Heisenberg Pentamer: Insights into Inelastic Neutron Scattering on Magnetic Clusters

J. T. Haraldsen

Phys. Rev. Lett. **107**, 037205 — Published 14 July 2011

DOI: 10.1103/PhysRevLett.107.037205

Heisenberg pentamer: Insights into inelastic neutron scattering on magnetic clusters

J. T. Haraldsen
Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA and
Department of Physics and Astronomy, University of Tennessee, Knoxville Tennessee 37996, USA

Assuming Heisenberg interactions and the symmetric case of a spin S-S' pentamer, the energy eigenstates can be determined exactly. With the energies known, the inelastic neutron scattering intensities are then calculated for the special case of a 1-1/2 pentamer. Through an analysis of these results, two main insights are gained: 1) Due to symmetry constraints, not all $\Delta S_{tot} = \pm 1$ transitions are accessible by INS. This constrains the standard selections rules for magnetic excitations. 2) the INS signatures of magnetic clusters are directly dependent on the state and component that is excited.

Magnetic clusters have gained much attention over recent years [1–3], and with a demand for faster and newer technologies, the area of molecular magnetism has become very focused[4, 5]. The need for both detailed experimental and theoretical work is of great importance to it the understanding of magnetic clusters. Most clusters typically have a larger number of spin ions, which restricts the ability to gain analytical understanding of the magnetic structure [6, 7]. Therefore, to access a more basic understanding of larger clusters, it is necessary to analyze smaller clusters that can be solved exactly.

Spin-1/2 clusters have been discussed in great detail in literature. In 2004, Whangbo *et al*. gave a comprehensive review of dimers with increasing spin[8], while Ref. [9] presented a review for the magnetic properties and inelastic neutron scattering (INS) excitations and intensities of spin-1/2 clusters. O. Waldmann examined the INS cross section of spin clusters with high molecular symmetry[10], and R. A. Klemm and D. V. Efremov have reviewed the single molecule anisotropy in small clusters of varying spin using first degree perturbation theory[11, 12]. Most cases have restricted the Hilbert space from two to four magnetic ions within the clusters with small spin quantum numbers.

Many different probes are used to understand the interactions and structure for magnetic spin clusters. Most notable are the bulk probes of magnetic susceptibility, heat capacity, and electron spin resonance. While bulk properties provide a wealth of knowledge and are of interest, the INS energies and intensities are the main focus of this paper. INS allows one to probe the microscopic nature of the clusters and gain direct knowledge of the magnetic interactions.

In 2009, the INS intensities of general tetramers and hexamers were examined in detail[13, 14]. An examination of the INS intensities revealed that the neutron excitations are restricted by sub-magnetic structures in a cluster and the functional form is directly linked to the specific component that is excited. However, these were always in the lowest spin ground state and similar valance. By expanding to pentamers and examining a mixed valance system with a non-zero ground state, it is possible to gain a clearer view of the way neutrons interact with clusters. Using the model of a general spin pentamer, the exact eigenstates can be determined, while the intensities utilize the convenience of smaller component basis sets. The pentamer discussed in this letter uses a basis of a dimer and a trimer. Although other general geometries can be examined, the specific case of a spin-S trimer coupled to a spin-S' dimer is of particular experimental interest[19]. From this basis, the energy eigenstates and INS intensities can be determined, while a more fundamental understanding of the cluster and its magnetic states is achieved. Though an analysis of these results and comparison to that of previous work, a clarification of INS selection rules and an understanding of the nature of INS excitations becomes clear.

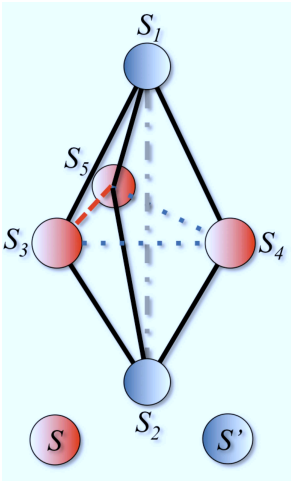

FIG. 1: A spin pentamer consisting of a spin-S trimer (white/red circles) and a spin-S' dimer (blue/white circles). The magnetic interactions consist of a six trimer to dimer J (solid black - d_1), two intra-trimer ηJ (dotted dark blue - d_2), one trimer-dimer αJ (dashed red - d_3), and one apical-dimer γJ (dash-dot grey - d_4) interactions.

As shown in Fig. 1, the pentamer model consists of an isosceles trimer cluster that interacts with two apical ions. Assuming pairwise Heisenberg interactions, this

TABLE I: Energy levels and INS properties for a 1-1/2 pentamer

Spin State $\mid \mathbf{S}_{tot}\ \mathbf{S}^z_{tot} >_{\Delta,d_t,d_a}$	**Energy Level**	**INS Energy Gap**	**INS Powder Intensity**[a]
$\mid 4\ \mathrm{S}^z_{tot} >_{3,2,1}$	$\frac{J}{4}(12+8\eta+4\alpha+\gamma)$		
$\mid 3\ \mathrm{S}^z_{tot} >_{3,2,1}$	$\frac{J}{4}(-4+8\eta+4\alpha+\gamma)$	$3J$	$\frac{10}{189}[15+9j_0(qd_4)-36j_0(qd_1)+4j_0(qd_3)+8j_0(qd_2)]$
$\mid 3\ \mathrm{S}^z_{tot} >_{2,2,1}$	$\frac{J}{4}(8-4\eta+4\alpha+\gamma)$	$6J$	$\frac{1}{4725}[3-4j_0(qd_2)+j_0(qd_3)]$
$\mid 3\ \mathrm{S}^z_{tot} >_{2,1,1}$	$\frac{J}{4}(8+4\eta-4\alpha+\gamma)$	$6J$	0
$\mid 3\ \mathrm{S}^z_{tot} >_{3,2,0}$	$\frac{J}{4}(8\eta+4\alpha-3\gamma)$	$4J$	$\frac{1}{14}[1-j_0(qd_4)]$
$\mid 2\ \mathrm{S}^z_{tot} >_{3,2,1}$	$\frac{J}{4}(-16+8\eta+4\alpha+\gamma)$	Ground State	
$\mid 2\ \mathrm{S}^z_{tot} >_{2,2,1}$	$\frac{J}{4}(-4+4\eta+4\alpha+\gamma)$	$3J$	$\frac{41}{4725}[3-4j_0(qd_2)+j_0(qd_3)]$
$\mid 2\ \mathrm{S}^z_{tot} >_{2,1,1}$	$\frac{J}{4}(-4+4\eta-4\alpha+\gamma)$	$3J$	0
$\mid 2\ \mathrm{S}^z_{tot} >_{1,2,1}$	$\frac{J}{4}(4-12\eta+4\alpha+\gamma)$	$5J$	0
$\mid 2\ \mathrm{S}^z_{tot} >_{1,1,1}$	$\frac{J}{4}(4-4\eta-4\alpha+\gamma)$	$5J$	0
$\mid 2\ \mathrm{S}^z_{tot} >_{1,0,1}$	$\frac{J}{4}(4-8\alpha+\gamma)$	$5J$	0
$\mid 2\ \mathrm{S}^z_{tot} >_{2,2,0}$	$\frac{J}{4}(-4\eta+4\alpha-3\gamma)$	$4J$	0
$\mid 2\ \mathrm{S}^z_{tot} >_{2,1,0}$	$\frac{J}{4}(4\eta-4\alpha-3\gamma)$	$4J$	0
$\mid 1\ \mathrm{S}^z_{tot} >_{2,2,1}$	$\frac{J}{4}(-12-4\eta+4\alpha+\gamma)$	J	$\frac{7}{75}[3-4j_0(qd_2)+j_0(qd_3)]$
$\mid 1\ \mathrm{S}^z_{tot} >_{2,1,1}$	$\frac{J}{4}(-12+4\eta-4\alpha+\gamma)$	$6J$	0
$\mid 1\ \mathrm{S}^z_{tot} >_{1,2,1}$	$\frac{J}{4}(-4-12\eta+4\alpha+\gamma)$	$3J$	0
$\mid 1\ \mathrm{S}^z_{tot} >_{1,1,1}$	$\frac{J}{4}(-4-4\eta-4\alpha+\gamma)$	$3J$	0
$\mid 1\ \mathrm{S}^z_{tot} >_{1,0,1}$	$\frac{J}{4}(-4-8\alpha+\gamma)$	$3J$	0
$\mid 1\ \mathrm{S}^z_{tot} >_{1,2,0}$	$\frac{J}{4}(-12\eta+4\alpha-3\gamma)$	$4J$	0
$\mid 1\ \mathrm{S}^z_{tot} >_{1,1,0}$	$\frac{J}{4}(-4\eta-4\alpha-3\gamma)$	$4J$	0
$\mid 1\ \mathrm{S}^z_{tot} >_{1,0,0}$	$\frac{J}{4}(-8\alpha-3\gamma)$	$4J$	0
$\mid 1\ \mathrm{S}^z_{tot} >_{0,1,1}$	$\frac{J}{4}(-8\eta-4\alpha+\gamma)$	$4J$	0
$\mid 0\ 0 >_{1,2,1}$	$\frac{J}{4}(-8-12\eta+4\alpha+\gamma)$		
$\mid 0\ 0 >_{1,1,1}$	$\frac{J}{4}(-8-4\eta-4\alpha+\gamma)$		
$\mid 0\ 0 >_{1,0,1}$	$\frac{J}{4}(-8-8\alpha+\gamma)$		
$\mid 0\ 0 >_{1,1,0}$	$\frac{J}{4}(-4-4\eta-4\alpha-3\gamma)$		

[a]For comparison to real materials, the powder intensities must be multiplied by the magnetic form factor for that material.

system is described by the Hamiltonian

$$\mathcal{H} = J\Big[\eta\big(\vec{S}_3\cdot\vec{S}_4+\vec{S}_4\cdot\vec{S}_5\big)+\alpha\,\vec{S}_3\cdot\vec{S}_5+\gamma\vec{S}_1\cdot\vec{S}_2+ \vec{S}_1\cdot\vec{S}_3+\vec{S}_2\cdot\vec{S}_3+\vec{S}_1\cdot\vec{S}_4+\vec{S}_2\cdot\vec{S}_4+\vec{S}_1\cdot\vec{S}_5+\vec{S}_2\cdot\vec{S}_5\Big] -g_i\mu_B B\sum_i^5 S_i^z \tag{1}$$

For positive and negative values, the magnetic interactions are antiferromagnetic and ferromagnetic, respectively. $\vec{S}_i$ is the quantum spin operator for a spin-S ion at site i (i=1...5.) The Zeeman term describes the interaction with a magnetic field, and splits the degenerate magnetic substates, where g_i is the landé factor for the respective ions[16]. Note that the model consists of two separate dimers. One is a dimer within the trimer (d_t) and the other is the apical dimer (d_a).

The energy eigenstates and eigenvectors may be found by diagonalizing the magnetic Hamiltonian on a basis of dimers and trimers. Here, a set of $\hat{z}$-polarized magnetic basis states are employed. The energy eigenvalues for the general $S-S'$ pentamer are determined exactly, and are given by

$$E = \tfrac{J}{2}\Big[\eta\big(\int_\Delta - \int_{d_t} - \int\big)+\alpha\big(\int_{d_t}-2\int\big)+\gamma\big(\int_{d_a}-2\int'\big)+ \int_{tot}-\int_{d_a}-\int_\Delta\Big]-g\mu_B B S^z_{tot}, \tag{2}$$

where $\int_i = S_i(S_i+1)$. Here S_{tot} denotes the total spin of the pentamer, S_Δ is the spin of the trimer, S_{d_t} and S_{d_a} are the spins of the individual dimers, S and S' are the spins of the ions, and S^z_{tot} is the total spin z-component of the pentamer.

Since this is a rotationally invariant Hamiltonian in spin space, the total spin S_{tot} and S^z_{tot} 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 INS structure factors requires the exact magnetic states to be know.

If one considers a pentamer consisting of a dimer of spin-$\frac{1}{2}$ ions coupled to a trimer of spin-1 ions. There are $(2\big(\frac{1}{2}\big)+1)^2\cdot(2\big(1\big)+1)^3 = 108$ magnetic basis states, which have the spin decomposition of

$$4\oplus 3^4\oplus 2^8\oplus 1^9\oplus 0^4. \tag{3}$$

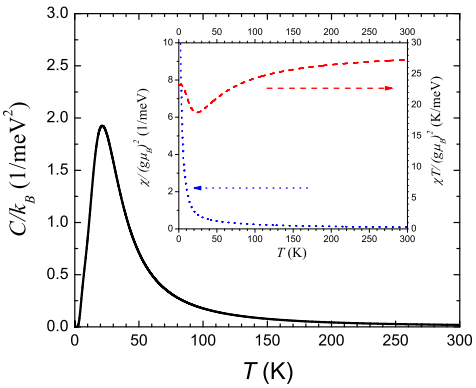

FIG. 2: Predicted heat capacity for a pentamer with $\alpha = \eta = \gamma = 0$ and $J = 2.0$ meV. The inset shows the magnetic susceptibility for the same cluster.

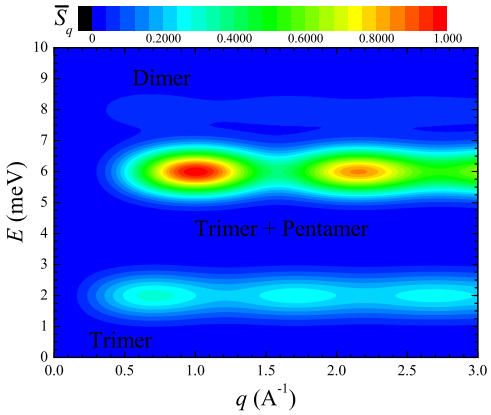

FIG. 3: Predicted energy versus wavevector powder INS spectra for a pentamer system with $\alpha = \eta = \gamma = 0$ and $J = 2.0$ meV. Here, distances are $d_1 = 5.0$ Å, $d_2 = 6.5$ Å, $d_3 = 7.0$ Å, and $d_4 = 6.6$ Å. The excitation at $6J$ is too weak to be observed, but will be similar in shape as the J excitations. The magnetic form factor is not included.

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. 5. These degenerate states will be split by an applied magnetic field.

Table I gives the energy eigenstates of the 1-1/2 pentamer Hamiltonian. The complete set of pentamer interactions includes coupling 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 the pentamer eigenstates is due to the equality of the couplings. If the coupling strengths were different, there would be mixing between the dimer and trimer basis states, which would greatly complicate the system.

Various bulk magnetic properties can be calculated in general form from the determined energy levels using methods described in Ref. [9]. However, due to the overall size of the exact analytical solutions, these quantities are not shown. For comparison, the heat capacity can be used to calculate the entropy of the pentamer, which can be compared to the zero-temperature entropy expected for this system. Through numerical integration, the zero-temperature entropy of the pentamer does indeed satisfy

$$\begin{aligned} \tfrac{S}{k_B} &= \textstyle\int_0^\infty \tfrac{C}{k_B}\,\tfrac{d\beta}{\beta} = \ln(\mathcal{N}/\mathcal{N}_0) \\ &= \begin{cases} 3\ln(3) & \alpha=\gamma=\eta=1 \\ \ln(\frac{108}{5}) & \alpha=\gamma=\eta=0, \end{cases} \end{aligned} \tag{4}$$

where $\mathcal{N}$ is the dimensionality of the full Hilbert space and $\mathcal{N}_0$ is the degeneracy of the ground state[9, 24]. The zero-temperature entropy clearly changes discontinuously if the degeneracy of the ground state changes.

Over the past few years, a number of heterobimetallic inorganic compounds have been characterized as pentanuclear clusters. [17–19] Most notably are the cyanide-bridged complexes of transition metals, [19–23] where mixed valance systems produce strong magnetic coupling along with controllable structural properties. These complexes are based from the building block or modular approach. Here, material growth is limited to a finite size through the use of transition metal complexes.[22] This helps to produce cyanide-bridge compounds with properties ranging from single molecule behavior to spin crossover. [20]

For a comparison to similar materials, interactions similar to those presented by Shatruk *et al.*[19] are used, where $\alpha = \eta = \gamma = 0$. Here, the Hamiltonian

$$\begin{aligned} \mathcal{H} = J\Big[&\vec{S}_1\cdot\vec{S}_3 + \vec{S}_2\cdot\vec{S}_3 + \vec{S}_1\cdot\vec{S}_4 + \\ &\vec{S}_2\cdot\vec{S}_4 + \vec{S}_1\cdot\vec{S}_5 + \vec{S}_2\cdot\vec{S}_5\Big] \end{aligned} \tag{5}$$

is greatly reduced due to the symmetry of the cluster. Figure 2 shows the predicted heat capacity with magnetic susceptibility in the inset. Here, $J = 2.0$ meV, which is in decent agreement with Ref. [19]. The magnetic susceptibility clearly indicates a non-zero ground state. Through an examination of the energy levels, the pentamer is in a spin-2 ground state. Table I shows our results for the INS energy gaps and powder average intensities for the spin pentamer, which are determined from the pentamer energy eigenstates and eigenvectors using methods described in Ref. [9]. Here, d_i are the inter-atomic distances (described in Fig. 1) and $j_0(x) = \sin(x)/x$. The excitation energies for these discrete levels are 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 INS powder average intensity $\bar{S}_q$, which is determined through an average of the unpolarized single-crystal neutron scattering structure factor over all orientations.

For a $S_{tot} = 2$ ground state state, it is typically thought that any final state of S_{tot} = 1,2, or 3 could be excited by INS. However, as shown in Table I, it is clear that only some of the states can be accessed. For the spin 1-1/2 pentamer, there are five possible INS observable excitations. This limitation is due to the magnetic sub-states of the pentamer. Since the pentamer ground state has trimer and dimer (d_t and d_a) states of 3, 2, and 1, respectively, only S_{tot} states whose magnetic sub-states either match or deviate by ± 1 can be observed by INS. This restricts the S_{tot} state to have sub-states of (3,2,1), (3,2,0), and (2,2,1). This is due to the inability of a neutron to excite more than one component at a time. Other excitations would be excitable by a two-neutron interaction those would be very small due to the improbability of that interaction.

Figure 3 shows the INS powder spectra for $J = 2.0$ meV assuming $\alpha = \eta = \gamma = 0$. By examining the functional form of the powder intensities of the pentamer and comparing to the known intensities of the smaller components[9], the excitation of an individual component of a leads to an INS intensity representative of that component, where overall pentamer structure does not add any more complexity to the given intensity. In this system, three of the excitations are that of the trimer, one an excitation of the axial dimer, and the fifth is an excitation of the full pentamer. It should be noted that there are no uncoupled excitations of d_t. This is due to the inability to change the state of d_t without changing the overall state of the trimer. This cannot be accomplished through a single neutron excitation, since there is no spin-3 trimer state given that d_t is in a spin-1 state, this transition is not allowed.

This is also been predicted in tetramer and hexamer calculations [13, 14]. Here, the tetramer (coupled dimers) and hexamer (coupled trimers) excitations followed this same pattern. Therefore, it is expected that excitations observed in larger clusters will also be composed of the individual components. It is hoped that this will allow for a deeper understanding of large magnetic clusters.

In conclusion, the exact solution for the energy eigenstates of the general spin pentamer are presented, and the INS energies and intensities for a pentamer composed of a spin-1 trimer and spin-1/2 dimer have been determined. This may be of particular interest for the materials described by Shatruk *et al*. [19]. A further analysis of this work and previous work on clusters has shown that specific excitations are restricted in INS due to sub-magnetic structure of clusters. This provides a deeper understanding of the INS selection rules for magnetic clusters. It is also determined that the excitations that do occur will have a functional form representative of component being excited. These insights are particularly important for those investigating nanomagnetic materials. Further analysis of this type of phenomena may have direct consequences in other fields of physics.

I would like to acknowledge useful discussions with T. Barnes and H. Dahal. This research was partially sponsored by the Joint Institute for Neutron Sciences and The University of Tennessee, as well as, the Center for Integrated Nanotechnologies, a U.S. Department of Energy, Office of Basic Energy Sciences user facility. Los Alamos National Laboratory is operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396.

[1] W. Heisenberg, Z. Phys. **38**, 411 (1926)
[2] D. Gatteschi, R. Sessoli, and J. Villain *Molecular Nanomagnets* (Oxford University Press, 2006).
[3] E.Dagotto and T.M.Rice, Science **271**, 618 (1996).
[4] O.Kahn, *Molecular Magnetism* (VCH Publishers, New York, 1993).
[5] M.A.Nielsen and I.L.Chuang, *Quantum Computation and Quantum Information* (Cambridge, 2000).
[6] E. Micotti *et al*., J. Mag. Mag. Mater. **272-276**, 1099 (2004).
[7] C. Schröder *et al*., Phys. Rev. Lett. **94**, 207203 (2005).
[8] M. H. Whangbo, H. J. Koo, and D. Dai, J. Solid State Chem. **176**, 417 (2003).
[9] J. T. Haraldsen, T. Barnes, and J. L. Musfeldt, Phys. Rev. B **71**, 064403 (2005)
[10] O. Waldmann, Phys. Rev. B **68**, 174406 (2003)
[11] D. V. Efremov and R. A. Klemm Phys. Rev. B **74**, 064408 (2006)
[12] R. A. Klemm and D. V. Efremov, Phys. Rev. B **77**, 184410 (2008)
[13] J. T. Haraldsen *et al*., J. Phys.: Condens. Matter **21**, 506003 (2009).
[14] J.T. Haraldsen *et al*., Phys. Rev. B **80**, 064406 (2009).
[15] K. Kambe, J. Phys. Soc. Jpn. **5**, 48 (1950)
[16] R.M. White, *Quantum Theory of Magnetism: Magnetic Properties of Materials* (Springer, 2010).
[17] M. M. Najafpour *et al*., Inorg. Chem. Comm. **14**, 125 (2011).
[18] U. Kortza *et al*., Coordination Chem. Revs. **253**, 2315 (2009)
[19] M. Shatruk *et al*., Inorg. Chem. **46**, 5155 (2007).
[20] K.R. Dunbar and R. A. Heintz, Prog. Inorg. Chem. **45**, 283 (1997).
[21] M. Shatruk, C. Avendano, and K. R. Dunbar, *Cyanide-Bridged Complexes of Transition Metals: A Molecular Magnetism Perspective, in Progress in Inorganic Chemistry*, **56** (Ed. K. D. Karlin, John Wiley & Sons, 2009).
[22] K. E. Funck *et al*., Inorg. Chem. **50**, 2782 (2011).
[23] J. H. Lim *et al*., Inorg. Chem. **50**, 1749 (2011).
[24] G.L.Squires, *Introduction to the Theory of Thermal Neutron Scattering* (Dover, 1996).