Online lectures accessible at:
http://neutrons.ornl.gov/neutrons-videos
Quantum magnetism in insulating solids

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Coulomb + Pauli = Heisenberg

Coulomb interactions plus Pauli principle split 4-fold spin degeneracy

The level scheme is reproduced by Heisenberg Exchange Hamiltonian

\[ \mathcal{H} = J S_i \cdot S_j \]

\( S_{tot} = 0 \) \( S_{tot} = 1 \)

Triplet gnd. State: \( J < 0 \)

Singlet gnd. State: \( J > 0 \)
Overview

✧ Neutron Scattering
  ○ Inelastic scattering
  ○ Sum-rules

✧ Singlet formation in 1D
  ○ Alternating spin-1/2 chain (static singlets)
  ○ Uniform spin-1/2 chain (resonating singlets)

✧ Frustrated Quantum Magnetism
  ○ Continuum scattering from kagome magnet
  ○ Quantum spin-ice
  ○ Spin-orbital systems
  ○ Magneto-structural effects

✧ Conclusions
Neutron Scattering

n-matter Interactions:
• Weak (Born limit)
• Energy independent
• Well characterized
• Similar strengths

\[ E = \frac{\hbar^2}{2m} k^2 \]

\[ = 2.072 \text{ meVÅ}^2 k^2 \]

\[ \frac{d^2\sigma}{d\Omega dE_f} = \frac{\text{Rate of neutrons into } d\Omega \text{ and } dE_f}{\Phi \times d\Omega \times dE_f} \]

\[ V_M(r) = -\mu_N \cdot H \]
\[ \sigma \sim \left( \gamma \frac{e^2}{m_e c^2} \right)^2 = 0.2916 \text{ barn} \]

n-matter Interactions:
• Weak (Born limit)
• Energy independent
• Well characterized
• Similar strengths

\[ V_N(r) = \frac{2\pi \hbar^2}{m} b\delta(r) \]
\[ \sigma = 4\pi b^2 \sim 1 \text{ barn} \]

\[ S^{\alpha\beta} (Q,\omega) = \frac{1}{2\pi \hbar} \int dt e^{-i\omega t} \frac{1}{2\pi \hbar^N} \sum_{RR'} e^{iQ(\mathbf{R}-\mathbf{R}')/N} \left\langle \rho_{QR}(0) S^{\alpha}_{RQ}(t) S^{\beta}_{RQ}(t) \right\rangle \]
Understanding Inelastic Magnetic Scattering:

Isolate the “interesting part” of the cross section

\[
\frac{d^2 \sigma}{d\Omega dE'} \equiv \frac{k'}{k} N r_0^2 \frac{g}{2} F(Q) \left| \frac{e^{-2w(Q)}}{2} \sum_{\alpha\beta} \left( \delta_{\alpha\beta} - \hat{Q}_\alpha \hat{Q}_\beta \right) S^{\alpha\beta}(Q,\omega) \right|^2
\]

The dynamic correlation function (“scattering law”):

\[
S^{\alpha\beta}(Q,\omega) \equiv \frac{1}{2\pi \hbar} \int dt e^{-i\omega t} \frac{1}{N} \sum_{ll'} e^{iQ \cdot (r_l - r_{l'})} \left\langle S^\alpha_l(0) S^\beta_{l'}(t) \right\rangle
\]

In thermodynamic equilibrium (detailed balance):

\[
S(Q,\omega) = \exp(\beta \hbar \omega) S(-Q,-\omega)
\]
Useful exact sum-rules:

Total moment sum-rule (general result from Fourier analysis)

$$\frac{1}{\int d^3Q \sum_\alpha \int \hbar d\omega} S^{\alpha\alpha}(Q\omega) = \langle S(0) \cdot S(0) \rangle = s(s+1)$$

Correlations in space & time rearrange intensity in space leaving the total scattering unaffected

Definition of the equal time correlation function:

$$S^{\alpha\alpha}(Q) \equiv \sum_{ll'} \langle S_l^\alpha S_{l'}^\alpha \rangle e^{iQ \cdot (r_l - r_{l'})} = \int S^{\alpha\alpha}(Q\omega) \hbar d\omega$$

The wave vector dependence of the energy-integrated intensity probe a snap-shot of the fluctuating spin configuration
Fluctuation Dissipation Theorem

Define the following t-dependent “response” function:

$$\Phi_\mathbf{Q}(t) = \frac{i}{\hbar} \langle [S_\mathbf{Q}(t), S_{-\mathbf{Q}}] \rangle$$

The generalized susceptibility can be expressed as:

$$\chi(Q\omega) = -\left(g\mu_B\right)^2 \lim_{\varepsilon \to 0^+} \int_0^\infty dt e^{-i(\omega - i\varepsilon)t} \Phi_\mathbf{Q}(t)$$

The “scattering law” can be expressed as:

$$\mathcal{S}(Q\omega) = \frac{1}{1 - e^{-\beta\hbar\omega}} \frac{1}{2\pi i} \int e^{i\omega t} \Phi_\mathbf{Q}(t) dt$$

From which, the “fluctuation-dissipation” theorem:

$$\mathcal{S}(Q\omega) = \frac{1}{1 - e^{-\beta\hbar\omega}} \frac{\chi''(Q\omega)}{\pi \left(g\mu_B\right)^2}$$
First Moment Sum-rule

Fourier transform of expression for scattering law:

\[ \Phi_Q(t) = i \int d\omega e^{-i\omega t} S(Q\omega)(1 - e^{-\beta \hbar \omega}) \]

Time derivative of left side evaluated for \( t=0 \):

\[ \partial_t \Phi_Q(t = 0) = -\frac{1}{2} \left\langle \left[ S_Q, \left[ S_{-Q}, \mathcal{H} \right] \right] \right\rangle \]

Time derivative of right side evaluated at \( t=0 \):

\[ \int \omega \, d\omega \, S(Q\omega)(1 - e^{-\beta \hbar \omega}) = 2 \int \omega \, d\omega \, S(k\omega) \]

Equating these leads to the first moment sum-rule:

\[ \int \hbar \omega \, \hbar \, d\omega \, S(Q\omega) = -\frac{1}{2} \left\langle \left[ S_Q, \left[ S_{-Q}, \mathcal{H} \right] \right] \right\rangle \]
Overview

- **Neutron Scattering**
  - Inelastic scattering
  - Sum-rules

- **Singlet formation in 1D**
  - Alternating spin-1/2 chain (static singlets)
  - Uniform spin-1/2 chain (resonating singlets)

- **Frustrated Quantum Magnetism**
  - Continuum scattering from kagome magnet
  - Quantum spin-ice
  - Spin-orbital systems
  - Magneto-structural effects

- **Conclusions**
Singlet product state on alternating spin-1/2 chain

\[ \langle S_0 \rangle \]

Temperature (K)

\[ \frac{1}{\sqrt{2}} \left( |\uparrow \downarrow \rangle + |\downarrow \uparrow \rangle \right), \]

\[ |\downarrow \downarrow \rangle \]

\[ S_{tot} = 1 \]

|\uparrow \uparrow \rangle, |\uparrow \downarrow \rangle, |\downarrow \uparrow \rangle, |\downarrow \downarrow \rangle \]

\[ \frac{1}{\sqrt{2}} \left( |\uparrow \downarrow \rangle - |\downarrow \uparrow \rangle \right) \]

\[ S_{tot} = 0 \]

Cu(NO₃)₂·2.5D₂O: Alternating spin chain
Quantum critical spin-1/2 chain

Hammar et al. (1999)

\[ \text{Cu(C}_4\text{H}_4\text{N}_2)(\text{NO}_3)_2 \]
Probing matter through scattering

\[ \hat{p}_f \quad \hat{h}Q_1 \quad \hat{h}Q \quad \hat{h}Q_2 \]

\[ \hat{p}_i = \hat{p}_f - \hat{p}_f \]

\[ \epsilon(Q_1) \theta(Q_2) E_i = E_f E_f - E_f \]

Intensity

Single Particle Process

Intensity

Multi Particle Process
Emergent quasi-particles at QCP

\[ |\Psi\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \]
Quantum Critical Spin-1/2 chain

\[ H = \sum_{n} \left( J_2 S_{2n} \cdot S_{2n+1} + J_1 S_{2n+1} S_{2n+2} \right) \]

\[ \Delta \]

Odd bond singlets

Even bond singlets

\[ \delta = \frac{J_2 - J_1}{J_2 + J_1} \]

Damle and Huse PRL (2002)
Magnetic excitations near quantum criticality

- No order parameter from which to form harmonic modes
- Excitations from quasi-particles in a strongly fluctuating medium
- Angular momentum conservation precludes single particle scattering
- Expect a broad continuum of scattering

\[ |\langle S_i \rangle| = 0 \]
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Corner-linked simplexes

Kagome

Hyper Kagome

Pyrochlore

Takagi et al.

Balents et al.
Herbertsmithite: \((\text{Zn}_{0.85}\text{Cu}_{0.15})\text{Cu}_3(\text{OD})_6\text{Cl}_2\)

Synthetic HS From MIT:
Small, clean, & deuterated
Y. S. Lee & Tianheng Han

Natural Herbertsmithite
From Chile: Big & dirty
Correlations in quantum kagome magnet

- “Rigid” extended structures in momentum space
- Consistent with structure factor for spinon


Hao & Tchernyshyov, PRB (2010)
Continuum in 2D quantum magnet

Spinons on kagome

$S = \frac{1}{2}$ kagome AFM has a finite concentration of spinons in its ground state.

Spinons are solitons with spin $S = \frac{1}{2}$ and fermionic statistics.

Exchange-mediated attraction binds spinons into pairs with spin $S=0$.

The ground state appears to be a Z2 spin liquid.

Y. Wan and O. Tchernysnyov, ArXiv 1301.5008v1 (2013)
Topological excitations and the dynamic structure factor of spin liquids on the kagome lattice

Matthias Punk, Debanjan Chowdhury, and Subir Sachdev
Department of Physics, Harvard University, Cambridge MA 02138

Decoupled impurity spins

Interacting impurity spins have simple cubic connectivity. The 15% concentration is below the 31.16% percolation threshold.
A gap in the spectrum of kagome planes

M. Fu et al., Science (2015)

Han et al., submitted to PRL (2016)

The NMR gap size of 0.9 meV is
• Consistent with neutron scattering
• Consistent with DMRG results
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Ising FM: Spin-Ice

\[ S_i = \sigma_i d_k \text{ where } d_k \cdot d_{k'} = -\frac{1}{3} \]

\[ \mathcal{H} = -J \sum_{\langle ij \rangle} S_i \cdot S_j = \frac{1}{3} J \sum_{\langle ij \rangle} \sigma_i \sigma_j \]

\[ = \frac{1}{6} J \sum \sigma^2 + c \text{st} \]

Ground state: \( \sigma = \sum_{i \in \downarrow} \sigma_i = 0 \)

6 out of 16 states have \( \sigma = 0 \)

\[ S_{\text{Pauling}} = k_B \ln \left( 2^N \left( \frac{6}{16} \right)^\frac{N}{2} \right) = \frac{1}{2} R \ln \frac{3}{2} \]
Pinch points and monopoles in spin ice
Fennell et al. Science (2009)
Quantum Spin Ice in Pr$_2$Zr$_2$O$_7$?

Exchange spin ice

\[ H = \sum_{\langle ij \rangle} [J_{zz} S_i^z S_j^z - J_\pm (S_i^+ S_j^- + S_i^- S_j^+) + J_{\pm \pm} (\gamma_{ij} S_i^+ S_j^+ + \gamma_{ij}^* S_i^- S_j^-)] \]
Quantum fluctuations in spin-ice

Pr$_2$Zr$_2$O$_7$: Quantum Spin Ice

Pr$_2$Zr$_2$O$_7$ Powder DCS

Only 5% of the scattering is elastic
Elastic scattering $|\hbar \omega| < 0.2 \text{ meV}$

$I(T = 0.1 \text{ K}) - I(T = 20 \text{ K})$

$\nabla \cdot \mathbf{M} \approx 0$
No pinch points for inelastic scattering

\[ \nabla \cdot M \neq 0 \]

0.25 meV
Excitation in (001) magnetized Pr$_2$Zr$_2$O$_7$
Elastic Scattering from (001) magnetized Pr$_2$Zr$_2$O$_7$

The induced “static” (|\(\hbar \omega| < 1\) K) magnetization is not lattice periodic!
Inhomogeneous Level Splitting in Pr$_{2-x}$Bi$_x$Ru$_2$O$_7$

J. van Duijn,$^{1,2}$ K. H. Kim,$^{3,*}$ N. Hur,$^4$ D. Adroja,$^2$ M. A. Adams,$^2$ Q. Z. Huang,$^5$ M. Jaime,$^3$ S.-W. Cheong,$^4$ C. Broholm,$^{1,5}$ and T. G. Perring$^2$

• The level distribution function:

\[ \rho(\Delta) \]

• Singlet-singlet susceptibility:

\[ \chi''(\omega) = \pi \left( g \mu_B \alpha \right)^2 \left( \delta(\omega - \Delta) - \delta(\omega + \Delta) \right) \frac{1 - e^{-\beta\Delta}}{1 + e^{-\beta\Delta} + e^{-\beta\Delta/2} Z'(\beta)} \]

• Sample averaged susceptibility

\[ \bar{\chi}''(\omega) = \int_{0}^{\infty} \rho(\Delta) \chi''_{\Delta}(\omega) d\Delta = \pi \left( g \mu_B \alpha \right)^2 \rho(\omega) \frac{1 - e^{-\beta\omega}}{1 + e^{-\beta\omega} + e^{-\beta\omega/2} Z'(\beta)} \]

• Fluctuation-dissipation theorem yields

\[ \rho(\omega) = \frac{1}{\alpha^2} \frac{1}{\bar{S}(\omega)} \left( 1 + e^{-\beta\omega} + e^{-\beta\omega/2} Z'(\beta) \right) \]
Inhomogeneous level splitting in Pr$_2$Zr$_2$O$_7$?

- The $E \gg h$ excitations result from inhomogeneous level splitting.
- For $E \sim h$ inter-site interactions (collective physics) is important.
- Population of the 9.5 meV singlet may account for quasi-elastic response for $T > 100$ K.
Origin of inhomogeneous level splitting?

- T-independent distribution function \( \rho(\Delta) \)
  \( \Rightarrow \) Static not dynamic phenomenon

- Continuous spectrum in stoichiometric sample
  \( \Rightarrow \) Large unit cell or density wave: distribution of environments
  \( \Rightarrow \) Dynamic Jahn-Teller type effect

- Distribution changes in \( \text{Pr}_{2+x}\text{Zr}_{2-x}\text{O}_{7-x/2} \)
  \( \Rightarrow \) Cr stuffing narrows the distribution so exchange dominates
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_conclusions
Spin and Orbital Frustration in MnSe₂S₄ and FeSe₂S₄

V. Fritsch, J. Hemberger, N. Büttgen, E-W. Scheidt, H-A. Krug von Nidda, A. Loedl, and V. Tsaruk

Department of Physics, University of Augsburg, Germany

Diamond lattice

Vibronic and Magnetic Excitations in the Spin-Orbital Liquid State of FeSe₂S₄

A. Krimmel, M. Mücksch, V. Tsaruk, M. M. Koza, H. Mutka, and A. Loedl

Department of Physics, University of Augsburg, Germany

Diamond lattice

Spin-Orbital Singlet and Quantum Critical Point on the Diamond Lattice: FeSe₂S₄

Gang Chen, Leon Balents, and Andreas P. Schnyder

Department of Physics, University of California, Santa Barbara, USA

Diamond lattice

Singlet-Triplet Excitations and Long-Range Entanglement in the Spin-Orbital Liquid Candidate FeSe₂S₄

N. J. Laurita, J. Deisenhofer, LiDong Pan, C. M. Morris, M. Schmidt, M. Johnsson, V. Tsaruk, and N. P. Armitage

Department of Physics, University of Maryland, USA

Diamond lattice
A dynamic state of affairs in FeSc$_2$S$_4$

K. Plumb et al. submitted to PRX

\[
\langle \delta m^2 \rangle = \int \int Q^2 S(Q, E) dQ dE / \int Q^2 dQ = 12(1) < g^2 S(S + 1) = 24
\]
Detection of spin and orbital order

MACS and CNCS

K. Plumb et al. submitted to PRX

11BM at APS
Ordered moment only 50% of the full ordered moment:
Strong quantum fluctuations and proximity to spin-orbital quantum criticality
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Why is Mott transition “exposed” in V$_2$O$_3$?

McWhan et al. PRB (1973)
Spin-Waves in AFI phase of $V_2O_3$

\[ E_1 = 100 \text{ meV} \]

\[ [-L 1 L] \]

\[ [-2 1 L] \]

4 meV

17 meV

J. Leiner
A frustrated paramagnet

V2O₃ (4% Cr-doped) T = 205K
Frustration: Bandwidth Narrowing

V$_2$O$_3$(4% Cr-doped) T = 205K
Frustrated Honeycomb AFM

DFT for V$_2$O$_3$ (Valenti et al.)

Albuquerque et al PRB (2011)
Bao et al. (1995)

\( \nu_{2O_3} \) at 200K

\( h\omega \) (meV)

\( 2k_f \)

\( (10\ell) \)

Bao et al. (1995)

\( \nu_{10.9O_3} \) at 1.4K

\( h\omega \) (meV)

\( (10\ell) \)

V\(_2\)O\(_3\)

Bao et al.
Summary

• Inelastic magnetic scattering probes dynamic spin correlation function:

• Scattering theory is essential to interpret data

• Tremendous progress in instrumentation: Join us!

• Challenges in Frustrated Quantum Magnetism
  – Static or dynamic valence bonds?
  – Local or collective singlet in Q-spin-ice
  – Static or dynamic orbital configuration?
  – Rigid or compliant lattice?