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Abstract. We examine the ground state of a Heisenberg model with arbitrary spin S on a one-dimensional lattice composed of diamond-shaped units. A unit includes two types of antiferromagnetic exchange interaction which frustrate each other. The system undergoes phase changes when the ratio λ between the exchange parameters varies. In some phases, strong frustration leads to larger local structures or *clusters* of spins than a dimer. We prove for arbitrary S that there exists a phase with four-spin cluster states, which was previously found numerically for a special value of λ in the $S = 1/2$ case. For $S = 1/2$ we show that there are three ground-state phases, and determine their boundaries.

Effects of frustration in quantum antiferromagnets are of great current interest in solid-state physics. In a classical system, strong frustration obstructs a simple antiferromagnetic (AF) ordering and produces another magnetic order characteristic of each system, e.g. the 120° structure or a spiral [1]. In a quantum system, the interplay of quantum fluctuations and frustration makes the situation more complicated. There may appear an exotic ground state which does not have magnetic order and has no classical analogue. A typical example is the complete dimer state in the Majumdar–Ghosh (MG) model (see [2]).

There are two types of frustrated quantum spin system. One is a system the classical version of which has a locally stable spin configuration in the ground state; i.e. any local deformation for a spin configuration always raises the energy. We say that such a system is *elastic*. The MG model, the model with linearly decreasing AF interactions [3, 4] and the AF Heisenberg model on the triangular lattice are of this type. For the other type, the classical version of a system has ground-state spin configurations which can be locally deformed without raising the energy. Then the set of these configurations is a manifold with dimensions proportional to the system size. We say that a system of this type is *floppy*. The AF Heisenberg models on the Δ chain [5], the double chain with diagonal interaction [6] and the Kagomé lattice [7] are of this type. Some other floppy spin systems are also seen in [3].

Especially interesting are floppy systems. For example, it is argued that the Kagomé antiferromagnet has a mysterious peak in a low-temperature part of the specific heat [7]. In spite of quite a few theoretical studies on this system, its quantum ground state and the low-temperature thermodynamic properties are hardly clarified. The difficulty of the problem originates from the floppiness. In a classical floppy system, the configuration of a local set of spins can be deformed without affecting the other part. In the corresponding quantum system the local set may form a nearly closed state, or a *cluster*. A part surrounded by such clusters forms another cluster. Thus the total wave function becomes approximately

of a direct product form. To confirm this picture, it is important to examine a simple floppy model in which the structure of the ground state is clearly seen.

The singlet dimer is the smallest cluster. Ground states with dimer structures are possible in both elastic and floppy systems with $S = 1/2$. The difference appears in their low-lying energy spectra. An elastic quantum system has usually unique or finitely degenerate ground states. The lowest excitation mode is expected to have an energy gap and a dispersion both of the order of the typical exchange parameters. On the other hand, unusual situations such as a macroscopic degeneracy of the dimer ground state [3] or dispersionless low-energy excitations [5] occur in floppy systems. These seem to be two different quantum manifestations of the classical floppiness.

In this paper we report exact ground states with larger clusters than dimers in a frustrated AF chain. The system contains a parameter which regulates the strength of the frustration, and can be either elastic or floppy according to the value of the parameter. Wave functions with periodic cluster structures appear in the floppy regime.
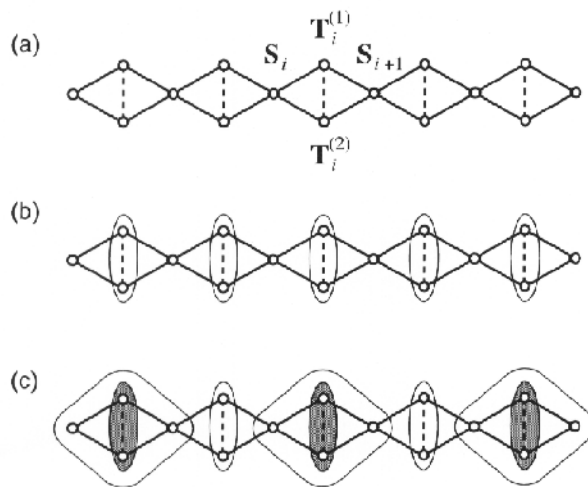

Figure 1. (a) The diamond chain. The circle represents a spin with magnitude S and the solid (dashed) line represents exchange parameter J (J'). (b) The dimer–monomer (DM) state. The unshaded oval represents a dimer ($T_i = 0$). There are free spins (monomers) on the sites not enclosed by ovals. (c) The tetramer–dimer (TM) state. The shaded oval represents a triplet pair ($T_i = 1$) and the closed loop including four spins represents a tetramer.

The system is described by the Hamiltonian

$$H = \sum_{i=1}^{N} h_i \tag{1a}$$

$$h_i = J(\mathbf{S}_i + \mathbf{S}_{i+1}) \cdot (\mathbf{T}_i^{(1)} + \mathbf{T}_i^{(2)}) + J'\mathbf{T}_i^{(1)} \cdot \mathbf{T}_i^{(2)} \tag{1b}$$

where $\mathbf{S}_i$, $\mathbf{T}_i^{(1)}$ and $\mathbf{T}_i^{(2)}$ are spins with magnitude S in the ith unit cell. We assume that J is positive. The sub-Hamiltonian h_i corresponds to a diamond shape and so we call the total lattice shown in figure 1(a) simply a *diamond chain*.

The system was studied earlier briefly by Sutherland and Shastry as an example of the superstability [8]. The case of $S = 1/2$ and $J' = 2J$ was discussed as an example in the context of a general method to derive spin models with complete dimer ground states [3].

The cases with $J' = \pm J$ were studied by Long *et al* [9]. They found numerically the ground state with four-site clusters for $S = 1/2$ and $J' = J$.

Recently it was reported that the magnetic properties of a mixed molecular crystal of organic mono- and di-radicals are described by the Hamiltonian (1) for $S = 1/2$ with $J \simeq 30$ K and $J' \simeq -20$ K [10].

We treat the whole region of J', though our main interest is in the frustrated region where J' is positive. For a given S the ratio $\lambda \equiv J'/J$ is the only parameter which determines the properties of the system. We assume periodic boundary conditions in the following, though most of the results do not depend on this assumption.

Before proceeding to the full quantum treatment, we examine the ground-state spin configuration in the classical limit ($S \to \infty$ with JS^2 finite). The ground state is given by a spin configuration which minimizes the energy of all the unit diamonds. Equation (1b) is rewritten as

$$h_i = \frac{J}{2}\{(\mathbf{T}_i + \tilde{\mathbf{S}}_i)^2 + (\lambda - 1)\mathbf{T}_i^2 - \tilde{\mathbf{S}}_i^2 - 2\lambda S(S + 1)\} \tag{2}$$

by using $\mathbf{T}_i \equiv \mathbf{T}_i^{(1)} + \mathbf{T}_i^{(2)}$ and $\tilde{\mathbf{S}}_i \equiv \mathbf{S}_i + \mathbf{S}_{i+1}$. In the classical limit $S(S+1)$ is replaced by S^2 in (2). For $\lambda < 1$ it is seen that the energy is minimized when the following conditions are satisfied: $|\mathbf{T}_i| = 2S$, $|\tilde{\mathbf{S}}_i| = 2S$ and $|\mathbf{T}_i + \tilde{\mathbf{S}}_i| = 0$. These conditions imply that $\mathbf{T}_i^{(1)}$ and $\mathbf{T}_i^{(2)}$, and $\mathbf{S}_i$ and $\mathbf{S}_{i+1}$ are parallel to each other, respectively, and further $\mathbf{T}_i^{(j)}$ ($j = 1$ or 2) and $\mathbf{S}_i$ are antiparallel to each other. So this is a ferrimagnetic state where all the $\mathbf{S}_i$s ($\mathbf{T}_i^{(j)}$s) are aligned parallel (antiparallel) to an axis. The ground-state energy and the magnetization are given by $-(4 - \lambda)JS^2$ and S per unit diamond, respectively. The ground state is elastic in this region.

For $\lambda > 1$, another expression of h_i is useful, i.e.

$$h_i = (J\lambda/2)\{(\mathbf{T}_i + \tilde{\mathbf{S}}_i/\lambda)^2 - (\tilde{\mathbf{S}}_i/\lambda)^2 - 2S(S + 1)\}.$$

The energy minimum is realized if $|\tilde{\mathbf{S}}_i| = 2S$ and $|\mathbf{T}_i + \tilde{\mathbf{S}}_i/\lambda| = 0$. The former condition leads to all the $\mathbf{S}_i$s being parallel to an axis. The latter condition is satisfied if and only if $\lambda \geqslant 1$, and means that $\mathbf{T}_i^{(1)}$ and $\mathbf{T}_i^{(2)}$ form a triangle with $\tilde{\mathbf{S}}_i/\lambda$. They make an angle $\theta = \cos^{-1}(1/\lambda)$ to the axis through $\mathbf{S}_i$ and may be rotated about this axis simultaneously without raising the energy. The ground state contains N degrees of freedom of free rotations and hence is floppy. The ground-state energy is $-(\lambda + 2/\lambda)JS^2$ per unit diamond. The ground state is again ferrimagnetic except for when $\lambda = 2$ with a magnetization $|2/\lambda - 1|S$ per unit. Thus in the classical limit the diamond chain has two different ground-state phases, the elastic one for $\lambda < 1$ and the floppy one for $\lambda > 1$.

We turn to the quantum case with general S. Hereafter we take an energy unit of $J = 1$. We find easily from (2) that $[\mathbf{T}_i^2, H] = 0$; i.e., for all i, $\mathbf{T}_i^2 = T_i(T_i + 1)$ are good quantum numbers ($T_i = 0, 1, \ldots, 2S$). With fixed $\{T_i\}$, the original problem of $3N$ spins reduces to a problem of a linear chain with $2N$ spins, where the $(2i - 1)$th site is occupied by the spin $\mathbf{S}_i$ and the $2i$th by $\mathbf{T}_i$. The energy of J'-bonds (i.e. a part of the energy proportional to λ) is determined solely by $\{T_i\}$. It should be noted that if $T_i = 0$ then there is no interaction between the left-hand and the right-hand sides of $\mathbf{T}_i$ and the whole lattice is decoupled.

Let us first consider the eigenstates of an isolated unit diamond described by h_i. In the lowest eigenstate of h_i for a given T_i, the energy is

$$E_1(T_i) = T_i\left[\frac{\lambda}{2}(T_i + 1) - (2S + 1)\right] - \lambda S(S + 1) \tag{3}$$

and the total spin is $2S - T_i$. Then we obtain the following.

Lemma 1. For $T \geqslant 1$ and for $\lambda > \lambda_D(T)$ where $\lambda_D(T) \equiv 2(2S+1)/(T+1)$, it holds that $T_i \neq T$ for any i in the ground state of the diamond chain.

Proof. The total Hamiltonian is divided as $H = H' + h_m$, where H' is the sum of h_is with $i \neq m$. Let us take a state $|\Psi_0\rangle$ whose wave function is given by the direct product of the ground-state wave function of H' and the singlet wave function of T_m. Then $\langle\Psi_0|H|\Psi_0\rangle = E_1(0) + E'$, where E' is the ground-state energy of H'. Let $|\Psi\rangle$ be any state with $T_m = T \geqslant 1$. Then $\langle\Psi|H|\Psi\rangle = \langle\Psi|h_m|\Psi\rangle + \langle\Psi|H'|\Psi\rangle$. Clearly $\langle\Psi|h_m|\Psi\rangle \geqslant E_1(T)$ and $\langle\Psi|H'|\Psi\rangle \geqslant E'$; also $E_1(T) > E_1(0)$ for $\lambda > \lambda_D(T)$. Therefore $\langle\Psi|H|\Psi\rangle > \langle\Psi_0|H|\Psi_0\rangle$ and $|\Psi\rangle$ cannot be the ground state of H. QED

Since $\lambda_D(T)$ decreases with T from $\lambda_D(1) = 2S + 1$ to $\lambda_D(2S) = 2$, we obtain the following result.

Proposition 1. For $\lambda > 2S + 1$, $T_i = 0$ for all i in the ground state. That is, all pairs of $T_i^{(1)}$ and $T_i^{(2)}$ form singlet dimers.

In this state all S_is are decoupled from other spins and behave as free spins. So we call this state a *dimer–monomer* (DM) state (figure 1(b)). Due to the free spins there is a $(2S+1)^N$-fold degeneracy in the DM state.

For $\lambda < 2S + 1$, the DM state is not a ground state since one can lower the energy by introducing an isolated $T_i = 1$ in the DM state. For $S = 1/2$ the ground state is composed of T_is with their magnitude 0 or 1. It is also true for $S \geqslant 1$ if $2S + 1 > \lambda > \lambda_D(2) = 2(2S+1)/3$. For example, let us assume the configuration of $\{T_i\}$ as $\{1010111011110110\}$ in the chain with 16 diamonds. Since zero T_is decouple the system to n-diamond clusters, the lowest energy for this configuration is simply given by $5E_1(0) + 2E_1 + E_2 + E_3 + E_4$, where E_n ($n \geqslant 1$) is the lowest energy of a cluster with n diamonds for the configuration with all T_is equal to 1. Taking account of an $E_1(0)$ accompanying each n-diamond cluster, the average energy of this cluster per diamond measured from the DM state is given by $e_n = (E_n - nE_1(0))/(n+1)$. If the minimum value of e_n occurs at $n = n_m$, then the ground state in the thermodynamic limit ($N \to \infty$) is realized by a regular array of n_m-clusters with isolated $T_i = 0$s between them. A finite N may cause a mismatch of the cluster size. If the minimum e_n is realized at more than one value of n, then the ground state will have a macroscopic degeneracy. It seems plausible that the ground state is the state with 1-diamond clusters on every other diamond for λ less than but close to $2S+1$, since a simple variational argument leads to $E_n \geqslant nE_1$ and usually the difference between the two sides of the inequality is fairly large. The wave function of this state is a direct product of those of four spin clusters ($T_i = 1$) and dimers ($T_i = 0$) as shown in figure 1(c) [9]. Therefore we call this state a *tetramer–dimer* (TD) state [11].

Proposition 2. There exists a finite region $\lambda_{C1} < \lambda < 2S + 1$ in which the TD state is the ground state of the diamond chain in the thermodynamic limit.

Proof. We show that e_n is the minimum only at $n = 1$ for a region $\lambda_{C1} < \lambda < 2S + 1$. We denote the ground-state energy of a nearest-neighbour AF linear chain with $n+1$ spins of magnitude S on odd sites and n spins of magnitude unity on even sites as $\tilde{E}_n$. Then we have $E_n - nE_1(0) = \tilde{E}_n + n\lambda$. Let us first assume $\delta \equiv \tilde{E}_2 - 2\tilde{E}_1 > 0$. If n is even, the Hamiltonian for $\tilde{E}_n$ is divided into $n/2$ sub-Hamiltonians, each equivalent to that for $\tilde{E}_2$. A variational argument gives an upper bound on $\tilde{E}_n$ as $n\tilde{E}_1 + n\delta/2$ for even n, and as $n\tilde{E}_1 + (n-1)\delta/2$ for odd n ($\geqslant 3$). Since $e_1 = [\lambda - (2S+1)]/2$, a lower bound on $e_n - e_1$ is given as $(1/2)(n-1)(n+1)^{-1}[\lambda - (2S+1) + \delta]$, which is positive for $\lambda > 2S + 1 - \delta$ and $n \geqslant 2$. So we obtain $\lambda_{C1} \leqslant 2S + 1 - \delta$.

Next we assume that $\delta = 0$ and deduce a contradiction. We divide the Hamiltonian

for $\tilde{E}_2$ with five spins as $\tilde{h}_1 + \tilde{h}_2$, where each one is the Hamiltonian for three spins, two of magnitude S and one of magnitude unity in the middle. A simple variational argument proves that $\delta \geqslant 0$ and the assumption implies that the ground state of $\tilde{h}_1 + \tilde{h}_2$ is also the ground state of $\tilde{h}_1$. The Lieb–Mattis theorem [12] holds in this case and implies that the total spin of the ground state is $|3S - 2|$ and that for $\tilde{h}_1$ is $2S - 1$. The theorem also tells us that the ground state with the z-component of the total spin S_{T}^z contains all the S^z-diagonal states compatible with S_{T}^z. The state $|S, 0, S, -1, S - 1\rangle$ is contained in the ground state with $S_{\text{T}}^z = 3S - 2$. But the fact that the total spin of three spins on the left must be $2S - 1$ eliminates the presence of the above state in the ground state and proves the failure of the assumption. QED

Remark. We can show that $\lambda_{\text{C1}} \leqslant 1$ for $S = 1/2$. The proof will be given elsewhere [13].

For each S, we need numerical studies of finite-size systems to determine the precise value of λ_{C1} and to find the ground-state structure for $\lambda < \lambda_{\text{C1}}$. The analysis for $S = 1/2$ and 1 will be given later.

For negative or positive but small λ, we expect that the ground state is a ferrimagnetic state corresponding to the complete ferrimagnetic ground state in the classical limit. For $\lambda \leqslant 0$ we have a general result.

Proposition 3. For $\lambda \leqslant 0$ the ground state is ferrimagnetic, i.e. it has both ferromagnetic and AF long-range order. For all i, $T_i = 2S$ in the ground state.

Proof. We divide the total lattice into two sublattices, where $\mathbf{S}_i$s are on the A sublattice and $\mathbf{T}_i^{(j)}$s on the B sublattice. For $\lambda \leqslant 0$ the Lieb–Mattis theorem [12] implies that the total spin of the ground state is given by NS; i.e. ferromagnetic long-range order (FLRO) exists. The positive (or negative) definiteness of the ground-state wave function in terms of the S^z-diagonal basis implies that the AFLRO is not less than the FLRO [14] and that $T_i = 2S$ for all i. QED

The ferrimagnetic ground-state phase is expected to extend to positive λ and we determine the phase boundary for $S = 1/2$ by numerical methods.

There is macroscopic degeneracy of the ground states at $\lambda = 2S + 1$. Since $E_1(1) = E_1(0)$ at this value of λ, any configuration of $\{T_i\}$ with only $T_i = 1$ or 0 and satisfying $\{T_i, T_{i+1}\} \neq \{1, 1\}$ for any i gives ground states. We estimate the total degeneracy D by using an asymptotic expansion for large N as $\log D \approx N \log[(2S + 1)(\sqrt{1 + 4/\alpha} + 1)/2]$ where $\alpha = (2S + 1)^2/(4S - 1)$. The ratio of the residual to the total entropy is 0.424 for $S = 1/2$ and decreases with S to 1/3 for $S = \infty$. Macroscopic degeneracy of the ground state can occur at other phase boundaries.
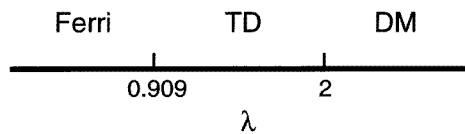
Ferri   TD   DM

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0.909   2

λ

Figure 2. The phase diagram for $S = 1/2$ in the parameter space of λ ($= J'/J$).

Let us inspect the case of $S = 1/2$. We estimate the minimum energy of a cluster composed of n unit diamonds where all T_is are unity. For this purpose, we numerically calculated the ground-state energy $\tilde{E}_n$ of finite linear chains with $n + 1$ spin one-halves and n spin unities alternatingly aligned. By employing the Lanczos technique we obtained the

energy up to $n = 7$. The data obtained for $\tilde{E}_n$ fit nicely to an assumed asymptotic formula $\tilde{E}_n/(n + 1) \simeq \tilde{e}_\infty + a/(n + 1)$ with $\tilde{e}_\infty = -1.454$. We have estimated the values of λ where the state with n-diamond clusters gives the same energy with the TD state by using the $\tilde{E}_n$s obtained. The values are $0.763\,012$, $0.819\,171$, $0.847\,024$, $0.862\,127$, $0.871\,321$, and $0.877\,464$ for $n = 2, 3, \ldots, 7$. From the monotonically increasing behaviour of these values, and the linear dependence of e_n on λ we conclude that the TD phase changes directly to the ferrimagnetic phase where $T_i = 1$ for all i. The critical λ is estimated as 0.909 from the value of $\tilde{e}_\infty$. Thus we have completely determined the ground-state phase diagram of the diamond chain for $S = 1/2$. It consists of three phases: the DM phase for $\lambda > 2$, the TD phase for $0.909 < \lambda < 2$ and the ferrimagnetic phase for $\lambda < 0.909$ (figure 2).

In the case of $S = 1$ we have obtained ground states with clusters larger than tetramers. The ground state changes its character successively from the DM state to the TD state at $\lambda = 3$, then to the heptamer ($n = 2$)–dimer state at $\lambda = 2.660$, to the state with 3-diamond clusters at $\lambda = 2.583$ and suddenly to the state where $T_i = 1$ for all i (i.e. $n = \infty$) at $\lambda = 2.577$. Therefore the ground-state phase diagram has at least six phases. The detail will be reported elsewhere [13].

Above we have shown that the spin system on the diamond chain has several ground-state phases with cluster structures [15]. There appear clusters larger than conventional dimers. For $S = 1/2$ the TD state is especially interesting since it is nonmagnetic. We believe that these cluster structures are quantum manifestations of the classical floppiness. The results might give some insight into the ground state of other floppy systems such as the Kagomé antiferromagnet.

Acknowledgments

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However, the model has no ground state with clusters larger than dimers for all parameter values.