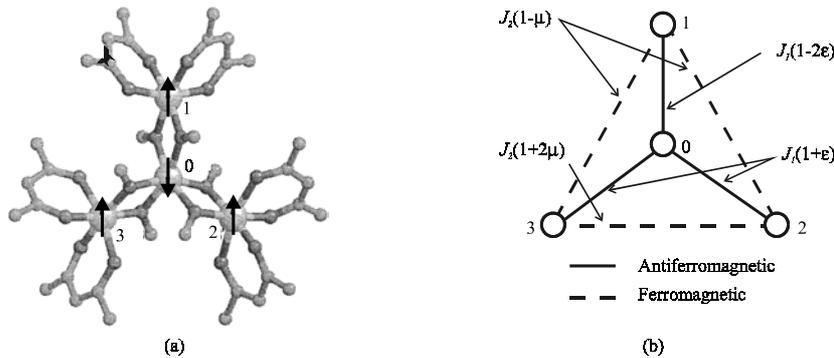


Fig. 1 – (a) The Fe₄ cluster (from [3]), (b) a model of the exchange interactions.

The energy levels are determined by a Heisenberg Hamiltonian,

$$H = \sum_{\langle ij \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

and in general must be obtained numerically, although in the perfectly equilateral case for which $\varepsilon = \mu = 0$ we can derive an analytical expression. The spin operators $\mathbf{S}_p = \mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3$ and $\mathbf{S}_t = \mathbf{S}_0 + \mathbf{S}_p$ are mutually commuting, so after some manipulations we may express the energy levels in terms of the quantum numbers S_p and S_t :

$$E(S_p, S_t) = -\frac{1}{2}(J_1 + J_2)S_p(S_p + 1) + \frac{1}{2}J_1S_t(S_t + 1) - \frac{35}{8}(J_1 - 3J_2)$$

Using experimentally obtained values for the exchange constants [4], we find that the first excited state is a doubly degenerate $S_t = 4$ state lying 86.3K above the ground state, followed by a triply degenerate $S_t = 3$ state, in agreement with independent experimental results [3]. To establish qualitatively the effect of the structure not being perfectly equilateral we have numerically diagonalized the Hamiltonian matrix for the case of small nonzero ε, μ and found that this splits the otherwise degenerate states, as expected since the threefold symmetry of the cluster has been removed.

On a finer scale each state is split by fine structure terms in the Hamiltonian and external magnetic fields. At low temperature we can assume that the cluster remains in its ground state and thus treat it as an $S = 5$ object, with the second order spin Hamiltonian:

$$H = D(\mathbf{S}_z^2 - S(S+1)/3) + E(\mathbf{S}_x^2 - \mathbf{S}_y^2) - g\mu_B \mathbf{B} \cdot \mathbf{S}$$

where D and E are the standard axial and transverse anisotropy coefficients respectively. Rearranging and discarding a constant term yields a more convenient form [2]:

$$H = -k_1 \mathbf{S}_z^2 - k_1 \delta \mathbf{S}_y^2 - g\mu_B \mathbf{B} \cdot \mathbf{S} \\ = -k_1 \mathbf{S}_z^2 - (k_1 \delta / 4)(\mathbf{S}_+ \mathbf{S}_- + \mathbf{S}_- \mathbf{S}_+ - \mathbf{S}_+ \mathbf{S}_+ - \mathbf{S}_- \mathbf{S}_-) - g\mu_B \mathbf{B} \cdot \mathbf{S}$$

where $k_1 = -D + E$ and $\delta = 2E/(E - D)$. Using the coefficients D and E evaluated in [5], we determine $k_1 = 0.32\text{K}$ and $\delta = 0.18$. In zero field an anisotropy barrier of approximately $25k_1 \sim 8\text{K}$ prevents reversal of the magnetization. Due to the transverse anisotropy of the Fe_4 system the coefficient δ is nonzero, so the second term causes mixing between states with $S_z = \pm 5, \pm 3, \pm 1$ and those with $S_z = \pm 4, \pm 2, 0$. There is a transition matrix element coupling states on either side of the anisotropy barrier so that tunneling between them is allowed. S_z is not a good quantum number and the pairs of states approximately described by $\pm S_z$ are split in energy. This splitting between states on either side of the anisotropy barrier is important to the quantum spin tunneling process, and due to the symmetry of the Hamiltonian we can obtain an analytical expression for this splitting in the zero field case. As we are primarily interested in the splitting between the lowest pair of levels, approximately described by $S_z = \pm 5$, we look at the sector spanning the states $S_z = \pm 5, \pm 3, \pm 1$. We define a symmetric subspace

$$|\alpha\rangle = 1/\sqrt{2}(|5\rangle + |-5\rangle) \\ |\beta\rangle = 1/\sqrt{2}(|3\rangle + |-3\rangle) \\ |\gamma\rangle = 1/\sqrt{2}(|1\rangle + |-1\rangle)$$

and find the 3×3 Hamiltonian matrix in this basis. Solving the cubic secular equation perturbatively we obtain the lowest eigenvalue in this sector in terms of δ . We repeat the process in the antisymmetric subspace, and find that the expressions are identical up to terms of order δ^4 , so that the splitting is given by $\Delta = k_1(1575/32768 \delta^5 + \dots) \approx 3.48\mu\text{K}$.

The most interesting aspect of the ground state multiplet structure is the behaviour of the levels in the presence of an external magnetic field. Experimental observations on Fe_8 have shown that the splitting between pairs of energy levels oscillates in the presence of a magnetic field [6]. It has recently been theoretically determined that these oscillations should go to exactly zero at special points known as ‘‘diabolical points’’, where the degeneracy cannot be explained by any obvious symmetry in the Hamiltonian [2]. It is of interest to evaluate if such points exist in the Fe_4 spectrum and whether or not the semiclassical and

perturbation theory approaches developed with Fe_8 in mind can effectively predict the location of these points in the Fe_4 system. In Fig. 2 we show the splitting between the lowest pair of states as a function of reduced transverse field $b_x \equiv g\mu_B B_x / 2k_1 S$, obtained from a full diagonalization of the 11×11 Hamiltonian matrix.

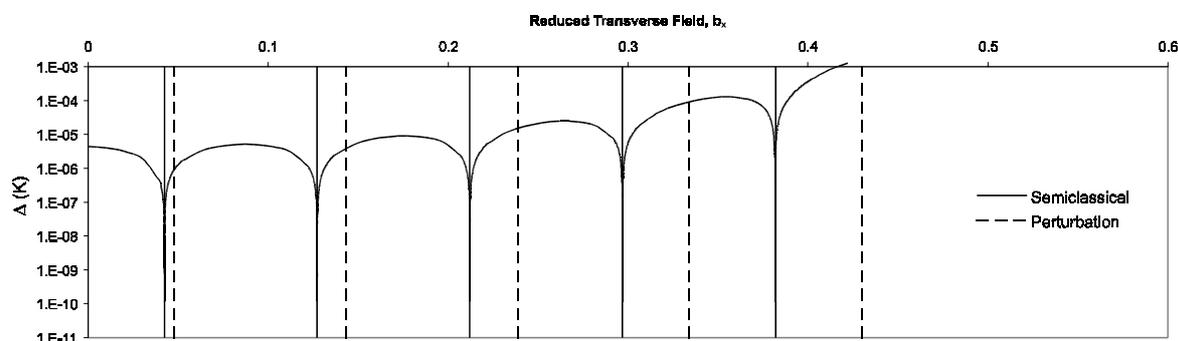


Fig. 2 – Tunnel splitting Δ between the lowest two levels in a transverse field.

One can clearly see points at which Δ becomes zero to within numerical accuracy, and we believe these are points of exact degeneracy. Although the perturbation theory approach is not able to predict accurately the location of such points, the semiclassical approach is clearly very accurate even for this small spin of five, which supports Garg's assertion that it may in fact be exact. It was also found that there is a set of exact degeneracies between the next highest pair of states located at regular intervals parallel to the b_x axis at a nonzero longitudinal field b_z , and these are once again accurately predicted by the semiclassical approach. To the best of our knowledge, diabolical points have only been predicted for second order crystal field Hamiltonians, so we have investigated the effect of including higher order anisotropy terms using the coefficients quoted in [5]. There appears to be little effect on the degeneracies between the lowest pair, although the degeneracies between the next highest pair are no longer observed parallel to the b_x axis but are found at other points in the b_x - b_z plane. Experimental observation of diabolical points in the Fe_4 spectrum remains an open problem. The experimental technique which was applied to Fe_8 would be well suited to Fe_4 , since the magnitudes of the splitting and magnetic fields required are similar, although Fe_4 would require temperatures as low as 0.1K to prevent higher levels from becoming populated.

Although many aspects of the energy spectrum of Fe_4 are well understood, there is still scope for further theoretical developments. Specifically there is a need for a more quantitative understanding of the effect of the structure not being equilateral and the effect that high order anisotropies have on the location of diabolical points in the spectrum.

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