Spin Gap in Two-Dimensional Heisenberg Model for CaV$_4$O$_9$

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Abstract

**ABSTRACT:** We investigate the mechanism of spin gap formation in a
two-dimensional model relevant to Mott insulators such as CaV$_4$O$_9$. From
the perturbation expansion and quantum Monte Carlo calculations, the origin
of the spin gap is ascribed to the four-site plaquette singlet in contrast to the
dimer gap established in the generalized dimerized Heisenberg model.

**KEYWORDS:** CaV$_4$O$_9$, spin gap, four-site plaquette singlet

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In previous papers, [1–3] we have investigated the mechanism of spin gap formation in a class of two-dimensional generalized antiferromagnetic Heisenberg (AFH) models with dimerization. From this analysis, the origin of the spin gap in low-dimensional systems such as the spin-Peierls system, the ladder system and the Haldane system has been identified as the dimer gap in a unified way.

Recently, Taniguchi et al. found that the temperature dependence of the uniform magnetic susceptibility and the nuclear magnetic relaxation time $T_1$ of CaV$_4$O$_9$ indicate the existence of the spin gap\cite{4}. In this paper, we investigate the possible mechanism of the spin gap in CaV$_4$O$_9$.

The crystal structure of VO$_5$ pyramid layer in CaV$_4$O$_9$ is shown in Fig. 1(a). Since the valence of V atom is 4+, V atom can be treated as the localized spin with $S = 1/2$. In the case of copper oxide systems such as high-$T_c$ materials and Sr$_{n-1}$Cu$_{n+1}$O$_{2n}$, the electrons are localized in the $d_{\gamma}$ orbitals on Cu$^{2+}$ sites. However in this system, the Fermi level lies in the $d_{\epsilon}$ orbital and hence the localized spins should mainly come from electrons in the $d_{\epsilon}$ orbitals on V$^{4+}$ sites. The degree of the orbital degeneracy with three-fold degenerate $d_{\epsilon}$ orbitals has not been clarified yet, because the anisotropic crystal field due to possible Jahn-Teller distortion has not been estimated precisely. In any case, the antiferromagnetic exchange coupling is expected between the adjacent $d_{\epsilon}$ orbitals on the nearest-neighbor V atoms. We also expect that the exchange coupling between the nearest neighbors is dominant due to the $d_{\epsilon}$ character. Based on these facts, the $S = 1/2$ AFH model with the network shown in Fig. 1(b) is a good starting point to discuss the Mott insulating phase. The Hamiltonian is written as

$$\mathcal{H} = J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1)$$

where $\langle i,j \rangle$ denotes the nearest-neighbor bonds.

We first calculate the spin gap by quantum Monte Carlo (QMC) simulation to check whether our model is relevant or not. Here the spin gap $\Delta_S$ is defined as the energy difference between the lowest state with $S_{\text{total}}^z = \sum_i S_i^z = 1$ and the singlet ground state. The algorithm
of the QMC simulation is based on the world-line method combined with the Suzuki-Trotter 
method [6] and the checker-board decomposition [7,8]. The temperature $T$ scaled by $J$ is 
taken as 0.1, which is sufficiently low to observe the ground state properties for the present 
purpose. The Trotter numbers $N_T$ are 40, 60, 80 and 100. The number of QMC steps is 
$(1 \sim 5) \times 10^7$ for each Trotter number. The extrapolation formula used to obtain $\Delta_s$ from 
the finite $N_T$ is given by $\Delta_s(L) = \Delta_s(\infty) + A/N_T^2$. The lattices we have calculated have 
sizes $1 \times 1$, $2 \times 2$, $3 \times 3$ and $4 \times 4$ cells under the periodic boundary condition, where a 
cell includes 20 sites. The value of the spin gap extrapolated to the thermodynamic limit is 
estimated to be $(0.11 \pm 0.03)J$ with the form of the fitting function $\Delta_s + A/L^2$, as is shown 
in Fig. 2.

We also calculate the temperature dependence of the uniform susceptibility for $2 \times 2$ cells, 
which is shown in Fig. 3. The susceptibility in the thermodynamic limit should be close to 
this result, since the spin gap for $2 \times 2$ cells is close to the value in the thermodynamic 
limit. As a reference, the susceptibility of the conventional square-lattice AFH model on 
$8 \times 8$ lattice is also shown in Fig. 3, which may describe the thermodynamic properties 
within statistical errors. This also shows the existence of the spin gap in our model.

Next we investigate the origin of the spin gap. The four-site plaquette is treated as 
the unperturbed Hamiltonian while the other bonds are taken as the perturbation. As is 
shown in Fig. 4, the strength of the spin exchange couplings in the four-site plaquette is 
taken as $J$, while the strength of the others is $J'$. The ground state of the unperturbed 
Hamiltonian is the product state of singlets on the four-site plaquettes, in other words, a 
resonating valence bond state in each plaquette. The first excited states consist of the triplet 
state on one of the plaquettes and the singlet on the others. The degeneracy is lifted by 
the first-order perturbation expansion (PE) through the hopping of the triplet due to the 
translational symmetry. Then the energy of the triplet state has a wave-number dependence. 
We calculate the energy of the ground state and triplet states using the second-order PE. 
Then the ground state energy per site $\epsilon^{(2)}_s(k)$ and the energy difference between the ground 
state and the triplet state $\Delta^{(2)}_s(k)$ are obtained as
\[ \epsilon_{G}^{(2)} = \frac{1}{2} J [1 + \frac{43}{576} J' J^2 + O((J'/J)^3)], \]  

(2)

\[ \Delta_s^{(2)}(\mathbf{k}) = J + \frac{1}{3} J'(\cos k_x a + \cos k_y a) - \frac{47}{864} \frac{J'^2}{J} J^2 + \frac{1}{54} J'^2 J (\cos^2 k_x a + \cos^2 k_y a) - \frac{1}{9} J'^2 J \cos k_x a \cos k_y a, \]  

(3)

where \( a \) is the lattice constant between plaquettes, as is shown in Fig. 4. The dispersion of the triplet excitation \( \Delta_s^{(2)}(\mathbf{k}) \) is shown in Fig. 5. The lowest triplet excitation is located at \( \mathbf{k} = (\pi, \pi) \). An interesting point is that the spin gap survives \((0.205J)\) even if the value of \( J' \) is equal to \( J \). On the other hand, if we take the unperturbed Hamiltonian as \( J' \) bonds with \( J/J' \) taken as the perturbation, the ground state energy per site given by the second-order PE \( \epsilon_{G}^{(2)} \) is obtained as

\[ \epsilon_{G}^{(2)} = - \frac{3}{8} J' (1 + \frac{1}{4} \frac{J^2}{J'^2}). \]  

(4)

When \( J' \) is equal to \( J \), \( \epsilon_{G}^{(2)} = -0.537J \) obtained from eq. (2) is lower than \( \epsilon_{G}^{(2)} = -0.469J \) in eq. (3). The dispersion of the triplet state given by the first-order PE in terms of \( J/J' \) is described as

\[ \Delta_s^{(1)}(\mathbf{k}) = J' - \frac{1}{2} J (\cos k_x a + \cos k_y a). \]  

(5)

The perturbation breaks down and the spin gap closes at \( J/J' = 1 \) even in the first-order PE.

The above results imply that the origin of the spin gap is basically the four-site plaquette singlet state rather than the dimer singlet. The spin gap in \( \text{CaV}_4\text{O}_9 \) has been estimated from the susceptibility as \( \Delta_s \sim 100K \), whereas the gap amplitude obtained from the QMC is \( \Delta_s/J \sim 0.11 \). Although at present we do not have available data for \( J \) in \( \text{CaV}_4\text{O}_9 \), one may argue that the calculated value of the spin gap appears to be smaller than the observed value because the exchange interaction in vanadium oxides is expected to be at most several hundred K. One possible origin of the gap enhancement is the frustration effect arising from the next-nearest-neighbor exchange coupling. It is also noted that the effect of
the orbital degeneracy and the orbital correlation effect could be important for a quantitative estimation of the gap.

In order to investigate the mechanism of the spin gap in more detail from the viewpoint of the four-site plaquette singlet formation, we investigate the one-dimensional analog of this model. The lattice structure is shown in Fig. 6(a). We calculate the spin gap by the exact diagonalization (ED) method. The size dependence of the spin gap is shown in Fig. 7. After the extrapolation to the thermodynamic limit, we estimate the spin gap as $\Delta_s \sim 0.60J$, which is larger than the value of the spin gap in the ladder model. [10,11] The fitting function is the same as the one in the previous analysis. In the second-order PE, the triplet state energy is obtained as

$$\Delta_s(k) = J + \frac{1}{3} J' \cos k_x a - \frac{31}{1728} J'\cos k_x a - \frac{1}{108} J'^2 \cos 2k_x a.$$  

(6)

When $J'$ is equal to $J$, the value of the spin gap is $\Delta_s = 0.658J$ at $k = \pi$, which is close to the estimation from the ED. These results in the one-dimensional model show that the four-site plaquette singlet is a good starting point for discussing the ground state in a class of lattices constructed from the four-site plaquettes connected by a small number of bonds. This one-dimensional model may be not a toy model but a relevant model in some transition metal oxide compounds if a lattice structure such as that in Fig. 6(b) is realized.

In summary, we have studied the mechanism of the spin gap in CaV$_4$O$_9$. From the QMC as well as the PE, the origin of the spin gap formation is found to be the four-site plaquette singlets.

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FIGURES

FIG. 1. (a) The lattice structure of VO$_5$ pyramid layer in CaV$_4$O$_9$. Open circles represent V sites, while solid circles show oxygen sites. (b) The network of the $S = 1/2$ AFH model. In the QMC calculation, we take 20 sites as a cell as shown by the wavy-line square.

FIG. 2. Size dependence of the spin gap in our model.

FIG. 3. Temperature dependence of the uniform magnetic susceptibility for 2 $\times$ 2 cells. Solid circles represent the susceptibility of our model for 2 $\times$ 2 cells, while open circles show the susceptibility for the conventional square lattice AFH model for 8 $\times$ 8 lattices.

FIG. 4. The lattice structure in the perturbation calculation. Bold lines represent the bonds with $J$ and thin lines those with $J'$. The distance between the nearest-neighbor four-site plaquettes is $a$.

FIG. 5. The wave-number dependence of the triplet excitation energy in the second-order perturbation calculation. The inset shows the route of the wave vector taken for the abscissa.

FIG. 6. (a) The one-dimensional four-site plaquette model. The definitions of the symbols are the same as in Fig.1(b). (b) The lattice structure of a possible quasi-one-dimensional four-site-plaquette system of transition metal oxides.

FIG. 7. Size dependence of the spin gap in the one-dimensional model. The sizes we have calculated are 8, 16 and 24 sites.