Exchange interactions in two-state systems: rare earth pyrochlores

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Received 7 February 2018, revised 23 April 2018
Accepted for publication 26 April 2018
Published 14 May 2018

Abstract

The general form of the nearest neighbour exchange interaction for rare earth pyrochlores is derived based on symmetry. Generally, the rare earth angular momentum degeneracy is lifted by the crystal electric field (CEF) into singlets and doublets. When the CEF ground state is a doublet that is well-separated from the first excited state the CEF ground state doublet can be treated as a pseudo-spin of some kind. The general form of the nearest neighbour exchange interaction for pseudo-spins on the pyrochlore lattice is derived for three different types of pseudo-spins. The methodology presented in this paper can be applied to other two-state spin systems with a high space group symmetry.

Keywords: frustrated magnets, pyrochlore crystals, exchange interaction

(Some figures may appear in colour only in the online journal)

1. Introduction

Rare earth pyrochlores are crystals that are famous for the wide variety of unusual magnetic states they host at low temperatures, including spin ice in Ho2Ti2O7 and Dy2Ti2O7 [1, 2], anti-ferromagnetic order in Er2Ti2O7 [3] and Nd2Zn2O7 [4, 5], and spin liquid in Tb2Ti2O7 [6]. In all of these materials, the rare earth ions (Pr, Nd, Gd, Tb, Dy, Ho and Yb) have relatively large values of total angular momentum J, with a corresponding 2J + 1-fold degeneracy of the single ion states. However, this degeneracy is lifted into singlets and doublets in the presence of the crystal electric field (CEF), the electric field produced by all of the other ions in the crystal. In many of the pyrochlore magnets the splitting between the CEF ground state and first excited state is large, of the order of 100 K, so that magnetic properties can be modelled using only the CEF ground state of the magnetic ion, neglecting the excited states. Models based on this restriction are further constrained by symmetry—the symmetry of the CEF and the character of the CEF ground state, as well as the space group symmetry of the crystal. Altogether, with their highly symmetric octahedral space group and small number (often two) of single ion states, rare earth pyrochlore crystals are an intriguing example of how symmetry can reduce the complexity of magnetic interactions.

Magnetic interactions are generally modelled in terms of short range exchange interactions and longer range magnetic dipole–dipole interactions. The nearest-neighbour exchange interaction is anisotropic in general and can be written as

\[ H_{\text{ex}} = \sum_{\langle ij \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \]

(1)

where \( \langle ij \rangle \) are pairs of nearest neighbours at magnetic ion sites i and j, \( \alpha, \beta = x, y, z \), and \( J_{ij}^{\alpha\beta} \) are phenomenological exchange coupling constants constrained by symmetry.

The dipole–dipole interaction takes the form

\[ H_{\text{dipole}} = \frac{1}{2} D a^3 \sum_{ij} \frac{\mathbf{J}_i \cdot \mathbf{J}_j}{|\mathbf{R}_{ij}|^3} - \frac{3(\mathbf{J}_i \cdot \mathbf{R}_{ij})(\mathbf{J}_j \cdot \mathbf{R}_{ij})}{|\mathbf{R}_{ij}|^5}, \]

(2)

where D is the dipolar interaction strength, a is the distance between nearest neighbours, and \( \mathbf{R}_{ij} \) is the displacement vector between sites i and j. The nearest-neighbour part of the dipole–dipole interaction can be included in the exchange interaction by renormalising the exchange coupling constants. Although essential to the description of correlations in some systems (for example, in spin ices), longer range contributions to the dipole–dipole interaction are often neglected.
In both (1) and (2) $\vec{J}_i$ is the total angular momentum (which shall be henceforth shortened to ‘spin’) of the magnetic ion at site $i$, and may represent either the classical quantity or the quantum mechanical operator. In the following, we will be concerned with quantum systems.

The spin $J$ of rare earth ions is determined by Hund’s rules, however in the environment of a CEF, the $2J + 1$-fold degeneracy is lifted according to the symmetry of the CEF. The character table of the group $D_h$ (the relevant symmetry group of the CEF at the rare earth site in pyrochlore crystals) is shown in the appendix. This table classifies spin states according to their transformation properties under the symmetry operations of $D_h$. According to the table, if $J$ is an integer then there are two different singlets ($\Gamma_1$ and $\Gamma_2$) and a single ‘non-Kramers’ (\(\Gamma_3\)) doublet. If $J$ is a half-integer then by Kramers’ theorem all states are necessarily doublets, and there are two different ‘Kramers’ doublets, one of which transforms the same way as a $J = 1/2$ spinor ($\Gamma_4$), and the other not ($\Gamma_{5,6}$). Some examples of pyrochlores in the titanate family with CEF ground state doublets are TB$_2$Ti$_2$O$_7$ and HO$_2$Ti$_2$O$_7$ ($\Gamma_3$), Yb$_2$Ti$_2$O$_7$ and Er$_2$Ti$_2$O$_7$ ($\Gamma_4$) and Dy$_2$Ti$_2$O$_7$ ($\Gamma_{5,6}$). In this article, we will review anisotropic nearest neighbour exchange interactions for pyrochlores crystals where the magnetic ion ground states are either Kramers or non-Kramers doublets.

The exchange interaction must be invariant under the symmetry operations of the crystallographic space group, which, for the pyrochlore crystals, is $Fd3m$. This space group has a face-centre cubic (fcc) Bravais lattice and its underlying point group is $O_h$ (octahedral). The most general form of the exchange Hamiltonian between rare earth ions in the pyrochlore crystals has four independent terms [7],

$$H_{ex} = J_1X_1 + J_2X_2 + J_3X_3 + J_4X_4,$$

where $J_i$ are four independent anisotropic exchange constants.

It is convenient to write the exchange terms $X_i$ using a set of local axes, defined such that the local $z$-axis (the spin quantisation axis) is the three-fold symmetry axis of the CEF at the rare earth site (see figure A1 in the appendix). This coordinate system is defined in appendix A. Using this notation, the exchange terms are

$$X_1 = \frac{1}{3} \sum_{\langle ij \rangle} J_{ij} J_z,$$

$$X_2 = -\frac{\sqrt{2}}{3} \sum_{\langle ij \rangle} [\Lambda_{ij} (J_{ix} J_{jx} + J_{ix} J_{jz}) + \text{h.c.}],$$

$$X_3 = \frac{1}{3} \sum_{\langle ij \rangle} \Lambda_{ij} J_{ix} J_{jx} + \text{h.c.},$$

$$X_4 = \frac{1}{6} \sum_{\langle ij \rangle} (J_{ix} J_{jx} + \text{h.c.}),$$

where h.c. stands for ‘Hermitian conjugate’ and $J_{\pm} = J_x \pm iJ_y$. The rare earth ions are found at the 16d Wyckoff position of the space group $Fd3m$, which has four inequivalent sites, therefore each rare earth ion site $i$ or $j$ can be specified by a fcc lattice vector and a site number, 1, 2, 3 or 4. Sites which are nearest neighbours will either belong to the same lattice vector or will differ by a single fcc translation. The complex coefficients $\Lambda_{ij}$ depend only on the site numbers, and not the lattice vectors. They are $\Lambda_{12} = \Lambda_{34} = 1$ and $\Lambda_{13} = \Lambda_{24} = \Lambda_{23} = \varepsilon = \exp(\frac{2\pi i}{3})$. The numerical coefficients in front of each term in (4)–(7) are selected so that the sum over all four terms is just the isotropic exchange interaction

$$X_1 + X_2 + X_3 + X_4 = \sum_{\langle ij \rangle} \vec{J}_i \cdot \vec{J}_j. \quad (8)$$

Several different forms of $H_{ex}$ have appeared in the literature which amount to different linear combinations of the exchange terms $X_i$. Some alternative forms are given in appendix B.

To prove that $H_{ex}$ (equation (3)) is the most general form of the exchange interaction we must demonstrate the following: (i) that there are exactly four independent terms that are bilinear in the spin operators, (ii) that the four terms (4)–(7) are in fact independent and (iii) invariant under the space group operations and time reversal. In order to prove any of these assertions, one needs to know how each spin operator transforms under the operations of $O_h$, the point group associated with $Fd3m$. The transformations of the spin operators are listed in appendix A, along with the calculation that shows that there are four independent terms in the nearest neighbour exchange interaction. It is obvious that (4)–(7) are independent because they contain different kinds of operators, and their invariance can be checked using the transformations given in appendix A.

This paper is concerned with nearest neighbour interactions between each of the three different types of CEF ground state doublets ($\Gamma_3$, $\Gamma_4$, and $\Gamma_{5,6}$). We begin by finding the restriction of the exchange interaction $H_{ex}$ (3) to the CEF ground state doublet. Clearly the restriction of $H_{ex}$ will be non-trivial only when there are non-vanishing matrix elements for $J_z$ and for $J_{\pm}$ within the restriction. Generally, $J_z$ has non-vanishing matrix elements for each of the three kinds of doublet, however $J_{\pm}$ is only non-vanishing for a $\Gamma_4$ doublet: symmetry requirements (including time reversal) force the matrix elements for $J_{\pm}$ to vanish within $\Gamma_3$ and $\Gamma_{5,6}$ doublets. Therefore when $H_{ex}$ is restricted to a $\Gamma_3$ or a $\Gamma_{5,6}$ subspace the model contains no quantum mechanical effects because the matrix elements of the $J_{\pm}$ operators vanish within either of these restrictions. However, because a spin-1/2 spinor belongs to the $\Gamma_4$ representation, when $H_{ex}$ is restricted to a $\Gamma_4$ doublet the resulting model will be the $J = 1/2$ version of $H_{ex}$ (3).

Physically, there are other interactions which may be relevant besides the exchange interaction that can generate non-zero matrix elements between the states in $\Gamma_3$ or $\Gamma_{5,6}$ doubles. Two that have been previously studied are (i) mixing with higher CEF levels [8, 9], and (ii) higher multipole (quadrupolar or octupolar) interactions [4, 5, 10–12]. These two types of interactions are handled differently.
The relevance of excited state CEF levels in Tb$_2$Ti$_2$O$_7$ was recognised long ago, in the first studies of magnetostriction [14, 15]. In Tb$_2$Ti$_2$O$_7$, the ground state and first excited CEF levels are both $\Gamma_3$ doublets, separated by an energy difference of only about 18 K. The first excited state admixes to the ground state to second order in perturbation theory via the exchange interaction, and gives rise to non-vanishing $J_{\pm}$ matrix elements which are recorded in the intensity patterns of diffuse neutron scattering experiments [8, 9]. To model these interactions we make use of a map between $\Gamma_3$ doublets and spin-1/2 ($\Gamma_4$) doublets. If the rare earth spins are considered in groups of four (the four sites of a tetrahedron) there is an exact symmetry match between $\Gamma_3$ doublets and $\Gamma_4$ doublets [9]. This map allows one to write the interactions between the states in a $\Gamma_3$ doublet as an effective spin-1/2 exchange interaction; i.e. the effective Hamiltonian is the $J = 1/2$ version of (3), with all four coupling constants $\tilde{J}_i$ of the effective $J = 1/2$ model non-zero. There is no similar map for $\Gamma_{5,6}$ doublets.

On the other hand, higher multipole interactions have been invoked to model praseodymium pyrochlores with $\Gamma_3$ CEF ground states, such as Pr$_2$Zr$_2$O$_7$ [11] and Pr$_2$Sn$_2$O$_7$ [10], since quadrupolar interactions are the lowest order interactions which yield non-zero $J_{\pm}$ matrix elements within the $\Gamma_3$ restriction (no mixing with excited CEF levels is required). Similarly, octupole interactions can yield non-zero matrix elements for $\Gamma_{5,6}$ states, as in Nd$_2$Zr$_2$O$_7$ [4, 5, 12, 13, 28]. This article describes how to cast these higher multipole interactions as effective exchange interactions.

In the following sections we use symmetry methods to derive general effective nearest neighbour exchange interaction models for each of the three different kinds of CEF ground state doublets, $\Gamma_4$, $\Gamma_{5,6}$ and $\Gamma_3$.

2. Exchange interaction for $\Gamma_4$ CEF ground states

We first consider $H_{\alpha\alpha}$ (equation (3)) for $J = 1/2$, using an alternate approach, as follows. The components of the spin operator $\mathbf{S}$ are defined in terms of the spin-1/2 states $|\pm\rangle$.

$$S_z = |+\rangle\langle-| + |-\rangle\langle+|,$$

$$S_x = -i(|+\rangle\langle-| + |-\rangle\langle+|),$$

$$S_y = |+\rangle\langle+| - |-\rangle\langle-|.$$  (11)

The quantisation axis (the $z$-axis) implied by this notation points in the direction of the three-fold symmetry axis of the rare earth site (the local $z$-axis). The transformation properties of $\mathbf{S}$ under rotations and time reversal follow from the transformation properties of the spin-1/2 bras and kets, where the rotation operator is given by $\exp(-i\mathbf{J} \cdot \mathbf{\hat{n}})$ for $J = 1/2$. We find that $\tilde{S}$ transforms the same way as the angular momentum $\mathbf{J}$ (as it must), and so the general form of the exchange interaction for $\tilde{S}$ is the $J = 1/2$ version of $H_{\alpha\alpha}$ (3). We also note that under $D'_3$, $S$ transforms as $\Gamma_2$, while $S_x$ transforms as $\Gamma_3$, and $\tilde{S}$ changes sign under time reversal.

More generally, any $\Gamma_4$ doublet, such as the CEF ground state of erbium in Er$_2$Ti$_2$O$_7$,

$$|\Gamma_{4(\text{Er})}\rangle = 0.471|\pm 13/2\rangle \mp 0.421|\pm 7/2\rangle \mp 0.569|\pm 1/2\rangle \mp 0.240|\mp 5/2\rangle + 0.469|\mp 11/2\rangle,$$  (12)

can be used to define operators analogous to (9)–(11),

$$\tilde{S}_3 = |\Gamma_4^+\rangle\langle\Gamma_4^-| + |\Gamma_4^-\rangle\langle\Gamma_4^+|,$$

$$\tilde{S}_y = -i|\Gamma_4^+\rangle\langle\Gamma_4^-| + i|\Gamma_4^-\rangle\langle\Gamma_4^+|,$$

$$\tilde{S}_z = |\Gamma_4^+\rangle\langle\Gamma_4^-| - |\Gamma_4^-\rangle\langle\Gamma_4^+|.$$  (15)

These operators transform in the same way as $\mathbf{S}$ under the $D'_3$ group operations. Moreover, these operators can be scaled by appropriate factors so that they have the same eigenvalues as $\tilde{S}$ (i.e. $\pm h/2$): $\tilde{S}_{3,y} = tS_{3,y}$ and $\tilde{S}_z = JS_z$, where $t = (J_{4t}^+J_{4t}^-+J_{4t}^-J_{4t}^+)/\hbar^2$. Therefore the general form of the exchange interaction using such operators will be the $J = 1/2$ version of $H_{\alpha\alpha}$ (3) with the constants $j$ and $t$ absorbed into the exchange constants $\tilde{J}_i$. This Hamiltonian has been used to model Yb$_2$Ti$_2$O$_7$ [16–18], Er$_2$Ti$_2$Ti$_7$ [18–24], and Er$_2$Sn$_2$O$_7$ [18, 25].

3. Exchange interaction for $\Gamma_{5,6}$ CEF ground states

Examples of rare earth pyrochlores with a $\Gamma_{5,6}$ CEF ground state include Dy$_2$Ti$_2$O$_7$ [26], Nd$_2$Ir$_2$O$_7$ [27], and Nd$_2$Zr$_2$O$_7$ [4, 5]. The CEF ground state of dysprosium in Dy$_2$Ti$_2$O$_7$ is [26]

$$|\Gamma_{5,6(\text{Dy})}\rangle = 0.981|\pm 15/2\rangle \mp 0.190|\pm 9/2\rangle - 0.022|\pm 3/2\rangle \mp 0.037|\mp 3/2\rangle + 0.005|\mp 9/2\rangle \pm 0.001|\mp 15/2\rangle.$$  (16)

In this rendering of the doublet the coefficients are real and the matrix elements of $J_z$ within this doublet are

$$|7.379 \quad 0.005\rangle$$

$$|0.005 \quad -7.379\rangle.$$  (17)

That is, within this restriction, $J_z$ can be represented by the matrix $7.379 \sigma_z + 0.005 \sigma_x$. The matrix elements for $J_x$ and $J_y$ are zero within this restriction, and we find that quadrupolar operators of the form $J_x^2J_x^2$ are proportional to the identity, while $J_x^3J_x^3$ and $J_y^3J_y^3$ vanish. The non-zero octupolar moments are $J_x^3J_x^3$, $J_y^3J_y^3$, and $J_z^3J_z^3$, proportional to combinations of $\sigma_x$, $\sigma_y$, and $J_{4t}^3J_{4t}^3$ proportional to $\sigma_z$.

We can define a set of operators based on these kets similar to (9)–(11) and (13)–(15),

$$\tau_x = |\Gamma_{5,6}^+\rangle\langle\Gamma_{5,6}^-| + |\Gamma_{5,6}^-\rangle\langle\Gamma_{5,6}^+|.$$  (17)
\[
\tau_y = -i|\Gamma_{5,6}^+\rangle\langle \Gamma_{5,6}^-| + i|\Gamma_{5,6}^-\rangle\langle \Gamma_{5,6}^+| \tag{18}
\]
\[
\tau_z = |\Gamma_{5,6}^+\rangle\langle \Gamma_{5,6}^+| - |\Gamma_{5,6}^-\rangle\langle \Gamma_{5,6}^-|. \tag{19}
\]

The \(\tau_{\alpha}\) are represented by the matrices \(\sigma_{\alpha}\) in the \{|\Gamma_{5,6}^+, \Gamma_{5,6}^-\rangle\} basis. Therefore, the actions of \(J_x, J_y, J_z, J^x, J^y\) and \(J^z\) in the restricted space of the \(\Gamma_{5,6}\) doublets are equivalent to linear combinations of \(\tau_x\) and \(\tau_y\), while \(J^z\) and \(J^x, J^y\) are proportional to \(\tau_z\). In other words, the operator \(\tau_z\) is only present in models which include octupole moments.

The doublet can also be written as
\[
|\Gamma_5\rangle = (|\Gamma_{5,6}^+\rangle + i|\Gamma_{5,6}^-\rangle)/\sqrt{2} \tag{20}
\]
\[
|\Gamma_6\rangle = (|\Gamma_{5,6}^+\rangle - i|\Gamma_{5,6}^-\rangle)/\sqrt{2}. \tag{21}
\]

The rendering of the doublet as \{|\Gamma_{5,6}^+, \Gamma_{5,6}^-\rangle\} has the physical interpretation of a spin that points into \(|\Gamma_{5,6}^+\rangle\) or out of \(|\Gamma_{5,6}^-\rangle\) a tetrahedron, while \(|\Gamma_5\rangle, |\Gamma_6\rangle\) is a pair of states that are time-reversed partners which transform according to two separate representations, \(\Gamma_5\) and \(\Gamma_6\), in table A2. Either rendering is a valid basis for the space spanned by these kets.

Let us define pseudo-spin operators based on the kets \(|\Gamma_5\rangle, |\Gamma_6\rangle\).

\[
\beta_x = |\Gamma_5\rangle\langle \Gamma_6| + |\Gamma_6\rangle\langle \Gamma_5| = \tau_z \tag{22}
\]
\[
\beta_y = -i|\Gamma_5\rangle\langle \Gamma_6| + i|\Gamma_6\rangle\langle \Gamma_5| = \tau_x \tag{23}
\]
\[
\beta_z = |\Gamma_5\rangle\langle \Gamma_5| - |\Gamma_6\rangle\langle \Gamma_6| = \tau_y. \tag{24}
\]

The transformation of these operators under the operations of the point group \(D_3\) is determined by the transformation of their constituent bras and kets under rotations. It is found that \(\beta_x, \beta_y\) transform as \(\Gamma_2\), while \(\beta_z\) transforms as \(\Gamma_1\), and all components of \(\beta\) change sign under time reversal. The transformations of these operators under the space group operations are given in table A3 of appendix A. By analysing the decomposition of the representation generated by bilinears in \(\beta\), we find that there are exactly four exchange terms allowed by the space group symmetry of the pyrochlore lattice, with slightly different forms compared to the \(\Gamma_4\) case [28]:

\[
X_{\Gamma_{5,6},1} = \sum_{\langle ij \rangle} \beta_i \beta_j \tag{25}
\]
\[
X_{\Gamma_{5,6},2} = \sum_{\langle ij \rangle} \beta_i \beta_j. \tag{26}
\]

\[
X_{\Gamma_{5,6},3} = \sum_{\langle ij \rangle} \beta_i \beta_j \tag{27}
\]
\[
X_{\Gamma_{5,6},4} = \sum_{\langle ij \rangle} (\beta_i \beta_j + \beta_j \beta_i)/2. \tag{28}
\]

The total Hamiltonian therefore has four terms,
\[
H = J_1 X_{\Gamma_{5,6},1} + J_2 X_{\Gamma_{5,6},2} + J_3 X_{\Gamma_{5,6},3} + J_4 X_{\Gamma_{5,6},4}. \tag{29}
\]

However, last three terms in \(H\) can be replaced by two terms [28],
\[
\tilde{X}_{\Gamma_{5,6},3} = \sum_{\langle ij \rangle} \tilde{\beta}_i \tilde{\beta}_j \tag{30}
\]
\[
\tilde{X}_{\Gamma_{5,6},4} = \sum_{\langle ij \rangle} \tilde{\beta}_i \tilde{\beta}_j, \tag{31}
\]

where \(\tilde{\beta}_i = \cos \theta \beta_i + \sin \theta \beta_i\) and \(\tilde{\beta}_i = -\sin \theta \beta_i + \cos \theta \beta_i\) are the operators rotated in the local \(xy\) plane. Then the Hamiltonian (29) is equivalent to
\[
\tilde{H} = J_1 \tilde{X}_{\Gamma_{5,6},1} + \tilde{J}_2 \tilde{X}_{\Gamma_{5,6},2} + \tilde{J}_3 \tilde{X}_{\Gamma_{5,6},3}. \tag{32}
\]

where
\[
\tilde{J}_2 = \frac{J_2 + J_3 + \sqrt{(J_2 - J_3)^2 + J_4^2}}{2} \tag{33}
\]
\[
\tilde{J}_3 = \frac{J_2 + J_3 - \sqrt{(J_2 - J_3)^2 + J_4^2}}{2} \tag{34}
\]
\[
\tan 2\theta = \frac{J_4}{J_2 - J_3}. \tag{35}
\]

This three-parameter model has been applied to \(\text{Nd}_2\text{Zr}_2\text{O}_7\) [12, 13]. As noted in [12], the phase diagram of the exchange model (29) or (32) does not depend on the angle \(\theta\), however the response of the system to an applied magnetic field is sensitive to this angle because it corresponds to a rotation in the local \(xz\) plane of each rare earth magnetic moment.

Considering the model on a single tetrahedron yields further insight about the symmetry of the spin states. On a single tetrahedron the \(\Gamma_{5,6}\) doublet space is spanned by sixteen kets of the pyrochlore lattice, with slightly different forms compared to the \(\Gamma_4\) case [28]:

\[
|\alpha_{11}\rangle = (|+++\rangle + |---\rangle)/\sqrt{2} \tag{36}
\]
(37) 
\[ |A_{1}^{(2)}\rangle = (|++--+| -+++ +| -+++=| +++++| +--+-| -+++-| +--+-| +--+1) / \sqrt{b} \]

(38) 
\[ |A_{3}^{(3)}\rangle = (|++++--| +--+1| -+++--| -++++1| -+++--| -++++1| -+++--| -++++1) / \sqrt{b} \]

(39) 
\[ |A_{1}^{(1)}\rangle = (|++++++|--| -+++--| -++++1| -+++--| -++++1| -+++--| -++++1) / \sqrt{2} \]

(40) 
\[ |A_{2}^{(0)}\rangle = (|++++--| +--+1| -+++--| -++++1| -+++--| -++++1| -+++--| -++++1) / \sqrt{b} \]

(41) 
\[ |E_{4}\rangle = (|+++--| -+++--| +++++1| -+++--| -++++1| -+++--| -++++1) / \sqrt{12} \]

(42) 
\[ |E_{2}\rangle = (|+++--| -+++--| -+++--| -++++1| -+++--| -++++1| -+++--| -++++1) / \sqrt{4} \]

(43) 
\[ |T_{1}(1)\rangle = (|+++--| -+++--| -+++--| -++++1| -+++--| -++++1| -+++--| -++++1) / \sqrt{2} \]

(44) 
\[ |T_{1y}(1)\rangle = (|+++--| -+++--| -+++--| -++++1| -+++--| -++++1| -+++--| -++++1) / \sqrt{2} \]

(45) 
\[ |T_{1z}(1)\rangle = (|+++--| -+++--| -+++--| -++++1| -+++--| -++++1| -+++--| -++++1) / \sqrt{2} \]

These kets can be used to block diagonalise the effective anisotropic exchange interaction on a single tetrahedron. The \( 16 \times 16 \) matrix representing the Hamiltonian (29) is reduced to a \( 3 \times 3 \) block for the \( A_{1} \) sector: \[
\begin{pmatrix}
6J_{2} & 2\sqrt{3}(J_{1} + J_{3}) & 3J_{1} \\
2\sqrt{3}(J_{1} + J_{3}) & 4J_{1} - 2J_{2} + 4J_{3} & \sqrt{3}J_{4} \\
3J_{4} & \sqrt{3}J_{4} & 6J_{1}
\end{pmatrix}
\]
a \( 2 \times 2 \) block for the \( A_{2} \) sector, \[
\begin{pmatrix}
6J_{2} & 3J_{4} \\
3J_{4} & 6J_{1}
\end{pmatrix}
\]
two degenerate blocks for the \( E \) sector, and \( 2 \times 2 \) blocks for the \( T_{2} \) sector, \[
\begin{pmatrix}
-2J_{2} & -J_{1} \\
-J_{1} & -2J_{2}
\end{pmatrix}
\]
three degenerate blocks for the \( T_{2} \) sector, -2\( J_{1} + J_{2} + J_{3} \). These blocks are equivalent to the blocks representing the three-parameter Hamiltonian (32) \[
\begin{pmatrix}
6J_{2} & 2\sqrt{3}(J_{1} + J_{3}) & 0 \\
2\sqrt{3}(J_{1} + J_{3}) & 4J_{1} - 2J_{2} + 4J_{3} & 0 \\
0 & 0 & 6J_{1}
\end{pmatrix}
\]
and \( -2(J_{1} + J_{2} + J_{3}) \). We note that \( I_{3} \) and \( I_{4} \) states on single tetrahedron yield a different decomposition than for \( I_{3,8} \) states. In both of these cases, the decomposition is \( A_{1} \oplus 3E \oplus 27T_{1} \oplus T_{2} \). This leads to a completely different set of degeneracies in the energy spectrum, and to different linear combinations of single tetrahedron kets in the eigenstates.

4. Exchange interaction for \( I_{3} \) CEF ground state

We follow the same approach as in section 3 to find a general effective exchange interaction for non-Kramers \( I_{3} \) doublet, such as the CEF ground state of Pr in \( Pr_{2}Sn_{2}O_{7} \) (neglecting J mixing) [10]:

\[ |\Gamma_{3}^{\pm}(3_{1})\rangle = 0.93\pm 4 \pm 0.37|1\rangle + 0.05|2\rangle \].

The operator \( \vec{\gamma} \) is defined analogously to \( \vec{S} \) and \( \vec{J} \),

\[ \gamma_{x} = |\Gamma_{3}^{+}\rangle (\langle \Gamma_{3}^{-}| + |\Gamma_{3}^{-}\rangle (\langle \Gamma_{3}^{+}| \]

\[ \gamma_{y} = -i|\Gamma_{3}^{+}\rangle (\langle \Gamma_{3}^{-}| + i|\Gamma_{3}^{-}\rangle (\langle \Gamma_{3}^{+}| \]

\[ \gamma_{z} = |\Gamma_{3}^{+}\rangle (\langle \Gamma_{3}^{-}| - |\Gamma_{3}^{-}\rangle (\langle \Gamma_{3}^{+}| \]

The transformation of \( \vec{\gamma} \) under the various symmetry operations is derived from the transformation of the kets \( |\Gamma_{3}^{\pm}\rangle \). We find that \( \vec{\gamma} \) transforms like \( \Gamma_{2} \) of \( D_{4}^{h} \), while \( \gamma_{x,y} \) transforms like \( \Gamma_{3} \), the same as for the operators \( \vec{S} \) and \( \vec{J} \). However, \( \gamma_{z} \) changes sign under time reversal, while \( \gamma_{xy} \) does not. Therefore the effective exchange interaction contains only three terms [30],
\[ X_{\Gamma,1} = \sum_{(j)} \gamma_i \gamma_j \]  
\[ X_{\Gamma,2} = \frac{1}{3} \sum_{(j)} (\lambda_j^+ \gamma_i \gamma_j + \text{h.c.}) \]  
\[ X_{\Gamma,3} = -\frac{1}{6} \sum_{(j)} (\gamma_j^+ \gamma_j^- + \text{h.c.}) \hspace{1cm} (50) \]  
These terms are the same as \( X_1, X_3 \) and \( X_4 \) in \( H_{\text{ex}} \) (4)–(7); here \( X_2 \) is missing because it is not invariant under time reversal.

As noted in the Introduction, in the restriction to the CEF ground state \( |\Gamma^+\rangle \), \( J_{\text{ex}} \) vanish while \( J_z \) is represented by \( \sigma_z \). Non-vanishing operators with matrix elements proportional to \( \sigma_x \) are the quadratic operators \( J_y J_z \) and \( J_z^2 - J_y^2 \), while \( J_y J_z \) and \( J_z J_y \) yield \( \sigma_y \). The terms \( X_{\Gamma,2} \) and \( X_{\Gamma,3} \) can therefore arise from interactions between nearest neighbour quadrupole moments. This model has been used to describe Pr spin ice pyrochlores [11, 29–31].

5. Summary

In modelling exchange interactions in spin systems with symmetry constraints there are two aspects that must be considered: the local site symmetry (the local CEF) and the global space group symmetry. This paper concerns models for those systems which have doubly degenerate CEF ground states, which include many of the rare earth pyrochlores. Different kinds of CEF doublets may have different symmetries, but each may be cast either as a true spin-1/2 spinor or as a pseudospin of some kind. The states in a doublet are used to construct operators that can be represented as the Pauli matrices, whose symmetry properties are derived from the doublet upon which they are constructed. These operators act in pairs as nearest neighbour exchange interactions that are invariant under the global space group symmetry.

The method presented in this paper is an alternative proof of previously proposed models for the rare earth pyrochlores, and can be generalised to any magnetic system in which the first excited CEF energy level is well-separated from the ground state.

Acknowledgment

This work was supported by NSERC.

Appendix A. Symmetry considerations

The magnetic rare earth ions are located at the 16d Wyckoff position of the cubic space group \( Fd\overline{3}m \). Considering origin choice 1 in the International Tables for Crystallography [32], the four sites of a primitive unit cell are located at the positions listed in table A1. The remaining 12 sites found in the cubic cell are obtained by fcc lattice translations. The cubic cell and the primitive cell are shown in figure A1. The underlying point group symmetry is the octahedral group \( O_h \), which includes two-fold rotations and four-fold screw rotations about the cubic axes, three-fold rotations about the cube diagonals (shown as black arrows in the figure), and two-fold screw rotations about the [1 1 0] directions, as well as inversion centres at each rare earth site.

It is convenient to adopt a local coordinate system for each of the four sites of the 16d Wyckoff position. Global coordinates are denoted by superscripts while the local coordinates are denoted by subscripts. The angular momentum operators for local coordinates are given in terms of the global coordinates as follows:

| Site # | Position | Three-fold axis |
|-------|----------|-----------------|
| 1     | (5/8, 5/8, 5/8) | (1, 1, 1) |
| 2     | (3/8, 3/8, 5/8) | (−1, −1, 1) |
| 3     | (3/8, 5/8, 3/8) | (−1, 1, −1) |
| 4     | (5/8, 3/8, 3/8) | (1, −1, −1) |

Table A1. Locations of the four sites of the 16d Wyckoff position.

Figure A1. The top figure shows the rare earth ions at the 16d Wyckoff position and the exchange paths within a cubic cell. The green/red paths correspond to type A/B tetrahedra. The black arrows indicate the direction of the local \( z \)-axes. The bottom figure is a part of the top figure and shows the four rare earth ions and the 12 exchange paths of a primitive cell.
The local z-axes are the three-fold symmetry axes of the crystal, and in particular they are three-fold symmetry axes for the 16d Wyckoff position. The local z-axes are shown as black arrows in figure A1. Different choices of the local x and y axes are possible, provided they are perpendicular to z and obey the right hand rule.

The 16d positions form a corner-sharing tetrahedral lattice. The tetrahedra alternate between two orientations, which we label A and B. Each site is on a corner that is shared between an A tetrahedron and a B tetrahedron. (We can assume that the tetrahedra alternate between two orientations, which obey the right hand rule.

The site symmetry of the 16d position is $D_{3d}$, where the three-fold axes point in the [1 1 1] directions of the crystal. The inversion element of $D_{3d}$ is usually handled separately, because within a given J manifold the orbital angular momentum $L$ is fixed, and is simply either even or odd under inversion. However, the double set of rotations must be considered for half-integral J, so the relevant point group for the 16d positions is the double group $D_{3d}$.

Table A2 shows the character table for the double group $D_{3d}$. The CEF levels of ions at the 16d positions can be classified by these representations. For integral J ions, there are three representations, two singlets and a doublet. For half-integral J, (which change sign under rotations by $2\pi$), there are two representations, that are necessarily (by Kramers theorem) two dimensional.

Table A3 shows how different sites, tetrahedra, and operators transform under the space group operations and time reversal $K$. The operations are two-fold, three-fold and four-fold rotations around a global axis specified by the subscript and inversion I. Some of the rotations are screw rotations (for details see [32]). For example, under a $C_{4z}$ screw rotation, $J_{1x} \rightarrow -J_{4x}$ and type A paths become type B paths.

Using the results in table A3, the characters associated with each kind of bilinear spin operator can be calculated, as listed in table A4. Each bilinear operator is associated with two nearest neighbour sites within a unit cell. There are 12 such pairs altogether: six pairings of the four sites, and two of each of these corresponding to A-type and B-type paths. The first column of characters (under the identity operation $E$) simply counts the number of operators of a given type. Among the remaining operations, only those that preserve the path (A versus B) of the bilinear can yield a non-zero character. These are $C_{1z}$, $C_{2z}$, $IC_{1z}$ and $IC_{2z}$. Among these, $C_{1z}$ and $IC_{1z}$ have vanishing characters because $C_3$ permutes three sites and $IC_4$ permutes four sites (so the site numbers on the bilinear must change). Therefore the only classes with non-vanishing characters are $C_{2z}$ and $IC_{2z}$. These characters can be calculated by considering the operations $C_{2z}$, $C_{2z}[1110]$ and $I$ in table A3 for $J$ and $\beta \gamma$ transforms the same way as $J$ under the space group operations, but differs under time reversal, as discussed in section 4.

The entries under the column labelled $A_{1g}$ in table A4 are the number of bilinear invariants for the pyrochlore crystal. Each invariant corresponds to a term in the Hamiltonian.

**Table A2.** The character table of the double group $D_{3d}$.

| $D_{3d}$ | $E$ | $R$ | $2C_{3}$ | $2RC_{3}$ | $3C_{3}'$ | $3RC_{3}$ |
|---------|-----|-----|---------|---------|---------|---------|
| $I'$   | 1   | 1   | 1       | 1       | 1       | 1       |
| $I''$  | 1   | 1   | 1       | 1       | -1      | -1      |
| $\Gamma_3$ | 2   | 2   | -1      | -1      | 0       | 0       |
| $\Gamma_4$ | 2   | -2  | 1       | -1      | 0       | 0       |
| $\Gamma_{5,6}$ | 1   | -1  | -1      | 1       | -1      | -i      |

$J_{1x} = (J_1^x + J_3^x - 2J_2^x)/\sqrt{6}$, $J_{2x} = (-J_1^x - J_3^x - 2J_2^x)/\sqrt{6}$, $J_{1y} = (-J_1^y + J_3^y)/\sqrt{2}$, $J_{3y} = (J_1^y + J_3^y)/\sqrt{2}$, $J_{1z} = (J_1^z + J_3^z + J_2^z)/\sqrt{3}$, $J_{2z} = (-J_1^z - J_3^z + J_2^z)/\sqrt{3}$, $J_{3z} = (J_1^z + J_2^z - J_3^z)/\sqrt{3}$.

$\beta_1 = \sqrt{2}$, $\beta_2 = \sqrt{2}$, $\beta_3 = \sqrt{2}$, $\beta_4 = \sqrt{2}$, $\beta_5 = \sqrt{2}$, $\beta_6 = \sqrt{2}$, $\gamma_1 = \sqrt{2}$, $\gamma_2 = \sqrt{2}$, $\gamma_3 = \sqrt{2}$, $\gamma_4 = \sqrt{2}$, $\gamma_5 = \sqrt{2}$, $\gamma_6 = \sqrt{2}$.

**Table A3.** Transformation of site numbers, tetrahedron type, and various operators under the space group generators and time reversal. $x' = -x/2 + \sqrt{3}y/2$, $y' = -y/2 - \sqrt{3}x/2$.

| | $C_{2z}$ | $C_{2z}'$ | $C_{2z}[1110]$ | $C_{4z}$ | $I'$ | $K$ |
|-------|---------|----------|----------------|---------|-----|-----|
| 1     | 2       | 3        | 1              | 2       | 4   | 1   |
| 2     | 1       | 4        | 4              | 1       | 3   | 2   |
| 3     | 4       | 1        | 2              | 3       | 1   | 3   |
| 4     | 3       | 2        | 3              | 4       | 2   | 4   |

$A/B$ | $A/B$ | $A/B$ | $A/B$ | $A/B$ | $A/B$ |
|------|------|------|------|------|------|

**Appendix B. The anisotropic exchange interaction**

The exchange interaction written as (4)–(7) is a useful form for analytic calculations. Alternatively, the four terms in the Hamiltonian can be written as

$$-3X_1 = \sum_{\text{tetra}} J_{14}J_{24} + J_{14}J_{34} + J_{14}J_{44} + J_{24}J_{34} + J_{24}J_{44} + J_{34}J_{44}$$

(B.1)
Table A4. Characters associated with each type of bilinear spin operator. The first part of the top row lists the classes of the point group \( O_h \); the second part lists the irreducible representations of \( O_h \). The first column lists the different types of bilinears. The left-hand-side array of numbers is the characters, and the right-hand-side array of numbers gives the representation decomposition for each type of bilinear. The \( C_2 \) operations are rotations about the main cubic axes (the [1 0 0] directions), and \( C_4 \) are rotations about the [1 1 0] directions.

\[
\begin{array}{|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline
\text{Operator} & \text{symbol} & E & C_3 & C_2 & C_4 & I & IC_3 & IC_2 & IC_4 & A_{1g} & A_{2g} & E_x & T_{1g} & T_{2g} & A_{1u} & A_{2u} & E_u & T_{1u} & T_{2u} \\
\hline
J_xJ_y & J_{xy} & 12 & 0 & 4 & 0 & 0 & 0 & 0 & 0 & 4 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
J_yJ_z & J_{yz} & 48 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 2 & 3 & 3 & 1 & 1 & 2 & 3 \\
J_zJ_x & J_{zx} & 24 & 0 & 8 & 0 & 0 & 0 & 0 & 0 & 8 & 0 & 2 & 2 & 2 & 2 & 2 & 2 & 2 & 2 & 2 \\
J_{y}J_{z} & J_{x} & 24 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -4 & 0 & 1 & 1 & 2 & 1 & 1 & 1 & 1 & 2 & 1 \\
\hline
\text{Total} & & 108 & 0 & 12 & 0 & 0 & 0 & 0 & 8 & 0 & 4 & 2 & 6 & 5 & 7 & 7 & 2 & 4 & 6 & 7 & 5 \\
\hline
\beta_{0}J_{y} & J_{y} & 24 & 0 & 8 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 2 & 1 & 1 & 1 & 2 & 1 & 1 \\
\beta_{0}J_{z} & J_{z} & 24 & 0 & 0 & 0 & 0 & 0 & 0 & 4 & 0 & 1 & 1 & 1 & 2 & 1 & 1 & 1 & 2 & 1 & 1 \\
\beta_{0}J_{x} & J_{x} & 48 & 0 & 0 & 0 & 0 & 0 & 0 & -8 & 0 & -2 & 2 & 4 & 2 & 2 & 2 & 2 & 4 & 2 \\
\beta_{0}J_{y} & J_{y} & 12 & 4 & 0 & 0 & 0 & 0 & 0 & 4 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
\beta_{0}J_{z} & J_{z} & 12 & 4 & 0 & 0 & 0 & 0 & 0 & 4 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
\beta_{0}J_{x} & J_{x} & 24 & 0 & 0 & 0 & 0 & 0 & 0 & 4 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
\beta_{0}J_{y} & J_{y} & 24 & 0 & 0 & 0 & 0 & 0 & 0 & 4 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
\beta_{0}J_{z} & J_{z} & 48 & 0 & 0 & 0 & 0 & 0 & 0 & -8 & 0 & -2 & 2 & 4 & 2 & 2 & 2 & 2 & 4 & 2 \\
\beta_{0}J_{x} & J_{x} & 12 & 4 & 0 & 0 & 0 & 0 & 0 & 4 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
\beta_{0}J_{y} & J_{y} & 12 & 4 & 0 & 0 & 0 & 0 & 0 & 4 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
\beta_{0}J_{z} & J_{z} & 24 & 0 & 0 & 0 & 0 & 0 & 0 & 4 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
\beta_{0}J_{x} & J_{x} & 24 & 0 & 0 & 0 & 0 & 0 & 0 & 4 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
\hline
\end{array}
\]

\[
-\frac{3}{\sqrt{2}}X_2 = \sum_{\text{teta}} J_{11}J_{22} + J_{11}J_{33} + J_{11}J_{44} + J_{11}J_{14} + J_{11}J_{12}
\]

\[
+ J_{11}J_{13} + J_{22}J_{33} + J_{22}J_{44} + J_{22}J_{14} + J_{22}J_{12}
\]

\[
\frac{3}{4}X_1 - \frac{3}{2}X_2 = \sum_{\text{teta}} J_{11}J_{23} + J_{11}J_{43} + J_{11}J_{43} + J_{11}J_{14} + J_{11}J_{12}
\]

\[
- \frac{3}{4}X_1 - \frac{3}{2}X_2 = \sum_{\text{teta}} J_{11}J_{23} + J_{11}J_{34} + J_{11}J_{43} + J_{11}J_{14} + J_{11}J_{12}
\]

where \( x' = -\frac{1}{2} + \frac{\sqrt{7}}{2} \), \( y' = -\frac{1}{2} - \frac{\sqrt{7}}{2} \), \( x'' = -\frac{1}{2} - \frac{\sqrt{7}}{2} \), and \( y'' = -\frac{1}{2} + \frac{\sqrt{7}}{2} \). The sums are over all tetrahedra (both A and B orientations) in the pyrochlore lattice. This allows us to compare the terms in this Hamiltonian with the terms of the \( \Gamma_{5,6} \) model (25)–(28); in this Hamiltonian some of the operators are rotated by 120 degrees and by 240 degrees in the \( xy \)-plane, while in the \( \Gamma_{5,6} \) model, all of the operators are rotated by the same angle \( \theta \).

The exchange interaction can also be written using global axes:

\[
X_{t1} = \sum_{\text{teta}} J_{11}J_{22} + J_{11}J_{33} + J_{11}J_{44} + J_{11}J_{14} + J_{11}J_{12}
\]

\[
= -X_1 + \frac{1}{2}X_2 + \frac{1}{2}X_3 - X_4
\]

\[
X_{t2} = \sum_{\text{teta}} J_{11}J_{23} + J_{11}J_{33} + J_{11}J_{43} + J_{11}J_{14} + J_{11}J_{12}
\]

\[
= 2X_1 + \frac{1}{2}X_2 + \frac{1}{2}X_3 + 2X_4
\]

\[
X_{t3} = \sum_{\text{teta}} J_{11}J_{23} + J_{11}J_{33} + J_{11}J_{43} + J_{11}J_{14} + J_{11}J_{12}
\]

\[
= -X_1 + \frac{1}{2}X_2 + \frac{1}{2}X_3 - X_4
\]
Here, the sum of the first two terms \( X_{11} + X_{12} \) yields the isotropic exchange interaction. The third term is another completely symmetric contribution while the fourth is completely anti-symmetric.

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