On the presence of mid-gap states in CaV$_4$O$_9$

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Using exact diagonalizations of finite clusters with up to 32 sites, we study the $J_1 - J_2$ model on the 1/5 depleted square lattice. Spin-spin correlation functions are consistent with plaquette order in the spin gap phase which exists for intermediate values of $J_2/J_1$. Besides, we show that singlet states will be present in the singlet-triplet gap if $J_2/J_1$ is not too small ($J_2/J_1\approx 0.47$). We argue that this property should play a central role in determining the exchange integrals in CaV$_4$O$_9$.

The interest in 2D frustrated magnets has recently increased with the discovery of the first 2D spin 1/2 system exhibiting a spin gap, namely CaV$_4$O$_9$ [5]. This material consists of V$_4$O$_9$ planes separated by calcium layers [3], each vanadium atom being at the centre of a VO$_5$ square-pyramid of oxygens. Vanadium having an oxidation number 4+ in this compound, there is a single electron in the d-shell of each vanadium atom. These electrons behave as localized spins 1/2 coupled by some exchange interactions. The relative magnitudes of the various possible exchange mechanisms cannot be easily deduced from quantum chemistry, and to get a better understanding of the magnetic properties of this compound, a direct comparison of physical properties of model Hamiltonians to experimental results is necessary.

The minimal model to describe this compound, namely the 1/5 depleted Heisenberg model with nearest neighbour interactions $J_1$, has been studied in great details. Contrary to early results [4], it is now clear that this model has Néel long range order and no spin gap. This was first proposed on the basis of exact diagonalizations and Schwinger boson mean field calculations [4] and confirmed by Monte Carlo simulations [5] and other methods [5, 6].

One way to go beyond this minimal model is to take into account the fact that intra- and inter–plaquette exchange integrals might have different values, say $J_1$ and $J'_1$, in particular because of the distortion of the lattice described in Ref. [3]. However, it seems difficult to explain the magnitude of the gap without assuming that the ratio $J'_1/J_1$ is unphysically small.

In fact, in analogy with the non-depleted square lattice [6], it has been suggested that a spin gap can be opened by frustration e.g. through the inclusion of exchange integrals between next nearest neighbours [6, 9, 11], a very reasonable assumption as far as quantum chemistry is concerned. This model corresponds to the Hamiltonian:

$$H = J_1 \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j + J_2 \sum_{\langle i\rangle j \rangle} \vec{S}_i \cdot \vec{S}_j ,$$

where $J_1$ ($J_2$) is the exchange integral between (next) nearest neighbours on the lattice shown in figure [1]. Again, to account for the detailed properties of CaV$_4$O$_9$, it might prove necessary to allow for different values of intra- and inter–plaquette exchange integrals, but these differences can be neglected in a first approximation.

![FIG. 1. Schematic structure of the V$_4$O$_9$ plane. The oxygen have been omitted for clarity.](image)

A number of results have already been obtained on that model [6, 8, 11]. According to the “spin-wave”–like calculation of Starykh et al. [6], there is a phase with a spin gap and plaquette order when $0.25 < J_2/J_1 < 0.8$. The cluster expansion of Gelfand et al. [8] suggests that the model has a plaquette–like ground state when $J_2/J_1 = 1/2$ with a large gap $\Delta/J_1\approx 0.5$. This value of the gap was confirmed by White [11] using a density matrix renormalization group (DMRG) calculation, who also showed that the gap should open for a frustration ratio of $J_2/J_1\approx 0.05$, i.e. earlier than predicted by Starykh et al. Even if these studies are somehow convergent, a
number of points remain to be definitely clarified. First, the nature of the ground state in the intermediate frustration domain has only been determined by perturbative methods. In principle, they are valid when the perturbation involves small parameters, which is not the case here. More importantly, the values of the coupling constants could not be deduced from experiments so far. In particular, the interpretation of the temperature dependence of the susceptibility is not conclusive [3]. Alternative ways of getting information about the exchange integrals directly from experimental results are clearly needed.

In order to address these issues, we have performed exact diagonalizations of small clusters with 8, 16 and 32 spins with periodic boundary conditions. To reduce numerical effort, we have taken advantage of all the symmetries of the Hamiltonian: The translations (the basis vectors are shown in Fig. 1), the point group C4 (the centre of rotation is at the middle of a plaquette) and the spin inversion. The elementary cell has four atoms labelled by α = 1, 2, 3, 4 (see Fig. 1). In the classical limit, the system will exhibit Néel order for \( J_2/J_1 < 1/2 \) and a collinear order with alternating rows (or columns) of up and down spins for \( J_2/J_1 > 1/2 \). A state with Néel (resp. collinear) long-range order will then be defined by its wave vector \((\pi, \pi)\) (resp. \((0, \pi)\)) and by the orientation \( \epsilon_\alpha = \pm 1 \) of the spins of an elementary cell \((\epsilon_1 = -\epsilon_2 = \epsilon_3 = -\epsilon_4 = 1 \) for Néel order, \( \epsilon_1 = \epsilon_2 = -\epsilon_3 = -\epsilon_4 = 1 \) for collinear order).

To test the presence of magnetic long-range order in the system, we have calculated the ground state energy \( E_N \), the singlet-triplet gap \( \Delta_N \), the magnetic susceptibility \( \chi_N \) and the staggered magnetizations \( M_N(\vec{Q}) \) corresponding to Néel and collinear orders and defined by:

\[
M_N^\alpha(\vec{Q}) = \frac{1}{N(N+2)} \langle \Phi | \sum_\alpha \epsilon_\alpha e^{i\vec{Q} \cdot \vec{r}_i} \phi_i, \alpha \rangle^2 | \Phi \rangle , \tag{2}
\]

where \( \vec{r}_i \) is the position of the centre of the plaquette \( i \), and \( \epsilon_\alpha \) depends on the nature of the phase. The normalisation of the staggered magnetizations is chosen so that the order parameter is independent of the size in a perfect Néel or collinear state. In an ordered phase, these various quantities should have the following finite size scaling [13]:

\[
\frac{E_N}{N} = E_0 + \frac{C_1}{N^{3/2}}, \quad \Delta_N = \frac{(\chi_0)^{-1}}{N} \tag{3}
\]

\[
\chi_N = \chi_0 + \frac{C_2}{N^{1/2}}, \quad M_N(\vec{Q}) = M_0^\alpha(\vec{Q}) + \frac{C_3(\vec{Q})}{N^{1/2}} \tag{4}
\]

Actually, for \( J_2 \neq 0 \), these asymptotic laws are not very well satisfied for the available sizes (8, 16 and 32 sites) [13], and the information we could extract on that problem is only qualitative. The ground-state energy has always a scaling reasonably well described by Eq. (3), so it cannot really help deciding whether a state is ordered or not. Finite size effects for the triplet gap and for the magnetic susceptibility, for such sizes, become large when \( J_2 \neq 0 \) so that no reasonable scaling could be performed. However, the scaling of the staggered magnetization was satisfactory enough so that we were able to extract useful informations. Let us start with Néel order for the non-frustrated model with intra- and inter-plaquette exchange integrals \( J_1 \) and \( J_1' \) studied by two of us in a previous paper [3]. We are now in a position to improve the finite-size analysis by considering the results for 32 spins. It turns out that the scaling of Eq. (4) is not yet satisfied for such sizes. Meaningful results can nevertheless be obtained by adding further corrections of order \( 1/N \). They are shown in figure 2.

![FIG. 2. Staggered magnetisation of the non–frustrated model for N=8,16,32 and extrapolated values. Quantum Monte Carlo results are from Troyer et al. [3].](image_url)

They are in reasonable agreement with the Quantum Monte Carlo results of Troyer et al. [3]. The slight discrepancy for small \( J_1'/J_1 \) shows however that such a scaling should not be taken too seriously at a quantitative level. For the model of Eq. (1), the Néel staggered magnetization deduced from a similar finite size scaling analysis is shown in figure 3. It vanishes for \( J_2/J_1 \approx 0.2 \). This is larger than the value \( J_2/J_1 \approx 0.05 \) deduced from a recent density matrix renormalisation group (DMRG) calculation by White [14], which again suggests that large clusters have to be studied to get quantitative estimates. As far the collinear order is concerned, we first note that the 8 site cluster cannot be used because the collinear order is frustrated by periodic boundary conditions in that case. Using Eq. (4) with 16 and 32 sites, we found that there is a non–vanishing collinear order parameter for \( J_2/J_1 \geq 0.7 \), in reasonable agreement with Starykh et al. [3]. This order parameter drops abruptly, which suggests that the transition with the disordered state is first order, as in the case of the non-depleted lattice [10].


So, our results are consistent with the previous results that there is no magnetic long-range order for intermediate values of $J_2/J_1$, although very precise bounds cannot be deduced from a finite-size scaling of the results for 8, 16 and 32 sites.

Exact diagonalizations turn out to be very useful to study the nature of the intermediate phase. The basic idea is that, for intermediate values of $J_2/J_1$, the system will more or less behave as isolated plaquettes. For $J_2/J_1 = 1/2$, this can be understood very simply for the following reason: Let us write the Hamiltonian as $H = H_P + H_{IP}$ where $H_P$ describes independent plaquettes while $H_{IP}$ describes the coupling between them, and let us denote by $|\Phi_0\rangle$ the ground state of $H_P$. Then, for $J_2/J_1 = 1/2$, $\langle \Phi_0 | H_{IP} | \Phi_0 \rangle = 0$, which shows that the perturbation due to $H_{IP}$ will have a very small effect on $|\Phi_0\rangle$.

In order to check this assumption, we have computed $\langle \vec{S}_i \cdot \vec{S}_j \rangle$ on different links of the lattice: Along the side of a plaquette (P1), along the diagonal of a plaquette (P2), or along inter–plaquette links (IP1 and IP2 for $J_1$ and $J_2$ respectively). A signature of such a phase would be a set of correlation functions $\langle \vec{S}_i \cdot \vec{S}_j \rangle$ close to their values in the pure plaquette phase [14]. Results for $N=32$ and $N=16$ are shown on figure 4. The general features of these correlation functions are the same for both sizes. There is an abrupt variation of all the spin correlations which occurs for $J_2/J_1 \approx 0.67$ for $N=32$ and $J_2/J_1 \approx 0.6$ for $N=16$. This difference in the “critical” frustration is the main finite size effect. These curves give us information about the nature of the disordered phase: For $0.2 \lesssim J_2/J_1 \lesssim 0.7$, the correlations on all the links are close to their values in the plaquette phase. The best agreement is for $J_2/J_1 = 1/2$. For this particular value of the frustration, the correlation functions on the different links are comparable to their values in the pure plaquette state: $-0.4623 \pm 0.5$ for P1, $-0.2201 \pm 0.25$ for P2, $-0.0963 \pm 0$ for IP1, and $-0.0009 \pm 0$ for IP2. Hence, it seems clear that the ground-state is a plaquette resonating valence bond state. Note that there is no sign of the ground-state being degenerate, which allows one to eliminate the alternative broken symmetry state proposed by Sachdev and Read [15].

![FIG. 3. Staggered magnetisation and collinear order parameter for the $J_1 - J_2$ model for the $N=16,32$ sites clusters and extrapolated values (including also $N=8$ for the staggered case).](image1)

![FIG. 4. $\langle \vec{S}_i \cdot \vec{S}_j \rangle$ on different links for the $N=16$ (a) and $N=32$ (b) clusters: P1 (●), P2 (■), IP1 (○) and IP2 (□).](image2)

We now discuss the low-lying excitations in the intermediate frustration regime where the system has a plaquette ground state. For a single plaquette of four spins, the ground state is a singlet of energy $-2J_1 + J_2/2$ as long as $J_2 < J_1$. However, the first excited state is a triplet only if $J_2 < J_1/2$. Beyond that value, there is a singlet state in the singlet-triplet gap. Let us see what remains of that picture when plaquettes are coupled. The lowest energy levels versus $J_2/J_1$ for the $N = 32$ spin cluster are shown in figure 4. The other clusters have the same behaviour. The ground state is always a singlet totally symmetric under the symmetries of the Hamiltonian. The nature of the first triplet excitation depends on the value of $J_2/J_1$. When $J_2/J_1$ is small, the first triplet excitation has a wave vector $\vec{Q} = (\pi, \pi)$, while for $J_2/J_1 \simeq 0.56$ the first triplet has a wave vector $\vec{Q} = (0, \pi)$. This change in the position of the lowest triplet in the Brillouin zone is...
consistent with the prediction of Starykh et al. [8] and of Gelfand et al. [9] who both found such a change around $J_2/J_1 = 1/2$. A Schwinger boson mean field calculation [10] actually suggests that the position of the maximum of the spin structure factor moves continuously from $(\pi, \pi)$ to $(0, \pi)$. Now, more importantly, we found that, for intermediate values of $J_2/J_1$, there are singlet states in the triplet gap when $0.49 < J_2/J_1 < 0.7$. One of these excitations has the same wave vector as the ground state but has a d-wave symmetry. For the $N = 16$ clusters, this energy level crosses the ground state energy but this is probably an artifact of this cluster. The existence of a first excitation which is a singlet had not been reported so far for this model.

![FIG. 5. Lowest energy levels for N=32. Solid symbols are for spin 0 state, while open are for spin 1. Dashed lines indicate the position of the change of the nature of the first excitations described in the text.](image)

Testing experimentally the presence of singlet states in the singlet-triplet gap in CaV$_4$O$_9$ should give useful information about the frustration ratio for the following reasons. We first note that two related compounds have been studied recently, suggesting that the value of the coupling constants could be quite different from the commonly accepted value, i.e. $J_2/J_1 \approx 1/2$ and $J_1$ ranging from 100K to 200K. A parent compound of CaV$_4$O$_9$, CaV$_3$O$_7$, which has a similar structure as far as the local geometry in the VO plane is concerned, has been studied by Harashina et al. [17]. Using neutron diffraction, they have shown that it has a collinear magnetic long range order. This is the signature of a large frustration: A modified spin wave calculation of Kontani et al. [18] suggests that this state is the ground state only if $J_2/J_1$ is bigger than 0.7. More recently, a quasi-one dimensional vanadate, NaV$_2$O$_5$, has been studied [19]. This material consists of spin 1/2 chains corresponding to corner sharing VO$_2$ square pyramids. So it involves only one coupling constant which should correspond to $J_2$. A fit of the temperature dependence of the susceptibility has been performed leading to $J_2 \approx 530K$. The local geometry being essentially the same in these compounds and in CaV$_4$O$_9$, the exchange integrals should be comparable. So these results suggest that $J_2$ should be of order 500 K, and that $J_2/J_1$ should be around 0.7. Note that large values of $J_1$ and $J_2$ are compatible with the reported value for the gap (107K) because the gap is much smaller than $J_1$ close to the boundary to collinear order. Observing singlet states in the singlet–triplet gap would be a direct confirmation of this picture.

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