Convergent expansions for properties of the Heisenberg model for CaV$_4$O$_9$

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We have carried out a wide range of calculations for the $S = 1/2$ Heisenberg model with nearest- and second-neighbor interactions on a two-dimensional lattice which describes the geometry of the vanadium ions in the spin-gap system CaV$_4$O$_9$. The methods used were convergent high-order perturbation expansions (“Ising” and “Plaquette” expansions at $T = 0$, as well as high-temperature expansions) for quantities such as the uniform susceptibility, sublattice magnetization, and triplet elementary excitation spectrum. Comparison with the data for CaV$_4$O$_9$ indicates that its magnetic properties are well described by nearest-neighbor exchange of about 200K in conjunction with second-neighbor exchange of about 100K.

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Since the discovery of high temperature superconductivity in the cuprates there has been much interest in two-dimensional antiferromagnetism. From a theoretical point of view, there has been an extensive search for the so-called spin liquid ground state in models with realistic interactions. A possible link between such a ground state and high temperature superconductivity has often been suggested though not demonstrated. For square lattice Heisenberg models it is believed that sufficient further-neighbor interactions will destabilize the Néel state and lead to a spin-gap phase; however, such a phase typically has spin-Peierls order and hence is not a true spin liquid. A spin-gap phase without other spontaneously broken symmetries has been found experimentally in quasi-one-dimensional spin ladders and theoretically in strongly coupled two-plane models.

In light of these developments, it is interesting that the quasi-two-dimensional Heisenberg system CaV$_4$O$_9$ has been found to exhibit a spin gap. Within each layer, the spins form a one-fifth depleted square lattice, which we denote the CAVO lattice (see Fig. 1). Recently this system has attracted much attention from theorists and experimentalists such as the uniform susceptibility, sublattice magnetization, and triplet elementary excitation spectrum. Comparison with the data for CaV$_4$O$_9$ indicates that its magnetic properties are well described by nearest-neighbor exchange of about 200K in conjunction with second-neighbor exchange of about 100K.

Hence it is appropriate to study a Heisenberg model with interactions

$$\mathcal{H} = J_1 \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + J'_1 \sum_{\langle i,k \rangle} \mathbf{S}_i \cdot \mathbf{S}_k + J_2 \sum_{\langle i,l \rangle} \mathbf{S}_i \cdot \mathbf{S}_l + J'_2 \sum_{\langle i,m \rangle} \mathbf{S}_i \cdot \mathbf{S}_m,$$

where the first sum runs over nearest-neighbor bonds within plaquettes, the second over nearest-neighbor bonds between plaquettes, the third over second-neighbor bonds within plaquettes, and the last over second-neighbor bonds between plaquettes.

We have carried out a variety of high-order convergent perturbation expansions for this Hamiltonian that are comparable in accuracy to the best available quantum Monte Carlo calculations (which have been limited to $J_2 = J'_2 = 0$) and that provide the only reliable results for the parameter values most relevant to CaV$_4$O$_9$. An outline of the calculations and results is as follows: (1) Ising expansion estimates of the sublattice magnetization and phase boundary for models with $J_2 = J'_2 = 0$ are consistent with the quantum Monte Carlo calculations of Troyer et al.; (2) Plaquette expansions for the triplet elementary excitation spectrum are highly convergent and informative in the plaquette phase, and (3) High-temperature expansions for the susceptibility, combined with plaquette expansion results, can be compared with the existing experimental data to fix the model’s parameters for CaV$_4$O$_9$. In this Letter we can only describe the highlights of the results; details are reserved for a separate publication.

For the Ising expansions we have considered the Hamiltonian

$$\mathcal{H} = J_1 \sum_{\langle i,j \rangle} [S_i^x S_j^x + \alpha (S_i^y S_j^y + S_i^z S_j^z)] + J'_1 \sum_{\langle i,k \rangle} [S_i^z S_k^z + \alpha (S_i^x S_k^x + S_i^y S_k^y)] + t(1-\alpha) \sum_i \epsilon_i S_i^z,$$

where $\epsilon_i = \pm 1$ on the two sublattices. (The last term is a local field term, which can be included to improve convergence and proves useful in that regard when $J'_1 \approx J_1$.) We have developed expansions up to order $\alpha^{14}$, for several values of $J'_1/J_1$, for the ground state energy, the sublattice magnetization $M$, and the longitudinal and
transverse susceptibilities. The expansion techniques have been reviewed earlier \[11\,12\). When the Heisenberg model has a spin gap, one expects these expansions to break down at some $a < 1$ and the system to exhibit $d = 3$ Ising criticality. Such considerations can be used to estimate the domain of long-range Néel order. Within the Néel-ordered phase our estimates of $M$ are presented in Fig. 2 along with those of Troyer et al. \[9\].

For the plaquette expansions we return to the original Hamiltonian of interest, Eq. (1), but with the interplaquette interactions parametrized as $J'_1 = \lambda_1 J_1$, $J'_2 = \gamma J_1$, and $J'_2 = \lambda_2 J_2$. For convenience we have taken $\lambda_1 = \lambda_2 \equiv \lambda$ in our calculations; that restriction could be relaxed if desired. Let us restrict our attention to $\gamma < 1$, since there is both a ground state and lowest excited state level crossing for an isolated plaquette when $J_1 = J_2$, and $J_1 > J_2$ is certainly more relevant to CaV$_4$O$_9$. When $\lambda = 0$ the ground state is a product of singlets on the non-interacting plaquettes, while the lowest-lying triplet excitations are gapped and completely local. For $\lambda \neq 0$, the excitations are mobile and develop a well-defined dispersion. Using a recently developed method for computing the excitation spectra \[13\], the complete dispersion for these triplet excitations has been constructed to order $\lambda^5$ for various values of $\gamma$. Following the convention of Katoh and Imada \[6\] for the wave vectors, to second order in $\lambda$ the dispersion has the form

$$
\Delta(q_x, q_y)/J_1 = 1 + \lambda^2 c_2^{(0,0)}(\gamma) + \frac{1}{2} \lambda (\cos q_x + \cos q_y) c_2^{(1,0)}(\gamma) + \lambda^2 \cos q_x \cos q_y c_2^{(2,0)}(\gamma) + \frac{1}{2} \lambda^2 \cos q_x \cos q_y c_2^{(2,0)}(\gamma)
$$

The coefficients $c_n^r$ for $\gamma = 0$, 0.4 and 0.5 are presented in Table 2. (Because $\gamma$ is a parameter in both the unperturbed and perturbing Hamiltonians, a simple double expansion in which $c_n^r$ can be expressed as a polynomial of order $n$ in $\gamma$ does not exist.) Second-order excitation-spectrum expansions have been presented earlier: for $J_2 = 0$ by Katoh and Imada \[6\] and at $q_x = q_y = \pi$ for $J_2 = J_2'$ (that is, $\lambda_1$ and $\gamma$ arbitrary and $\lambda_2 = 1$) by Ueda et al. \[6\]. However, in both cases the authors failed to consider the $O(\lambda^2)$ term associated with the $(\cos q_x + \cos q_y)$ part of the dispersion; in effect they set $c_2^{(1,0)}$ to zero. For the case $\lambda = 1$ and $\gamma = 0$ one finds from summing the correct series terms to $O(\lambda^2)$ a gap $\Delta(\pi, \pi) = 0.010 J_1$, in contrast to the previous perturbative estimates of 0.205 $J_1$. As evidenced by the Ising expansions and the Monte Carlo results of Troyer et al., this point lies in the Néel-ordered phase and should have a zero gap. This shows that already in second order the plaquette expansion for the gap locates the phase boundary fairly well, at least for $\gamma \approx 0$.

Another important point not discussed in earlier perturbation-theoretic work is that the minimum of $\Delta$ is not necessarily found at $q = (\pi, \pi)$. For small $\lambda$ the minimum shifts from $(\pi, \pi)$ when $\gamma < 1/2$ to $(0,0)$ when $\gamma > 1/2$. Precisely at $\gamma = 1/2$ the minimum for small $\lambda$ is achieved at $q = (\tilde{q}, \tilde{q})$ with $\tilde{q}/\pi = 0.7044$. . . . To the extent one can trust estimates of $\Delta$ based on simply summing series coefficients, such an incommensurate minimum persists at finite $\lambda$ and for $\gamma \approx 1/2$. (A similar incommensuration for sufficiently large $\gamma$ was found in the mean-field calculations of Starykh et al. \[10\].)

The present plaquette expansions are also the first which are sufficiently long to reflect the absence of reflection symmetry in the Hamiltonian: in third order and above $\Delta(q_x, q_y) \neq \Delta(q_y, q_x)$. It is not a dominant feature of the excitation spectrum but if $\gamma$ is sufficiently large it may be observable: at $\gamma = 0.5$ and $\lambda = 1$ the asymmetry parameter

$$
2[\Delta(q, \pi - q) - \Delta(q - \pi, q)]/[\Delta(q, \pi - q) + \Delta(q - \pi, q)]
$$

may be 10% for $q/\pi \approx 0.15$.

The fact that the excitation spectrum minimum is not fixed at $q = (\pi, \pi)$ could in principle complicate the matter of estimating the gap in the plaquette phase. However, for $\gamma \leq 1/2$ and $\lambda \leq 1$ the value of $\Delta(\pi, \pi)$ exceeds the true gap by at most 0.05 $J_1$ and usually by far less. So it is not too bad to identify estimates of $\Delta(\pi, \pi)$ with estimates of the gap in the parameter region of most physical interest. Another consideration is that the uncertainty in the estimates of $\Delta(\pi, \pi)$, which can be judged by spread in the direct sums and Padé approximants, become noticeable precisely in the part of $\gamma$-$\lambda$ space where the gap minimum apparently moves away from $q = (\pi, \pi)$. See Fig. 2 for some examples of $\Delta(\pi, \pi)$ estimates. Fortunately, for the parameters expected to be relevant to CaV$_4$O$_9$ the estimates of the gap appear to be fairly reliable, if not quite as good as when $\gamma \approx 0$. For those parameters, $J'_1 = J_1 = 2J'_2 = 2J_2$ ($\lambda = 1, \gamma = 1/2$), the gap is 0.57$\pm$0.03 $J_1$. Taking the experimental gap value of 107 K for CaV$_4$O$_9$ leads to the estimate $J_1 = 190 \pm 10$ K. The Curie temperature ($= 9 J_1/8$, for the given parameter ratios) should then be 215$\pm$10 K, which is consistent with the experimental value of 220 K and shows that the present parameter estimates are entirely plausible.

If magnetic neutron scattering data can be obtained, comparison with the plaquette expansion for the gap should allow for precise determination of model parameters. The structure of the triplet excitation spectrum is strongly dependent on the ratio of nearest- to second-neighbor couplings: see Fig. 2 for some illustrative plots.

We now turn to the high temperature expansions for the uniform susceptibility. The uniform susceptibility per spin can be defined as $\beta \chi(T) = \frac{1}{N} \sum_i \sum_j \langle S^z_i S^z_j \rangle$ where the angular brackets represent thermal averaging and $\beta = 1/T$. For $J_2 = J'_2 = 0$ we have determined
the expansion to order $\beta^{14}$. The integrated differential approximants have been used to extrapolate $\chi$ to low $T$; we find that they agree with Monte Carlo calculations down to $T \approx J_1/10$ when the ground state lies in the plaquette phase.

High temperature expansions have also been developed for the models with $J_1 = J_1'$, $J_2 = J_2' \neq 0$, to order $\beta^{30}$. They should be more relevant for comparison with the CaV$_4$O$_9$ data, however, they have proven more difficult to extrapolate to lower temperatures. In order to improve the convergence, we have developed differential approximants for $\chi e^{\Delta/T}$, with $\Delta$ taken from our studies at $T = 0$. This biases the leading exponential behavior of the susceptibility at low temperatures to be of the form $e^{-\Delta/T}$. Despite this biasing there remain significant uncertainties in the location of the peak temperature, where $\chi$ is maximized; the best we can say is that it lies in the range $0.4$–$0.6$ $J_1$ for $J_2 = J_1/2$. The susceptibility of CaV$_4$O$_9$ peaks at about 110 K, which is consistent with a $J_1$ value of approximately 200 K.

A comparison of experimental data with the calculated susceptibility, using $J_1 = 190$ K as estimated above, is shown in Fig. 1. In order to convert the susceptibility for the Heisenberg model into units of emu/g, we multiply the theoretical value (calculated with $J_1 = 1$) by $(g^2\mu_B^2/J_1k_B)(4N_A/M)$, where $\mu_B$ is the Bohr magneton, $k_B$ is the Boltzmann constant, $N_A$ is Avogadro’s number, $M$ is gram molecular weight, and the factor of 4 comes from the four vanadium spins per CaV$_4$O$_9$ formula unit. The $g$-factor can be used as a fitting parameter, and the comparison shown uses the value 1.77. We note that the calculated susceptibility does not fully agree with the data at high temperatures: this may be in part due to the existence of other phases above 340 K as noted in the experimental paper, or due to the lattice distortions discussed by Starzyk et al., which can make the exchange constants temperature dependent. A more detailed examination of the high temperature susceptibility for CaV$_4$O$_9$ in context of the Heisenberg models will be given elsewhere.

In summary, we have carried out a wide range of high-order perturbation expansions for $S = 1/2$ Heisenberg antiferromagnets on the CAVO lattice. The existing susceptibility data for CaV$_4$O$_9$ is generally consistent with the coupling ratios $J_1 = J_1' = 2J_2 = 2J_2'$ suggested by Ueda et al., Measurements of the wave vector resolved triplet excitation spectrum should be compared with estimates of the spectrum based on the present plaquette expansions for a definitive test of the model.

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FIG. 1. The CAVO lattice, with sites indicated by circles. The couplings $J_1$, $J_1'$, $J_2$, and $J_2'$ are indicated by thick solid, thick dashed, thin solid, and thin dashed lines, respectively. Note that the plaquette centers lie on a square lattice with spacing $b$ which is $\sqrt{3}$ times the distance between nearest-neighbor sites. In characterizing the excitation spectrum (see Eq. (4) below) we take $b = 1$ and rotate the coordinate system so that the lines between nearest-neighbor plaquette centers define the $x$ and $y$ axes.

FIG. 2. Sublattice magnetization versus $J_1'/J_1$ (with second-neighbor couplings $J_2 = J_2' = 0$) as estimated by Ising expansions (filled symbols) and the Troyer et al. quantum Monte Carlo calculations (open symbols).

FIG. 3. The excitation energy $\Delta(\pi, \pi)$ versus $\lambda$ for several values of $\gamma$.

FIG. 4. The triplet excitation spectrum $\Delta(q_x, q_y)$ along high-symmetry cuts through the Brillouin zone for coupling ratios $\lambda = 1$ and $\gamma = 0.1$, 0.3 and 0.5 (from greatest to least values of $\Delta(0, 0)$). The ends of the bars indicate the values of the direct sums to fourth and fifth order in $\lambda$. 
FIG. 5. A comparison of the calculated susceptibility for the Heisenberg model with $J_2 = J_1/2$ (the solid lines representing various approximants), with the experimental data of Taniguchi et al. for CaV$_4$O$_9$.

TABLE I. Coefficients in the expansion of the triplet elementary excitation spectrum $\Delta(q_x,q_y)$, to second order in $\lambda$, for selected $\gamma$ values: see Eq. (3).

| γ | $c_{2}^{0,0}$ | $c_{1}^{1,0}$ | $c_{2}^{1,0}$ | $c_{2}^{1,1}$ | $c_{2}^{2,0}$ |
|---|---|---|---|---|---|
| 0 | -0.0358796 | 0.6666666 | 0.1944444 | -0.1111111 | 0.0185185 |
| 0.4 | -0.1950309 | 0.1333333 | 0.1799242 | -0.0444444 | 0.0570370 |
| 0.5 | -0.2279762 | 0 | 0.1597222 | 0 | 0.0666667 |
\[ \chi [10^{-6} \text{ emu/g}] \]

\[ T [\text{K}] \]

\[ J_1 = J'_1 = 190 \text{K} \]

\[ J_2 = J'_2 = J_1/2 \]

\[ g = 1.77 \]