Exact Nonmagnetic Ground State and Residual Entropy of $S = 1/2$ Heisenberg Diamond Spin Lattices

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Exactly solvable frustrated quantum spin models consisting of a diamond unit structure are presented. The ground states are characterized by tetramer-dimer states with a macroscopic degeneracy in a certain range of isotropic exchange interaction. The lower bound of the excitation gap is exactly calculated to be finite, and the bulk entropy in the limit of zero temperature remains finite depending on the shape of the boundary of the system. Residual entropy is in the range of 0 - 6.1% of the entropy at high temperature for a hexagonal diamond lattice and 0 - 8.4% for a square diamond lattice. These diamond spin lattices are generalized to any dimensions and some of them are likely to be synthesized experimentally.

Quantum spin systems are fundamental theoretical models of interacting electrons, and much effort has been devoted to understanding the properties of the system for several decades. Even though their interactions are simple, the quantum nature of the spins sometimes leads to unexpected behavior at low temperatures. The quantum spin liquid (QSL) proposed by Anderson in 1973 [1] is an example of such a state widely considered to be realized in frustrated systems such as the Kagome lattice[2 -4]. The QSL state is generally understood as a resonating valence bond (RVB) state[1] where all electrons forming singlet dimers with each other are dynamically distributed in a certain range of the system without any static orders. Although extensive studies have been directed to find such a QSL state, the exact ground state of RVB has not yet been obtained in two- and three-dimensional Heisenberg spin systems.

One of the few exactly solvable quantum spin models in 2D is the Kitaev model [5]. The interaction of this model, however, has strong anisotropy and it is not a general model of magnetic materials forming an isotropic spin singlet. If we restrict the interaction to isotropic exchange coupling, the Shastry-Sutherland model is known to have an exact solution. [6] In this model, the ground state is not QSL but a valence bond solid (VBS) with static dimer order [6, 7].

As naively expected, if any configurations of the dimers on a lattice have the same energy and they contribute to the ground state with equal weight, it would be a similar state to the RVB state although it is not a unique ground state. In this Letter, we present models whose ground state is equivalent to an arbitrary configuration of dimers completely covering the lattice. The model is composed of a diamond unit structure consisting of one dimer $S_k^{(d1)} - S_k^{(d2)}$ and two monomers $S_i$ and $S_j$ as shown in Fig. 1(a). The exactly solvable model is obtained by replacing the nearest-neighbor bonds on a regular lattice with the diamond unit structure provided that the original lattice can be completely covered by dimers. With this replacement the Heisenberg chain is mapped onto the diamond chain[8], and square and hexagonal lattices are converted to square diamond and hexagonal diamond lattices as shown in Figs. 1(b) - 1(d).

The Hamiltonian of the models is then written as

$$H = J \sum_{<i,k>} S_i \cdot (S_k^{(d1)} + S_k^{(d2)}) + J_d \sum_k S_k^{(d1)} \cdot S_k^{(d2)}$$

$$= J \sum_{<i,k>} S_i \cdot T_k + J_d \sum_k \left( \frac{|T_k|^2}{2} - S(S+1) \right), \quad (1)$$

where $J$ and $J_d$ are the dimer-monomer interaction and dimer interaction, respectively. In this paper, we focus on the case of quantum spins with $S = 1/2$. $S_i$ and $S_k^{(d1)}$ represent monomer and dimer spins of $S = 1/2$, respectively, and $T_k$ represents the total spin of the

![FIG. 1. (Color online). (a) Diamond unit structure. (b) Conversion from Heisenberg chain to diamond chain. (c) Square diamond lattice[9]. (d) Hexagonal diamond lattice[9].](attachment:image.png)
dimer, \(\mathbf{T}_k = \mathbf{S}_k^{(d1)} + \mathbf{S}_k^{(d2)}\). Since \([H, \mathbf{T}_k^2] = 0\) and \(\mathbf{T}_k^2 = T_k(T_k + 1)\), each eigenstate of \(H\) is characterized by a set of \(\{T_k\}\). In the following, we show that the ground state of the Hamiltonian is exactly solvable when \(J_d > J > 0\).

We first decompose \(H\) to the sum of partial Hamiltonians \(h_i\) as

\[
H = \sum_{i}^{N} h_i, \tag{2}
\]

where \(N\) is the number of units in the diamond spin lattice that encloses one monomer spin as shown in Figs. 1(c) and 1(d) by the broken lines. Then, the minimum energy \(E_{\text{min}}\) of \(H\) and the sum of the minimum energy \(e_{i\text{min}}\) of \(h_i\) satisfy the inequality

\[
E_{\text{min}} \geq \sum_{i}^{N} e_{i\text{min}} \tag{3}
\]

for any choice of \(h_i\) based on the variational principle. The equality occurs only when the eigenstate of \(H\) is also the lowest energy eigenstate of each \(h_i\). Here, we chose \(h_i\) as one unit of the lattice shown in Fig. 2, where the exchange interaction between the spins \(S_k^{(d1)}\) and \(S_k^{(d2)}\) is written as \(J_d/2\) because of the double counting of the interaction at the interface between the two neighboring units,

\[
h_i = J \sum_{k}^{n_d} S_i \cdot \mathbf{T}_k + \frac{J_d}{2} \sum_{k}^{n_d} \left( \frac{|\mathbf{T}_k|^2}{2} - S(S + 1) \right). \tag{4}
\]

We first consider the eigenstates of the partial Hamiltonian \(h_i\), where the number of dimers is \(n_d\). Since the total spin of the dimer is a conserved quantity, \([h_i, \mathbf{T}_k^2] = 0\), their sum \(n_t = \sum_{k}^{n_d} T_k\) in each unit is a good quantum number. This means that both the numbers of triplet dimers, \(n_t\), and singlet dimers, \(n_d - n_t\), are conserved quantities in each unit. The eigenstates of \(h_i\) are then obtained by solving a problem of interacting \(S = 1\) triplet dimer spins and the \(S = 1/2\) monomer spin at the center of the unit. The local Hamiltonian \(h_i\) is now reduced to

\[
h_i = J \sum_{k}^{n_d} S_i \cdot \mathbf{T}_k + \frac{1}{8} J_d(4n_t - 3n_d), \tag{5}
\]

where \(S_i\) is \(S = 1/2\) spin at the center and \(T_k\) is \(S = 1\) spin representing three states of triplet dimers. From the Lieb–Mattis theorem\(^{[1,2]}\), the ground state belongs to \(S_{\text{tot}} = n_t - 1/2\) for the antiferromagnetic coupling \(J > 0\), and is exactly solvable with the energy \(e_{\text{min}} = -J(n_t + 1)/2\). The lowest energy \(e_{\text{min}}\) of \(h_i\) under the condition of fixed \(n_t\) is

\[
e_{\text{min}}(n_t) = \begin{cases} -\frac{1}{2}J(n_t + 1) + \frac{1}{2}J_d(4n_t - 3n_d) & (n_t \geq 1) \\ -\frac{3}{8}J_d n_d & (n_t = 0). \end{cases} \tag{6}
\]

The lowest energy \(e_{\text{min}}\) of \(h_i\) is then obtained as

\[
e_{\text{min}} = \begin{cases} -\frac{1}{2}J(n_d + 1) + \frac{1}{2}J_d n_d & (J_d < J, \ n_t = n_d) \\ -J + \frac{1}{4}J_d(4n_t - 3n_d) & (J < J_d < 2J, \ n_t = 1) \\ -\frac{3}{8}J_d n_d & (2J < J_d, \ n_t = 0). \end{cases} \tag{7}
\]

depending on the ratio \(J_d/J\). In the region of \(J_d > J\), the number of triplet dimers in \(h_i\) is 0 or 1. As shown in the following, the ground state and its energy of \(H\) are exactly obtained. The ground state of \(H\) in the case of \(n_t = 0\) in each unit is obvious. All the spins of dimers, \(S_k^{(d1)}\) and \(S_k^{(d2)}\), form spin singlet states and decouple from the other part of the system. The ground state is then characterized by the dimer–monomer (DM) state.

Here, we concentrate on the case of \(J < J_d < 2J\) where only one triplet dimer is confined in each unit (\(n_t = 1\)). Since spin singlet dimers are decoupled from the rest of the system, we consider three spins on one triangle in the unit consisting of one triplet dimer and one monomer spin, as shown in Fig. 3(a). The ground states of the three spins are doubly degenerate with different \(z\)-components of the total spin as shown below:

\[
|g_s\rangle_{123}^{+} = \frac{1}{\sqrt{3}} \left[ |\uparrow\rangle_1|\downarrow\rangle_2|\uparrow\rangle_3 + |\downarrow\rangle_1|\uparrow\rangle_2|\downarrow\rangle_3 \right]; \tag{8}
\]

\[
|g_s\rangle_{123}^{-} = \frac{1}{\sqrt{3}} \left[ |\uparrow\rangle_1|\downarrow\rangle_2|\downarrow\rangle_3 + |\downarrow\rangle_1|\uparrow\rangle_2|\uparrow\rangle_3 \right]; \tag{9}
\]

where

\[
|\uparrow\rangle_{ij} = |\uparrow\rangle_i|\uparrow\rangle_j, \tag{10}
\]
\[ |\psi\rangle_{ij}^{0} = \frac{1}{\sqrt{2}} (|\uparrow\rangle_i |\downarrow\rangle_j + |\downarrow\rangle_i |\uparrow\rangle_j), \]
\[ |\phi\rangle_{ij} = |\downarrow\rangle_i |\downarrow\rangle_j. \]

The energy of these states is obtained as

\[ e_{\text{tri(min)}} = -J + \frac{1}{8} J_d \]

with the interaction of \( J_d/2 \) between the two spins of the triplet dimer labeled by the numbers 2 and 3 in Fig. 3(a). We then couple two triangles by joining the edge bonds of \( J_d/2 \) to form a quadrangle shown in Fig. 3(b). The exact ground state \( |gs\rangle_{\text{qua}} \) and its energy \( e_{\text{qua(min)}} \) are obtained as

\[ |gs\rangle_{\text{qua}} = \frac{1}{\sqrt{2}} \left[ |t\rangle_{14}^{+} |t\rangle_{23}^{0} + |t\rangle_{14}^{0} |t\rangle_{23}^{-} - |t\rangle_{14}^{0} |t\rangle_{23}^{0} \right], \]
\[ e_{\text{qua(min)}} = -2J + \frac{1}{4} J_d, \]

where \( |gs\rangle_{\text{qua}} \) is rewritten using Eqs. (8) and (9) as

\[ |gs\rangle_{\text{qua}} = \frac{1}{\sqrt{2}} \left( |gs\rangle_{123}^{+} |\downarrow\rangle_4 + |gs\rangle_{123}^{0} |\uparrow\rangle_4 \right), \]
\[ = \frac{1}{\sqrt{2}} \left( |gs\rangle_{123}^{+} |\downarrow\rangle_1 + |gs\rangle_{123}^{0} |\uparrow\rangle_1 \right) \]

with \( |gs\rangle_{123}^{(+)0} \) being obtained by replacing “1” with “4” in Eqs. (8) and (9).

Comparing Eqs. (13) and (15), we find that the minimum energy of the quadrangle is just twice the minimum energy of the triangle. This means that the minimum energy of the sum of two partial Hamiltonians \( h_i + h_j \) sharing one triplet dimer state at the interface is equal to twice the minimum energy of each partial Hamiltonian. Indeed, we find that the minimum energy eigenstates of \( h_i + h_j \) are also the minimum energy eigenstates of each \( h_i \), as shown in Eq. (16). Since the eigenstates of the quadrangle \( |gs\rangle_{\text{qua}} \) are decoupled from the rest of the system by the singlet dimer states, \( |gs\rangle_{\text{qua}} \) is also an eigenstate of \( H \). If \( H \) is composed of such coupled partial Hamiltonian \( h_i + h_j \), the ground state is exactly obtained as product states of \( |gs\rangle_{\text{qua}} \) surrounded by spin singlet dimer states. We refer to this state as the tetramer-dimer (TD) state. The ground-state energy of \( H \) per unit of the diamond spin lattice is then given by

\[ E_{\text{min}}/N = -J + \frac{1}{8} (4 - 3\bar{n}_d) J_d, \]

where \( \bar{n}_d = N_d/N \) is the ratio of the total number of dimers, \( N_d \), to the total number of monomers, \( N \), in the diamond spin lattice. The condition to compose \( H \) from the coupled partial Hamiltonian \( h_i + h_j \) whose eigenstate consists of quadrangle \( |gs\rangle_{\text{qua}} \) is to find a complete dimer covering the original lattice of monomers, as shown in Fig. 4. The number of dimer configurations depends on the shape of the boundary but it generally increases to a macroscopic number with the increase in the system size yielding finite residual entropy in the ground state as shown later. Note that even in the case of \( J_d < J \), where equality in Eq. (3) does not hold, there is a possibility that the TD state is still the ground state. Equation (4) is the inequality determining the lower limit of the total Hamiltonian, and thus \( J_d = J \) is the upper bound of the transition to the TD state. Indeed, the diamond chain has the transition point from Ferri to TD state at \( J_d \sim 0.909J \).

We next show that only TD states have the lowest energy in the region of \( J < J_d < 2J \). Each eigenstate of \( H \) is characterized by a set of \( \{ T_k \} \) and there is the inequality Eq. (3) requiring that each \( h_i \) in \( H \) has the lowest energy with one triplet dimer \( (n_t = 1) \). Since each triplet dimer is shared by the neighboring two units of the diamond spin lattice, the minimum energy state has triplet dimers whose number \( N_t \) in the total system is half the number of units, \( N_t = N/2 \). This condition is equivalent to the complete dimer covering and the definition of the TD state. The uniqueness of the ground state in the subspace of \( N_t = N/2 \) and \( n_t = 1 \) in each unit is shown by exactly solving a tetramer of 4 spins. Since the condition of \( N_t = N/2 \) and \( n_t = 1 \) in each unit means that the spin singlet dimers completely surround the tetramer of 4 spins, all the tetramers in the system are independent of each other. The exact diagonalization of the tetramer shows that the ground state is singlet and separated from the lowest excited states by the energy gap \( \Delta E = J \), which shows that only the TD states are the lowest energy states.

Since \( \{ h_i, T_k^z \} = 0 \) and \( \{ h_i, T_k^x \} = 0 \), the lower bound of the energy of any subspace of \( \{ T_k \} \) is obtained by the variational principle represented by Eq. (3). The elemental excitations from the TD states are then classified by the quantum numbers \( N_t \) and \( n_t \) as follows:

- \( N_t = N/2 - 1 \) that is obtained by replacing one tetramer with one spin singlet dimer and two monomers, as in Fig. 5(a). The lowest excitation energy is obtained as \( \Delta E_t = 2J - J_d \).
See the text for the description of the diagrams and the content of the page.

We therefore conclude that in the region of \( J < J_4 < 2J \), only the TD state is the ground state and a finite excitation gap separates the TD ground state from the other excited state. The lowest excitation energy \( \Delta E_{\text{min}} \) is then summarized as

\[
\Delta E_{\text{min}} \geq J_d - J, \quad (J < J_4 < \frac{3}{2}J), \\
\Delta E_{\text{min}} = 2J - J_d, \quad (\frac{3}{2}J \leq J_d < 2J).
\]

All the above results on the ground state and excitation energy are common features of the diamond spin lattice including one- and three-dimensional systems and any boundary conditions provided that TD states are constructed on the lattice. Experimentally, it would be relatively easy to synthesize 2D hexagonal or square diamond lattices, because the lattice structure is equivalent even if dimers are disposed perpendicular to the 2D plane. There are several reports on the bimetallic polymeric coordination compounds that have a hexagonal diamond lattice structure\(^{13, 15} \) and a square diamond lattice structure\(^{16, 17} \). We do not discuss the case of \( J_d < J \), because results are model-dependent.

We finally comment on the residual entropy of the TD ground state. The number of degenerate TD ground states is equivalent to the number of configurations of dimer covering the original lattice of the monomer spin. This is known as dimer problems and the number of dimer configurations, \( N_{g}\), is given for an \( m \times n \) square lattice\(^{18, 19} \) with torus and open boundary conditions as

\[
\lim_{N \to \infty} \frac{1}{N} \ln N_{g} = 0.2915609, \quad (N = nm) \quad (18)
\]

which corresponds to the residual bulk entropy of the ground state per unit of diamond spin lattice. For a hexagonal lattice under torus boundary conditions, it is shown that\(^{20, 21} \)

\[
\lim_{N \to \infty} \frac{1}{N} \ln N_{g} = 0.169157 \quad (19)
\]

in the bulk limit. However, it is also known that \( N_{g} \) depends on the shape of the boundary of the lattice even in the bulk limit. For example, \( \lim_{N \to \infty} \frac{1}{N} \ln N_{g} = 0.130812 \) for a hexagonal lattice with open boundary conditions\(^{22} \), and \( \lim_{N \to \infty} \frac{1}{N} \ln N_{g} = 0 \) for a square lattice of almost square-shaped open boundaries\(^{23} \). Since the entropy under the torus boundary condition is expected to be the largest, the residual entropy of the TD ground state is distributed at least in the range of 0 – 6.1% of the entropy at high temperature for a hexagonal diamond lattice and 0 – 8.4% for a square diamond lattice depending on the boundary conditions. These results show that the residual entropy of diamond spin lattices is boundary-dependent even in the bulk limit, which may lead to quite unusual thermodynamic behavior at low temperatures. If we include next-nearest-neighbor exchange interactions in a square diamond lattice, the second-order perturbation analysis shows that the low-energy effective model will be a quantum dimer model\(^{24} \) that releases the residual entropy and may lead to a quantum spin liquid state.

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