Spin Correlations on the Pyrochlore Lattice

by

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Abstract

Pyrochlores have the chemical formula $A_2B_2O_7$ with A, B, or both A and B magnetic. It has corner-sharing tetrahedra in the structure, therefore, frustration phenomena naturally occurs in these systems. Because of the frustration, pyrochlore have many interesting properties, including the spin glass in $Y_2Mo_2O_7$, spin liquid in $Tb_2Ti_2O_7$, disordered spin ice in $Ho_2Ti_2O_7$, and ordered spin ice in $Tb_2Sn_2O_7$.

In this thesis we will focus on $Tb_2Ti_2O_7$. Our goal is to find the spin correlation functions between different sites of Tb ions. The Hamiltonian of Tb ions is an anisotropic nearest neighbour exchange interaction. We apply perturbation theory to the Hamiltonian, and it will separate the Hamiltonian into two parts. The unperturbed part of Hamiltonian is the spin ice Hamiltonian, and other parts of the Hamiltonian are perturbative. The perturbative parts of Hamiltonian can be written in the local coordinates to give three different terms X_2, X_3, X_4. In order to find the spin correlation function, we calculate time dependent spin operators in the interaction picture. Then we apply them to the unperturbed and perturbed terms of Hamiltonian to calculate the spin correlation functions. Finally, we discuss the neutron scattering experiment and how to apply it to test our results.

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Chapter 1

Introduction

1.1 Geometric Frustration

Geometric frustration occurs when a system cannot minimize its total classical energy by minimizing the interaction energy between each pair of interacting degrees of freedom pair by pair due to the geometric structure of its lattice [1]. A simple example of geometric frustration is shown in Figure 1; three spins lie at the vertices of an equilateral triangle with antiferromagnetic interactions between them. If we want to minimize the energy of each spin pair, all those spins should be anti-parallel. However, when we align the first two spins be anti-parallel, the third spin can either point up or down. Therefore, we say the third spin is frustrated [1].

In three dimensions, geometrical frustration can occur in a tetrahedra. Suppose we have a tetrahedron which contains four spins on its corners (Figure 1.2). If there is an antiferromagnetic interaction between spins, then it is not possible to arrange the spins so that all interactions between spins are antiparallel [2].

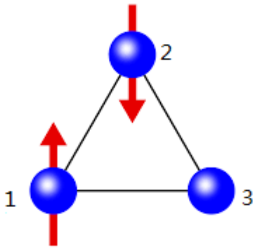

Figure 1.1: Geometric frustration on a triangle. It is impossible to align all spins anti-parallel.

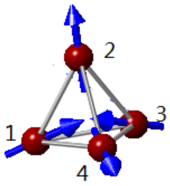

Figure 1.2: Geometric frustration on a tetrahedron (spin ice).

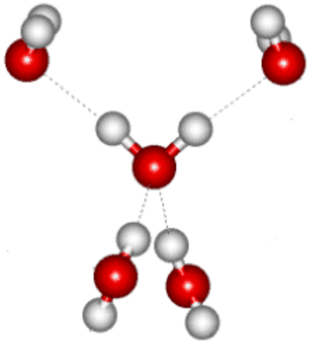

Figure 1.3: Crystal water ice structure.

1.2 Ice Rule and Residual Entropy

In 1935, Linus Pauling noted that the structure of water ice (Figure 1.3) exhibits degrees of freedom that would be expected to remain disordered even at absolute zero. In his research he used the ice rule to explain the disordered property of crystalline water ice. The ice rule states that in water ice two protons (H^+ ions) are near to and two are further away from each oxygen ion [5]. It was previously proposed by Bernal and Fowler [4]. Pauling noted that the number of configurations conforming to this “two-in and two-out” rule grows exponentially with the system size, and, therefore, that the zero-temperature entropy of ice was expected to be extensive [5]. Pauling’s findings were confirmed by specific heat measurements, though pure crystals of water ice are particularly hard to create.

Pauling also noticed that because of the ice rule, crystal ice has residual entropy even at zero temperature. Moreover, he calculated the residual entropy of crystal ice which is $R = \frac{1}{2} \ln \frac{3}{2}$ [5].

1.3 Spin Ice

In 1956, Philip Anderson noted that the frustrated Ising ferromagnet on a (pyrochlore) lattice of corner-sharing tetrahedra is equivalent to Pauling's water ice problem [3]. It is called spin ice, and it consists tetrahedra of spins, which must satisfy the same two-in and two-out ice rule analogous to water ice [3]. We can see the spin ice structure in Figure 1.2.

Spin ice has many interesting properties, one of which is the residual entropy as T→ 0 [3]. Moreover, recent experiments found the evidence for the existence of magnetic monopoles in these materials [3]. If one atom flips its spin, we can have three-in and one-out, or three-out and one-in spin structures on tetrahedra in these materials which can be treated as magnetic monopoles locally [3].

1.4 Spin Ice Degeneracy: Pauling's Argument

In water ice, suppose there are N oxygen ions and $2N$ hydrogen ions in a mole a ice. There are 2^{2N} configurations of hydrogen bonds between adjacent oxygen atoms, each hydrogen nucleus having two choices of two positions, either near one oxygen ion or the other. Now, let us consider a given oxygen atom with four surrounding hydrogen atoms. Since each hydrogen ion has two possible positions, there are sixteen arrangements of the four hydrogen nuclei. Among of these 6 satisfy the ice rule. Hence the total number of configurations satisfies the ice rule is estimated to be $W = 2^{2N}(6/16) = (3/2)^N$ [2].

Now we apply Pauling's argument to spin ice. Suppose there are N magnetic ions each magnetic moment can be in one of two configurations (points into or out of a tetrahedron), there are 2^N configurations. Now let us consider a single tetrahedron: which has 4 magnetic ions. Thus, there will be $2^4 = 16$ possible configurations for each tetrahedron, and among these only 6 of them satisfy the spin ice rule, therefore we have the fraction $(\frac{6}{16})^{N/2}$ for spin ice. Therefore, the total number of configuration is $2^N(\frac{6}{16})^{N/2} = (3/2)^{N/2}$ [2].

1.5 Pyrochlore Lattice

The cubic pyrochlores have the chemical formula $A_2B_2O_7$, where A is a rare earth and B is a transition metal [1]. In practice, the formula of cubic pyrochlores can be expressed as $A_2B_2O_7$. It has corner-sharing tetrahedra in the structure, therefore, frustration phenomena naturally occurs in these systems [1].

The pyrochlores have space group Fd$\bar{3}$m (No.227). The details of the structure are listed in Table 1.1 and 1.2 and shown in Figure 1.4.

Table 1.1: Atomic Positions of Pyrochlore

Ions	Site	Coordinate Position
A	16d	$(0.5, 0.5, 0.5)$
B	16c	$(0, 0, 0)$
O’	8b	$(0.375, 0.375, 0.375)$
O	48f	$(x, 0.125, 0.125)$

Atom number	Equivalent Position	Local z-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 1.2: Position of the 16*d* Wyckoff of origin choice 1

Recently, pyrochlores are well-studied, and many interesting properties have been revealed. Pyrochlores have residual entropy even at zero temperature [1]. Moreover, pyrochlore can have spin ice structure, for example, disordered spin ice in $Ho_2Ti_2O_7$, ordered spin ice in $Tb_2Sn_2O_7$ and quantum spin ice in $Tb_2Ti_2O_7$, as well as different

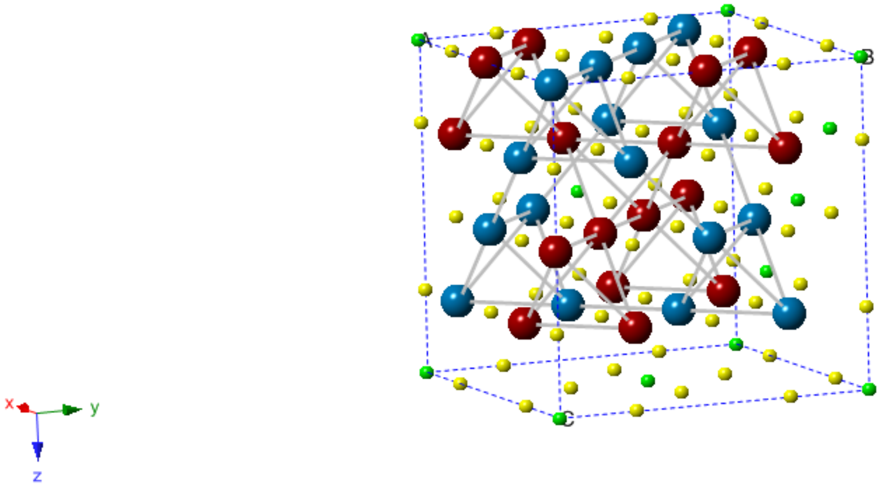

Figure 1.4: Crystal structure of $R_2Ti_2O_7$. The red ions are R^{3+}, the blue ions are Ti^{4+}, and the yellow and green ions are oxygen.

kinds of magnetic ordering in $Er_2Ti_2O_7$ and $Yb_2Ti_2O_7$ [1]. Most recently, a spin liquid state was discovered in pyrochlores such as $Ce_2Sn_2O_7$ [31]; it is a disordered state in a system of interacting quantum spins [28]. Spin liquid was first proposed by Philip Anderson in 1973 as the ground state for a system of spins on a triangular lattice [28]. Moreover, he proposed a theory that described high temperature superconductivity in terms of a disordered spin-liquid state in 1987 [28].

1.6 $Tb_2Ti_2O_7$

In the past few years, many experiment has been achieved to reveal the physical properties of $Tb_2Ti_2O_7$. Muon spin relaxation measurements show that at low temperature $Tb_2Ti_2O_7$ has paramagnetic behaviour [6]. High-resolution neutron powder-diffraction showed that the crystal structure of $Tb_2Ti_2O_7$ is the pyrochlore structure without disorder [8]. The diffuse neutron scattering is used to examine correlations in $Tb_2Ti_2O_7$. It showed at 9 K, $Tb_2Ti_2O_7$ has only short range correlations [5]. The neutron spin echo experiment is used to study the dynamics of the magnetic state of $Tb_2Ti_2O_7$. From the experiment, it shows the magnetic state of $Tb_2Ti_2O_7$ appears to be freezing close to 200 mK, however, the majority of spins have dynamic fluctuations down to below 50 mK [10]. Moreover, ultrasonic measurements show that $Tb_2Ti_2O_7$ exhibits strong softening effects [11].

Recently, $Tb_2Ti_2O_7$ was treated as a quantum mechanical version of the classical spin ice [6]. Therefore, it can be used to explain some properties of $Tb_2Ti_2O_7$. For example, diffuse neutron scattering patterns cannot be explained by a classical spin ice model [17]. Moreover, we can treat $Tb_2Ti_2O_7$ as effective spin 1/2 system [17]. Hence, we can write down the Hamiltonian as effective spin 1/2 system to find the spin correlations. The Hamiltonian of $Tb_2Ti_2O_7$ is a spin ice Hamiltonian with additional spin flip terms, which lift the macroscopic degeneracy of the classical 2-in and 2-out ground state [7].

1.7 Outline of Thesis

In this chapter we introduced the pyrochlores. Because of the corner-shared tetrahedron structure in pyrochlores, the geometric frustration phenomenon occurs. More particularly, we will focus on one of the pyrochlores: $Tb_2Ti_2O_7$, a quantum spin ice material. We treat $Tb_2Ti_2O_7$ using perturbation theory, by considering 3 of the 4 terms in the Hamitonian as small [32].

In the following chapter, we will introduce the perturbation theory on Tb ions in $Tb_2Ti_2O_7$ and do the first order perturbation to calculate the spin correlation of Tb ions. In Chapter 3, we will use it on the Hamiltonian of Tb ions to find the spin correlations between different sites of Tb ions. In Chapter 4, I will summarize the work I did in this thesis, as well as the results I got. Moreover, I will suggest what work can be done in the future.

Chapter 2

Spin Correlations using Perturbation Theory

In this chapter we will use perturbation theory to find the spin correlation function between different sites of Tb ions in $Tb_2Ti_2O_7$. Therefore, we will discuss why can we use perturbation theory and how to use it.

2.1 Spin Correlation

In statistical mechanics, the correlation function is a measure of the order in a system. Correlation functions describe how microscopic variables, such as spin and density, at different positions are related. Therefore, the spin correlation function can be used to find the relationship between spins. More specifically, if we know the spin for one atom, then based on the spin correlation function we can find the spin for another atom [21]. We can use neutron scattering to measure the spin correlation [21].

2.2 Perturbation Theory

Perturbation theory is a mathematical method for finding an approximate solution to a problem, by starting from the exact solution of a related problem. By using perturbation theory, we can break the problem into "solvable" and "perturbation" parts. Perturbation theory is applicable if the problem at hand cannot be solved exactly, but can be formulated by adding a "small" term to the mathematical description of the exactly solvable problem [21].

By using perturbation theory, we can express the the problem as a power series in some "small" parameter which is known as a perturbation series. The leading term in this power series is the solution of the exactly solvable problem, while further terms describe the deviation in the solution, due to the deviation from the initial problem [21]. For example, if we use the perturbation theory on A, we have

$$A = A_0 + \epsilon^1 A_1 + \epsilon^2 A_2 + \epsilon^3 A_3 + \dots$$

where ϵ is a small quantity, A_0 is the known solution to the exactly solvable initial problem and A_1, A_2, $\dots$ represent the higher-order terms which may be found iteratively by some systematic procedure.

An approximate "perturbative solution" is obtained by truncating the series, usually by keeping only the first two terms, the initial solution and the "first-order" perturbation correction

$$A \approx A_0 + \epsilon A_1$$

2.3 Hamiltonian of Tb ions

In quantum mechanics, Kramers theorem states that the energy levels of a system with an odd total number of fermions remain at least doubly degenerate in the absence of a magnetic field [20]. In $Tb_2Ti_2O_7$, the 13-fold degeneracy of the $J = 6$ Tb ions is lifted by the local crystal electric field into singlets and doublets. The ground state doublet of Tb^{3+} is a non-Kramers doublet. However, on a tetrahedron, which has point group symmetry T_d, the symmetry classification of the 4 Tb^{3+} ions is $A_1 \oplus 3E_2 \oplus 2T_1 \oplus T_2$ which happens to be isomorphic to a tetrahedron of 4 spin 1/2 spins. Hence, there is a map from the Tb non-Kramers doublet to a spin 1/2 spinor. Therefore, one can treat Tb ions in $Tb_2Ti_2O_7$ as a spin 1/2 problem [17].

The Hamiltonian of the Tb ions can be expressed by

$$H = H_0 + H_1 \tag{2.1}$$

$$H_0 = \mathcal{J}_1 X_1 \tag{2.2}$$

$$H_1 = [\mathcal{J}_2 X_2 + \mathcal{J}_3 X_3 + \mathcal{J}_4 X_4]\epsilon(t) \tag{2.3}$$

where the $\mathcal{J}_i$ are the anisotropic exchange constants for the effective spin 1/2 model, X_i are the anisotropic exchange interaction terms, and $\epsilon(t)$ is a function which is approximately 1 for finite times, and that vanishes as $t \to \pm\infty$. In $Tb_2Ti_2O_7$, $\mathcal{J}_{2,3,4} \ll \mathcal{J}_1$ [17].

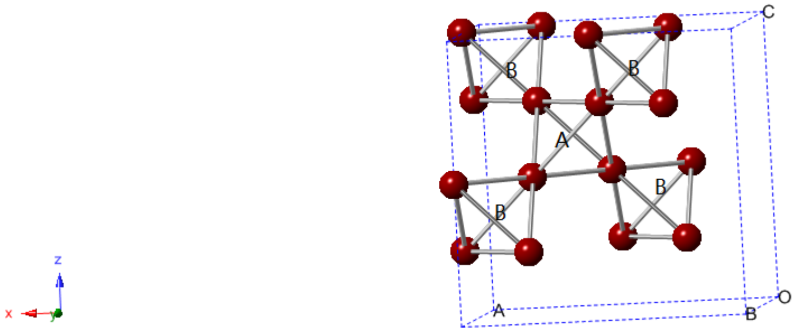

Figure 2.2: The structure of Tb ions, it has the corner-shared tetrahedron structure.

Tb ions located at the 16d position have a site symmetry D$_{3d}$, where the 3-fold axes point in the [111] direction. For convenience we will use local coordinates for the Hamiltonian. The local coordinates are locally rotated so that the local z-axis is the 3-fold axis, while the local x and y axes are chosen such that they obey the right hand rule [32]. This is convenient because the spin quantisation axis is the z-axis by convention, and this choice allows the spin states to be written in a symmetrical form that maps to effective spin 1/2 states. We will discuss the transformation relations in detail in Appendix.

In the following we will write down the angular momentum operators in local coordinates in terms of global coordinates (superscripts are the global coordinates and subscripts are the local coordinates) [17].

for ion 1, at $(5/8, 5/8, 5/8)$ we have the local coordinates

$$
\begin{aligned}
J_{1x} &= J_1^x/\sqrt{6} + J_1^y/\sqrt{6} - 2J_1^z/\sqrt{6} \\
J_{1y} &= -J_1^x/\sqrt{2} + J_1^y/\sqrt{2} \\
J_{1z} &= J_1^x/\sqrt{3} + J_1^y/\sqrt{3} + J_1^z/\sqrt{3};
\end{aligned}
$$

for ion 2, at $(3/8, 3/8, 5/8)$ we have the local coordinates

$$\begin{aligned}
J_{2x} &= -J_2^x/\sqrt{6} - J_2^y/\sqrt{6} - 2J_2^z/\sqrt{6} \\
J_{2y} &= J_2^x/\sqrt{2} - J_2^y/\sqrt{2} \\
J_{2z} &= -J_2^x/\sqrt{3} - J_2^y/\sqrt{3} + J_2^z/\sqrt{3};
\end{aligned}$$

for ion 3, at $(3/8, 5/8, 3/8)$ we have the local coordinates

$$\begin{aligned}
J_{3x} &= -J_3^x/\sqrt{6} + J_3^y/\sqrt{6} + 2J_3^z/\sqrt{6} \\
J_{3y} &= J_3^x/\sqrt{2} + J_3^y/\sqrt{2} \\
J_{3z} &= -J_3^x/\sqrt{3} + J_3^y/\sqrt{3} - J_3^z/\sqrt{3};
\end{aligned}$$

for ion 4, at $(5/8, 3/8, 3/8)$ we have the local coordinates

$$\begin{aligned}
J_{4x} &= J_4^x/\sqrt{6} - J_4^y/\sqrt{6} + 2J_4^z/\sqrt{6} \\
J_{4y} &= -J_4^x/\sqrt{2} - J_4^y/\sqrt{2} \\
J_{4z} &= J_4^x/\sqrt{3} - J_4^y/\sqrt{3} - J_4^z/\sqrt{3}.
\end{aligned}$$

The exchange interaction terms can be expressed in local coordinates as

$$X_1 = -\frac{1}{3}\sum_{<ij>} J_{iz}J_{jz} \tag{2.4}$$

$$X_2 = -\frac{\sqrt{2}}{3}\sum_{<ij>} [\Lambda_{s_i s_j}(J_{iz}J_{j+} + J_{jz}J_{i+}) + h.c.] \tag{2.5}$$

$$X_3 = \frac{1}{3}\sum_{<ij>} [\Lambda^*_{s_i s_j} J_{i+}J_{j+} + h.c.] \tag{2.6}$$

$$X_4 = -\frac{1}{6}\sum_{<ij>} (J_{i+}J_{j-} + h.c.) \tag{2.7}$$

where *h.c.* stands for Hermitian conjugate, i and j are sites on the lattice while S_i and S_j are the corresponding Wyckoff positions ($S_i, S_j = 1, 2, 3, 4$). $\Lambda_{12} = \Lambda_{34} = 1$ and $\Lambda_{13} = \Lambda_{24} = \Lambda_{14}^* = \Lambda_{23}^* = \varepsilon \equiv \exp(\frac{2\pi i}{3})$, and $\langle i, j \rangle$ are nearest neighbours. These terms are written explicitly in Table 2.1 for a single tetrahedron.

Term	X$_1$	X$_2$	X$_3$	X$_4$
$\vec{J}_1 \cdot \vec{J}_2$	$-\frac{1}{3}J_{1z}J_{2z}$	$-\frac{\sqrt{2}}{3}[J_{1z}(J_{2+} + J_{2-}) + (J_{1+} + J_{1-})J_{2z}]$	$\frac{1}{3}(J_{1+}J_{2+} + J_{1-}J_{2-})$	$-\frac{1}{6}(J_{1+}J_{2-} + J_{1-}J_{2+})$
$\vec{J}_3 \cdot \vec{J}_4$	$-\frac{1}{3}J_{3z}J_{4z}$	$-\frac{\sqrt{2}}{3}[J_{3z}(J_{4+} + J_{4-}) + (J_{3+} + J_{3-})J_{4z}]$	$\frac{1}{3}(J_{3+}J_{4+} + J_{3-}J_{4-})$	$-\frac{1}{6}(J_{3+}J_{4-} + J_{3-}J_{4+})$
$\vec{J}_1 \cdot \vec{J}_3$	$-\frac{1}{3}J_{1z}J_{3z}$	$-\frac{\sqrt{2}}{3}[J_{1z}(\varepsilon J_{3+} + \varepsilon^2 J_{3-}) + (\varepsilon J_{1+} + \varepsilon^2 J_{1-})J_{3z}]$	$\frac{1}{3}(\varepsilon^2 J_{1+}J_{3+} + \varepsilon J_{1-}J_{3-})$	$-\frac{1}{6}(J_{1+}J_{3-} + J_{1-}J_{3+})$
$\vec{J}_2 \cdot \vec{J}_4$	$-\frac{1}{3}J_{2z}J_{4z}$	$-\frac{\sqrt{2}}{3}[J_{2z}(\varepsilon J_{4+} + \varepsilon^2 J_{4-}) + (\varepsilon J_{2+} + \varepsilon^2 J_{2-})J_{4z}]$	$\frac{1}{3}(\varepsilon^2 J_{2+}J_{4+} + \varepsilon J_{2-}J_{4-})$	$-\frac{1}{6}(J_{2+}J_{4-} + J_{2-}J_{4+})$
$\vec{J}_1 \cdot \vec{J}_4$	$-\frac{1}{3}J_{1z}J_{4z}$	$-\frac{\sqrt{2}}{3}[J_{1z}(\varepsilon^2 J_{4+} + \varepsilon J_{4-}) + (\varepsilon^2 J_{1+} + \varepsilon J_{1-})J_{4z}]$	$\frac{1}{3}(\varepsilon J_{1+}J_{4+} + \varepsilon^2 J_{1-}J_{4-})$	$-\frac{1}{6}(J_{1+}J_{4-} + J_{1-}J_{4+})$
$\vec{J}_2 \cdot \vec{J}_3$	$-\frac{1}{3}J_{2z}J_{3z}$	$-\frac{\sqrt{2}}{3}[J_{2z}(\varepsilon^2 J_{3+} + \varepsilon J_{3-}) + (\varepsilon^2 J_{2+} + \varepsilon J_{2-})J_{3z}]$	$\frac{1}{3}(\varepsilon J_{2+}J_{3+} + \varepsilon^2 J_{2-}J_{3-})$	$-\frac{1}{6}(J_{2+}J_{3-} + J_{2-}J_{3+})$

Table 2.1: The exchange interaction over a single tetrahedron expressed in terms of local coordinates for each Tb ion.

2.4 Interaction Picture and Perturbative Expansion

If we want to calculate $\langle J_i^\alpha(t) J_j^\beta(t') \rangle$ in $Tb_2Ti_2O_7$, we can express it in the Heisenberg representation as

$$\frac{\mathrm{Tr}[\rho_H J_{Hi}^\alpha(t) J_{Hj}^\beta(t')]}{\mathrm{Tr}[\rho_H]},$$

where the time $t = 0$ will be used as the reference time. Here $H = H_0 + H_1$, where $H_0 = \mathcal{J}_1 X_1$ and H_1 contains the other exchange terms [21]. When $\mathcal{J}_1 < 0$, the ground state of H_0 is the spin ice manifold, which can be described as a density matrix

$$\rho_0 = \frac{1}{g} \sum |\text{spin ice}\rangle\langle\text{spin ice}|$$

where $|\text{spin ice}\rangle$ is any configuration constrained by the spin ice rule, $g = (3/2)^{N/2}$ is the spin ice degeneracy and $\mathrm{Tr}[\rho_0] = 1$.

In the interaction picture, we need to introduce a time-dependent Hamiltonian

$$H = H_0 + \epsilon(t)H_1(t)$$

When $t \to \pm\infty$, the Hamiltonian is H_0 [21]. If $|\Phi_0\rangle$ is the ground state at $t = 0$ then the ground state at different times is $|\Phi_I(t)\rangle = U_I(t, 0)|\Phi_0\rangle$. As $t \to -\infty$, the "in" state is

$$|\Phi_0\rangle = U_I(-\infty, 0)|\Psi_0\rangle = U_I^\dagger(0, -\infty)|\Psi_0\rangle$$

since we assume that the interaction H_1 is turned off at $t \to -\infty$ and $|\Psi_0\rangle$ is the ground state of H_0. Using density operators instead of pure states, we have the Schrödinger density at this time

$$\rho_0 = \rho_S(-\infty)$$

is the spin ice manifold, and

$$\begin{aligned}
&\rho_I(t) = U_0^\dagger(t, 0)\rho_S(t)U_0(t, 0)\\
&\rho_I(-\infty) = U_0^\dagger(-\infty, 0)\rho_S(-\infty)U_0(-\infty, 0) = \rho_S(-\infty)
\end{aligned}$$

since U_0 commutes with H_0. At the reference time $t = 0$, we have

$$\begin{aligned}
\rho_H &= \rho_S(0) = U(0, -\infty)\rho_S(-\infty)U^\dagger(0, -\infty)\\
&= \rho_I(0) = U_I(0, -\infty)\rho_S(-\infty)U_I^\dagger(0, -\infty)
\end{aligned}$$

where $U(t, t')$ satisfies

$$i\hbar\frac{\partial U(t, t')}{\partial t} = H_1(t)U(t, t')$$

$$U_I(t,t') = U_0^\dagger(t)U(t,t')U_0$$
$$i\hbar\frac{\partial}{\partial t}U_0(t,t_0) = H_0(t)U_0(t,t_0),$$

and U_I can be solved perturbatively [21] to give

$$U_I(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} H_1(t')dt' + \ldots$$

From this point forward, we set set $\hbar = 1$ in our expressions. Therefore, we have

$$\begin{aligned}&\mathrm{Tr}[\rho_H] = \mathrm{Tr}[U(0,-\infty)\rho_S(\infty)U^\dagger(0,-\infty]\\ &= \mathrm{Tr}[\rho(\infty)]\\ &= \mathrm{Tr}[\rho_0]\\ &= 1.\end{aligned}$$

For operators in the different pictures, we have the following relationships

$$\begin{aligned}O_I(t) &= U_0^\dagger(t,0)O_S U_0(t,0)\\ O_H(t) &= U^\dagger(t,0)O_S U(t,0)\\ &= U^\dagger(t,0)U_0(t,0)O_I(t)U_0^\dagger(t,0)U(t,0)\\ &= U_I^\dagger(t,0)O_I(t)U_I(t,0)\end{aligned}$$

This yields

$$\begin{aligned}&\mathrm{Tr}[\rho_H J^\alpha_{iH}(t)J^\beta_{jH}(t')]\\ &= \mathrm{Tr}[\rho_0 U_I(-\infty,t)J^\alpha_{iI}(t)U_I(t,t')J^\beta_{jI}(t')U_I(t',-\infty)]\end{aligned}$$

We will calculate this using the perturbative expansion for U_I, to first order in perturbation theory [17]. There will be three terms to calculate, which take the form

$$\begin{aligned}\mathrm{Tr}[\rho_H J_{1I}(t)J_{2I}(t')] &= \mathrm{Tr}[\rho_0 J_{1I}(t)J_{2I}(t')] - i\mathrm{Tr}\left[\rho_0\left(\int_t^{-\infty} H_1(t'')dt''\right)J_{1I}(t)J_{2I}(t')\right]\\ &- i\mathrm{Tr}\left[\rho_0 J_{1I}(t)\left(\int_{t'}^{t} H_1(t'')dt''\right)J_{2I}(t')\right] - i\mathrm{Tr}\left[\rho_0 J_{1I}(t)J_{2I}(t')\left(\int_{-\infty}^{t'} H_1(t'')dt''\right)\right].\end{aligned} \tag{2.8}$$

Here we are using the interaction picture operators. The interaction picture operators satisfy

$$i\hbar\frac{\partial O_I(t)}{\partial t} = U_0^\dagger(t)[O_S, H_0]U_0(t)$$

Using the commutation relations $[J_{i\alpha}, J_{j\beta}] = 0$ for $i \neq j$ and $[J_{i\pm}, J_{iz}] = \mp\hbar J_{i\pm}$, we have the following

$$\begin{aligned}&[J_{iz}, H_0] = 0\\ &J_{izI}(t) = J_{iz}\\ &[J_{i+}, H_0] = \frac{\mathcal{J}_1}{6}J_{i+}\sum_j J_{jz}\\ &[J_{i-}, H_0] = -\frac{\mathcal{J}_1}{6}J_{i-}\sum_j J_{jz}\\ &i\frac{\partial J_{i+I}(t)}{\partial t} = \frac{\mathcal{J}_1}{6}J_{i+I}(t)\sum_j J_{jz}\\ &J_{i+I}(t) = J_{i+}e^{-it\mathcal{J}_1/6\sum_j J_{jz}}\\ &J_{i-I}(t) = J_{i-}e^{it\mathcal{J}_1/6\sum_j J_{jz}}\end{aligned}$$

where in each exponent the sum over j is the sum over nearest neighbours of i. For each time dependent operator $J_{i\pm I}(t)$, the summation in the exponent depends on j which is the nearest neighbour of i. Therefore, when we apply the time dependent operator on spin states, we need to know the states of its nearest neighbours based on the spin ice rule.

In this chapter we introduced the Hamiltonian of Tb ions and expressed the Hamiltonian in interaction picture. Moreover, we described how to use perturbation theory to find the spin correlation between different sites of Tb ions.

In next chapter we will do the calculation and find the spin correlation between site 1 and site 2. We can find the spin correlations on other sites by applying symmetry transformations on the spin correlation of site 1 and site 2.

Chapter 3

Calculation

In this chapter, we will calculate the spin correlation function using perturbation theory. For simplicity, we only consider about the spin correlations between site 1 and site 2, the same procedure can be performed when we change the sites.

3.1 Spin Ice States

First, let us define the spin ice states based on the ice rule. If we only consider one tetrahedron, based on the two in and two out states, we can have six possible spin ice states,

$$|\Psi\rangle_1 = \begin{pmatrix} |++--\rangle \\ |+-+-\rangle \\ |+--+\rangle \\ |--++\rangle \\ |-+-+\rangle \\ |-++-\rangle \end{pmatrix}, \tag{3.1}$$

where the index 1 refers to 1 tetrahedron.

If there is a spin “+” on site 1, we have a restriction to the kets

$$|\Psi_{1+}\rangle_1 = \begin{pmatrix} |++--\rangle \\ |+-+-\rangle \\ |+--+\rangle \end{pmatrix} \tag{3.2}$$

Moreover, if there is a spin "-" on site 1, we have

$$|\Psi_{1-}\rangle_1 = \begin{pmatrix} |--++\rangle \\ |-+-+\rangle \\ |-++-\rangle \end{pmatrix} \tag{3.3}$$

with the same analogy we can also define the subspace for spin “+” or “-” on site two, three and four.

If we only consider three sites in a tetrahedron, we can define the following kets:

$$|\Phi_{1+}\rangle_1 = \begin{pmatrix} |+--\rangle \\ |-+-\rangle \\ |--+\rangle \end{pmatrix}$$

the subscript “1+” indicates the spin ice kets with spin “+” on site one, but in $|\Phi_{1+}\rangle_1$ we does not include site one. Similarly, we also define the kets

$$|\Phi_{1-}\rangle_1 = \begin{pmatrix} |-++\rangle \\ |+--\rangle \\ |+--\rangle \end{pmatrix}$$

the subscript ”1−” indicates the spin ice kets with spin “+” on site one, but in $|\Phi_{1+}\rangle_1$ we does not include site one.

Now, let us consider two tetrahedra that are joined by site number one. We define additional states satisfying the spin ice rule as:

$$|\Psi_1\rangle_2 = \begin{pmatrix} |\Psi_{1+}\rangle_1 \otimes |\Phi_{1+}\rangle_1 \\ |\Psi_{1-}\rangle_1 \otimes |\Phi_{1-}\rangle_1 \end{pmatrix} \tag{3.4}$$

where the subscript "1" in $|\Psi_1\rangle_2$ indicates the two tetrahedra are joined by site one. Here $|\Psi_1\rangle_2$ is a column vector containing 18 spin ice kets on two corner shared tetrahedra.

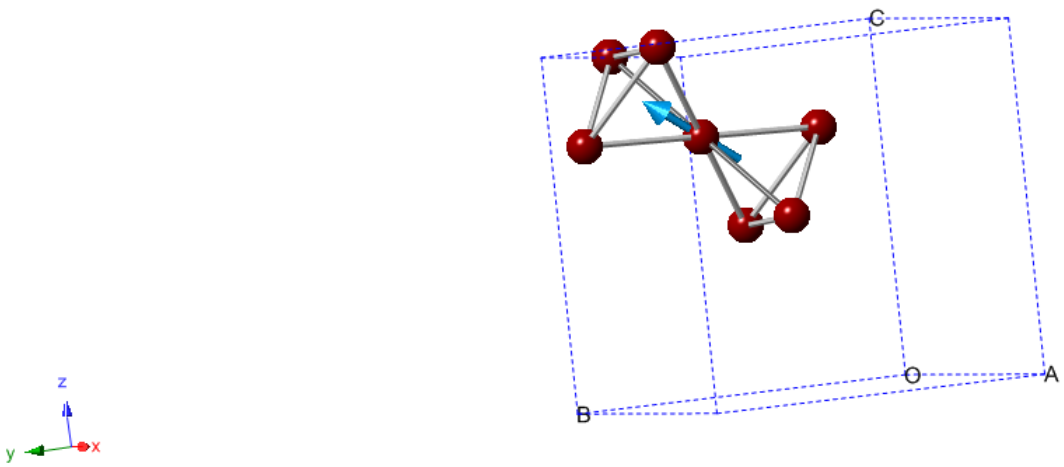

Figure 3.1: Two corner shared tetrahedra.

We will also need to consider states on three tetrahedra that satisfy the ice rule.

Here the tetrahedra are joined by site one and two.

$$|\Psi_{12}\rangle_3 = \begin{pmatrix} |--++\rangle \otimes |\Phi_{1-}\rangle_1 \otimes |\Phi_{2-}\rangle_1 \\ \begin{pmatrix} |+-+-\rangle \\ |+--+\rangle \end{pmatrix} \otimes |\Phi_{1+}\rangle_1 \otimes |\Phi_{2-}\rangle_1 \\ \begin{pmatrix} |-+-+\rangle \\ |-++-\rangle \end{pmatrix} \otimes |\Phi_{1-}\rangle_1 \otimes |\Phi_{2+}\rangle_1 \\ |++--\rangle \otimes |\Phi_{1+}\rangle_1 \otimes |\Phi_{2+}\rangle_1 \end{pmatrix} \tag{3.5}$$

Here $|\Psi_{12}\rangle_3$ is a column vector containing 54 spin ice kets.

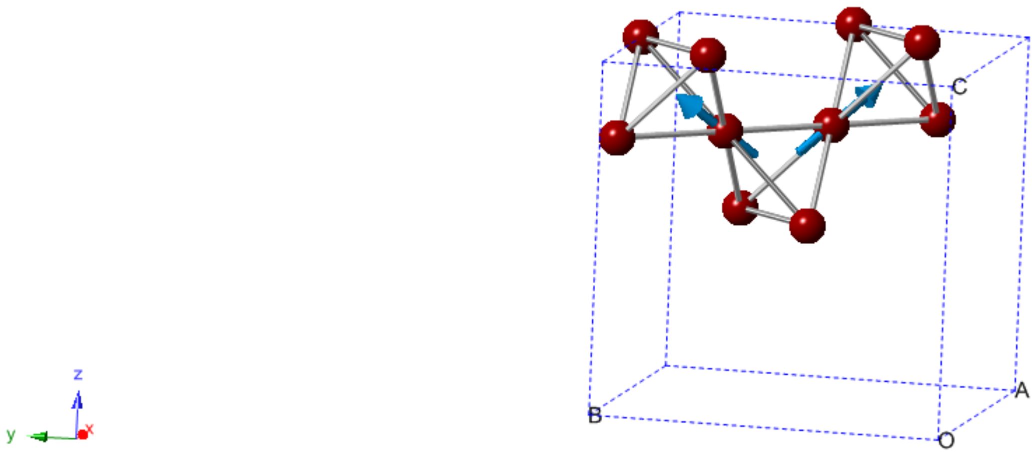

Figure 3.2: Three corner shared tetrahedra.

3.2 Lattice of Tetrahedra

The Tb ions define a corner shared tetrahedron structure. We define the tetrahedra in the middle as the A type tetrahedra, and each of the four surrounding tetrahedrons as B type tetrahedra (see Figure 3.3), type A and B tetrahedra differ by their orientation. The Tb lattice has an overall face-centered cubic (fcc) structure, hence, we also define the fcc lattice vectors. We have

$$\begin{aligned} f_{12} &= (1/2, 1/2, 0) & f_{13} &= (1/2, 0, 1/2) \\ f_{14} &= (0, 1/2, 1/2) & f_{23} &= (0, -1/2, 1/2) \\ f_{24} &= (-1/2, 0, 1/2) & f_{34} &= (-1/2, 1/2, 0) \end{aligned}$$

Also, $f_{ij} = -f_{ji}$ and $f_{ij} + f_{jk} = f_{ik}$ [17]. The set of all type A (or type B) tetrahedra forms an fcc lattice. Hence f_{ij} connect neighbouring type A tetrahedra on the line defined by the Wyckoff positions (i, j).

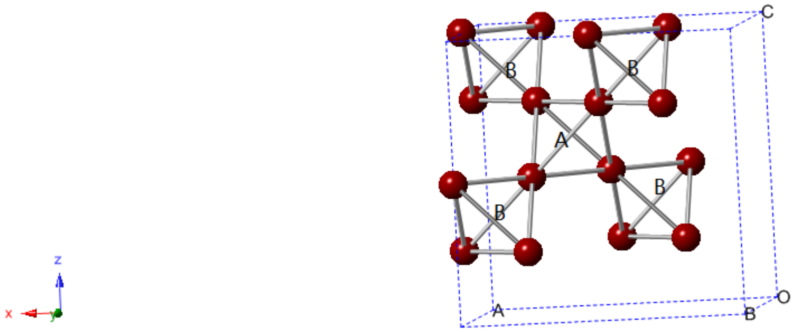

Figure 3.3: Tb lattice. The tetrahedron in the middle is type A, the surrounding tetrahedra are type B.

3.3 Spin Correlation Functions

From Chapter 2 we know the Hamiltonian can be expressed by the unperturbed term H_0 and perturbed term H_1. Recall H_0 and H_1 from Chapter 2

$$H = H_0 + H_1$$

$$H_0 = \mathcal{J}_1 X_1$$

$$H_1 = [\mathcal{J}_2 X_2 + \mathcal{J}_3 X_3 + \mathcal{J}_4 X_4]\epsilon(t)$$

We begin by calculating the spin correlation function $\langle J_{in\alpha}(t) J_{jn'\beta}(t')\rangle$, where $i, j = 1, 2, 3, 4$ are the Wychoff sites, n, n' are fcc lattice vectors, which label the A-type tetrahedra, α, β refer to the local coordinate system. (Note that sometimes the notation $J_{i\alpha}(t)$ is used, where i represents any site on the lattice.) When $\alpha, \beta = z$, the operators J_z acting on the spin ice manifold simply measure spins to be in or out, while $J_\pm$ raise or lower spins. In general, the action of $J_\pm$ takes a state that is in the spin ice manifold to a state that is outside the manifold, so in order to get a non-zero expectation values, each J_+ must appear with a J_- and vice versa. Hence, the spin correlation $\langle J_{inz} J_{jn'-}\rangle$ will be non-zero with a X_2 perturbation, $\langle J_{in+}(t) J_{jn'+}(t')\rangle$ needs a X_3 perturbation and $\langle J_{in+}(t) J_{jn'-}(t')\rangle$ needs a X_4 perturbation. $\langle J_{inz}(t) J_{jn'z}(t')\rangle$ has no first order correlations.

3.4 Spin correlation $\langle J_{1nz}(t) J_{2n'z}(t')\rangle$

From the above we know that the only non-zero unperturbed spin correlation term of site 1 and site 2 is the unperturbed contribution,

$$\langle J_{1nz}(t) J_{2n'z}(t')\rangle = \mathrm{Tr}[\rho_0 J_{1nz}(t) J_{2n'z}(t')] = \mathrm{Tr}[\rho_0 J_{1nz} J_{2nz}] \tag{3.6}$$

We know that $J_{1z}|+\rangle = j|+\rangle$ and $J_{1z}|-\rangle = -j|+\rangle$ where $j = 1/2$ for spin 1/2 system. Moreover, from Chapter 2 we know $J_z(t) = J_z$. If site 1 and site 2 are both in the same tetrahedron, we can get

$$\begin{aligned} &\mathrm{Tr}[\rho_0 J_{1nz}(t) J_{2n'z}(t')] = {}_1\langle\Psi|J_{1nz}J_{2n'z}|\Psi\rangle_1 \\ &= (j^2 + j^2 - j^2 - j^2 - j^2 - j^2)[\delta_{nn'} + \delta_{n,n'-f_{12}}] \\ &= -2j^2[\delta_{nn'} + \delta_{n,n'-f_{12}}] \end{aligned} \tag{3.7}$$

Here $\delta_{nn'}$ means both site 1 and site 2 are in the same A tetrahedron, $\delta_{n,n'-f_{12}}$ means both site 1 and site 2 are in the same B tetrahedron which corresponds to adjacent A tetrahedra ($n = n' - f_{12}$). When site 1 and site 2 are on different tetrahedra the correlation function vanishes.

3.5 Spin correlation $\langle J_{1nz}(t) J_{2n'+}(t')\rangle$

We now consider $\langle J_{1nz}(t) J_{2n'+}(t')\rangle$. The first order correction comes from X_2.

$$\begin{aligned} &\langle J_{1nz}(t) J_{2n'+}(t')\rangle = -i\mathrm{Tr}\left[\rho_0 \left(\int_t^{-\infty} X_2(t'')\epsilon(t'')dt''\right) J_{1nz}(t) J_{2n'+}(t')\right] \\ &- i\mathrm{Tr}\left[\rho_0 J_{1nz}(t)\left(\int_{t'}^{t} X_2(t'')\epsilon(t'')dt''\right) J_{2n'+}(t')\right] - i\mathrm{Tr}\left[\rho_0 J_{1nz}(t) J_{2n'+}(t')\left(\int_{-\infty}^{t'} X_2(t'')\epsilon(t'')dt''\right)\right] \\ &= -i\mathrm{Tr}\left[\rho_0\left(\int_t^{-\infty} -\frac{\sqrt{2}}{3}\mathcal{J}_2 \sum_{\langle ij\rangle}[\Lambda_{ij}(J_{inz}(t'')J_{jn'-}(t'')]\epsilon(t'')dt''\right) J_{1nz}(t) J_{2n'+}(t')\right] \\ &- i\mathrm{Tr}\left[\rho_0 J_{1nz}(t)\left(\int_{t'}^{t} -\frac{\sqrt{2}}{3}\mathcal{J}_2 \sum_{\langle ij\rangle}[\Lambda_{ij}(J_{inz}(t'')J_{jn'-}(t'')]\epsilon(t'')dt''\right) J_{2n'+}(t')\right] \\ &- i\mathrm{Tr}\left[\rho_0 J_{1nz}(t) J_{2n'+}(t')\left(\int_{-\infty}^{t'} -\frac{\sqrt{2}}{3}\mathcal{J}_2 \sum_{\langle ij\rangle}[\Lambda_{ij}(J_{inz}(t'')J_{jn'-}(t'')]\epsilon(t'')dt''\right)\right] \end{aligned}$$

Here $\langle ij\rangle$ is all pairs of nearest neighbours. In order to get a non-zero expectation value of the $\langle J_{1nz}(t) J_{2n'+}(t')\rangle$, we must have that $j = 2n'$ and $1n$ and i in the same tetrahedron, or adjoining ones. Considering that i and j are nearest neighbours, we

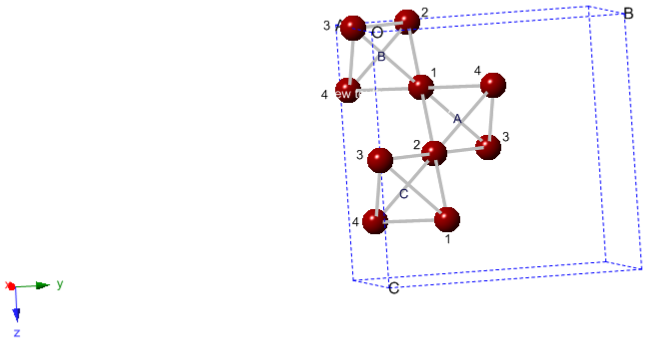

Figure 3.4: Two tetrahedron joined by site 2.

have

$$
\begin{aligned}
&i = 1n' \quad \text{and} \quad n = n' \\
&i = 3n' \quad \text{and} \quad n = n' \;\text{ or }\; n = n' + f_{31} \\
&i = 4n' \quad \text{and} \quad n = n' \;\text{ or }\; n = n' + f_{41} \\
&i = 1n' + f_{21} \quad \text{and} \quad n = n' + f_{21} \\
&i = 3n' + f_{23} \quad \text{and} \quad n = n' + f_{23} \;\text{ or }\; n = n' + f_{21} \\
&i = 4n' + f_{24} \quad \text{and} \quad n = n' + f_{24} \;\text{ or }\; n = n' + f_{21}
\end{aligned}
$$

In the following, we will calculate the spin correlation functions from these different contributions.

3.5.1 First three contributions

We begin with the following 3 contributions:

$$
\begin{aligned}
&i = 1n' \quad \text{and} \quad n = n' \\
&i = 3n' \quad \text{and} \quad n = n'
\end{aligned}
$$

$$i = 4n' \quad \text{and} \quad n = n'$$

In each case, there are three first order terms that involve different ordering of the operators. We use the set of spin ice states on two tetrahedra joined by site number two: $|\Psi_2\rangle_2$, to compute the trace.

The first contribution:

$$\begin{aligned}
&\Lambda_{12} i \frac{\sqrt{2}}{3} \mathcal{J}_2 \int_t^{-\infty} dt'' \epsilon(t'')_2 \langle \Psi_1 | J_{1n'z} J_{2n'-}(t'') J_{1n'z} J_{2n'+}(t') | \Psi_1 \rangle_2 \delta_{n,n'} \\
&= \Lambda_{12} \int_t^{-\infty} e^{-i(t'-t'')2j\mathcal{J}_1/3} \epsilon(t'') dt'' s^2 j^2 9 \delta_{n,n'} \\
&= \Lambda_{12} i \frac{\sqrt{2}}{3} \mathcal{J}_2 9 s^2 j^2 e^{-it'/3\mathcal{J}_2} \left[\frac{e^{it''\mathcal{J}_1 2j/3}}{i\mathcal{J}_1 2j/3} \epsilon(t'')|_t^{-\infty} - \int_t^{-\infty} e^{it''\mathcal{J}_1 2j/3} \epsilon'(t'') dt'' \right] \delta_{n,n'} \\
&= -\Lambda_{12} \frac{9\mathcal{J}_2}{\sqrt{2}\mathcal{J}_1} s^2 j e^{i(t-t')2j\mathcal{J}_1/3} \delta_{n,n'}
\end{aligned}$$

where s is the matrix elements of the $J_\pm$ operators, $s = \langle + | J_+ | - \rangle = \langle - | J_- | + \rangle$. Please see the detail of how to apply the time dependent operator $J_{i\pm}(t)$ on states in the Appendix. The second contribution:

$$\begin{aligned}
&\Lambda_{13} i \frac{\sqrt{2}}{3} \mathcal{J}_2 \int_t^{-\infty} dt'' \epsilon(t'')_2 \langle \Psi_1 | J_{3n'z} J_{2n'-}(t'') J_{1n'z} J_{2n'+}(t') | \Psi_1 \rangle_2 \delta_{n,n'} \\
&= \Lambda_{13} i \frac{\sqrt{2}}{3} \mathcal{J}_2 \int_t^{-\infty} e^{-i(t'-t'')2j\mathcal{J}_1/3} \epsilon(t'') dt'' t^2 j^2 3 \delta_{n,n'} \\
&= \Lambda_{13} \frac{3\mathcal{J}_2}{\sqrt{2}\mathcal{J}_1} s^2 j e^{i(t-t')2j\mathcal{J}_1/3} \delta_{n,n'}
\end{aligned}$$

The third contribution:

$$\begin{aligned}
&\Lambda_{14} i \frac{\sqrt{2}}{3} \mathcal{J}_2 \int_t^{-\infty} dt'' \epsilon(t'')_2 \langle \Psi_1 | J_{4n'z} J_{2n'-}(t'') J_{1n'z} J_{2n'+}(t') | \Psi_1 \rangle_2 \delta_{n,n'} \\
&= \Lambda_{14} i \frac{\sqrt{2}}{3} \mathcal{J}_2 \int_t^{-\infty} e^{-i(t'-t'')2j\mathcal{J}_1/3} \epsilon(t'') dt'' t^2 j^2 3 \delta_{n,n'} \\
&= \Lambda_{14} \frac{3\mathcal{J}_2}{\sqrt{2}\mathcal{J}_1} s^2 j e^{i(t-t')2j\mathcal{J}_1/3} \delta_{n,n'}
\end{aligned}$$

The sum of the above 3 terms is

$$
\begin{aligned}
&\frac{3\mathcal{J}_2}{\sqrt{2}\mathcal{J}_1}s^2 j e^{i(t-t')2j\mathcal{J}_1/3}(-3\Lambda_{12}+\Lambda_{13}+\Lambda_{14})\delta_{n,n'}\\
&=6\sqrt{2}\frac{\mathcal{J}_2}{\mathcal{J}_1}s^2 j e^{i(t-t')2j\mathcal{J}_1/3}
\end{aligned}
$$

The second term in the perturbation is as follows:

The first contribution:

$$
\begin{aligned}
&\Lambda_{12} i\frac{\sqrt{2}}{3}\mathcal{J}_2\int_{t'}^{t} dt''\epsilon(t'')_2\langle\Psi_1|J_{1n'z}J_{1n'z}J_{2n'-}(t'')dt''J_{2n'+}(t')|\Psi_1\rangle_2\delta_{n,n'}\\
&=\Lambda_{12} i\frac{\sqrt{2}}{3}\mathcal{J}_2\int_{t'}^{t} e^{-i(t'-t'')2j\mathcal{J}_1/3}\epsilon(t'')dt''s^2j^2 9\delta_{n,n'}\\
&=\Lambda_{12}\frac{9}{\sqrt{2}}\frac{\mathcal{J}_2}{\mathcal{J}_1}s^2 j(e^{i(t-t')2j\mathcal{J}_1 1/3}-1)
\end{aligned}
$$

The second contribution:

$$
\begin{aligned}
&\Lambda_{13} i\frac{\sqrt{2}}{3}\mathcal{J}_2\int_{t'}^{t} dt''\epsilon(t'')_2\langle\Psi_1|J_{1n'z}J_{3n'z}J_{2n'-}(t'')dt''J_{2n'+}(t')|\Psi_1\rangle_2\delta_{n,n'}\\
&=\Lambda_{13} i\frac{\sqrt{2}}{3}\mathcal{J}_2\int_{t'}^{t} e^{-i(t'-t'')2j\mathcal{J}_1/3}\epsilon(t'')dt''s^2j^2 3\delta_{n,n'}\\
&=-\Lambda_{13}\frac{3}{\sqrt{2}}\frac{\mathcal{J}_2}{\mathcal{J}_1}s^2 j(e^{i(t-t')2j\mathcal{J}_1 1/3}-1)
\end{aligned}
$$

The third contribution:

$$
\begin{aligned}
&\Lambda_{14} i\frac{\sqrt{2}}{3}\mathcal{J}_2\int_{t'}^{t} dt''\epsilon(t'')_2\langle\Psi_1|J_{1n'z}J_{4n'z}J_{2n'-}(t'')dt''J_{2n'+}(t')|\Psi_1\rangle_2\delta_{n,n'}\\
&=\Lambda_{14} i\frac{\sqrt{2}}{3}\mathcal{J}_2\int_{t'}^{t} e^{-i(t'-t'')2j\mathcal{J}_1/3}\epsilon(t'')dt''s^2j^2 3\delta_{n,n'}\\
&=-\Lambda_{14}\frac{3}{\sqrt{2}}\frac{\mathcal{J}_2}{\mathcal{J}_1}s^2 j(e^{i(t-t')2j\mathcal{J}_1 1/3}-1)
\end{aligned}
$$

The sum of the above 3 terms is

$$\begin{aligned}
&\frac{3\sqrt{2}}{2}\frac{\mathcal{J}_2}{\mathcal{J}_1}s^2 j(e^{i(t-t')2j\mathcal{J}_1 1/3}-1)(3\Lambda_{12}-\Lambda_{13}-\Lambda_{14}) \\
&=-6\sqrt{2}\frac{\mathcal{J}_2}{\mathcal{J}_1}s^2 j(e^{i(t-t')2j\mathcal{J}_1 1/3}-1)
\end{aligned}$$

The third term in the perturbation is as follows:

The first contribution:

$$\begin{aligned}
&\Lambda_{12} i\frac{\sqrt{2}}{3}\mathcal{J}_2\int_{-\infty}^{t'} dt''\epsilon(t'')_2\langle\Psi_1|J_{1n'z}J_{2n'+}(t')J_{1n'z}J_{2n'-}(t'')dt''|\Psi_1\rangle_2\delta_{n,n'} \\
&=\Lambda_{12} i\frac{\sqrt{2}}{3}\mathcal{J}_2\int_{-\infty}^{t'} e^{-i(t'-t'')2j\mathcal{J}_1/3}\epsilon(t'')dt''s^2j^2 9]\delta_{n,n'} \\
&=\Lambda_{12} i\frac{\sqrt{2}}{3}\mathcal{J}_2 e^{-it'2j\mathcal{J}_1/3}\left[\frac{e^{it''\mathcal{J}_1 2j/3}}{i\mathcal{J}_1 2j/3}\epsilon(t'')|_{-\infty}^{t'}-\int_{-\infty}^{t'} e^{it''\mathcal{J}_1 2j/3}\epsilon'(t'')dt''\right]\delta_{n,n'} \\
&=\Lambda_{12}\frac{9\mathcal{J}_2}{\sqrt{2}\mathcal{J}_1}s^2 j
\end{aligned}$$

The second contribution:

$$\begin{aligned}
&\Lambda_{13} i\frac{\sqrt{2}}{3}\mathcal{J}_2\int_{-\infty}^{t'} dt''\epsilon(t'')_2\langle\Psi_1|J_{1n'z}J_{2n'+}(t')J_{3n'z}J_{2n'-}(t'')dt''|\Psi_1\rangle_2\delta_{n,n'} \\
&=-\Lambda_{13} i\frac{\sqrt{2}}{3}\mathcal{J}_2\int_{-\infty}^{t'} e^{-i(t'-t'')2j\mathcal{J}_1/3}\epsilon(t'')dt''s^2j^2 3\delta_{n,n'} \\
&=-\Lambda_{13}\frac{3\mathcal{J}_2}{\sqrt{2}\mathcal{J}_1}s^2 j
\end{aligned}$$

The third contribution:

$$\begin{aligned}
&\Lambda_{14} i\frac{\sqrt{2}}{3}\mathcal{J}_2\int_{-\infty}^{t'} dt''\epsilon(t'')_2\langle\Psi_1|J_{1n'z}J_{2n'+}(t')J_{4n'z}J_{2n'-}(t'')dt''|\Psi_1\rangle_2\delta_{n,n'} \\
&=-\Lambda_{14} i\frac{\sqrt{2}}{3}\mathcal{J}_2\int_{-\infty}^{t'} e^{-i(t'-t'')2j\mathcal{J}_1/3}\epsilon(t'')dt''s^2j^2 3\delta_{n,n'} \\
&=-\Lambda_{14}\frac{3\mathcal{J}_2}{\sqrt{2}\mathcal{J}_1}s^2 j
\end{aligned}$$

The sum of the above 3 terms is

$$\begin{aligned}
&\frac{3\sqrt{2}\mathcal{J}_2}{2\mathcal{J}_1}s^2j(3\Lambda_{12}-\Lambda_{13}-\Lambda_{14})\\
&=6\sqrt{2}\frac{\mathcal{J}_2}{\mathcal{J}_1}s^2j
\end{aligned}$$

The sum of all three contributions is:

$$\begin{aligned}
&-6\sqrt{2}\frac{\mathcal{J}_2}{\mathcal{J}_1}s^2je^{i(t-t')2j\mathcal{J}_1/3}\\
&+6\sqrt{2}\frac{\mathcal{J}_2}{\mathcal{J}_1}s^2j(e^{i(t-t')2j\mathcal{J}_1/3}-1)\\
&+6\sqrt{2}\frac{\mathcal{J}_2}{\mathcal{J}_1}s^2j\\
&=0
\end{aligned}$$

Hence, the sum of all three contributions vanishes. In fact, each contribution vanishes by itself.

3.5.2 Next three contributions

We will now consider the contributions coming from:

$$\begin{aligned}
i &= 1n' + f_{21} \quad \text{and} \quad n = n' + f_{21}\\
i &= 3n' + f_{23} \quad \text{and} \quad n = n' + f_{23}\\
i &= 4n' + f_{24} \quad \text{and} \quad n = n' + f_{24}
\end{aligned}$$

These contributions are similar to the first three, because each contribution can be calculated using two tetrahedra. Therefore, they also vanish.

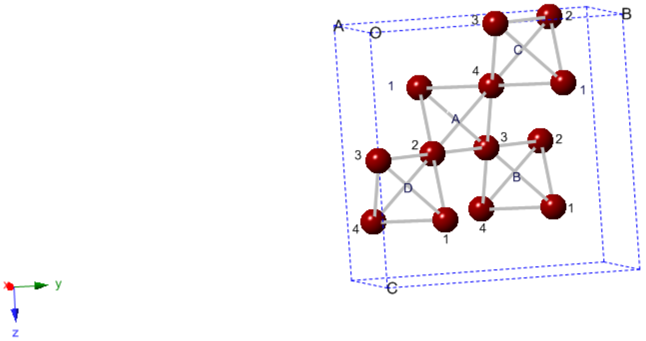

Figure 3.5: Three tetrahedrons joined by site 1 and 2.

3.5.3 Last four contributions

Finally, we consider the contributions:

$$i = 3n' \quad \text{and} \quad n = n' + f_{31}$$

$$i = 4n' \quad \text{and} \quad n = n' + f_{41}$$

$$i = 3n' + f_{23} \quad \text{and} \quad n = n' + f_{21}$$

$$i = 4n' + f_{24} \quad \text{and} \quad n = n' + f_{21}$$

To compute these we need spin ice states on three tetrahedra (see Figure 3.5). For the first contribution, the first term in perturbation,

$$\begin{aligned}
&\Lambda_{13} \int_t^{-\infty} dt'' \frac{\sqrt{2}}{3} \mathcal{J}_2 \epsilon(t'')_3 \langle \Psi_{23} | J_{3n'z} J_{2n'-}(t'') J_{1(n'+f_{31})z} J_{2n'+}(t') | \Psi_{23} \rangle_3 \delta_{n,n'+f_{31}} \\
&= \Lambda_{13} \int_t^{-\infty} \frac{\sqrt{2}}{3} \mathcal{J}_2 \epsilon(t'') e^{-i(t'-t'')2j\mathcal{J}_1 1/3} dt'' 9 s^2 j^2 \delta_{n,n'+f_{31}} \\
&= \Lambda_{13} \frac{9\mathcal{J}_2}{\sqrt{2}\mathcal{J}_1} s^2 j e^{i(t-t')2j\mathcal{J}_1 1/3} \delta_{n,n'+f_{31}}
\end{aligned}$$

The first contribution, second term in perturbation is:

$$\begin{aligned}
&\Lambda_{13}\int_{t'}^{t} dt''\frac{\sqrt{2}}{3}\mathcal{J}_2\epsilon(t'')_3\langle\Psi_{23}|J_{1(n'+f_{31})z}J_{3n'z}J_{2n'-}(t'')J_{2n'+}(t')|\Psi_{23}\rangle_3\delta_{n,n'+f_{31}}\\
&=\Lambda_{13}\int_{t'}^{t}\frac{\sqrt{2}}{3}\mathcal{J}_2\epsilon(t'')e^{-i(t'-t'')2j\mathcal{J}_1 1/3}dt''9s^2j^2\delta_{n,n'+f_{31}}\\
&=\Lambda_{13}\frac{9\mathcal{J}_2}{\sqrt{2}\mathcal{J}_1}s^2j(e^{i(t-t')2j\mathcal{J}_1/3}-1)\delta_{n,n'+f_{31}}
\end{aligned}$$

The first contribution, third term in perturbation is:

$$\begin{aligned}
&\Lambda_{13}\int_{-\infty}^{t'} dt''\frac{\sqrt{2}}{3}\mathcal{J}_2\epsilon(t'')_3\langle\Psi_{23}|J_{1(n'+f_{31})z}J_{2n'+}(t')J_{3n'z}J_{2n'-}(t'')|\Psi_{23}\rangle_3\delta_{n,n'+f_{31}}\\
&=\Lambda_{13}\int_{-\infty}^{t'}\frac{\sqrt{2}}{3}\mathcal{J}_2\epsilon(t'')e^{-i(t'-t'')2j\mathcal{J}_1 1/3}dt''9s^2j^2\delta_{n,n'+f_{31}}\\
&=\Lambda_{13}\frac{9\mathcal{J}_2}{\sqrt{2}\mathcal{J}_1}s^2j\delta_{n,n'+f_{31}}
\end{aligned}$$

The sum of all these contributions gives an zero value, hence, the spin correlation function vanishes. The other contributions are also zero. Hence we find that $\langle J_{1nz}(t)J_{2n'+}(t')\rangle$ vanishes to first order in perturbation theory.

3.6 Spin correlation $\langle J_{1n+}J_{2n'+}\rangle$

For $\langle J_{1n+}J_{2n'+}\rangle$, the X_3 term in the perturbation gives the non-zero spin correlations

$$\begin{aligned}
&\langle J_{1n+}(t)J_{2n'+}(t')\rangle=-i\mathrm{Tr}\left[\rho_0\left(\int_{t}^{-\infty}X_3(t'')\epsilon(t'')dt''\right)J_{1n+}(t)J_{2n'+}(t')\right]\\
&-i\mathrm{Tr}\left[\rho_0J_{1n+}(t)\left(\int_{t'}^{t}X_3(t'')\epsilon(t'')dt''\right)J_{2n'+}(t')\right]-i\mathrm{Tr}\left[\rho_0J_{1n+}(t)J_{2n'+}(t')\left(\int_{-\infty}^{t'}X_3(t'')\epsilon(t'')dt''\right)\right]
\end{aligned}$$

There are three tetrahedra involved for $\langle J_{1n+}J_{2n'+}\rangle$ (see Figure 3.6). Only nearest neighbours will give non-zero spin correlation function, hence site 1 and site 2 need

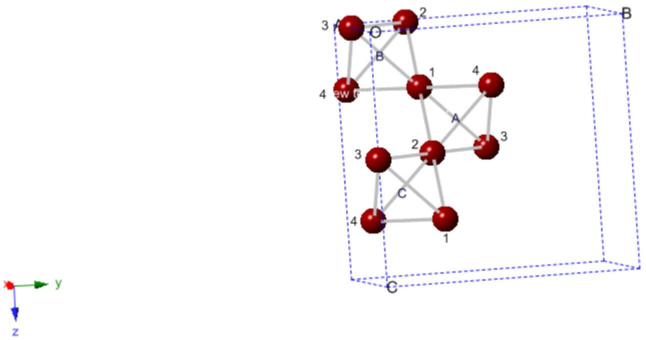

Figure 3.6: Three tetrahedrons joined by site 1 and 2..

to be in the same tetrahedron i.e. $n = n'$ or $n = n' + f_{12}$. Therefore, we have

$$
\begin{aligned}
&\langle J_{1n+}(t) J_{2n'+}(t') \rangle = -i\frac{i\mathcal{J}_3}{3}\Bigg(\mathrm{Tr}\left[\rho_0 \left(\int_t^{-\infty} J_{1n-}(t'') J_{2n'-}(t'') \epsilon(t'') dt'' \right) J_{1n+}(t) J_{2n'+}(t') \right] \\
&- i\mathrm{Tr}\left[\rho_0 J_{1n+}(t) \left(\int_{t'}^{t} J_{1n-}(t'') J_{2n'-}(t'') \epsilon(t'') dt'' \right) J_{2n'+}(t') \right] \\
&- i\mathrm{Tr}\left[\rho_0 J_{1n+}(t) J_{2n'+}(t') \left(\int_{-\infty}^{t'} J_{1n-}(t'') J_{2n'-}(t'') \epsilon(t'') dt'' \right) \right] \Bigg) (\delta_{n,n'} + \delta_{n,n'+f_{12}})
\end{aligned} \tag{3.8}
$$

Now we will calculate the above term by term, using the same methods as in section 3.5. The first term in perturbation is

$$
\begin{aligned}
&{}_3\langle \Psi_{12} | \left(\int_t^{-\infty} \frac{1}{3} \mathcal{J}_3 J_{1n-}(t'') J_{2n'-}(t'') \epsilon(t'') dt'' \right) J_{1n+}(t) J_{2n'+}(t') | \Psi_{12} \rangle_3 \\
&= \frac{3\mathcal{J}_3}{4j\mathcal{J}_1} s^4 e^{i(t-t')2j\mathcal{J}_1/3} (\delta_{n,n'} + \delta_{n,n'+f_{21}})
\end{aligned}
$$

The second term in perturbation is

$$
\begin{aligned}
&{}_3\langle \Psi_{12} | J_{1n+}(t) \left(\int_{t'}^{t} \frac{1}{3} \mathcal{J}_3 J_{1n-}(t'') J_{2n'-}(t'') \epsilon(t'') dt'' \right) J_{2n'+}(t') | \Psi_{12} \rangle_3 \\
&= 6i\mathcal{J}_3 (t - t') s^4 e^{i(t-t')2j\mathcal{J}_1/3} (\delta_{n,n'} + \delta_{n,n'+f_{21}})
\end{aligned}
$$

The third term in perturbation is

$$\begin{aligned}
&{}_3\langle\Psi_{12}|J_{1n+}(t)J_{2n'+}(t')\left(\int_{-\infty}^{t'}\frac{1}{3}\mathcal{J}_3 J_{1n-}(t'')J_{2n'-}(t'')\epsilon(t'')dt''\right)|\Psi_{12}\rangle_3\\
&=\frac{3\mathcal{J}_3}{4j\mathcal{J}_1}s^4 e^{i(t-t')2j\mathcal{J}_1/3}(\delta_{n,n'}+\delta_{n,n'+f_{21}})
\end{aligned}$$

Now let us consider the number of configurations. For $\langle J_{1+n}J_{2+n'}\rangle$, there are three tetrahedron involved and for each tetrahedron we have 6 possible spin ice configurations, hence we have $3\times 3\times 6 = 54$ configurations. Hence we have

$$\langle J_{1n+}(t)J_{2n'+}(t')\rangle = -\frac{\mathcal{J}_3 s^4 e^{i(t-t')\mathcal{J}_1 1/3}}{54}(6i(t-t')+\frac{3}{4j\mathcal{J}_1}) \tag{3.9}$$

3.7 Spin correlation $\langle J_{1n-}(t)J_{2n'+}(t')\rangle$

For $\langle J_{1n-}(t)J_{2n'+}(t')\rangle$, the X_4 term of the perturbation gives the non-zero spin correlations

$$\begin{aligned}
&\langle J_{1n-}(t)J_{2n'+}(t')\rangle = -i\mathrm{Tr}\left[\rho_0\left(\int_t^{-\infty}X_4(t'')\epsilon(t'')dt''\right)J_{1n-}(t)J_{2n'+}(t')\right]\\
&-i\mathrm{Tr}\left[\rho_0 J_{1n-}(t)\left(\int_{t'}^{t}X_4(t'')\epsilon(t'')dt''\right)J_{2n'+}(t')\right]-i\mathrm{Tr}\left[\rho_0 J_{1n-}(t)J_{2n'+}(t')\left(\int_{-\infty}^{t'}X_4(t'')\epsilon(t'')dt''\right)\right]
\end{aligned}$$

There are three tetrahedra involved for $\langle J_{1n-}J_{2n'+}\rangle$ (see Figure 3.6). Only the nearest neighbour will give non-zero spin correlation function, hence site 1 and site 2

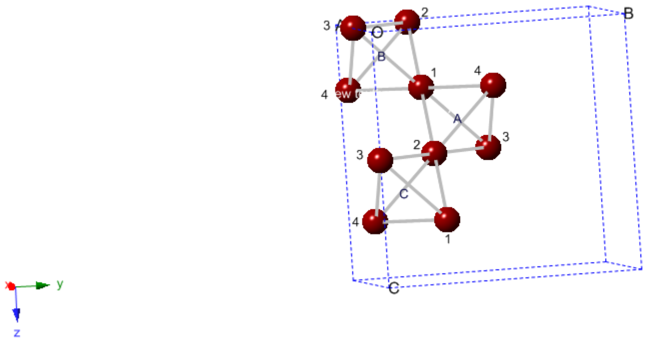

Figure 3.7: Three tetrahedra joined by site 1 and 2..

need to be in the same tetrahedron i.e. $n = n'$ or $n = n' + f_{12}$ Therefore, we have

$$
\begin{aligned}
&\langle J_{1n-}(t)J_{2n'+}(t')\rangle = -\frac{i\mathcal{J}_4}{6}\left(\mathrm{Tr}\left[\rho_0\left(\int_t^{-\infty} J_{1n+}(t'')J_{2n'-}(t'')\epsilon(t'')dt''\right) J_{1n-}(t)J_{2n'+}(t')\right]\right.\\
&+\mathrm{Tr}\left[\rho_0 J_{1n-}(t)\left(\int_{t'}^{t} J_{1n+}(t'')J_{2n'+}(t'')\epsilon(t'')dt''\right) J_{2n'+}(t')\right]\\
&\left.+\mathrm{Tr}\left[\rho_0 J_{1n-}(t)J_{2n'+}(t')\left(\int_{-\infty}^{t'} J_{1n+}(t'')J_{2n'-}(t'')\epsilon(t'')dt''\right)\right]\right)(\delta_{n,n'}+\delta_{n,n'+f_{12}})
\end{aligned}
\tag{3.10}
$$

Now we will calculate the above term by term, using the same methods as before. The first term in perturbation is

$$
\begin{aligned}
&\int_t^{-\infty} dt''\frac{1}{6}\mathcal{J}_4\epsilon(t'')_3\langle\Psi_{12}|J_{1n+}(t'')J_{2n'-}(t'')J_{1n-}(t)J_{2n'+}(t')|\Psi_{12}\rangle_3\\
&=\frac{3\mathcal{J}_4}{4j\mathcal{J}_1}s^4 e^{i(t'-t)2j\mathcal{J}_1/3}(\delta_{n,n'}+\delta_{n,n'+f_{21}})
\end{aligned}
$$

The second term in perturbation is

$$
\begin{aligned}
&\int_{t'}^{t} dt''\frac{1}{6}\mathcal{J}_4\epsilon(t'')_3\langle\Psi_{12}|J_{1-n}(t)J_{1+n}(t'')J_{2-n'}(t'')J_{2+n'}(t')|\Psi_{12}\rangle_3\\
&=3i\mathcal{J}_4(t'-t)s^4 e^{i(t'-t)2j\mathcal{J}_11/3}(\delta_{n,n'}+\delta_{n,n'+f_{21}})
\end{aligned}
$$

The third term in perturbation is

$$\int_{-\infty}^{t'} dt'' \frac{1}{6} \mathcal{J}_4 \epsilon(t'')_3 \langle \Psi_{12} | J_{1+n}(t) J_{2+n'}(t') J_{1-n}(t'') J_{2-n'}(t'') | \Psi_{12} \rangle_3$$
$$= \frac{3\mathcal{J}_4}{4j\mathcal{J}_1} s^4 e^{i(t'-t)2j\mathcal{J}_1 1/3} (\delta_{n,n'} + \delta_{n,n'+f_{21}})$$

For $\langle J_{1-n} J_{2+n'} \rangle$, there are three tetrahedron involved and for each tetrahedron we have 6 possible spin ice configurations, hence we have $3 \times 3 \times 6 = 54$ configurations. Hence we have

$$\langle J_{1n+}(t) J_{2n'+}(t') \rangle = -\frac{3\mathcal{J}_4 s^4 e^{i(t'-t)\mathcal{J}_1 1/3}}{54} (i(t'-t) + \frac{1}{4j\mathcal{J}_1}) \tag{3.11}$$

where N is the number of total ions in the lattice.

3.8 Spin Correlation in Global Coordinates

In this section we express our results in global coordinates using the relations between local and global coordinates described in the Appendix. We use symmetry arguments to generalise our results for site 1 and 2 correlations to other sites. Since $J_+ = J_x + iJ_y$ and $J_- = J_x - iJ_y$, hence $J_+ = (J_-)^\dagger$. Therefore, we have the following

$$\langle J_{1z} J_{2-} \rangle = (\langle J_{1z} J_{2+} \rangle)^\dagger$$
$$\langle J_{1+} J_{2+} \rangle = (\langle J_{1-} J_{2-} \rangle)^\dagger$$
$$\langle J_{1+} J_{2-} \rangle = (\langle J_{1-} J_{2+} \rangle)^\dagger$$

There are 4 independent correlation functions out of 54. As we shall show, the rest are related by symmetry. By using the group theory, we can do the transformation between local coordinates with global coordinates which is provided in Appendix. Let us define $J_1^x J_2^x = a$, $J_1^x J_2^y = b$, $J_1^z J_2^x = c$, $J_1^z J_2^z = d$, we have the relationship between local coordinates with global coordinates in table 3.1. In the following section, we will write the global spin correlation functions using the local spin correlation functions.

	$J^x J^x$	$J^x J^y$	$J^x J^z$	$J^y J^x$	$J^y J^y$	$J^y J^z$	$J^z J^x$	$J^z J^y$	$J^z J^z$
$J_1 J_2$	a	b	$-c$	b	a	c	c	$-c$	d
$J_1 J_3$	a	$-c$	b	c	d	$-c$	b	c	d
$J_1 J_4$	d	c	$-c$	$-c$	a	b	c	b	a
$J_2 J_3$	d	c	c	$-c$	a	$-b$	$-c$	$-b$	d
$J_2 J_4$	a	$-c$	b	c	d	c	b	c	a
$J_3 J_4$	a	$-b$	c	$-b$	a	c	$-c$	$-c$	d

Table 3.1: Equivalent spin correlations between different sites.

$\langle J_1^z J_2^z \rangle$

For ion 1 and 2, the global spin correlation function of $J_1^z J_2^z$ can be expressed by

$$\begin{aligned}\langle J_1^z J_2^z \rangle &= \frac{1}{6}(\langle J_{1+} J_{2+} \rangle + \langle J_{1+} J_{2-} \rangle + \langle J_{1-} J_{2+} \rangle + \langle J_{1-} J_{2-} \rangle) \\ &- \frac{1}{3\sqrt{2}}(\langle J_{1z} J_{2-} \rangle + \langle J_{1z} J_{2+} \rangle) + \langle J_{1-} J_{2z} \rangle + \langle J_{1+} J_{2z} \rangle) + \frac{1}{3}\langle J_{1z} J_{2z} \rangle\end{aligned}$$

$\langle J_1^z J_2^x \rangle$

For ion 1 and 2, the global spin correlation function of $J_1^z J_2^x$ can be expressed by

$$\begin{aligned}\langle J_1^z J_2^x \rangle &= \frac{1}{12}(\langle J_{1-} J_{2-} \rangle + \langle J_{1+} J_{2-} \rangle + \langle J_{1-} J_{2+} \rangle + \langle J_{1+} J_{2+} \rangle) \\ &- \frac{i}{4\sqrt{3}}(\langle J_{1-} J_{2-} \rangle + \langle J_{1+} J_{2-} \rangle - \langle J_{1-} J_{2+} \rangle - \langle J_{1+} J_{2+} \rangle) \\ &- \frac{1}{6\sqrt{2}}(\langle J_{1z} J_{2-} \rangle + \langle J_{1z} J_{2+} \rangle) + \frac{i}{2\sqrt{6}}(\langle J_{1z} J_{2-} \rangle - \langle J_{1z} J_{2+} \rangle)\end{aligned}$$

$$+\frac{1}{3\sqrt{2}}(\langle J_{1-}J_{2z}\rangle+\langle J_{1+}J_{2z}\rangle)-\frac{1}{3}\langle J_{1z}J_{2z}\rangle$$

$\langle J_1^x J_2^y\rangle$

For ion 1 and 2, the global spin correlation function of $J_1^x J_2^y$ can be expressed by

$$\begin{aligned}
&\langle J_1^x J_2^y\rangle=-\frac{1}{6}(\langle J_{1-}J_{2-}\rangle+\langle J_{1+}J_{2+}\rangle)+\frac{1}{12}(\langle J_{1+}J_{2-}\rangle+\langle J_{1-}J_{2+}\rangle)\\
&-\frac{i}{4\sqrt{3}}(\langle J_{1+}J_{2-}\rangle-\langle J_{1-}J_{2+}\rangle)-\frac{1}{6\sqrt{2}}(\langle J_{1z}J_{2-}\rangle+J_{1z}J_{2+}\rangle+\langle J_{1-}J_{2z}\rangle\\
&+\langle J_{1+}J_{2z}\rangle)-\frac{i}{2\sqrt{6}}(\langle J_{1z}J_{2-}\rangle-\langle J_{1z}J_{2+}\rangle-\langle J_{1-}J_{2z}\rangle+\langle J_{1+}J_{2z}\rangle)\\
&-\frac{1}{3}\langle J_{1z}J_{2z}\rangle
\end{aligned}$$

$\langle J_1^x J_2^x\rangle$

For ion 1 and 2, the global spin correlation function of $J_1^x J_2^x$ can be expressed by

$$\begin{aligned}
&\langle J_1^x J_2^x\rangle=\frac{1}{12}(\langle J_{1-}J_{2-}\rangle+\langle J_{1+}J_{2+}\rangle)+\frac{i}{4\sqrt{3}}(\langle J_{1-}J_{2-}\rangle-\langle J_{1+}J_{2+}\rangle)\\
&-\frac{1}{6}(\langle J_{1+}J_{2-}\rangle+\langle J_{1-}J_{2+}\rangle)-\frac{1}{6\sqrt{2}}(\langle J_{1z}J_{2-}\rangle+\langle J_{1z}J_{2+}\rangle+\langle J_{1-}J_{2z}\rangle\\
&+\langle J_{1+}J_{2z}\rangle)+\frac{i}{2\sqrt{6}}(\langle J_{1z}J_{2-}\rangle-\langle J_{1z}J_{2+}\rangle+\langle J_{1-}J_{2z}\rangle-\langle J_{1+}J_{2z}\rangle)\\
&-\frac{1}{3}\langle J_{1z}J_{2z}\rangle
\end{aligned}$$

3.9 Neutron Scattering

Neutron scattering is an experiment which is sensitive to the spin correlation function. The neutron cross-section for the scattering by identical magnetic ions situated at the sites R_{in} of a crystal is

$$\begin{aligned}\frac{d^2\sigma}{d\Omega dE'} =& r_0^2\frac{k'}{k}[\frac{1}{2}gF(\kappa)]^2\sum_{\alpha,\beta}(\delta_{\alpha,\beta}-\kappa_\alpha\kappa_\beta)\sum_{\lambda,\lambda'}p_\lambda\sum_{i,n}\sum_{i',n'}\langle\lambda|\exp(-i\kappa\cdot R_{in}J^\alpha_{in}|\lambda'\rangle\\ &\times\langle\lambda'|\exp(i\kappa\cdot R_{in}J^\beta_{i'n'}|\lambda\rangle\delta(\hbar\omega+E_\lambda-E_{\lambda'})\end{aligned}$$

where $\vec{k}$ is variable in the momentum space, $\kappa=\frac{\vec{k}}{|k|}$ is the unit vector of $\vec{k}$, g is a constant which can be determined by experiment, R_{in} is the position vector, J^α_{in} is the spin function, i is the site number and n is the Wyckoff position of Tb atoms, $|\lambda\rangle$ is a state, and E_λ is the energy of the state.

The partial differential cross-section is

$$\frac{d^2\sigma}{d\Omega dE'} = r_0^2\frac{k'}{k}[\frac{1}{2}gF(\kappa)]^2\sum_{\alpha,\beta}(\delta_{\alpha,\beta}-\kappa_\alpha\kappa_\beta)\frac{N}{2\pi\hbar}\int_{-\infty}^{\infty}dt\int dr\exp(i\kappa\cdot r-i\omega t)\Gamma_{\alpha\beta}(r,t) \tag{3.12}$$

where N is the number of unit cells in the crystal, and

$$\Gamma_{\alpha\beta}(r,t)=\frac{1}{N}\sum_{i,n}\sum_{i',n'}\int dr'\langle\delta(r+R_{in}-r')J^\alpha_{in}\delta(r'-R_{in}(t))J^\beta_{i'n'}(t)\rangle \tag{3.13}$$

Because the spin-dependent forces are small, therefore, we can approximate the motion of an ion as independent of its spin orientation. Then the above equation becomes

$$\Gamma_{\alpha\beta}(r,t)=\frac{1}{N}\sum_{i,n}\sum_{i',n'}\langle J^\alpha_{in}J^\beta_{i'n'}(t)\rangle\int dr'\langle\delta(r+R_{in}-r')\delta(r'-R_{i'n'}(t))\rangle. \tag{3.14}$$

and $\langle J^\alpha_{in}J^\beta_{i'n'}(t)\rangle$ are the spin correlation functions between different sites. Essentially, in order to calculate the neutron scattering intensity, we need to convert the spin correlation function into k space, which is the Fourier transformation of the spin correlation function with position.

By substituting the spin correlation functions into the above equation and setting

$\mathcal{J}_1 = 1, \mathcal{J}_2 = \mathcal{J}_3 = \mathcal{J}_4 = 0.1$ and setting $\omega = 0$ for the elastic neutron scattering. By using equation 3.12, we can plot the neutron scattering intensity as a function of k, as shown in Figure 3.8.

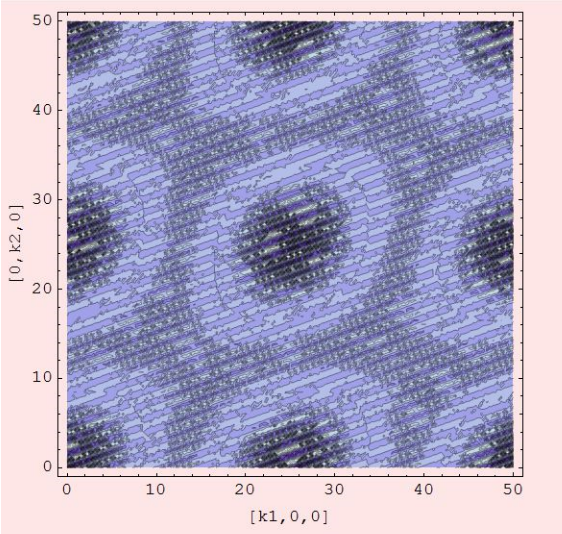

Figure 3.8: The neutron scattering intensity along $(k_1, k_2, 0)$ plane.

Figure 3.8 is a contour plot in k_1 and k_2 plane with $k_3 = 0$. Figure 3.8 was obtained using Mathematica. We plot (3.12) in Mathematica and for simplicity set $k_3 = 0$. From the plot we can find the partial cross-section by substituting k_1 and k_2 into (3.12). The dark colour in the plot indicates the higher intensity and the light colour indicates the lower intensity. From Fig 3.8 we can see that the spin correlation function is periodic in k-space. These results are preliminary; further studies are needed to compare with experiment.

In this chapter, we used the first order perturbation theory on the interaction Hamiltonian to find the spin correlations between site 1 and 2. We found the spin correlation of $\langle J_{iz} J_{j+} \rangle$ vanishes to the nearest and next nearest neighbours, the spin correlations of $\langle J_{i+} J_{j+} \rangle$ and $\langle J_{i+} J_{j-} \rangle$ will give non-zero results only to the nearest neighbour. We also converted the spin correlation from local coordinates to global coordinates and used group generator of space group to find the spin correlations on different sites. Finally, we discussed about the neutron scattering experiment and how to find the scattering intensity by using the spin correlation functions. Moreover, we did a plot of the scattering intensity along the k_1 and k_2 plane.

Chapter 4

Conclusion

In this thesis, we use the perturbation theory to find the spin correlations on Tb ions in $Tb_2Ti_2O_7$.

In the first chapter, we discussed the structure of pyrochlores. We also talked about geometric frustration in the tetrahedron structure in pryochlores. We reviewed the ice rule and residual entropy on crystal ice and applied it to spin ice materials. Particularly, we focused our interest on one of the pryochlores, $Tb_2Ti_2O_7$, which is believed to be a quantum spin ice material. $Tb_2Ti_2O_7$ has many interesting properties such as residual entropy and elastic softening effects.

In Chapter 2, we described the spin 1/2 exchange Hamiltonian for $Tb_2Ti_2O_7$. The largest term in H has a spin ice ground state. We use perturbation theory on the rest of the terms in the Hamiltonian to find the spin correlations between different sites of Tb ions. In order to use perturbation theory, we found the interaction picture representation of our operators.

In Chapter 3, we did the calculation to find the spin correlation function. From our calculation, we found that the spin correlation $\langle J_{iz}(t)J_{j+}(t')\rangle$ vanishes not only on the nearest neighbours, but also on the next nearest neighbours. $\langle J_{i+}(t)J_{j+}(t')\rangle$

and $\langle J_{i+}(t) J_{j-}(t') \rangle$ only give spin correlations between nearest neighbours. From our calculation we find that there are only short range spin correlation of Tb ions. After the calculation, we discussed the neutron scattering theory which is one method to test our result experimentally. Although neutron scattering is the typical method to find the spin correlation function, there are also other experiment methods such as muon spin relaxation and dc susceptibility can be used to text the spin correlation function [29].

Experiments reveal that the correlations are mainly short-range, but there are longer range correlation seen as “pinch points” in neutron scattering patterns [31]. From higher order perturbation theory, we can reveal more details of spin correlation function and find the spin correlation function in longer range [24]. Therefore, in the future, we can apply higher order perturbation theory to the interaction Hamiltonian. Recently, neutron scattering experiment shows that spin correlations in $Tb_2Ti_2O_7$ extend over larger distances near 20 K [30]. Therefore, in the mean time, we can also use neutron scattering experiments to test our theoretical calculations.

Chapter 5

Appendix

In this thesis, we use the angular momentum operators: J_z and $J_\pm$. In the interaction picture, the operator J_z is time independent, and the operator $J_\pm$ is time dependent. From Chapter two we know $J_{i\pm}(t) = J_{i\pm}e^{\mp it\mathcal{J}_1/6\sum_j J_{jz}}$, where the sum over j means we need to apply the operator J_z to all the nearest neighbours of site i.

In this appendix we will discuss how to apply J_z and $J_\pm$ on the spin ice states. First, let us consider the operator J_z. Because J_z is time independent, therefore, when we apply it on the spin ice state it will give the eigenvalue of the state but will not change the state. For example, if we have a spin ice state $|++--\rangle$, then we apply J_{1z} on it, it will give a eigenvalue of site 1, i.e. $J_{1z}|++--\rangle = j|++--\rangle$. Therefore, when J_{1z} acts on the states

$$|\Psi\rangle_1 = \begin{pmatrix} |++--\rangle \\ |+-+-\rangle \\ |+--+\rangle \\ |--++\rangle \\ |-+-+\rangle \\ |-++-\rangle \end{pmatrix}$$

It will produce the eigenvalue of site 1. Therefore, we have

$$J_{1z}|\Psi\rangle = \begin{pmatrix} |++--\rangle \\ |+-+-\rangle \\ |+--+\rangle \\ |--++\rangle \\ |-+-+\rangle \\ |-++-\rangle \end{pmatrix} = \begin{pmatrix} j|++--\rangle \\ j|+-+-\rangle \\ j|+--+\rangle \\ -j|--++\rangle \\ -j|-+-+\rangle \\ -j|-++-\rangle \end{pmatrix}.$$

then if we want to find ${}_1\langle\Psi|J_{1z}J_{2z}|\Phi\rangle_1$, we start by computing the following:

$$J_{1z}J_{2z}|\Psi\rangle_1 = \begin{pmatrix} |++--\rangle \\ |+-+-\rangle \\ |+--+\rangle \\ |--++\rangle \\ |-+-+\rangle \\ |-++-\rangle \end{pmatrix} = \begin{pmatrix} jj|++--\rangle \\ j(-j)|+-+-\rangle \\ j(-j)|+--+\rangle \\ -j(-j)|--++\rangle \\ -jj|-+-+\rangle \\ -jj|-++-\rangle \end{pmatrix}.$$

Therefore, we have

$${}_1\langle\Psi|J_{1z}J_{2z}|\Psi\rangle_1 = j^2 - j^2 - j^2 + j^2 - j^2 - j^2 = -2j^2$$

Now let us consider the time dependent angular momentum operator $J_{\pm}(t)$. We know that when J_+ act on a state $|+\rangle$, it will eliminate it, and when J_+ act on a state $|-\rangle$, it will raise it to $|+\rangle$. Therefore, when we apply J_{i+} on the spin ice state, the only non-zero result is contributed by the site i with spin "$-$". The exponent part of $J_{i+}(t)$ has the summation part $\sum_j J_{jz}$, hence we need to apply J_z to all the nearest neighbour of site i. For example, if we apply $J_{1+}(t)$ on spin ice state $|--++>$, we need to find out the nearest neighbour of site 1. By applying the spin ice rule, we know that the nearest neighbours of site 1 have spin state "-", "+", "+", "-", "+", "+". Therefore, $\sum_j J_{jz} = -j + j + j - j + j + j = 2j$. Hence,

$$J_{1+}(t)|--++\rangle = J_{1+}e^{-it\mathcal{J}_1/6\sum_j J_{jz}}|--++\rangle = e^{-it2j\mathcal{J}_1/6}|+-++\rangle$$

Moreover, in order to have a non-zero result for $\langle --++|J|--++\rangle$ we need to pair the operator $J_{1-}(t)J_{1+}(t')$. Therefore, we have

$$\begin{aligned}
&\langle --++|J_{1-}(t)J_{1+}(t')|--++\rangle \\
&= \langle --++|J_{1-}(t)J_{1+}e^{-it'\mathcal{J}_1/6\sum_j J_{jz}}|--++\rangle \\
&= \langle --++|J_{1-}(t)e^{-i(-2j)t'\mathcal{J}_1/6}|+-++\rangle \\
&= \langle --++|e^{i(2j)t\mathcal{J}_1/6}e^{-i(2j)t'\mathcal{J}_1/6}|--++\rangle \\
&= e^{i(2j)(t-t')\mathcal{J}_1/6}
\end{aligned}$$

Therefore, we can apply the above argument to other spin ice state in our calculation to give the results in Chapter 3.

Here we will present some examples of calculation detail in Chapter 3. First, in the spin correlation functions contain X_2, if we want to find ${}_2\langle\Psi_2|J_{1nz}(t'')J_{2n'-}(t'')J_{1nz}J_{2n'+}|\Psi_2\rangle_2$, we can start by computing the following:

$$J_{1nz}J_{2-n'}(t'')J_{1nz}J_{2+n'}(t')\left(\begin{matrix}\left(\begin{matrix}|++--\rangle\\ |-+-+\rangle\\ |-++-\rangle\end{matrix}\right\}\otimes|\Phi_{2+}\rangle\\ \left\{\begin{matrix}|--++\rangle\\ |+-+-\rangle\\ |+--+\rangle\end{matrix}\right)\otimes|\Phi_{2-}\rangle\end{matrix}\right)\delta_{n,n'n'+f_{31}}$$

$$=J_{1nz}J_{2-n'}(t'')J_{1nz}e^{-it'2j\mathcal{J}_1 1/3}s\left(\begin{matrix}0\\ \begin{pmatrix}|-+++\rangle\\ |+++-\rangle\\ |++-+\rangle\end{pmatrix}\otimes|\Phi_{2-}\rangle\end{matrix}\right)\delta_{n,n'}$$

$$=e^{-i(t'-t'')2j\mathcal{J}_1 1/3}s^2j^2\left(\begin{matrix}0\\ \begin{pmatrix}|--++\rangle\\ |+-+-\rangle\\ |+--+\rangle\end{pmatrix}\otimes|\Phi_{2-}\rangle\rangle\end{matrix}\right)$$

where s is the matrix elements of the $J_\pm$ operators, $s=\langle+|J_+|-\rangle=\langle-|J_-|+\rangle$. Therefore, we have

$${}_2\langle\Psi_2|J_{1nz}(t'')J_{2n'-}(t'')J_{1nz}J_{2n'+}|\Psi_2\rangle_2=e^{-i(t'-t'')2j\mathcal{J}_1 1/3}s^2j^2$$

In the spin correlation functions contain X_3, if we want to find

$${}_3\langle\Psi_{12}|J_{1n-}(t'')J_{2n'-}(t'')J_{1n+}J_{2n'+}|\Psi_{12}\rangle_3$$

we need to compute the following:

$$J_{1n-}(t'')J_{2n'-}(t'')J_{1n+}(t)J_{2n'+}(t')\begin{pmatrix} |++--\rangle\otimes|\Phi_{2+}\rangle_1\otimes|\Phi_{1+}\rangle_1 \\ \begin{pmatrix} |-+-+\rangle \\ |-++-\rangle \end{pmatrix}\otimes|\Phi_{2+}\rangle_1\otimes|\Phi_{1-}\rangle_1 \\ |--++\rangle\otimes|\Phi_{2-}\rangle_1\otimes|\Phi_{1-}\rangle_1 \\ \begin{pmatrix} |+-+-\rangle \\ |+--+\rangle \end{pmatrix}\otimes|\Phi_{2-}\rangle_1\otimes|\Phi_{1+}\rangle_1 \end{pmatrix}(\delta_{n,n'}+\delta_{n,n'+f_{21}})$$

$$= J_{1n-}(t'')J_{2n'-}(t'')J_{1n+}(t)e^{-it'2j\mathcal{J}_1 1/3}s\begin{pmatrix} 0 \\ 0 \\ 0 \\ |-+++\rangle\otimes|\Phi_{2-}\rangle_1\otimes|\Phi_{1-}\rangle_1 \\ \begin{pmatrix} |+++-\rangle \\ |++-+\rangle \end{pmatrix}\otimes|\Psi_{2-}\rangle_1\otimes|\Psi_{1+}\rangle_1 \end{pmatrix}(\delta_{n,n'}+\delta_{n,n'+f_{21}})$$

$$= J_{1n-}(t'')J_{2n'-}(t'')e^{-i(t'+t)2j\mathcal{J}_1 1/3}s^2\begin{pmatrix} 0 \\ 0 \\ 0 \\ |++++\rangle\otimes|\Phi_{2-}\rangle_1\otimes|\Phi_{1-}\rangle_1 \\ 0 \\ 0 \end{pmatrix}(\delta_{n,n'}+\delta_{n,n'+f_{21}})$$

$$= e^{-i(t'+t-2t'')2j\mathcal{J}_1 1/3}s^4\begin{pmatrix} 0 \\ 0 \\ 0 \\ |--++\rangle\otimes|\Psi_{2-}\rangle_1\otimes|\Psi_{1-}\rangle_1 \\ 0 \\ 0 \end{pmatrix}(\delta_{n,n'}+\delta_{n,n'+f_{21}})$$

Hence,

$$ {}_3\langle \Psi_{12} | J_{1n-}(t'') J_{2n'-}(t'') J_{1n+} J_{2n'+} | \Psi_{12} \rangle_3 = s^4 e^{-i(t'+t-2t'')2j\mathcal{J}_1 1/3} $$

In the spin correlation functions contain X_4, if we want to find

$$ {}_3\langle \Psi_{12} | J_{1n+}(t'') J_{2n'-}(t'') J_{1n-} J_{2n'+} | \Psi_{12} \rangle_3 $$

, we need to compute the following:

$$ J_{1n+}(t'') J_{2n'-}(t'') J_{1n-}(t) J_{2n'+}(t') \begin{pmatrix} |++--\rangle \otimes |\Phi_{2+}\rangle_1 \otimes |\Phi_{1+}\rangle_1 \\ \begin{pmatrix} |-+-+\rangle \\ |-++-\rangle \end{pmatrix} \otimes |\Psi_{2+}\rangle_1 \otimes |\Phi_{1-}\rangle_1 \\ |--++\rangle \otimes |\Phi_{2-}\rangle_1 \otimes |\Phi_{1-}\rangle_1 \\ \begin{pmatrix} |+-+-\rangle \\ |+--+\rangle \end{pmatrix} \otimes |\Phi_{2-}\rangle_1 \otimes |\Phi_{1+}\rangle_1 \end{pmatrix} (\delta_{n,n'} + \delta_{n,n'+f_{21}}) $$

$$ = J_{1n+}(t'') J_{2n'-}(t'') J_{1n-}(t) e^{-it'2j\mathcal{J}_1 1/3} s \begin{pmatrix} 0 \\ 0 \\ 0 \\ |-+++\rangle \otimes |\Phi_{2-}\rangle \otimes |\Phi_{1-}\rangle \\ \begin{pmatrix} |+++-\rangle \\ |++-+\rangle \end{pmatrix} \otimes |\Phi_{2-}\rangle_1 \otimes |\Phi_{1+}\rangle_1 \end{pmatrix} (\delta_{n,n'} + \delta_{n,n'+f_{21}}) $$

$$= J_{1n+}(t'')J_{2n'-}(t'')e^{-i(t'-t)2j\mathcal{J}_1 1/3}s^2 \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ \begin{pmatrix} |-++-\rangle \\ |-+-+\rangle \end{pmatrix} \otimes |\Phi_{2-}\rangle_1 \otimes |\Phi_{1+}\rangle_1 \end{pmatrix} (\delta_{n,n'} + \delta_{n,n'+f_{21}})$$

$$= e^{-i(t'-t)2j\mathcal{J}_1 1/3}s^4 \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ \begin{pmatrix} |+-+-\rangle \\ |+--+\rangle \end{pmatrix} \otimes |\Phi_{2-}\rangle_1 \otimes |\Phi_{1+}\rangle_1 \end{pmatrix} (\delta_{n,n'} + \delta_{n,n'+f_{21}})$$

Hence,

$${}_3\langle\Psi_{12}|J_{1n+}(t'')J_{2n'-}(t'')J_{1n-}J_{2n'+}|\Psi_{12}\rangle_3 = s^4 e^{-i(t'-t)2j\mathcal{J}_1 1/3}$$

.

Now let us find the spin correlation function of other sites by applying symmetry transformations. We will use generators of the space group: C_z^2, C_x^2, $C_{[111]}^3$, $C_{[110]}^2$.

By applying C_z^2, we will have the following:

$$1 \leftrightarrow 2$$

$$3 \leftrightarrow 4$$

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} -x \\ -y \\ z \end{pmatrix}$$

hence we have:

$$J_1^x J_2^y = J_1^y J_2^x$$

$$J_1^x J_2^z = -J_1^z J_2^x$$

$$J_1^y J_2^z = -J_1^z J_2^y$$

$$J_1^x J_3^x = J_2^x J_4^x$$

$$J_1^x J_3^y = J_2^x J_4^y$$

$$J_1^x J_3^z = -J_2^x J_4^z$$

$$J_1^y J_3^x = J_2^y J_4^x$$

$$J_1^y J_3^y = J_2^y J_4^y$$

$$J_1^y J_3^z = -J_2^y J_4^z$$

$$J_1^z J_3^x = J_2^z J_4^x$$

$$J_1^z J_3^y = -J_2^z J_4^y$$

$$J_1^z J_3^z = J_2^z J_4^z$$

$$J_1^x J_4^x = J_2^x J_3^x$$

$$J_1^x J_4^y = J_2^x J_3^y$$

$$J_1^x J_4^z = -J_2^x J_3^z$$

$$J_1^y J_4^x = J_2^y J_3^x$$

$$J_1^y J_4^y = J_2^y J_3^y$$

$$J_1^y J_4^z = -J_2^y J_3^z$$

$$J_1^z J_4^x = -J_2^z J_3^x$$

$$J_1^z J_4^y = -J_2^z J_3^y$$

$$J_1^z J_4^z = J_2^z J_3^z$$

$$J_3^x J_4^y = J_3^y J_4^x$$

$$J_3^x J_4^z = -J_3^z J_4^x$$

$$J_3^y J_4^z = -J_3^z J_4^y$$

By applying C_x^2, we will have the following:

$$1 \leftrightarrow 4$$

$$2 \leftrightarrow 3$$

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} x \\ -y \\ -z \end{pmatrix}$$

hence we have:

$$J_1^x J_2^x = J_3^x J_4^x$$

$$J_1^x J_2^y = -J_3^x J_4^y$$

$$J_1^x J_2^z = -J_3^x J_4^z$$

$$J_1^y J_2^x = -J_3^y J_4^x$$

$$J_1^y J_2^y = J_3^y J_4^y$$

$$J_1^y J_2^z = J_3^y J_4^z$$

$$J_1^z J_2^x = -J_3^z J_4^x$$

$$J_1^z J_2^y = J_3^z J_4^y$$

$$J_1^z J_2^z = J_3^z J_4^z$$

$$J_1^x J_3^x = J_2^x J_4^x$$

$$J_1^x J_3^y = -J_2^y J_4^x$$

$$J_1^x J_3^z = -J_2^z J_4^x$$

$$J_1^y J_3^x = -J_2^x J_4^y$$

$$J_1^y J_3^y = J_2^y J_4^y$$

$$J_1^y J_3^z = J_2^z J_4^y$$

$$J_1^z J_3^x = -J_2^x J_4^z$$

$$J_1^z J_3^y = J_2^y J_4^z$$

$$J_1^z J_3^z = J_2^z J_4^z$$

$$J_1^x J_4^y = -J_1^y J_4^x$$

$$J_1^x J_4^z = -J_1^z J_4^x$$

$$J_1^y J_4^z = J_1^z J_4^y$$

$$J_2^x J_3^y = -J_2^y J_3^x$$

$$J_2^x J_3^z = -J_2^z J_3^x$$

$$J_2^y J_3^z = J_2^z J_3^y$$

By apply $C_{[111]}^3$, we will have the following:

$$1 \leftrightarrow 1$$

$$3 \rightarrow 2 \rightarrow 4 \rightarrow 3$$

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} y \\ z \\ x \end{pmatrix}$$

hence we have:

$$J_1^x J_2^x = J_1^y J_4^y$$

$$J_1^x J_2^y = J_1^y J_4^z$$

$$J_1^x J_2^z = J_1^y J_4^x$$

$$J_1^y J_2^x = J_1^z J_4^y$$

$$J_1^y J_2^y = J_1^z J_4^z$$

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$$J_2^x J_4^y = J_2^y J_4^z$$

$$J_2^x J_4^z = J_2^y J_4^x$$

$$J_3^x J_4^x = J_3^y J_4^y$$

$$J_3^x J_4^y = J_3^y J_4^z$$

$$J_3^x J_4^z = J_3^y J_4^x$$

By apply $C^2_{[110]}$, we will have the following:

$$1 \leftrightarrow 2$$

$$3 \leftrightarrow 3$$

$$4 \leftrightarrow 4$$

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} y \\ x \\ -z \end{pmatrix}$$

hence we have:

$$J_1^x J_2^x = J_1^y J_2^y$$

$$J_1^x J_2^y = J_1^y J_2^x$$

$$J_1^x J_2^z = -J_1^y J_2^z$$

$$J_1^z J_2^x = -J_1^z J_2^y$$

$$J_1^x J_3^x = J_2^y J_3^y$$

$$J_1^x J_3^y = J_2^y J_3^x$$

$$J_1^x J_3^z = -J_2^y J_3^z$$

$$J_1^y J_3^x = J_2^x J_3^y$$

$$J_1^y J_3^y = J_2^x J_3^x$$

$$J_1^y J_3^z = -J_2^x J_3^z$$

$$J_1^z J_3^x = -J_2^z J_3^y$$

$$J_1^z J_3^y = -J_2^z J_3^x$$

$$J_1^z J_3^z = J_2^z J_3^z$$

$$J_1^x J_4^x = J_2^y J_4^y$$

$$J_1^x J_4^y = J_2^y J_4^x$$

$$J_1^x J_4^z = -J_2^y J_4^z$$

$$J_1^y J_4^x = J_2^x J_4^y$$

$$J_1^y J_4^y = J_2^x J_4^x$$

$$J_1^y J_4^z = -J_2^x J_4^z$$

$$J_1^z J_4^x = -J_2^z J_4^y$$

$$J_1^z J_4^y = -J_2^z J_4^x$$

$$J_1^z J_4^z = J_2^z J_4^z$$

$$J_3^x J_4^x = J_3^y J_4^y$$

$$J_3^x J_4^y = J_3^y J_4^x$$

$$J_3^x J_4^z = -J_3^y J_4^z$$

$$J_3^z J_4^x = -J_3^z J_4^y$$

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