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Quantum to classical transition for small magnetic clusters in a field

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Abstract
We study the zero-temperature magnetization of small clusters in which the atoms are coupled by an isotropic Heisenberg antiferromagnetic interaction. We obtain either a full or partial energy spectrum. From this we obtain the magnetization curves as a series of steps for finite S. Each step is characterized by the space group symmetry of the cluster and many different representations may be present. We then investigate the classical limit, $S \to \infty$, in which the magnetization curves are typically piecewise smooth curves or straight lines. We find two basic types of behaviour, depending on whether or not the steps are characterized by a single or many different representations. This latter case is associated with extra hidden symmetry.

1. Introduction

Symmetry is an important concept in physics. In cluster physics the symmetry properties of clusters can be used to simplify the problem and so, for instance, to reduce computation times. In this paper the main interest is the symmetry of the ground state of small antiferromagnetic (AFM) Heisenberg clusters and how it changes as a function of external field. We are also interested in the limit of infinite spin length, in which case we obtain classical AFM Heisenberg systems.

In a recent paper [1] we considered the magnetization of eight different clusters of antiferromagnetically coupled ions as a function of the applied magnetic field. The eight clusters have octahedral, icosahedral, fcc and hcp structures and various sizes. The exchange interaction is nearest-neighbour isotropic Heisenberg. We considered both the quantum case with $S = 1/2$ and also the classical case for all these systems.

Although there are some broad similarities between the quantum and classical cases the detailed behaviour is very different. At zero temperature the quantum systems show stepped magnetization curves in which the step width is sometimes constant and sometimes varies in a non-uniform way. (The normalized step height is $1/(2S)$ or occasionally a multiple of this.) The magnetization curve of a classical system is a piecewise smooth curve or a straight line.

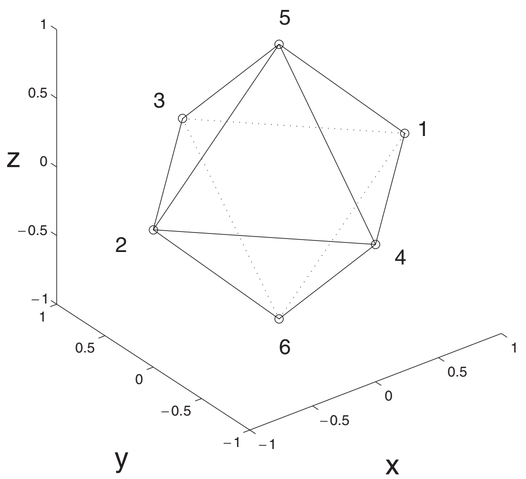

Figure 1. The octahedron, showing the labelling of the sites.

It is to be expected that, if we study quantum systems in which the spin S is increased, then in the limit $S \to \infty$ the classical result should be obtained as the height of the steps tends to 0. However, for the systems we studied numerically in the earlier paper, we were unable to proceed beyond $S = 5/2$ because the size of matrix to be diagonalized becomes too great. For the largest clusters we could only use spin lengths up to $S = 3/2$ and even then it was only possible to obtain the eigenvalues and corresponding eigenstates for the largest values of magnetization.

In this paper we shall mainly consider smaller clusters, up to the octahedron shown in figure 1, with a brief mention of larger clusters.

For several of these we shall obtain the magnetization curves at zero temperature for general S and hence we shall be able to study the limit $S \to \infty$. For clusters larger than the octahedron we are only able to study finite S by directly diagonalizing the Hamiltonian numerically and obtaining the relevant eigenstates. Our main focus will be on the *symmetry* of the lowest-lying states for each value of the magnetization M (the z component of the total spin), which are the only relevant states for the magnetization curve at zero temperature.

The Hamiltonians studied here have extra symmetries in that the space operations, which act on the cluster by permuting the sites and form a point group, are independent of the operations which rotate the spins. The latter form the full rotation group R_3 in the absence of the field and R_2 about the field axis when $B \neq 0$. This is the equivalent of the 'spin-space' group studied earlier [2] adapted to systems with point symmetry. It means that the states of the system can be characterized by a representation of the point group Γ_i and values of total spin T and total z component M. The relevant theory of group representations is described in many standard works, e.g. [3] or [4].

It will be found that in several of the systems studied here extra degeneracies occur when several states of different Γ_i and the same or different T and M have the same energy. These are due to extra symmetries hidden in the Hamiltonian, as is familiar in the degeneracies found in the three-dimensional harmonic oscillator or Coulomb potential.

In this paper we use the notation $\boldsymbol{s}_i$ for a spin of length S at site i, with z component s_i^z. The total spin of the cluster is written $\boldsymbol{t} = \sum_i \boldsymbol{s}_i$ with length T. The z component of this is the magnetization $M = t^z$. $\boldsymbol{t}_k$ refers to a particular combination of two or more spins and has length T_k and z component t_k^z.

2. Pair of spin-S atoms

Although this is very simple it illustrates the general features of most of the clusters. The Hamiltonian is

$$\begin{aligned}\mathcal{H} &= \boldsymbol{s}_1 \cdot \boldsymbol{s}_2 - B(s_1^z + s_2^z) \\ &= \tfrac{1}{2}[(\boldsymbol{s}_1 + \boldsymbol{s}_2)^2 - \boldsymbol{s}_1^2 - \boldsymbol{s}_2^2] - B(s_1^z + s_2^z) \\ &= \tfrac{1}{2}[\boldsymbol{t}^2 - \boldsymbol{s}_1^2 - \boldsymbol{s}_2^2] - Bt^z \\ &= \tfrac{1}{2}[T(T+1) - 2S(S+1)] - BM \end{aligned} \tag{1}$$

where $\boldsymbol{t} = \boldsymbol{s}_1 + \boldsymbol{s}_2$ is the spin of the pair, which in this case equals the total spin. $T(T+1)$ is the eigenvalue of $\boldsymbol{t}^2$ and $T = 0, 1, 2, \ldots, 2S$. $M = t^z$ is the magnetization of the cluster and so $-T \leqslant M \leqslant T$. The lowest energy for a given M is obtained for $T = M$. Crossover from M to $M + 1$ occurs at B given by

$$\tfrac{1}{2}M(M+1) - BM = \tfrac{1}{2}(M+1)(M+2) - B(M+1)$$

i.e. $B = M + 1$. Thus the magnetization curve is a series of steps of equal width 1 and height 1.

To determine the symmetry of each of the states which occur at each step we note that a complete *basis* for the states with given M is the set $|q, M-q\rangle_b$ with $-T+M \leqslant q \leqslant T$. The subscript b indicates a basis state.

The space group of the pair is C_2 with two one-dimensional representations, Γ_1, the identity representation, and Γ_2. Provided $q \neq M - q$, the pair $|q, M-q\rangle_b$, $|M-q, q\rangle_b$ can be written in two linear combinations:

$$\frac{1}{\sqrt{2}}[|q, M-q\rangle_b + |M-q, q\rangle_b] \qquad \text{with symmetry} \quad \Gamma_1$$

and

$$\frac{1}{\sqrt{2}}[|q, M-q\rangle_b - |M-q, q\rangle_b] \qquad \text{with symmetry} \quad \Gamma_2.$$

If $q = M - q$ then there is a single state with symmetry Γ_1.

Starting with the maximum $M = 2S$, there is only one state $|S, S\rangle_b$, so the symmetry is Γ_1. This is clearly an eigenstate with $T = 2S$, $M = 2S$ and energy $E = S^2 - 2BS$. Eigenstates will be written $|T, M\rangle$ without a subscript, so this is $|2S, 2S\rangle$.

For the next highest $M = 2S - 1$ the basis has two states $|S, S-1\rangle_b$ and $|S-1, S\rangle_b$ with linear combinations with symmetries Γ_1 and Γ_2. The allowed values of T are $2S$ and $2S - 1$, so the eigenstates will be $|2S, 2S-1\rangle$ and $|2S-1, 2S-1\rangle$. Since T is a good quantum number the first of these is obtained from $|2S, 2S\rangle$ by operating with the lowering operator t^- and must have the same symmetry Γ_1. The energy is $S^2 - B(2S-1)$. The other state, $|2S-1, 2S-1\rangle$ must have symmetry Γ_2 and it has a lower energy $S(S-2) - B(2S-1)$ since T is lower. In conclusion, the step on the magnetization curve with $M = 2S - 1$ corresponds to a state with symmetry Γ_2.

If $S = \frac{1}{2}$ there are no other steps (we consider only $B \geqslant 0$). For larger S the next highest M is $2S - 2$. The basis has three elements with symmetries Γ_1 (twice) and Γ_2 (once). Two of these have $T > M$ and are obtained from the two $M = 2S - 1$ states by operating with t^- and have the same symmetries. The remaining state with $T = M$ has the lowest energy $S^2 - 4S + 1 - B(2S-2)$ and must have symmetry Γ_1. This is the symmetry of the $M = 2S - 2$ step.

We can now continue the process and find that the symmetry of the steps alternates Γ_1, Γ_2 as M decreases, starting with Γ_1 at the maximum $M = 2S$. The final step, for $0 \leqslant B < 1$, $M = 0$, has symmetry Γ_1 for $2S$ even and Γ_2 for $2S$ odd.

In the limit $S \to \infty$ the magnetization steps become infinitesimal and the magnetization curve becomes the straight line $M = B$ for $0 \leqslant B \leqslant 2S$, with $M = 2S$ for $B > 2S$. The symmetry is Γ_1 for $B > 2S$, but for $0 \leqslant B \leqslant 2S$ there is not a unique symmetry. Instead both Γ_1 and Γ_2 are present with equal weights. The actual form of the classical state in this region is that the two spins point at equal and opposite angles to the z axis.

This result is, to our knowledge, the first full analysis of the symmetry of a *classical* magnetic system in terms of the irreducible representations of the space group.

3. Triangle of spin-S atoms

Three spins arranged in an equilateral triangle with equal exchange between each pair have the Hamiltonian

$$\begin{aligned}\mathcal{H} &= \boldsymbol{s}_1 \cdot \boldsymbol{s}_2 + \boldsymbol{s}_2 \cdot \boldsymbol{s}_3 + \boldsymbol{s}_3 \cdot \boldsymbol{s}_1 - B(s_1^z + s_2^z + s_3^z) \\ &= \tfrac{1}{2}[(\boldsymbol{s}_1 + \boldsymbol{s}_2 + \boldsymbol{s}_3)^2 - \boldsymbol{s}_1^2 - \boldsymbol{s}_2^2 - \boldsymbol{s}_3^2] - B(s_1^z + s_2^z + s_3^z) \\ &= \tfrac{1}{2}[\boldsymbol{t}^2 - \boldsymbol{s}_1^2 - \boldsymbol{s}_2^2 - \boldsymbol{s}_3^2] - Bt^z \\ &= \tfrac{1}{2}[T(T+1) - 3S(S+1)] - BM \end{aligned} \qquad (2)$$

where $\boldsymbol{t} = \boldsymbol{s}_1 + \boldsymbol{s}_2 + \boldsymbol{s}_3$ is the total spin, $T = 0, 1, 2, \ldots, 3S$, and $-T \leqslant M \leqslant T$.

The use of an equilateral triangle is not strictly necessary as any triangular arrangement with equal exchange interactions will produce the same magnetization curve. However, the equilateral triangle is the natural arrangement in this case and will enable us to characterize the eigenstates in terms of the space group $C_{3\mathrm{v}}$ of the equilateral triangle, which is equivalent to the permutation group acting on the three equivalent vertices. The group has six elements and there are [5] two one-dimensional irreducible representations Γ_1 and Γ_2 and one two-dimensional representation Γ_3.

Just as for the pair, the lowest state with a given M has $T = M$. Crossover from M to $M + 1$ occurs at $B = M + 1$.

A complete basis is the set $|a, b, c\rangle_b$ where a, b, c are the z components of the three spins. For a given M the requirement $a + b + c = M$ defines a plane with a normal in the (1, 1, 1) direction. The requirements $-S \leqslant a, b, c \leqslant S$ define a cube centred at the origin. The plane and the cube intersect to form a triangle with corners $(S, S, M - 2S)$, $(S, M - 2S, S)$ and $(M - 2S, S, S)$, provided $M \geqslant S$. For $0 \leqslant M \leqslant S$ the intersection is a six-sided figure with corners at $(S, -S, M)$ and its permutations. We need to find the number of points lying on each of these plane areas and their types.

For conciseness we show only the states with $a \leqslant b \leqslant c$ explicitly in this section.

For example, for $S = 4$, $M = 7$ we have

$$|-1, 4, 4\rangle_b \; |0, 3, 4\rangle_b \; |1, 2, 4\rangle_b \; |1, 3, 3\rangle_b \; |2, 2, 3\rangle_b$$

and for $M = 6$

$$\begin{aligned}&|-2, 4, 4\rangle_b \; |-1, 3, 4\rangle_b \; |0, 2, 4\rangle_b \; |0, 3, 3\rangle_b \; |1, 1, 4\rangle_b \\ &|1, 2, 3\rangle_b \; |2, 2, 2\rangle_b\end{aligned}$$

while for $M = 3$ we have

$$\begin{aligned}&|-4, 3, 4\rangle_b \; |-3, 2, 4\rangle_b \; |-3, 3, 3\rangle_b \; |-2, 1, 4\rangle_b \; |-2, 2, 3\rangle_b \\ &|-1, 0, 4\rangle_b \; |-1, 1, 3\rangle_b \; |-1, 2, 2\rangle_b \; |0, 0, 3\rangle_b \; |0, 1, 2\rangle_b \\ &|1, 1, 1\rangle_b.\end{aligned}$$

Evaluation of all the states for general S, M is somewhat lengthy and is given in appendix A.

A state with $a = b = c$ has symmetry Γ_1. A state with $a = b \neq c$, $a = c \neq b$ or $a \neq b = c$, has three permutations which can be written in linear combinations with symmetries Γ_1 and Γ_3. A state with $a \neq b \neq c$ has six permutations with linear combinations with symmetries Γ_1, Γ_2 and $2 \times \Gamma_3$. (This combination forms the regular representation of the group C_{3v}.) Thus the complete basis for $S = 4$, $M = 7$, for example, has symmetries

$$3(\Gamma_1 + \Gamma_3) + 2(\Gamma_1 + \Gamma_2 + 2\Gamma_3) = 5\Gamma_1 + 2\Gamma_2 + 7\Gamma_3$$

and for $M = 6$

$$\Gamma_1 + 3(\Gamma_1 + \Gamma_3) + 3(\Gamma_1 + \Gamma_2 + 2\Gamma_3) = 7\Gamma_1 + 3\Gamma_2 + 9\Gamma_3.$$

All the states with $M = 7$ have $T \geqslant 7$. Operating on each of these with t^- produces a state with the same symmetry and T but with $M = 6$. Consequently the states with $T = M = 6$ must have symmetries

$$2\Gamma_1 + \Gamma_2 + 2\Gamma_3.$$

Hence there are 7 states in all which form the $M = 6$ step of the magnetization curve.

This method of finding the degeneracies and symmetries of each step is generalized to arbitrary S, arbitrary M in appendix A. The final result is as follows.

For integer S and $M \leqslant S$ there is a cycle of 6 steps with the following symmetries:

$$\begin{aligned}
M &= 6k &&: 2kZ + \Gamma_a \\
M &= 6k+1 &&: 2kZ + \Gamma_b + \Gamma_3 \\
M &= 6k+2 &&: 2kZ + \Gamma_a + 2\Gamma_3 \\
M &= 6k+3 &&: 2kZ + \Gamma_a + 2\Gamma_b + 2\Gamma_3 \\
M &= 6k+4 &&: 2kZ + 2\Gamma_a + \Gamma_b + 3\Gamma_3 \\
M &= 6k+5 &&: 2kZ + \Gamma_a + 2\Gamma_b + 4\Gamma_3
\end{aligned}$$

where $\Gamma_a = \Gamma_1$, $\Gamma_b = \Gamma_2$ if S is even and $\Gamma_a = \Gamma_2$, $\Gamma_b = \Gamma_1$ if S is odd, and $Z = \Gamma_1 + \Gamma_2 + 2\Gamma_3$, the regular representation.

For $S =$ integer $+\frac{1}{2}$ and $M \leqslant S$ there is a cycle of 3:

$$\begin{aligned}
M &= 3k + \tfrac{1}{2} &&: \Gamma_1 + \Gamma_3 + kZ \\
M &= 3k + \tfrac{3}{2} &&: \Gamma_1 + \Gamma_2 + \Gamma_3 + kZ \\
M &= 3k + \tfrac{5}{2} &&: (k+1)Z.
\end{aligned}$$

For $M \geqslant S$, putting $M = 3S - n$, the sequence for all S is

$$\begin{aligned}
n &= 6k &&: kZ + \Gamma_1 \\
n &= 6k+1 &&: kZ + \Gamma_3 \\
n &= 6k+2 &&: kZ + \Gamma_1 + \Gamma_3 \\
n &= 6k+3 &&: kZ + \Gamma_1 + \Gamma_2 + \Gamma_3 \\
n &= 6k+4 &&: kZ + \Gamma_1 + 2\Gamma_3 \\
n &= 6k+5 &&: (k+1)Z.
\end{aligned}$$

For large S, and in the classical limit $S \to \infty$, the steps have massive degeneracy, and each representation is present with large multiplicity. Also we note that, for large S with M not close to 0 or $3S$, the dominant feature is a multiple of Z. Therefore we conclude that the dominant symmetry of the corresponding classical system is defined by Z. This result reflects the fact that the regular representation has zero character for all classes except the unit element, where $\chi = g$, the number of elements in the group. The states represented by Z therefore are different but equivalent for any permutation of the sites. In the classical state the spins can have any orientation such that

$$t^x = t^y = 0 \qquad t^z = M$$

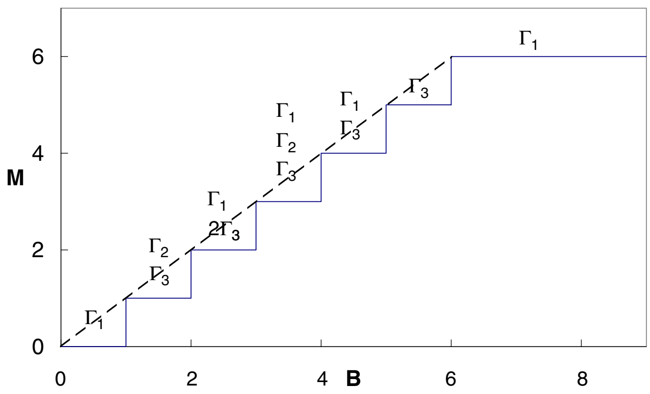

Figure 2. Zero-temperature magnetization curve of the $S = 2$ triangle, showing the symmetries of each step. The broken line is the classical magnetization curve for a spin of this length. The magnetization curve of the $S = 1$ octahedron is identical except that Γ_i is replaced by Γ_i^+ everywhere.

and these conditions remain satisfied by any interchange of sites 1, 2 and 3, even though the detailed pattern is then changed to an energetically equivalent one.

It seems clear that the triangle is a rather special case in which there is additional hidden symmetry present. This shows up in various ways. Firstly the Hamiltonian factorizes into a simple form. Secondly each spin is coupled to each other spin, and thirdly the quantum states which determine the ground state for a given M are massively degenerate. The dominance of the regular representation Z is presumably also associated with the hidden symmetry.

These results have been checked numerically for many different S. The magnetization curve for $S = 2$ is shown in figure 2.

4. Square of spin-S atoms

Four spins arranged in a square with equal nearest-neighbour exchange between each pair have C_{4v} symmetry. This group [5] has four one-dimensional representations Γ_1, Γ_2, Γ_3 and Γ_4 and one two-dimensional representation Γ_5. The Hamiltonian is

$$\begin{aligned}\mathcal{H} &= \boldsymbol{s}_1\cdot\boldsymbol{s}_2 + \boldsymbol{s}_2\cdot\boldsymbol{s}_3 + \boldsymbol{s}_3\cdot\boldsymbol{s}_4 + \boldsymbol{s}_4\cdot\boldsymbol{s}_1 - B(s_1^z + s_2^z + s_3^z + s_4^z)\\ &= (\boldsymbol{s}_1 + \boldsymbol{s}_3)\cdot(\boldsymbol{s}_2 + \boldsymbol{s}_4) - B(s_1^z + s_2^z + s_3^z + s_4^z)\\ &= \boldsymbol{t}_1\cdot\boldsymbol{t}_2 - B(t_1^z + t_2^z)\end{aligned} \tag{3}$$

where $\boldsymbol{t}_1 = \boldsymbol{s}_1 + \boldsymbol{s}_3$ and $\boldsymbol{t}_2 = \boldsymbol{s}_2 + \boldsymbol{s}_4$. This behaves as a pair of coupled spins with not necessarily equal lengths. In fact, the lengths satisfy $0 \leqslant T_1, T_2 \leqslant 2S$ and

$$\begin{aligned}\mathcal{H} &= \tfrac{1}{2}[(\boldsymbol{t}_1 + \boldsymbol{t}_2)^2 - \boldsymbol{t}_1^2 - \boldsymbol{t}_2^2] - B(t_1^z + t_2^z)\\ &= \tfrac{1}{2}[\boldsymbol{t}^2 - \boldsymbol{t}_1^2 - \boldsymbol{t}_2^2] - Bt^z\\ &= \tfrac{1}{2}[T(T+1) - T_1(T_1+1) - T_2(T_2+1)] - BM\end{aligned} \tag{4}$$

where $\boldsymbol{t} = \boldsymbol{t}_1 + \boldsymbol{t}_2$ is the total spin, $T(T+1)$ is the eigenvalue of $\boldsymbol{t}^2$ and $M = t^z$.

For a given T and M the lowest energy is obtained by choosing the largest values for T_1, T_2, namely $T_1 = T_2 = 2S$. All values of $0 \leqslant T \leqslant 4S$ can be obtained with this choice. For a given M the lowest energy state has $T = M$ so the energy is

$$E = \tfrac{1}{2}[M(M+1) - 4S(2S+1)] - BM.$$

The situation in these lowest states is therefore equivalent to a pair of atoms, each of spin $2S$, and the results are analogous to those of section 2, which are determined from the group C_2. The relationship can be seen as follows. If we treat the pairs as fixed entities there are elements in the group C_{4v} which leave the whole invariant; they are E, C_2 (about the perpendicular axis) and $2C_2'$ (about the diagonals). These are therefore equivalent to E in C_2. Similarly the other four elements interchange the pairs, and are all equivalent. The only representations with characters which satisfy this equivalence are $\Gamma_1(C_{4v}) \to \Gamma_1(C_2)$ and $\Gamma_4(C_{4v}) \to \Gamma_2(C_2)$.

In our numerical studies of finite S for this system we found that the representations of the relevant states alternated between Γ_1 and Γ_4 in the same way as the representations of the relevant states for the pair alternated between Γ_1 and Γ_2. We therefore believe that, for all S, the magnetization steps of the square have representation Γ_1 if M is even and Γ_4 if M is odd. Thus the symmetry of the classical system is governed by the sum of Γ_1 and Γ_4, reflecting the extra symmetry in the Hamiltonian, and giving states with fixed pairs and then the regular representation of C_2.

5. Five-atom ring of spin-S atoms

The group in this case is C_{5v}. This group [5] has two one-dimensional representations Γ_1 and Γ_2 and two two-dimensional representations Γ_3 and Γ_4. The Hamiltonian is

$$\mathcal{H} = s_1 \cdot s_2 + s_2 \cdot s_3 + s_3 \cdot s_4 + s_4 \cdot s_5 + s_5 \cdot s_1 - B(s_1^z + s_2^z + s_3^z + s_4^z + s_5^z). \tag{5}$$

This Hamiltonian cannot be factorized in the same way as the previous ones, so we cannot obtain the representations for general S. Our numerical calculations on finite $S \leqslant \frac{5}{2}$ systems show the following pattern.

For $M = 5S - n$, the representation r is given by

n	0	1	2	3	4	5	6	7	8	9	10	11	12
r	Γ_1	Γ_4	Γ_3	Γ_3	Γ_4	Γ_2	Γ_4	Γ_3	Γ_3	Γ_4	Γ_1	Γ_4	Γ_3

.

We speculate that the pattern is of period 10 and repeats indefinitely.

The quantum magnetization curve for 5 atoms shows steps whose width decreases as the applied field increases, whereas the classical curve is a straight line. As S increases the variation in the width of the steps becomes less and the quantum curve tends to a straight line classical curve.

This difference between the quantum and classical behaviour is known for long chains of spin-$\frac{1}{2}$ atoms [6]. For a ring of spin-$\frac{1}{2}$ atoms the curve of $\frac{M}{NS}$ becomes a smooth curve with monotonically increasing gradient as $N \to \infty$. The classical curve ($S \to \infty$) remains a straight line for all N. The smooth quantum curve would tend to the classical curve as S is increased from $\frac{1}{2}$ to ∞.

6. Tetrahedron

The group is the tetrahedral group T_d with 24 elements. There are [5] two one-dimensional representations Γ_1 and Γ_2, one two-dimensional representation Γ_3 and two three-dimensional representations Γ_4 and Γ_5.

Each atom has three neighbours and the Hamiltonian is

$$\begin{aligned}\mathcal{H} &= s_1 \cdot s_2 + s_1 \cdot s_3 + s_1 \cdot s_4 + s_2 \cdot s_3 + s_3 \cdot s_4 + s_4 \cdot s_2 - B(s_1^z + s_2^z + s_3^z + s_4^z) \\ &= \tfrac{1}{2}[(s_1 + s_2 + s_3 + s_4)^2 - s_1^2 - s_2^2 - s_3^2 - s_4^2] - B(s_1^z + s_2^z + s_3^z + s_4^z) \\ &= \tfrac{1}{2}[t^2 - 4S(S+1)] - Bt^z = \tfrac{1}{2}[T(T+1) - 4S(S+1)] - BM\end{aligned} \tag{6}$$

where $\boldsymbol{t} = \boldsymbol{s}_1 + \boldsymbol{s}_2 + \boldsymbol{s}_3 + \boldsymbol{s}_4$ is the total spin and $0 \leqslant T \leqslant 4S$. The lowest state for a given M has $T = M$.

For a given M the basis states of the form $|a, b, c, d\rangle_b$ have $a + b + c + d = M$ which defines a 'plane' in $4D$ space which intersects a hypercube defined by $-S \leqslant a, b, c, d \leqslant S$. For $2S \leqslant M \leqslant 4S$ the intersection is a tetrahedron with four vertices given by $(S, S, S, M - 3S)$ and its permutations. For $0 \leqslant M \leqslant 2S$ the intersection is a truncated tetrahedron with 12 vertices given by $(S, S, -S, M - S)$ and its permutations, which becomes a regular octahedron at $M = 0$.

We have not analysed this situation in the same way as for the triangle, but the numerical results for $S \leqslant \frac{5}{2}$ show the following pattern.

For $2S \leqslant M \leqslant 4S$ with $M = 4S - n$ the representations r are

n	r
0	Γ_1
1	Γ_5
2	$\Gamma_1 + \Gamma_3 + \Gamma_5$
3	$\Gamma_1 + \Gamma_4 + 2\Gamma_5$
4	$2\Gamma_1 + 2\Gamma_3 + \Gamma_4 + 2\Gamma_5$
5	$\Gamma_1 + \Gamma_3 + 2\Gamma_4 + 4\Gamma_5$

.

For $0 \leqslant M \leqslant 2S$ we do not have sufficient numerical data to identify a regular pattern. Note, however, that the basis state $|a, b, c, d\rangle_b$ with $a \neq b \neq c \neq d$ and its 24 permutations form a set of states with symmetries (the regular representation of T_d)

$$Z = \Gamma_1 + \Gamma_2 + 2\Gamma_3 + 3\Gamma_4 + 3\Gamma_5.$$

For large S this combination will dominate the overall symmetry of the massively degenerate steps in the magnetization curve. Again we note the connection of the massive degeneracy and the dominance of the regular representation to the factorizability of the Hamiltonian, reflecting the presence of hidden symmetry. In both this case and the triangle we also note that each spin is a nearest neighbour of every other spin.

7. Octahedron

The group is O_h with 48 elements. There are [5] four irreducible representations, ${\Gamma_1}^+$, ${\Gamma_2}^+$, ${\Gamma_1}^-$ and ${\Gamma_2}^-$, of dimension 1, two, ${\Gamma_3}^+$ and ${\Gamma_3}^-$, of dimension 2, and four, ${\Gamma_4}^+$, ${\Gamma_5}^+$, ${\Gamma_4}^-$ and ${\Gamma_5}^-$, of dimension 3.

The Hamiltonian is

$$\mathcal{H} = (\boldsymbol{s}_1 + \boldsymbol{s}_2) \cdot (\boldsymbol{s}_3 + \boldsymbol{s}_4 + \boldsymbol{s}_5 + \boldsymbol{s}_6) + \boldsymbol{s}_3 \cdot \boldsymbol{s}_5 + \boldsymbol{s}_5 \cdot \boldsymbol{s}_4 + \boldsymbol{s}_4 \cdot \boldsymbol{s}_6 + \boldsymbol{s}_6 \cdot \boldsymbol{s}_3 \\ -B(s_1^z + s_2^z + s_3^z + s_4^z + s_5^z + s_6^z) = \boldsymbol{t}_1 \cdot \boldsymbol{t}_2 + \boldsymbol{t}_2 \cdot \boldsymbol{t}_3 + \boldsymbol{t}_3 \cdot \boldsymbol{t}_1 - B(t_1^z + t_2^z + t_3^z) \tag{7}$$

where $\boldsymbol{t}_1 = \boldsymbol{s}_1 + \boldsymbol{s}_2$, $\boldsymbol{t}_2 = \boldsymbol{s}_3 + \boldsymbol{s}_4$ and $\boldsymbol{t}_3 = \boldsymbol{s}_5 + \boldsymbol{s}_6$. This is not exactly the Hamiltonian of the triangle discussed earlier because the lengths of the three spins do not have to be equal. Hence

$$\begin{aligned} \mathcal{H} &= \tfrac{1}{2}[(\boldsymbol{t}_1 + \boldsymbol{t}_2 + \boldsymbol{t}_3)^2 - \boldsymbol{t}_1^2 - \boldsymbol{t}_2^2 - \boldsymbol{t}_3^2] - B(t_1^z + t_2^z + t_3^z) \\ &= \tfrac{1}{2}[\boldsymbol{t}^2 - \boldsymbol{t}_1^2 - \boldsymbol{t}_2^2 - \boldsymbol{t}_3^2] - Bt^z \\ &= \tfrac{1}{2}[T(T+1) - T_1(T_1+1) - T_2(T_2+1) - T_3(T_3+1)] - BM \end{aligned} \tag{8}$$

where $\boldsymbol{t} = \boldsymbol{t}_1 + \boldsymbol{t}_2 + \boldsymbol{t}_3$ is the total spin. T, T_1, T_2 and T_3 are the lengths of the combined spins $\boldsymbol{t}$, $\boldsymbol{t}_1$, $\boldsymbol{t}_2$ and $\boldsymbol{t}_3$, respectively, so that $0 \leqslant T_1, T_2, T_3 \leqslant 2S$. T satisfies $T_{\min} \leqslant T \leqslant T_1 + T_2 + T_3$, where $T_{\min}$ is the smallest length that can be formed from the three spins $\boldsymbol{t}_1$, $\boldsymbol{t}_2$ and $\boldsymbol{t}_3$. $M = t^z$ so $-T \leqslant M \leqslant T$.

From equation (8) it is clear that the lowest energy for a given M will be obtained by choosing the largest values for T_1, T_2 and T_3, namely $T_1 = T_2 = T_3 = 2S$. With this choice the Hamiltonian becomes the same as for the triangle and so the earlier results will apply, replacing S by $2S$.

The symmetry of the relevant states for the triangle are in terms of the irreducible representations of $C_{3\mathrm{v}}$. The relation between these and the corresponding states of the octahedron is similar to that between the pair and the four-atom ring. In this case we find the equivalence of the elements is as follows:

O_h		$C_{3\mathrm{v}}$
$E + 3C_{2m}$	$\rightarrow$	E
$8C_3$	$\rightarrow$	$2C_3$
$6C_{2p} + 6C_{4m}$	$\rightarrow$	$3C_2$

and thus $\Gamma_i^+(O_h) \rightarrow \Gamma_i(C_{3\mathrm{v}})$ for $i = 1, 2, 3$. Our numerical studies confirm that the relevant states of the octahedron have symmetries in which the Γ_a of $C_{3\mathrm{v}}$ is replaced by Γ_a^+ of O_h. Of course, states with symmetry Γ_a^- do occur but these are never the lowest for a given M and so do not have any effect on the zero-temperature magnetization curve. If the temperature was not zero then they would have to be taken into account.

The cycles of length 3 or 6 seen for the triangle are seen in exactly the same way for the octahedron as for the triangle.

8. FCC-12, ICO-12, FCC-13 and ICO-13 clusters

These large clusters were investigated in the earlier paper. The ICO-12 is particularly interesting because there appear to be two distinct regions of the magnetization curve. We have obtained the symmetries of the low-lying states for $S = \frac{1}{2}$ only. For FCC-12 the group is O_h and the symmetries r are

M	0	1	2	3	4	5	6
r	$\Gamma_1{}^-$	$\Gamma_5{}^-$	$\Gamma_1{}^+$	$\Gamma_1{}^+$	$\Gamma_1{}^+ + \Gamma_3{}^+$	$\Gamma_3{}^+ + \Gamma_5{}^-$	$\Gamma_1{}^+$

For ICO-12 the group is I_h and the symmetries are

M	0	1	2	3	4	5	6
r	$\Gamma_3{}^+$	$\Gamma_5{}^-$	$\Gamma_4{}^-$	$\Gamma_5{}^+$	$\Gamma_3{}^-$	$\Gamma_1{}^+$	$\Gamma_1{}^+$

For $S = 1$ we obtained only a few results for high M, and found that the symmetries of the states with $M = 12S - n$ for $n = 0, 1, 2, 3, 4$ were the same as for $S = \frac{1}{2}$.

Clusters with an additional central atom, FCC-13 and ICO-13, show exactly the same symmetries except for one or more additional steps with $\Gamma_1{}^+$ symmetry at large M. The number of these additional steps is $2S$.

The number of steps obtained for all these clusters is too small to determine a pattern which would apply at general S and would enable symmetry of the different regions of the classical FCC-12, ICO-12, FCC-13 or ICO-13 curves to be described.

9. Conclusion

For quantum spin systems with small numbers of spins arranged in clusters with high symmetry, it is possible to categorize the ground state wavefunction in a magnetic field in terms of the irreducible representations of the space group of the cluster. We have shown, for certain of these clusters, how to obtain the complete decomposition of the states in terms of these representations for arbitrary spin S. Sometimes a single irreducible representation is present, although of course if this has dimension greater than one there will be degeneracy. Sometimes several representations are present, giving additional degeneracy. Sometimes massive degeneracy occurs, of the order of NS, due to the fact that some representations occur many times, although some do not occur at all.

The fact that we have results for arbitrary S, and assuming that the limiting process $S \to \infty$ is smooth, means that we should be able to describe the symmetry of the *classical* ground states in a similar way to the quantum.

We find that, even if the quantum states belong to a single irreducible representation, the representation varies in a systematic way as the applied field changes so that the classical system cannot normally be described by a single representation. Clearly this is even more true in the case when a quantum system has degeneracies between states of different irreducible representations. For some clusters the dominant representation is the combination of irreducible representations known as the regular representation. The numerical results indicate that this is the case if the topology of the cluster is such that every spin is connected to all other spins.

Typically in the quantum case we find that there is a well defined repeating cycle of irreducible representations as a function of B. This suggests that the symmetry of the classical state should be described as a combination of all the representations which are present in the cycle. For example, for the two-atom pair the classical state should be described by $\Gamma_1 + \Gamma_2$. For the triangle and octahedron we find two different regions in which the periodicity of the cycle of representations on the steps of the magnetization curve is different. However, in both regions the dominant linear combination of representations is the regular representation and the classical curve is a straight line which is not divided into two regions of different symmetry.

Unfortunately we were not able to fully analyse any system in which the classical magnetization curve $M = M(B)$ has two distinct regions of different symmetry, e.g. ICO-12. We expect that in the quantum case, for general S, there would be two regions with different cycles and the transition point between the two cycles would tend to the classical crossover point in the limit $S \to \infty$, characterized by a discontinuity in the gradient of the magnetization curve.

Finally we note that it would be interesting to study other types of exchange interaction and possibly other single-atom terms in the Hamiltonian, in the hope that they might shed further light on the question of the relation between the quantum and classical symmetries.

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Appendix A. Lowest states for a triangle of general spin

In this appendix we give the details of the symmetries of the lowest states for a triangle of spin-S atoms. As noted, there are two distinct regions depending whether M is less than or greater than S.

First the region $M \leqslant S$. The plane area bounded by the six corners $(S, -S, M)$ and its permutations contains a total of

$$N_T = 3S(S+1) - M^2 + 1$$

states. Let the number of states of the form (a, a, a) be N_3, of the form (a, a, b) with $b \neq a$ (and permutations) be N_2, and of the form (a, b, c) with $a \neq b \neq c$ be N_1. Clearly $N_3 = 1$ if $2M$ is divisible by 3 and $N_3 = 0$ otherwise. For states of the form (a, a, b) we have $2a+b = M$ and $-S \leqslant b \leqslant S$ so

$$-A_1 \leqslant a \leqslant A_2 \qquad \text{where} \quad A_1 = \frac{S-M}{2} \quad \text{and} \quad A_2 = \frac{S+M}{2}.$$

The minimum value of a will be equal to $-A_1$ if $S - M$ is even and the maximum will be equal to A_2 if $S + M$ is even. If S is an integer and both $S - M$ and $S + M$ are even then the number of values of a is $N_a = S + 1$. If S is an integer and both $S - M$ and $S + M$ are odd then $N_a = S$. If S is an integer plus $\frac{1}{2}$ then one of $S - M$ and $S + M$ is even and one odd. In this case N_a is $S + \frac{1}{2}$. States of the form (a, a, b) have three permutations unless $b = a$ so

$$N_2 = 3(N_a - N_3).$$

Finally

$$N_1 = N_T - N_2 - N_3.$$

For integer S the alternation between even and odd values of N_a for successive values of M and the cycle of 3 in N_3 results in a cycle of 6 overall. For integer plus $\frac{1}{2}$ the cycle is of length 3.

The symmetries of the states for a given M are given by

$$X_M = N_3(\Gamma_1) + \tfrac{1}{3}N_2(\Gamma_1 + \Gamma_3) + \tfrac{1}{6}N_1(\Gamma_1 + \Gamma_2 + 2\Gamma_3).$$

The symmetries of the lowest states of a given M are those for which $T = M$ and these are given by $X_M - X_{M+1}$. The final result is

For $S =$ integer $+\frac{1}{2}$:

$$\begin{aligned} M &= 3k + \tfrac{1}{2} \ : \ \Gamma_1 + \Gamma_3 + kZ \\ M &= 3k + \tfrac{3}{2} \ : \ \Gamma_1 + \Gamma_2 + \Gamma_3 + kZ \\ M &= 3k + \tfrac{5}{2} \ : \ (k+1)Z \end{aligned}$$

where $0 \leqslant k \leqslant S/3$, $Z = \Gamma_1 + \Gamma_2 + 2\Gamma_3$.

For $S =$ even integer:

$$\begin{aligned} M &= 6k & &: \ 2kZ + \Gamma_1 \\ M &= 6k+1 & &: \ 2kZ + \Gamma_2 + \Gamma_3 \\ M &= 6k+2 & &: \ 2kZ + \Gamma_1 + 2\Gamma_3 \\ M &= 6k+3 & &: \ 2kZ + \Gamma_1 + 2\Gamma_2 + 2\Gamma_3 \\ M &= 6k+4 & &: \ 2kZ + 2\Gamma_1 + \Gamma_2 + 3\Gamma_3 \\ M &= 6k+5 & &: \ 2kZ + \Gamma_1 + 2\Gamma_2 + 4\Gamma_3. \end{aligned}$$

For $S =$ odd integer the result is the same as for even integers except that Γ_1 and Γ_2 are interchanged.

Now consider the region $S \geqslant M \geqslant 3S$. The plane region bounded by the corners $(S, S, M - 2S)$ and its permutations contains a total of

$$N_T = \tfrac{1}{2}(3S - M + 1)(3S - M + 2)$$

states. Again $N_3 = 1$ if $2M$ is divisible by 3 and $N_3 = 0$ otherwise.

States of the form (a, a, b) occur for $M - 2S \leqslant b \leqslant S$ and so

$$\frac{M-S}{2} \leqslant a \leqslant S.$$

Hence, $N_a = \frac{1}{2}(3S - M) + 1$ if $M - S$ is even and $N_a = \frac{1}{2}(3S - M)$ if $M - S$ is odd.

Here there is a cycle of length 6 for all S. The symmetries are

$$\begin{aligned} M &= 3S - 6k & &: \ kZ + \Gamma_1 \\ M &= 3S - 6k - 1 & &: \ kZ + \Gamma_3 \\ M &= 3S - 6k - 2 & &: \ kZ + \Gamma_1 + \Gamma_3 \\ M &= 3S - 6k - 3 & &: \ kZ + \Gamma_1 + \Gamma_2 + \Gamma_3 \\ M &= 3S - 6k - 4 & &: \ kZ + \Gamma_1 + 2\Gamma_3 \\ M &= 3S - 6k - 5 & &: \ (k+1)Z. \end{aligned}$$

Appendix B. $S = 1/2$ octahedron symmetry

In this section we present a full symmetry analysis of the $S = 1/2$ octahedron.

The character table of the octahedral group O_h is

$$\begin{array}{|cc|}\hline \chi & \chi \\ \chi & -\chi \\ \hline\end{array}$$

where χ is the table without inversion, i.e. pure rotations:

$$\chi = \begin{array}{|l|ccccc|}\hline \text{Class } i & E & C_3 & C_{2m} & C_{2p} & C_{4m} \\ \text{Rot. axis} & & (111) & (100) & (110) & (100) \\ n_i & 1 & 8 & 3 & 6 & 6 \\ \hline \Gamma_1^+ & 1 & 1 & 1 & 1 & 1 \\ \Gamma_2^+ & 1 & 1 & 1 & -1 & -1 \\ \Gamma_3^+ & 2 & -1 & 2 & 0 & 0 \\ \Gamma_4^+ & 3 & 0 & -1 & -1 & 1 \\ \Gamma_5^+ & 3 & 0 & -1 & 1 & -1 \\ \hline\end{array}$$

Here n_i is the number of elements in class i. The five irreducible representations in the lower half of the table are labelled Γ_1^-, Γ_2^-, Γ_3^- , Γ_4^- and Γ_5^-.

The Hamiltonian is equation (8). We use the usual Ising-like basis with states of the form $|a_1a_2a_3a_4a_5a_6\rangle$, where a_i is either + or $-$ and refers to the ith site, with the sites labelled as shown in figure 1. We choose axes so that sites 1 and 2 are $(1, 0, 0)$ and $(-1, 0, 0)$, sites 3 and 4 are at $(0, 1, 0)$ and $(0, -1, 0)$ and sites 5 and 6 are at $(0, 0, 1)$ and $(0, 0, -1)$. This choice is for convenience and it is not necessary for the axes of the octahedron to be aligned with the magnetic field.

M is a good quantum number so we can consider each M separately. We shall also consider $B = 0$ initially since the effect of the magnetic field is merely to lift the degeneracy without altering the eigenstates.

For $M = 3$ there is only one basis state, $|{+}{+}{+}{+}{+}{+}\rangle$, which must therefore be an eigenstate with energy 3. This state is invariant under all group operations so the ten character columns associated with each class all contain 1 and the symmetry is Γ_1^+.

For $M = 2$ there are 6 basis states of the form $|-+++++\rangle$ where the $-$ may be in each of the six positions. The ten characters for this group of states are

$$6 \quad 0 \quad 2 \quad 0 \quad 2 \quad 0 \quad 0 \quad 4 \quad 2 \quad 0.$$

Using the rules for character decomposition, or by inspection, this gives $\Gamma_1^+ + \Gamma_3^+ + \Gamma_4^-$.

Since T is also a good quantum number in the absence of a magnetic field, the states with $M = 2$ must include states with $T = 3$ and 2. For $T = 3$ the states are obtained by operating on the $M = 3$ state with the lowering operator

$$t^- = \sum_i s_i^-$$

which does not alter the symmetry. Consequently the Γ_1^+ state has $T = 3$ while the five states with $\Gamma_3^+ + \Gamma_4^-$ have $T = 2$.

For $M = 1$ there are 15 basis states, each with 2 minuses and 4 pluses. Three states (type A) have the two minuses at opposite vertices, e.g. $|--++++\rangle$, while the remaining twelve (type B) have minuses on adjacent sites along one edge, e.g. $|-++-++\rangle$. The rotations and inversion do not mix these two types so we can consider their symmetry separately. For the first three the characters are

$$3 \quad 0 \quad 3 \quad 1 \quad 1 \quad 3 \quad 0 \quad 3 \quad 1 \quad 1$$

giving $\Gamma_1^+ + \Gamma_3^+$.

For the twelve of type B the characters are

12 0 0 2 0 0 0 4 2 0

giving $\Gamma_1^+ + \Gamma_3^+ + \Gamma_4^- + \Gamma_5^+ + \Gamma_5^-$.

Of these twelve states, six have $T > 1$ with the symmetries obtained above, leaving the six states with $T = 1$ as having irreducible representations $\Gamma_1^+ + \Gamma_3^+ + \Gamma_5^+ + \Gamma_5^-$.

Finally we consider $M = 0$. There are 20 states in the basis. Eight states (type A) have the three minus spins at the three corners of one face, e.g. $|-++--+\rangle$, and twelve (type B) have three minuses on two perpendicular joined edges, e.g. $|---+++\rangle$.

The characters for the first type are

8 2 0 0 0 0 0 0 4 0

giving $\Gamma_1^+ + \Gamma_2^- + \Gamma_4^- + \Gamma_5^+$.
While for the second type the characters are

12 0 4 0 0 0 0 4 0 0

giving $\Gamma_1^+ + \Gamma_2^+ + 2\Gamma_3^+ + \Gamma_4^- + \Gamma_5^-$.

Subtracting states with $T > 0$ gives the five states with $T = 0$ as having irreducible representations $\Gamma_2^+ + \Gamma_2^- + \Gamma_4^-$.

We now determine to which representation each of the possible energies correspond.

For $M = 3$ the only state has energy 3 and symmetry Γ_1^+.

As already noted, the Hamiltonian can be written in terms of $\boldsymbol{t}_1, \boldsymbol{t}_2, \boldsymbol{t}_3$ and $\boldsymbol{T}$. A complete set of states for the pair $\boldsymbol{t}_1 = \boldsymbol{s}_1 + \boldsymbol{s}_2$ are the states of the form $|T_1, t_1^z\rangle$ given by

$$\begin{aligned}
|1,1\rangle &= |++\rangle \\
|1,0\rangle &= \frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle) \\
|1,-1\rangle &= |--\rangle \\
|0,0\rangle &= \frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle).
\end{aligned} \tag{B.1}$$

As can be seen the three states with $T_1 = 1$ are unchanged under inversion and have positive parity while the state with $T_1 = 0$ changes sign under inversion and so has negative parity.

We now draw up a table of all possible states of the octahedron.

M	T	T_1	T_2	T_3	Energy	Parity	Deg.	Rep.
3	3	1	1	1	3	+	1	Γ_1^+
2	3	1	1	1	3	+	1	Γ_1^+
	2	1	1	1	0	+	2	Γ_3^+
		1	1	0	1	−	3	Γ_4^-
1	3	1	1	1	3	+	1	Γ_1^+
	2	1	1	1	0	+	2	Γ_3^+
		1	1	0	1	−	3	Γ_4^-
	1	1	1	1	−2	+	3	$\Gamma_1^+ + \Gamma_3^+$
		1	1	0	−1	−	3	Γ_5^-
		1	0	0	0	+	3	Γ_5^+
0	3	1	1	1	3	+	1	Γ_1^+
	2	1	1	1	0	+	2	Γ_3^+
		1	1	0	1	−	3	Γ_4^-
	1	1	1	1	−2	+	3	$\Gamma_1^+ + \Gamma_3^+$
		1	1	1	−1	−	3	Γ_5^-
		1	1	1	0	+	3	Γ_5^+
	0	1	1	1	−3	+	1	Γ_2^+
		1	1	0	−2	−	3	Γ_4^-
		0	0	0	0	−	1	Γ_2^-

All the representations in the above table can be deduced from knowledge of the parity and the degeneracy of the states together with the list of representations for each M obtained above. The only exception to this are the two positive parity states with $T = 1$ and $M = 1$, both of which have degeneracy 3.

To determine these we consider the three states with $T = 1$, $M = 1$ which have $T_1 = 1$, $T_2 = T_3 = 0$ and permutations. A basis for these is the set

$$\begin{aligned} |b_1\rangle &= |1, 1\rangle_{12}|0, 0\rangle_{34}|0, 0\rangle_{56} \\ |b_2\rangle &= |0, 0\rangle_{12}|1, 1\rangle_{34}|0, 0\rangle_{56} \\ |b_3\rangle &= |0, 0\rangle_{12}|0, 0\rangle_{34}|1, 1\rangle_{56} \end{aligned} \tag{B.2}$$

using the notation of equation (B.1). Under the pure rotations of the group the characters of this set of three basis states are

$$3 \quad 0 \quad -1 \quad 1 \quad -1$$

so these must belong to Γ_5^+.

An alternative method of obtaining these results is to obtain explicit expressions for the eigenstates in terms of basis states similar to those of equation (B.2). For $S = 1/2$ this can be done analytically. The symmetry can then be determined directly by studying how the eigenstates transform under the group operations.

For larger S the eigenstates have to be determined numerically and for the octahedron this can be done for $S \leqslant 4$ without much difficulty. However, as noted earlier, only the lowest states for each M are needed for the $T = 0$ magnetization curve and these can be determined using the method of appendix A.

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