Resonating-Valence-Bond Ground-state of CaV$_4$O$_9$

Studied by the Gutzwiller-projected Schwinger-boson method

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Abstract

An antiferromagnetic Heisenberg model on a 1/5-depleted two-dimensional square-lattice, a model of CaV$_4$O$_9$, is investigated by variational Monte Carlo simulation. A prototype of a trial wave function is made by projecting out the doubly occupied states from the Schwinger-boson mean-field solution. Then variational Monte Carlo simulation is performed up to 40 × 40 sites (including 320 vacant sites). The optimized state has the lowest energy, $-0.5510J$, ever reported. For this state energies of a dimer bond and a plaquette bond, staggered magnetization, static structure factor, and excitation spectrum are calculated. It is shown that the Néel order survives and there is no gap at isotropic coupling.

75.10.-b, 75.10.Jm, 75.50.Ee
Recent discovery of the energy gap in CaV$_4$O$_9$ has given rise to the question of the origin of the two-dimensional spin-gap. Though it has been suggested that the pseudo-gap is observed for the underdoped bilayer YBCO system, this is the first material to show the gapful ground-state for spin system in the two-dimensional single layer experimentally. Considering the fact that the two-dimensional square-lattice Heisenberg layer has an antiferromagnetic long-range order, the periodic lattice-defects intrinsic to the material may play an important role to destroy the magnetic ordering to make the spin-gap.

The planer lattice-structure of CaV$_4$O$_9$ is shown in Fig.1. Each closed circle stands for the V atom which has a localized spin with $S = 1/2$. It interacts with the nearest neighbor spins antiferromagnetically. Though topologically there are two different types of bonds, dimer bond $J_0$ and plaquette bond $J_1$, both couplings are believed to have the same magnitude in the material. Thus in this rapid communication, we consider only the model with $J \equiv J_0 = J_1$. In addition to the above coupling, it has also been pointed out that in the real material there is a frustrated next nearest neighbor coupling of the order of $J' = J/2$, which we neglect in the present work. Thus we investigate here the possibility to have a ground-state with spin-gap in a system represented by the following Hamiltonian,

$$H = J \sum_i \sum_w S_i \cdot S_{i+w}. \tag{1}$$

Here, $i = (i_x, i_y)$, $i_x$ and $i_y$ being integers, $i + w = (i_x + 1, i_y)$ or $(i_x, i_y + 1)$, and the summation over $w$ is done only for sites where spin exists.

There has been several investigations to explain the experimental spin-gap. The essential problem of this CaV$_4$O$_9$ is whether the gap is made by the depletion of the square-lattice or the additional frustration. Imada and Katoh have proposed that the gap is explained by the resonating local singlets of the four spins on a plaquette, which they call plaquette RVB state. They investigated this model by Quantum Monte Carlo (QMC) method and the second order perturbation expansions (PE) from the plaquette limit. It is found that the system has a gapful excitation without frustration. The estimated spin-gap is $\Delta = 0.11 \pm 0.03J$ for QMC and $0.205J$ for PE. On the other hand, linear spin-wave theory
and Schwinger-boson mean-field approximation resulted in the gapless excitation as far as frustrated couplings are not included. In the latter method it has been found that the Néel state is stable at $0.60 < J_0/J_1 < 2.40$. Contrary to ref. these results suggest that the next nearest neighbor coupling is needed to make the gap. Exact diagonalization study gives a contradictory result. It shows a small spin-gap with a finite staggered magnetization. This may result from the difficult extrapolation to the infinite size. Quite recently, QMC simulation done by Troyer et al. shows there is no gap without frustration. They make a phase diagram as a function of the ratio of dimer coupling $J_0$ to plaquette one $J_1$. In both limits of $J_0 \gg J_1$ and $J_1 \gg J_0$, the system has a gapful state. Thus ordered state is realized only in a limited region of the phase diagram. The estimated ordered region is at $0.60 \pm 0.05 < J_0/J_1 < 1.07 \pm 0.05$. This shows that the isotropic point is quite close to the order-disorder transition and suggests that other kinds of investigations are needed for this isotropic coupling.

In this paper, we study this model by Gutzwiller-projected Schwinger-boson method. In this method, first, the Hamiltonian is solved by Schwinger-boson mean-field theory. Then the solution is Gutzwiller projected to fix the spin at each site to be $S = 1/2$. The obtained ground-state is a kind of long-range RVB state with amplitude for a constituent bond depending on the distance between the sites. The mean-field solution is used only for the determination of these bond amplitudes. As for the mean field solution we could use that by Albrecht and Mila. However, for simplicity we here use the bond amplitudes obtained from the solution of the simple square-lattice, except those for the nearest neighbor bond amplitudes. Namely, in this paper, we modify the plaquette and dimer bond amplitudes by scaling them by $\alpha_p$ and $\alpha_d$, respectively, where $\alpha_p$ and $\alpha_d$ are variational parameters.

This type of Gutzwiller-projected wave functions have already given some good results for other models. It was first applied to the square-lattice Heisenberg model. The resultant ground-state is quite close to the true ground-state: the energy agrees with the best estimated value within the error of less than 0.1%. This method has then been applied to other similar models and also gave good results for each of them. We will see later in
this paper that the ground state energy is low enough in this system also. The optimized wavefunction is used to calculate the staggered magnetization and the excitation spectrum.

Using these methods, we did the variational Monte Carlo simulation for systems with $10 \times 10$, $20 \times 20$, $30 \times 30$, and $40 \times 40$ lattice points. The variational parameters are the ratios $\alpha_p$ and $\alpha_d$. It was found that the optimal state is realized at $\alpha_p = 1.08$ and $\alpha_d = 0.93$. This anisotropy is strongly enhanced in the result of the energy for the dimer coupling per bond ($E_d$), and that for the plaquette one ($E_p$). Actually, they take quite different values: $E_d = -0.303J$, $E_p = -0.400J$. This shows that the system favors the plaquette RVB state even in the isotropic coupling. The total energy per site can be scaled by $1/L^3$ as shown in Fig.2. Here, $L$ is the lattice size. It is clear from Fig.2 that our system size is large enough to estimate the energy in the thermodynamic limit. The obtained optimal energy is $-0.5510 \pm 0.0005$ per site, which is the lowest value that has already been reported.

To determine whether the system has gap or not without frustrated coupling, we have calculated staggered magnetization and excitation spectrum. The result of staggered magnetization per site can be scaled by inverse lattice-size $1/L$. The magnetization is evaluated from the longest spin-spin correlation as,

$$M(L) \equiv \sqrt{\frac{1}{N} \sum_{i,j} \langle |S_i \cdot S_j| \rangle}, \quad (2)$$

where the summation is taken over the longest possible distance in the plane and $N$ is the number of spin sites. From this analysis we have concluded that there is an antiferromagnetic long-range order. The staggered magnetization per site in the thermodynamic limit is $0.25 \pm 0.01$.

Although the existence of the long-range order indicates the absence of excitation gap, we also confirmed this by calculation of the excitation spectrum. We use the single mode approximation. Since this is a variational calculation, the upper bound of the spectrum is obtained. The true unit cell of this system is defined by the lattice vectors, $a_1 = (2, 1)$ and $a_2 = (-1, 2)$, and contains four spins. Therefore in the Brillouin zone there are four spin excitation modes. From the experience in the simple square-lattice, we expect that
the lowest modes among the four are those where the nearest neighbor spin moves almost in-phase or out-of-phase. Such modes can be expressed by

$$|k⟩ = \sum_i S_i^- e^{i \mathbf{k} \cdot \mathbf{r}_i} |G⟩,$$

(3)

where $|G⟩$ is the ground state, and the value of the wave vectors are around $\mathbf{k} = (0, 0)$ or around $\mathbf{k} = (\pi, \pi)$, i.e. the wave vectors around the $\Gamma$ or $M$ points of the original square-lattice. The upper bound of the spectrum, $\omega(\mathbf{k})$, is expressed as

$$\omega(\mathbf{k}) = \frac{f(\mathbf{k})}{S(\mathbf{k})},$$

(4)

$$S(\mathbf{k}) = \frac{1}{N} \sum_{i,j} \langle G|S_i^+ S_j^- |G⟩ e^{i \mathbf{k} \cdot \mathbf{r}_{i,j}},$$

(5)

$$f(\mathbf{k}) = \frac{J}{N}(2 - \cos k_x - \cos k_y) \sum_{i,w'} \langle G|S_{i+w'}^+ S_i^- S_{i+w'}^z|G⟩.$$

(6)

Here, $i + \omega' = (i_x \pm 1, i_y)$ or $(i_x, i_y \pm 1)$, $S(\mathbf{k})$ is the static structure factor, and $f(\mathbf{k})$ is a 3-point correlation function of spin operators, which is proportional to the ground-state energy.\(^\text{13}\) Static structure factor, $S(\mathbf{k})$, and the excitation spectrum, $\omega(\mathbf{k})$, for $40 \times 40$ lattices are shown in Figs.3 and 4, respectively. Here, $\Gamma = (0, 0)$, $X = (\pi, 0)$, and $M = (\pi, \pi)$ in the momentum space.\(^\text{28}\) Error bar is the statistical error. The value of $S(\mathbf{k})$ at $M$ point is too large to be plotted in this figure. The structure factor also suggests the strong antiferromagnetic correlation. The excitation is gapless at the $\Gamma$ and $M$ points. It should be noted that in the true Brillouin zone this $M$ point is folded into the $M$ point of the true Brillouin zone, which is at $(\pi/5, 3\pi/5)$.

To discuss the detailed properties of our results, we first see the accuracy of our trial wave function. The energy per site of the obtained ground-state is quite good. As for the energy, there is no elaborated estimation. It is easily estimated that the energy per site for an isolated plaquette RVB state is $-0.5J$.\(^\text{7}\) In the presence of inter-plaquette coupling, the energy should be lowered. By the second order perturbation expansions from the plaquette
RVB state, Katoh and Imada gives it as $-0.5373J$. This value is quite close to the result of the linear spin-wave theory, $-0.5376J$. On the other hand, our Monte Carlo result shows that the energy is $-0.5510 \pm 0.0005J$ which is the lowest energy that has already been reported. This means that the Gutzwiller-projected Schwinger-boson RVB wave function is useful to investigate other physical properties as well as the single-layer two-dimensional Heisenberg model.

Our results of the finite staggered magnetization and excitation spectrum show gapless spin excitation at the isotropic coupling. The result of finite magnetization coincides with the Schwinger-boson mean-field theory. The Gutzwiller-projection slightly changes the magnitude of the magnetic ordering. The magnitude of the staggered magnetization, $0.25 \pm 0.01$ per site, is slightly larger than that of the Schwinger-boson mean-field theory, about $0.22$. The gapless points exist at the $\Gamma$ and $M$ point. The gap closing at the former point is made by the behavior of $S(k)$ near the $\Gamma$ point. Since $f(k)$ is proportional to $k^2$, linear $k$ dependence of $S(k)$, Fig.3, makes the spectrum gapless. The antiferromagnetic long-range order makes the excitation spectrum gapless at the $M$ point, since structure factor diverges here. These results show that other ingredients are necessary to explain the experimental results on CaV$_4$O$_9$. The most probable mechanism is the destruction of the ordered state by additional next nearest neighbor couplings. Another candidate is subtle deformation of the lattice-structure which makes the dimer or plaquette couplings change to make the spin-gap.

Compared with the simple square-lattice, the bond energy of the plaquette, $E_p$, is enhanced, while that of the dimer bond, $E_d$, is suppressed. Namely $E_p$ is larger than that of the square-lattice, $-0.334J$, and about $80\%$ of the pure plaquette state. On the other hand, $E_d = -0.303J$ is reduced from $-0.334J$. This suggests that the system is approaching the plaquette RVB state in spite of the isotropic coupling. This result is consistent with the phase diagram given by QMC method. There, the isotropic point is quite close to the order-disorder transition beyond which the gap originated by the plaquette RVB opens.

In the present system the energy per site, $-0.5510J$ is smaller than that of the square-
lattice, $-0.6696J$. However, if energy is compared per bond, the average energy per bond $-0.3674J$ of this system is lower than $-0.3348J$ of the latter. This enhancement of the bond strength comes from the smaller coordination number, and also indicates closeness of the present system towards the spin-gap state. This tendency is also seen in the long-range spin-correlation. The magnetization per site is reduced to 83% of the square-lattice. These results suggest that more vacancies make the system gapful.

The spin wave velocity of the CaV$_4$O$_9$ is lower than that of the square-lattice. The renormalized factor, $Z_c$, which is rescaled by the classical spin-wave velocity, does not show the size-dependence. The estimated $Z_c$ is $1.94 \pm 0.02$, which is smaller than our result of the square-lattice, $1.99^{31}$. The decrease of the spin-velocity can be understood by the decrease of the coordination number, which effectively weakens the spin-stiffness.

In conclusion, we have investigated the antiferromagnetic Heisenberg model on a 1/5-depleted two-dimensional square-lattice as a model of CaV$_4$O$_9$ by variational Monte Carlo simulation. In our model, where the interaction exists only between the nearest neighbor spin pairs, the antiferromagnetic long-range order survives and the excitation is gapless. The gapless points exist at the Γ and $M$ points. Plaquette energy is larger than dimer energy, which shows the system favors the plaquette RVB state. Our conclusion is consistent with the recent QMC result done by Troyer et al.$^{32}$ These results show that the additional mechanism is needed to destroy the magnetic ordering and to make the experimental spin-gap state of CaV$_4$O$_9$.

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27. If we consider the position of apical oxygen, i.e. three dimensional structure, the unit cell should be doubled. Here, we only consider the planer structure of $\text{CaV}_4\text{O}_9$.

28. The results are shown in the extended zone scheme, namely in the Brillouin zone of the two-dimensional square-lattice. The actual Brillouin zone for the $\text{CaV}_4\text{O}_9$ is one fifth of that.

29. It is believed that the renormalization factor is about $1.18 \pm 0.02$ for the square-lattice Heisenberg model. Here, to compare the spin-wave velocity within the same method, we take our Monte Carlo result based on the same method. Such large $Z_c$ comes from the multi-magnon effect on our single-mode approximation.
FIGURE CAPTIONS

FIG. 1. Lattice structure for V-spins in a layer of CaV$_4$O$_9$. Dimer(plaquette) coupling is shown by a thick(thin) solid line.

FIG. 2. Energy per site as a function of $1/L^3$. The optimal parameters are taken as $\alpha_p = 1.08$ and $\alpha_d = 0.93$. The obtained value in the thermodynamic limit is $-0.5510 \pm 0.005$.

FIG. 3. Structure factor, $S(k)$, for $40 \times 40$ lattice. The value at $M$ point is too large to show in the figure.

FIG. 4. Excitation spectrum, $\omega(k)$, for $40 \times 40$ lattice. The spectrum is gapless at $\Gamma$ and $M$ point.
FIG. 1 Miyazaki et al.
for PRB rapid communication
Excitation energy

\( \Gamma \)