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I am submitting herewith a thesis written by Jason Thomas Haraldsen entitled “Nanomagnets: Magnetic Properties and Inelastic Neutron Scattering Studies.” I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Physics.

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Nanomagnets: Magnetic Properties and Inelastic Neutron Scattering Studies

A Thesis

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Jason Thomas Haraldsen

May 2008

Acknowledgments

I would like to acknowledge and thank my advisor Ted Barnes (Department of Physics and Astronomy), for his guidance, support, and patience throughout the process of this work. I am very grateful for Dr. Barnes' helpful suggestions and encouragement throughout my time as a graduate student.

I extend great appreciation to my committee members (Elbio Dagotto, Robert Hinde, and Pengcheng Dai) for taking the time to be on my committee, review my work, and provide helpful insight. I would also like to acknowledge useful discussions and work with Matt Stone, Mark Lumsden, James Thompson, John Turner, and Steve Nagler.

I dedicate this thesis to my loving wife, Beth, for coming down to Tennessee for these years and being there to help me throughout my career. I also dedicate this work to my family for their encouragement and support.

Abstract

In this thesis, small quantum spin systems, known as nano-magnets or molecular magnets, have been investigated. This is an area of great interest in the development of nanotechnology and quantum computers. Previous research on molecular magnets has concentrated on large, complex materials, which have many magnetic ions competing for superexchange pathways. Due to the large number of magnetic ions, the Hamiltonians resulted in very large Hilbert spaces, which makes it difficult for the magnetic interactions to be characterized and analyzed. Through the analysis of smaller and simpler magnetic clusters, insight can be gained from the interactions of the magnetic ions in these systems. Because many quantum spin systems can be accurately modeled using an antiferromagnetic Heisenberg Hamiltonian, we will assume this as a starting point for the theoretical description of molecular magnets.

Our previous work on these systems considered only clusters of $S=1/2$ ions. Here, we derived closed form results for the magnetothermal properties and inelastic neutron scattering structure factors for dimers, trimers, and tetramers in various geometries, and in several cases were able to compare these calculations to known molecular magnets, and assist in the identification of the dominant magnetic interaction pathways.

Using similar methods, these results are extended to clusters of two to six ions of spin S . An analysis of magnetic properties and observables for these clusters reveal a distinct pattern for that may be useful for the understanding of large clusters that

cannot be determined analytically. From the specific case examined, the analysis of data from experiments on some magnetic materials shows the use and need for these calculations. This study of magnetic interactions in small quantum magnets develops clearer insight into the nature of excitations of larger, more complicated systems, which at present can only be investigated phenomenologically or through the use of numerical methods.

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Chapter 1

Introduction to Nanomagnetism

Throughout recent years, the field of low-dimensional magnetism has seen greatly increased interest to the area of finite quantum spin systems, also known as molecular magnets or nanomagnets [1–11]. Nanomagnets typically consist of clusters of interacting magnetic ions that are quasi-isolated from each other by nonmagnetic ligands within a molecular solid. They are usually defined as materials in which the ground state of the cluster has a nonzero total spin [3, 12]. Here, we generalize this definition to include all systems of largely isolated clusters of interacting quantum spins.

The study of nanomagnets provides interesting research opportunities that help extend and expand the field of condensed matter physics [1–6]. With the properties and phenomena of quantum tunneling, cascade excitations, and anisotropic properties, as well as the possibility of technological applications, the excitement and focus on new and upcoming magnetic materials becomes more apparent [5–8]. With the large influx of experimental data and questions about these materials, there is a great need to provide fundamental theory that helps analyze and understand these questions. This thesis will focus on considering simple and complicated models to help analyze and predict excitations for nanomagnets, and help determine fundamental

properties for finite spin clusters.

Many realizations of spin cluster materials with numerous spin ions and magnetic structure have been reported in the literature [7,8,10,11]. Most of the work published on nanomagnets has been on large, complex materials with high-spin ground states. A familiar example is “Mn₁₂-acetate” [13], which consists of four $S = 3/2$ and eight $S = 2$ magnetic ions with a 10^8 -dimensional Hilbert space. The magnetic properties of clusters with large Hilbert spaces can only be treated using numerical techniques. Therefore, to understand the underlying physics, we will investigate qualitatively similar, but smaller molecular magnets. By specializing our calculations to smaller systems and starting with a fundamental Hamiltonian, we can apply theoretical techniques to the full magnetic Hilbert space and derive the magnetic observables in closed form [11]. Through an analysis of these properties and observations, an overall understanding of the nature of finite clusters can be achieved.

Previous theoretical studies of molecular magnets in the literature have usually specialized to individual materials and their associated model Hamiltonians. Whereas this work is intended to be general and useful for the interpretation of data on many candidate nanomagnets. Few general theoretical results have been reported for finite spin systems beyond dimers and trimers, since there are many possible independent geometries and superexchange sets. Specific cases of tetramers have been considered by Procissi *et al.* [14] ($S=1/2$ square tetramer), Gros *et al.* [15] and Jensen *et al.* [16] (an unsymmetric $S=1/2$ tetrahedral model of $\text{Cu}_2\text{Te}_2\text{O}_5(\text{Br}_{1-x}\text{Cl}_x)$), Kortz *et al.* [17] (unsymmetric tetramer model of $\text{K}_7\text{Na}[\text{Cu}_4\text{K}_2(\text{H}_2\text{O})_6(\alpha\text{-AsW}_9\text{O}_{33})_2] \cdot 5.5\text{H}_2\text{O}$), and Ciftja [18] (symmetric trimer with apical spin). More general reviews of quantum spin systems have been published by Kahn [3] (thermodynamics) and Whangbo *et al.* [19] (local origins of magnetism, thermodynamics properties, and materials). Studies of the dynamics of Heisenberg spin clusters using a quasiclassical formalism have been reported in a series of papers by Ameduri, Efremov and

Klemm [20–22]. Waldmann has reported results for the inelastic neutron structure factor of cyclic Heisenberg spin clusters [23], which are similar to the calculations we propose to carry out on higher-spin systems.

A more detailed investigation of the properties and interaction of small quantum spin systems is necessary for a complete understanding of nanomagnets. For simple theoretical models such as the Heisenberg model, small clusters that consist of only a few interacting magnetic ions can be treated and solved analytically, and closed-form results can be obtained for many physical observables [11]. One property of special interest is the inelastic neutron scattering (INS) structure factor, which is required for the interpretation of INS experiments. INS is very well suited to the investigation of magnetic interactions at an interatomic level, since the measured structure factor is sensitive to the local geometry and interactions with the magnetic ions [11]. As this study is intended to assist in the analysis of future neutron scattering experiments, evaluation of this structure factor is one of our principal concerns. Other properties that are of special interest are magnetic susceptibility and magnetic heat capacity, since these bulk measurements compliment the local probe of neutron scattering [3].

Previous work on inelastic neutron scattering of small spin systems concentrated only on clusters consisting of $S = \frac{1}{2}$ ions [11], where bulk and microscopic observations were determined. In this thesis, the work is generalized to small clusters of spin S ions, assuming isotropic Heisenberg interactions. We derive closed-form results for the properties of N ions (where $N = 1 \dots 6$) with various geometries and interaction strengths. In the next chapter, we will define the superexchange interaction and the Heisenberg model, as well as the magnetic observables that we plan to investigate. These include the standard bulk thermodynamic quantities for magnetic materials (partition function, magnetic heat capacity, and magnetic susceptibility), as well as the inelastic neutron scattering structure factor. Since the number of geometries become more complicated as N increases, the pentamer ($N=5$) and hexamer ($N=6$)

clusters are mainly examined in general terms. Overall, this study will show that the magnetic properties of nano-magnetic materials change in a predictable manner. This becomes apparent through the method of using dimer and trimer bases for the calculation of the eigenstates.

This thesis is organized as follows: in the second chapter, the theoretical basis for this research and the models that are used in these studies are discussed. Chapter three considers the magnetic properties of small antiferromagnetic clusters of N ($N = 1 \dots 6$) ions (covering magnetic observables and in some sections, experimental cases). Finally, the last chapter contains the summary and conclusions.

Chapter 2

Theory of Super-Exchange and Magnetic Excitations

In this chapter, the theory of super-exchange and magnetic excitations is discussed. Starting from basic electron orbitals, we discuss the interactions between magnetic atoms to the bulk properties and excitations of these magnetic interactions.

2.1 Super-Exchange and Magnetic Interactions

For a better understanding of magnetic interactions, it is important to give a brief review into the nature of the magnetism and the creation of interactions between ions. In 1897, the electron was discovered by J.J. Thomson. The property of the electron's intrinsic spin has been analyzed through many experiments and provides an electron with a magnetic moment through its angular momentum [24, 25], where a single electron has a moment of $\frac{\hbar}{2}$. Since most atoms consist of electrons, the individual magnetic moments can combine to give the atom an overall magnetic moment. This combination of electrons helps develop a system that follows specific rules, known as Hund's rules, which result in an overall magnetic moment of 0, $1/2$, 1, $3/2$, 2, or $5/2$ [26]. This is especially true of the transition elements on the periodic

table, where higher moments can be found in the more exotic larger atoms.

When a material is synthesized using magnetic elements, the magnetic moments of the atoms can interact by a transfer of electrons through the molecular bonds with non-magnetic neighbors. This interaction is called super-exchange [3] and can provide a material with ordered magnetism: ferromagnetic and anti-ferromagnetic. These describe the directionality of the interacting spins, where ferromagnetic interactions consist of spin ions that are aligned parallel to each other and anti-ferromagnetic interactions are aligned in an anti-parallel manner. A simple model dealing mainly with spin alignment was proposed by Ising in 1925. However, this did not consider the more complicated interactions between ions [27]. While super-exchange provides magnetic order, magnetic disorder can result from randomization of spins called paramagnetism.

To understand the super-exchange between ions, one must examine the bonds and interactions more closely. The molecular bonds that produce a magnetic super-exchange usually involve the d -orbital valence electrons [3, 26]. Through orbital overlap, the valence electrons are provided a pathway for which they may interact. While the strongest magnetic interactions form through orbitals with a 180° bond angle, the super-exchange pathway can still exist with smaller bond angles; although they will be substantially weakened. [3]

In 1963, J. Hubbard proposed a model that contained the basic elements of the interactions between magnetic ions [9]. This Hamiltonian contains two types of terms that represent the states from the model. The Hubbard Hamiltonian is stated as

$$\mathcal{H} = U \sum_i n_{i\uparrow} n_{i\downarrow} - t \sum_{\langle ij \rangle, \sigma} c_{i,\sigma}^\dagger c_{j,\sigma}, \quad (2.1)$$

where U represents the potential energy arising from the charges on the electrons and t represents the kinetic energy of electrons hopping between atoms [3, 9]. The

first term in the Hubbard model is the on-site repulsion between ions multiplied by the number of doubly occupied levels. Here, the up and down arrows denote the spin state of each electrons and is diagonal in these states. The second component is the hopping integral that represents the off-diagonal states with non-vanishing matrix elements between states that differ by one electron that move with changing spin state. When the limit of $U \gg t$ is examined, it is possible to derive the anti-ferromagnetic Heisenberg spin Hamiltonian with an overall exchange constant of J , which is equal to $4t^2/U$. It is this super-exchange constant that provides the interaction between two spin ions. This limited model was first discussed by Heisenberg in 1926 and is the basis for the work presented here [1].

2.2 The Heisenberg Magnet

Within the limit of the Hubbard model, the magnetic Hamiltonian can be examined as individual ions interacting through either a ferromagnetic or anti-ferromagnetic interaction. The nearest-neighbor Heisenberg magnet, which we shall assume as our standard model for molecular magnets, is defined by the Hamiltonian

$$\mathcal{H} = \sum_{\langle ij \rangle} J_{ij} \vec{S}_i \cdot \vec{S}_j, \quad (2.2)$$

where the superexchange constants J_{ij} are positive for antiferromagnetic interactions and negative for ferromagnetic ones, and $\vec{S}_i$ is the quantum spin operator for a spin S ion at site i [1,3]. Chapter 3 will be discussing varying spin clusters of spin S ions.

It is important to understand that Eq. 2.2 is the basic Hamiltonian approached in this thesis. This is the isotropic interaction that is the fundamental building block. However, multiple perturbations can be added to the Hamiltonian to correct for anisotropic interactions, addition of magnetic field, or crystal field splitting. The

full magnetic Hamiltonian with all terms is described as

$$\mathcal{H} = \sum_{\langle ij \rangle} [J_{ij} \vec{S}_i \cdot \vec{S}_j + \vec{S}_i \cdot \mathbf{D}_{ij} \cdot \vec{S}_j + \mathbf{d}_{ij} \vec{S}_i \wedge \vec{S}_j] + \sum_i \vec{L}_i \cdot \vec{S}_i - \sum_i^N g\mu_B S_i^z B, \quad (2.3)$$

where the second term describes anisotropic and dipolar interactions, the third term is the Dzyaloshinski/Moriya interaction that describes antisymmetric interactions, the forth evaluates the spin-orbit coupling, and the last term is the Zeeman magnetic field splitting term [3]. Since this work focuses on looking at small clusters in the analytical limit, the Hamiltonian will stick mainly to the isotropic term with magnetic field splitting. It is important to keep in mind that by completely understanding the isotropic Hamiltonian, we can examine the other terms as perturbations of the original.

2.3 Magnetic Observables

Magnetic excitations of spin S systems display various interesting properties. These magnetic excitations will be considered for various models including clusters of N ions with ($N = 1 \dots 6$). Examples of the application of our results to novel materials will be presented in detail. All our results will be derived assuming an isotropic Heisenberg antiferromagnetic Hamiltonian [1, 3]. These Hamiltonians are then used to determine thermodynamical properties (magnetic susceptibility and heat capacity), magnetic excitations, inelastic neutron scattering structure factors and powder average intensities [4, 28]. Each experimental technique will, in general, bring new information regarding the physics of a systems. The idealized isolated cluster results discussed here may also be useful in the study of infinite quantum spin systems, especially in the regime of weak intercluster coupling.

The energy eigenstates and eigenvalues may be found by diagonalizing the magnetic Hamiltonian on a convenient basis. (In practice we will employ the usual set of

$\hat{z}$ -polarized magnetic basis states.) This can be simplified by extending the Kambe approach of rewriting the Hamiltonian in terms of not only total spin of the whole cluster, but total spin of the individual components (Dimers and Trimers) [4, 29]. Several physically interesting quantities may be computed directly from the energy eigenvalues; in this work we evaluate the partition function, specific heat and magnetic susceptibility, which are given by

$$Z = \sum_{i=1}^N e^{-\beta E_i} = \sum_{E_i} (2S_{tot} + 1) e^{-\beta E_i} , \quad (2.4)$$

$$C = k_B \beta^2 \frac{d^2 \ln(Z)}{d\beta^2} , \quad (2.5)$$

and

$$\begin{aligned} \chi &= \frac{\beta}{Z} \sum_{i=1}^N (M_z^2)_i e^{-\beta E_i} \\ &= \frac{1}{3} (g\mu_B)^2 \frac{\beta}{Z} \sum_{E_i} (2S_{tot} + 1) (S_{tot} + 1) S_{tot} e^{-\beta E_i} . \end{aligned} \quad (2.6)$$

In these central formulas, the sum $i = 1 \dots N$ is over all N independent energy eigenstates (including magnetic substates), the sum $\sum_{E_i}$ is over energy levels only, $M_z = m g \mu_B$ where $m = S_{tot}^z / \hbar$ is the integral or half-integral magnetic quantum number, and g is the electron g -factor [2, 3, 24]. While these bulk properties are important to examine and consider, they do not provide a microscopic picture of the magnetic structure. Therefore, it is necessary to use a probe that interacts directly with the magnetism in materials. This would be inelastic neutron scattering.

2.4 Inelastic Neutron Scattering

The neutron is one of the fundamental particles in nature and consists of two down quarks and an up quark [30]. This combination of quarks leaves the neutron with

no net charge, spin of $1/2$, and a magnetic moment [24, 28, 31]. It is the charge neutrality that makes the neutron useful for magnetism in condensed matter physics. The neutrons energy is defined by

$$E = k_B T = \frac{h^2}{2m\lambda^2} = h\nu. \quad (2.7)$$

For the neutron to be useful, we have to take advantage of the neutrons wave-like nature using the de Broglie relationship of

$$\lambda = \frac{h}{p} = \frac{h}{mv}, \quad (2.8)$$

where the wavelength is inversely proportional to the momentum and therefore inversely proportional to its velocity [28]. The nature of the neutron allows it to have a wavelength and energy that is ideal for material analysis. Since wavelength is inversely proportional to the velocity, it can be easily tuned. With the wavelength of neutron being a few Angstroms, it is possible for the neutron to be used to easily investigate the atomic length scales. For example, a neutron with 81.8 meV of energy will be travelling ≈ 4000 m/s and have a wavelength of 1 Å. By cooling down the neutrons, the wavelength can be increased to about 9 Å [31]. This makes it possible to investigate larger micro-structures. However, for this thesis, the magnetic moment of the neutron is going to be key. Since the magnetic moment provides a neutron with spin, it can interact directly with magnetic atoms; ignoring the charge of the electrons and the nucleus of the atoms.

The magnetic properties of the neutron makes inelastic neutron scattering (INS) an important tool when you want to investigate dynamic properties like vibrational and magnetic excitations [32]. This is possible due to the nature of inelastic collisions, where neutrons lose some energy to excite phonons and magnetic excitations. These can be examined as the complete picture of the structure factor, $S(\mathbf{Q}, \omega)$,

as function of energy and momentum. Individual energy excitations have distinct energy and momentum transfers, which are dependent on atomic position and magnetic cross section, that acts like a finger print to specific materials. Since we are examining magnetism, phonon excitations can be a hinderance to the observation of magnetic excitations due to the possible cross-over in energy levels [31]. Therefore, a method to distinguish magnetic excitations from phonons must be considered. Luckily, thermodynamic statistics provides an answer for this excitation problem. As temperature increases, magnetic excitations lose statistical intensity while phonons have an increase in intensity with temperature [31], which in turn allows the two excitations to be clarified. Now that neutrons have been introduced, the more detailed and densely theoretical calculation of the structure factor can now be discussed.

In “spin-only” magnetic neutron scattering at zero temperature, the differential cross section for the inelastic scattering of an incident neutron from a magnetic system in an initial state $|\Psi_i\rangle$, with momentum transfer $\hbar\vec{q}$ and energy transfer $\hbar\omega$, is proportional to the neutron scattering structure factor tensor

$$S_{ba}(\vec{q}, \omega) = \int_{-\infty}^{\infty} \frac{dt}{2\pi} \sum_{\vec{x}_i, \vec{x}_j} e^{i\vec{q}\cdot(\vec{x}_i - \vec{x}_j) + i\omega t} \langle \Psi_i | S_b^\dagger(\vec{x}_j, t) S_a(\vec{x}_i, 0) | \Psi_i \rangle . \quad (2.9)$$

The site sums in Eq.(2.9) run over all magnetic ions in one unit cell, and a, b are the spatial indices of the spin operators.

For transitions between discrete energy levels, the time integral gives a trivial delta function $\delta(E_f - E_i - \hbar\omega)$ in the energy transfer, so it is useful to specialize to an “exclusive structure factor” for the excitation of states within a specific magnetic multiplet (generically $|\Psi_f(\lambda_f)\rangle$) from the given initial state $|\Psi_i\rangle$,

$$S_{ba}^{(fi)}(\vec{q}) = \sum_{\lambda_f} \langle \Psi_i | V_b^\dagger | \Psi_f(\lambda_f) \rangle \langle \Psi_f(\lambda_f) | V_a | \Psi_i \rangle , \quad (2.10)$$

where the vector $V_a(\vec{q})$ is a sum of spin operators over all magnetic ions in a unit

cell,

$$V_a = \sum_{\vec{x}_i} S_a(\vec{x}_i) e^{i\vec{q} \cdot \vec{x}_i} . \quad (2.11)$$

This exclusive structure factor is related to the exclusive differential inelastic neutron scattering cross section by

$$\frac{d\sigma^{(fi)}}{d\Omega} = (\gamma r_0)^2 \frac{k'}{k} (\delta_{ab} - \hat{q}_a \hat{q}_b) S_{ba}^{(fi)}(\vec{q}) |F(\vec{q})|^2, \quad (2.12)$$

where $\gamma \approx -1.193$ is the neutron gyromagnetic ratio, $r_o = \hbar\alpha/m_e c$ is the classical electron radius, k and k' are the magnitudes of the initial and final neutron wavevectors, and $F(\vec{q})$ is the ionic form factor. (This relation is abstracted from Eq.(7.61) of Ref. [28], specialized to an exclusive process.)

For a rotationally invariant magnetic interaction and an $S_{tot} = 0$ initial state (as is often encountered in $T=0$ inelastic scattering from an antiferromagnet), only $S_{tot} = 1$ final states are excited, and $S_{ba}^{(fi)}(\vec{q}) \propto \delta_{ab}$. In this case we may define a scalar neutron scattering structure factor $S(\vec{q})$ by

$$S_{ba}^{(fi)}(\vec{q}) = \delta_{ab} S(\vec{q}) . \quad (2.13)$$

The result for $S_{ba}^{(fi)}(\vec{q})$ is more complicated for neutron scattering from a magnetic ($S_{tot} > 0$) initial state. If we assume an isotropic magnetic Hamiltonian and a spherical basis for the spin operators S_a , the tensor $S_{ba}^{(fi)}(\vec{q})$ is diagonal but is not $\propto \delta_{ab}$; it instead has entries that are proportional to a universal function of $\vec{q}$ times a product of Clebsch-Gordon coefficients, since

$$\langle \Psi_f(\lambda_f) | V_a | \Psi_i(\lambda_i) \rangle = \langle S_f \lambda_f | 1a S_i \lambda_i \rangle \mathcal{V}^{(fi)}(\vec{q}) , \quad (2.14)$$

where $\mathcal{V}^{(fi)}(\vec{q})$ is the reduced matrix element for the transition $|\Psi_i\rangle \rightarrow |\Psi_f\rangle$. Here we simplify the presentation by quoting the unpolarized result $\langle S_{ba}^{(fi)}(\vec{q}) \rangle$, obtained

by summing over final and averaging over initial polarizations. This unpolarized $\langle S_{ba}^{(fi)}(\vec{q}) \rangle$ is $\propto \delta_{ab}$, so it suffices to give the function $S(\vec{q})$;

$$\langle S_{ba}^{(fi)}(\vec{q}) \rangle = \delta_{ab} S(\vec{q}) =$$

$$\frac{1}{2S_i + 1} \sum_{\lambda_i, \lambda_f} \langle \Psi_i(\lambda_i) | V_b^\dagger | \Psi_f(\lambda_f) \rangle \langle \Psi_f(\lambda_f) | V_a | \Psi_i(\lambda_i) \rangle . \quad (2.15)$$

If desired, the general results for polarized scattering can be recovered by reintroducing the appropriate Clebsch-Gordon coefficients of Eq.(2.14) in Eq.(3.134).

The results given above apply to neutron scattering from single crystals. Frequently magnetic materials are only available as powders, so neutron scattering experiments measure an orientation average of the unpolarized neutron scattering structure factor. We define this powder average by

$$\bar{S}(q) = \int \frac{d\Omega_{\hat{q}}}{4\pi} S(\vec{q}) . \quad (2.16)$$

Chapter 3

Magnetic Excitations and Observables of Spin Cluster Systems

This chapter is a lightly revised version of a paper published in the Physical Review B in 2004 by Jason T. Haraldsen, Ted Barnes, and Janice Musfeldt: J.T. Haraldsen, T. Barnes, and J.L. Musfeldt, Neutron Scattering and Magnetic Observables for $S = 1/2$ Molecular Magnets, *Phys. Rev. B* 72, 064403 (2005). This chapter is a review of the work completed and to be submitted for publication on spin S spin clusters and is shown as an explanation of the calculations performed on the high spin systems.

Recent years have seen a rapid increase in the interest in finite quantum spin systems, also known as molecular magnets or nanomagnets [7,8,10,18,33–38]. Molecular magnets typically consist of clusters of interacting spins that are magnetically isolated from the other clusters in the molecular solid by nonmagnetic ligands. Formally, molecular magnets are materials in which the ground state has nonzero total spin. Here we generalize this definition to include all systems of largely isolated clusters of interacting quantum spins. These materials are interesting both as simple model

Table 3.1: Some examples of small $S = \frac{1}{2}$ clusters and molecular magnets.

Material	Spin System	Ground State S_{tot}	Refs.
$\text{VO}(\text{HPO}_4) \cdot 0.5\text{H}_2\text{O}$	dimer	0	[39–41]
$\text{Cu}_3(\text{O}_2\text{C}_{16}\text{H}_{23})_6 \cdot 1.2\text{C}_6\text{H}_{12}$	symmetric trimer	1/2	[42, 43]
$\text{Na}_9[\text{Cu}_3] \cdot 26\text{H}_2\text{O}^1$	symmetric trimer	1/2	[17]
$[\text{Cu}_3(\text{cpse})_3(\text{H}_2\text{O})_3] \cdot 8.5\text{H}_2\text{O}$	symmetric trimer	1/2	[44]
$(\text{CN}_3\text{H}_6)_4\text{Na}_2[\text{V}_6] \cdot 14\text{H}_2\text{O}^2$	isosceles trimer	1/2	[45]
$\text{Na}_6[\text{V}_6] \cdot 18\text{H}_2\text{O}^2$	general trimer	1/2	[45]
$\text{K}_6[\text{V}_{15}\text{As}_6\text{O}_{42}(\text{H}_2\text{O})] \cdot 8\text{H}_2\text{O}$	symmetric trimer	1/2	[46–50]
NaCuAsO_4	linear tetramer	0	[51, 52]
$(\text{NHEt}_3)[\text{V}_{12}\text{As}_8\text{O}_{40}(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$	rectangular tetramer	0	[53]
$\text{K}_7\text{Na}[\text{Cu}_4] \cdot 5.5\text{H}_2\text{O}^3$	distorted tetramer	1	[17]

$$^1[\text{Cu}_3] = [\text{Cu}_3\text{Na}_3(\text{H}_2\text{O})_9(\alpha\text{-AsW}_9\text{O}_{33})_2]$$

$$^2[\text{V}_6] = [\text{H}_4\text{V}_6\text{O}_8(\text{PO}_4)_4((\text{OCH}_2)_3\text{CCH}_2\text{OH})_2]$$

$$^3[\text{Cu}_4] = [\text{Cu}_4\text{K}_2(\text{H}_2\text{O})_6(\alpha\text{-AsW}_9\text{O}_{33})_2]$$

systems for the study of quantum magnetism and because they have possible applications as nanoscale computer memory elements [7, 8]. Many realizations of finite spin clusters with various ionic spins, ground state spins and geometries have been reported in the literature; some recent examples with $S=1/2$ ions are given in Table 3.1.

Theoretical results for the properties of finite $S=1/2$ quantum spin systems have appeared in several recent references, primarily in the context of experimental studies of specific materials. Dimer results are reported in several studies of the $S=1/2$ spin dimer $\text{VO}(\text{HPO}_4) \cdot 0.5\text{H}_2\text{O}$; see for example Johnson *et al.* [39], Tennant *et al.* [40] and Koo *et al.* [41]. Theoretical properties of $S=1/2$ spin trimers have similarly been given in studies of candidate trimer materials; see for example Refs. [17, 42, 43, 45, 54].

Rather few general theoretical results have been reported for $S=1/2$ spin tetramers, since the results are more complicated and there are many more independent geometries and sets of superexchanges. Specific cases of tetramers are considered by Pro-

cissi *et al.* [14] ($S=1/2$ square tetramer), Gros *et al.* [15] and Jensen *et al.* [16] (an unsymmetric $S=1/2$ tetrahedral model of $\text{Cu}_2\text{Te}_2\text{O}_5(\text{Br}_{1-x}\text{Cl}_x)$), Kortz *et al.* [17] (unsymmetric tetramer model of $\text{K}_7\text{Na}[\text{Cu}_4\text{K}_2(\text{H}_2\text{O})_6(\alpha\text{-AsW}_9\text{O}_{33})_2]\cdot 5.5\text{H}_2\text{O}$), and Ciftja [18] (symmetric trimer with apical spin). More general reviews of quantum spin systems have been published by Kahn [3] (thermodynamics) and Whangbo *et al.* [19] (local origins of magnetism, thermodynamics properties, and materials). Studies of the dynamics of Heisenberg spin clusters using a quasiclassical formalism have been reported in a series of papers by Ameduri, Efremov and Klemm [20–22].

This increased level of interest in molecular magnets motivates more detailed theoretical investigation of the properties of finite quantum spin systems. For simple theoretical models such as the Heisenberg model, clusters that consist of only a few interacting magnetic ions can be treated analytically, and closed-form results can be obtained for many physical observables. One especially interesting quantity is the inelastic neutron scattering structure factor, which is required for the interpretation of inelastic neutron scattering experiments. Inelastic neutron scattering is very well suited to the investigation of magnetic interactions at interatomic scales, since the measured structure factor is sensitive to the local geometry and interactions of the magnetic ions. As this work is intended in part to facilitate future neutron scattering studies, the evaluation of this structure factor is one of our principal concerns.

3.1 Spin Dimers

3.1.1 Dimer of General Spin S

The magnetic spin dimer is the most basic of spin cluster models. Whangbo *et al.* has examined the dimer in great detail [19]. Here we review and present the magnetic properties for the general S dimer. We then expand the dimer for use as a basis for the general S trimer systems. We present the magnetic properties and INS structure

factor for the $S = 0$ ground to the $S = 1$ excited state. The spin dimer consists of two spins interacting through the isotropic Heisenberg Hamiltonian,

$$\mathcal{H} = J \vec{S}_1 \cdot \vec{S}_2 , \quad (3.1)$$

where J is the magnetic interaction and S is the quantum spin operator. From the Clebsch-Gordon series, the spin decomposition of the general spin dimer is given as

$$\mathbf{S} \otimes \mathbf{S} = \sum_0^S \mathbf{S}, \quad (3.2)$$

where $\mathbf{S} = 2S + 1$. Therefore, any magnetic dimer will have $(2S_1 + 1)(2S_2 + 1)$ magnetic states and the energy eigenstates are give by

$$E = \frac{J}{2} [\mathfrak{J}_{tot} - \mathfrak{J}_1 - \mathfrak{J}_2], \quad (3.3)$$

where $\mathfrak{J}_{tot} = S_{tot}(S_{tot} + 1)$ and S_{tot} is the total spin state of the dimer and $\mathfrak{J}_i = S_i(S_i + 1)$ ($i=1,2$) and S_1 and S_2 are individual spins for each ion. While this allows for mixed valence systems, these systems are not discussed in detailed. From the magnetic states and energy levels, bulk properties and inelastic neutron scattering can be determine. The bulk properties can be determine through equations 3.143-2.6. The inelastic neutron scattering structure factor and powder average intensities can be determine in general form.

From an analysis the of the general energy levels, the excitation energy of the first transition is always J , while the general excitations are give by $J(S_{tot} + 1)$. The structure factor for inelastic neutron scattering can be determined in general form to be

$$S(\vec{q}) = \frac{2S(S+1)}{3} (1 - \cos(\vec{q} \cdot \vec{r}_{12})), \quad (3.4)$$

where S is the spin of the system and r_{12} is the distance between ions. Using these

results we can give clarity to the spin-1/2 case, as well as the higher spin cases of spin-1 and spin-3/2.

3.1.2 Spin $\frac{1}{2}$ Dimer

The “minimal” spin cluster model is the $S = 1/2$ spin dimer (Fig.3.1), which consists of a single pair of $S = 1/2$ spins interacting through the Heisenberg Hamiltonian,

$$\mathcal{H} = J \vec{S}_1 \cdot \vec{S}_2 . \quad (3.5)$$

Since this is an isotropic magnetic Hamiltonian, the total spin is a good quantum number, and from the Clebsch-Gordon series $1/2 \otimes 1/2 = 1 \oplus 0$ we expect the spectrum to consist of an $S_{tot} = 1$ triplet and an $S_{tot} = 0$ singlet. In a $\hat{z}$ -diagonal basis

$$\begin{bmatrix} |\uparrow\uparrow\rangle \\ |\uparrow\downarrow\rangle \\ |\downarrow\uparrow\rangle \\ |\downarrow\downarrow\rangle \end{bmatrix} \quad (3.6)$$

the Hamiltonian matrix is

$$\mathcal{H} = J \begin{bmatrix} 1/4 & & & \\ & -1/4 & 1/2 & \\ & 1/2 & -1/4 & \\ & & & 1/4 \end{bmatrix} . \quad (3.7)$$

Diagonalizing this Hamiltonian matrix gives the energy eigenvalues and eigenvectors,

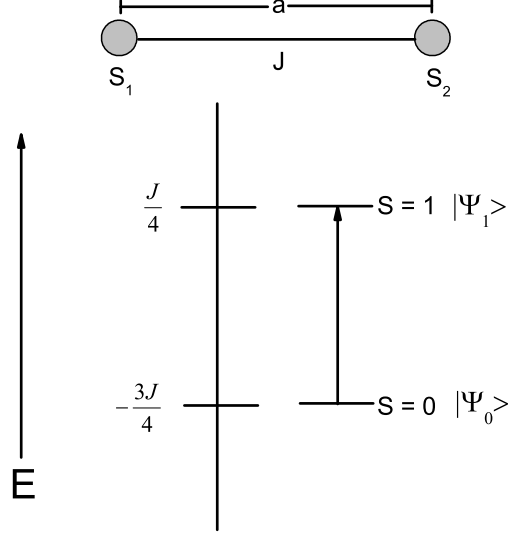


Figure 3.1: The geometry and energy levels of a Heisenberg spin dimer.

$$E_1 = \frac{1}{4} J \quad (3.8)$$

$$E_0 = -\frac{3}{4} J ,$$

$$\left[\begin{array}{l} |\Psi_1(+1)\rangle = |\uparrow\uparrow\rangle \\ |\Psi_1(0)\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |\Psi_1(-1)\rangle = |\downarrow\downarrow\rangle \end{array} \right] \quad (3.9)$$

$$|\Psi_0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) . \quad (3.10)$$

The specific heat and magnetic susceptibility for the dimer are especially simple, since there is only a single excited level. The results are (in a dimensionless form)

$$Z = e^{\frac{3}{4}\beta J} + 3e^{-\frac{1}{4}\beta J} \quad (3.11)$$

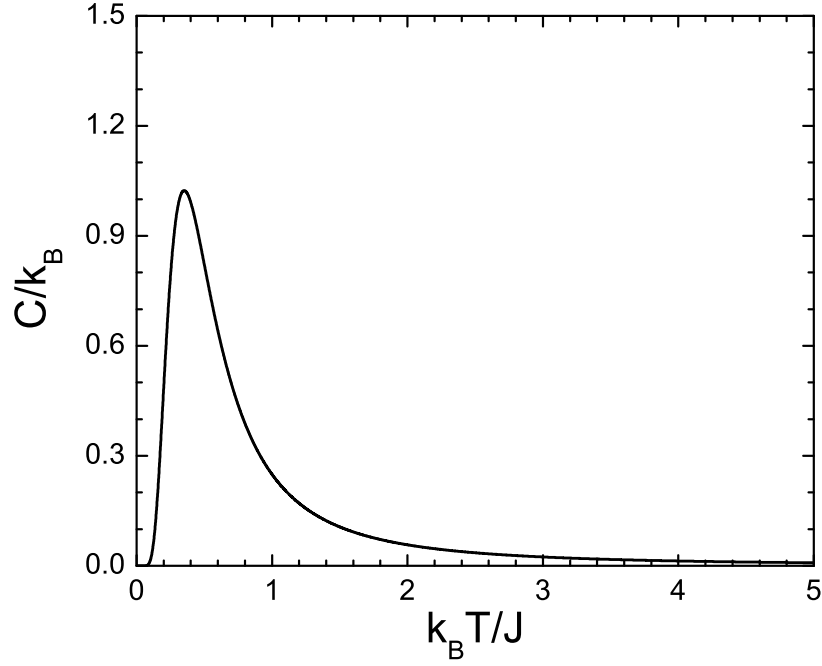


Figure 3.2: The magnetic contribution to the specific heat of a spin dimer, Eq.(3.12) (dimensionless units).

$$\frac{C}{k_B} = 3(\beta J)^2 \frac{e^{-\beta J}}{(1 + 3e^{-\beta J})^2} , \quad (3.12)$$

and

$$\frac{\chi}{(g\mu_B)^2/J} = 2\beta J \frac{e^{-\beta J}}{(1 + 3e^{-\beta J})} . \quad (3.13)$$

Plots of the dimensionless specific heat and susceptibility of the spin dimer are shown in Figures 3.2 and 3.3. These results are summarized in Tables 3.2 and 3.3, as are the corresponding results we find for the other spin 1/2 clusters systems.

One may confirm that this specific heat formula gives the correct entropy for a dimer of $S=1/2$ ions,

$$S = \int_0^\infty C \frac{d\beta}{\beta} = k_B 2 \ln(2) . \quad (3.14)$$

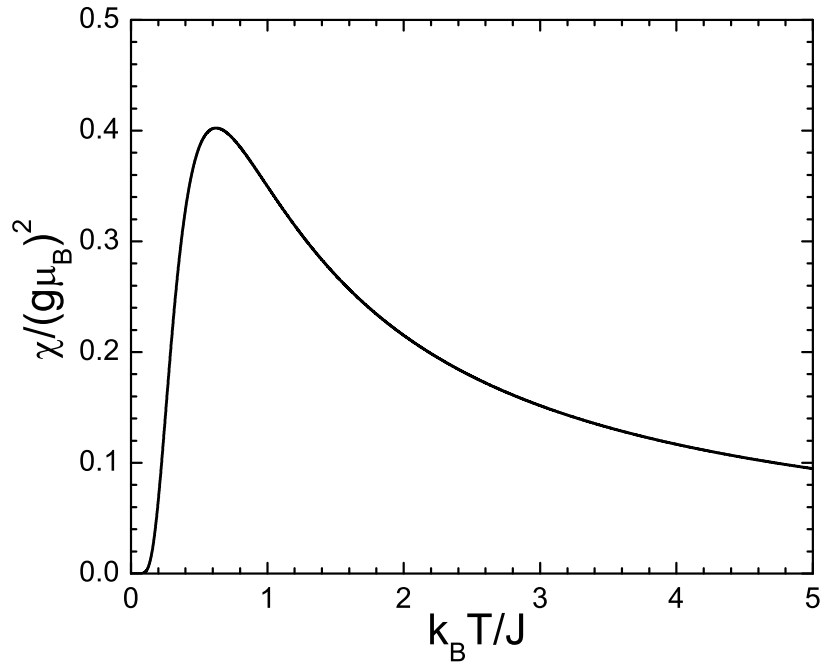


Figure 3.3: The magnetic susceptibility of a spin dimer, Eq.(3.13) (dimensionless units).

Table 3.2: Magnetic heat capacities¹ for $S = \frac{1}{2}$ dimers, trimers, and tetramers

Spin System	C/k_B
Dimer	$3(\beta J)^2 e^{\beta J} / (3 + e^{\beta J})^2$
Symmetric Trimer	$\frac{9}{4}(\beta J)^2 e^{\frac{3}{2}\beta J} / (1 + e^{\frac{3}{2}\beta J})^2$
Isosceles Trimer	$\frac{1}{2}(\beta J)^2 \left(2(1 - \alpha)^2 e^{(1+2\alpha)\beta J} + (2 + \alpha)^2 e^{(1+\frac{1}{2}\alpha)\beta J} + 9\alpha^2 e^{\frac{3}{2}\alpha\beta J} \right) / \left(2 + e^{\frac{3}{2}\alpha\beta J} + e^{(1+\frac{1}{2}\alpha)\beta J} \right)^2$
General Trimer	$\frac{1}{16}(\beta J)^2 e^{\frac{1}{2}(1+\alpha_s)\beta J} \left(f_0^2 e^{\frac{1}{2}(1+\alpha_s)\beta J} + (4(1 + \alpha_s)^2 + f_0^2) \cosh(f_0\beta J/4) + 4f_0(1 + \alpha_s) \sinh(f_0\beta J/4) \right) / \left(1 + e^{\frac{1}{2}(1+\alpha_s)\beta J} \cosh(f_0\beta J/4) \right)^2$
Tetrahedron	$18(\beta J)^2 \left(10e^{2\beta J} + 5e^{3\beta J} + e^{5\beta J} \right) / \left(5 + 9e^{2\beta J} + 2e^{3\beta J} \right)^2$

¹This table uses the abbreviation $f_0 = \sqrt{(2 - \alpha_s)^2 + 3\alpha_d^2}$.

Table 3.3: Magnetic susceptibilities¹ for $S = \frac{1}{2}$ dimers, trimers, and tetramers

Spin System	$\chi/(g\mu_B)^2$
Dimer	$2\beta/(3 + e^{\beta J})$
Symmetric Trimer	$\frac{1}{4}\beta(5 + e^{\frac{3}{2}\beta J})/(1 + e^{\frac{3}{2}\beta J})$
Isosceles Trimer	$\frac{1}{4}\beta(10 + e^{\frac{3}{2}\alpha\beta J} + e^{(1+\frac{1}{2}\alpha)\beta J})/(2 + e^{\frac{3}{2}\alpha\beta J} + e^{(1+\frac{1}{2}\alpha)\beta J})$
General Trimer	$\frac{1}{4}\beta(5 + e^{\frac{1}{2}(1+\alpha_s)\beta J} \cosh(f_0\beta J/4))/(1 + e^{\frac{1}{2}(1+\alpha_s)\beta J} \cosh(f_0\beta J/4))$
Tetrahedron	$2\beta(5 + 3e^{2\beta J})/(5 + 9e^{2\beta J} + 2e^{3\beta J})$
Rectangular Tetramer	$2\beta(5 + e^{\beta J} + e^{\alpha\beta J} + e^{(1+\alpha)\beta J})/$ $(5 + 3e^{\beta J} + 3e^{\alpha\beta J} + 3e^{(1+\alpha)\beta J} + 2e^{(1+\alpha)\beta J} \cosh(f_1\beta J/2))$
Linear Tetramer	$2\beta(5 + e^{\beta J} + 2e^{\frac{1}{2}(1+\alpha)\beta J} \cosh(f_3\beta J/2))/$ $(5 + 3e^{\beta J} + 2e^{(1+\frac{1}{2}\alpha)\beta J} \cosh(f_2\beta J) + 6e^{\frac{1}{2}(1+\alpha)\beta J} \cosh(f_3\beta J/2))$

¹ This table uses the abbreviations $f_0 = \sqrt{(2 - \alpha_s)^2 + 3\alpha_d^2}$, $f_1 = \sqrt{1 - \alpha + \alpha^2}$, $f_2 = \sqrt{1 - \alpha/2 + \alpha^2/4}$, $f_3 = \sqrt{1 + \alpha^2}$.

The corresponding result for a general spin system is

$$S = k_B \ln(\mathcal{N}/\mathcal{N}_0) , \quad (3.15)$$

where $\mathcal{N}$ is the dimensionality of the full Hilbert space and $\mathcal{N}_0$ is the degeneracy of the ground state; for the S=1/2 dimer, $\mathcal{N} = 2^2$ and $\mathcal{N}_0 = 1$.

3.1.3 Application to VO(HPO₄)·0.5H₂O

As an example of the application of the dimer susceptibility of Eq.(3.13) (known as the Bleaney-Bowers formula [55]), in Fig.3.4 we show a fit to the susceptibility of the spin dimer VO(HPO₄)·0.5H₂O [56]. (The molar susceptibility shown is related to the single dimer susceptibility of Eq.(3.13) by $\chi_{molar} = N_A/2 \cdot \chi$.) The parameters of the fit are $g = 2.05$ and $J = 7.76$ meV (consistent with the results of inelastic neutron scattering [40]). A $1/T$ defect contribution was also included in the fit.

Finally we evaluate the inelastic neutron scattering intensities, which are given by the structure factors of Eqs.(2.15,2.16). (A complete set of inelastic neutron scattering transitions for all the spin systems we consider in this work is given in Table 3.4 and 3.5; typically we will only evaluate the structure factors for the ground state of the antiferromagnetic system.) We evaluate Eq.(2.15) for the dimer using the energy eigenvectors $|\Psi_1(m)\rangle$ and $|\Psi_0\rangle$ of Eqs.(3.9,3.10). This gives

$$S(\vec{q}) = \frac{1}{2}(1 - \cos(\vec{q} \cdot \vec{a})) \quad (3.16)$$

where $\vec{a} = \vec{x}_1 - \vec{x}_2 = \vec{x}_{12}$ is a spatial vector that coincides with the dimer. Evidently there should be no excitation of the dimer spin-triplet state when the neutron momentum transfer $\vec{q}$ is perpendicular to the dimer axis $\hat{a}$.

In scattering from powder samples one measures the powder average $\bar{S}(q)$ of the

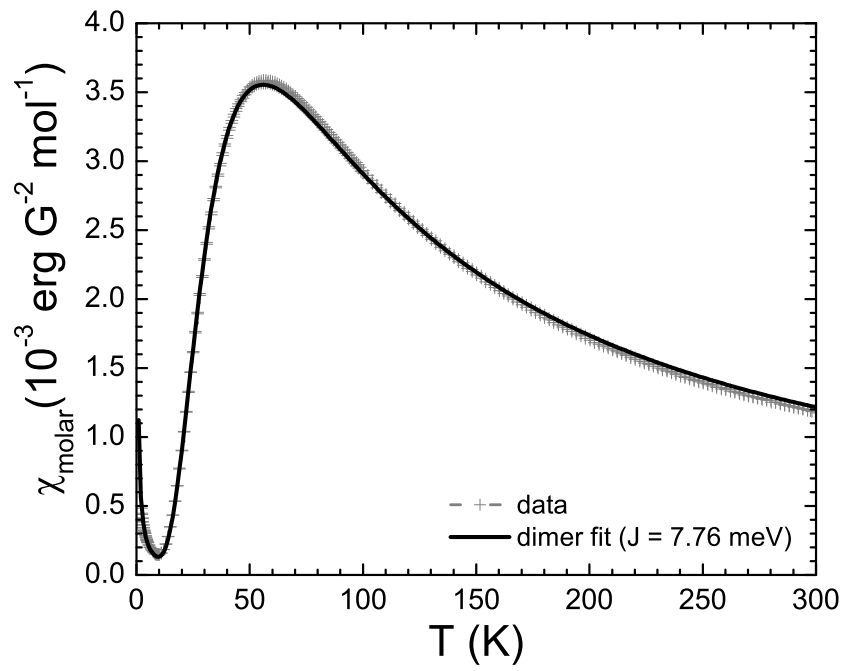


Figure 3.4: A fit of the dimer susceptibility formula of Eq.(3.13) to the measured susceptibility of VO(HPO₄)·0.5H₂O. A defect term was also included.

Table 3.4: Magnetic spin excitations for $S = \frac{1}{2}$ dimers and trimers¹

System	Transition	ΔE
Dimer	I. $ \Psi_0\rangle \rightarrow \Psi_1\rangle$	J
Symmetric Trimer	I. $ \Psi_{\frac{1}{2},1}\rangle \rightarrow \Psi_{\frac{3}{2}}\rangle$ II. $ \Psi_{\frac{1}{2},2}\rangle \rightarrow \Psi_{\frac{3}{2}}\rangle$	$\frac{3}{2} J$
Isosceles Trimer	I. $ \Psi_{\frac{1}{2},1}\rangle \rightarrow \Psi_{\frac{3}{2}}\rangle$ II. $ \Psi_{\frac{1}{2},2}\rangle \rightarrow \Psi_{\frac{3}{2}}\rangle$ III. $ \Psi_{\frac{1}{2},1}\rangle \rightarrow \Psi_{\frac{1}{2},2}\rangle$	$(1 + \frac{1}{2}\alpha) J$ $\frac{3}{2}\alpha J$ $(1 - \alpha) J$
General Trimer	I. $ \Psi_{\frac{1}{2},1}\rangle \rightarrow \Psi_{\frac{3}{2}}\rangle$ II. $ \Psi_{\frac{1}{2},2}\rangle \rightarrow \Psi_{\frac{3}{2}}\rangle$ III. $ \Psi_{\frac{1}{2},1}\rangle \rightarrow \Psi_{\frac{1}{2},2}\rangle$	$(\frac{1}{2}(1 + \alpha_s) + \frac{1}{4}f_0) J$ $(\frac{1}{2}(1 + \alpha_s) - \frac{1}{4}f_0) J$ $\frac{1}{2}f_0 J$

¹ This table uses the abbreviation $f_0 = \sqrt{(2 - \alpha_s)^2 + 3\alpha_d^2}$.

structure factor, defined by Eq.(2.16). For the dimer this is

$$\bar{S}(q) = \int \frac{d\Omega_{\hat{q}}}{4\pi} \frac{1}{2} (1 - \cos(\vec{q} \cdot \vec{a})) = \frac{1}{2} (1 - j_0(qa)) \quad (3.17)$$

where $j_0(x) = \sin(x)/x$ is a spherical Bessel function. This result is shown in Fig.3.5 for pointlike magnetic ions ($F(\vec{q}) = 1$). The location of the first maximum, at $q \approx 4.493 a^{-1}$, provides a convenient estimate of the separation between the interacting ions in the dimer. Of course in real materials the incorporation of ionic form factors will reduce the location of this maximum.

Experimental studies of real magnetic materials typically proceed by establishing the approximate magnetic parameters of a model Hamiltonian through a fit to the susceptibility. Given a model Hamiltonian, one can predict the inelastic neutron

Table 3.5: Magnetic spin excitations for $S = \frac{1}{2}$ tetramers¹

System	Transition	ΔE
Tetrahedron	I. $ \Psi_{0,1}\rangle \rightarrow \Psi_{1,1}\rangle$	J
	II. $ \Psi_{0,1}\rangle \rightarrow \Psi_{1,2}\rangle$	
	III. $ \Psi_{0,1}\rangle \rightarrow \Psi_{1,3}\rangle$	
	IV. $ \Psi_{0,2}\rangle \rightarrow \Psi_{1,1}\rangle$	
	V. $ \Psi_{0,2}\rangle \rightarrow \Psi_{1,2}\rangle$	
	VI. $ \Psi_{0,2}\rangle \rightarrow \Psi_{1,3}\rangle$	
	VII. $ \Psi_{1,1}\rangle \rightarrow \Psi_2\rangle$	$2J$
	VIII. $ \Psi_{1,2}\rangle \rightarrow \Psi_2\rangle$	
	IX. $ \Psi_{1,3}\rangle \rightarrow \Psi_2\rangle$	
Rectangular Tetramer	I. $ \Psi_{0,1}\rangle \rightarrow \Psi_{1,1}\rangle$	$f_1 J$
	II. $ \Psi_{0,1}\rangle \rightarrow \Psi_{1,2}\rangle$	$(f_1 + \alpha) J$
	III. $ \Psi_{0,1}\rangle \rightarrow \Psi_{1,3}\rangle$	$(f_1 + 1) J$
	IV. $ \Psi_{1,1}\rangle \rightarrow \Psi_{0,2}\rangle$	$f_1 J$
	V. $ \Psi_{1,1}\rangle \rightarrow \Psi_{1,2}\rangle$	αJ
	VI. $ \Psi_{1,1}\rangle \rightarrow \Psi_{1,3}\rangle$	J
	VII. $ \Psi_{1,1}\rangle \rightarrow \Psi_2\rangle$	$(1 + \alpha) J$
	VIII. $ \Psi_{1,2}\rangle \rightarrow \Psi_{0,2}\rangle$	$(f_1 - \alpha) J$
	IX. $ \Psi_{1,2}\rangle \rightarrow \Psi_{1,3}\rangle$	$(1 - \alpha) J$
	X. $ \Psi_{1,2}\rangle \rightarrow \Psi_2\rangle$	J
	XI. $ \Psi_{0,2}\rangle \rightarrow \Psi_{1,3}\rangle$	$(1 - f_1) J$
	XII. $ \Psi_{1,3}\rangle \rightarrow \Psi_2\rangle$	αJ
Linear Tetramer	I. $ \Psi_{0,1}\rangle \rightarrow \Psi_{1,1}\rangle$	$(f_2 - \frac{1}{2}(f_3 - 1)) J$
	II. $ \Psi_{0,1}\rangle \rightarrow \Psi_{1,2}\rangle$	$(f_2 + \frac{1}{2}\alpha) J$
	III. $ \Psi_{0,1}\rangle \rightarrow \Psi_{1,3}\rangle$	$(f_2 + \frac{1}{2}(f_3 + 1)) J$
	IV. $ \Psi_{1,1}\rangle \rightarrow \Psi_{0,2}\rangle$	$(f_2 + \frac{1}{2}(f_3 - 1)) J$
	V. $ \Psi_{1,1}\rangle \rightarrow \Psi_{1,2}\rangle$	$\frac{1}{2}(f_3 - 1 + \alpha) J$
	VI. $ \Psi_{1,1}\rangle \rightarrow \Psi_{1,3}\rangle$	$f_3 J$
	VII. $ \Psi_{1,1}\rangle \rightarrow \Psi_2\rangle$	$\frac{1}{2}(f_3 + 1 + \alpha) J$
	VIII. $ \Psi_{1,2}\rangle \rightarrow \Psi_{0,2}\rangle$	$(f_2 - \frac{1}{2}\alpha) J$
	IX. $ \Psi_{1,2}\rangle \rightarrow \Psi_{1,3}\rangle$	$\frac{1}{2}(f_3 + 1 - \alpha) J$
	X. $ \Psi_{1,2}\rangle \rightarrow \Psi_2\rangle$	J
	XI. $ \Psi_{0,2}\rangle \rightarrow \Psi_{1,3}\rangle$	$(-f_2 + \frac{1}{2}(f_3 + 1)) J$
	XII. $ \Psi_{1,3}\rangle \rightarrow \Psi_2\rangle$	$\frac{1}{2}(-f_3 + 1 + \alpha) J$

¹ This table uses the abbreviations $f_1 = \sqrt{1 - \alpha + \alpha^2}$, $f_2 = \sqrt{1 - \alpha/2 + \alpha^2/4}$, and $f_3 = \sqrt{1 + \alpha^2}$.

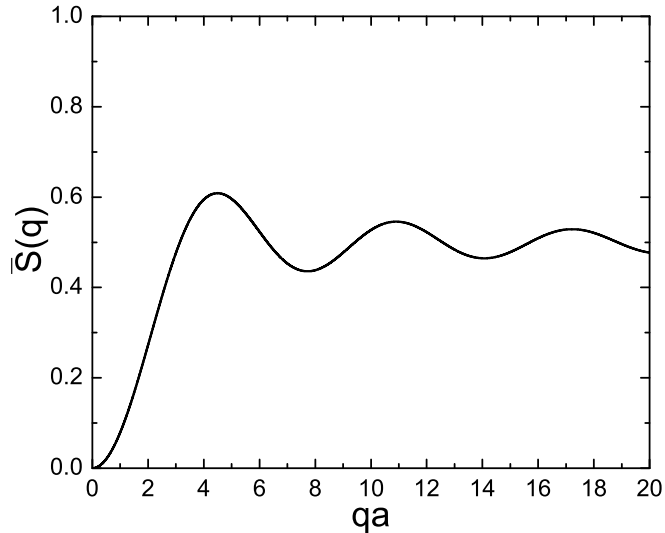


Figure 3.5: The powder average, unpolarized neutron structure factor $\bar{S}(q)$ for a spin dimer with pointlike magnetic ions.

scattering structure factor, which is then compared to experiment. (Ideally this is done on single crystal samples, but more frequently only powder samples are available.) Unlike the bulk susceptibility, the inelastic neutron scattering structure factor allows a sensitive and microscopic test of the assumed magnetic Hamiltonian, since it is determined by the relative positions of the interacting magnetic ions. The spin-dimer material $\text{VO}(\text{DPO}_4) \cdot 0.5\text{D}_2\text{O}$ provides a recent illustration of the use of inelastic neutron scattering in identifying magnetic interaction pathways; the susceptibility data of Johnson *et al.* [39] was well known to give an excellent fit to the dimer formula Eq.(3.13), however the separation of the interacting V-V pair inferred from inelastic neutron scattering data [40] using Eq.(3.17) showed that the interacting V-V pair had been misidentified in the literature.

3.1.4 Spin 1 and $\frac{3}{2}$ Dimers

The spin decomposition for the spin 1 and spin 3/2 dimers is given as

$$1 \otimes 1 = 2 \oplus 1 \oplus 0$$

$$\frac{3}{2} \otimes \frac{3}{2} = 3 \oplus 2 \oplus 1 \oplus 0. \quad (3.18)$$

When compared to the spin 1/2 dimer, it is clear that as spin increases in the dimer system the number of energy level increases linearly. The diagonalization of the spin 1 dimer Hamiltonian gives the following energy eigenvalues. The energy levels are

$$E_2 = J$$

$$E_1 = -J \quad (3.19)$$

$$E_0 = -2J .$$

Magnetic susceptibility can be simply calculated from the eigenvalues of each spin state. For the spin 1 dimer, the magnetic susceptibility (in dimension form) is given by

$$\frac{\chi}{(g\mu_B)^2/J} = 2\beta J \frac{5 + e^{2\beta J}}{(5 + 3e^{2\beta J} + e^{3\beta J})} . \quad (3.20)$$

We evaluate the INS structure factors and intensities for the spin transition from $|\Psi_0\rangle$ and $|\Psi_1(m)\rangle$. Without the introduction of a magnetic form factor, the structure factor and powder average intensity

$$S(\vec{q}) = \frac{4}{3}(1 - \cos(\vec{q} \cdot \vec{r}_{12})) \quad (3.21)$$

and

$$\bar{S}(q) = \int \frac{d\Omega_{\hat{q}}}{4\pi} \frac{4}{3} (1 - \cos(\vec{q} \cdot \vec{r}_{12})) = \frac{4}{3} (1 - j_0(qr_{12})), \quad (3.22)$$

respectively. Here, $j_0(x) = \frac{\sin(x)}{x}$.

Diagonalization of the spin 3/2 dimer Hamiltonian produces four energy eigenvalues, consistent with the decomposition shown in eq. 3.18. the energy levels are given by

$$\begin{aligned} E_3 &= \frac{9}{4}J \\ E_2 &= -\frac{3}{4}J \\ E_1 &= -\frac{11}{4}J \\ E_0 &= -\frac{15}{4}J . \end{aligned} \quad (3.23)$$

The magnetic susceptibility for the spin 3/2 dimer, although more complex than the spin 1 dimer, is considerably trivial to determine, and is given by

$$\frac{\chi}{(g\mu_B)^2/J} = 2\beta J \frac{14 + 5e^{3\beta J} + e^{5\beta J}}{(7 + 5e^{3\beta J} + 3e^{5\beta J} + e^{6\beta J})} . \quad (3.24)$$

The INS structure factor and intensity for the first transition of the spin 3/2 dimer system is determined to be

$$S(\vec{q}) = \frac{5}{2} (1 - \cos(\vec{q} \cdot \vec{r}_{12})) \quad (3.25)$$

and

$$\bar{S}(q) = \frac{5}{2} (1 - j_0(qr_{12})), \quad (3.26)$$

respectively. It should be noted that the structure factors for the spin 1 and spin 3/2 system are similar in every aspect except of the scaling coefficient in front. This is true of the structure of the spin 1/2 dimer system, shown in ref. [11]. It should also be noted that the excitation energy for the first transition for the spin 1/2, 1, and 3/2 dimers are all J . This is particularly interesting, because it shows that even with increasing complexity of increased spin, the transition from the $S=0$ ground state and the $S=1$ first excited state is the same in energy and overall phase of the structure factor. The excitation energies for the inelastic neutron scattering transitions, as well as, the inelastic structure factors for the excitations from the ground state for both the spin 1 and 3/2 dimers and trimers have been tabulated in Tables 3.6 and 3.7 along with the trimer systems discussed below.

Since the spin dimer systems are fairly trivial to solve, it becomes clear that the dimer systems can be used as basis for expanding the simple two spin model. The expansion of the dimer to that of an increased finite cluster model is a simple addition of Clebsch-Gordon coefficients. This is useful because as the size of the model increased, complexity of the calculations are held to a minimum.

3.2 Spin Trimers

We will consider the most general case of a spin trimer with Heisenberg magnetic interactions. It is useful to present the results as special cases with decreasing symmetry, since the formulas are simpler in the more symmetric cases, and examples of both symmetric and isosceles trimers are known in the literature.

3.2.1 Trimers of General Spin S

The spin trimer consists to three spins interacting in various ways. The introduction of a third spin increases not only the number of overall spins, but it presents a

Table 3.6: Inelastic neutron scattering excitations and structure factors for $S = 1$ and $S = \frac{1}{2}$ dimers and trimers

System	Transition	ΔE^a	Structure Factors ^{b,c}
Spin 1 Dimer	$ \Psi_0\rangle \rightarrow \Psi_1\rangle$	J	$\frac{3}{4}(1-\cos(\vec{q} \cdot \vec{r}_{12}))$
	$ \Psi_1\rangle \rightarrow \Psi_2\rangle$	$2J$	
Spin 3/2 Dimer	$ \Psi_0\rangle \rightarrow \Psi_1\rangle$	J	$\frac{5}{2}(1-\cos(\vec{q} \cdot \vec{r}_{12}))$
	$ \Psi_1\rangle \rightarrow \Psi_2\rangle$	$2J$	
	$ \Psi_2\rangle \rightarrow \Psi_3\rangle$	$3J$	
Spin 1 Isosceles Trimer	$ \Psi_{0,1}\rangle \rightarrow \Psi_{1,2}\rangle$	$(2\alpha - 1)J$	$\frac{5}{9}(1-\cos(\vec{q} \cdot \vec{r}_{12}))$
	$ \Psi_{0,1}\rangle \rightarrow \Psi_{1,1}\rangle$	J	$\frac{1}{3}(3+\cos(\vec{q} \cdot \vec{r}_{12})-2\cos(\vec{q} \cdot \vec{r}_{23})-2\cos(\vec{q} \cdot \vec{r}_{31}))$
	$ \Psi_{0,1}\rangle \rightarrow \Psi_{1,0}\rangle$	$(2 - \alpha)J$	$\frac{4}{9}(1-\cos(\vec{q} \cdot \vec{r}_{12}))$
	$ \Psi_{1,2}\rangle \rightarrow \Psi_{1,1}\rangle$	$(2 - 2\alpha)J$	$\frac{5}{36}(1-\cos(\vec{q} \cdot \vec{r}_{12}))$
	$ \Psi_{1,2}\rangle \rightarrow \Psi_{1,0}\rangle$	$(3 - 3\alpha)J$	0
	$ \Psi_{1,2}\rangle \rightarrow \Psi_{2,2}\rangle$	$2J$	$\frac{3}{40}(3+\cos(\vec{q} \cdot \vec{r}_{12})-2\cos(\vec{q} \cdot \vec{r}_{23})-2\cos(\vec{q} \cdot \vec{r}_{31}))$
	$ \Psi_{1,2}\rangle \rightarrow \Psi_{2,1}\rangle$	$(4 - 2\alpha)J$	$\frac{1}{180}(1-\cos(\vec{q} \cdot \vec{r}_{12}))$
	$ \Psi_{1,1}\rangle \rightarrow \Psi_{1,0}\rangle$	$(1 - \alpha)J$	
	$ \Psi_{1,1}\rangle \rightarrow \Psi_{2,2}\rangle$	$2\alpha J$	
	$ \Psi_{1,1}\rangle \rightarrow \Psi_{2,1}\rangle$	$2J$	
	$ \Psi_{1,0}\rangle \rightarrow \Psi_{2,2}\rangle$	$(3\alpha - 1)J$	
	$ \Psi_{1,0}\rangle \rightarrow \Psi_{2,1}\rangle$	$(1 - 3\alpha)J$	
	$ \Psi_{2,2}\rangle \rightarrow \Psi_{2,1}\rangle$	$(2 - 2\alpha)J$	
	$ \Psi_{2,2}\rangle \rightarrow \Psi_{3,2}\rangle$	$3J$	
	$ \Psi_{2,1}\rangle \rightarrow \Psi_{3,2}\rangle$	$(1 + 2\alpha)J$	

Due to the INS structure factor being zero, some transitions cannot be seen in INS.

² Structure factors have been calculated for the excitations from the ground state.

³ The calculation of the powder intensity replaces cosine with a zeroth order bessel function.

Table 3.7: Inelastic neutron scattering excitations and structure factors for $S = 1$ and $S = \frac{1}{2}$ dimers and trimers (cont.)

System	Transition	ΔE^a	Structure Factors ^{b,c}
Spin 3/2	$ \Psi_{1/2,2}\rangle \rightarrow \Psi_{1/2,1}\rangle$	$(2 - 2\alpha)J$	$(1 - \cos(\vec{q} \cdot \vec{r}_{12}))$
Isosceles Trimer	$ \Psi_{1/2,2}\rangle \rightarrow \Psi_{3/2,3}\rangle$	$(3\alpha - \frac{3}{2})J$	$\frac{21}{40}(1 - \cos(\vec{q} \cdot \vec{r}_{12}))$
	$ \Psi_{1/2,2}\rangle \rightarrow \Psi_{3/2,2}\rangle$	$\frac{3}{2}J$	$\frac{3}{8}(3 + \cos(\vec{q} \cdot \vec{r}_{12}) - 2\cos(\vec{q} \cdot \vec{r}_{23}) - 2\cos(\vec{q} \cdot \vec{r}_{31}))$
	$ \Psi_{1/2,2}\rangle \rightarrow \Psi_{3/2,1}\rangle$	$(\frac{7}{2} - 2\alpha)J$	$\frac{3}{40}(1 - \cos(\vec{q} \cdot \vec{r}_{12}))$
	$ \Psi_{1/2,2}\rangle \rightarrow \Psi_{3/2,0}\rangle$	$(\frac{9}{2} - 3\alpha)J$	0
	$ \Psi_{1/2,1}\rangle \rightarrow \Psi_{3/2,3}\rangle$	$(5\alpha - \frac{7}{2})J$	0
	$ \Psi_{1/2,1}\rangle \rightarrow \Psi_{3/2,2}\rangle$	$(2\alpha - \frac{1}{2})J$	
	$ \Psi_{1/2,1}\rangle \rightarrow \Psi_{3/2,1}\rangle$	$\frac{3}{2}J$	
	$ \Psi_{1/2,1}\rangle \rightarrow \Psi_{3/2,0}\rangle$	$(\frac{5}{2} - \alpha)J$	
	$ \Psi_{3/2,3}\rangle \rightarrow \Psi_{3/2,2}\rangle$	$(3 - 3\alpha)J$	$\frac{21}{100}(1 - \cos(\vec{q} \cdot \vec{r}_{12}))$
	$ \Psi_{3/2,3}\rangle \rightarrow \Psi_{3/2,1}\rangle$	$5 - 5\alpha)J$	0
	$ \Psi_{3/2,3}\rangle \rightarrow \Psi_{3/2,0}\rangle$	$(6 - 6\alpha)J$	0
	$ \Psi_{3/2,3}\rangle \rightarrow \Psi_{5/2,3}\rangle$	$\frac{5}{2}J$	$\frac{1}{5}(3 + \cos(\vec{q} \cdot \vec{r}_{12}) - 2\cos(\vec{q} \cdot \vec{r}_{23}) - 2\cos(\vec{q} \cdot \vec{r}_{31}))$
	$ \Psi_{3/2,3}\rangle \rightarrow \Psi_{5/2,2}\rangle$	$(\frac{11}{4} - 3\alpha)\alpha J$	$\frac{1}{200}(1 - \cos(\vec{q} \cdot \vec{r}_{12}))$
	$ \Psi_{3/2,3}\rangle \rightarrow \Psi_{5/2,1}\rangle$	$(\frac{15}{2} - 5\alpha)J$	0
	$ \Psi_{3/2,2}\rangle \rightarrow \Psi_{3/2,1}\rangle$	$(2 - 2\alpha)J$	
	$ \Psi_{3/2,2}\rangle \rightarrow \Psi_{3/2,0}\rangle$	$(3 - 3\alpha)J$	
	$ \Psi_{3/2,2}\rangle \rightarrow \Psi_{5/2,3}\rangle$	$(3\alpha - \frac{1}{2})J$	
	$ \Psi_{3/2,2}\rangle \rightarrow \Psi_{5/2,2}\rangle$	$\frac{5}{2}J$	
	$ \Psi_{3/2,2}\rangle \rightarrow \Psi_{5/2,1}\rangle$	$(\frac{9}{2} - 2\alpha)J$	
	$ \Psi_{3/2,1}\rangle \rightarrow \Psi_{3/2,0}\rangle$	$(1 - \alpha)J$	
	$ \Psi_{3/2,1}\rangle \rightarrow \Psi_{5/2,3}\rangle$	$(5\alpha - \frac{5}{2})J$	
	$ \Psi_{3/2,1}\rangle \rightarrow \Psi_{5/2,2}\rangle$	$(\frac{1}{2} + 2\alpha)J$	
	$ \Psi_{3/2,1}\rangle \rightarrow \Psi_{5/2,1}\rangle$	$\frac{5}{2}J$	
	$ \Psi_{3/2,0}\rangle \rightarrow \Psi_{5/2,3}\rangle$	$(6\alpha - \frac{7}{2})J$	
	$ \Psi_{3/2,0}\rangle \rightarrow \Psi_{5/2,2}\rangle$	$(3\alpha - \frac{1}{2})J$	
	$ \Psi_{3/2,0}\rangle \rightarrow \Psi_{5/2,1}\rangle$	$(\alpha + \frac{3}{2})J$	
	$ \Psi_{5/2,3}\rangle \rightarrow \Psi_{5/2,2}\rangle$	$(3 - 3\alpha)J$	
	$ \Psi_{5/2,3}\rangle \rightarrow \Psi_{5/2,1}\rangle$	$(5 - 5\alpha)J$	
	$ \Psi_{5/2,3}\rangle \rightarrow \Psi_{7/2,3}\rangle$	$\frac{7}{2}J$	
	$ \Psi_{5/2,3}\rangle \rightarrow \Psi_{7/2,2}\rangle$	$(\frac{13}{2} - 3\alpha)J$	
	$ \Psi_{5/2,3}\rangle \rightarrow \Psi_{5/2,2}\rangle$	$(2 - 2\alpha)J$	
	$ \Psi_{5/2,3}\rangle \rightarrow \Psi_{5/2,1}\rangle$	$(\frac{1}{2} + 3\alpha)J$	
	$ \Psi_{5/2,3}\rangle \rightarrow \Psi_{7/2,3}\rangle$	$\frac{7}{2}J$	
	$ \Psi_{5/2,1}\rangle \rightarrow \Psi_{7/2,3}\rangle$	$(5\alpha - \frac{3}{2})J$	
	$ \Psi_{5/2,1}\rangle \rightarrow \Psi_{7/2,2}\rangle$	$(\frac{3}{2} + 2\alpha)J$	
	$ \Psi_{7/2,3}\rangle \rightarrow \Psi_{7/2,2}\rangle$	$(3 - 3\alpha)J$	
	$ \Psi_{7/2,3}\rangle \rightarrow \Psi_{9/2,3}\rangle$	$\frac{9}{2}J$	
	$ \Psi_{7/2,2}\rangle \rightarrow \Psi_{9/2,3}\rangle$	$(\frac{3}{2} + 3\alpha)J$	

¹ Due to the INS structure factor being zero, some transitions cannot be seen in INS.

² Structure factors have been calculated for the excitations from the ground state.

³ The calculation of the powder intensity replaces cosine with a zeroth order bessel function.

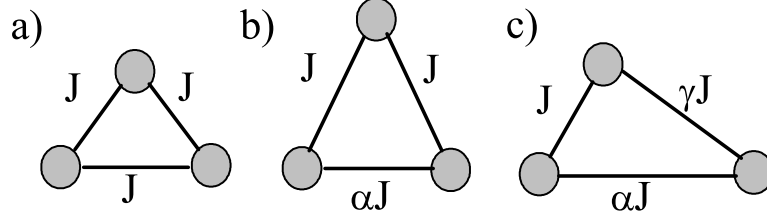


Figure 3.6: Three basic trimers. a) Symmetric, b) Isosceles, and c) Scalene.

geometry aspect as well. Figure 3.6 shows that there are three main geometries for the spin trimer (Symmetric(a), Isosceles(b), Scalene(c)). The equilateral is given by equal interactions on all sides, while the isosceles and scalene have two or no sides equal, respectively. The trimer can be described as a three spins with only two interactions (linear trimer), but this is just a limiting case of the isosceles or scalene trimer. The general spin trimer with isotropic interactions is given by the Hamiltonian shown as

$$\mathcal{H} = J \left(\vec{S}_1 \cdot \vec{S}_2 + \alpha \vec{S}_2 \cdot \vec{S}_3 + \gamma \vec{S}_3 \cdot \vec{S}_1 \right), \quad (3.27)$$

where $\alpha = J'/J$, $\gamma = J''/J$, and J , J' , and J'' are the interactions between spins.

The eigenfunctions for the trimer system can be determined using the dimers as a basis. This is done by allowing an extra spin to interact with another spins of the dimer. Using Clebsch-Gordon coefficients, the eigenfunctions for the spin 1 and $\frac{3}{2}$ trimers can be determined. By using a dimer basis, it becomes clear that there is no mixing of spin states for all but the scalene trimer. Therefore, simple calculation of the energy states for any isosceles trimer, symmetric, and linear of any spin can be given by

$$E = \frac{J}{2} \left[\mathcal{S}_{tot} - \mathcal{S}_d - \mathcal{S}_1 + \alpha (\mathcal{S}_d - \mathcal{S}_2 - \mathcal{S}_3) \right], \quad (3.28)$$

where $\mathcal{J}_{tot} = S_{tot}(S_{tot} + 1)$ and S_{tot} is the total spin state of the trimer, $\mathcal{J}_d = S_d(S_d + 1)$ and S_d is the total spin state of the dimer, and $\mathcal{J}_i = S_i(S_i + 1)$ ($i=1,2,3$) and S_i are the individual spins of the ions. By having the spin general energy level, one can examine mixed valence systems. However, due to the complexity of scalene trimer, the general form will not be determined in closed form. This is due to mixing of states when the system deviates from the symmetrical Hamiltonians. However, the spin- $\frac{1}{2}$ case for the scalene trimer will be examined. Overall, the isosceles trimer will be examined in closed form. This is due to the fact that the equilateral and linear trimers can be found as limits of the isosceles trimers.

3.2.2 Spin $\frac{1}{2}$ Trimers

Symmetric Spin $\frac{1}{2}$ Trimer

The completely symmetric, equilateral trimer has equal magnetic couplings and bond lengths between all three pairs of spins. The Hamiltonian for this model is

$$\mathcal{H} = J \left(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_2 \cdot \vec{S}_3 + \vec{S}_3 \cdot \vec{S}_1 \right). \quad (3.29)$$

Since this Hamiltonian is invariant under any permutation of the three spin labels, it has a discrete S_3 symmetry in addition to the magnetic rotational symmetry. In the S_z -diagonal basis

$$\begin{bmatrix} |\uparrow\uparrow\uparrow\rangle \\ |\uparrow\uparrow\downarrow\rangle \\ |\uparrow\downarrow\uparrow\rangle \\ |\downarrow\uparrow\uparrow\rangle \\ |\uparrow\downarrow\downarrow\rangle \\ |\downarrow\uparrow\downarrow\rangle \\ |\downarrow\downarrow\uparrow\rangle \\ |\downarrow\downarrow\downarrow\rangle \end{bmatrix} \quad (3.30)$$

the full Hamiltonian matrix is

$$J \begin{bmatrix} 3/4 & & & & & & & \\ & -1/4 & 1/2 & 1/2 & & & & \\ & 1/2 & -1/4 & 1/2 & & & & \\ & 1/2 & 1/2 & -1/4 & & & & \\ & & & & -1/4 & 1/2 & 1/2 & \\ & & & & 1/2 & -1/4 & 1/2 & \\ & & & & 1/2 & 1/2 & -1/4 & \\ & & & & & & & 3/4 \end{bmatrix} \quad (3.31)$$

This matrix is block diagonal within subspaces of definite $S_{z\,tot}$, as expected for a rotationally invariant Hamiltonian. The energy levels of the symmetric trimer are shown in Figure 3.7a. For the $J > 0$ (antiferromagnetic) case the ground state is a quadruplet (the two $S_{tot} = 1/2$ multiplets are degenerate), and there is an energy gap of $\frac{3}{2}J$ to the $S_{tot} = 3/2$ excited state. Representative symmetric trimer energy

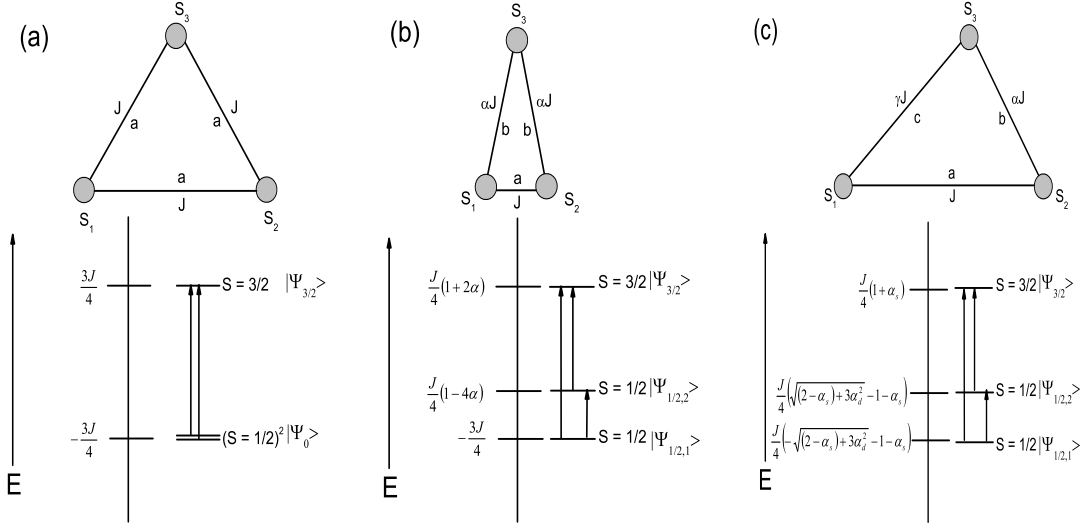


Figure 3.7: Geometries and energy levels of (a) symmetric, (b) isosceles and (c) general trimer systems. These systems have one $S_{tot} = \frac{3}{2}$ multiplet and two $S_{tot} = \frac{1}{2}$ multiplets.

eigenstates (those with maximum $S_{z\,tot}$) are given in Table 3.8 and 3.9. Since the two $S_{tot} = 1/2$ levels are degenerate, there is no unique ground state for this system; we use the Jacobi $|\rho\rangle = |(12)_A\rangle$ and $|\lambda\rangle = |(12)_S\rangle$ three-body basis states of definite (12)-exchange symmetry as our two independent basis vectors.

We may determine the specific heat and magnetic susceptibility of the symmetric trimer from these energy levels, using Eqs.(3.145,2.6). The results are

$$\frac{C}{k_B} = \frac{9}{4}(\beta J)^2 \frac{e^{-\frac{3}{2}\beta J}}{(1 + e^{-\frac{3}{2}\beta J})^2} \quad (3.32)$$

and

$$\frac{\chi}{(g\mu_B)^2/J} = \frac{1}{4}\beta J \frac{(1 + 5e^{-\frac{3}{2}\beta J})}{(1 + e^{-\frac{3}{2}\beta J})} . \quad (3.33)$$

It is notable that the integral of this specific heat gives an entropy of

$$S = \int_0^\infty C \frac{d\beta}{\beta} = k_B \ln(2) \quad (3.34)$$

Table 3.8: Energy eigenvalues and eigenvectors of $S = \frac{1}{2}$ dimer and trimers.

Spin System	Eigenvector $ \Psi_{S_{tot}}\rangle$ ($S_{z\ tot} = S_{tot}$)	Energy
Dimer	$ \Psi_1\rangle = \sigma(+1)\rangle = \uparrow\uparrow\rangle$	$E_1 = \frac{1}{4} J$
	$ \Psi_0\rangle = \rho\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow\rangle - \downarrow\uparrow\rangle)$	$E_0 = -\frac{3}{4} J$
Symmetric Trimer	$ \Psi_{\frac{3}{2}}\rangle = \sigma(+3/2)\rangle = \uparrow\uparrow\uparrow\rangle$	$E_{\frac{3}{2}} = \frac{3}{4} J$
	$ \Psi_{\frac{1}{2},2}\rangle = \lambda(+1/2)\rangle =$ $\frac{1}{\sqrt{6}}(\uparrow\downarrow\uparrow\rangle + \downarrow\uparrow\uparrow\rangle - 2 \uparrow\uparrow\downarrow\rangle)$	$E_{\frac{1}{2}} = -\frac{3}{4} J$
	$ \Psi_{\frac{1}{2},1}\rangle = \rho(+1/2)\rangle =$ $\frac{1}{\sqrt{2}}(\uparrow\downarrow\uparrow\rangle - \downarrow\uparrow\uparrow\rangle)$	
Isosceles Trimer	$ \Psi_{\frac{3}{2}}\rangle = \sigma(+3/2)\rangle$	$E_{\frac{3}{2}} = (\frac{1}{4} + \frac{1}{2}\alpha) J$
	$ \Psi_{\frac{1}{2},2}\rangle = \lambda(+1/2)\rangle$	$E_{\frac{1}{2},2} = (\frac{1}{4} - \alpha) J$
	$ \Psi_{\frac{1}{2},1}\rangle = \rho(+1/2)\rangle$	$E_{\frac{1}{2},1} = -\frac{3}{4} J$
General Trimer	$ \Psi_{\frac{3}{2}}\rangle = \sigma(+3/2)\rangle$	$E_{\frac{3}{2}} = \frac{1}{4}(1 + \alpha_s) J$
	$ \Psi_{\frac{1}{2},2}\rangle = +\cos(\theta) \lambda(+1/2)\rangle +$ $\sin(\theta) \rho(+1/2)\rangle$	$E_{\frac{1}{2},2} = \frac{1}{4}(+\sqrt{(2 - \alpha_s)^2 + 3\alpha_d^2} -$ $1 - \alpha_s) J$
	$ \Psi_{\frac{1}{2},1}\rangle = -\sin(\theta) \lambda(+1/2)\rangle +$ $\cos(\theta) \rho(+1/2)\rangle$	$E_{\frac{1}{2},1} = \frac{1}{4}(-\sqrt{(2 - \alpha_s)^2 + 3\alpha_d^2} -$ $1 - \alpha_s) J$

Table 3.9: Energy eigenvalues and eigenvectors of $S = \frac{1}{2}$ tetramers

Spin System	Eigenvector $ \Psi_{S_{tot}}\rangle$ ($S_{z\ tot} = S_{tot}$)	Energy
Tetrahedron	$ \Psi_2\rangle = \sigma\sigma\rangle_2 = \uparrow\uparrow\uparrow\uparrow\rangle$	$E_2 = \frac{3}{2} J$
	$ \Psi_{1,3}\rangle = \sigma\sigma\rangle_1$	$E_1 = -\frac{1}{2} J$
	$ \Psi_{1,2}\rangle = (\rho\sigma)_S\rangle$	
	$ \Psi_{1,1}\rangle = (\rho\sigma)_A\rangle$	
	$ \Psi_{0,2}\rangle = \sigma\sigma\rangle_0$	$E_0 = -\frac{3}{2} J$
	$ \Psi_{0,1}\rangle = \rho\rho\rangle$	
Rectangular tetramer	$ \Psi_2\rangle = \sigma\sigma\rangle_2$	$E_2 = (\frac{1}{2} + \frac{1}{2}\alpha) J$
	$ \Psi_{1,3}\rangle = \sigma\sigma\rangle_1$	$E_{1,3} = (\frac{1}{2} - \frac{1}{2}\alpha) J$
	$ \Psi_{1,2}\rangle = (\rho\sigma)_S\rangle$	$E_{1,2} = (-\frac{1}{2} + \frac{1}{2}\alpha) J$
	$ \Psi_{1,1}\rangle = (\rho\sigma)_A\rangle$	$E_{1,1} = (-\frac{1}{2} - \frac{1}{2}\alpha) J$
	$ \Psi_{0,2}\rangle = +\cos(\theta_0) \sigma\sigma\rangle_0 +$ $\sin(\theta_0) \rho\rho\rangle$	$E_{0,2} = (+\sqrt{1 - \alpha + \alpha^2}$ $-\frac{1}{2} - \frac{1}{2}\alpha) J$
	$ \Psi_{0,1}\rangle = -\sin(\theta_0) \sigma\sigma\rangle_0 +$ $\cos(\theta_0) \rho\rho\rangle$	$E_{0,1} = (-\sqrt{1 - \alpha + \alpha^2}$ $-\frac{1}{2} - \frac{1}{2}\alpha) J$
Linear Tetramer	$ \Psi_2\rangle = \sigma\sigma\rangle_2$	$E_2 = (\frac{1}{2} + \frac{1}{4}\alpha) J$
	$ \Psi_{1,3}\rangle = +\cos(\theta_1) \sigma\sigma\rangle_1 +$ $\sin(\theta_1) (\rho\sigma)_S\rangle$	$E_{1,3} = (+\frac{1}{2}\sqrt{1 + \alpha^2} - \frac{1}{4}\alpha) J$
	$ \Psi_{1,2}\rangle = (\rho\sigma)_A\rangle$	$E_{1,2} = (-\frac{1}{2} + \frac{1}{4}\alpha) J$
	$ \Psi_{1,1}\rangle = -\sin(\theta_1) \sigma\sigma\rangle_1 +$ $\cos(\theta_1) (\rho\sigma)_S\rangle$	$E_{1,1} = (-\frac{1}{2}\sqrt{1 + \alpha^2} - \frac{1}{4}\alpha) J$
	$ \Psi_{0,2}\rangle = +\cos(\theta_0) \sigma\sigma\rangle_0 +$ $\sin(\theta_0) \rho\rho\rangle$	$E_{0,2} = (+\sqrt{1 - \frac{1}{2}\alpha + \frac{1}{4}\alpha^2}$ $-\frac{1}{2} - \frac{1}{4}\alpha) J$
	$ \Psi_{0,1}\rangle = -\sin(\theta_0) \sigma\sigma\rangle_0 +$ $\cos(\theta_0) \rho\rho\rangle$	$E_{0,1} = (-\sqrt{1 - \frac{1}{2}\alpha + \frac{1}{4}\alpha^2}$ $-\frac{1}{2} - \frac{1}{4}\alpha) J$

which is only half as large as the entropy of the dimer, despite the larger trimer Hilbert space, $\mathcal{N} = 2^3 = 8$. The lower entropy is due to the fourfold degenerate ground state of this highly frustrated system;

$$S = k_B \ln(\mathcal{N}/\mathcal{N}_0) = k_B \ln(2^3/4) = k_B \ln(2) . \quad (3.35)$$

The susceptibility of the symmetric trimer, Eq.3.33, agrees with Eq.2 of Veit *et al.* [57] (after specializing to a single g -factor and a change of variables). This result is shown in Figure 3.8. Note that $\chi(T)$ diverges as we approach zero temperature, since the ground state has nonzero spin. This divergence is present independent of whether the intrinsic spin-spin coupling J is antiferromagnetic (as we normally assume) or ferromagnetic, since both cases have ground states of nonzero spin. A more detailed comparison of the susceptibility suffices to distinguish these; see the inset of Figure 3.8, which shows χT versus T for both cases. A recently reported $S=1/2$ V^{4+} vanadium trimer, $(\text{CN}_3\text{H}_6)_4\text{Na}_2[\text{H}_4\text{V}_6\text{O}_8(\text{PO}_4)_4((\text{OCH}_2)_3\text{CCH}_2\text{OH})_2] \cdot 14\text{H}_2\text{O}$ (material **1** of Luban *et al.* [45]) provides an illustration of this behavior; in Figure 3 of Ref. [45] one can see that χT for this material clearly follows the lower trimer curve, confirming that it is accurately described by the symmetric trimer model and has an $S_{tot} = 1/2$ ground state. At high temperatures the spin-spin coupling J is unimportant, and both results approach the same Curie's law limit.

Next we consider the neutron scattering structure factors for the symmetric trimer. Since this system has two degenerate $S_{tot} = 1/2$ ground states and a single $S_{tot} = 3/2$ excitation, there are two distinct exclusive inelastic neutron structure factors but only a single transition energy, $E_1 - E_0 = \frac{3}{2}J$. We have chosen $|\rho\rangle$ and $|\lambda\rangle$ basis states for our orthogonal $S_{tot} = 1/2$ eigenstates, and will give neutron structure factors for each of these. The same structure factors follow for the isosceles trimer, although in that case the two $S_{tot} = 1/2$ states are nondegenerate.

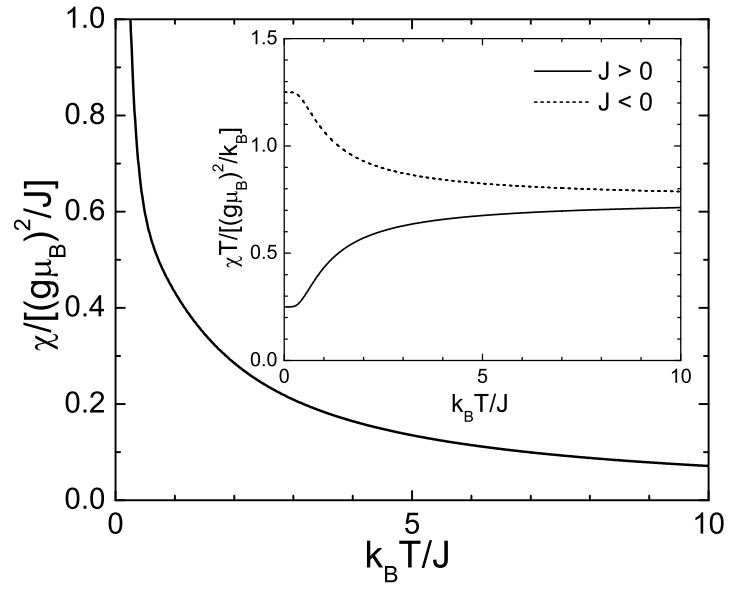


Figure 3.8: The magnetic susceptibility of a symmetric trimer. The inset shows χT versus T for ferromagnetic (dashed) and antiferromagnetic (solid) couplings.

The structure factors for excitation of the $S_{tot} = 3/2 \ |\sigma\rangle$ level (using Eq.(2.15)) are given by

$$S^{(\rho \rightarrow \sigma)}(\vec{q}) = \frac{1}{3}(1 - \cos(\vec{q} \cdot \vec{x}_{12})) , \quad (3.36)$$

$$S^{(\lambda \rightarrow \sigma)}(\vec{q}) = \frac{1}{3} \left(1 + \frac{1}{3} \cos(\vec{q} \cdot \vec{x}_{12}) - \frac{2}{3} \cos(\vec{q} \cdot \vec{x}_{13}) - \frac{2}{3} \cos(\vec{q} \cdot \vec{x}_{23}) \right) . \quad (3.37)$$

These results may be understood in terms of the different natures of the $|\rho\rangle$ and $|\lambda\rangle$ initial states. In the $|\rho\rangle$ ground state the (12)-dimer is in a pure $S_{(12)} = 0$ state, which must be excited to $S_{(12)} = 1$ to couple to the $|\sigma\rangle$ excited state. The $|\rho\rangle \rightarrow |\sigma\rangle$ excitation problem is thus identical to the dimer problem, to within an overall constant. It follows that $S^{(\rho \rightarrow \sigma)}(\vec{q})$ is proportional to the dimer structure factor of Eq.(3.16). In contrast, in the $|\lambda\rangle$ initial state the (12)-dimer is pure $S_{(12)} = 1$ and the (23)- and (31)-dimers have amplitudes to be in both spin 0 and 1, so there are contributions to $S^{(\lambda \rightarrow \sigma)}$ due to the excitation of each of the three dimer subsystems.

As $S^{(\rho \rightarrow \sigma)}$ and $S^{(\lambda \rightarrow \sigma)}$ differ considerably for moderate qa it will certainly be possible to distinguish between $|\rho\rangle$ and $|\lambda\rangle$ states from their single crystal structure factors. The powder averages however are identical, and cannot be distinguished experimentally;

$$\bar{S}^{(\rho \rightarrow \sigma)}(q) = \bar{S}^{(\lambda \rightarrow \sigma)}(q) = \frac{1}{3}(1 - j_0(qa)) . \quad (3.38)$$

These powder structure factors are identical because of the identical dimer lengths, $r_{12} = r_{23} = r_{31} = a$, so the powder average of each cosine in Eqs.(3.36,3.37) gives the same $j_0(qa)$ Bessel function. The dependence $(1 - j_0(qa))$ follows from the requirement that $\bar{S}(0) = 0$.

As we shall discuss in the next section, an isosceles trimer would be a more favorable system for the identification of $|\rho\rangle$ and $|\lambda\rangle$ initial states in inelastic neutron

scattering; these levels are nondegenerate in the isosceles system, and the $|\rho\rangle \rightarrow |\sigma\rangle$ and $|\lambda\rangle \rightarrow |\sigma\rangle$ powder average structure factors are no longer equal, due to the different leg lengths.

Isosceles Spin $\frac{1}{2}$ Trimer

The isosceles spin trimer, Figure 3.7b, has two equal magnetic interactions and bond lengths. The Hamiltonian is given by

$$\mathcal{H} = J(\vec{S}_1 \cdot \vec{S}_2 + \alpha(\vec{S}_2 \cdot \vec{S}_3 + \vec{S}_3 \cdot \vec{S}_1)). \quad (3.39)$$

To find the energy eigenvalues of this Hamiltonian it suffices to consider the $S_{z\text{tot}} = +1/2$ sector, since the $S_{\text{tot}} = 1/2$ and $3/2$ multiplets both have $S_{z\text{tot}} = +1/2$ members. The remaining symmetry of this problem suggests that we use the three $\{|S_{\text{tot}}, +1/2\rangle\}$ energy eigenstates of the symmetric trimer as our basis,

$$\begin{bmatrix} |\sigma(3/2, +1/2)\rangle = \sqrt{\frac{1}{3}}(|\uparrow\uparrow\downarrow\rangle + |\uparrow\downarrow\uparrow\rangle + |\downarrow\uparrow\uparrow\rangle) \\ |\lambda(1/2, +1/2)\rangle = \sqrt{\frac{1}{6}}(|\uparrow\uparrow\uparrow\rangle + |\downarrow\uparrow\uparrow\rangle - 2|\uparrow\uparrow\downarrow\rangle) \\ |\rho(1/2, +1/2)\rangle = \sqrt{\frac{1}{2}}(|\uparrow\uparrow\uparrow\rangle - |\downarrow\uparrow\uparrow\rangle) \end{bmatrix}. \quad (3.40)$$

The Hamiltonian is necessarily diagonal on this basis, since these three basis states have different values of the conserved quantities S_{tot} and (12)-exchange symmetry.

The result is

$$\mathcal{H} = \frac{1}{4}J \begin{bmatrix} 1 + 2\alpha & & \\ & 1 - 4\alpha & \\ & & -3 \end{bmatrix}. \quad (3.41)$$

The two $S_{\text{tot}} = \frac{1}{2}$ levels are split as a result of the reduced symmetry of the isosceles trimer; the full S_3 symmetry of the symmetric trimer has been reduced to S_2

((12)-exchange symmetry), and since S_2 is Abelian no degeneracies follow from this symmetry.

The specific heat and susceptibility of the isosceles trimer, which follow from the energy levels of Eq.(3.41) and the formulas Eqs.(3.145,2.6), are given in Tables 3.3 and 3.2. Note that one recovers the symmetric trimer result in the limit $\alpha = 1$.

We have confirmed by numerical integration of the rather complicated isosceles trimer specific heat formula given in Table 3.2 that the entropy of the isosceles trimer satisfies

$$\frac{S}{k_B} = \int_0^\infty \frac{C}{k_B} \frac{d\beta}{\beta} = \begin{cases} 2 \ln(2) & \alpha \neq 1 \\ \ln(2) & \alpha = 1 \end{cases}, \quad (3.42)$$

as expected from Eq.(3.15) for an eight-dimensional Hilbert space which has a fourfold-degenerate ground state for $\alpha = 1$, and a twofold-degenerate ground state otherwise.

There are three inelastic transitions excited by neutron scattering from an isosceles spin trimer, $|\rho\rangle \rightarrow |\sigma\rangle$, $|\lambda\rangle \rightarrow |\sigma\rangle$ and $|\rho\rangle \rightarrow |\lambda\rangle$. The first two were considered in the discussion of the symmetric trimer, and the results for the isosceles trimer are identical (except that the ΔE values of the transitions differ). The $|\rho\rangle \rightarrow |\lambda\rangle$ transition was not considered previously because these states are degenerate in the symmetric trimer. The result we find for the structure factor of this transition is

$$S^{(\rho \rightarrow \lambda)}(\vec{q}) = \frac{1}{6} \left(1 - \cos(\vec{q} \cdot \vec{x}_{12}) \right). \quad (3.43)$$

This has the same form as the dimer and $|\rho\rangle \rightarrow |\sigma\rangle$ structure factors because it also involves the excitation of the $S_{(12)} = 0$ (12)-dimer to an $S_{(12)} = 1$ state. It can evidently be distinguished from the $|\rho\rangle \rightarrow |\sigma\rangle$ transition by the overall intensity, but not by the functional dependence on q .

To illustrate these single crystal structure factors, in Figure 3.9, we show the two

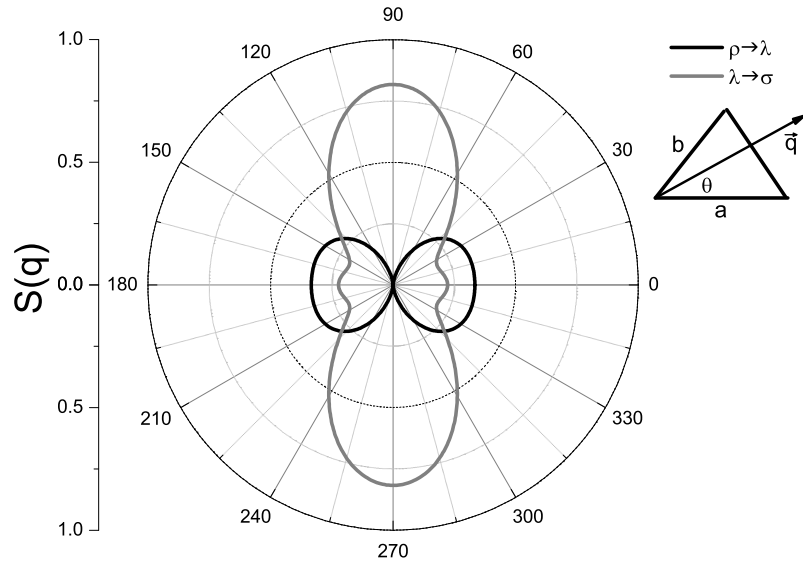


Figure 3.9: The unpolarized structure factors $\{\bar{S}(\vec{q})\}$ (proportional to the angular scattering intensities) predicted for inelastic neutron scattering from the $|\lambda\rangle$ ground state of a single crystal of an isosceles trimer material (see text).

ground state structure factors for $(\text{CN}_3\text{H}_6)_4\text{Na}_6[\text{H}_4\text{V}_6\text{O}_8(\text{PO}_4)_4((\text{OCH}_2)_3\text{CCH}_2\text{OH})_2] \cdot 14\text{H}_2\text{O}$ described by Luban *et al.* [45]. The parameters are $a = 3.22 \text{ \AA}$ and $b = 3.364 \text{ \AA}$. We show the predictions of Eqs.(3.37,3.43) for in-plane scattering, with momentum transfer $q = \pi/a$. Since this material has two strong bonds and a weak dimer ($\alpha \approx 9$) [45], $|\lambda\rangle$ should be the ground state, and the $|\lambda\rangle \rightarrow |\rho\rangle$ and $|\lambda\rangle \rightarrow |\sigma\rangle$ transitions shown in the figure should both be observable (These are expected at 4.2 meV and 7.0 meV respectively, given the parameters of Luban *et al.*) The very different angular distributions predicted for the scattered neutrons show that it should be straightforward to distinguish between these transitions in an inelastic neutron scattering experiment, given a single crystal of this or a similar trimer material.

The powder average eliminates much of the difference between these neutron scattering transitions, although it still should be possible to distinguish them exper-

imentally. On carrying out the powder average we find

$$\begin{aligned}
\bar{S}^{(\rho \rightarrow \sigma)}(q) &= \frac{1}{3}(1 - j_0(qa)) \\
\bar{S}^{(\lambda \rightarrow \sigma)}(q) &= \frac{1}{3}\left(1 + \frac{1}{3}j_0(qa) - \frac{4}{3}j_0(qb)\right) \\
\bar{S}^{(\rho \rightarrow \lambda)}(q) &= \frac{1}{6}(1 - j_0(qa)) \quad .
\end{aligned} \tag{3.44}$$

In the symmetric limit $b/a = 1$ these transitions are proportional to the same function, $1 - j_0(qa)$; at best it may be possible to distinguish the $|\rho\rangle \rightarrow |\lambda\rangle$ transition from the others through their relative intensities. However for significantly different leg lengths the $|\lambda\rangle \rightarrow |\sigma\rangle$ powder average structure factor may differ enough from the $1 - j_0(qa)$ of the $|\rho\rangle \rightarrow |\sigma\rangle$ and $|\rho\rangle \rightarrow |\lambda\rangle$ transitions to distinguish them. As an example, in Figure 3.10, we show the powder structure factors of Eq.(3.44) for the three transitions, for an elongated triangle with $b/a = 2$. (These results are independent of the magnetic coupling ratio α .) As there is considerable variation in form and magnitude between these powder structure factors, it should be possible to distinguish them experimentally in similar isosceles trimer materials. If more than one transition is clearly observed, it may also be useful to compare structure factor ratios, to eliminate the effect of ionic form factors.

Scalene Spin $\frac{1}{2}$ Trimer

The general trimer of Figure 3.7c has three different magnetic couplings and ion pair separations, and is described by the Hamiltonian

$$\mathcal{H} = J\left(\vec{S}_1 \cdot \vec{S}_2 + \alpha_{23} \vec{S}_2 \cdot \vec{S}_3 + \alpha_{31} \vec{S}_3 \cdot \vec{S}_1\right). \tag{3.45}$$

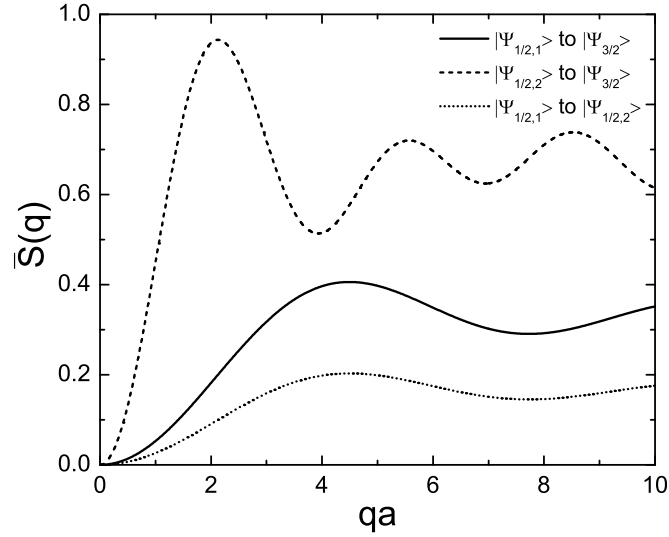


Figure 3.10: The powder average inelastic neutron structure factor $\bar{S}(q)$ for the three allowed transitions of an isosceles trimer, with $b/a = 2$.

We may again determine all the trimer energy eigenvalues by specializing to the $S_{z\,tot} = +1/2$ sector and using the symmetric trimer basis of Eq.(3.40), which gives the Hamiltonian matrix

$$\mathcal{H} = \frac{1}{4} J \begin{bmatrix} 1 + \alpha_s & & \\ & 1 - 2\alpha_s & \sqrt{3}\alpha_d \\ & \sqrt{3}\alpha_d & -3 \end{bmatrix} \quad (3.46)$$

where $\alpha_s = \alpha_{31} + \alpha_{23}$ and $\alpha_d = \alpha_{31} - \alpha_{23}$. The $|\sigma\rangle$ basis states again must be energy eigenstates, since they are the only $S_{tot} = 3/2$ states in the Hilbert space. They have energies of

$$E_{\frac{3}{2}} = \frac{1 + \alpha_s}{4} J . \quad (3.47)$$

The $S_{tot} = 1/2$ basis states $|\rho\rangle$ and $|\lambda\rangle$ mix in this problem, since the general trimer

Hamiltonian with $\alpha_{23} \neq \alpha_{31}$ breaks (12)-exchange symmetry. The resulting energies are

$$E_{\frac{1}{2},\{\frac{1}{2}\}} = -\frac{(1 + \alpha_s \pm \sqrt{(2 - \alpha_s)^2 + 3\alpha_d^2})}{4} J . \quad (3.48)$$

The specific heat and magnetic susceptibility of the general trimer follow from the energy levels of Eqs.(3.47,3.48) and the formulas Eqs.(3.145,2.6). The resulting expressions are given in Tables 3.2 and 3.3. One may confirm recovery of the isosceles and symmetric trimer results as special cases of these results. We have also confirmed numerically that integration of the rather lengthy general trimer specific heat formula given in Table 3.2 leads to an entropy of $S = k_B 2 \ln(2)$, provided that at least one of the parameters α_{23} and α_{31} differs from unity.

The neutron scattering structure factors for the general trimer involve coherent superpositions of the previously derived $|\rho\rangle$ and $|\lambda\rangle$ excitation functions, since the energy eigenstates are superpositions of these basis states. The $S_{tot} = 1/2$ energy eigenstates of Eq.(3.46) are explicitly

$$|\Psi_{\frac{1}{2},1}\rangle = -\sin(\theta)|\lambda\rangle + \cos(\theta)|\rho\rangle \quad (3.49)$$

and

$$|\Psi_{\frac{1}{2},2}\rangle = +\cos(\theta)|\lambda\rangle + \sin(\theta)|\rho\rangle, \quad (3.50)$$

where the mixing angle θ satisfies

$$\tan(\theta) = \frac{x}{1 + \sqrt{1 + x^2}} \quad (3.51)$$

with $x = \sqrt{3}\alpha_d/(2 - \alpha_s)$. The $S_{tot} = 3/2$ energy eigenstate is, as for all the trimers we have considered,

$$|\Psi_{\frac{3}{2}}\rangle = |\sigma\rangle . \quad (3.52)$$

The structure factor for the transition from the $S_{tot} = 1/2$ state $|\Psi_{\frac{1}{2},1}\rangle$ to the $S_{tot} = 3/2$ state is given by

$$S^{(\Psi_{\frac{1}{2},1} \rightarrow \Psi_{\frac{3}{2}})}(\vec{q}) = \frac{1}{3} \left(\left(1 - \frac{1}{3}(C_{12} + C_{23} + C_{31}) \right) + \frac{1}{3} \mathcal{C}_2 (C_{31} + C_{23} - 2C_{12}) + \frac{1}{\sqrt{3}} \mathcal{S}_2 (C_{31} - C_{23}) \right) \quad (3.53)$$

where $C_{ij} = \cos(\vec{q} \cdot \vec{x}_{ij})$, $\mathcal{C}_2 = \cos(2\theta)$ and $\mathcal{S}_2 = \sin(2\theta)$. The structure factor for the second transition, $\Psi_{\frac{1}{2},2} \rightarrow \Psi_{\frac{3}{2}}$, follows from Eq.(3.53) on changing the overall signs of the $\mathcal{C}_2$ and $\mathcal{S}_2$ terms. The third transition, between the two $S_{tot} = 1/2$ states, has the structure factor

$$S^{(\Psi_{\frac{1}{2},1} \rightarrow \Psi_{\frac{1}{2},2})}(\vec{q}) = \frac{1}{6} \left(\left(1 - \frac{1}{3}(C_{12} + C_{23} + C_{31}) \right) + \frac{1}{3} \mathcal{C}_4 (C_{31} + C_{23} - 2C_{12}) + \frac{1}{\sqrt{3}} \mathcal{S}_4 (C_{31} - C_{23}) \right), \quad (3.54)$$

where the new quantities are $\mathcal{C}_4 = \cos(4\theta)$ and $\mathcal{S}_4 = \sin(4\theta)$. One may confirm that the previously derived symmetric and isosceles trimer structure factors of Eqs.(3.36,3.37,3.43) follow from these general trimer results in the limit $\theta \rightarrow 0$.

The powder averages of these general trimer unpolarized structure factors may also be evaluated; the result for the transition $\Psi_{\frac{1}{2},1} \rightarrow \Psi_{\frac{3}{2}}$ is

$$\bar{S}^{(\Psi_{\frac{1}{2},1} \rightarrow \Psi_{\frac{3}{2}})}(\vec{q}) = \frac{1}{3} \left(1 - \frac{(1 + 2\mathcal{C}_2)}{3} j_0(qr_{12}) - \frac{(1 - \mathcal{C}_2 + \sqrt{3}\mathcal{S}_2)}{3} j_0(qr_{23}) - \frac{(1 - \mathcal{C}_2 - \sqrt{3}\mathcal{S}_2)}{3} j_0(qr_{31}) \right). \quad (3.55)$$

The powder average results for the two remaining transitions can be obtained from Eq.(3.55) by simple substitutions. To obtain $\bar{S}^{(\Psi_{\frac{1}{2},2} \rightarrow \Psi_{\frac{3}{2}})}$ simply change the overall signs of $\mathcal{C}_2$ and $\mathcal{S}_2$ in Eq.(3.55), and to obtain $\bar{S}^{(\Psi_{\frac{1}{2},1} \rightarrow \Psi_{\frac{1}{2},2})}$, divide Eq.(3.55) by a

factor of two and replace $\mathcal{C}_2$ and $\mathcal{S}_2$ by $\mathcal{C}_4$ and $\mathcal{S}_4$ respectively.

These results may be useful for the interpretation of neutron scattering data on real materials. One example of a candidate general trimer is $\text{Na}_6[\text{H}_4\text{V}_6\text{O}_8(\text{PO}_4)_4((\text{OCH}_2)_3\text{CCH}_2\text{OH})_2] \cdot 18\text{H}_2\text{O}$ of Luban *et al.* [45]; this has three distinct V-V separations between the $S=1/2$ V^{+4} ions within each vanadium trimer, 3.212 Å, 3.252 Å and 3.322 Å.

3.2.3 Spin 1 and Spin $\frac{3}{2}$ Isosceles Trimers

The Heisenberg Hamiltonian for the isosceles trimer is given by

$$\mathcal{H} = \alpha J \vec{S}_1 \cdot \vec{S}_2 + J (\vec{S}_2 \cdot \vec{S}_3 + \vec{S}_3 \cdot \vec{S}_1) \quad (3.56)$$

The energy levels, E_{S_t, S_d} , of the spin 1 isosceles trimer as determined from Eq. 3.28 are shown in Fig. 3.11.

From these energies, the partition function, heat capacity, and magnetic susceptibility can be determined. The partition function for the spin 1 isosceles trimer and is given by

$$Z = 7e^{-\beta J(2+\alpha)} + 10\cosh(\beta J(1-\alpha)) + 3(e^{2\alpha\beta J} + e^{\beta J(1+\alpha)} + e^{-\beta J(\alpha-3)}) + e^{\beta J(2+\alpha)} . \quad (3.57)$$

From the partition function. The magnetic susceptibility can be calculated from eq. 2.6, and is found to be

$$\frac{\chi}{(g\mu_B)^2/J} = \frac{2\beta J}{Z} (14e^{-\beta J(2+\alpha)} + 10\cosh(\beta J(1-\alpha)) + e^{2\alpha\beta J} + e^{\beta J(1+\alpha)} + e^{-\beta J(\alpha-3)}) , \quad (3.58)$$

Figure 3.11(a) shows the spin 1 isosceles trimer energies as a function of E/J vs.

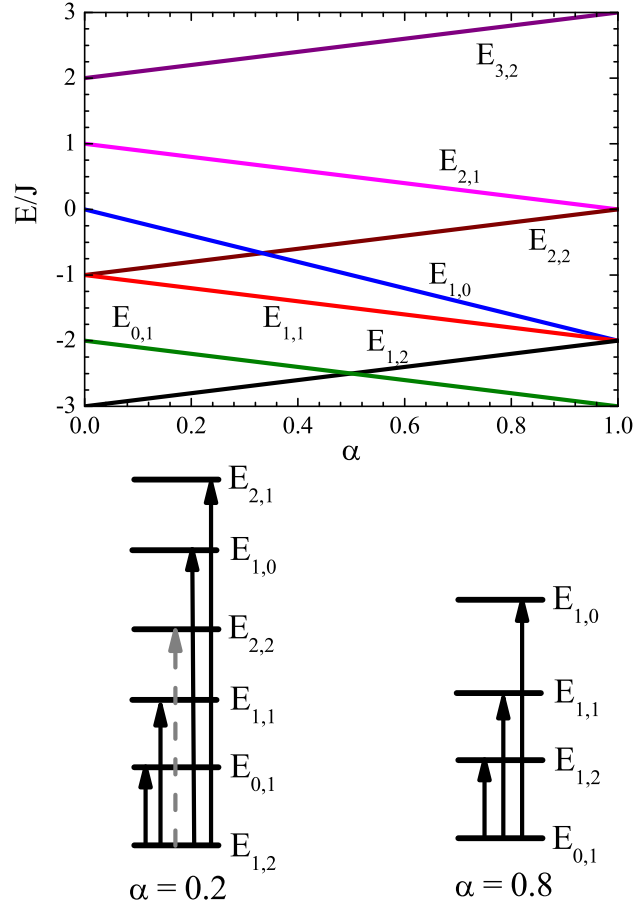


Figure 3.11: a) $S = 1$ isosceles trimer energy levels plotted as a function of E/J vs. α . b) The INS transitions. Arrows indicate transitions allowed by a regular $\Delta S = \pm 1$ or 0 selection rule. Gray arrows show the transition that are blocked by the dimer basis state selection rule. The energy levels are $E_{3,2} = J(2 + \alpha)$, $E_{2,1} = J(1 - \alpha)$, $E_{2,2} = J(\alpha - 1)$, $E_{1,0} = -2\alpha J$, $E_{1,1} = -J(1 + \alpha)$, $E_{1,2} = J(\alpha - 3)$, and $E_{0,1} = -J(2 + \alpha)$.

α . The different excitations for INS are given in table 3.4. Arrows indicate different transitions from the different trimer ground states. If one is to take the limit as $\alpha \rightarrow 0$, then one would have the solution for the linear trimer. In the other direction it is easy to see that the limit as $\alpha \rightarrow 1$ would give the equilateral case. Further discussion of the energy diagram will later.

The spin $\frac{3}{2}$ isosceles trimer is a fairly complex system to solve. However, by using the basis of the $S = \frac{3}{2}$ dimer, the complexity of the trimer becomes greatly simplified. The decomposition of the $S = \frac{3}{2}$ trimer states goes as

$$\frac{3}{2} \otimes \frac{3}{2} \otimes \frac{3}{2} = \frac{3}{2} \otimes (3 \oplus 2 \oplus 1 \oplus 0) =$$

$$\frac{9}{2} \oplus \frac{7}{2} \oplus \frac{5}{2} \oplus \frac{3}{2} \quad (\text{for } S_d = 3)$$

$$\frac{7}{2} \oplus \frac{5}{2} \oplus \frac{3}{2} \oplus \frac{1}{2} \quad (\text{for } S_d = 2)$$

$$\frac{5}{2} \oplus \frac{3}{2} \oplus \frac{1}{2} \quad (\text{for } S_d = 1)$$

$$\frac{3}{2} \quad (\text{for } S_d = 0)$$

$$= \frac{9}{2} \oplus \frac{7^2}{2} \oplus \frac{5^3}{2} \oplus \frac{3^4}{2} \oplus \frac{1^2}{2} \quad (\text{Total}). \quad (3.59)$$

where the dimer states are in parenthesis. These dimer basis states play an important role in the INS structure factors to be discussed later. The energy levels, E_{S_t, S_d} , for the $S = \frac{3}{2}$ isosceles trimer are given in Fig. 3.12.

The magnetic susceptibility of the spin 3/2 isosceles trimer is quite a complex equa-

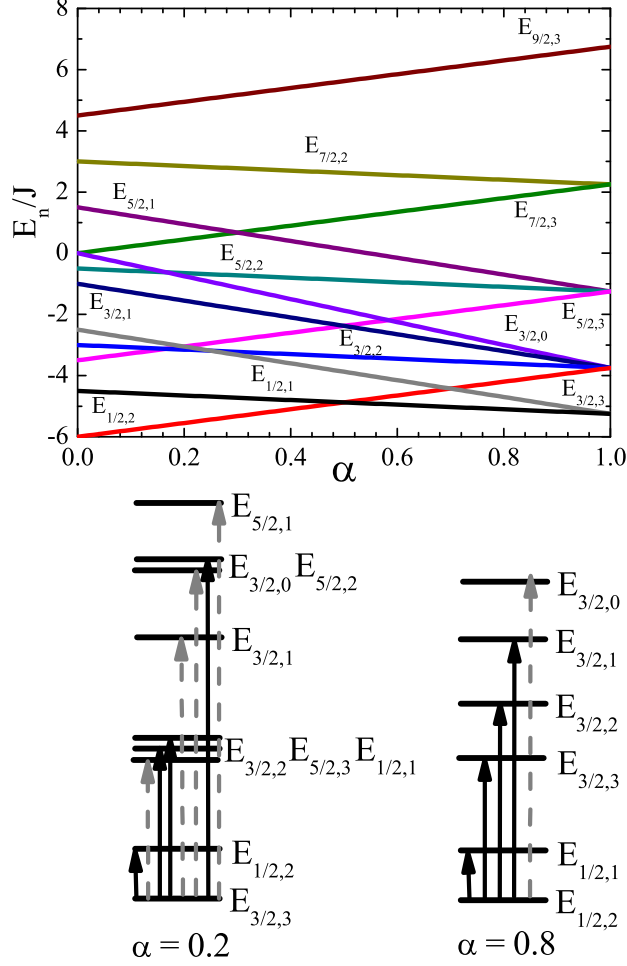


Figure 3.12: a) $S = \frac{3}{2}$ isosceles trimer energy levels plotted as a function of E/J vs. α . b) The INS transitions. Arrows indicate transitions allowed by a regular $\Delta S = \pm 1$ or 0 selection rule. Gray arrows show the transition that are blocked by the dimer basis state selection rule. The energy levels are $E_{9/2,3} = J(\frac{9}{2} + \frac{9}{4}\alpha)$, $E_{7/2,2} = J(3 - \frac{3}{4}\alpha)$, $E_{7/2,3} = \frac{9}{4}\alpha J$, $E_{5/2,1} = J(\frac{3}{2} - \frac{11}{4}\alpha)$, $E_{5/2,2} = -J(\frac{1}{2} + \frac{3}{4}\alpha)$, $E_{5/2,3} = J(\frac{9}{4}\alpha - \frac{7}{2})$, $E_{3/2,0} = -\frac{15}{4}\alpha J$, $E_{3/2,1} = -J(1 + \frac{11}{4}\alpha)$, $E_{3/2,2} = -J(3 + \frac{3}{4}\alpha)$, $E_{3/2,3} = J(\frac{9}{4}\alpha - 6)$, $E_{1/2,1} = -J(\frac{5}{2} + \frac{11}{4}\alpha)$, $E_{1/2,2} = -J(\frac{9}{2} + \frac{3}{4}\alpha)$.

tion. However, it is the exact solution for this particular model and is given by

$$\frac{\chi}{(g\mu_B)^2/J} = \frac{\beta J}{2Z} (165e^{-\beta E_{9/2,3}} + 84(e^{-\beta E_{7/2,2}} + e^{-\beta E_{7/2,3}}) + 35(e^{-\beta E_{5/2,1}} + e^{-\beta E_{5/2,2}} + e^{-\beta E_{5/2,3}}) + 10(e^{-\beta E_{3/2,0}} + e^{-\beta E_{3/2,1}} + e^{-\beta E_{3/2,2}} + e^{-\beta E_{3/2,3}}) + (e^{-\beta E_{1/2,1}} + e^{-\beta E_{1/2,2}})) , \quad (3.60)$$

where Z is the partition function for the spin $3/2$ isosceles trimer and is given by

$$Z = 10e^{-\beta E_{9/2,3}} + 8(e^{-\beta E_{7/2,2}} + e^{-\beta E_{7/2,3}}) + 6(e^{-\beta E_{5/2,1}} + e^{-\beta E_{5/2,2}} + e^{-\beta E_{5/2,3}}) + 4(e^{-\beta E_{3/2,0}} + e^{-\beta E_{3/2,1}} + e^{-\beta E_{3/2,2}} + e^{-\beta E_{3/2,3}}) + 2(e^{-\beta E_{1/2,1}} + e^{-\beta E_{1/2,2}}) . \quad (3.61)$$

The energy levels of the $S=3/2$ isosceles trimer are presented in Fig. 3.12 as a function of E/J vs. α . As with $S=1$ transitions, the arrows indicate different transition in INS from the ground state. Transition energies for INS are given in Table 3.4.

Because the ground state, in Figs. 3.11 and 3.12, changes from $S=0$ to $S=1$ (spin 1 trimer) and $S=\frac{1}{2}$ to $S=\frac{3}{2}$ (spin $\frac{3}{2}$ trimer) as α goes from 1 to 0, it is necessary to calculate the INS structure factors and intensities for the different transitions from the ground state to all possible excited states. The structure factors and intensities for ground state transitions for the spin trimers are presented in Table 3.4.

In figure 3.11(b) and 3.12(b), we show the possible INS transitions for the spin 1 and spin $\frac{3}{2}$ isosceles trimers, respectively. The black and gray arrows are the possible transitions according to the $\Delta S = \pm 1$ or 0 selection rule. The black arrows are the transitions that have a nonzero structure factor, while the gray arrows indicate a transition with a zero structure factor and are therefore unexcitable by INS.

The structure factors for the different transitions in both the spin 1 and spin $\frac{3}{2}$

cases illustrates and interesting phenomenon in INS. According to known INS selection rules, the transitions of $\Delta S = \pm 1$ or 0 should be allowed and should therefore have a calculated structure factor. However, it is easy to see that there are structure factors that, regardless of the selection rules, are determined to be zero. This is particularly interesting because INS is typically thought to be able to measure any $\Delta S = \pm 1$ or 0 transition. Therefore, by examining the transition that mysteriously have zero structure factors symmetry selection rule for INS comes clear, at least for finite clusters. It is evident that the transitions have to obey a selection of dimer basis state. The transition must have a $\Delta S_d = \pm 1$ or 0 along with the previous selection rule. This comes about through the symmetry of the isosceles trimer.

Another point of interest is the change in ground state at $\alpha=0.5$. This brings a discontinuity to the neutron scattering intensities and helps clarify the spin states of the ions. The sudden change from a $S = 0$ to a $S = 1$ ground state in the $S = 1$ trimer immediately allows two more transitions.

This is described in Fig. 3.13, where at $\alpha=0.8$ there are only three possible transitions and at $\alpha=0.3$ there are five possible transitions. As α decreases below 0.5 for the $S = 1$ case, the trimer is allowed to order itself into a less frustrated state with an overall spin of 1, but a dimer spin state of 2 (both ions are in spin up states). Whereas with $\alpha > 0.5$, the trimer experiences a greater frustration that pushes the spins into a $S = 1$ dimer state (one spin and one neutral), which gives the overall spin of the trimer to be zero. This is illustrated in Fig. 3.14. The $S = \frac{3}{2}$ trimer has an analogous state flip at $\alpha=0.5$. Therefore, the use of the spin dimer basis states allows for the spin configurations to be known and a better understanding of the frustration of the trimer becomes clear. The nature of the change in ground state can be attributed to a change in the dimer basis.

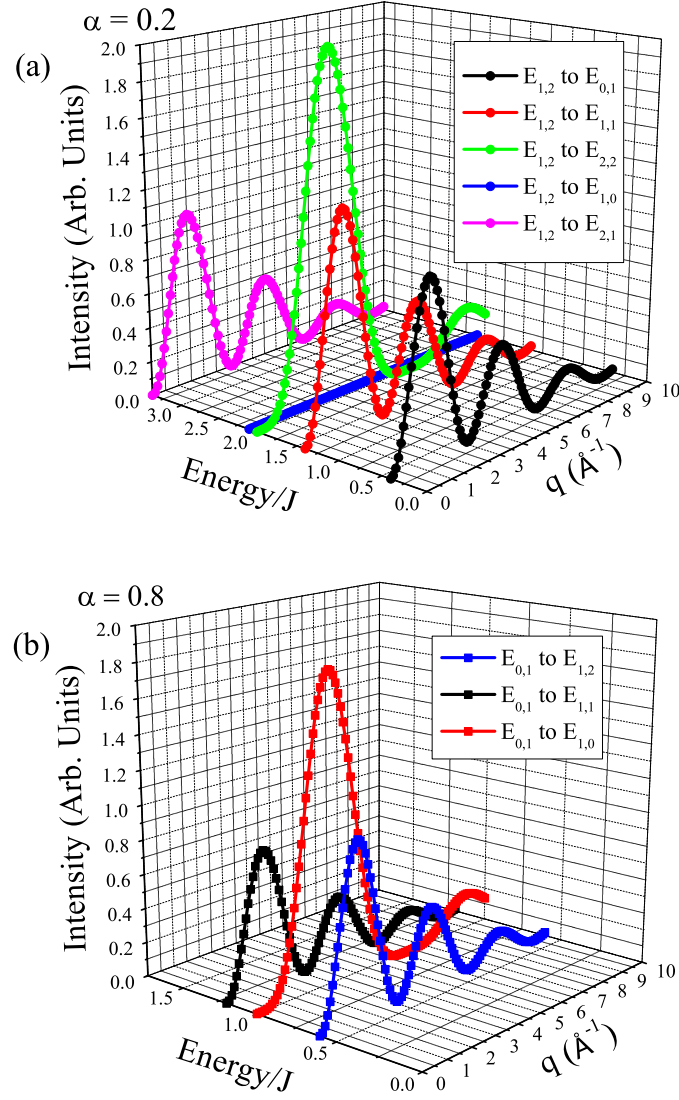


Figure 3.13: a) $S = 1$ isosceles trimer structure factors as a function of E/J vs. q with $S = 0$ ground state at $\alpha=0.8$. b) $S = 1$ isosceles trimer structure factors as a function of E/J vs. q with $S = 1$ ground state at $\alpha=0.3$ (red). Note: Different colors were used to differentiate the different transitions for that particular α .

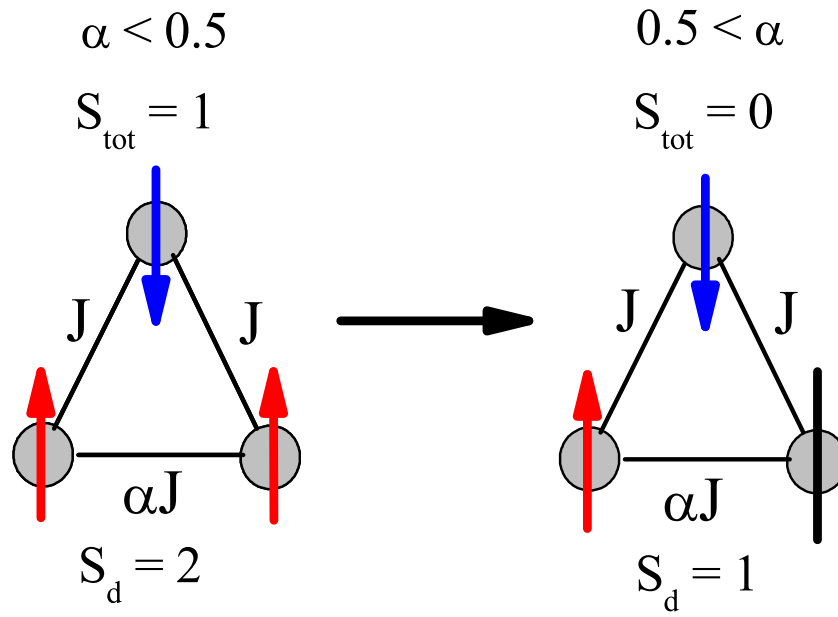


Figure 3.14: The transition as α is increased through the spin ground state transition. Red arrows indicate spin up states, blue arrows are spin down states, black double headed arrow is the spin neutral state.

3.3 Spin Tetramers

The general tetramer can be solved exactly for different symmetric cases. This section will cover the formation of the tetramer of general spin S and then followed by the calculation of some diagonalizable spin- $\frac{1}{2}$ tetramers. The section will close with the discussion of spin- $\frac{3}{2}$ tetramers with application to Na_3RuO_4 .

3.3.1 Tetramer of General Spin S

Tetramers are the first area where there are now too many configurations to consider. For the general spin case, there are three main configurations that will be examined. These configurations are based from the purely symmetric coupled dimer model shown in Fig. 3.15 (b-d). All three of the tetramer configurations can be described by a single Hamiltonian. By using this model, we can clearly examine the three possible configurations that may describe Na_3RuO_4 , which will be discussed later in this section. Using nearest-neighbor Heisenberg interactions and a Zeeman magnetic field term for magnetic fields $\mathbf{B}$ defining the z -axis, the general Hamiltonian is

$$\mathcal{H} = J \left[(\vec{S}_1 \cdot \vec{S}_3 + \vec{S}_1 \cdot \vec{S}_4 + \vec{S}_2 \cdot \vec{S}_3 + \vec{S}_2 \cdot \vec{S}_4) + \alpha \vec{S}_1 \cdot \vec{S}_2 + \gamma \vec{S}_3 \cdot \vec{S}_4 \right] - (S_1^z + S_2^z + S_3^z + S_4^z) g \mu_B B. \quad (3.62)$$

where $\alpha = J'/J$, $\gamma = J''/J$ and μ_B is the Bohr magneton. We define the exchange interaction as positive for antiferromagnetic interactions, and $\vec{S}_i$ is the quantum spin operator for a spin- S ion at site $i=1,2,3,4$. The Zeeman term interacts with the z -component of the spin Hamiltonian, lifting the degeneracy of magnetic substates in applied magnetic fields.

The Hamiltonian, Eq. 3.62, is rotationally invariant in spin space, such that the total spin, S_{tot} , and S_z are good quantum numbers. For the general case of a spin- S

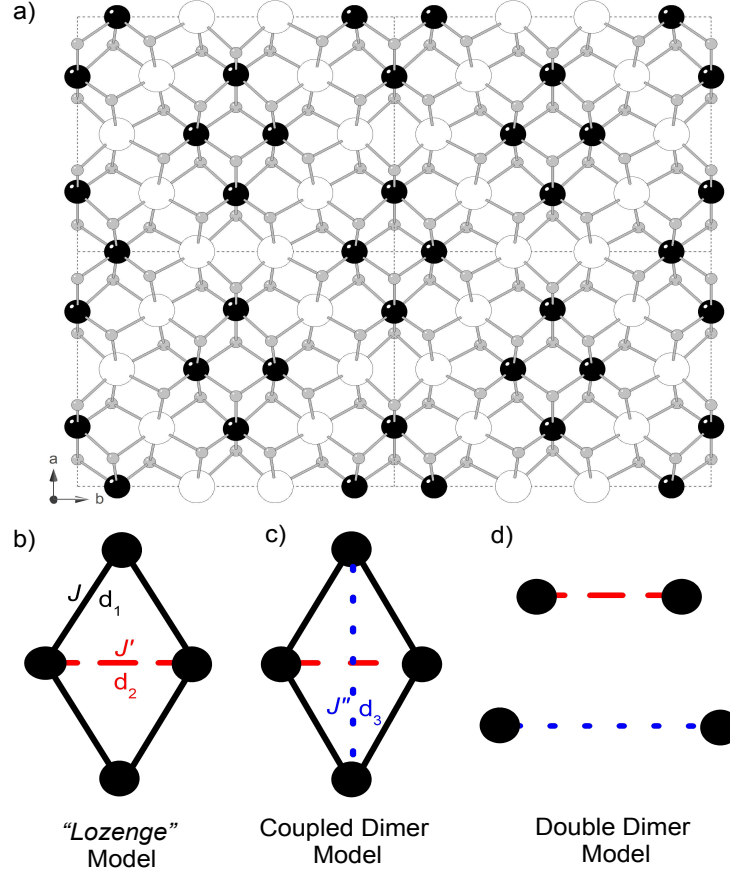


Figure 3.15: Crystal structure and potential exchange interactions for Na_3RuO_4 . (a) Crystal structure as viewed along the c -axis showing a single plane of atomic sites for $\pm \frac{c}{4}$ unit cells. Ru, O and Na sites are black, gray, and white respectively. The monoclinic $C 2/m$ unit cell is shown as dashed grey lines. (b)-(d) are three possible models of exchange interactions between Ru sites in the ab plane as discussed in the text.

tetramer cluster, the energy eigenstates have the total spin decompositions given by

$$\prod_{S_{tot}=1}^4 S_n = \sum_{S_{tot}=0}^{2S} (4S - S_{tot})^{\binom{(S_{tot}+1)(S_{tot}+2)}{2}} \oplus \sum_{S_{tot}=0}^{2S-1} S_{tot}^{\frac{1}{2}(4S+2+8S_{tot}S+S_{tot}-3S_{tot}^2)}, \quad (3.63)$$

where the total number of magnetic states in a general S tetramer are $(2S + 1)^4$. Therefore for the S=3/2 tetramer, the energy eigenstates have $S^4 = 256$ magnetic states and the spin decomposition is given by

$$\frac{3}{2} \otimes \frac{3}{2} \otimes \frac{3}{2} \otimes \frac{3}{2} =$$

Individual Spins

$$(3 \oplus 2 \oplus 1 \oplus 0) \otimes (3 \oplus 2 \oplus 1 \oplus 0) =$$

Dimer States

$$6 \oplus 5^3 \oplus 4^6 \oplus 3^{10} \oplus 2^{11} \oplus 1^9 \oplus 0^4 \quad (3.64)$$

Tetramer States.

The superscript in the tetramer states denote multiple S_{tot} states. Each multiplet containing $2S_{tot}+1$ magnetic states, which are degenerate given an isotropic magnetic Hamiltonian such as the Heisenberg form of Eq. 3.62, where the degenerate states can be split by a magnetic field. This breakdown of the dimer and tetramer states clarifies which dimer states interact to create the separate tetramer states.

Through the use of the Kambe approach [4, 29], we can rewrite the Hamiltonian in terms of total spin, in which the eigenstates and eigenvalues of the Hamiltonian may be found by diagonalization in the convenient basis of two dimers. This ap-

proach gives information about the states of the dimers as the tetramer states are determined. In practice we employ the usual set of $\hat{z}$ -polarized magnetic basis states. The energy levels are then determined simply by considering a dimer basis, where S_α corresponds to the spin state of the α dimer and S_γ corresponds to the spin state of a γ dimer as described in the Hamiltonian, Eq. 3.62. Using this dimer basis, the energy levels for the general S coupled dimer can be determined exactly and are given by

$$E = \frac{J}{2} [\mathfrak{J}_{tot} + \mathfrak{J}_\alpha(\alpha - 1) + \mathfrak{J}_\gamma(\gamma - 1) - 2(\alpha + \gamma)\mathfrak{J}] \quad (3.65)$$

where $\mathfrak{J}_{tot} = S_{tot}(S_{tot} + 1)$ with S_{tot} denoting the magnetic state of the system, $\mathfrak{J}_\alpha = S_\alpha(S_\alpha + 1)$ and S_α is the spin state of the α dimer (S_1 - S_2 dimer), $\mathfrak{J}_\gamma = S_\gamma(S_\gamma + 1)$ and S_γ is the spin state of the γ dimer (S_3 - S_4 dimer), and $\mathfrak{J} = S(S + 1)$ with S being the spin of the system. The individual states can be split into $2S_{tot} + 1$ states with magnetic field. Therefore, the energy levels split by $g\mu_B B S_{tot}^z$, where S_{tot}^z is from $0 \dots (2S_{tot} + 1)$.

3.3.2 Spin $\frac{1}{2}$ Tetramers

Tetramer basis states and their matrix elements

We will consider three $S = 1/2$ tetramer spin clusters of decreasing symmetry, the regular tetrahedron, the rectangular tetramer, and the linear (dimer-pair) tetramer. Our definitions for the magnetic couplings and geometry of these systems are shown in Figure 3.16. As with the dimer and trimer systems we will give results for the partition function, specific heat, magnetic susceptibility and neutron inelastic scattering structure factors, the latter for both single crystal and powder average cases.

Since there is a natural separation of the rectangle and linear tetramer systems into dimer components, we will use a $|(12)(34)\rangle$ dimer basis to represent tetramer

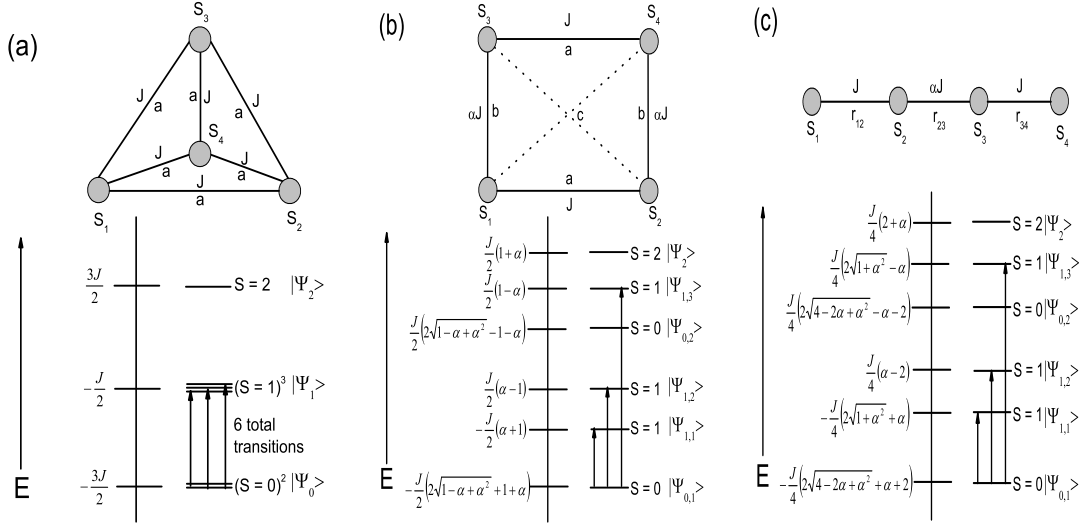


Figure 3.16: Energy level diagrams for (a) the tetrahedron, (b) the rectangular tetramer, and (c) the linear (dimer-pair) tetramer.

energy eigenvectors. The dimer basis states are

$$|\rho\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \quad (3.66)$$

and

$$|\sigma(m)\rangle = \begin{bmatrix} |\uparrow\uparrow\rangle & m = +1 \\ \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) & m = 0 \\ |\downarrow\downarrow\rangle & m = -1 \end{bmatrix}. \quad (3.67)$$

These are combined as Clebsch-Gordan series to form tetramer basis states of definite total spin and symmetry, which are $|(\sigma\sigma)_S\rangle$, $S_{tot} = 0, 2$; $|(\sigma\sigma)_A\rangle$, $S_{tot} = 1$; $|(\rho\sigma)_{S,A}\rangle$, $S_{tot} = 1$; $|\rho\rho\rangle$, $S_{tot} = 0$. In the interest of clarity we will occasionally specify the total spin of one of these basis state with a subscript; thus $|\sigma\sigma\rangle_0$ refers to the $|(\sigma\sigma)_S\rangle$ state with $S_{tot} = 0$.

Using these states as basis vectors reduces the 16-dimensional full tetramer Hilbert space to 1-, 2- and 3-dimensional subspaces, which are spanned by the basis sets

$$| S_{tot} = 2 \rangle = | \sigma \sigma \rangle_2 \quad (3.68)$$

$$\{ | S_{tot} = 1 \rangle \} = \begin{bmatrix} | \sigma \sigma \rangle_1 \\ | (\rho \sigma)_S \rangle \\ | (\rho \sigma)_A \rangle \end{bmatrix} \quad (3.69)$$

$$\{ | S_{tot} = 0 \rangle \} = \begin{bmatrix} | \sigma \sigma \rangle_0 \\ \\ | \rho \rho \rangle \end{bmatrix} . \quad (3.70)$$

Thus symmetry arguments alone determine the eigenvectors for one level, and the eigenvectors for the remaining levels involve at most 2×2 and 3×3 diagonalizations. As we shall see, for the three tetramer models we consider here we actually encounter at most 2×2 diagonalization problems using this basis.

These basis states are also convenient for determining neutron scattering structure factors, since they have relatively simple matrix elements of the spin transition operator V_a of Eq.(3.135). The complete set of matrix elements of V_a (spherical components) between single (12)-dimer basis states is

$$\langle \rho | V_a | \rho \rangle = 0 \quad (3.71)$$

$$\langle \sigma(m) | V_a | \rho \rangle = \delta_{a,m} \frac{f_1 - f_2}{2} \quad (3.72)$$

$$\langle \rho | V_a | \sigma(m) \rangle = -\delta_{a,-m} \frac{f_1 - f_2}{2} \quad (3.73)$$

$$\langle \sigma(m') | V_a | \sigma(m) \rangle = -\delta_{m',m+a} \frac{f_1 + f_2}{2} \quad (3.74)$$

where $f_i = e^{i\vec{k} \cdot \vec{x}_i}$.

These dimer results may be combined to give the complete set of matrix elements of V_a between tetramer basis states, which is all that we require to determine all neutron scattering structure factors for all the spin tetramer problems we consider. These tetramer matrix elements (with explicit S_{tot} or S_{tot} , $S_{z\ tot}$ subscripts on the states where required for clarity) are

$$\langle \rho\rho | V_a | \rho\rho \rangle = 0 \quad (3.75)$$

$$\begin{aligned} {}_{1,m} \langle (\rho\sigma)_S | V_a | \rho\rho \rangle = \\ \delta_{a,m} \frac{f_1 - f_2 + f_3 - f_4}{2\sqrt{2}} \end{aligned} \quad (3.76)$$

$$\begin{aligned} {}_{1,m} \langle (\rho\sigma)_A | V_a | \rho\rho \rangle = \\ \delta_{a,m} \frac{f_1 - f_2 - f_3 + f_4}{2\sqrt{2}} \end{aligned} \quad (3.77)$$

$$\langle \sigma\sigma | V_a | \rho\rho \rangle = 0 \quad (3.78)$$

$$\langle \rho\rho | V_a | \sigma\sigma \rangle = 0 \quad (3.79)$$

$$\begin{aligned} {}_{1,m} \langle (\rho\sigma)_S | V_a | \sigma\sigma \rangle_0 = \\ -\delta_{a,m} \frac{f_1 - f_2 + f_3 - f_4}{2\sqrt{6}} \end{aligned} \quad (3.80)$$

$$\begin{aligned} {}_{1,m} \langle (\rho\sigma)_A | V_a | \sigma\sigma \rangle_0 = \\ -\delta_{a,m} \frac{f_1 - f_2 - f_3 + f_4}{2\sqrt{6}} \end{aligned} \quad (3.81)$$

$${}_0 \langle \sigma\sigma | V_a | \sigma\sigma \rangle_0 = 0 \quad (3.82)$$

$$\begin{aligned} {}_{1,m} \langle \sigma\sigma | V_a | \sigma\sigma \rangle_0 = \\ \delta_{a,m} \frac{f_1 + f_2 - f_3 - f_4}{\sqrt{6}} \end{aligned} \quad (3.83)$$

$${}_2 \langle \sigma\sigma | V_a | \sigma\sigma \rangle_0 = 0 \quad (3.84)$$

These matrix elements suffice for the evaluation of the inelastic neutron scattering transitions between $S_{tot} = 0$ and $S_{tot} = 1$ tetramer energy eigenstates considered here. The remaining matrix elements between $S_{tot} = 1$ pairs and $S_{tot} = 1$ and $S_{tot} = 2$ states may be evaluated similarly.

Spin $\frac{1}{2}$ Tetrahedron

This system has four $S = 1/2$ ions at the vertices of a regular tetrahedron, with Heisenberg interactions of strength J between each pair of ions (see Figure 3.16a).

The Hamiltonian of this system is given by

$$\mathcal{H} = J \sum_{\substack{i,j=1 \\ i < j}}^4 \vec{S}_i \cdot \vec{S}_j . \quad (3.85)$$

The invariance of this Hamiltonian under permutation of any site labels implies an S_4 symmetry, in addition to the spin rotation symmetry $SU(2)$. Since the group S_4 is non-Abelian and has irreducible representations of dimensionality 1, 2 and 3, we anticipate that one may find twofold and threefold degeneracies in the spectrum of tetrahedron energy eigenstates. We will see that this is indeed the case.

As with the dimer and symmetric trimer we may determine the energy eigenvalues of this system by simply squaring the total spin operator $\vec{S}_{tot} = \sum_{i=1}^n \vec{S}_i$, which gives for this case

$$E_{S_{tot}} = \frac{1}{2} J \left(S_{tot}(S_{tot} + 1) - 3 \right) = \begin{cases} +\frac{3}{2} J & S_{tot} = 2 \\ -\frac{1}{2} J & S_{tot} = 1 \\ -\frac{3}{2} J & S_{tot} = 0. \end{cases} \quad (3.86)$$

The Clebsch-Gordon series of Eq.(3.142) implies that these $S_{tot} = 1$ and $S_{tot} = 0$ energy levels are respectively threefold and twofold degenerate.

Given these energy levels, the specific heat and susceptibility of the tetrahedron may then be determined using Eqs.(3.145,2.6), with the results

$$\frac{C}{k_B} = \frac{9}{2} (\beta J)^2 e^{-\beta J} \frac{(1 + 5e^{-2\beta J} + 10e^{-3\beta J})}{(1 + \frac{9}{2}e^{-\beta J} + \frac{5}{2}e^{-3\beta J})^2} \quad (3.87)$$

and

$$\frac{\chi}{(g\mu_B)^2/J} = 3\beta J e^{-\beta J} \frac{(1 + \frac{5}{3}e^{-2\beta J})}{(1 + \frac{9}{2}e^{-\beta J} + \frac{5}{2}e^{-3\beta J})} . \quad (3.88)$$

These quantities are shown in Figure 3.17 and Figure 3.18, respectively. The specific heat of the tetrahedron gives an entropy of $S = k_B 3 \ln(2)$, as expected for a

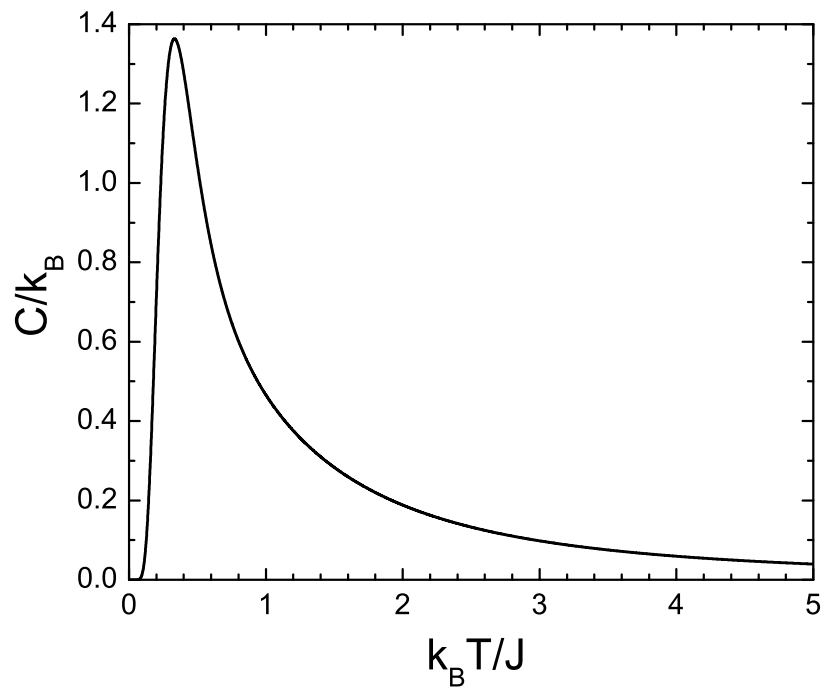


Figure 3.17: Magnetic contribution to the specific heat of a regular tetrahedron.

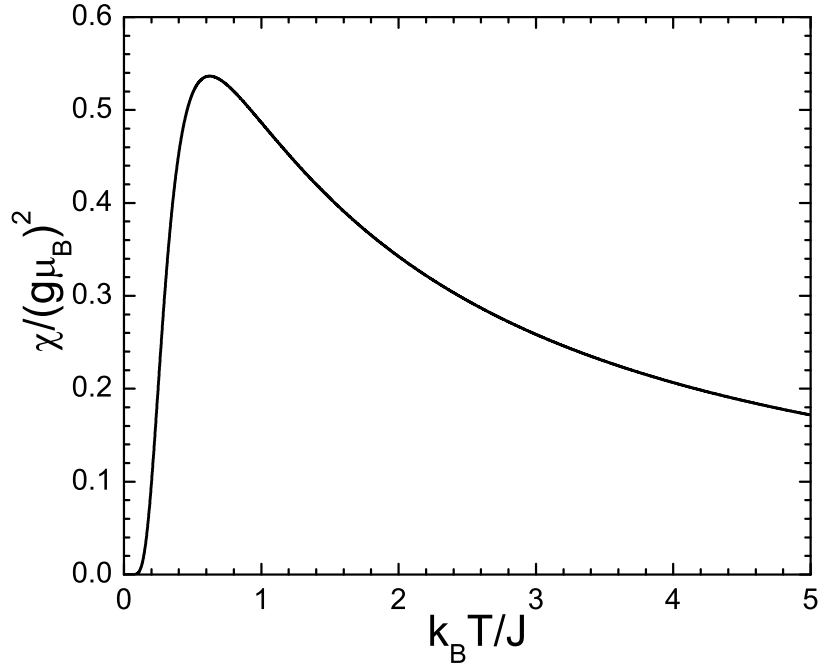


Figure 3.18: Susceptibility of a regular tetrahedron.

16-dimensional Hilbert space and a doubly-degenerate ground state.

Note that the susceptibility is rather similar to that of the spin dimer, since the tetrahedron also has an $S_{tot} = 0$ ground state and a gap of J to the magnetized $S_{tot} = 1$ excited states. (The fact that the ground state is twofold degenerate does not affect this result, since both are $S_{tot} = 0$ states and neither makes a contribution to the susceptibility.)

Determination of the energy eigenvectors requires diagonalization of the Hamiltonian on a specific basis. Operating on our $|(12)(34)\rangle$ dimer basis of Eqs.(3.68-3.70) with the tetrahedron Hamiltonian, Eq.(3.85), we find that the Hamiltonian matrix is already fully diagonal; each of these basis states is an energy eigenvector of the tetrahedron Hamiltonian.

In our discussion of neutron scattering structure factors of the tetrahedron and

the other spin tetramers considered in this paper, we will specialize to $S_{tot} = 0$ initial states. Structure factors for $S_{tot} > 0$ initial states, which are of interest for systems with magnetized ground states and at finite temperatures, and can be derived using similar methods.

The tetrahedron has two degenerate ground states, which we take to be $|\Psi_{0,1}\rangle = |\rho\rho\rangle$ and $|\Psi_{0,2}\rangle = |\sigma\sigma\rangle_0$. The three degenerate $S_{tot} = 1$ excited states, which can be reached from the $S_{tot} = 0$ levels using inelastic neutron scattering, are taken to be $|\Psi_{1,1}\rangle = |(\rho\sigma)_S\rangle$, $|\Psi_{1,2}\rangle = |(\rho\sigma)_A\rangle$ and $|\Psi_{1,3}\rangle = |(\sigma\sigma)_S\rangle_1$. The choice of this specific set of initial and final states is rather arbitrary; in a real material we would expect a spontaneous distortion of the lattice, which would select nearly degenerate energy eigenstates that need not be these specific basis states. However these will suffice to illustrate the neutron scattering structure factors expected for nearly tetrahedral systems.

The single crystal structure factors for all of these transitions may be read directly from Eqs.(3.76-3.83). For example, the transition $|\Psi_{0,1}\rangle \rightarrow |\Psi_{1,1}\rangle$ is specified by the matrix element of Eq.(3.76); using the structure factor definition in Eq.(2.15), we find

$$S^{(\Psi_{0,1} \rightarrow \Psi_{1,1})}(\vec{q}) = \frac{1}{2} - \frac{1}{4} \left(C_{12} - C_{13} + C_{14} + C_{23} - C_{24} + C_{34} \right) \quad (3.89)$$

where as before $C_{ij} = \cos(\vec{q} \cdot \vec{x}_{ij})$. This characteristic angular distribution and its five partner distributions could be used in an inelastic neutron scattering experiment from a single crystal sample to characterize the spin states of the individual $S_{tot} = 0$ and $S_{tot} = 1$ levels. (Note however that one specific transition, $|\Psi_{0,1}\rangle \rightarrow |\Psi_{1,3}\rangle$, has a zero matrix element.)

The powder average structure factors for a tetrahedron are much less characteristic. Since there is only a single ion pair separation, each cosine in the single crystal

structure factors such as Eq.(3.89) powder-averages to the same factor of $j_0(qa)$. This gives a powder structure factor that is proportional to $1 - j_0(qa)$ for each transition, just as we found for the dimer and symmetric tetramer; only the overall coefficients distinguish the different transitions. These results are

$$\begin{aligned}
\bar{S}^{(\Psi_{0,1} \rightarrow \Psi_{1,1})}(q) &= \frac{1}{2}(1 - j_0(qa)) \\
\bar{S}^{(\Psi_{0,1} \rightarrow \Psi_{1,2})}(q) &= \frac{1}{2}(1 - j_0(qa)) \\
\bar{S}^{(\Psi_{0,1} \rightarrow \Psi_{1,3})}(q) &= 0 \\
\bar{S}^{(\Psi_{0,2} \rightarrow \Psi_{1,1})}(q) &= \frac{1}{6}(1 - j_0(qa)) \\
\bar{S}^{(\Psi_{0,2} \rightarrow \Psi_{1,2})}(q) &= \frac{1}{6}(1 - j_0(qa)) \\
\bar{S}^{(\Psi_{0,2} \rightarrow \Psi_{1,3})}(q) &= \frac{2}{3}(1 - j_0(qa)) .
\end{aligned} \tag{3.90}$$

A generalization of the tetrahedron problem in which the Hamiltonian has couplings of strength αJ between ions in different dimers may also be of interest. This generalized Hamiltonian is

$$\begin{aligned}
\mathcal{H}(\alpha) &= J \left((\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_3 \cdot \vec{S}_4) \right. \\
&\quad \left. + \alpha (\vec{S}_1 \cdot \vec{S}_3 + \vec{S}_1 \cdot \vec{S}_4 + \vec{S}_2 \cdot \vec{S}_3 + \vec{S}_2 \cdot \vec{S}_4) \right).
\end{aligned} \tag{3.91}$$

The dimer-pair basis of Eqs.(3.68-3.70) is also diagonal under this Hamiltonian, with the eigenvalues given below. (We have added an S_{tot} subscript to all these state vectors for clarity.)

$$\mathcal{H}(\alpha)|\sigma\sigma\rangle_{S_{tot}=2} = \left(\frac{1}{2} + \alpha\right) |\sigma\sigma\rangle_2 \quad (3.92)$$

$$\mathcal{H}(\alpha)|\sigma\sigma\rangle_1 = \left(\frac{1}{2} - \alpha\right) |\sigma\sigma\rangle_1 \quad (3.93)$$

$$\mathcal{H}(\alpha)|(\rho\sigma)_S\rangle_1 = -\frac{1}{2} |(\rho\sigma)_S\rangle_1 \quad (3.94)$$

$$\mathcal{H}(\alpha)|(\rho\sigma)_A\rangle_1 = -\frac{1}{2} |(\rho\sigma)_A\rangle_1 \quad (3.95)$$

$$\mathcal{H}(\alpha)|\sigma\sigma\rangle_0 = \left(\frac{1}{2} - 2\alpha\right) |\sigma\sigma\rangle_0 \quad (3.96)$$

$$\mathcal{H}(\alpha)|\rho\rho\rangle_0 = -\frac{3}{2} |\rho\rho\rangle_0 \quad (3.97)$$

Since the energy eigenvectors of this generalized problem are exactly the basis states we used for the tetrahedron, the neutron scattering structure factors for the $S_{tot} = 0$ to $S_{tot} = 1$ transitions are unchanged. In this system however all these levels are nondegenerate, so unlike the pure tetrahedron problem one encounters no structure factor ambiguities due to an arbitrary choice between degenerate basis states.

Spin $\frac{1}{2}$ Rectangular Tetramer

The rectangular tetramer, shown in Figure 3.16b, has (12) and (34) dimers of interaction strength J coupled by interactions of strength αJ between ion pairs (13) and (24). The Hamiltonian is

$$\mathcal{H} = J\left(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_3 \cdot \vec{S}_4 + \alpha(\vec{S}_1 \cdot \vec{S}_3 + \vec{S}_2 \cdot \vec{S}_4)\right). \quad (3.98)$$

This Hamiltonian is already diagonal on the $S_{tot} = 1, 2$ dimer-pair basis states of Eqs.(3.68,3.69); the energy eigenvalues are

$$E_2 = +\frac{(1+\alpha)}{2} J \quad (3.99)$$

$$E_{1,3} = +\frac{(1-\alpha)}{2} J \quad (3.100)$$

$$E_{1,2} = -\frac{(1-\alpha)}{2} J \quad (3.101)$$

$$E_{1,1} = -\frac{(1+\alpha)}{2} J \quad (3.102)$$

$$(3.103)$$

The 2×2 Hamiltonian matrix in the $S_{tot} = 0$ subspace spanned by Eq.(3.70) is

$$\mathcal{H}_{S_{tot}=0} = \frac{1}{2} J \begin{bmatrix} 1-2\alpha & -\sqrt{3}\alpha \\ -\sqrt{3}\alpha & -3 \end{bmatrix}, \quad (3.104)$$

which has eigenvalues

$$E_{0,\{1_2\}} = \left(-\frac{1}{2} - \frac{1}{2}\alpha \mp \sqrt{1-\alpha+\alpha^2} \right) J. \quad (3.105)$$

The specific heat and susceptibility of the rectangular tetramer may be evaluated using these energy levels and the general formulas of Eqs.(3.145,2.6). The susceptibility, which is the more relevant experimental quantity for this study, is given in Table 3.3. Although the specific heat is straightforward to evaluate, the result is too complicated to tabulate here.

The neutron scattering structure factors of the rectangular tetramer are especially interesting in because this is the first tetramer we have considered in which the ground state is a linear combination of the dimer-pair basis states; this mixing leads to coupling-dependent structure factors. The $S_{tot} = 0$ ground state of the rectangular

tetramer is a linear superposition of unexcited and doubly-excited dimer pairs,

$$|\Psi_{0,1}\rangle = -\sin(\theta_0)|\sigma\sigma\rangle_0 + \cos(\theta_0)|\rho\rho\rangle \quad (3.106)$$

where the mixing angle θ_0 between these basis states satisfies

$$\tan(\theta_0) = -\frac{\sqrt{3}\alpha/2}{1 - \alpha/2 + \sqrt{1 - \alpha + \alpha^2}}. \quad (3.107)$$

The matrix elements of the neutron scattering transition operator V_α of Eq.(3.135) between the ground state $|\Psi_{0,1}\rangle$ and the three $S_{tot} = 1$ final states $|\Psi_{1,1\dots 3}\rangle$ may then be determined using the results of Eqs.(3.76-3.83). Specializing to $S_{z\,tot} = +1$ final states for illustration, these matrix elements are

$${}_{1,1}\langle\Psi_{1,n}|V_+|\Psi_{0,1}\rangle = \begin{cases} \frac{(C_0+S_0/\sqrt{3})}{2\sqrt{2}} (f_1 - f_2 - f_3 + f_4), & n = 1 \\ \frac{(C_0+S_0/\sqrt{3})}{2\sqrt{2}} (f_1 - f_2 + f_3 - f_4), & n = 2 \\ -\frac{S_0}{\sqrt{6}} (f_1 + f_2 - f_3 - f_4), & n = 3 \end{cases} \quad (3.108)$$

where C_0 and S_0 are $\cos(\theta_0)$ and $\sin(\theta_0)$ respectively.

On converting these matrix elements to structure factors using Eqs.(2.13,2.15) we find different functional forms for each transition for both the single crystal and powder average results, as a result of the different weight factors and the three distinct ion pair separations. The powder average, unpolarized structure factors are

$$\bar{S}^{\Psi_{0,1} \rightarrow \Psi_{1,n}}(q) =$$

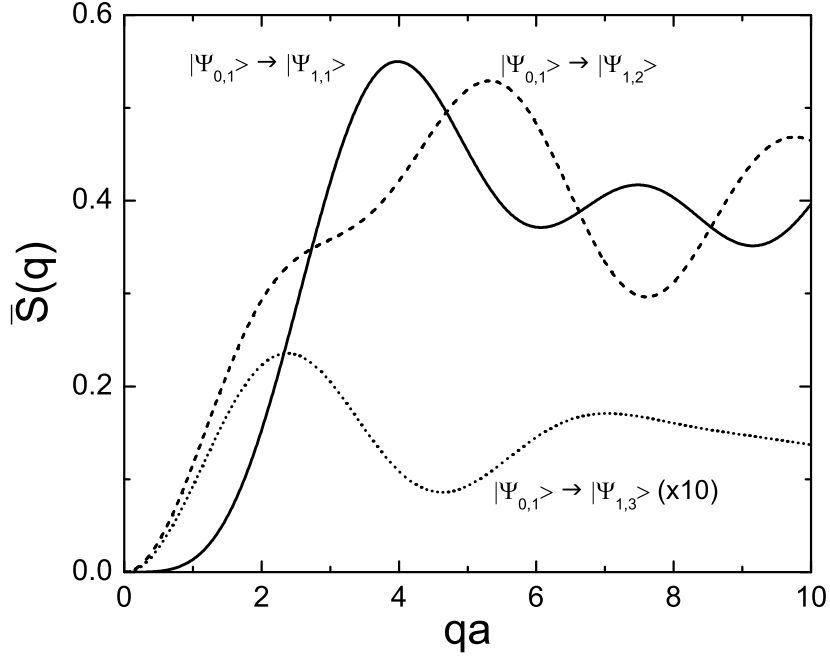


Figure 3.19: Powder average, unpolarized structure factors $\bar{S}(q)$ for the excitation of the three $S_{tot} = 1$ excited states of the rectangular spin tetramer from the $S_{tot} = 0$ ground state $|\Psi_{0,1}\rangle$. The interdimer coupling strength is $\alpha = 0.3$, and the side length ratio is $b/a = 1.5$. The structure factor to the third state is scaled up by a factor of 10 for visibility.

$$\left\{ \begin{array}{ll} \frac{(C_0 + S_0/\sqrt{3})^2}{2} (1 - j_0(qa) - j_0(qb) + j_0(qc)), & n = 1 \\ \frac{(C_0 + S_0/\sqrt{3})^2}{2} (1 - j_0(qa) + j_0(qb) - j_0(qc)), & n = 2 \\ \frac{2}{3} S_0^2 (1 + j_0(qa) - j_0(qb) - j_0(qc)), & n = 3 \end{array} \right. \quad (3.109)$$

where $c = \sqrt{a^2 + b^2}$. In Figure 3.19 we show these structure factors for a case with moderate interdimer coupling ($\alpha = 0.3$) for a rectangle of side ratio $b/a = 1.5$. The transition to the highest $S_{tot} = 1$ excited state $|\Psi_{1,3}\rangle$ is much weaker than the other two, and so is multiplied by a factor of 10 in the figure for visibility.

Note that the excitation of the highest $S_{tot} = 1$ state $|\Psi_{1,3}\rangle$, which is a doubly-

excited dimer ($|\sigma\sigma\rangle$), is only possible because the ground state has an $O(\alpha)$ excited component, in addition to the dominant “bare” $|\rho\rho\rangle$ basis state. The weakness of the $|\Psi_{1,3}\rangle$ signal is because the structure factor is proportional to the nonleading ground state amplitude squared, so that it is $O(\alpha^2)$. The observation of similar “non-valence state” transitions which are forbidden at $O(\alpha^0)$ should allow direct experimental tests of the “interaction” terms in quantum spin Hamiltonians such as this one. The strength alone is a sensitive measure of α , and the spatial modulation of $\bar{S}(q)$ is clearly different from the $O(\alpha^0)$ transitions that dominate the structure factors of the lower-lying $S_{tot} = 1$ states.

The detailed q -dependence of the structure factors can be used as a “fingerprint” to test whether a given structure is indeed the magnetically active system. As an example, in Figure 3.20 we show that the detailed form of the structure factor to the first $S_{tot} = 1$ state shows significant variation as we vary the rectangle side length ratio b/a . (Values of $b/a = 1, 2$ and 4 are shown.) This type of dependence could be used to establish the geometry of a magnetic subsystem, or to check powder neutron scattering results against the geometry of a proposed spin system.

Spin $\frac{1}{2}$ Linear Tetramer

The linear tetramer is the simplest of the spin tetramer systems; it consists of two dimers with internal magnetic couplings of strength J , with a single interdimer coupling between two adjacent end spins, of strength αJ (see Figure 3.16). The term “linear” refers only to the pattern of magnetic couplings; the actual spatial geometry of our linear tetramer is not assumed to be a straight line. The “Clemson tetramer” NaCuAsO_4 [51] is a recent example of a possible “linear tetramer” that does not have a true collinear dimer geometry.

The linear tetramer Hamiltonian matrix is also relatively simple in the dimer pair basis of Eqs.(3.68-3.70). The single $S_{tot} = 2$ basis state $|\langle\sigma\sigma\rangle_2$ is diagonal, with

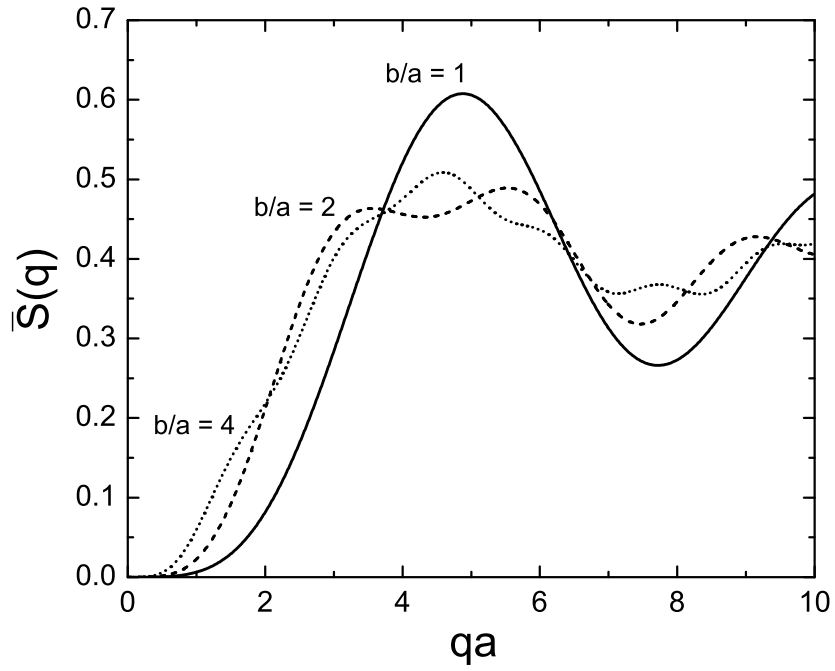


Figure 3.20: Variation of the $\bar{S}(q)$ structure factors for excitation of the lowest $S_{tot} = 1$ state of the rectangular spin tetramer with side length ratio b/a . This illustrates the use of powder structure factors in establishing the internal geometry of spin clusters. The dimer coupling is $\alpha = 0.3$, however this only affects the overall scale.

energy

$$E_2 = \left(\frac{1}{2} + \frac{1}{4}\alpha \right) J . \quad (3.110)$$

The $S_{tot} = 1$ basis state $|(\rho\sigma)_A\rangle$ is also diagonal, with energy

$$E_{1,2} = -\left(\frac{1}{2} - \frac{1}{4}\alpha \right) J . \quad (3.111)$$

The remaining $S_{tot} = 1$ and $S_{tot} = 0$ two-dimensional Hamiltonian matrices are

$$\mathcal{H}_{S_{tot}=1} = \frac{1}{2} J \begin{bmatrix} 1 - \frac{1}{2}\alpha & \alpha \\ \alpha & -1 - \frac{1}{2}\alpha \end{bmatrix} \quad (3.112)$$

and

$$\mathcal{H}_{S_{tot}=0} = \frac{1}{2} J \begin{bmatrix} 1 - \alpha & \frac{\sqrt{3}}{2}\alpha \\ \frac{\sqrt{3}}{2}\alpha & -3 \end{bmatrix} \quad (3.113)$$

with eigenvalues

$$E_{1,\{1_3\}} = -\left(\frac{1}{4}\alpha \pm \frac{1}{2}\sqrt{1 + \alpha^2} \right) J \quad (3.114)$$

and

$$E_{0,\{1_2\}} = -\left(\frac{1}{2} + \frac{1}{4}\alpha \pm \sqrt{1 - \frac{1}{2}\alpha + \frac{1}{4}\alpha^2} \right) J \quad (3.115)$$

respectively.

The susceptibility of the linear tetramer, which follows from these energy levels and Eq.(2.6), is given in Table 3.3. As was the case with the rectangular tetramer, the expression we find for the (less experimentally relevant) specific heat is too lengthy to tabulate here.

The neutron scattering structure factors from the linear tetramer $S_{tot} = 0$ ground state $|\Psi_{0,1}\rangle$ to the three $S_{tot} = 1$ excited states $|\Psi_{1,1...3}\rangle$ may be calculated using the same techniques we applied to the rectangular tetramer. The results are somewhat more complicated, since two of the $S_{tot} = 1$ linear tetramer states are rotated be-

tween the dimer-pair basis states, in addition to the ground state basis rotation we found for the rectangular tetramer. The energy eigenvectors in these sectors are the superpositions of dimer-pair basis states given in Table 3.9, with mixing angles that satisfy

$$\tan(\theta_1) = \frac{\alpha}{1 + \sqrt{1 + \alpha^2}} , \quad (3.116)$$

$$\tan(\theta_0) = \frac{\sqrt{3}\alpha/4}{1 - \alpha/4 + \sqrt{1 - \alpha/2 + \alpha^2/4}} . \quad (3.117)$$

This more complicated basis mixing pattern introduces a new feature, which is that the functional forms of the structure factors for the two mixed $S_{tot} = 1$ states, $|\Psi_{1,1}\rangle$ and $|\Psi_{1,3}\rangle$, depend on the dimer coupling α . (In the rectangular tetramer system discussed previously we found that changing the dimer coupling α only changed the overall normalization of the structure factors, not their detailed q dependence.)

We will give explicit results for the first transition, $|\Psi_{0,1}\rangle \rightarrow |\Psi_{1,1}\rangle$, and then simply quote the results for the two remaining final states. The matrix element of the neutron scattering transition operator V_a is

$${}_{11}\langle\Psi_{1,1}|V_+|\Psi_{0,1}\rangle = c_{14}(f_1 - f_4) + c_{23}(f_2 - f_3) \quad (3.118)$$

where

$$\begin{Bmatrix} c_{14} \\ c_{23} \end{Bmatrix} = \pm \frac{(C_0 + S_0/\sqrt{3})C_1}{2\sqrt{2}} + \frac{S_0S_1}{\sqrt{6}} \quad (3.119)$$

and $C_{0,1}$ and $S_{0,1}$ are respectively cos and sin of the linear tetramer basis state mixing angles, which were defined in Eqs.(3.116,3.117). The resulting unpolarized powder structure factor for this transition, using Eqs.(2.15,2.16), is

$$\bar{S}^{\Psi_{0,1} \rightarrow \Psi_{1,1}} =$$

$$2\left(c_{14}^2(1 - j_0(qr_{14})) + c_{23}^2(1 - j_0(qr_{23})) - 2c_{14}c_{23}((j_0(qr_{12}) - j_0(qr_{13})))\right). \quad (3.120)$$

The transition from the ground state to the second linear tetramer $S_{tot} = 1$ excited state is given by a matrix element we encountered previously in the rectangular tetramer problem, except for a change in spatial geometry. The result for the unpolarized powder structure factor with completely general ion positions is

$$\begin{aligned} \bar{S}^{\Psi_{0,1} \rightarrow \Psi_{1,2}}(q) = \\ \frac{(C_0 + S_0/\sqrt{3})^2}{2} \left(1 + \frac{1}{2}(-j_0(qr_{12}) - j_0(qr_{13}) + j_0(qr_{14}) \right. \\ \left. + j_0(qr_{23}) - j_0(qr_{24}) - j_0(qr_{34})) \right). \end{aligned} \quad (3.121)$$

The structure factor for the third $S_{tot} = 1$ state $\Psi_{1,3}$ may be found from the $\Psi_{1,1}$ structure factor of Eq.(3.120) with the simple substitutions $(C_1 \rightarrow S_1), (S_1 \rightarrow -C_1)$.

We will illustrate the predicted structure factors for the linear tetramer assuming parameters appropriate for the candidate material NaCuAsO₄ [51, 52]. The ion pair separations are $r_{12} = r_{34} = 3.641 \text{ \AA}$, $r_{13} = r_{24} = 3.863 \text{ \AA}$ and $r_{23} = 3.151 \text{ \AA}$. The copper positions are consistent with planarity, although our results do not require this assumption. There are indications of three $S_{tot} = 1$ levels in this material from a recent inelastic neutron scattering experiment, with energies of approximately 9, 11 and 18 meV [52]; in the linear tetramer model this suggests parameters of $J \approx 10 \text{ meV}$ and $\alpha \approx 0.4$, which we will assume here. (The structure factors only depend on α .) We also incorporated a simple Cu²⁺ ionic form factor, $F(q) = 1/(1 + q^2/q_0^2)^3$ with $q_0 = 8.0 \text{ \AA}^{-1}$, which agrees with the online ILL Cu²⁺ form factor [58] to $\lesssim 0.5 \%$ over the range of q shown. Our results are shown in Figure 3.21; characteristic features include the displaced relative maxima of the intensities of the two lower states, and the much weaker transition to the highest $S_{tot} = 1$ state. The results for the two

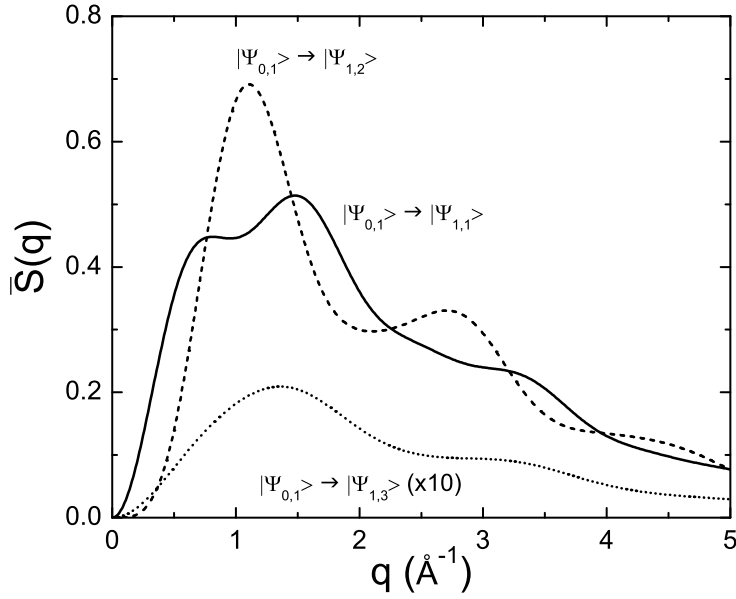


Figure 3.21: Powder average, unpolarized structure factors $\bar{S}(q)$ for the excitation of the three $S_{tot} = 1$ states of the linear tetramer, including the ionic form factor, with magnetic coupling ratio $\alpha = 0.4$ and ion positions taken from the NaCuAsO_4 structure [51]. The structure factor to the third state is scaled up by a factor of 10 for visibility.

lower states are rather insensitive to α . The overall scale of the $|\Psi_{1,3}\rangle$ structure factor however is quite sensitive to α , and scales approximately as α^2 . A measurement of the relative strength of these transitions would provide a useful determination of α , which could be compared with the value extracted from the energy levels. (In principle the susceptibility could also be used to determine α , but we have found that it has a rather weak α dependence in this system.)

In Figure 3.22, we show these results in a contour plot, approximately as would be observed in a neutron scattering experiment. (Our results should be multiplied by the energy-dependent factor k'/k of Eq.(2.12) for a direct comparison with experiment.) To generate this plot we have convolved a Gaussian energy resolution function, $\exp(-(E - E_i)^2/2\sigma_E^2)$ with $\sigma_E = 0.5$ meV, with the structure factors to the

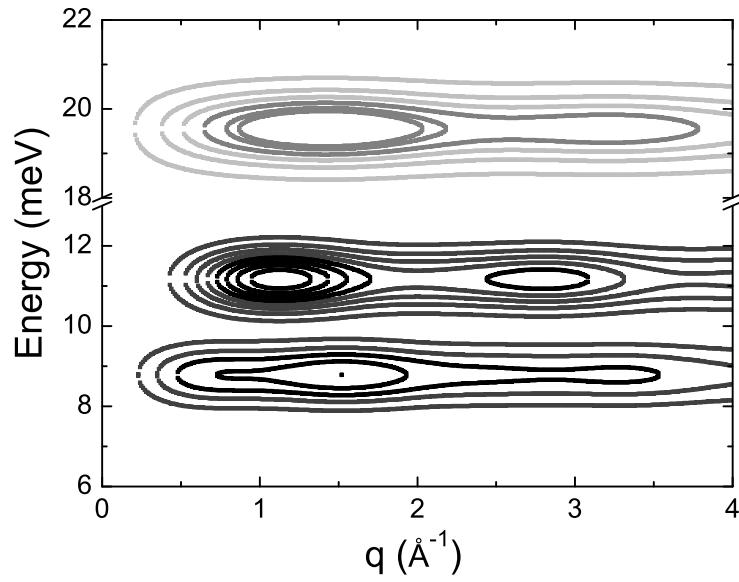


Figure 3.22: Contours of equal intensity of the powder average, unpolarized structure factors of the linear tetramer, with parameters appropriate to NaCuAsO_4 , as in Fig.3.21. The contours are normalized to the peak of the first transition, and intervals of 0.1 in intensity are shown for the two lower states. The much weaker third transition shows intervals of 0.01.

three $S_{tot} = 1$ states. The intensities are shown relative to the maximum excitation intensity of the transition to the lowest $S_{tot} = 1$ state, $|\Psi_{0,1}\rangle \rightarrow |\Psi_{1,1}\rangle$. Note the characteristic strong peak in intensity of the second transition, $|\Psi_{0,1}\rangle \rightarrow |\Psi_{1,2}\rangle$, near $1.1 \text{ \AA}^{-1}$. Comparison of these general features with the data of Nagler *et al.* [52] suggests that the linear tetramer model does indeed give a realistic description of neutron scattering from NaCuAsO_4 .

3.3.3 Spin $\frac{3}{2}$ Tetramer

For the $S = \frac{3}{2}$ tetramer, the energy eigenstates of the isotropic Heisenberg Hamiltonian with general S_{tot}^z are given in Table 3.10. The magnetic substates are all degenerate in the absence of an applied magnetic field, but can be split linearly in accordance with the Zeeman field term. The ground state of the $S = \frac{3}{2}$ tetramer can either have a nonmagnetic $S = 0$ ground state or a magnetic $S = 1$ ground state depending upon the values of α and γ . Simple examination of the energy levels in Table 3.10 indicates that, assuming antiferromagnetic exchange for J , the ground state will be non-magnetic when both α and γ are less than $\frac{4}{3}$.

We now present the method for determining the partition function and magnetic susceptibility for the $S=3/2$ coupled dimer model. Due to the length of the equations, we present the eigenstates and eigenvalues explicitly in Table 3.10 and represent the magnetic observables as summations over energy eigenvalues. Using this method, the partition function is given by

$$\begin{aligned}
Z = \sum_{i=1}^N e^{-\beta E_i} &= \sum_{E_i} (2S_{tot} + 1) e^{-\beta E_i} = \\
&5 e^{\frac{3J\beta}{4}(8-3\alpha+\gamma)} + 3 e^{-\frac{J\beta}{4}(-32-3\alpha+9\gamma)} + 7 e^{\frac{J\beta}{4}(-8+11\alpha+3\gamma)} + e^{\frac{J\beta}{4}(8+11\alpha+11\gamma)} + \\
&7 e^{\frac{J\beta}{4}(4-9\alpha+11\gamma)} + 3 e^{\frac{J\beta}{4}(12+11\alpha+3\gamma)} + e^{-\frac{3J\beta}{4}(-16+3\alpha+3\gamma)} + 5 e^{\frac{J\beta}{4}(4+11\alpha+3\gamma)} +
\end{aligned}$$

Table 3.10: Energy levels of a coupled dimer of spin- $\frac{3}{2}$ ions.

S_{tot}	Spin State $ S_{tot} S_z\rangle_{S_\alpha, S_\gamma}$	Energy Level	INS Energy Gap	INS Structure Factor
6	$6 S_z > 3,3$	$J(9 + \frac{9}{4}\alpha + \frac{9}{4}\gamma)$		
5	$5 S_z > 3,3$	$J(3 + \frac{9}{4}\alpha + \frac{9}{4}\gamma)$		
	$5 S_z > 3,2$	$J(6 + \frac{9}{4}\alpha - \frac{3}{4}\gamma)$		
	$5 S_z > 2,3$	$J(6 - \frac{3}{4}\alpha + \frac{9}{4}\gamma)$		
4	$4 S_z > 3,3$	$J(-2 + \frac{9}{4}\alpha + \frac{9}{4}\gamma)$		
	$4 S_z > 3,2$	$J(1 + \frac{9}{4}\alpha - \frac{3}{4}\gamma)$		
	$4 S_z > 3,1$	$J(3 + \frac{9}{4}\alpha - \frac{11}{4}\gamma)$		
	$4 S_z > 2,3$	$J(1 - \frac{3}{4}\alpha + \frac{9}{4}\gamma)$		
	$4 S_z > 1,3$	$J(3 - \frac{11}{4}\alpha + \frac{9}{4}\gamma)$		
	$4 S_z > 2,2$	$J(4 - \frac{3}{4}\alpha - \frac{3}{4}\gamma)$		
3	$3 S_z > 3,3$	$J(-6 + \frac{9}{4}\alpha + \frac{9}{4}\gamma)$		
	$3 S_z > 3,2$	$J(-3 + \frac{9}{4}\alpha - \frac{3}{4}\gamma)$		
	$3 S_z > 3,1$	$J(-1 + \frac{9}{4}\alpha - \frac{11}{4}\gamma)$		
	$3 S_z > 2,3$	$J(-3 - \frac{3}{4}\alpha + \frac{9}{4}\gamma)$		
	$3 S_z > 1,3$	$J(-1 - \frac{11}{4}\alpha + \frac{9}{4}\gamma)$		
	$3 S_z > 2,2$	$J(-\frac{3}{4}\alpha - \frac{3}{4}\gamma)$		
	$3 S_z > 2,1$	$J(2 - \frac{3}{4}\alpha - \frac{11}{4}\gamma)$		
	$3 S_z > 1,2$	$J(2 - \frac{11}{4}\alpha - \frac{3}{4}\gamma)$		
	$3 S_z > 3,0$	$J(\frac{9}{4}\alpha - \frac{15}{4}\gamma)$		
	$3 S_z > 0,3$	$J(-\frac{15}{4}\alpha + \frac{9}{4}\gamma)$		
2	$2 S_z > 3,3$	$J(-9 + \frac{9}{4}\alpha + \frac{9}{4}\gamma)$		
	$2 S_z > 3,2$	$J(-6 + \frac{9}{4}\alpha - \frac{3}{4}\gamma)$		
	$2 S_z > 3,1$	$J(-4 + \frac{9}{4}\alpha - \frac{11}{4}\gamma)$		
	$2 S_z > 2,3$	$J(-6 - \frac{3}{4}\alpha + \frac{9}{4}\gamma)$		
	$2 S_z > 1,3$	$J(-4 - \frac{11}{4}\alpha + \frac{9}{4}\gamma)$		
	$2 S_z > 2,2$	$J(-3 - \frac{3}{4}\alpha - \frac{3}{4}\gamma)$		
	$2 S_z > 2,1$	$J(-1 - \frac{3}{4}\alpha - \frac{11}{4}\gamma)$		
	$2 S_z > 1,2$	$J(-1 - \frac{11}{4}\alpha - \frac{3}{4}\gamma)$		
	$2 S_z > 1,1$	$J(1 - \frac{11}{4}\alpha - \frac{11}{4}\gamma)$		
	$2 S_z > 2,0$	$J(-\frac{3}{4}\alpha - \frac{15}{4}\gamma)$		
	$2 S_z > 0,2$	$J(-\frac{15}{4}\alpha - \frac{3}{4}\gamma)$		
1	$1 S_z > 3,3$	$J(-11 + \frac{9}{4}\alpha + \frac{9}{4}\gamma)$	J	$2 F(\vec{q}) ^2(2 - 4j_0(qd_1) + j_0(qd_2) + j_0(qd_3))$
	$1 S_z > 3,2$	$J(-8 + \frac{9}{4}\alpha - \frac{3}{4}\gamma)$	$4J$	$\frac{ F(\vec{q}) ^2}{2}(1 - j_0(qd_3))$
	$1 S_z > 2,3$	$J(-8 - \frac{3}{4}\alpha + \frac{9}{4}\gamma)$	$J(4 - 3\alpha)$	$\frac{ F(\vec{q}) ^2}{2}(1 - j_0(qd_2))$
	$1 S_z > 2,2$	$J(-5 - \frac{3}{4}\alpha - \frac{3}{4}\gamma)$		
	$1 S_z > 2,1$	$J(-3 - \frac{3}{4}\alpha - \frac{11}{4}\gamma)$		
	$1 S_z > 1,2$	$J(-3 - \frac{11}{4}\alpha - \frac{3}{4}\gamma)$		
	$1 S_z > 1,1$	$J(-1 - \frac{11}{4}\alpha - \frac{11}{4}\gamma)$		
	$1 S_z > 1,0$	$J(-\frac{11}{4}\alpha - \frac{15}{4}\gamma)$		
	$1 S_z > 0,1$	$J(-\frac{15}{4}\alpha - \frac{11}{4}\gamma)$		
0	$0 S_z > 3,3$	$J(-12 + \frac{9}{4}\alpha + \frac{9}{4}\gamma)$	Ground State	
	$0 S_z > 2,2$	$J(-6 - \frac{3}{4}\alpha - \frac{3}{4}\gamma)$		
	$0 S_z > 1,1$	$J(-2 - \frac{11}{4}\alpha - \frac{11}{4}\gamma)$		
	$0 S_z > 0,0$	$J(-\frac{15}{4}\alpha - \frac{15}{4}\gamma)$		

$$\begin{aligned}
& 9e^{-\frac{J\beta}{4}(12-11\alpha+9\gamma)} + 5e^{\frac{J\beta}{4}(-4+11\alpha+11\gamma)} + 7e^{\frac{3J\beta}{4}(\alpha+\gamma)} + 11e^{\frac{3J\beta}{4}(-8-3\alpha+\gamma)} + 5e^{\frac{3J\beta}{4}(\alpha+5\gamma)} + \\
& 7e^{-\frac{3J\beta}{4}(-5\alpha+3\gamma)} + 7e^{-\frac{J\beta}{4}(-4-11\alpha+9\gamma)} + 5e^{\frac{3J\beta}{4}(5\alpha+\gamma)} + 7e^{\frac{3J\beta}{4}(-3\alpha+5\gamma)} + e^{\frac{15J\beta}{4}(\alpha+\gamma)} + \\
& 3e^{\frac{J\beta}{4}(15\alpha+11\gamma)} + 9e^{\frac{J\beta}{4}(-12-9\alpha+11\gamma)} + 3e^{\frac{J\beta}{4}(11\alpha+15\gamma)} + 3e^{\frac{J\beta}{4}(4+11\alpha+11\gamma)} + 11e^{-\frac{3J\beta}{4}(4+3\alpha+3\gamma)} + \\
& 9e^{-\frac{J\beta}{4}(4-3\alpha+9\gamma)} + 9e^{\frac{J\beta}{4}(-4-9\alpha+3\gamma)} + 7e^{\frac{3J\beta}{4}(4-3\alpha+\gamma)} + 9e^{\frac{J\beta}{4}(-16+3\alpha+3\gamma)} + 9e^{-\frac{J\beta}{4}(-8+9\alpha+9\gamma)} + \\
& 5e^{\frac{J\beta}{4}(16-9\alpha+11\gamma)} + 5e^{\frac{3J\beta}{4}(4+\alpha+\gamma)} + 3e^{\frac{J\beta}{4}(20+3\alpha+3\gamma)} + 7e^{-\frac{3J\beta}{4}(-4-\alpha+3\gamma)} + 7e^{-\frac{3J\beta}{4}(-8+3\alpha+3\gamma)} + \\
& 11e^{-\frac{3J\beta}{4}(8-\alpha+3\gamma)} + 3e^{-\frac{J\beta}{4}(-44+9\alpha+9\gamma)} + 7e^{\frac{J\beta}{4}(-8+3\alpha+11\gamma)} + 3e^{\frac{J\beta}{4}(12+3\alpha+11\gamma)} + 3e^{\frac{J\beta}{4}(32-9\alpha+3\gamma)} + \\
& 5e^{\frac{J\beta}{4}(4+3\alpha+11\gamma)} + 13e^{-\frac{9J\beta}{4}(4+\alpha+\gamma)} + 5e^{-\frac{9J\beta}{4}(-4+\alpha+\gamma)} + 5e^{-\frac{3J\beta}{4}(-8-\alpha+3\gamma)} + \\
& 5e^{-\frac{J\beta}{4}(-16-11\alpha+9\gamma)} + e^{\frac{3J\beta}{4}(8+\alpha+\gamma)}, \tag{3.122}
\end{aligned}$$

and the magnetic susceptibility is given by

$$\begin{aligned}
\chi &= \frac{\beta}{Z} \sum_{i=1}^N (M_z^2)_i e^{-\beta E_i} = \frac{1}{3} (g\mu_B)^2 \frac{\beta}{Z} \sum_{E_i} (2S_{tot} + 1) (S_{tot} + 1) S_{tot} e^{-\beta E_i} \\
&= \frac{N_A \beta (\mu g)^2}{4Z} \left(2e^{-\frac{J\beta}{4}(-32+9\alpha-3\gamma)} + 28e^{-\frac{3J\beta}{4}(3\alpha-5\gamma)} + 28e^{\frac{J\beta}{4}(-8+11\alpha+3\gamma)} + 10e^{-\frac{3J\beta}{4}(-8+3\alpha-\gamma)} + \right. \\
& 2e^{\frac{J\beta}{4}(12+11\alpha+3\gamma)} + 10e^{\frac{J\beta}{4}(4+11\alpha+3\gamma)} + 60e^{-\frac{J\beta}{4}(12+9\alpha-11\gamma)} + 10e^{-\frac{J\beta}{4}(-16+9\alpha-11\gamma)} + \\
& 10e^{\frac{3J\beta}{4}(8+\alpha-3\gamma)} + 10e^{\frac{J\beta}{4}(16+11\alpha-9\gamma)} + 60e^{\frac{J\beta}{4}(-4+3\alpha-9\gamma)} + 28e^{-\frac{3J\beta}{4}(-4+3\alpha-\gamma)} + \\
& 10e^{\frac{J\beta}{4}(-4+11\alpha+11\gamma)} + 28e^{\frac{3J\beta}{4}(\alpha+\gamma)} + 10e^{\frac{3J\beta}{4}(\alpha+5\gamma)} + 60e^{\frac{J\beta}{4}(-12+11\alpha-9\gamma)} + 28e^{\frac{3J\beta}{4}(4+\alpha-3\gamma)} + \\
& 28e^{-\frac{J\beta}{4}(-4+9\alpha-11\gamma)} + 10e^{\frac{3J\beta}{4}(5\alpha+\gamma)} + 2e^{\frac{J\beta}{4}(15\alpha+11\gamma)} + 2e^{\frac{J\beta}{4}(11\alpha+15\gamma)} + 2e^{\frac{J\beta}{4}(4+11\alpha+11\gamma)} + \\
& 110e^{-\frac{3J\beta}{4}(4+3\alpha+3\gamma)} + 110e^{\frac{3J\beta}{4}(-8+\alpha-3\gamma)} + 60e^{\frac{J\beta}{4}(-16+3\alpha+3\gamma)} + 60e^{-\frac{J\beta}{4}(-8+9\alpha+9\gamma)} + \\
& \left. 10e^{\frac{3J\beta}{4}(4+\alpha+\gamma)} + 2e^{\frac{J\beta}{4}(20+3\alpha+3\gamma)} + 28e^{-\frac{3J\beta}{4}(-8+3\alpha+3\gamma)} + 2e^{-\frac{J\beta}{4}(-44+9\alpha+9\gamma)} + \right)
\end{aligned}$$

$$\begin{aligned}
& 28 e^{\frac{J\beta}{4}(-8+3\alpha+11\gamma)} + 2 e^{\frac{J\beta}{4}(12+3\alpha+11\gamma)} + 10 e^{\frac{J\beta}{4}(4+3\alpha+11\gamma)} + 182 e^{-\frac{9J\beta}{4}(4+\alpha+\gamma)} + \\
& 10 e^{-\frac{9J\beta}{4}(-4+\alpha+\gamma)} + 28 e^{\frac{3J\beta}{4}(5\alpha-3\gamma)} + 110 e^{-\frac{3J\beta}{4}(8+3\alpha-\gamma)} + 60 e^{-\frac{J\beta}{4}(4+9\alpha-3\gamma)} + \\
& 2 e^{\frac{J\beta}{4}(32+3\alpha-9\gamma)} + 28 e^{\frac{J\beta}{4}(4+11\alpha-9\gamma)}. \tag{3.123}
\end{aligned}$$

In these formulas, the sum $\sum_{i=1}^N$ is over all N independent energy eigenstates (including magnetic substates), the sum $\sum_{E_i}$ is over energy levels only, $M_z = mg\mu_B$ where $m = S_{tot}^z/\hbar$ is the integral or half-integral magnetic quantum number, and g is the Lande g -factor, $\beta = \frac{1}{k_B T}$ and k_B is Boltzman's constant [28]. The heat capacity can also be determined from

$$C = k_B \beta^2 \frac{d^2 \ln(Z)}{d\beta^2}. \tag{3.124}$$

The heat capacity is especially useful for confirming the proper accounting of eigenstates, through a calculation of the magnetic entropy of the tetramer system at large temperature,

$$\begin{aligned}
\frac{S}{k_B} &= \int_0^\infty \frac{C}{k_B} \frac{d\beta}{\beta} = \\
\ln(\mathcal{N}/\mathcal{N}_0) &= \begin{cases} 2 \ln(2) & \alpha < \frac{4}{3}, \gamma < \frac{4}{3} \\ \ln(\frac{256}{3}) & \alpha > \frac{4}{3}, \gamma > \frac{4}{3}. \end{cases} \tag{3.125}
\end{aligned}$$

Here $\mathcal{N}$ is the dimensionality of the full Hilbert space and $\mathcal{N}_0$ is the degeneracy of the ground state manifold.

Using the methods presented in Haraldsen *et al.* [11], we next determine the excitation energies and structure factors for the observable transitions of the coupled dimer models shown in Figs. 3.15(b)-(d).

With respect to the spin-3/2 rhombus model, the values of the magnetic interactions quoted in literature [64] suggest a $S_{tot} = 0$ ground state, with dimer states $S_\alpha = 3$ and $S_\gamma = 3$. Therefore, only three of the nine $S_{tot} = 1$ states are accessible

from that ground state through INS. The respective excitation energies ($E_{S_{tot}, S_\alpha, S_\gamma}$) are determined to be

$$E_{0,3,3 \rightarrow 1,3,3} = J,$$

$$E_{0,3,3 \rightarrow 1,3,2} = J(4 - 3\gamma), \quad (3.126)$$

$$E_{0,3,3 \rightarrow 1,2,3} = J(4 - 3\alpha),$$

and the powder average INS structure factors intensities ($\bar{S}(q)_{S_{tot}, S_\alpha, S_\gamma}$) for these transitions are

$$\begin{aligned} \bar{S}(q)_{0,3,3 \rightarrow 1,3,3} = \\ 2|F(\vec{q})|^2(2 - 4j_0(qd_1) + j_0(qd_2) + j_0(qd_3)), \\ \bar{S}(q)_{0,3,3 \rightarrow 1,3,2} = \frac{|F(\vec{q})|^2}{2}(1 - j_0(qd_3)), \text{ and} \end{aligned} \quad (3.127)$$

$$\bar{S}(q)_{0,3,3 \rightarrow 1,2,3} = \frac{|F(\vec{q})|^2}{2}(1 - j_0(qd_2)),$$

where d_1 , d_2 , and d_3 are the inter-atomic separations (shown in Fig. 3.15) and $|F(\vec{q})|$ is the Ru^{5+} magnetic form factor (a parameterization is given in Ref. [59] and [60]). The $0, 3, 3 \rightarrow 1, 3, 3$ is an excitation of the full tetramer, and the other two transitions are excitations of individual dimers.

3.3.4 Application to Na_3RuO_4

The structure of Na_3RuO_4 was first reported by Darriet *et al.* [61]. Refinement of the crystal structure in these preliminary measurements shows that Na_3RuO_4 consists of oxygen coordinated sodium and ruthenium sites within the ab -plane, separated by a single layer of sodium sites displaced along the c -axis. The structure of Na_3RuO_4 was recently re-refined and was determined to be monoclinic, with space group $C2/m$ and lattice parameters $a = 11.0295(6)$ Å, $b = 12.8205(7)$ Å and $c = 5.7028(3)$ Å with

$\beta = 109.90(3)^\circ$ [62, 63]. Figure 3.15(a) illustrates a single plane of Ru ions together with coplanar oxygen and sodium ions. The Ru ions are octahedrally coordinated through shared oxygens, and each Ru^{+5} ion may be modeled as having a local spin $S = \frac{3}{2}$. This arrangement of ions suggests a local magnetic tetramer or lozenge spin system, as shown in Figs. 3.15(a) and (c). An isolated spin-tetramer with exchange constants $J = 3.36$ meV and $J' = 3.88$ meV was first proposed by Drillon *et al.* [64] to describe magnetic susceptibility measurements in this material. The existence of long range antiferromagnetic order below $T \approx 30$ K was also established using Mossbauer spectroscopy [65]. These measurements found that a model based on isolated tetramer clusters with antiferromagnetic interactions was incorrect. Recent measurements of magnetic susceptibility have also been interpreted in terms of a spin-tetramer model [62]. Temperature dependent neutron diffraction studies have confirmed the existence of long-range magnetic order below $T \approx 30$ K. The existence of this long range order immediately calls into question the accuracy of an isolated spin-tetramer model of Na_3RuO_4 . Through an examination of thermodynamic and spectroscopic properties of Na_3RuO_4 and a comparison with theoretical predictions for isolated spin tetramers, we shall see that the isolated spin-tetramer model is indeed inappropriate for Na_3RuO_4 .

Experimental Techniques

Powder samples of Na_3RuO_4 were prepared by solid-state reactions from stoichiometric amount of NaOH and RuO_2 . The stoichiometric mixture was initially ground together and then held at 500 °C for 20 hr. under an O_2 atmosphere. After re-grinding, the powder was heated to 650 °C for another 20 hr, again under an O_2 atmosphere. The resulting dark grey powder was reground and checked for impurity phases using X-ray powder diffraction. If any impurity phases were evident, the powder was refired and the process repeated. This growth procedure is similar to

that described in Ref. [62]. Powder refinement of room temperature X-ray diffraction measurements yielded lattice parameters of $a = 11.012(7)$, $b = 12.809(9)$ and $c = 5.687(3)$ Å and $\beta = 109.91(3)^\circ$ for the monoclinic unit cell with space group $C2/m$ [63]. These values compare well to the fully refined structure described in Ref. [62]. Single crystals of appropriate mass are unfortunately not yet available for INS measurements.

Heat capacity measurements were performed on a small single crystal of mass ≈ 10 mg, which was obtained through the synthesis procedure described above. This single crystal grew as a small platelet, with the c -axis normal to the plane of the platelet. Heat capacity measurements were performed with a commercial calorimeter between $T = 1.8$ K and 300 K using the relaxation technique. Measurements were carried out in zero and 8 T applied magnetic fields, with the magnetic field applied along the c -axis of the single crystal sample.

Magnetization measurements were performed on powder and single crystal samples using a commercial SQUID, as a function of applied magnetic field and temperature. SQUID measurements on the same single crystal sample that was used for heat capacity measurements agree well with those taken on a powder sample.

INS measurements were performed using the MARI time-of-flight spectrometer at the ISIS neutron scattering facility. The sample consisted of ≈ 45 g of Na_3RuO_4 powder in a square aluminum foil sachet (approximately 50 by 50 by 8 mm thick), suspended from the cold-tip of a closed-cycle He^4 refrigerator. The sachet was oriented with the 50x50 mm surface normal to the incident neutron beam. An incident energy of $E_i = 25$ meV was used, and data were taken at several temperatures between $T = 8$ K and $T = 305$ K. This configuration resulted in a measured instrumental energy resolution at the elastic position of $\delta(\hbar\omega) = 0.982(7)$ meV full width at half maximum (FWHM). Data were corrected for detector sensitivity through room temperature measurements on a vanadium standard.

INS measurements were also carried out using the HB3 triple-axis spectrometer at the high flux isotope reactor (HFIR) at Oak Ridge National Laboratory (ORNL). For these measurements, the sample consisted of 20.7 g of Na_3RuO_4 powder in a cylindrical 18 mm diameter and 57 mm tall aluminum sample can. The sample can was sealed under He gas and mounted to the cold-tip of a closed-cycle He^4 refrigerator. Horizontal collimation was chosen respectively as $48' - 40' - 40' - 120'$ between source and monochromator, monochromator and sample, sample and analyzer, and analyzer and detector. The spectrometer was operated with fixed final energy, $E_f = 14.7$ meV, using a pyrolytic graphite (PG 002) monochromator and analyzer. Pyrolytic graphite filters were placed after the sample to substantially reduce higher-order spurious scattering processes. In this configuration, the energy resolution at the elastic position was $\delta(\hbar\omega) = 1.10(2)$ meV FWHM, as measured from the incoherent scattering at $Q = 1.2 \text{ \AA}^{-1}$. The wave vector resolution was measured to be $\delta Q = 0.0407(7) \text{ \AA}^{-1}$ FWHM using the (110) nuclear Bragg peak. All measurements were made for fixed incident neutron monitor count.

Elastic neutron scattering measurements were also performed using the HB3 triple-axis spectrometer, with $E_i = E_f = 14.7$ meV. These measurements were performed on the same powder sample as the inelastic HB3 measurements, with horizontal collimation $48' - 20' - 20' - 70'$. This resulted in an energy resolution at the elastic position of $\delta(\hbar\omega) \approx 0.8$ meV FWHM. The wave vector resolution was measured to be $\delta Q = 0.0254(9) \text{ \AA}^{-1}$ FWHM using the (110) nuclear Bragg peak.

Experimental Results

Figure 3.23 shows the heat capacity as a function of temperature for $H = 0$ and 8 T. There are two clear lambda-like anomalies at $T \approx 23$ and $T \approx 28$ K, signifying phase transitions at these temperatures. Previous neutron diffraction measurements have shown the existence of only a single, broad phase transition around 30 K in

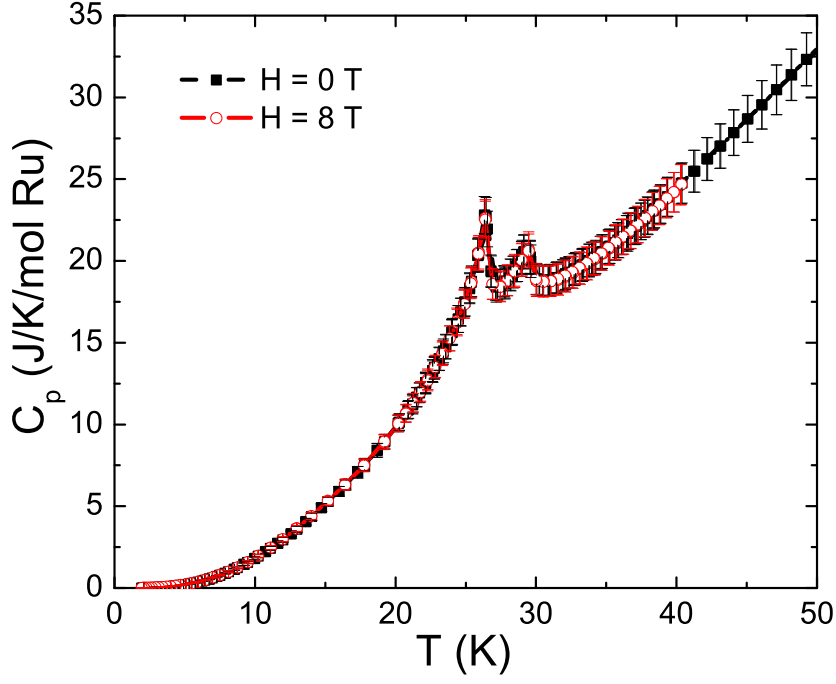


Figure 3.23: Heat capacity of a Na_3RuO_4 single crystal. Measurements were performed at zero field (black squares) and $H = 8$ T (red open circles), with $H \parallel c$. Error bars represent an estimated five percent error in the measurement.

Na_3RuO_4 , corresponding to the onset of long-range magnetic order [62]. Our heat capacity measurements indicate that the observed broad transition is likely due to two successive transitions that occur at similar temperatures. No change was noted in these transition temperatures when measured at $H = 0$ and $H = 8$ T.

The magnetic susceptibility of Na_3RuO_4 was measured over the range $2 \leq T \leq 350$ K; the resulting data is shown in Fig. 3.24. The susceptibility also shows evidence for a phase transition near $T \approx 30$ K. The negative intercept in $\chi^{-1}(T)$ and the decrease in $\chi(T)$ below the transition temperature are consistent with dominantly antiferromagnetic interactions.

Figure 3.25 shows the temperature dependent inelastic neutron scattering data taken on the MARI spectrometer at ISIS. There is significant inelastic scattering

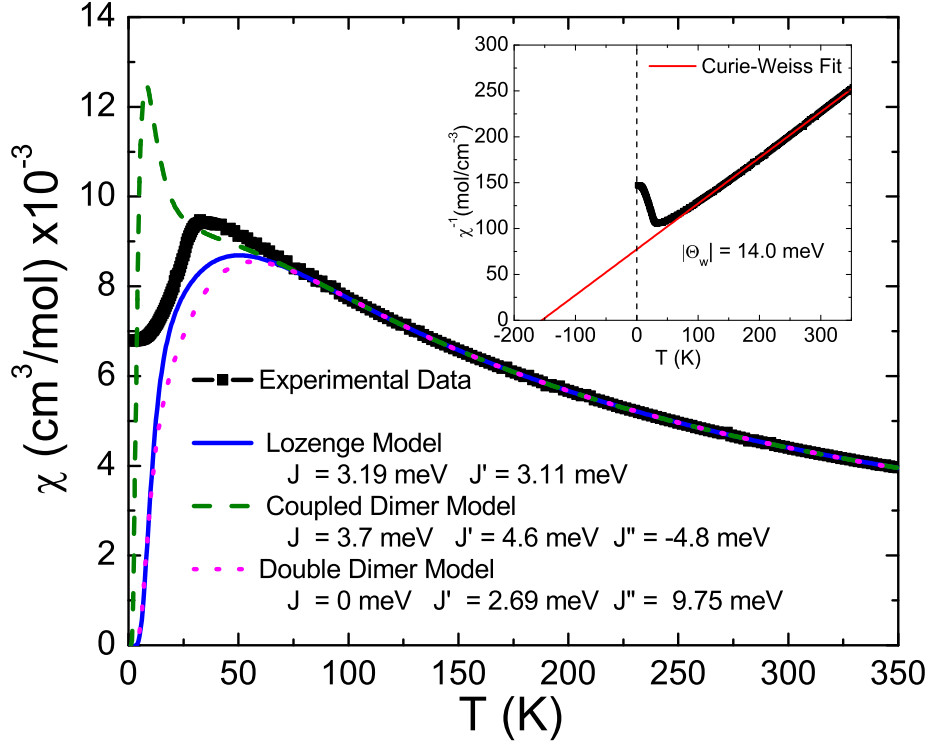


Figure 3.24: Magnetic susceptibility of Na_3RuO_4 (black squares), showing fits using the three models: Lozenge (solid blue), coupled dimer (dotted magenta), double dimer (dashed olive). The inset shows inverse χ with a Curie-Weiss fit as described in the text (which gives $|\Theta_{CW}| = 14.0$ meV, and is consistent with dominantly antiferromagnetic interactions.)

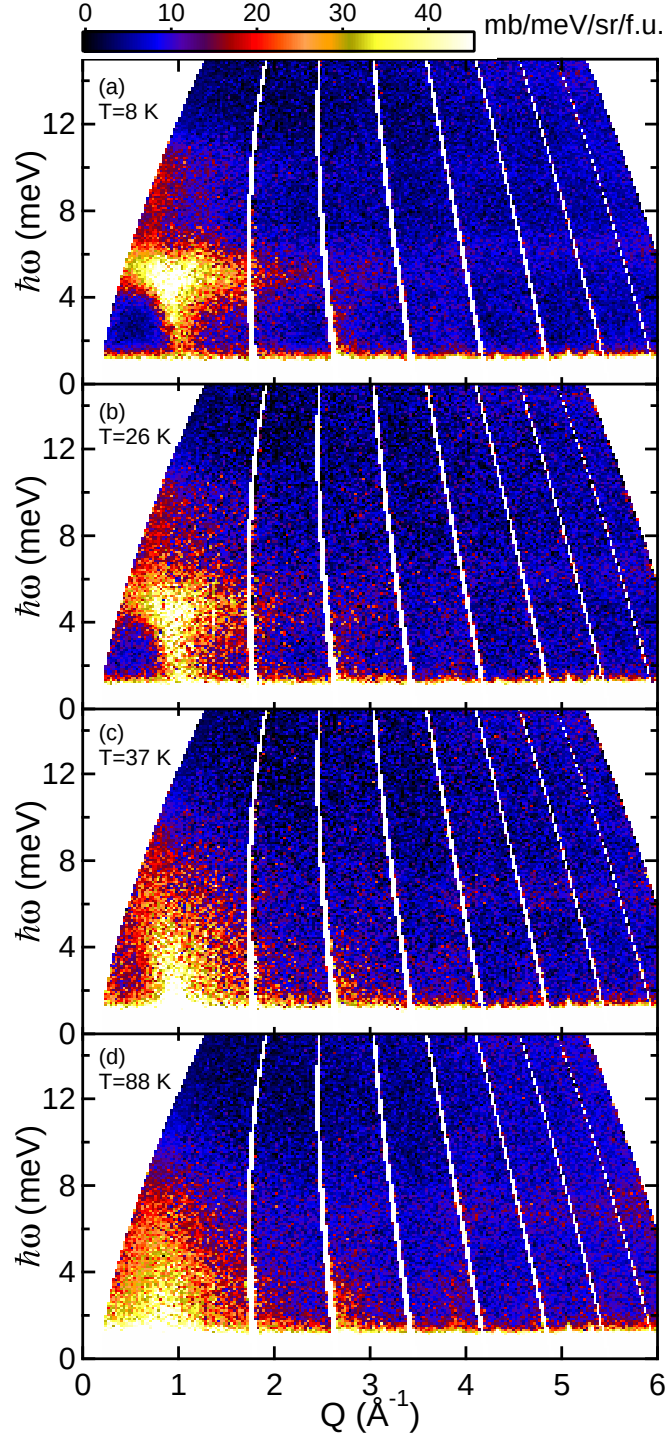


Figure 3.25: INS intensity from Na_3RuO_4 powder versus energy and momentum transfer at (a) $T = 8$ K, (b) $T = 26$ K, (c) $T = 37$ K and (d) $T = 88$ K. These measurements were carried out on the MARI spectrometer at an incident energy of $E_i = 25$ meV.

intensity in the vicinity of $\hbar\omega \approx 5$ meV, which decreases in intensity rapidly with increasing wave-vector. The wave-vector dependence implies that the scattering is magnetic in origin. In the $T = 8$ K data a weak excitation near $\hbar\omega \approx 10$ meV is also evident. As the temperature increases, the inelastic scattering intensity rapidly diminishes and moves to smaller wave-vectors, consistent with an evolution from antiferromagnetic spin-waves to paramagnetic scattering with increasing temperature. We speculate that the excitations observed below T_N are acoustic and optical spin waves associated with the long-range ordered phase. Higher incident energy measurements were also performed, which show evidence for phonon excitations above 20 meV.

In Fig. 3.26, we show plot the scattering intensity as a function of energy transfer for the single wave-vector $Q = 1. \text{ \AA}^{-1}$, measured on the HB3 spectrometer, as well as the integrated scattering intensity for $0.4 \text{ \AA}^{-1} < Q < 1.6 \text{ \AA}^{-1}$ on the MARI spectrometer. Single Lorentzian fits to the low-temperature data suggests modes at $\hbar\omega = 5.03 \pm 0.08$, 9.8 ± 0.2 and 17.9 ± 0.3 meV (for the data in Fig. 3.26(a)), and $\hbar\omega = 4.95 \pm 0.04$ and 9.8 ± 0.1 meV (for the data in Fig. 3.26(b)). The increase in intensity of the excitation at 18 meV for large temperatures implies that it is likely due to lattice excitations.

The temperature dependence of the 18 meV phonon excitation was investigated more carefully as a function of momentum transfer as shown in Fig. 3.27. These data indicate a monotonic increase in scattering intensity as the temperature is increased, and an increase in scattering intensity with increasing wave-vector. These results further support the identification of the 18 meV mode with a phonon excitation.

We also examined the temperature dependence of the elastic scattering in the vicinity of $Q \approx 1 \text{ \AA}^{-1}$. Figure 3.28 shows the scattering intensity observed in the HB3 Na_3RuO_4 powder measurement as a function of temperature and wave-vector. As the temperature is decreased, there is an increase in the scattering intensity at

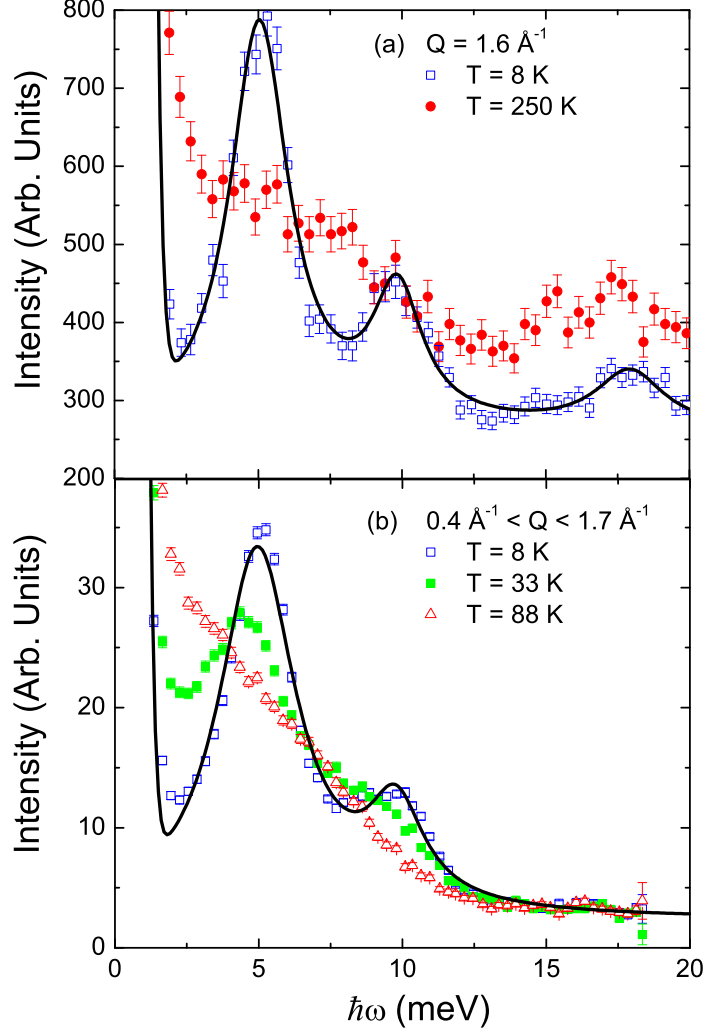


Figure 3.26: INS intensity for Na_3RuO_4 powder versus energy transfer at (a) $Q = 1.6 \text{ \AA}^{-1}$ at $T = 8$ and 250 K , and (b) integrated over the range $0.4 \text{ \AA}^{-1} < Q < 1.6 \text{ \AA}^{-1}$ at $T = 8 \text{ K}$, 30 K and 88 K . Black lines are Lorentzian fits as described in the text. The data in (a) are from HB3, and the data in (b) were acquired using MARI at ISIS.

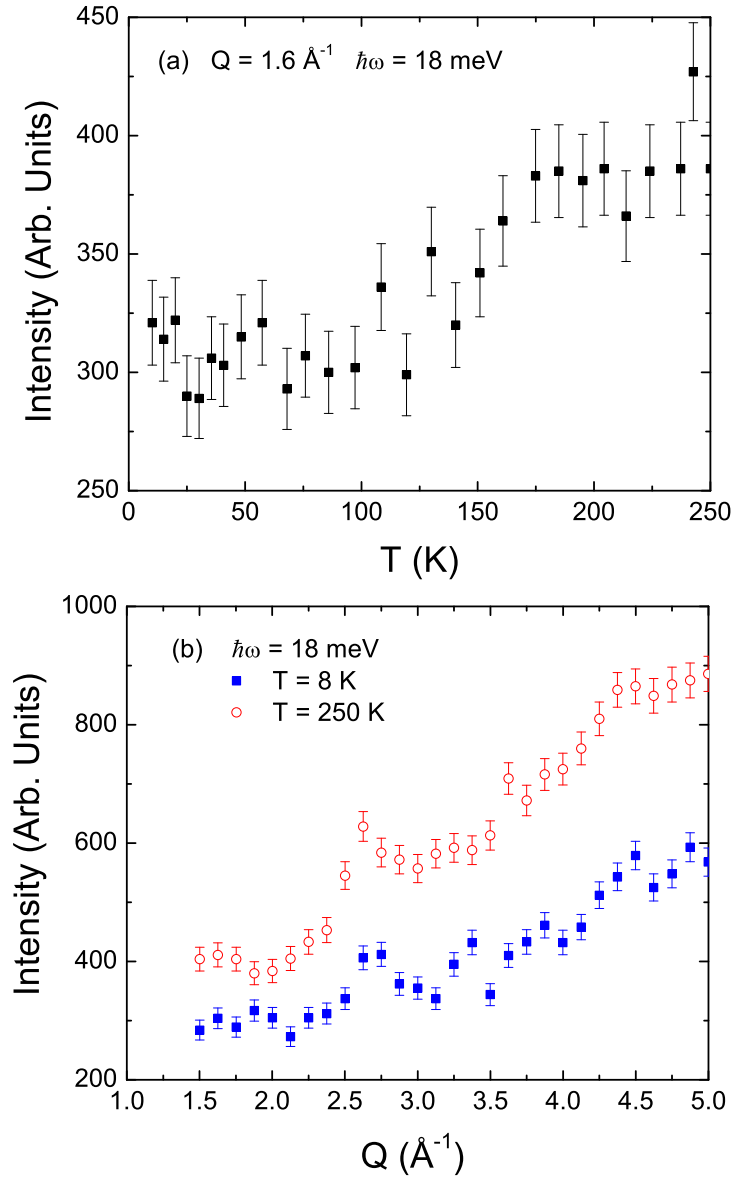


Figure 3.27: (a) INS intensity versus temperature for Na_3RuO_4 powder at $\hbar\omega = 18 \text{ meV}$ and $Q = 1.5 \text{ \AA}^{-1}$. (b) Intensity versus momentum transfer at $\hbar\omega = 18 \text{ meV}$ at $T = 8$ and $T = 250 \text{ K}$. Data were acquired using HB3.

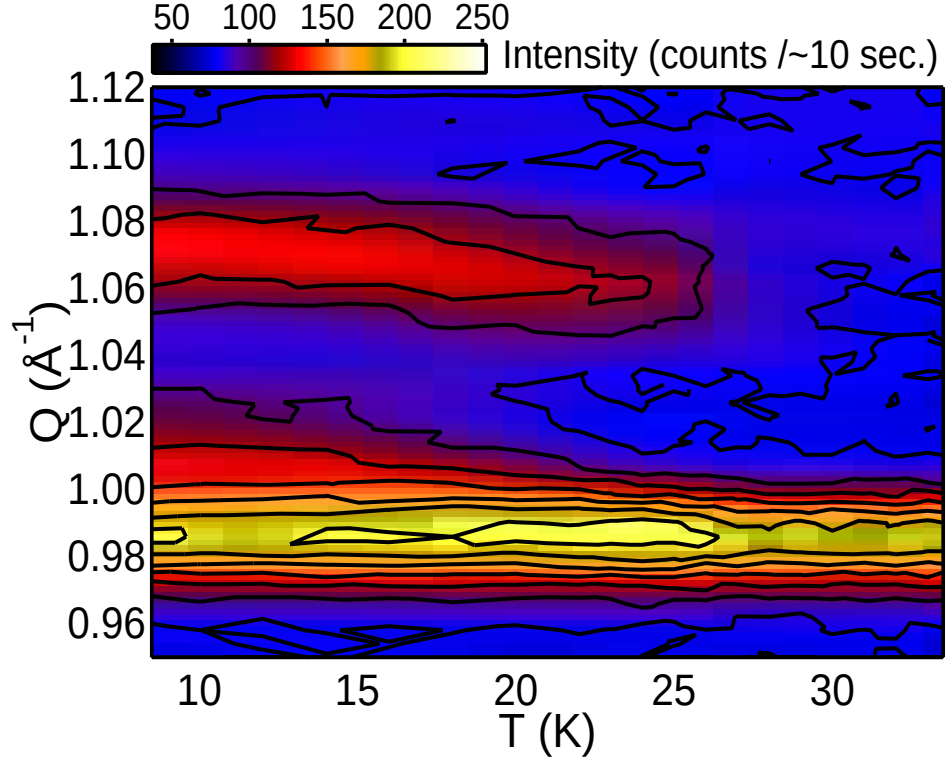


Figure 3.28: Elastic scattering intensity of Na_3RuO_4 as function of wave-vector transfer and temperature. Data were acquired using the HB3 spectrometer. The contour lines correspond to intervals 20 counts per ten seconds, and are only plotted for count rates between 80 and 200 counts per ten seconds. The data were obtained at 20 temperatures between $T = 8.5$ and 34 K.

$Q \approx 0.99$ and $\approx 1.07 \text{ \AA}^{-1}$. Below $T \approx 25 \text{ K}$, the magnetic Bragg peaks appear to move as a function of decreasing temperature. This is also evident in Fig. 3.29, which shows the scattering intensity as a function of temperature for various individual momentum transfers. For certain Q -values, the scattering intensity shows non-monotonic temperature dependence, for example at $Q = 0.99$ and $1.05 \text{ \AA}^{-1}$. This behavior may be due to the presence of magnetic phase transitions near 25 and 30 K.

Discussion

The high temperature magnetic susceptibility fitted using the finite cluster models for $T > 30 \text{ K}$, where there is no long-range magnetic order. Table 3.11 shows the

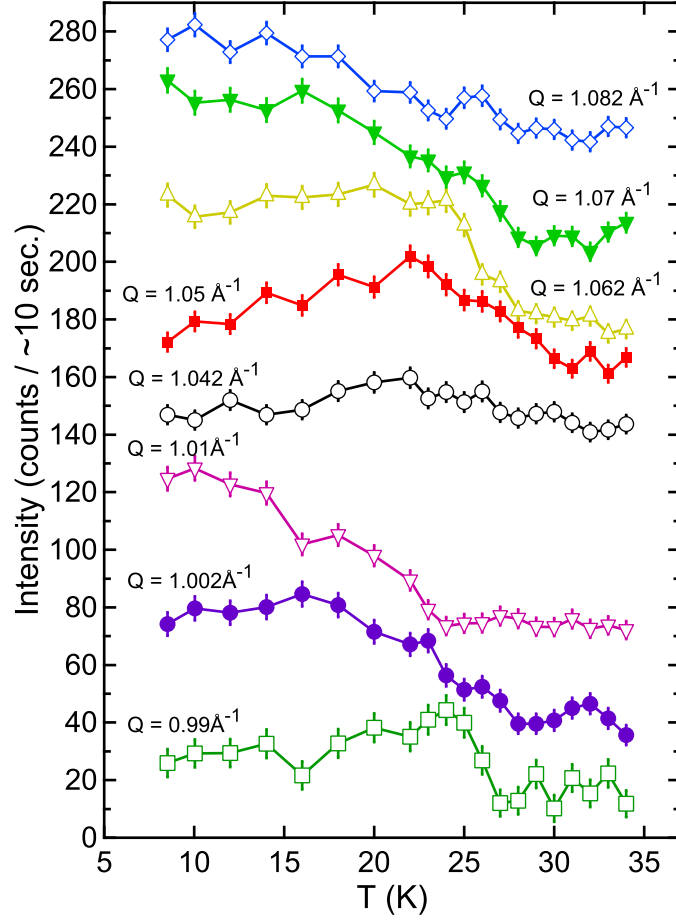


Figure 3.29: INS scattering intensity from Na_3RuO_4 powder versus temperature for several wave-vectors. The data corresponds to the individual wave-vectors shown in Fig. 3.28 (The data have been offset along the vertical axis for presentation.)

magnetic interactions determined from these fits for the three models considered. We also compare the extracted magnetic interaction parameters to the Curie-Weiss temperature. The Curie-Weiss temperature in the mean field approximation is

$$\Theta_W = \frac{S(S+1)}{3} J_0, \quad (3.128)$$

where in this case $S = \frac{3}{2}$ and J_0 is the sum of the magnetic exchange constants [24]. As shown in Figure 3.24, all three cluster models qualitatively reproduce the high temperature susceptibility data, and only deviate strongly close to the transition temperature. However, a comparison of the the calculated Curie-Weiss temperatures based upon the double dimer model is more consistent with the experimental Curie-Weiss temperature, $|\Theta_W| = 14.0$ meV (antiferromagnetic), illustrated in the inset of Fig. 3.24. Because the Curie-Weiss temperature is proportional to a sum of exchange constants, the presence of inter-cluster exchange could significantly effect the estimated values of Θ_W . For example, there are 28 bonds with distances of five to six angstroms between the Ru sites in one cluster and the Ru sites in all neighboring clusters. If inter-cluster interactions are larger, the Curie-Weiss temperature would deviate significantly from the values quoted in Table 3.11.

The inelastic neutron scattering energies and intensities can also be calculated using the exchange values determined from the magnetic susceptibility (shown in Table 3.11) and the ion positions given by Regan *et al.* [62] The three models predict observable INS energy gaps of 2.96, 3.08, and 12.16 meV for the lozenge model, 1.33, 3.49, and 23.53 meV for the coupled dimer model, and 2.47 and 9.16 meV for the double dimer model. We have already noted that the data shows magnetic excitations at approximately 5.0 and 9.8 meV (*cf.* Fig. 3.26.) Figure 3.25 also shows evidence for a spin-wave emerging from the antiferromagnetic Bragg peak in the vicinity of the $Q \approx 1 \text{ \AA}^{-1}$ for $T < T_N$. Although a clear transition to long range magnetic order is

Table 3.11: Exchange interactions estimated from magnetic susceptibility and inelastic neutron scattering data on Na_3RuO_4 powder.

Magnetic Susceptibility				
Model	J (meV)	J' (meV)	J'' (meV)	Θ_w (meV)
Lozenge	3.19 ± 0.01	3.11 ± 0.03	0	19.8 ± 0.1
Coupled Dimer	3.7 ± 0.1	4.6 ± 0.3	-4.8 ± 1.2	18.3 ± 1.3
Double Dimer	0	2.69 ± 0.01	9.75 ± 0.05	15.6 ± 0.1
Inelastic Neutron Scattering ¹				
Model	J (meV)	J' (meV)	J'' (meV)	Θ_w (meV)
Lozenge	5.5 ± 0.1	0	4.1 ± 0.1	32.6 ± 0.1
Double Dimer	0	5.5 ± 0.1	9.8 ± 0.1	19.1 ± 0.1

¹ There is insufficient information to determine the interaction strengths in the coupled dimer model.

evident at low-temperatures, it is nonetheless reasonable to examine the properties of these excitations as observed in INS especially their wave-vector dependence, since these are characteristic indicators of the nature of the interactions.

On comparing the predicted excitation spectrum using the magnetic susceptibility data to determine the interaction strengths, it is evident that only the double dimer model gives a realistic description of the excitation energies (note that the inter-cluster interactions, which produce long-range order may significantly affect the energy levels.) All three models predict an INS-visible excitation below 3 meV and above 9 meV. We also examine the wave vector dependence of these three models; Figure 3.30 shows constant wave-vector scans performed above and below T_N for 5 and 9.8 meV energy transfer. For comparison, we first calculate the wave-vector dependence of the INS scattering intensity at Eq. 3.127 for the lozenge model geometry. These lineshapes (shown in Fig. 3.30) are unable to account for the initial rapid rise in scattering intensity at small wave-vectors, which implies that there are significant exchange interactions between spins at larger separations than are present in the lozenge model. If the ionic distances are allowed to vary freely in fitting the data, an interesting result emerges. For the 9.8 meV excitation, the fitted dimer separation in a single dimer model is 5.66 ± 0.10 Å bond. This separation agrees with the length of the γ -dimer. This makes it unlikely that the coupled dimer model is realistic, as it predicts a 23 meV γ -dimer excitation using the magnetic susceptibility parameters. The lozenge and double dimer models with susceptibility-fitted parameters predict γ -dimer excitations at 12 meV and 9 meV, respectively. The double dimer model is evidently closer to the observed gap of 9.8 meV. Fitting the 5.0 meV data with a free dimer length in both the lozenge and dimer models gives a length of 4.60 ± 0.02 Å, which does not correspond to any Ru-Ru separation in the structure of Na_3RuO_4 . We conclude that the intercluster interactions are significant enough to modify the energies and wave-vector dependences of the excitations, three simple dimer models

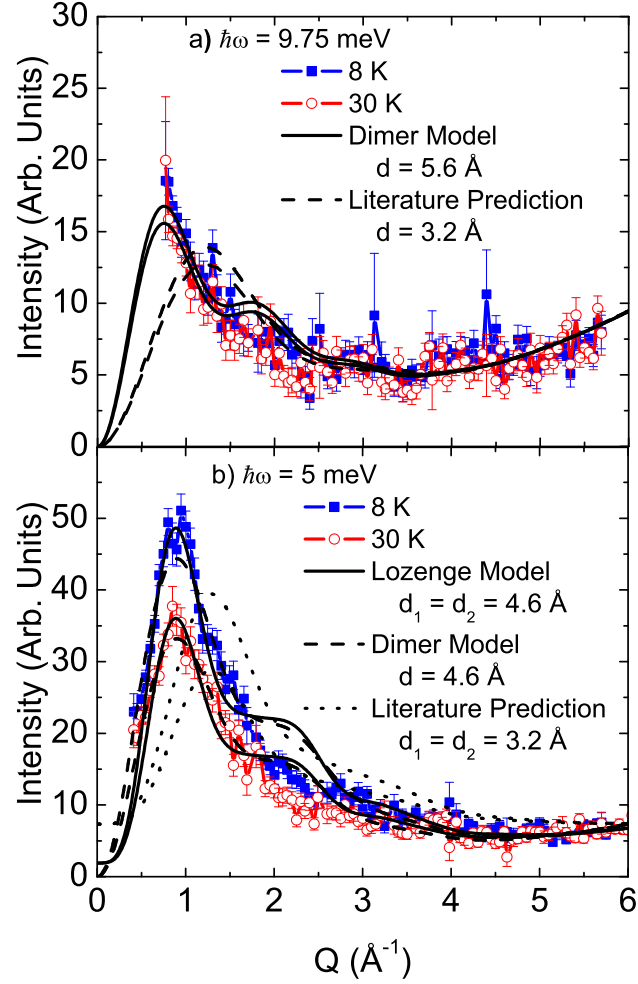


Figure 3.30: a) INS intensity versus momentum transfer of the 9.8 meV excitation in Na_3RuO_4 at $T = 8$ (blue squares) and 30 K (red circles); the black solid lines are fits to the dimer model, and the gray dashed lines are predictions given fixed physical distances. b) INS intensity versus momentum transfer at $T = 8$ (blue squares) and 30 K (red circles) for the 5.0 meV excitation. The solid black line is the lozenge model fit, the gray dashed line is the dimer model, and light gray dotted line is a prediction using the physical distances (The data was acquired using the HB3 spectrometer as described in the text.)

do not give a good description of the excitations.

Table 3.11 gives estimated magnetic interaction parameters for the various models using observed neutron scattering excitations at $\hbar\omega \approx 5.03$ and 9.8 meV as input. Since no third magnetic excitation was observed to 30 meV, the coupled dimer model cannot be uniquely constrained. Although the lozenge model also predicts three excitations, two of those excitations involve dimers alone, and we can therefore determine both of the exchange constants using the neutron scattering results. Using these exchange interactions, the lozenge model gives an estimated Curie-Weiss temperature of 32.6 meV, more than double the observed value. The double dimer model gives a value of $|\Theta_w| = 18.5$ meV; this is closer to the measured value, although it is still 30% larger than the observed value (from the magnetic susceptibility). If the excitations are indeed well described by the double dimer model, they demonstrate that the 5.0 and 9.8 meV modes correspond to excitations of the α - and γ -dimers, with the nature of the α -dimer excitation being significantly modified coupled-cluster effects and the onset of long range magnetic order.

Conclusions

In summary, we have given analytic results for the energy levels and energy eigenstates of coupled dimers with general ion spin S . We derive analytic closed-form results for the magnetic susceptibility and inelastic neutron scattering excitation functions and their wave-vector dependence for several tetramer models, and compare our results to experimental data on the $S = \frac{3}{2}$ tetramer spin lozenge candidate Na_3RuO_4 .

On considering the observed magnetic susceptibility and inelastic neutron scattering data and comparing these results to several tetramer models, we first find that the Na_3RuO_4 data is not consistent with the spin-lozenge model of Regan *et al.* [62]. Although no isolated tetramer model is able to describe all of the thermodynamic and

spectroscopic measurements simultaneously, a double dimer model with bond lengths of $d = 4.60 \text{ \AA}$ and $5.66 \text{ \AA}$ does provide a description of some aspects of the observed thermodynamic properties and the inelastic neutron scattering measurements on the two observed magnetic excitations.

Measurements of the heat capacity and elastic neutron scattering data show that there are two distinct magnetic phase transitions in this material, at $T \approx 23 \text{ K}$ and 28 K . This is the first evidence for two low-temperature phase transitions in this material. Clearly, an understanding the nature of these long-range ordered magnetic phases will provide useful additional information regarding the nature of magnetic interactions in Na_3RuO_4 . We anticipate that neutron diffraction measurements on single crystal samples of Na_3RuO_4 will be the most useful next step in the experimental studies of the this material.

3.4 Spin Pentamers

3.4.1 General Spin Pentamers

To further develop our symmetry-based methods, we next consider a specific model of a general spin pentamer. Using a basis of a dimer and trimer, the energy eigenstates can easily be determined exactly in case of specific symmetric geometries. Although more general geometries are of interest, the specific case of a spin- S dimer coupled to a spin- S' trimer is of particular experimental interest [66]. Previous work on these clusters have lead to bulk measurements that use only numerical applications to determine interactions. Though the methods presented below, we can determine the exact properties and learn more qualitative information about the clusters. While bulk properties are of interest, the inelastic neutron scattering energies and intensities are of greater interest due to underlying nature that the symmetric clusters present. Our results may be useful in particular for the analysis of the pentamer materials

being synthesized by the group of K.R. Dunbar *et al.* at Texas A&M [66].

Hamiltonian and Energy Eigenstates

As shown in figure 3.31, this model consists of an isosceles trimer cluster that interacts with two apical ions, which form a spin dimer. The lines denote interactions between the ions, with separations of d_1 (dashed red), d_2 (dotted blue), d_3 (dash-dot gray), and d_4 (solid black). Assuming pairwise Heisenberg interactions, this system is described by the Hamiltonian

$$\mathcal{H} = J \left[\eta (\vec{S}_3 \cdot \vec{S}_4 + \vec{S}_4 \cdot \vec{S}_5) + \alpha \vec{S}_3 \cdot \vec{S}_5 + \gamma \vec{S}_1 \cdot \vec{S}_2 + \right. \\ \left. \vec{S}_1 \cdot \vec{S}_3 + \vec{S}_2 \cdot \vec{S}_3 + \vec{S}_1 \cdot \vec{S}_4 + \vec{S}_2 \cdot \vec{S}_4 + \vec{S}_1 \cdot \vec{S}_5 + \vec{S}_2 \cdot \vec{S}_5 \right] - g_i \mu_B B \sum_i^5 S_i^z \quad (3.129)$$

where J is the trimer-apical interaction, $\alpha = J'/J$, $\gamma = J''/J$, and $\eta = J'''/J$. J' , J'' , and J''' are dimer 1, dimer 2, and trimer interactions, respectively. These magnetic interactions as usual are positive if antiferromagnetic and negative if ferromagnetic. $\vec{S}_i$ is the quantum spin operator for a spin- S ion at site i ($i=1\dots5$.) The Zeeman term describes the interaction with a magnetic field, and splits the degenerate magnetic substates. g_i is the lande factor for the respective ions.

The energy eigenstates and eigenvalues may be found by diagonalizing the magnetic Hamiltonian on a convenient basis. (Here, we employ the usual set of $\hat{z}$ -polarized magnetic basis states.) Using a trimer basis, the energy eigenvalues for the general $S - S'$ pentamer can be determined exactly, and are given by

$$E = \frac{J}{2} \left[\eta (\mathcal{S}_\Delta - \mathcal{S}_{d,1} - \mathcal{S}') + \alpha (\mathcal{S}_{d,1} - 2\mathcal{S}') + \gamma (\mathcal{S}_{d,2} - 2\mathcal{S}) + \right. \\ \left. \eta (\mathcal{S}_{\text{tot}} - \mathcal{S}_{d,2} - \mathcal{S}_\Delta) - g \mu_B B S_{\text{tot}}^z \right], \quad (3.130)$$

where $\mathcal{S}_i = S_i(S_i + 1)$. Here S_{tot} denotes the total spin of the pentamer, S_Δ is the

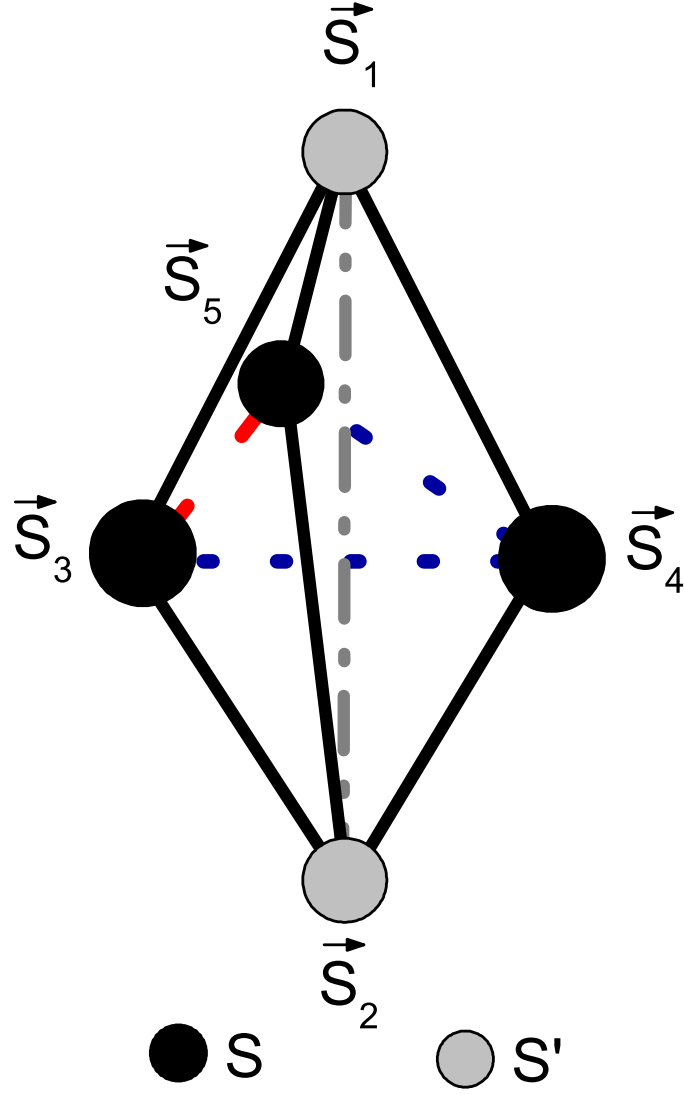


Figure 3.31: A spin pentamer, visualized as a coupled dimer-trimer system. The magnetic ions (black/gray circles) have interactions of strength J (solid black), ηJ (dotted dark blue), αJ (dashed red), and γJ (dash-dot grey). The black and grey denote different ion spin, S and S' .

spin of the trimer, $S_{d,(1,2)}$ are the spins of the individual dimers, S and S' are the spins of the ions, and S_{tot}^z is the total spin z -component of the pentamer.

The total spin states of the pentamer follow from the spin decomposition of

$$S_1 \otimes S_2 \otimes S_3 \otimes S_4 \otimes S_5. \quad (3.131)$$

Since this is a rotationally invariant Hamiltonian in spin space, the total spin S_{tot} and S_{tot}^z are good quantum numbers. The dimensionality of the Hilbert space is evidently $(2S+1)^3 \cdot (2S'+1)^2$. Given the individual energies and multiple spin substates, the partition function, magnetic susceptibility and heat capacity for the system can be determined. The inelastic neutron scattering structure factors can be determined from the given states.

3.4.2 Magnetic Observables for a Dimer of Spin- $\frac{1}{2}$ Coupled to a Trimer of Spin-1

We first consider a pentamer consisting of a dimer of spin- $\frac{1}{2}$ ions coupled to a trimer of spin-1 ions, with all interactions assumed equal. There are $(2(\frac{1}{2})+1)^2 \cdot (2(1)+1)^3 = 108$ magnetic basis states, which have the spin decomposition by

$$\left(\frac{1}{2} \otimes \frac{1}{2}\right) \otimes (1 \otimes 1 \otimes 1) =$$

Dimer and Trimer States

$$(1 \oplus 0) \otimes (1 \otimes (2 \oplus 1 \oplus 0)) =$$

Dimer and Dimer (in Trimer) States

$$(1 \oplus 0) \otimes (3 \oplus 2^2 \oplus 1^3 \oplus 0) =$$

Dimer and Trimer States

$$4 \oplus 3^4 \oplus 2^8 \oplus 1^9 \oplus 0^4. \quad (3.132)$$

Pentamer States

The superscript indicates the number of independent multiplets with each S_{tot} . Each multiplet contains $2S_{tot}+1$ magnetic substates, which are degenerate given an isotropic magnetic Hamiltonian such as the Heisenberg form of Eq. 3.129. These degenerate states will be split by an applied magnetic field.

Table 3.12 gives the energy eigenstates of the ($S = \frac{1}{2}$, $S' = 1$) isotropic Heisenberg pentamer Hamiltonian. The complete set of pentamer interactions includes couplings between the individual trimer and dimer states which lead to pentamer energy eigenstates that are linear combinations of dimer and trimer basis states. The simplicity of these full pentamer eigenstates is due to the equality of the two dimer-trimer couplings. If those coupling strengths were different, there would be mixing between more of the dimer and trimer basis states, which would greatly complicate the physics of this system.

Various bulk magnetic properties including the partition function, heat capacity and magnetic susceptibility can be calculated from these determined energy levels using results described in Chapter 2. Due to the length of the exact analytical solutions, the partition function, heat capacity, and magnetic susceptibility are not shown. As a check of these results, we can use the heat capacity to calculate the entropy of the pentamer, and compare this to the zero-temperature entropy expected for this system. Numerical integration shows that the zero-temperature entropy of the pentamer does indeed satisfy

$$\frac{S}{k_B} = \int_0^\infty \frac{C}{k_B} \frac{d\beta}{\beta} =$$

$$\ln(\mathcal{N}/\mathcal{N}_0) , \begin{cases} 3 \ln(3) & \alpha = \gamma = \eta = 1 \\ \ln(\frac{108}{5}) & \alpha = \eta = 0, 0 \leq \gamma < 3 , \end{cases} \quad (3.133)$$

where $\mathcal{N}$ is the dimensionality of the full Hilbert space and $\mathcal{N}_0$ is the degeneracy of the ground state [11, 28]. The zero-temperature entropy clearly changes discontinuously if the degeneracy of the ground state changes. In comparison to materials similar to those presented by Shatruk *et al.*, $\alpha = \eta = \gamma = 0$ [66]. This condition makes the pentamer have a spin-2 ground state.

Table 3.12 shows our results for the inelastic neutron scattering (INS) energy gaps and structure factors for a spin pentamer, which are determined from the pentamer energy eigenstates and eigenvectors. For these transitions between discrete energy levels, the excitation energy is equal to the energy difference of the levels, $\hbar\omega = E_f - E_i$, and the INS differential cross-section is shown to be proportional to the neutron scattering structure factor

$$S(\vec{q}) = |F(\vec{q})|^2 \left[\sum_{\lambda_f} \langle \Psi_f(\lambda_f) | V_a | \Psi_i \rangle^2 \right] , \quad (3.134)$$

where $F(\vec{q})$ is the ions magnetic form factor, and the vector $V_a(\vec{q})$ is a sum of spin operators over all magnetic ions in a unit cell,

$$V_a = \sum_{\vec{x}_i} S_a(\vec{x}_i) e^{i\vec{q} \cdot \vec{x}_i} . \quad (3.135)$$

For a rotationally invariant magnetic interaction and an $S_{tot} = 0$ initial state (as is often encountered in $T=0$ inelastic scattering from an antiferromagnet), only $S_{tot} = 1$ final states are excited (as shown in Table 3.12.)

The results given in Table 3.12 apply to neutron scattering from single crystals. To interpret neutron experiments on powder samples, we require an orientation average of the unpolarized single-crystal neutron scattering structure factor. This powder

Table 3.12: Energy levels and INS properties for a pentamer

Spin State $ \mathbf{S}_{tot} \mathbf{S}_{tot}^z \rangle_{\Delta, d1, d2}$	Energy Level	INS Energy Gap	INS Structure Factor
$ 4 \mathbf{S}_{tot}^z \rangle_{3,2,1}$	$\frac{J}{2}(6\eta - 4 + 2\alpha + \gamma)$		
$ 3 \mathbf{S}_{tot}^z \rangle_{3,2,1}$	$\frac{J}{2}(6\eta - 4 + 2\alpha + \gamma)$	$3J$	$\frac{10}{189}[15 + 9\cos(qd_3) - 36\cos(qd_4) + 4\cos(qd_1) + 8\cos(qd_2)]$
$ 3 \mathbf{S}_{tot}^z \rangle_{2,2,1}$	$\frac{J}{2}(2 + 2\alpha + \gamma)$	$J(6 - 3\eta)$	$\frac{1}{4725}[3 - 4\cos(qd_2) + \cos(qd_1)]$
$ 3 \mathbf{S}_{tot}^z \rangle_{2,1,1}$	$\frac{J}{2}(4\eta + 2 - 2\alpha + \gamma)$		
$ 3 \mathbf{S}_{tot}^z \rangle_{3,2,0}$	$\frac{J}{2}(6\eta - 2 + 2\alpha - \gamma)$	$J(4 - \gamma)$	$\frac{1}{14}[1 - \cos(qd_3)]$
$ 2 \mathbf{S}_{tot}^z \rangle_{3,2,1}$	$\frac{J}{2}(6\eta - 10 + 2\alpha + \gamma)$	Ground State	
$ 2 \mathbf{S}_{tot}^z \rangle_{2,2,1}$	$\frac{J}{2}(-4 + 2\alpha + \gamma)$	$3J(1 - \eta)$	$\frac{41}{4725}[3 - 4\cos(qd_2) + \cos(qd_1)]$
$ 2 \mathbf{S}_{tot}^z \rangle_{2,1,1}$	$\frac{J}{2}(4\eta - 4 - 2\alpha + \gamma)$		
$ 2 \mathbf{S}_{tot}^z \rangle_{1,2,1}$	$\frac{J}{2}(-4\eta + 2\alpha + \gamma)$		
$ 2 \mathbf{S}_{tot}^z \rangle_{1,1,1}$	$\frac{J}{2}(-2\alpha + \gamma)$		
$ 2 \mathbf{S}_{tot}^z \rangle_{1,0,1}$	$\frac{J}{2}(2\eta - 4\alpha + \gamma)$		
$ 2 \mathbf{S}_{tot}^z \rangle_{2,2,0}$	$\frac{J}{2}(-2 + 2\alpha - \gamma)$		
$ 2 \mathbf{S}_{tot}^z \rangle_{2,1,0}$	$\frac{J}{2}(2\eta - 2\alpha - \gamma - 2)$		
$ 1 \mathbf{S}_{tot}^z \rangle_{2,2,1}$	$\frac{J}{2}(-8\eta + 2\alpha + \gamma)$	$J(1 - 3\eta)$	$\frac{7}{75}[3 - 4\cos(qd_2) + \cos(qd_1)]$
$ 1 \mathbf{S}_{tot}^z \rangle_{2,1,1}$	$\frac{J}{2}(-4 - 2\alpha + \gamma)$		
$ 1 \mathbf{S}_{tot}^z \rangle_{1,2,1}$	$\frac{J}{2}(-4\eta + 2\alpha + \gamma - 4)$		
$ 1 \mathbf{S}_{tot}^z \rangle_{1,1,1}$	$\frac{J}{2}(-4 - 2\alpha + \gamma)$		
$ 1 \mathbf{S}_{tot}^z \rangle_{1,0,1}$	$\frac{J}{2}(2\eta - 4\alpha + \gamma - 2)$		
$ 1 \mathbf{S}_{tot}^z \rangle_{1,2,0}$	$\frac{J}{2}(-4\eta + 2\alpha - \gamma - 2)$		
$ 1 \mathbf{S}_{tot}^z \rangle_{1,1,0}$	$\frac{J}{2}(-2 - 2\alpha - \gamma)$		
$ 1 \mathbf{S}_{tot}^z \rangle_{1,0,0}$	$\frac{J}{2}(2\eta - 4\alpha - \gamma - 2)$		
$ 1 \mathbf{S}_{tot}^z \rangle_{0,1,1}$	$\frac{J}{2}(-2\eta - 2\alpha + \gamma - 2)$		
$ 0 0 \rangle_{1,2,1}$	$\frac{J}{2}(-4\eta - 6 + 2\alpha + \gamma)$		
$ 0 0 \rangle_{1,1,1}$	$\frac{J}{2}(-6 - 2\alpha + \gamma)$		
$ 0 0 \rangle_{1,0,1}$	$\frac{J}{2}(2\eta - 6 - 4\alpha + \gamma)$		
$ 0 0 \rangle_{1,1,0}$	$\frac{J}{2}(-4 - 2\alpha - \gamma)$		

average intensity, including the magnetic form factor, is given by

$$\bar{S}(q) = \frac{F^2(q)}{14} \left(1 - j_0(qd_3) \right), \quad (3.136)$$

(Dimer Excitation)

$$\begin{aligned} \bar{S}(q) &= \frac{F^2(q)}{4725} \left(3 + j_0(qd_1) - 4j_0(qd_3) \right), \\ \bar{S}(q) &= \frac{41F^2(q)}{4725} \left(3 + j_0(qd_1) - 4j_0(qd_3) \right), \\ \bar{S}(q) &= \frac{7F^2(q)}{75} \left(3 + j_0(qd_1) - 4j_0(qd_3) \right), \end{aligned} \quad (3.137)$$

(Trimer Excitations)

and

$$\bar{S}(q) = \frac{10F^2(q)}{189} [15 + 9\cos(qd_3) - 36\cos(qd_4) + 4\cos(qd_1) + 8\cos(qd_2)], \quad (3.138)$$

(Pentamer Excitation)

where $F(q)$ is the magnetic form factor, d is the inter-atomic separation, and $j_0(x) = \sin(x)/x$. For the spin pentamer, there are five possible INS-visible excitations, three of which are excitations of the trimer, one an excitation of the axial dimer, and the fifth is an excitation of the full pentamer. Note that there is no uncoupled excitation of the dimers within the trimer. This is an interesting point; in order to change the state of a dimer within the trimer one must also change the overall state of the trimer, which cannot be done by a single neutron. Since there is no spin-3 trimer state given a spin-1 "inner" dimer, this transition is not allowed.

3.5 Spin Hexamers

3.5.1 General Spin Hexamer

We introduce spin hexamers to model inter-trimer interactions. The energy eigenstates of this system in our model can be determined exactly, which allows us to evaluate the partition function, magnetic susceptibility, and heat capacity. The explicit result for the heat capacity is too lengthy to present here, but a numerical integration of the heat capacity allows a check of our results using the zero-temperature entropy. Fitting the magnetic susceptibility to data on a coupled V_3 system will allow an estimate of the exchange interactions in this case.

Hamiltonian and Energy Eigenstates

Our hexamer model (as shown in figure 3.32) consists of two isosceles trimers that interact through multiple superexchange pathway. Assuming nearest-neighbor Heisenberg interactions, the Hamiltonian of this system can be written as

$$\begin{aligned} \mathcal{H} = J & \left(\eta_a (\vec{S}_1 \cdot \vec{S}_3 + \vec{S}_2 \cdot \vec{S}_3) + \eta_b (\vec{S}_4 \cdot \vec{S}_5 + \vec{S}_4 \cdot \vec{S}_6) + \right. \\ & \alpha_a \vec{S}_1 \cdot \vec{S}_2 + \alpha_b \vec{S}_5 \cdot \vec{S}_6 + \gamma (\vec{S}_1 \cdot \vec{S}_4 + \vec{S}_1 \cdot \vec{S}_5 + \vec{S}_1 \cdot \vec{S}_6 + \vec{S}_2 \cdot \vec{S}_4 + \\ & \left. \vec{S}_2 \cdot \vec{S}_5 + \vec{S}_2 \cdot \vec{S}_6 + \vec{S}_3 \cdot \vec{S}_4 + \vec{S}_3 \cdot \vec{S}_5 + \vec{S}_3 \cdot \vec{S}_6) \right) - g\mu_B B \sum_i^6 S_{z_i} \end{aligned} \quad (3.139)$$

where J is an overall interaction scale, $\eta_{a,b} = J_{a,b}/J$, $\alpha_{a,b} = J'_{a,b}/J$, $\gamma = J''/J$, and $J_{a,b}$, $J'_{a,b}$ and J'' are the trimer, dimer and hexamer super-exchange interactions, respectively. As usual these magnetic interactions are positive for antiferromagnetic interactions and negative for ferromagnetic ones, and $\vec{S}_i$ is the quantum spin operator for a spin- $\frac{1}{2}$ ion at site $i=1\dots 6$.

The energy eigenvalues of the general spin hexamer model of figure 3.32 are given

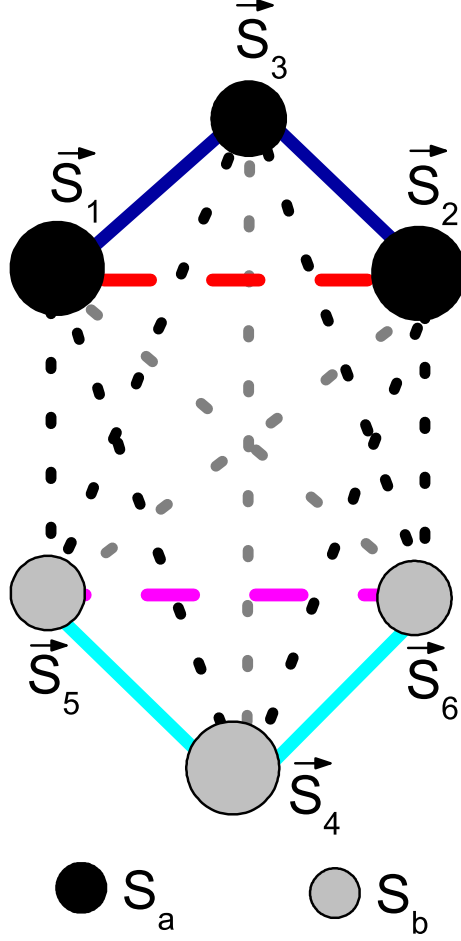


Figure 3.32: The hexamer model. The ions (black/gray circles) have intra-trimer interactions of strength $\eta_a J$ (solid dark blue), $\eta_b J$ (solid light blue), $\alpha_a J$ (dashed dark red), $\alpha_b J$ (dashed light red), and inter-trimer interaction γJ (dotted black/grey). The black and grey spin ions nominally denote trimers with different ion spins, S_a and S_b . (In the V_6 application discussed here, we specialize to $S_a = S_b = 1/2$.) The gray dotted lines represent the interactions that may not be present in the V_6 material. [67]

by

$$\begin{aligned}
E = \frac{J}{2} & \left(\eta_a (\mathfrak{J}_{\Delta,\mathbf{a}} - \mathfrak{J}_{\mathbf{d},\mathbf{a}} - \mathfrak{J}_{\mathbf{a}}) + \eta_b (\mathfrak{J}_{\Delta,\mathbf{b}} - \mathfrak{J}_{\mathbf{d},\mathbf{b}} - \mathfrak{J}_{\mathbf{b}}) + \right. \\
& \alpha_a (\mathfrak{J}_{d,a} - 2\mathfrak{J}_a) + \alpha_b (\mathfrak{J}_{d,b} - 2\mathfrak{J}_b) + \\
& \left. \gamma (\mathfrak{J}_{tot} - \mathfrak{J}_{\Delta,a} - \mathfrak{J}_{\Delta,b}) \right) - g\mu_B B S_{tot}^z, \tag{3.140}
\end{aligned}$$

where $\mathfrak{J}_{tot} = S_{tot}(S_{tot}+1)$ specifies the total hexamer spin, $\mathfrak{J}_{\Delta,(a,b)} = S_{\Delta,(a,b)}(S_{\Delta,(a,b)}+1)$ specifies the spin state of the individual trimers, $\mathfrak{J}_{d,(a,b)} = S_{d,(a,b)}(S_{d,(a,b)}+1)$ gives the spin state of the individual dimers, and $\mathfrak{J}_{(a,b)} = S_{(a,b)}(S_{(a,b)}+1)$ gives the spin of the individual ions in each trimer. S_{tot}^z is the total hexamer z -component .

The total spin states of the hexamer, trimers, and dimers can be determined by the examining the spin decomposition of

$$S_a \otimes S_a \otimes S_a \otimes S_b \otimes S_b \otimes S_b. \tag{3.141}$$

Since this is a rotationally invariant Hamiltonian in spin space, the total spin S_{tot} and z -component S_{tot}^z are good quantum numbers. The Hilbert space is evidently $(2S_a+1)^3 \cdot (2S_b+1)^3$ dimensional. Given the energy eigenvalues and eigenstates, we may determine the partition function, magnetic susceptibility and heat capacity as usual.

3.5.2 Magnetic Observables for $S = \frac{1}{2}$ Hexamer

Specializing to the case of $S = \frac{1}{2}$ ions, which has a $S^6 = (2(\frac{1}{2})+1)^6 = 64$ dimensional Hilbert space, the decomposition into spin states is as follows:

$$\left(\frac{1}{2} \otimes \frac{1}{2} \otimes \frac{1}{2} \right) \otimes \left(\frac{1}{2} \otimes \frac{1}{2} \otimes \frac{1}{2} \right) =$$

composition of two trimers

$$\left(\frac{1}{2} \otimes (1 \oplus 0)\right) \otimes \left(\frac{1}{2} \otimes (1 \oplus 0)\right) =$$

spin and dimer states

$$\left(\frac{3}{2} \oplus \frac{1}{2} \oplus \frac{1}{2}\right) \otimes \left(\frac{3}{2} \oplus \frac{1}{2} \oplus \frac{1}{2}\right) =$$

trimer states

$$3 \oplus 2^5 \oplus 1^9 \oplus 0^5. \quad (3.142)$$

hexamer states

The superscript specifies the number of independent multiplets of each S_{tot} . Each of these states contain $2S_{tot}+1$ magnetic substates, which are degenerate given an isotropic magnetic Hamiltonian such as the Heisenberg form we assume (Eq. 3.139).

The energy eigenvalues and INS properties are given for this $S = \frac{1}{2}$ hexamer model in Table 3.13 . Here, specializing the vanadium material simplifies the Hamiltonian by constraining $J_a = J_b = J$ and $J'_a = J'_b = J'$, so we may take $\eta_{(a,b)} = 1$ and $\alpha_1 = \alpha_2 = \alpha$. The inter-trimer interaction couples the individual trimer energy eigenstates; which Figure 3.33 qualitatively shows the affect of the coupling on the energy levels of the two spin- $\frac{1}{2}$ trimers. The origin of the hexamer energy eigenstates as coupled trimer states, as indicted by the spin decomposition (Eq. 3.142), is evident in the this figure. The relative simplicity of these hexamer states is largely due to the symmetry of this identical trimer problem. Were the inter-trimer interactions different, there would be additional mixing between the basis states, which would greatly complicate the energy eigenvalues and eigenstates.

The partition function, magnetic heat capacity and magnetic susceptibility can be determined directly from the energy eigenvalues. The zero-field partition function for the $S = \frac{1}{2}$ hexamer is given by

Table 3.13: Energy levels and INS properties of the $S = \frac{1}{2}$ hexamer

Spin State $ S_{tot} S_{tot}^z\rangle_{\Delta 1, \Delta 2, d1, d2}$	Energy Level	INS Energy Gap	INS Structure Factor
$ 3 S_{tot}^z > \frac{3}{2}, \frac{3}{2}, 1, 1\rangle$	$\frac{J}{2}(\frac{9\gamma}{2} + 2 + \alpha)$		
$ 2 S_{tot}^z > \frac{3}{2}, \frac{3}{2}, 1, 1\rangle$	$\frac{J}{2}(\frac{-3\gamma}{2} + 2 + \alpha)$		
$ 2 S_{tot}^z > \frac{1}{2}, \frac{3}{2}, 1, 1\rangle$	$\frac{J}{2}(\frac{3\gamma}{2} - 1 + \alpha)$		
$ 2 S_{tot}^z > \frac{1}{2}, \frac{3}{2}, 0, 1\rangle$	$\frac{J}{2}(\frac{3\gamma}{2} + 1 - \alpha)$		
$ 2 S_{tot}^z > \frac{3}{2}, \frac{1}{2}, 1, 1\rangle$	$\frac{J}{2}(\frac{3\gamma}{2} - 1 + \alpha)$		
$ 2 S_{tot}^z > \frac{3}{2}, \frac{1}{2}, 1, 0\rangle$	$\frac{J}{2}(\frac{3\gamma}{2} + 1 - \alpha)$		
$ 1 S_{tot}^z > \frac{3}{2}, \frac{3}{2}, 1, 1\rangle$	$\frac{J}{2}(\frac{-11\gamma}{2} + 2 + \alpha)$		
$ 1 S_{tot}^z > \frac{1}{2}, \frac{3}{2}, 1, 1\rangle$	$\frac{J}{2}(\frac{-5\gamma}{2} - 1 + \alpha)$	$\frac{J}{2}(3 - \gamma)$	$\frac{2}{7}[3 + \cos(qd_{\alpha_b}) - 4\cos(qd_{\eta_b})]$
$ 1 S_{tot}^z > \frac{1}{2}, \frac{3}{2}, 0, 1\rangle$	$\frac{J}{2}(\frac{-5\gamma}{2} + 1 - \alpha)$		
$ 1 S_{tot}^z > \frac{3}{2}, \frac{1}{2}, 1, 1\rangle$	$\frac{J}{2}(\frac{-5\gamma}{2} - 1 + \alpha)$	$\frac{J}{2}(3 - \gamma)$	$\frac{2}{7}[3 + \cos(qd_{\alpha_a}) - 4\cos(qd_{\eta_a})]$
$ 1 S_{tot}^z > \frac{3}{2}, \frac{1}{2}, 1, 0\rangle$	$\frac{J}{2}(\frac{-5\gamma}{2} + 1 - \alpha)$		
$ 1 S_{tot}^z > \frac{1}{2}, \frac{1}{2}, 1, 1\rangle$	$\frac{J}{2}(\frac{\gamma}{2} - 4 + \alpha)$	γJ	$\frac{3}{7}[9 + 8\cos(qd_{\alpha_a}) + 8\cos(qd_{\alpha_b}) - 8\cos(qd_{\eta_a}) - 8\cos(qd_{\eta_b}) - 9\cos(qd_{\gamma})]$
$ 1 S_{tot}^z > \frac{1}{2}, \frac{1}{2}, 1, 0\rangle$	$\frac{J}{2}(\frac{\gamma}{2} - 2 - \alpha)$	$J(\gamma + 1 - \alpha)$	$1 - \cos(qd_{\alpha_b})$
$ 1 S_{tot}^z > \frac{1}{2}, \frac{1}{2}, 0, 1\rangle$	$\frac{J}{2}(\frac{\gamma}{2} - 2 - \alpha)$	$J(\gamma + 1 - \alpha)$	$1 - \cos(qd_{\alpha_a})$
$ 1 S_{tot}^z > \frac{1}{2}, \frac{1}{2}, 0, 0\rangle$	$\frac{J}{2}(\frac{\gamma}{2} - 3\alpha)$		
$ 0 0 > \frac{3}{2}, \frac{3}{2}, 1, 1\rangle$	$\frac{J}{2}(\frac{-15\gamma}{2} + 2 + \alpha)$		
$ 0 0 > \frac{1}{2}, \frac{1}{2}, 1, 1\rangle$	$\frac{J}{2}(\frac{-3\gamma}{2} - 4 + \alpha)$	Ground State	
$ 0 0 > \frac{1}{2}, \frac{1}{2}, 0, 1\rangle$	$\frac{J}{2}(\frac{-3\gamma}{2} - 2 - \alpha)$		
$ 0 0 > \frac{1}{2}, \frac{1}{2}, 1, 0\rangle$	$\frac{J}{2}(\frac{-3\gamma}{2} - 2 - \alpha)$		
$ 0 0 > \frac{1}{2}, \frac{1}{2}, 0, 0\rangle$	$\frac{J}{2}(\frac{-3\gamma}{2} - 3\alpha)$		

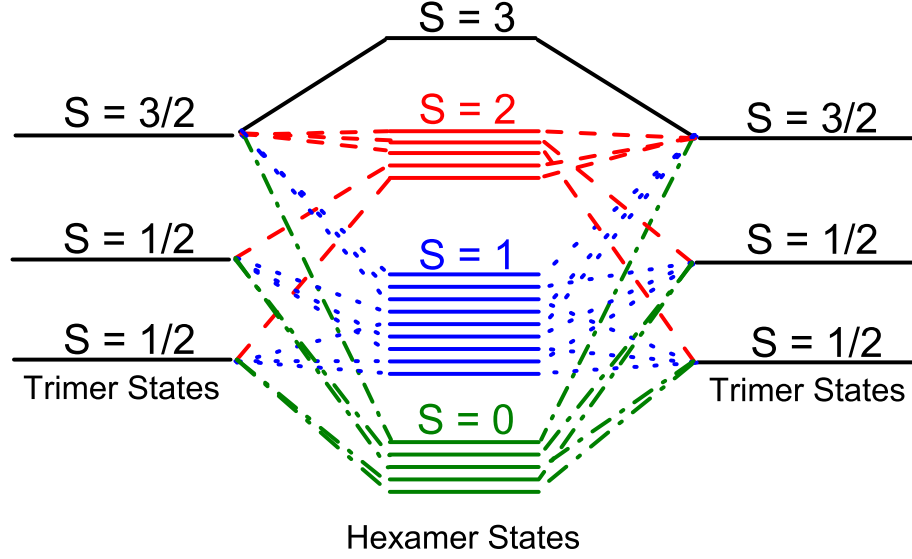


Figure 3.33: Energy levels of two spin-1/2 trimers coupling into a hexamer system. The trimer levels combine to give a spin-3 septet (black solid), 5 spin-2 quintets (red dashed), 9 spin-1 triplets (blue dotted), and 5 spin-0 singlets (green dot-dashed).

$$\begin{aligned}
Z = \sum_{i=1}^N e^{-\beta E_i} &= \sum_{E_i} (2S_{tot} + 1) e^{-\beta E_i} = e^{\frac{3J\beta(\gamma+2\alpha)}{4}} + 2e^{\frac{J\beta(3\gamma+4+2\alpha)}{4}} + e^{\frac{J\beta(3\gamma+8-2\alpha)}{4}} + \\
&e^{\frac{J\beta(15\gamma-4-2\alpha)}{4}} + 3e^{-\frac{J\beta(\gamma-6\alpha)}{4}} + 6e^{-\frac{J\beta(\gamma-4-2\alpha)}{4}} + 3e^{-\frac{J\beta(\gamma-8+2\alpha)}{4}} + 6e^{-\frac{J\beta(5\gamma-2+2\alpha)}{4}} \\
&+ 6e^{-\frac{J\beta(5\gamma+2-2\alpha)}{4}} + 3e^{-\frac{J\beta(11\gamma-4-2\alpha)}{4}} + 10e^{-\frac{J\beta(3\gamma+2-2\alpha)}{4}} + 10e^{-\frac{J\beta(3\gamma-2+2\alpha)}{4}} + \\
&5e^{-\frac{J\beta(3\gamma-4-2\alpha)}{4}} + 7e^{-\frac{J\beta(9\gamma+4+2\alpha)}{4}}
\end{aligned} \tag{3.143}$$

and the zero-field magnetic susceptibility per formula unit is

$$\chi = \frac{\beta}{Z} \sum_{i=1}^N (M_z^2)_i e^{-\beta E_i} = \frac{1}{3} (g\mu_B)^2 \frac{\beta}{Z} \sum_{E_i} (2S_{tot} + 1) (S_{tot} + 1) S_{tot} e^{-\beta E_i} =$$

$$\begin{aligned}
& \frac{N_A (g\mu_B)^2 \beta}{Z} \left(2 e^{-\frac{J\beta(\gamma-6\alpha)}{4}} + 4 e^{-\frac{J\beta(\gamma-4-2\alpha)}{4}} + 2 e^{-\frac{J\beta(\gamma-8+2\alpha)}{4}} + 4 e^{-\frac{J\beta(5\gamma-2+2\alpha)}{4}} + \right. \\
& 4 e^{-\frac{J\beta(5\gamma+2-2\alpha)}{4}} + 2 e^{-\frac{J\beta(11\gamma-4-2\alpha)}{4}} + 20 e^{-\frac{J\beta(3\gamma+2-2\alpha)}{4}} + 20 e^{-\frac{J\beta(3\gamma-2+2\alpha)}{4}} + \\
& \left. 10 e^{-\frac{J\beta(3\gamma-4-2\alpha)}{4}} + 28 e^{-\frac{J\beta(9\gamma+4+2\alpha)}{4}} \right) \quad (3.144)
\end{aligned}$$

In these formulas, the sum $i = 1 \dots N$ is over all N independent energy eigenstates (including magnetic substates), the sum $\sum_{E_i}$ is over energy levels only, $M_z = mg\mu_B$ where $m = S_{tot}^z/\hbar$ is the integral or half-integral magnetic quantum number, and g is the electron g -factor. Only zero-field susceptibility is shown, due to the length of the in-field expression. The result for the heat capacity is too large present here. It is implicitly determined by

$$C = k_B \beta^2 \frac{d^2 \ln(Z)}{d\beta^2}, \quad (3.145)$$

and can be evaluated using algebra programs. We have confirmed numerically that the zero-temperature entropy of the hexamer satisfies

$$\begin{aligned}
\frac{S}{k_B} &= \int_0^\infty \frac{C}{k_B} \frac{d\beta}{\beta} = \\
\ln(\mathcal{N}/\mathcal{N}_0) &= \begin{cases} \ln(\frac{2^6}{5}) & \alpha = \gamma = 1 \\ 2 \ln(2) & \alpha = 1, \gamma = 0 \\ 4 \ln(2) & \alpha \neq 1, \gamma = 0 \\ 6 \ln(2) & \alpha = 1, \gamma > 1, \end{cases} \quad (3.146)
\end{aligned}$$

where $\mathcal{N}$ is the dimensionality of the full Hilbert space and $\mathcal{N}_0$ is the degeneracy of the ground state; for the $S = \frac{1}{2}$ hexamer, $\mathcal{N} = 2^6$, and $\mathcal{N}_0 = 5$ for $\alpha = \gamma = 1$ [11,28]. Here, in the $\gamma \rightarrow 0$, the entropy of a trimer pair is recovered with the multiplicity of the ground state.

Table 3.13 shows the inelastic neutron scattering (INS) energy gaps and structure

factors for a spin- $\frac{1}{2}$ hexamer, which were determined from the energy eigenvalues and eigenvectors. For transitions between discrete energy levels, the excitation energy is equal to the energy difference, $\hbar\omega = E_f - E_i$. The resulting powder-average intensity including the magnetic form factor, is given by

$$\bar{S}(q) = F^2(q) \left(1 - j_0(qd_{\alpha_a/b}) \right), \quad (3.147)$$

(dimer excitation)

$$\bar{S}(q) = \frac{2F^2(q)}{7} \left(3 + j_0(qd_{\alpha_a/b}) - 4j_0(qd_{\eta_a/b}) \right), \quad (3.148)$$

(trimer excitation)

and

$$\begin{aligned} \bar{S}(q) = \frac{3F^2(q)}{7} & \left(9 + 8j_0(qd_{\alpha_a}) + 8j_0(qd_{\alpha_b}) \right. \\ & \left. - 8j_0(qd_{\eta_a}) - 8j_0(qd_{\eta_b}) - 9j_0(qd_{\gamma}) \right), \end{aligned} \quad (3.149)$$

(hexamer excitation)

where $F(q)$ is the magnetic form factor [58], d is the inter-atomic separation corresponding to the interaction, and $j_0(x) = \sin(x)/x$. For the spin- $\frac{1}{2}$ hexamer, there are five INS-observable excitations from the spin-0 ground state; two are dimer excitations, two are trimer excitations, and the fifth is an excitation of the full hexamer.

3.5.3 Application to V_6 Clusters

Experimental Techniques

All vanadium clusters, “ V_{green} ” and “ V_{blue} ”, were synthesized in a nitrogen atmosphere using the methods of Bogge *et al.* [68].

After synthesis the materials, the samples were stored in an inert gas atmosphere.

Several milligrams of the samples were prepared for measurement on a Quantum Design MPMS-XL magnetometer with a 6.5 Tesla magnet. For preparation, portions of the samples were wrapped in weighing paper lined with a very small amount of N grease to immobilize and protect them. The samples were then placed in the SQUID magnetometer. (The sample space of the SQUID magnetometer has a He atmosphere, so the samples were again in an inert atmosphere.) The backgrounds from the paper and grease was removed after the measurements. The measurements of the magnetic moments of the samples were carried out over the temperature range 2 K to 300 K in a weak applied field of 0.2 T.

Results and Discussion

In 2002, Luban *et al.* presented data for two vanadium molecular magnets that were found to consist of magnetically isolated V_3 trimers [45]. A trimer model was applied to the materials $(CN_3H_6)_4Na_2[H_4V_6O_8(PO_4)_4((OCH_2)_3CCH_2OH)_2] \cdot 14H_2O$ (“ V_{green} ”) and $Na_6[H_4V_6O_8(PO_4)_4((OCH_2)_3CCH_2OH)_2] \cdot 18H_2O$ (“ V_{blue} ”). (The shorthand name denotes the color of the material [68].) These molecular magnets consist of 6 $S = 1/2$ V^{4+} ions per formula unit, and the magnetic interactions were described by an isosceles trimer Heisenberg model. Fitting the data gave exchange constants of $J = 64.6$ K and $J' = 6.9$ K for V_{green} and $J = 63.8$ K and $J' = 5.9$ K for V_{blue} . Unpublished inelastic neutron scattering data purportedly confirmed the energy levels predicted by this model [69]. These two materials are good candidates for our hexamer model of possible weak inter-trimer interactions. From this model and a fit to the magnetic susceptibility, we will give predictions of the INS structure factors for the two V_6 materials we consider, which should be useful in future experiments.

In figure 3.34, we show the magnetic susceptibility data for V_{green} . The black and red lines show the fits to the isolated trimer and weakly interacting hexamer models,

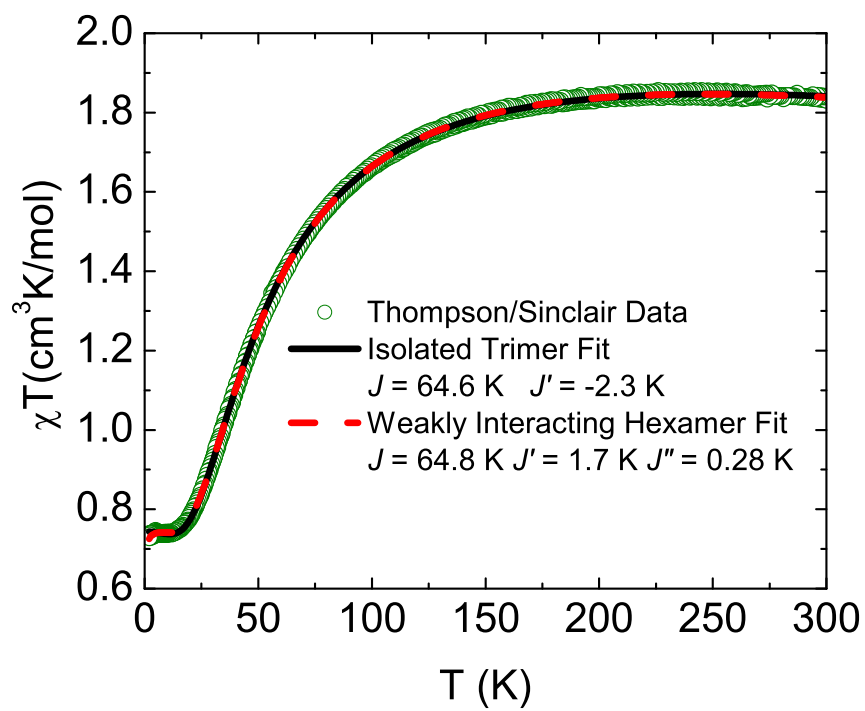


Figure 3.34: Magnetic susceptibility data for V_{green} (green circles), showing fits to the isolated trimer (solid black) and weakly interacting hexamer (dashed red) models.

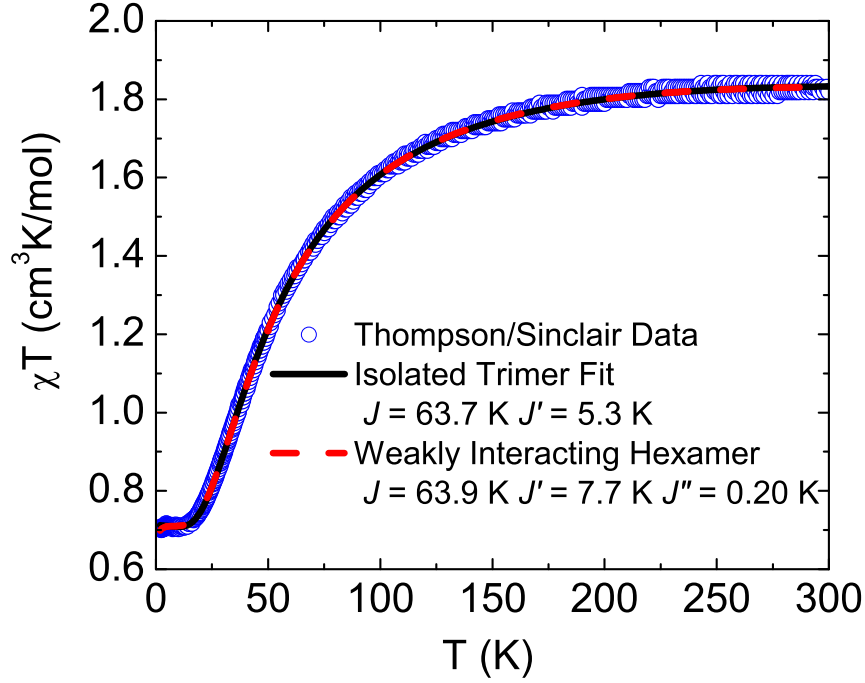


Figure 3.35: Magnetic susceptibility of V_{blue} (blue circles), showing fits to the isolated trimer (solid black) and weakly interacting hexamer (dashed red) models.

respectively. A fit to our data gives $J = 63.3$ K and $J' = -2.8$ K; this ferromagnetic J' is not in agreement with previous literature [45]. When we incorporate an intertrimer “hexamer” interaction, the value of J' is closer to that of Luban *et al.*; we find $J = 64.8$ K, $J' = 1.7$ K, and $J'' = 0.28$ K. Evidently the fitted J' has increased by 5 K and is anti-ferromagnetic. This fit suggests a possible scale for a very weak inter-trimer interaction (≈ 0.3 K). Note that the interaction J is dominant, and J' and J'' are much smaller and less well defined.

In figure 3.35, we show the magnetic susceptibility data for V_{blue} . The red and blue line show the fits to the isolated trimer and weakly interacting hexamer models. For the isolated trimer model, we find that our data leads to $J = 63.7$ K and $J' = 5.3$ K, which is in good agreement with the result of Luban *et al.* [45]. On incorporating

Table 3.14: Exchange interactions from magnetic susceptibility

$(\text{CN}_3\text{H}_6)_4\text{Na}_2[\text{H}_4\text{V}_6\text{O}_8(\text{PO}_4)_4((\text{OCH}_2)_3\text{CCH}_2\text{OH})_2] \cdot 14\text{H}_2\text{O}$ $(\text{V}_{\text{green}})$			
Model	$J(K)$	$J'(K)$	$J''(K)$
Isolated Trimer	64.6 ± 0.1	-2.3 ± 0.4	0
Hexamer	64.8 ± 0.1	1.7 ± 0.4	0.28 ± 0.01
Luban <i>et al.</i> [45]	64.6 ± 0.5	6.9 ± 1	0
$\text{Na}_6[\text{H}_4\text{V}_6\text{O}_8(\text{PO}_4)_4((\text{OCH}_2)_3\text{CCH}_2\text{OH})_2] \cdot 18\text{H}_2\text{O}$ (V_{blue})			
Model	$J(K)$	$J'(K)$	$J''(K)$
Isolated Trimer	63.7 ± 0.1	5.3 ± 0.6	0
Hexamer	63.9 ± 0.1	7.7 ± 0.6	0.20 ± 0.02
Luban <i>et al.</i> [45]	63.8 ± 0.6	5.9 ± 1.1	0

inter-trimer interaction, the fitting values change to $J = 63.9$ K, $J' = 7.7$ K, and $J'' = 0.20$ K. Again, the model suggests that a weak inter-trimer interaction of strength $J'' \approx 0.2$ K, similar to the previous ≈ 0.3 K may be present.

It is clear a weak inter-trimer interaction is consistent with the susceptibility data. As shown in Table 3.14, the fitted values of the dominant coupling, J , are all in close agreement. A slight discrepancy between theory and experiment is evident in fitting the isolated trimer model of V_{green} . Allowing a hexamer interaction, J'' , results in a shift in J' of a few K in these materials. While this is only a small change overall, it may be observable in the magnetic excitation spectrum in these materials.

Our fits suggest that $|0 \text{ S}_{\text{tot}}^z > \frac{1}{2}, \frac{1}{2}, 1, 1\rangle$ is the ground state in these materials. This

implies that only three excitations will be visible in INS (see Table 3.14). (Two of these states are doubly degenerate, which will split if the trimers are inequivalent). Therefore the presence of a hexamer interaction will allow the observation of additional inelastic neutron scattering excitations. Given out fitted values of the exchange interactions in the spin hexamer model, INS excitations would be visible at 0.02 meV, 5.46 meV, and 8.36 meV in V_{green} , and 0.02 meV, 4.84 meV, and 8.23 meV in V_{blue} . Although the low-lying excitation may be difficult to resolve, the two higher excitations should be clearly evident in INS. In an isolated trimer model these excitations would lie at 5.03 meV and 8.24 meV for V_{blue} . Allowing a hexamer interaction evidently has the effect of lowering the energies of these excitations. This difference should be evident in high resolution INS measurements. According to M. Luban, preliminary INS measurements show excitations at ~ 5.0 meV and ~ 8.25 meV, although this data is unpublished [69]. Future INS studies of deuterated samples would be very useful in clarifying magnetic interactions in these materials.

Figure 3.36 shows the predicted INS intensity for V_{blue} as a function of energy and momentum transfer for V_{blue} . In this system, the two highest visible excitations are excitations of the individual dimer and trimer subsystems. Since the individual trimers are identical and the coupling is weak, the two trimer excitations are at almost identical energies (similar for the dimer excitations.) It is evident that the effect of a weak hexamer interaction is a small shift in the energies and the presence of a new low-lying excitation. The structure factors of the two higher-energy excitations are not affected by the inter-trimer coupling. Only the first (low-lying) excitation shows a dependent on the inter-trimer distances. However, since the hexamer excitation is estimated to be quite small, $\sim 20 \mu\text{V}$, it may be difficult for INS to resolve this excitation. The two higher excitations arise from neutron interactions with the individual trimers and dimers; the 4.8 meV excitation is a dimer excitation, and the

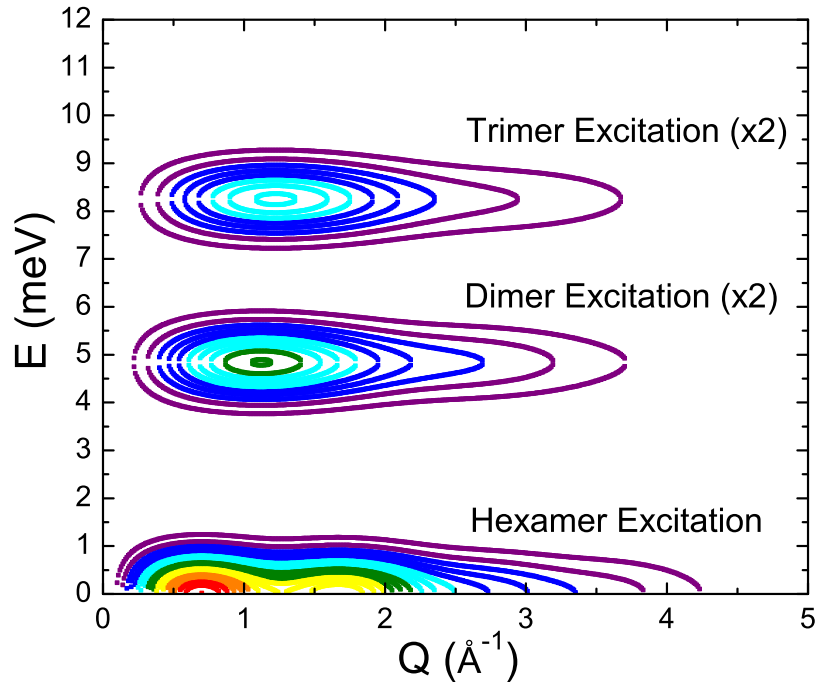


Figure 3.36: The predicted inelastic neutron scattering intensity for V_{blue} . Excitations of the dimer and trimer subsystems are expected at about 5 meV and 8 meV. The predicted intensity pattern for V_{green} is quite similar.

8.3 meV excitation is our excitation of the full trimer. It will be very interesting in future to see whether INS can indeed observe the effect of the weak inter-trimer interaction on the energy levels, and in particular observe the expected low-lying excitation.

Chapter 4

Summary and Conclusions

In this thesis, the magnetic properties and observables of quantum magnetic spin clusters consisting of two to six ions in various geometries were discussed. To derive closed-form expressions for the energy eigenvalues, we made extensive use of the Kambe approach, which involved rewriting the magnetic Hamiltonian in terms of the total spin of individual subsets of spins as well as the full cluster. Using this approach, our results for magnetic energy levels led to results for several bulk magnetic observables on the specific clusters we considered. These bulk observables are useful in the analysis of qualitative aspects of the magnetic interactions, and allow parameter determinations that are useful for inelastic neutron scattering.

In our studies of specific examples of spins and cluster geometries, we found that the inelastic neutron scattering structure factors we evaluated can provide a very valuable microscopic view of the inter-atomic magnetic interactions. We have found that the inelastic neutron scattering structure factors for the various transitions within larger systems often correspond to the excitations of smaller subsystems, which have very characteristics, experimentally accessible Q -dependence. This type of information can clearly be used to establish the nature of magnetic interactions in more complicated systems, and to distinguish between different models for the

magnetic interactions within a given material.

Extension of these studies of magnetic excitations in inelastic neutron scattering to the larger clusters of five to six ions clarified this "aufbau" principle with specific examples. Clusters larger than dimers consist of subsystems composed of the components of those clusters. The excitations observed in neutron scattering can only be transitions that satisfies $\Delta S = \pm 1$ or 0, for not only the full cluster, but also for the individual cluster components. Since larger clusters consist of multiple subsystems, these often control the nature of the allowed transitions if the transition only occurs within a subsystem. These restricted transitions introduce additional selection rules in neutron scattering. In neutron scattering, the possible INS excitations are usually considered to be transitions for which $\Delta S = \pm 1$ or 0. However, it is clear from the studies described here that the number of allowed transitions (with nonzero INS matrix element) is constrained by the allowed transitions within subsystems.

In a given cluster model, we have determined the energy eigenvectors we can calculate the inelastic neutron scattering structure factors. A study of the model's spatial geometry and the Q-dependence of the structure factors shows that the individual subsystems that comprise a cluster can often be identified in the structure factors. This is because a specific transition is often due to the excitation of a specific subsystem of the symmetry of that cluster. For example, a spin trimer consists of a dimer coupled to a single spin. Of the two transitions in the trimer, one is an excitation of the dimer alone and the other is an excitation of the full trimer. The dimer transition has the structure factor associated with the excitations of an isolated dimer.

This pattern may also be observed in larger clusters. The pentamer (consisting of a trimer coupling to a dimer) provides additional insight into the excitations of component subsystems. Different ground states allow variations in the types of components excited; the pentamer examined in this thesis was characterized by a

spin-2 ground state. In chapter 3, of the twenty a priori possible INS transitions, only five were allowed due to these subsystem constraints. These five transitions were excitations from the spin-2 ground state to spin-3,2, or 1 excited states, and the structure factors of those transitions corresponded directly to the component subsystem excited (3 were trimer excitations and the others were dimer and pentamer excitations.) If a dimer is excited, the structure factor has the characteristic dimer functional form. This is evident in Table 4.1, which gives results for all the spin systems examined in this thesis.

Another purpose of these calculations has been to consider the properties of some specific magnetic materials, in an attempt to help clarify their magnetic structures and properties. In some cases, this worked well and has given a clearer picture of the materials involved (*i.e.* the vanadium clusters). Other cases we considered have led to complications. For example, Na_3RuO_4 has been assumed in the literature to be a spin-3/2 tetramer. However, from comparisons between the experimental data and our theoretical results, it is clear that this system shows some properties that are more characteristic of an infinite, coupled system than a small isolated cluster.

In the case of the vanadium materials, we investigated two vanadium molecular magnets that had previously been discussed by Luban *et al.* [45] Comparison of our results for the magnetic susceptibility of a coupled trimer with data showed that a small inter-trimer interaction can indeed be accommodated and we were able to show how this interacts with the spectrum of excitations. Finally, we evaluated the inelastic neutron scattering structure factor for one of the materials, and showed that the inter-trimer interactions may lead to an observable change in the energy levels. The inter-trimer interactions primarily led to small level splittings, and did not significantly affect the INS intensities relative to the corresponding results for isolated trimers.

In the case of Na_3RuO_4 , we developed a new coupled dimer model in an attempt

Table 4.1: Cluster inelastic neutron scattering structure factor comparison

Cluster	Component of Excited	Structure Factor (Functional Form)
Dimer	Dimer	$S(q) = 1 - \cos(qd)$
Isosceles Trimer	Dimer Trimer	$S(q) = 1 - \cos(qd_1)$ $S(q) = 3 + \cos(qd_1) - 4\cos(qd_2)$
Tetramer (Coupled Dimer)	Dimer Dimer Tetramer	$S(q) = 1 - \cos(qd_1)$ $S(q) = 1 - \cos(qd_2)$ $S(q) = 2 + \cos(qd_1) + \cos(qd_2) - 4\cos(qd_3)$
Pentamer (Coupled Dimer/Trimer)	Dimer Trimer Trimer Trimer Pentamer	$S(q) = 1 - \cos(qd_3)$ $S(q) = 3 + \cos(qd_1) - 4\cos(qd_2)$ $S(q) = 3 + \cos(qd_1) - 4\cos(qd_2)$ $S(q) = 3 + \cos(qd_1) - 4\cos(qd_2)$ $S(q) = 15 + 9\cos(qd_3) - 36\cos(qd_4) + 4\cos(qd_1) + 8\cos(qd_4)$
Hexamer (Coupled Trimers)	Dimer Dimer Trimer Trimer Hexamer	$S(q) = 1 - \cos(qd_1)$ $S(q) = 1 - \cos(qd_2)$ $S(q) = 3 + \cos(qd_1) - 4\cos(qd_3)$ $S(q) = 3 + \cos(qd_2) - 4\cos(qd_4)$ $S(q) = 9 + 8\cos(qd_1) + 8\cos(qd_2) - 8\cos(qd_3) - 8\cos(qd_4) - 9\cos(qd_5)$

to understand new INS measurements of the excitations spectrum of this on the $S = \frac{3}{2}$ tetramer system. We determined the magnetic susceptibility and INS-visible excitation spectrum and intensities predicted by this model, which we compared to experiment. A comparison of the predictions of the “lozenge” model as presented by Regan *et al.* with the observed magnetic susceptibility and INS measurements showed that this is not a realistic model of Na_3RuO_4 . we instead found that a model for the system consisting of two separate dimers did explain some of the aspects of the data. It is clear from measurements of the heat capacity, that there are two distinct phase transitions in the material at 23 K and 28 K, which may provide useful information regarding long-range coupling in this material. Our conclusions are complicated by the presence of long range magnetic ordering and the possibility of a significant spin-orbit coupling; future studies of single crystals of Na_3RuO_4 , in particular neutron diffraction, may give a clearer picture of the overall magnetic structure.

In summary, in this thesis we have attempted to develop a deeper understanding of small, isolated clusters of magnetic ions. It is hoped that these results will be useful in the interpretation of the physics of larger, more complicated systems. Our examination of the magnetic properties of small clusters using analytical methods has shown how larger clusters may often be understood in terms of their smaller component subsystems.

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The V^{4+} magnetic form factor from ($g = 2$) can be modeled by $F = Ae^{as^2} + Be^{bs^2} + Ce^{cs^2} + D$, where $A = 0.3106$ ($a = 16.8160$), $B = 0.7198$ ($b = 7.0487$), $C = -0.0521$ ($c = 0.3020$), $D = 0.0221$, and $s = \sin\theta/\lambda = k/4\pi$.
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