

# Frustration effects in antiferromagnetic molecules: the cuboctahedron

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## Abstract

Frustration of magnetic systems which is caused by competing interactions is the driving force of several unusual phenomena such as plateaus and jumps of the magnetization curve as well as of unusual energy spectra with for instance many singlet levels below the first triplet state. The antiferromagnetic cuboctahedron can serve as a paradigmatic example of certain frustrated antiferromagnets. In addition it has the advantage that its complete energy spectrum can be obtained up to individual spin quantum numbers of  $s = 3/2$  (16,777,216 states).

*Key words:* Magnetic Molecules, Heisenberg model, Antiferromagnets, Frustration, Energy spectrum

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## 1 Introduction

The magnetism of antiferromagnetically coupled and geometrically frustrated spin systems is a fascinating subject due to the richness of phenomena that are observed [1,2]. Realizations of such systems exist in one, two, and three dimensions; the most famous being the two-dimensional kagome lattice [2,3,4,5,6,7] and the three-dimensional pyrochlore antiferromagnet [8,9,10,11,12,13,14,15,16].

It is very interesting and from the point of theoretical modeling appealing that similar but zero-dimensional spin systems – in the form of magnetic

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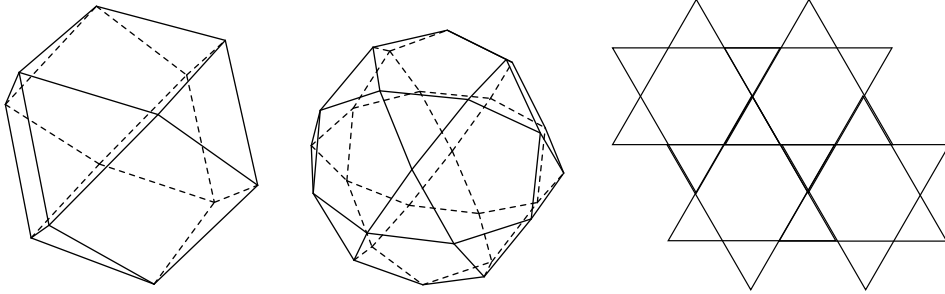


Fig. 1. Cuboctahedron, icosidodecahedron, and (part of the) kagome lattice

molecules [17,18,19,20,21] – exist that potentially could show many of the special features of geometrically frustrated antiferromagnets. Figure 1 displays the zero-dimensional “little brothers” of the kagome antiferromagnet: the cuboctahedron which consists of squares surrounded by triangles and the icosidodecahedron which consists of pentagons surrounded by triangles. Such finite size antiferromagnets offer the possibility to discover and understand properties that are shared by the infinitely extended lattices. An example is the discovery of localized independent magnons [6,22], which explain the unusual magnetization jump at the saturation field. Also the plateau at  $1/3$  of the saturation magnetization that appears in systems built of corner sharing triangles could be more deeply investigated by looking at the cuboctahedron and the icosidodecahedron [23,24].

In this article we continue investigations along this line. We focus on two points. First we discuss the physics of the regular cuboctahedron as a function of the single spin quantum number  $s = 1/2, 1, 3/2$ . For these cases all energy eigenvalues could be obtained with the help of Irreducible Tensor Operator (ITO) techniques [25,26,27] and by application of point group symmetries. As a second point we investigate irregular cuboctahedra. This study is motivated by recent magnetization measurements of the icosidodecahedral molecules  $\{\text{Mo}_{72}\text{Fe}_{30}\}$  [18] and  $\{\text{Mo}_{72}\text{Cr}_{30}\}$  [20] published in Ref. [28] which could successfully be interpreted by a *classical* Heisenberg model with random antiferromagnetic exchange couplings between the paramagnetic ions.

## 2 Theoretical model

The physics of many of the mentioned spin systems can be well understood with the help of the isotropic Heisenberg model,

$$\tilde{H} = -2 \sum_{u < v} J_{uv} \vec{\tilde{s}}(u) \cdot \vec{\tilde{s}}(v) . \quad (1)$$

Here the sum runs over pairs of spins given by spin operators  $\vec{S}$  at sites  $u$  and  $v$ . A negative value of the exchange interaction  $J_{uv}$  corresponds to antiferromagnetic coupling. We refer to a regular body, e.g. cuboctahedron, if there are only nearest neighbor couplings of constant size  $J$ . In the case of an irregular coupling the nearest-neighbor couplings can assume values according to the chosen distribution.

Since the Hamiltonian commutes with the total spin, we can find a common eigenbasis  $\{|\nu\rangle\}$  of  $\tilde{H}$ ,  $\tilde{S}^2$ , and  $\tilde{S}_z$  and denote the related eigenvalues by  $E_\nu$ ,  $S_\nu$ , and  $M_\nu$ , respectively. The eigenvalues of (1) are evaluated in mutually orthogonal subspaces  $\mathcal{H}(S, M)$  of total spin  $S$  and total magnetic quantum number  $M$  using Irreducible Tensor Operator (ITO) techniques [25,26,27]. In addition point group symmetries have been applied for the regular cuboctahedron.

### 3 The regular cuboctahedron

The regular cuboctahedron belongs to the class of geometrically frustrated antiferromagnets built of corner-sharing triangles. Such systems possess an extended magnetization plateau at  $1/3$  of the saturation magnetization  $\mathcal{M}_{\text{sat}}$  caused by dominant up-up-down contributions [23,24], an unusually high jump of the magnetization at the saturation field due to independent magnons [22,6] as well as low-lying singlets below the first triplet level [29,30,24]. These features are shared for instance by the icosidodecahedron and by the kagome lattice.

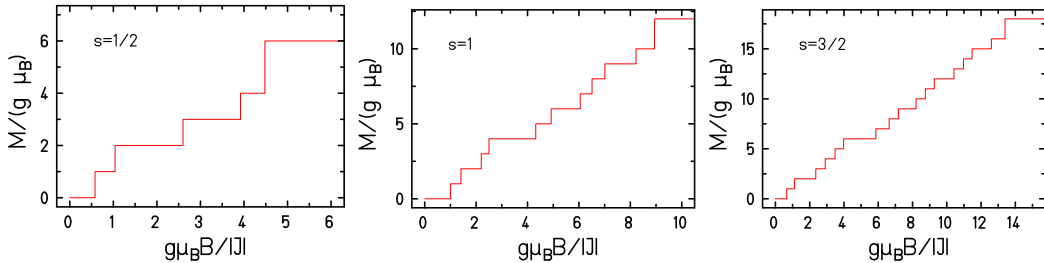


Fig. 2. Magnetization as a function of applied field at  $T = 0$  for the regular cuboctahedron with  $s = 1/2$ ,  $s = 1$ , and  $s = 3/2$ . The extended plateau at  $\mathcal{M}_{\text{sat}}/3$  is clearly visible.

Figure 2 shows the magnetization curves at  $T = 0$  for the regular cuboctahedron with  $s = 1/2$ ,  $s = 1$ , and  $s = 3/2$ . These curves show besides the plateau at  $\mathcal{M}_{\text{sat}}/3$  a jump to saturation of height  $\Delta M = 2$ . Both features are reflected by the differential susceptibility function which is displayed in Fig. 3. Each step in Fig. 2 corresponds to a peak in Fig. 3. One notices that the peaks are washed out for higher temperatures, but that the minimum that

corresponds to the plateau at  $\mathcal{M}_{\text{sat}}/3$  persists up to temperatures of the order of the exchange coupling.

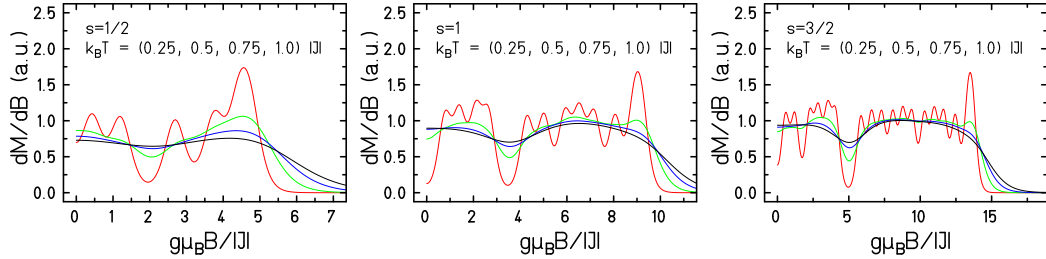


Fig. 3. Differential susceptibility as a function of applied field at  $k_B T/|J| = 0.25, 0.5, 0.75, 1.0$  for the regular cuboctahedron with  $s = 1/2$ ,  $s = 1$ , and  $s = 3/2$ . The smoother the curve, the higher the temperature.

As a function of the intrinsic spin  $s$  the differential susceptibility  $d\mathcal{M}/dB$  exhibits two properties. With increasing spin quantum number  $s$  the individual peaks oscillate more and more with smaller relative amplitude, but the minimum at  $1/3$  is actually sharpened. It is known that in the classical limit, i.e. for  $s \rightarrow \infty$ , the differential susceptibility is practically flat below the saturation field except for the dip at  $1/3$  [23].

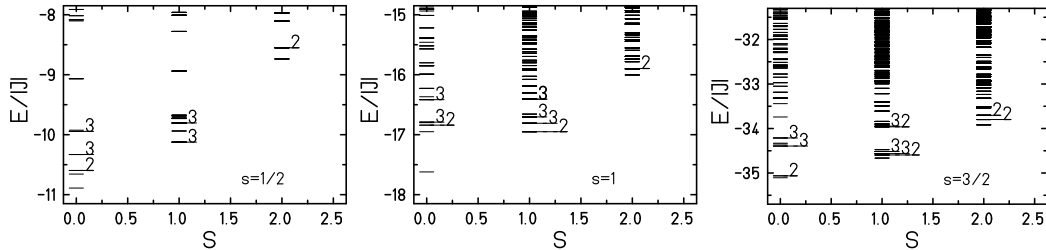


Fig. 4. Low-lying energy levels for the regular cuboctahedron with  $s = 1/2$ ,  $s = 1$ , and  $s = 3/2$ . Numbers attached to selected levels denote their multiplicities  $d_S$ ; unlabeled levels below the highest labeled level have  $d_S = 1$ .

For zero field Fig. 4 shows the low-lying energy levels. In the case of  $s = 1/2$  (l.h.s. of Fig. 4) one notices the low-lying singlets below the first triplet. These states are a cornerstone of geometric frustration and as well present in the kagome lattice and the icosidodecahedron with  $s = 1/2$  [29]. It is interesting to note that with increasing  $s$ , i.e. towards a more classical behavior, the number of these states decreases. For  $s = 1$  (middle of Fig. 4) the first excited singlet level is already (slightly) above the lowest triplet level. For  $s = 3/2$  (r.h.s. of Fig. 4) a doubly degenerate excited singlet level remains below the lowest triplet, the others have disappeared. This behavior, i.e. no excited singlets below the lowest triplet for integer spins and a doubly degenerate excited singlet below the lowest triplet, does not change anymore for higher spin quantum numbers as can be checked e.g. by Lanczos methods.

The rather high symmetry of the cuboctahedron leads to many degenerate energy levels. As examples we label some low-lying energy levels in Fig. 4

by their multiplicity  $d_S$ , i.e. by the degeneracy of the whole multiplet. The full degeneracy including the multiplicity of the magnetic sublevels  $d_M$  is then  $d = d_S \times d_M$ . Clearly, such high multiplicities have an important impact on the magnetocaloric behavior since they increase the entropy for low temperatures [30,31]. In the following we would like to discuss the impact of low-lying singlets below the first triplet which in the case of extended lattices are supposed to condense in infinite number onto the ground state.

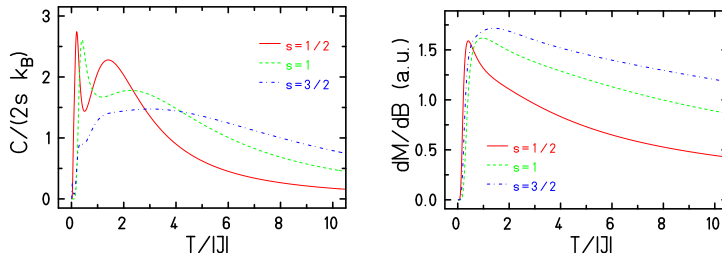


Fig. 5. Heat capacity (l.h.s.) and zero-field susceptibility (r.h.s.) for the regular cuboctahedron with  $s = 1/2$ ,  $s = 1$ , and  $s = 3/2$ .

Figure 5 compares the heat capacity (l.h.s.) and the zero-field susceptibility (r.h.s.) for the regular cuboctahedron with  $s = 1/2$ ,  $s = 1$ , and  $s = 3/2$ . The heat capacity shows a pronounced double peak structure for  $s = 1/2$  and  $s = 1$  which dissolves into a broad peak with increasing spin quantum number. The broad peak also moves to higher temperatures with increasing  $s$ . The reason for the first sharp peak is twofold. Since there are several gaps between the low-lying levels the density of states has a very discontinuous structure which results in the double peak structure. For  $s = 1/2$  the low-lying singlets provide a very low-lying non-magnetic density of states which is responsible for the fact that the first sharp peak is at such low temperatures. For  $s = 1$  the first sharp peak results from both excited singlet as well as lowest triplet levels. For  $s = 3/2$  a remnant of the first sharp peak is still visible; it is given by the low-lying singlets, but since they are so few, also influenced by the lowest triplet levels.

The behavior of the heat capacity is contrasted by the susceptibility on the r.h.s. of Fig. 5 which reflects mostly the density of states of magnetic levels and is only weakly influenced by low-lying singlets. Therefore, the first sharp peak, or any other structure at very low temperatures, is absent .

#### 4 The irregular cuboctahedron

In this section we investigate how the magnetic properties of the cuboctahedron change if random variations of the exchange coupling parameters are introduced. This study is motivated by recent magnetization measurements

of the icosidodecahedral molecules  $\{\text{Mo}_{72}\text{Fe}_{30}\}$  [18] and  $\{\text{Mo}_{72}\text{Cr}_{30}\}$  [20] published in Ref. [28], which were interpreted by assuming random distributions of exchange parameters in a classical Heisenberg model description.

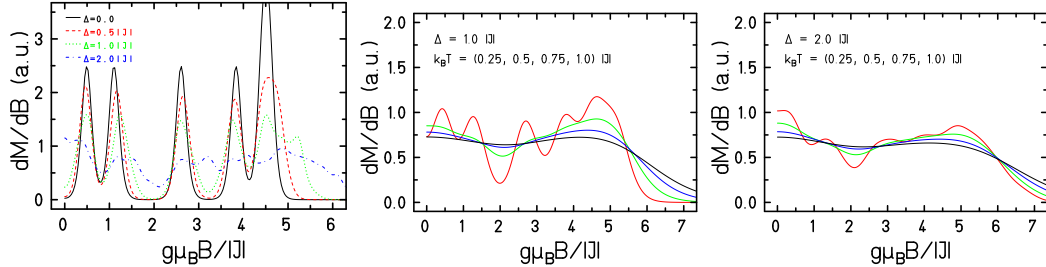


Fig. 6. Differential susceptibility as a function of applied field for the irregular cuboctahedron with  $s = 1/2$ . L.h.s.: dependence on the width  $\Delta$  of the random distribution. Middle: dependence on the temperature  $k_B T/|J| = 0.25, 0.5, 0.75, 1.0$  for  $\Delta = 1.0|J|$ . R.h.s.: same as middle for  $\Delta = 2.0|J|$ .

We introduce variations of the exchange parameters of the Hamiltonian (1) by replacing the common nearest neighbor exchange parameter  $J_{uv} = J$  with values of a flat random distribution  $J - 0.5\Delta \leq J_{uv} \leq J + 0.5\Delta$ . Thus the mean exchange parameter is kept to be  $J$ . In order to gain sufficient statistical certainty we use ensembles of 10,000 spectra for realizations of the irregular cuboctahedron with  $s = 1/2$ ; the results do not deviate from those for 1,000 realizations. For larger  $s$  the production of sufficiently large ensembles is hindered by prohibitively many diagonalizations of larger matrices.

Figure 6 shows the differential susceptibility that results from averages using distributions with various  $\Delta$ . The figure on the l.h.s. compares  $d\mathcal{M}/dB$  at the rather low temperature of  $k_B T = 0.1|J|$  for  $\Delta = 0$ , i.e. the regular cuboctahedron, with  $\Delta = 0.5|J|$ ,  $\Delta = 1.0|J|$ , and  $\Delta = 2.0|J|$ . One clearly sees that the pattern which mainly originates from ground state level crossings does not change much for  $\Delta = 0.5|J|$  and  $\Delta = 1.0|J|$ . It needs a variation as large as  $\Delta = 2.0|J|$ , i.e. ferromagnetic interactions occur, to qualitatively change the differential susceptibility function. The reason is that smaller variations do not alter the structure of low-lying energy gaps. The singlet-triplet gap, which is approximately  $0.765|J|$ , does not vary very much for the ensembles with smaller  $\Delta$ , and so does the singlet-triplet crossing which is determined by the singlet-triplet gap. It needs an appreciable variance of the exchange parameter distribution in order to impose large variations of the level crossing fields.

The middle and the r.h.s. of Fig. 6 display  $d\mathcal{M}/dB$  for temperatures  $k_B T/|J| = 0.25, 0.5, 0.75, 1.0$  and  $\Delta = 1.0|J|$  and  $\Delta = 2.0|J|$ , respectively. As already explained, there is only very little difference between the behavior of an irregular cuboctahedron with  $\Delta = 1.0|J|$  (middle) and the regular one. For  $\Delta = 2.0|J|$  (r.h.s.) the differential susceptibility is much more smeared out which includes an appreciable broadening at the saturation field. Considering the irregular cuboctahedron we can conclude that the magnetic properties are rather stable

against random fluctuations of the exchange parameters. This means that the striking behavior especially of the experimental differential susceptibility of  $\{\text{Mo}_{72}\text{Fe}_{30}\}$  and  $\{\text{Mo}_{72}\text{Cr}_{30}\}$  which shows no signs of level crossings at all [28] needs further theoretical exploration of the microscopic origin.

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## References

- [1] A. P. Ramirez, *Annu. Rev. Mater. Sci.* **24** (1994) 453
- [2] J. Greedan, *J. Mater. Chem.* **11** (2001) 37
- [3] H. Diep, editor, *Magnetic systems with competing interactions*, World Scientific, Singapore (1994)
- [4] Y. Narumi, K. Katsumata, Z. Honda, J.-C. Domenge, P. Sindzingre, C. Lhuillier, Y. Shimaoka, T. C. Kobayashi, K. Kindo, *Europhys. Lett.* **65** (2004) 705
- [5] M. E. Zhitomirsky, *Phys. Rev. Lett.* **88** (2002) 057204
- [6] J. Schulenburg, A. Honecker, J. Schnack, J. Richter, H.-J. Schmidt, *Phys. Rev. Lett.* **88** (2002) 167207
- [7] J. L. Atwood, *Nat. Mater.* **1** (2002) 91
- [8] O. Tchernyshyov, R. Moessner, S. L. Sondhi, *Phys. Rev. Lett.* **88** (2002), 6 067203
- [9] R. Moessner, *Can. J. Phys.* **79** (2001) 1283
- [10] S. T. Bramwell, M. J. P. Gingras, *Science* **294** (2001) 1495
- [11] E. Berg, E. Altman, A. Auerbach, *Phys. Rev. Lett.* **90** (2003) 147204
- [12] K. Penc, N. Shannon, H. Shiba, *Phys. Rev. Lett.* **93** (2004) 197203
- [13] J.-H. Chung, M. Matsuda, S.-H. Lee, K. Kakurai, H. Ueda, T. J. Sato, H. Takagi, K.-P. Hong, S. Park, *Phys. Rev. Lett.* **95** (2005) 247204

- [14] C. L. Henley, Phys. Rev. Lett. **96** (2006) 047201
- [15] H.-J. Schmidt, J. Richter, R. Moessner, J. Phys. A: Math. Gen. **39** (2006) 10673
- [16] M. E. Zhitomirsky, H. Tsunetsugu, Phys. Rev. B **75** (2007) 224416
- [17] A. J. Blake, R. O. Gould, C. M. Grant, P. E. Y. Milne, S. Parsons, R. E. P. Winpenny, J. Chem. Soc.-Dalton Trans. (1997) 485
- [18] A. Müller, S. Sarkar, S. Q. N. Shah, H. Bögge, M. Schmidtman, S. Sarkar, P. Kögerler, B. Hauptfleisch, A. Trautwein, V. Schünemann, Angew. Chem., Int. Ed. **38** (1999) 3238
- [19] A. Müller, A. M. Todea, J. van Slageren, M. Dressel, H. Bögge, M. Schmidtman, M. Luban, L. Engelhardt, M. Rusu, Angew. Chem., Int. Ed. **44** (2005) 3857
- [20] A. M. Todea, A. Merca, H. Bögge, J. van Slageren, M. Dressel, L. Engelhardt, M. Luban, T. Glaser, M. Henry, A. Müller, Angew. Chem. Int. Ed. **46** (2007) 6106
- [21] C. P. Pradeep, D.-L. Long, P. Kögerler, L. Cronin, Chem. Commun. (2007) 4254
- [22] J. Schnack, H.-J. Schmidt, J. Richter, J. Schulenburg, Eur. Phys. J. B **24** (2001) 475
- [23] C. Schröder, H. Nojiri, J. Schnack, P. Hage, M. Luban, P. Kögerler, Phys. Rev. Lett. **94** (2005) 017205
- [24] I. Rousochatzakis, A. M. Läuchli, F. Mila, Phys. Rev. B **77** (2008) 094420
- [25] D. Gatteschi, L. Pardi, Gazz. Chim. Ital. **123** (1993) 231
- [26] J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado, B. S. Tsukerblat, Inorg. Chem. **38** (1999) 6081
- [27] O. Waldmann, Phys. Rev. B **61** (2000) 6138
- [28] C. Schröder, R. Prozorov, P. Kögerler, M. D. Vannette, X. Fang, M. Luban, A. Matsuo, K. Kindo, A. Müller, A. M. Todea, Phys. Rev. B **77** (2008) 224409
- [29] R. Schmidt, J. Schnack, J. Richter, J. Magn. Magn. Mater. **295** (2005) 164
- [30] J. Schnack, R. Schmidt, J. Richter, Phys. Rev. B **76** (2007) 054413
- [31] A. Honecker, M. E. Zhitomirsky, J. Phys. Conf. Ser., in print; arXiv:0809.4414v1