SU(4) Theory for Spin Systems with Orbital Degeneracy

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The isotropic limit of spin systems with orbital degeneracy has global SU(4) symmetry. On many 2D lattices, the ground state does not possess long-range order, which may explain the observed spin liquid properties of $LiNiO_2$. In the SU(4) Néel-ordered state, spin-spin correlations can be antiferromagnetic between two neighboring sites with parallel magnetic moments. [S0031-9007(98)07416-X]

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In many transitional metal oxides, the electron configuration on the metal ions has orbital degeneracy in addition to spin degeneracy. In these systems, the sign and magnitude of the spin-spin couplings depend on the orbital occupancy. This may result in interesting magnetic properties of the Mott insulating phase, and is believed to be relevant to unusual properties of many vanadium, titanium, manganese, and nickel oxides [1–12]. It may be also relevant to the quasi-one-dimensional tetrahis-dimethylamino-ethylene (TDAE)-C_{60} [13], and to artificial quantum dot arrays [14]. Orbitals are much more difficult to measure in experiments than spins. Recent successful measurement of orbitals using a reflection technique in x ray [15] has opened a new avenue in the study of orbitals in spin systems. The Hamiltonian describing spin $s = 1/2$ systems with a twofold orbital degeneracy (isospin $\tau = 1/2$) was derived by Castellani *et al.* [2]. The Hamiltonian is generally rotationally symmetric in $\vec{s}$ space, but not in $\vec{\tau}$ space. The anisotropy of the latter is due to Hund's rule and the anisotropy in orbital wave functions.

In this Letter we study a simplified Hamiltonian, Eq. (1), which has SU(4) symmetry. The insight learned from this higher symmetric model should shed light on our understanding of more realistic systems. The model provides a new possibility for spin liquid ground states in higher dimensions. For the square lattice, using the fermion mean field theory, we find the flavor liquid state to be stable against flavor or generalized spin density wave formation. By comparing the energies of long-ranged ordered states to short-ranged ones on the triangular lattice, we argue the ground state is likely to be a resonant plaquette flavor liquid. In the SU(4) Néel ordered state, the spin-spin correlations can be antiferromagnetic (AF) between two neighboring sites with *parallel* magnetic moments.

The simplest AF quantum spin-1/2 system with twofold degenerate orbitals (τ-1/2) and rotational invariance in both $\vec{s}$ and $\vec{\tau}$ spaces is given by [5]

$$H = \sum_{\langle i,j\rangle} (2\vec{s}_i \cdot \vec{s}_j + 1/2)\,(2\vec{\tau}_i \cdot \vec{\tau}_j + 1/2)\,, \qquad (1)$$

where $\langle ij\rangle$ is the nearest neighbor (nn) pairs. Apparently, (1) has SU(2) × SU(2) symmetry, representing rotational invariance in both spin and orbital spaces, and also interchange symmetry between spins and orbitals. As we will see, the full symmetry of (1) is actually the higher symmetry group SU(4), which unifies the spin and orbital degrees of freedom. An intuitive way to see the SU(4) symmetry is to rewrite (1) as

$$H = (1/4) \sum_{\langle i,j\rangle} \left(\sum_{\gamma=1}^{15} A_i^\gamma A_j^\gamma + 1 \right), \qquad (2)$$

where $A^\gamma = 2s^\alpha, 2\tau^\alpha, 4s^\alpha\tau^\beta$ for $\alpha, \beta = x, y, z$. A^γ can be considered as the 15 generators of the SU(4) group [13]. The symmetry can be examined in terms of the more standard generators of group theory. The Hamiltonian (1) acts on a Hilbert space of four basis states at each site. Choosing these as $|s^z, \tau^z\rangle$, we label them as

$$\begin{aligned} |1\rangle &= |1/2, 1/2\rangle, \qquad |2\rangle = |-1/2, 1/2\rangle, \\ |3\rangle &= |1/2, -1/2\rangle, \qquad |4\rangle = |-1/2, -1/2\rangle. \end{aligned} \qquad (3)$$

These basis states form a fundamental representation of SU(4). The conventional SU(4) generators S_m^n act on a basis state $|\mu\rangle$ according to $S_m^n|\mu\rangle = \delta_{n,\mu}|m\rangle$. The SU(4) algebra is given by $[S_m^n, S_k^l] = \delta_{n,k}S_m^l - \delta_{m,l}S_k^n$. In terms of electron operators, $S_m^n(i) = c_{i,m}^\dagger c_{i,n}$, where $c_{i,\mu}$ is the annihilation operator of an electron at site i and state $|\mu\rangle$. The operators $\vec{s}$ and $\vec{\tau}$ can be expressed in terms of S_m^n. For example, $2s^z = \sum_{m=1,3}(S_m^m - S_{m+1}^{m+1})$, and $s^+ = \sum_{m=1,3} S_m^{m+1}$. The expressions for $\vec{\tau}$ are similar. In terms of S_m^n, (1) becomes

$$H = \sum_{\langle i,j\rangle} S_m^n(i) S_n^m(j)\,. \qquad (4)$$

The repeated indices n, m are summed in Eq. (4) and hereafter. It is clear from (4) that H has global SU(4) invariance.

Equation (1), or equivalently (4), gives the effective Hamiltonian for the corresponding Hubbard model in the large U-limit and at 1/4 filling. Equation (4) is equivalent to the model studied by Pokrovskii and Uimin [16], and to one of a class of models that has been solved by Sutherland in one dimension (1D) [17]. This model

was also studied by Arovas and Auerbach in connection with the quasi-one-dimensonal TDAE-C_{60}, and recently by Yamashita *et al.* [18].

We remark that the AF SU(4) model here is different from the SU(N) model studied using the large N expansion method in [19] and in [20]. These authors considered the AF SU(N) model on bipartite lattices, where the two sublattices have conjugate representations with respect to each other ("quarks" and "antiquarks"). In the present model, all of the sites have the same representation, which is not self-conjugate.

To get insight on the physical properties, we first consider systems with a few sites. Since H has global SU(4) invariance, the eigenstates are given by irreducible representations of SU(4). In Fig. 1, we show the Young tableaux for two- and four-site systems. In the two-site system, the lower energy ($\epsilon = -1$) states are sixfold degenerate (total spin $s = 1$ and total orbital $\tau = 0$ or $s = 0$ and $\tau = 1$), and higher energy ($\epsilon = 0$) states are tenfold degenerate ($s = \tau = 1$ or both $= 0$). In the four-site system, the ground state is a unique SU(4) singlet $|\mathrm{SGL}\rangle$, which is rotationally invariant under the SU(4) generators,

$$\sum_i A_i^\gamma |\mathrm{SGL}\rangle = 0\,. \tag{5}$$

In terms of S_m^n, the singlet satisfies $\sum_i [S_m^n(i) - \delta_{mn}/4]|\mathrm{SGL}\rangle = 0$. A SU(4) singlet is a singlet of spin, orbital, and the orbital-spin crossing operator $U^{\alpha,\beta} = 4s^\alpha \tau^\beta$, and is a generalization of the SU(2) singlet of spin only systems. The energy of the SU(4) singlet of the four-site is found to be $-N_b$, with N_b the number of pairs $\langle ij\rangle$ in (1). Hence, $N_b = 4$ for a four-site ring, $N_b = 3$ for an open chain, and $N_b = 6$ for a tetrahedron. It is interesting to note that the energy of each bond in the four-site system is $\epsilon_b = -1$, the best energy a single bond can have. This would be difficult to understand from the conventional valence bond picture for spin only systems, and again indicates the difference between (1) and spin only models including the four-site plaquette resonating-valence-bond state recently discussed in the literature [21]. In terms of the fermion operators $c_{i\mu}$, the SU(4) singlet can be written as

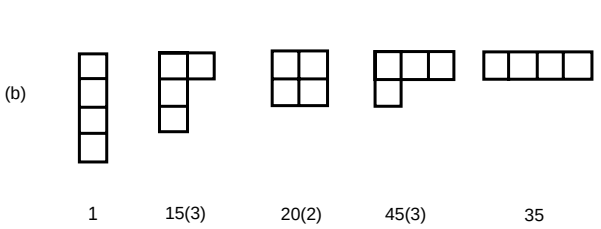

FIG. 1. Young tableaux for SU(4) model (1); (a) in a two-site system, and (b) in a four-site system. The dimensionality of representations is indicated for each tableau, and inside the parenthesis is the number of distinct representation.

$$|\mathrm{SGL}\rangle = \frac{1}{\sqrt{24}} \sum_{\{ijkl\}} c_{i1}^\dagger c_{j2}^\dagger c_{k3}^\dagger c_{l4}^\dagger |0\rangle\,, \tag{6}$$

where the sum is over all of the permutations of the four sites $ijkl = 1234$.

The SU(N) model in 1D was solved by Sutherland [17]. Affleck and Lieb [22] generalized the Lieb-Wu theorem [23] that the ground state is either gapless or has broken translational symmetry (dimerization) for SU(2) spin-1/2 chain to all 1/2-integer S, and to SU(N) chain. Their theorem for SU(4) can be extended to 2D in the same way as for the SU(2) case, but requires a long narrow strip as discussed by Affleck [24].

The SU(4) symmetry identified for model (1) has interesting consequences. Provided there is no symmetry breaking, it follows from the symmetry that the thermodynamic correlation functions, denoted by $\langle \ldots \rangle$,

$$\langle s_i^\alpha s_j^\alpha \rangle = \langle \tau_i^\alpha \tau_j^\alpha \rangle = \langle 4 s_i^\alpha \tau_i^\beta s_j^\alpha \tau_j^\beta \rangle = w_{ij}\,, \tag{7}$$

where w_{ij} is a function of i and j, independent of the indices α and $\beta = x, y, z$. This symmetry has been observed in quantum Monte Carlo calculations of the 1D system [25]. For translational invariant systems, the nn correlation is related to the energy per bond, ϵ_b,

$$w = \frac{1}{15}\left(\epsilon_b - \frac{1}{4}\right). \tag{8}$$

The nature of the ground state of (1) is of great potential interest. There have been numerous theoretical activities since the discovery of high temperature superconductivity to find possible spin liquid ground states in two or three dimensions. The additional orbital degrees of freedom provide a new possibility for such states. Since there are four *equivalent* single site states $|\mu\rangle$ in (1) in comparison with two states in the spin only systems, we expect quantum fluctuations to be stronger, making it more difficult to establish long-range order, hence, favoring flavor liquid states.

To illustrate this, we consider model (1) on a square lattice and carry out a fermion mean field theory. In fermion representation, $H = -\sum_{\langle ij\rangle} \chi_{ij}^\dagger \chi_{ij} + \text{const}$, where $\chi_{ij} = \sum_{\mu=1}^4 c_{i,\mu}^\dagger c_{j,\mu}$. The model is similar to the 2D SU(N) t-J model of Affleck and Marston [26], with the important difference that here one fermion per site implies that each flavor of fermions is 1/4 filled, while in their study each flavor of fermions is close to 1/2 filled, the case relevant to cuprates. We consider a uniform and real mean field bond amplitude $\chi = \langle \chi_{ij} \rangle$, and examine its stability against a generalized spin density wave (SDW) state with four sublattices B_ν, $\nu = 1, 2, 3, 4$. The uniform mean field state describes a flavor liquid. For the spin-1/2 Heisenberg model, the uniform state was found unstable against the (π, π) SDW state [27]. However, the instability is related to the nesting Fermi surface at 1/2 filling. We expect the uniform state to become stable against the SDW state at fillings sufficiently far away from 1/2, as in the present case. Minimizing the mean field energy with

respect to the generalized SDW order parameter m, defined so that the mean occupation number for the flavor μ at site $i \subset B_\nu$, $\langle c^\dagger_{i,\mu} c_{i,\mu}\rangle = (1 - m)/4 + m\delta_{\nu,\mu}$, we find that the uniform bond state is stable against the SDW. Thus, the mean field theory suggests the ground state of (1) on the square lattice is disordered. This flavor disordered state is gapless within mean field theory. However, the $1/4$ filled uniform mean field state is unstable against the commensurate flux phase of flux $hc/4e$ per plaquette [28,29]. The flux phase is also a flavor liquid, but has a gap and, hence, also a finite correlation length. The lack of long-range order is also suggested by considering the classical limit of (1) [30]. The classical limit of (1) in both square and triangular lattices are not frustrated, and the classical ground state is the same as the ground state of the corresponding Ising model:

$$H_{\text{Ising}} = \sum_{\langle i,j\rangle} (2s^z_i s^z_j + 1/2)\,(2\tau^z_i \tau^z_j + 1/2)\,,$$

which is identical to the four-component AF Potts model [31]. On the square lattice, this model has macroscopic ground state degeneracy, and is expected to be disordered even at $T = 0$ [32]. This expectation has been confirmed numerically [33].

Energetics also points to a disordered ground state. We consider the model on the triangular lattice. The AF Heisenberg spin-$1/2$ system on the triangular lattice is believed to order in a three-sublattice 120^0 structure [34]. With orbital degeneracy, such a spin ordering is no longer favored. In Fig. 2, we compare the estimated energies for various long-range ordered states, including the classical SU(4) Néel state [the same as the Ising-like Néel state for both triangular and square lattices (see Ref. [30])], the orbital polarized spin ordered state, and a valence bond state, with the SU(4) singlet plaquette solid state. Unlike the spin only problem, where the classical Néel state and the valence bond solid state are degenerate, here the plaquette state has much lower energy than all others. Since the plaquette state can resonate to further lower the energy (and becomes a flavor liquid), we speculate the ground state to be a resonant plaquette state with neither spin nor orbital long range order.

It is interesting to note that a spin liquid state with twofold orbital degeneracy may have already been realized in the best samples of $LiNiO_2$. The compound shows ferromagnetic spin-spin correlation at high temperature, but the measurements of magnetic susceptibility, specific heat, muon spin rotation μSR, and NMR at low temperature show no long-range ordering in spins, and the μSR also shows that Ni spins remain fluctuating even at 20 mK [6,35]. The NMR and specific heat measurements have ruled out the possibility of the spin glass phase [35]. These evidences strongly indicate a spin liquid ground state. In that material, a formal Ni^{3+} ion has spin $s = 1/2$ and a twofold e_g orbital degeneracy. The former is supported from the magnetic susceptibility at high temperatures, and the latter is implied from the absence of the Jahn-Teller distortion in the NiO_6 structure [6]. The Ni ions form layered triangular-lattices, separated by two oxygen and one Li layer, so that the interlayer coupling is weak. The basic physics can be described by a spin-$1/2$ system with twofold orbital degeneracy. We believe the orbital degeneracy is responsible for the observed spin liquid properties, and Eq. (1) may serve as a simple model to illustrate the role of the orbital degeneracy.

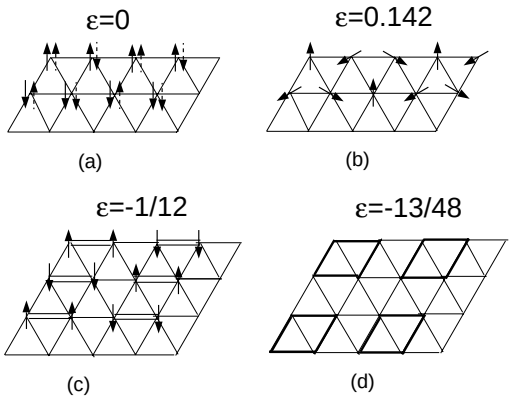

FIG. 2. Average energy per bond ϵ of (1) for various states for the triangular lattice. (a) Classical four-sublattice SU(4) Néel state, with each flavor shown by its orbital (dashed arrow) and spin (solid arrow) state. (b) State with orbital "ferromagnetic" and spin AF. In this case, Eq. (1) is reduced to $H = \sum_{\langle i,j\rangle}(2\vec{s}_i \cdot \vec{s}_j + 1/2)$. ϵ is deduced from Ref. [34]. (c) Valence bond state. Each double line represents a two-site valence bond of orbital singlet and spin triplet. Note the spin long-range order. (d) Plaquette state. Each plaquette (linked by four thick lines) represents a four-site SU(4) singlet.

The actual system in $LiNiO_2$ has anisotropic terms due to the Hund's rule and the anisotropy of the orbital wave functions, reducing the symmetry to just spin SU(2) symmetry. In the strong Hund's rule coupling limit, all of the spins are parallel while the orbitals will arrange themselves appropriately to have the lowest energy, and the system is ferromagnetic. However, since the ground state most likely has a gap in the SU(4) limit, it should be stable and remain disordered below a critical Hund's coupling. We believe the Hund's rule coupling in $LiNiO_2$ is below (but close to) the critical value, so that although the spin-spin correlations are ferromagnetic as indicated by the high temperature susceptibility, the low temperature physics can still be qualitatively described by the ground state of the SU(4) limit in that it is a spin liquid. It will be very interesting to experimentally further justify the spin liquid nature of the compound.

We now turn to the ordered states where the SU(4) symmetry is spontaneously broken. There are many ways to break SU(4), and here we discuss the generalized four-sublattice Néel state such as that shown in Fig. 2a. The remaining symmetry is $U(1) \times U(1) \times U(1)$. The nn correlation function can have very unusual properties in states with symmetry breaking. Consider, for example, the four-sublattice Néel state. Let the two nn sites i and j belong to the two sublattices with $\langle s^z_i\rangle = \langle s^z_j\rangle \geq 0$.

In spin only systems, this would imply a ferromagnetic coupling and the correlation $w(s^z) \equiv \langle s_i^z s_j^z \rangle > 0$. In the presence of the orbital degeneracy, the situation can be different. Let us start with the disordered state, where $w(s^z) < 0$ from (8). Provided the transition is continuous, this implies that $w(s^z)$ will remain negative at the transition point, or close to it on the ordered side of the transition. Therefore the system can have *antiparallel* spin correlation while both spins have *parallel* magnetic moments.

Such a broken symmetry state also supports very unusual generalized spin wave or flavor wave excitations. The usual linearized semiclassical spin wave approach [36] can be generalized to the SU(4) case. Assuming a four-sublattice ordered ground state in 2D systems such as in Fig. 2a. We find all of the flavor waves to be 1D in nature in spite of the 2D ordering pattern. While this behavior is a consequence of SU(4) symmetry, and if the Hamiltonian contains terms that break this symmetry (e.g., due to orbital anisotropy), 2D flavor waves will in general be observed; the flavor waves will remain quasi-1D-like if the deviation from the SU(4) limit is weak. The enhanced quantum fluctuations due to reduced dimensionality of the excitations may also provide a mechanism of disordering the ground state, in further support of our mean field theory result that the ground state of the SU(4) model (1) is a flavor liquid. The details will be the subject of a later publication. The unusual magnetic properties described above can be tested by neutron scattering.

In summary, we have examined the isotropic limit of spin systems with orbital degeneracy, and showed the ground states do not have long-range order in many 2D lattices. Our study may serve as a simple theory to illustrate the role of the orbital degeneracy responsible for the experimentally observed spin liquid properties in $LiNiO_2$.

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