

Ordering by quantum fluctuations in a strongly frustrated Heisenberg antiferromagnet

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The nature of the ordering of a quantum spin- $\frac{1}{2}$ Heisenberg antiferromagnet is considered in the presence of the strong lattice frustration associated with the pyrochlore lattice. A field theory indicates that quantum fluctuations lead to a state having dimerization that has long-range static correlations not in $\langle \mathbf{S} \rangle$ but rather in $\langle \mathbf{S}(\mathbf{r}) \cdot \mathbf{S}(\mathbf{r} + \boldsymbol{\delta}) \rangle$. A sublattice ordering is found that is consistent with results obtained using degenerate perturbation theory to analyze the ground-state manifold.

A well-known but still unsolved problem concerns the possible ordering, if any, of the quantum spin- $\frac{1}{2}$ Heisenberg antiferromagnet (QSHHA) with only nearest-neighbor interactions on a triangular lattice.¹ The difficulty of simultaneously treating the frustration of the lattice and the low-dimensional fluctuations has so far prevented a definitive analysis. Frustration effects are even more severe on the Kagome lattice.² An analogous system in three dimensions is the QSHHA with only nearest-neighbor interactions on the pyrochlore lattice, which can be regarded as an fcc lattice with a four-site basis:

$$\boldsymbol{\tau}_1 = (0,0,0), \quad \boldsymbol{\tau}_2 = \frac{1}{2}\mathbf{a}_1, \quad \boldsymbol{\tau}_3 = \frac{1}{2}\mathbf{a}_2, \quad \boldsymbol{\tau}_4 = \frac{1}{2}\mathbf{a}_3, \quad (1)$$

where $\mathbf{a}_1 = (0,a,a)/2$, $\mathbf{a}_2 = (a,0,a)/2$, and $\mathbf{a}_3 = (a,a,0)/2$ are the fcc Bravais lattice vectors. This lattice can be viewed either as corner-sharing tetrahedra in which each site is a member of two tetrahedra, or as a lattice of independent tetrahedra coupled by intertetrahedral bonds which, of course, have the same strength as the bonds within a tetrahedron. There are two corner-sharing tetrahedra per fcc unit cell or one independent tetrahedron per fcc unit cell. Here we briefly describe two approaches to this problem. The first is a field theory to describe quantum fluctuations in the quantity $\mathbf{S}(\mathbf{r}) \cdot \mathbf{S}(\mathbf{r} + \boldsymbol{\delta})$, where $\boldsymbol{\delta}$ is a nearest-neighbor vector. The second is a putative ground-state calculation starting from the highly degenerate manifold that results when the intertetrahedral bonds are omitted. We use degenerate perturbation theory to obtain the effective Hamiltonian that describes the splitting of this manifold when intertetrahedral bonds are included. Although neither approach is entirely convincing, it is significant that they do give identical results for the symmetry of the ordered phase, since the second assumes a broken symmetry, whereas the first does not. Experimental³ and theoretical⁴ studies suggest that the classical version of this model has no nonzero temperature phase transition, and previously Anderson⁵ predicted a nonzero entropy at zero temperature.⁴ Thus our results, if correct, imply that quantum fluctuations play an essential role in the ordering.

First we describe the field theory. We start from the identity for spin $\frac{1}{2}$:

$$(\mathbf{S}_i \cdot \mathbf{S}_j)^2 = \frac{3}{16} - \frac{1}{2} \mathbf{S}_i \cdot \mathbf{S}_j \quad (2)$$

We use Eq. (2) to write the partition function with only nearest-neighbor interactions on bonds b as

$$\mathcal{Z} = e^{-3\beta N_b J/8} \text{Tr} \exp\left(2\beta J \sum_b (\mathbf{S}_{i(b)} \cdot \mathbf{S}_{j(b)})^2\right), \quad (3)$$

where $\beta = (kT)^{-1}$, where T is the temperature, and N_b is the number of nearest neighbor bonds in the lattice. Here $i(b)$ and $j(b)$ are the sites associated with the bond b . We will henceforth drop the constant factor $\exp(-3\beta N_b J/8)$. In order to perform a Hubbard-Stratonovich transformation with noncommuting operators it is necessary to introduce time ordering.⁶ We write

$$\mathcal{Z} = \text{Tr} T \exp\left[\int_0^\beta d\tau \left(2J \sum_b [\mathbf{S}_{i(b)}(\tau) \cdot \mathbf{S}_{j(b)}(\tau)]^2\right)\right], \quad (4)$$

where T is the time-ordering operator. In Eq. (4) $\mathbf{S}_i(\tau)$ is identical to \mathbf{S}_i and the label τ is only relevant in that T orders operators according to their τ label. Now the Hubbard-Stratonovich transformation yields

$$\mathcal{Z} \equiv \int \mathcal{D} \bar{\phi}(\tau) \exp(-\mathcal{F}[\bar{\phi}]), \quad (5)$$

where

$$\begin{aligned} \mathcal{F}[\bar{\phi}] = & \frac{1}{2K} \sum_b \int_0^\beta \bar{\phi}_b(\tau)^2 d\tau \\ & - \ln \left[\text{Tr} T \exp\left(\int_0^\beta \sum_b \bar{\phi}_b(\tau) \mathbf{S}_{i(b)}(\tau) \cdot \mathbf{S}_{j(b)}(\tau) d\tau\right) \right]. \end{aligned} \quad (6)$$

In principle one obtains a free-energy functional that describes the ordering (if any) of the field $\bar{\phi}_b(\tau)$ conjugate to the operator $\mathbf{S}_{i(b)}(\tau) \cdot \mathbf{S}_{j(b)}(\tau)$. At nonzero temperature the free energy reduces to that of a classical system because fluctuations at nonzero frequency can be integrated out of

the free energy.⁶ The important point here is that the Landau parameters are influenced by quantum fluctuations, as we will see in a moment. We evaluate the free

energy of Eq. (6) up to order $\bar{\phi}^4$ omitting some nonzero frequency terms and find

$$F[\phi] = \frac{1}{2\beta K} \sum_b \sum_v \phi_b(z_v) \phi_b(-z_v) - \frac{3}{32} \sum_b \phi_b(0)^2 + \frac{1}{64} \sum_b \phi_b(0)^3 - \frac{1}{64} \sum_{\Delta} \phi_u(0) \phi_v(0) \phi_w(0) + \frac{1}{1024} \sum_b \phi_b(0)^4 + \frac{1}{256} \sum_{\Delta} \phi_u(0)^2 \phi_v(0) \phi_w(0) + \frac{1}{256} \sum_{\langle u,v \rangle} \phi_u(0)^2 \phi_v(0)^2 - \frac{3}{256} \sum_Q \phi_u(0) \phi_v(0) \phi_w(0) \phi_x(0), \quad (7)$$

where the sums are over bonds b , triangles Δ , quadrilaterals Q , and pairs of nearest-neighboring bonds $\langle u,v \rangle$, and $\phi(z_v)$ is the time-Fourier transform of $\bar{\phi}$, where $z_v = 2\nu\pi kT$, with ν an integer. This form gives the correct high-temperature limiting result, $(\beta J) \langle \mathbf{S}_{i(b)} \cdot \mathbf{S}_{j(b)} \rangle \sim \langle \phi_b \rangle = -A/T^2$, where A is a positive constant, which is nonzero only due to quantum fluctuations if one starts from the partition function of Eq. (3).

The quadratic terms in the free energy above are completely local. Even with the interactions contained in Eq. (7) critical correlations are confined to a single tetrahedron.⁷ Critical coupling between tetrahedra only arises when terms of order ϕ^6 are included. These terms describe correlations propagating around a hexagon of bonds spanning six corner-sharing tetrahedra. Replacing all possible choices of four ϕ 's in such a product by $\langle \phi \rangle$ leads to an effective nonlocal quadratic interaction which, although smaller than interactions within a tetrahedron, is nonetheless crucial in determining the nature of the critical fluctuations. To describe these interactions we need to introduce the basis of 12 bonds within a unit cell: bonds 1–6 on one of the two corner-sharing tetrahedra in a unit cell and bonds 7–12 on the other tetrahedron in the unit cell. At this level of approximation, we find that there are six symmetry-related modes that first become critical as the temperature is lowered. There are two modes for each of the wave vectors $\mathbf{k}_x = (2\pi, 0, 0)/a$, $\mathbf{k}_y = (0, 2\pi, 0)/a$, and $\mathbf{k}_z = (0, 0, 2\pi)/a$. For wave vector \mathbf{k}_x one of these is confined to one of the two tetrahedra and is

$$\eta_{x,1} \equiv \frac{1}{\sqrt{12}} [-\phi_1(0) - \phi_2(0) + 2\phi_3(0) - \phi_4(0) - \phi_5(0) + 2\phi_6(0)], \quad (8)$$

where the bonds on a tetrahedron are numbered so that bonds i and $i+3$ do not meet one another. The fluctuation in Eq. (8) is one in which one pair of nonintersecting bonds (3,6) is more dimerized than the average, and the other bonds are less dimerized than the average. The other mode at this wave vector $\eta_{x,2}$ has similar amplitudes on the bonds (7–12) of the other tetrahedron in the unit cell. The modes $\eta_{y,i}$ and $\eta_{z,i}$ with $i=1,2$ corresponding respectively to the wave vectors \mathbf{k}_y and \mathbf{k}_z are found (for $i=1$) by cyclic permutation of the subscripts in Eq. (8).

The final step is to understand whether these six critical modes fluctuate independently or not. Here the cubic terms in Eq. (7) lead to a free-energy contribution of the form

$$\delta F \sim \sum_{i=1}^2 \eta_{x,i} \eta_{y,i} \eta_{z,i} \quad (9)$$

The effect of this term is to favor simultaneous fluctuations like $\eta_{x,i} + \eta_{y,i} + \eta_{z,i}$ with $i=1$ or 2. Indeed, selection of $i=1$ (or 2) cooperatively breaks the symmetry at each site, selecting one of the two tetrahedra as the one to which the site in question will dimerize. Combinations of normal modes of Eq. (8) then lead to a dimerization on four sublattices: One sublattice is randomly dimerized; each of the other three sublattices is dimerized according to the three ways of forming four sites into two dimer pairs. In this connection a dimer is a state in which singlet correlations are beginning to develop. Presumably, higher-order terms in the Landau expansion will lead to induced order in the tetrahedra found here to be disordered.

We now turn to a perturbative treatment starting from noninteracting independent tetrahedra. For such a single tetrahedron the exact energy eigenstates are characterized by their total spin S_{tot} and their energy is $J S_{\text{tot}}(S_{\text{tot}} + 1) - \frac{3}{2} J$. The spin-zero ground state is two-fold degenerate.⁸ Thus, for a system containing N_T independent tetrahedra the ground manifold is 2^{N_T} -fold degenerate. The effect of intertetrahedral perturbations is then described by an effective Hamiltonian \mathcal{H}_{eff} within this ground manifold. This approach is similar in spirit to treating the Hubbard model with large on-site Coulomb interactions by confining one's attention to the manifold with no double occupancy. In n th order, perturbation theory gives contributions to \mathcal{H}_{eff} of order $J\lambda^n$, where $\lambda = J'/J$, where J' is the intertetrahedral interaction (which we eventually set equal to J). Since we take independent tetrahedra, we have one tetrahedron per unit cell, in contrast to the situation in the field theory. This arbitrary choice of one tetrahedron corresponds to an assumption of broken symmetry. This assumption is supported by the field theory, as discussed above.

In second order \mathcal{H}_{eff} is a (negative) constant and does not remove the degeneracy of the ground manifold. In third order this degeneracy is removed and \mathcal{H}_{eff} is de-

scribed in terms of a pseudospin- $\frac{1}{2}$ operator, σ_i , at the i th tetrahedron. This operator is defined with respect to the states

$$|\sigma\rangle = \frac{1}{\sqrt{6}} (|++--\rangle + |--++\rangle + \omega|+-+-\rangle + \omega|-+-+\rangle + \omega^2|-++-\rangle + \omega^2|+--+\rangle), \quad (10)$$

where $|++--\rangle$ is a state in which spins 1 and 2 are up and spins 3 and 4 are down, etc. Also in Eq. (10), $\omega = \exp(2\pi i\sigma/3)$, and $\sigma = 1$ (-1) corresponds to pseudospin up (down). To understand what these states mean, note that this manifold includes the spin-zero states formed by the product of two spin singlets which one obtains by dividing the four spins into two singlet pairs. Since this division can be done in three ways, there are three such singlet product states. However, they are not all linearly independent: they span the space formed by taking $\sigma = \pm 1$ in Eq. (10). Thus one can view the effective Hamiltonian as determining the nature of the dimerization in the ground state.

Since the results are complicated we will only summarize them here. In third-order perturbation theory we find two-spin and three-spin terms. As in the field theory, the two-spin terms determine the wave vector of the ground state and the three-spin terms determine whether one has a single wave vector or a superposition of wave vectors. The two-spin terms are

$$\mathcal{H}_{\text{eff}} = \frac{1}{96} J\lambda^3 \sum_{\mathbf{q}} A_{\alpha\beta}(\mathbf{q}) \sigma_{\alpha}(-\mathbf{q}) \sigma_{\beta}(\mathbf{q}), \quad (11)$$

where $\sigma(\mathbf{q})$ is the spatial Fourier transform of σ_i , α and β label Cartesian components, and

$$\mathbf{A}(\mathbf{q}) = \begin{bmatrix} 2c_x c_y + 2c_x c_z - c_y c_z & \sqrt{3}c_x c_y - \sqrt{3}c_x c_z \\ \sqrt{3}c_x c_y - \sqrt{3}c_x c_z & 3c_y c_z \end{bmatrix}, \quad (12)$$

where $c_{\alpha} = \cos(q_{\alpha}a/2)$. There is no reason to expect isotropy in pseudospin space.

The ground state of \mathcal{H}_{eff} is not easy to determine. If the pseudospins were classical spins and we treated Eq. (11) as a Landau free energy, then we would conclude that the minimum energy corresponds to condensing into a state with $\sigma(\mathbf{q})$ nonzero for $\mathbf{q} = \mathbf{k}_i$, where \mathbf{k}_i are the wave vectors that minimize the eigenvalues of $\mathbf{A}(\mathbf{q})$. In fact, the \mathbf{k}_i 's so obtained are identical to those found in the field theory. Indeed the ground-state calculation is quite similar

to the field theory. The three-spin terms, which we have not written down here, play exactly the same role as the cubic term in Eq. (9) and their effect leads to the same four-sublattice structure as found in the field theory. To assess the convergence of this scheme we give the ground-state energy per fcc unit cell in powers of λ :

$$\frac{E(\lambda)}{J} = -\frac{3}{2} - \frac{9}{16}\lambda^2 + \frac{104 - \delta}{384}\lambda^3, \quad (13)$$

where the term in $\delta \approx 61$ results from our approximate treatment of the splitting of \mathcal{H}_{eff} .

Some general comments on these results are in order. First of all, these theories describe an ordering in which $\langle \mathbf{S}(\mathbf{r}) \rangle = 0$. The order parameter is equivalent to the vector

$$\psi(\mathbf{r}) = - \sum_{\delta} \delta \langle \mathbf{S}(\mathbf{r}) \cdot \mathbf{S}(\mathbf{r} + \delta) \rangle. \quad (14)$$

When there is no symmetry breaking,

$$\langle \mathbf{S}(\mathbf{r}) \cdot \mathbf{S}(\mathbf{r} + \delta) \rangle = \langle \mathbf{S}(\mathbf{r}) \cdot \mathbf{S}(\mathbf{r} - \delta) \rangle,$$

and $\psi(\mathbf{r}) = 0$. One can interpret $\psi(\mathbf{r})$ as a vector field which locally points in the direction of dimerization. Our field theory describes the breaking of this symmetry. The degenerate perturbation theory assumes this symmetry to be partially broken. In both approaches one sublattice is found to be disordered. In a more complete theory this disorder would probably be removed, and it is plausible, but not obvious, that the nature of the ordering would not be substantially modified.

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¹For a recent treatment which uses a formalism similar to ours, see G. Baskaran, Phys. Rev. Lett. **63**, 2524 (1989).

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