Classical Dimers and Dimerized Superstructure in an Orbitally Degenerate Honeycomb Antiferromagnet

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We discuss the ground state of the spin-orbital model for spin-one ions with partially filled t_{2g} levels on a honeycomb lattice. We find that the orbital degrees of freedom induce a spontaneous dimerization of spins and drive them into nonmagnetic manifold spanned by hard-core dimer (spin-singlet) coverings of the lattice. The cooperative "dimer Jahn-Teller" effect is introduced through a magnetoelastic coupling and is shown to lift the orientational degeneracy of dimers leading to a peculiar valence bond crystal pattern. The present theory provides a theoretical explanation of nonmagnetic dimerized superstructure experimentally seen in Li_2RuO_3 compound at low temperatures.

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The nearest-neighbor Heisenberg antiferromagnet on a bipartite lattice has a Néel-type magnetically long-range ordered ground state. However, such a classical order of spins can be destabilized by introducing a frustration into the system through the competing interactions that may lead to the extensively degenerate classical ground states [1]. In such systems exotic quantum phases without long-range order can emerge as the true ground states. In this Letter we want to point out and discuss another scenario that can appear when magnetic ions on a bipartite lattice possess also an orbital degeneracy. The physics of such systems may be drastically different from that of pure spin models, as the occurrence of an orbital ordering can modulate the spin exchange and preclude the formation of magnetically ordered state on a bipartite lattice. In the following we focus on a system with threefold-orbitally degenerate $S = 1$ magnetic ions on a honeycomb lattice. This model is suitable to describe d^2 and d^4-type transition-metal compounds with partially filled t_{2g} levels, like the layered compound Li_2RuO_3 [2]. Here the layers are formed by edge-sharing network of RuO_6 and LiO_6 octahedra. The Ru ions make a honeycomb lattice and Li ions reside in the centers of hexagons. These layers are well separated by the remaining Li ions. The magnetically active Ru^{4+} ions are characterized by four electrons in the threefold degenerate t_{2g} manifold coupled into a $S = 1$ state. Li_2RuO_3 undergoes a metal-to-insulator transition on cooling below 540 K [2]. At the transition the magnetic susceptibility shows a steep decrease and its low-temperature value can be considered to be due almost entirely to the Van Vleck paramagnetism. The structural analyses have revealed the formation of dimerized superstructure of Ru-Ru bonds in the low-temperature phase. These observations indicate that Ruthenium spin-1 degrees of freedom are mysteriously missing at low temperatures and suggest the formation of an unusual spin-singlet dimer phase in the ground state of the system.

Here we describe the microscopic theory behind the stabilization of such a spin-singlet dimer state. We argue that, remarkably, such a novel phase can be realized on a honeycomb lattice because of orbital degeneracy, without invoking any exotic spin-only interactions. A possibility of formation of orbitally driven magnetically disordered states has been suggested within various coupled spin-orbital models [3–9]. The orbital induced frustration in t_{2g} based systems on a bipartite (cubic) lattice has also been considered [10,11]. The emergence of new phases due to the p-orbital degeneracy of cold atoms in optical lattices has been recently discussed within a spinless fermion model on a honeycomb and other two-dimensional lattices [12,13]. Yet, the peculiar case of partially filled t_{2g} levels on a honeycomb lattice leads to new results: the onset of an orbitally driven spin-singlet dimer phase in a spin-one system.

The model.—We assume that the low-temperature insulating phase of Li_2RuO_3 is of Mott-Hubbard type and describe the low energy physics within the Kugel-Khomskii type spin-orbital Hamiltonian [14]. We consider undistorted honeycomb lattice of Ru ions and look for possible instabilities towards symmetry reductions. In the Li_2RuO_3 crystal structure three distinct bonds of honeycomb lattice are in xy, xz, and yz planes (in cubic notations). We consider the leading part of the nearest-neighbor (NN) hopping integral of t_{2g} orbitals (d_{xy}, d_{yz}, and d_{xz}) due to the direct σ-type overlap. The $dd\sigma$ overlap in $\alpha\beta$ plane (α, $\beta = x, y, z$) connects only the orbitals of same $\alpha\beta$ type. The effective spin-orbital Hamiltonian for such a system been reported in Refs. [15,16]. It has the following form:

$$H = \sum_{\langle ij\rangle}\{J[\vec{S}_i\cdot\vec{S}_j - 1]\bar{O}_{ij} - [J_0\vec{S}_i\cdot\vec{S}_j + J_1]O_{ij}\}, \quad (1)$$

where the sum is taken over pairs of NN sites, $\vec{S}_i$ are spin-one operators, and the orbital contribution are described by

$\bar O_{ij}$ and O_{ij} operators. The second-order virtual processes locally conserve orbital index. The orbital degrees are thus static Potts-like variables and their contribution can be expressed simply in terms of projectors $P_{i,\alpha\beta}$ onto the singly occupied orbital state $\alpha\beta$ at site i. With this definition of the projectors the orbital part of the Hamiltonian can be written in the form equally valid for t_{2g}^2 and its particle-hole symmetry related t_{2g}^4 configurations. The orbital operators $\bar O_{ij}$ and O_{ij} along the bond ij in $\alpha\beta$ plane are given by $\bar O_{ij} = P_{i,\alpha\beta}P_{j,\alpha\beta}$ and $O_{ij} = P_{i,\alpha\beta}(1 - P_{j,\alpha\beta}) + P_{j,\alpha\beta}(1 - P_{i,\alpha\beta})$. For further analysis it is convenient to rewrite the Hamiltonian as the sum of three terms: $H = E_0 + H_{\rm AF} + H_{\rm FM}$,

$$H_{\rm AF} = \sum_{\langle ij\rangle} J[\vec S_i\cdot\vec S_j + \zeta]\bar O_{ij},\quad H_{\rm FM} = -J_0\sum_{\langle ij\rangle}\vec S_i\cdot\vec S_j O_{ij}, \tag{2}$$

$E_0 = -2J_1N$, N is number of lattice sites and $\zeta = 2J_1/J - 1$ [17]. For the full expressions of the exchange constants in terms of hopping integral t, on-site Coulomb repulsion U and Hund's coupling J_H we refer the reader to Refs. [15,16]. To the leading order in small parameter $\eta = J_H/U$, the coupling constants are given by $J \approx (1-\eta)\frac{t^2}{U}$, $J_0 \approx \eta\frac{t^2}{U}$, $J_1 \approx (1+2\eta)\frac{t^2}{U}$, and $\zeta \approx 1 + 6\eta$. For our further analysis, it will be important that $\zeta \geq 1$ for all values of the Hund's coupling. The inequality implies that any magnetically ordered ground state has a positive classical energy on antiferromagnetic (AF) bonds. It suggests that the formation of a low dimensional network of AF spin-coupling patterns are energetically favorable due to a larger gain of quantum spin-energy per bond. This picture is substantiated by the exact solution of the ground-state problem at zero Hund's coupling described in the next section.

Zero Hund's coupling.—The spin-orbital model defined in Eq. (2) has a small parameter $\eta \ll 1$. We start our analysis from the limit of zero Hund's coupling $\eta = 0$ ($H_{\rm FM} = 0$) and look for the possible spin-coupling patterns generated by $H_{\rm AF}$ term of the Hamiltonian.

The antiferromagnetic term $H_{\rm AF}$ is active only on the bonds with corresponding orbital being singly occupied at both ends of a bond (e.g., on a bond ij in xy plane both sites have xy orbital singly occupied). The AF bonds can only form nonintersecting linear open and/or closed chains [see Fig. 1(a)]. The longer the chain is, the more energy can be gained from the AF spin interaction. However, for each AF bond we pay a positive energy $\zeta \geq 1$ (the second term in $H_{\rm AF}$). Under these conditions the minimal possible AF energy is achieved when all AF chains are dimers. The proof of the stability of dimer states against the formation of longer open Heisenberg chains is based on the variational estimate on the ground-state energy of the M-site spin-one AF Heisenberg chain with open ends: $E_M \geq 1 - \frac{3M}{2}$, with the equality attained only at $M = 2$. This estimate can be obtained by dividing the chain into shorter overlapping subchains of lengths two and three with exactly known energies $E_2 = -2$ and $E_3 = -3$. The dimer states have a lower energy than the closed chains if $\bar E_M > -\frac{3M}{2}$, where $\bar E_M$ is the ground-state energy of the M-site spin-one AF Heisenberg ring. The last inequality is satisfied for any AF Heisenberg ring with $M > 4$ (see, for example, Ref. [18]). Note that on a honeycomb lattice only the closed chains with $M \geq 6$ can be formed. Therefore, at zero Hund's coupling $\eta = 0$, in the ground-state manifold the pattern of AF bonds corresponds to a hard-core dimer covering of the lattice and on each interdimer bond only one site has active orbital singly occupied. The $H_{\rm AF}$ term is inactive on such interdimer bonds, and spins of different dimers are decoupled. Spins are coupled into quantum spin-singlet state on dimer bonds and are thus gapped. Such spin-singlet dimer states form the exact ground-state manifold of spin-orbital Hamiltonian Eq. (2) in the limit of zero Hund's coupling.

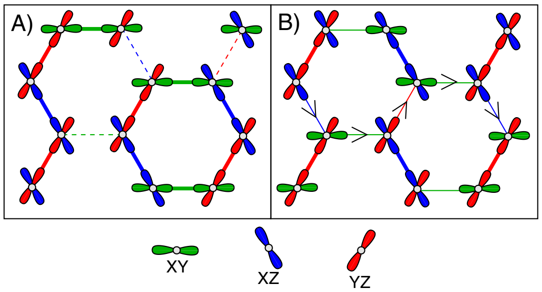

FIG. 1 (color online). Examples of orbital and spin-coupling patterns on the honeycomb lattice of Ru ions. (a) Decoupled AF chain and ring with corresponding orbital pattern. (b) An example of the spin-singlet dimer covering minimizing the energy at zero Hund's coupling. Thick (thin) lines denote AF (FM) intra- (inter-)dimer bonds, respectively. Dashed lines stand for the noninteracting bonds.

Ground-state manifold.—The ground-state manifold is extensively degenerate: there are infinitely many ways of covering a honeycomb lattice with hard-core dimers, and each dimer covering has its own Ising-type degeneracy connected with the orientation of an "inactive" orbital. Thus, in contrast to the case of one d electron ($S = 1/2$) where the state is determined by the covering of the lattice with spin-singlet dimers [9], here we have an extra degeneracy. At each site the second orbital points along one of two remaining bonds [the arrows in Fig. 1(b)], with the rule that at each of such "empty" bonds there should be only one orbital (one arrow). For any dimer covering the interdimer (empty) bonds form nonintersecting linear chains. Along an interdimer path all arrows must be directing along the same direction [see as an example the zigzag-like linear chain in Fig. 1(b)]. However, on each interdimer path we can inverse all the arrows and still remain in the ground-state manifold. Thus each interdimer path has a twofold degeneracy of Ising type. The degeneracy of a state with given dimer covering is thus equal to 2^{N_c}, where N_c is a number of decoupled interdimer chains. One finds that $N_c \sim \sqrt{N}$ for all dimer coverings except one case when all interdimer chains are hexagonal loops. In this case the honeycomb lattice is divided into nonoverlapping hexagons with no dimers, and the remaining hexagons are occupied by three dimers. This gives $N_c = N/6$ leading to a finite contribution to a bulk entropy from Ising-type degeneracy. The above degeneracy is, however, easily lifted by any interaction which induces a nonzero coupling of nonactive orbitals on dimer bonds and thus correlates the Ising-like variables (direction of arrows) of neighboring interdimer chains. For example, the coupling of Jahn-Teller distortions on NN edge-sharing oxygen octahedra favors the ferro-type orbital order of singly occupied nonactive orbitals on dimer bonds [see Fig. 1(b)] [19]. The π-type contribution to the hopping integral instead stabilizes an antiferro-type orbital order by increasing the AF coupling on a dimer bond [20]. In real materials the two mechanisms will have different energy scales and the dominant one will dictate the resulting orbital pattern. In both cases one completely lifts the degeneracy of a given dimer state.

The degeneracy of the second type originates from the orientational degeneracy of dimers and is exactly equal to the number of hard-core dimer coverings of the honeycomb lattice. The latter is well known to be an extensive quantity. The classical dimers on a honeycomb lattice exhibit a power-law decay of dimer-dimer correlation function and are thus in a critical state [21]. Therefore, one expects that any perturbation which may favor one or another type of dimer orientation may lift this extensive degeneracy, resulting in a long-range ordered pattern of dimers. We have considered a possibility of perturbing the exact dimer ground-state manifold by small but finite Hund's coupling $0 < \eta \ll 1$. The Hund's coupling produces a ferromagnetic (FM) term H_{FM} active on interdimer bonds [see Fig. 1(b)]. At small η, the dimer state is stable against the weak FM interdimer interaction. In this case the magnetic contribution along the FM bond is zero ($\langle \vec{S}_i \cdot \vec{S}_j \rangle = 0$ for i and j belonging to different dimers). However, the weak interdimer coupling may, in principle, lift the orientational degeneracy through order out of disorder by triplet fluctuations [9]. We find that on a honeycomb lattice these quantum fluctuations do not fully lift the dimer degeneracy. They only disfavor the configurations with three dimers on a hexagon because such a hexagonal loop of alternating AF and FM bonds is frustrated in the classical limit. In the next section we introduce a magnetoelastic coupling and show that it fully lifts the orientational degeneracy of dimers.

Degeneracy breaking by magnetoelastic coupling.—The magnetoelastic mechanism of lifting the extensive degeneracy of frustrated systems has been successful in explaining the experimentally observed structures [5,22–24]. The physics behind this mechanism is that the correlated nature of structural distortions that appear due to the modulation of magnetic energies on bonds may select a particular pattern of distortions and thus lift the extensive degeneracy of the ground-state manifold.

In the ground-state manifold the spin degrees of freedom are described by the product of spin-singlet dimer states. A shortening of a bond where the singlet is located enlarges the magnetic energy gain, because of the increase in the exchange coupling J on that bond. The magnetic energy gain, being linear in distortion, outweighs the increase in elastic energy and would always lead to such a contraction of singlet bonds for any dimer covering. But due to elastic coupling of these distortions different distorted patterns will lead to different elastic energy and hence to the lifting of dimer degeneracy. We, first, formalize this picture within the simplest model and later discuss its extension. The schematic structure of $\mathrm{Li_2RuO_3}$ is shown in Fig. 2(d). In the minimal model the exchange coupling is assumed to depend solely on a distance between Ru ions, and the lattice degrees of freedom are described within Einstein phonon model for Ru ions:

$$\mathcal{E}_{\mathrm{ME}} = -\gamma\epsilon \sum_{\langle ij \rangle} [\vec{u}_i - \vec{v}_j] \vec{l}_{ij} + \frac{k}{2} \sum_i \vec{u}_i^2, \tag{3}$$

where $\gamma = -\frac{1}{J}\frac{\partial J(r)}{\partial r}$ is a magnetoelastic coupling constant, ϵ is magnetic energy gain on a dimer bond, $\vec{u}_i$ is a displacement of Ru ions at site i, and k is Einstein phonon constant. The dimer positions are described by $\vec{l}_{ij}$: the latter is a unit vector along a bond ij occupied by dimer and is zero otherwise. We minimize the energy functional $\mathcal{E}_{\mathrm{ME}}$ with respect to set of $\vec{u}_i$ and eliminate them in favor of $\vec{l}_{ij}$. We find $\mathcal{E}_{\mathrm{ME}} = -\frac{k}{2}\sum_i \bar{\vec{u}}_i^2$ and $\bar{\vec{u}}_i = \frac{\gamma\epsilon}{k}\sum_j \vec{l}_{ij}$. The set of $\bar{\vec{u}}_i$ define the distortion pattern in which Ru ions on dimer bonds are moved towards each other. However, as the dimer bonds do not share a common site, $\mathcal{E}_{\mathrm{ME}}$ is a constant.

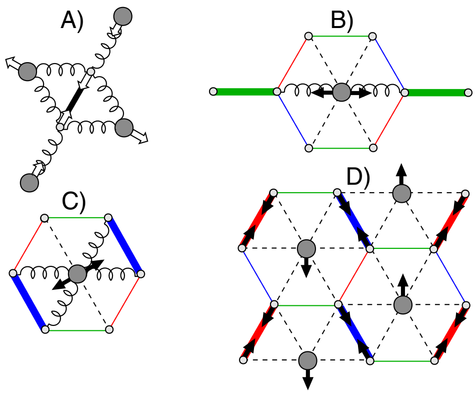

FIG. 2 (color online). Lifting dimer degeneracy by magnetoelastic coupling. The small light (large dark) circles denote Ru (Li) ions. The arrows show the displacements of corresponding ions. (a) The sketch of Li displacements induced by dimerized Ru-Ru bond. (b),(c) Two examples of destructive interference of Li displacements induced by neighboring dimers. (d) The ground-state dimer pattern selected by magnetoelastic coupling. This pattern exactly corresponds to the one found in $\mathrm{Li_2RuO_3}$ in Ref. [2].

It is independent of dimer variables $\vec{l}_{ij}$. In order to introduce the coupling between the dimers we extend the model by including a finite force induced on Li ions by distorted pattern of Ru ions. Consider an isolated complex of a Ru-Ru bond together with neighboring Li ions, shown in Fig. 2(a). When this bond is occupied by spin-singlet dimer it gets contracted, and the displacements of Ru ions induce the corresponding distortion of Li complex as seen in Fig. 2(a). On a lattice the distorted dimer bonds will now be coupled through the force induced on a common Li ion, an effect similar to a cooperative Jahn-Teller physics. The dimer configurations for which the induced forces on Li sites interfere in a nondestructive manner result in a larger distortion and hence more gain in energy. The two orientations of neighboring dimers shown in Figs. 2(b) and 2(c) are energetically unfavorable, as in both cases the induced forces exactly cancel each other. Thus the ground-state dimer pattern should satisfy the constraint of no-B and no-C type configurations. Note that a dimer covering satisfying the former constraint automatically satisfies the latter. It is possible to check that the only possibility to fulfill such a no-B constraint is realized for the dimer pattern shown in Fig. 2(d). This dimerization pattern exactly reproduces the one observed in the insulating phase of $\mathrm{Li_2RuO_3}$ [2].

We note that the above described mechanism of the selection of spin-singlet dimer pattern equally applies to the case when singlets are formed by spin-one-half degrees of freedom. The spin-singlet dimer nature of the ground-state manifold for d^1 systems on a honeycomb lattice has been proven in Ref. [9]. We therefore predict the same dimerized superstructure also for d^1 systems, such as V^{4+} and Ti^{3+} based compounds with such structure (if orbital degeneracy will not be lifted by some external mechanism like trigonal distortion, often present in such structure).

Summary.—To summarize, we have studied the ground state of spin-one honeycomb antiferromagnet with partially filled t_{2g} levels. We have demonstrated that the orbital degeneracy induces spontaneous dimerization of spins and drives them into extensively degenerate manifold of spin-singlet dimer states. The orientational degeneracy of dimers is then lifted through the magnetoelastic interaction that stabilizes a peculiar valence bond crystal state. Our theory provides an explanation for the observed nonmagnetic dimerized superstructure in $\mathrm{Li_2RuO_3}$ compound.

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