Quantum melting of magnetic order due to orbital fluctuations

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We have studied the phase diagram and excitations of the spin-orbital model derived for a three dimensional perovskite lattice, as in KCuF₃. The results demonstrate that the orbital degeneracy drastically increases quantum fluctuations and suppresses the classical long-range order near the multicritical point in the mean-field phase diagram. This generates a qualitatively new spin liquid, providing the first example of a valence bond ground state in three dimensions.

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It is common wisdom that macroscopic ensembles of interacting particles tend to behave classically. This is not always true, however, and the study of collective quantum systems starts to become a prominent theme in condensed matter physics. Central to this pursuit are low-dimensional quantum spin systems (spin chains [1] and ladders [2]), and it proves difficult to achieve quantum melting of magnetic long-range order (LRO) in empirically relevant systems in higher dimensions. Here we want to suggest a class of systems in which quantum-melting occurs even in three dimensions: small spin, orbital degenerate magnetic insulators, the so-called Kugel-Khomskii (KK) systems [3]. There might exist already large local Coulomb interactions (Hubbard U), in orbital degenerate Mott-Hubbard insulators one has to consider in first instance the purely electronic problem. Because of the large local Coulomb interactions (Hubbard U), a low energy Hilbert space splits off, spanned by spin and orbital configuration space, with superexchange-like couplings between both spin and orbital local degrees of freedom. The orbital sector carries a discrete symmetry and the net outcome is that the clock-like orbital degrees of freedom get coupled into the SU(2) spin problem. Such a system might undergo symmetry breaking in states with simultaneous spin- and orbital order. The lattice has to react to the symmetry lowering in the orbital sector, but it was recently convincingly shown, at least in the archetypical compound KCuF₃, that the structural distortion is a side effect [4].

The fundamental question arises if these forms of classical order are always stable against quantum fluctuations. Although the subject is much more general (singlet-triplet models in rare earth compounds [10], V₂O₅ [11], LaMnO₃ [12], heavy fermions [13]), we focus here on the simplest situation encountered in KCuF₃ and related systems [3]. These are JT-distorted cubic, 3D analogues of the cuprate superconductors [14]. The magnetic ion is in a 3d⁹ state, characterized in the absence of JT-distortion by two degenerate e₉ (x² – y² ~ |x⟩, 3z² – 1 ~ |z⟩) orbitals, next to the S = 1/2 spin degeneracy. Kugel and Khomskii derived the effective Hamiltonian [3] with AF superexchange J = t²/U (where t is the hopping between |z⟩ orbitals along the c-axis),
\[ H_1 = J \sum_{(ij), \alpha} \left[ 4(\hat{S}_i \cdot \hat{S}_j)(\sigma_i^{\alpha} - \frac{1}{2})(\sigma_j^{\alpha} - \frac{1}{2}) + (\sigma_i^{\alpha} + \frac{1}{2})(\sigma_j^{\alpha} + \frac{1}{2}) - 1 \right], \] (1)

neglecting the Hund’s rule splittings of the intermediate \( d^8 \) states. Including those up to order \( \eta = J_H/U \) (\( J_H \) is the singlet-triplet splitting) yields in addition,

\[ H_2 = J_H \sum_{(ij), \alpha} \left[ (\hat{S}_i \cdot \hat{S}_j)(\sigma_i^{\alpha} + \sigma_j^{\alpha} - 1) + \frac{1}{2}(\sigma_i^{\alpha} - 1)(\sigma_j^{\alpha} - 1) + 3(\sigma_i^{\alpha}\sigma_j^{\alpha} - \frac{1}{4}) \right]. \] (2)

In Eqs. (1) and (2), \( \hat{S}_i \) refers to the spin at site \( i \), while \( \alpha \) refers to the cubic \((a, b, c)\) axes, and the orbital degrees of freedom are represented by

\[ \sigma_i^{\alpha(b)} = \frac{1}{4}(\tau_i^{\alpha} \pm \sqrt{3}\tau_i^{\beta}), \quad \sigma_i^z = \frac{1}{2}\tau_i^z. \] (3)

The \( \tau \)'s are Pauli matrices acting on the orbital pseudo-spins \( |z\rangle = (\frac{1}{\sqrt{2}}, 0) \), \( |x\rangle = (0, \frac{1}{\sqrt{2}}) \). Hence, we find a Heisenberg Hamiltonian for the spins, coupled into an orbital problem which is clock-model-like (there are three directional orbitals: \( 3x^2-1, 3y^2-1, \) and \( 3z^2-1 \), but they are not independent) \([15]\). As we will see in a moment, the Hund’s rule coupling term \([2]\) acts to lift the degeneracy. Next to this, we introduce another control parameter,

\[ H_3 = -E_z \sum_i \sigma_i^z, \] (4)

a ”magnetic field” for the orbital pseudo-spins, loosely associated with an uniaxial pressure along the \( c \)-axis.

The classical phase-diagram of the spin-orbital model \( H = H_1 + H_2 + H_3 \), shown in Fig. 1, demonstrates the competition between the spin and orbital interactions similar to that found before in two dimensions \([14]\). It consists of five phases with staggered (two-sublattice) magnetic long-range order (LRO): (i) At large positive \( E_z \), the orbital system is uniformly polarized along \( x^2 - y^2 \). As no superexchange is possible in the \( c \)-direction, the \((a,b)\) planes decouple magnetically, and we recognize the two-dimensional (2D) antiferromagnet, called further AFxx, well known from the cuprate superconductors. (ii) At large negative \( E_z \), the orbitals polarize along \( 3z^2 - 1 \), and the spin system is an anisotropic 3D antiferromagnet, called AFzz. These two AF phases (AFxx and AFzz) are stabilized by the anisotropic superexchange which amounts to 4\( J \) between \( z \) orbitals along the \( c \)-axis, and to 9\( J/4 \) (\( J/4 \)) between the \( x \) (\( z \)) orbitals in the \((a,b)\)-planes, respectively. In contrast, the Hund’s rule coupling \( J_H \) stabilizes mixed-orbital (MO) phases in which both AF and ferromagnetic (FM) couplings occur: (iii) At large \( J_H/U \) and \( E_z < 0 \), a MOFA phase is found, characterized at each site by orbitals, \( |\alpha\rangle = \cos \theta_i |x\sigma\rangle + \sin \theta_i |z\sigma\rangle \), with the sign of \( \theta \) alternating between the two sublattices in the \((a,b)\) planes. At small \( |E_z| \) the orbitals stagger like \( x^2 - z^2 \), \( y^2 - z^2 \), \( x^2 - z^2 \), and point towards each other along the \( c \)-axis which results there in strong (\( \sim J \)) AF interactions. In contrast, weak FM interactions (\( \sim J_H \)) occur within the \((a,b)\) planes. (iv) A similar MO state, called MOAFF, is found at large \( J_H/U \) and \( E_z > 0 \), with the directional orbitals staggered in FM \((b,c)\) planes, and AF order along the \( a \) direction \([17]\). Both states are degenerate at the line \( E_z = 0 \) (where \( \cos 2\theta_i = 1 \)), or in a disordered spin system due to the orbital sector.

It is instructive to consider the stability of the classical phase diagram to Gaussian quantum fluctuations \([15]\). The collective modes can be calculated using, e.g., a random phase approximation (RPA) within the Green function technique \([13]\). Next to the Goldstone modes of the spin system, one finds optical modes corresponding to orbital excitations which occur both in the presence (’transverse’) and in the absence (’longitudinal’) of a simultaneous spin-flip. The new feature is that the spin and transverse orbital excitations are coupled, so that fluctuations in the orbital sector also affect the spin sector. The approach of the critical lines is signalled by the softening of both longitudinal and transverse orbital modes. The (mixed) transverse modes give the dominating contribution to the renormalization of energy and magnetic order parameter. In the AFxx (AFzz) phase the lowest transverse mode softens along \( \vec{k} = (\pi, 0, k_z) \) \([\vec{k} = (k_x, 0, 0)]\), and equivalent lines in the Brillouin zone (BZ), regardless how one approaches the critical lines. Thus, these modes become dispersionless along particular (soft-mode) lines in the BZ, where we find finite masses in the perpendicular directions,

\[ \omega_{AFxx}(\vec{k}) \rightarrow \Delta_x + B_x \left( k_x^2 + 14k_x^2 k_y^2 + k_y^4 \right)^{1/2}, \]
\[ \omega_{\text{AF}_{zz}}(k) \to \Delta_z + B_z (k_y^2 + 4k_z^2), \]

with \( \Delta_i = 0 \) and \( B_i \neq 0 \) at the \( M \) point, and the quantum fluctuations diverge logarithmically, \( \langle \delta S \rangle \sim \int d^3 k / \omega(k) \sim \int d^2 k / (\Delta_i + B_i k^2) \sim \ln \Delta_i \), if \( \Delta_i \to 0 \) at the transition. An analytic expansion could not be performed in the MO phases, but the numerical results reported below suggest a qualitatively similar behavior.

We have verified that the above behavior of the soft mode results in large quantum corrections \( \langle \delta S \rangle \) to the order parameter in all magnetic phases close to the critical lines. As an example we show \( \langle \delta S \rangle \) in AFxx and AFzz phases, being significantly lower than in a 2D HAF in a broad parameter regime (Fig. 2). Similarly as in two dimensions [4], the LRO is overwhelmed by quantum fluctuations at particular lines, where \( |\langle \delta S \rangle| = \langle \delta S \rangle \) (Fig. 1). Unlike \( \langle \delta S \rangle \), the RPA energies of the ordered phases show no divergence, with quite similar energy gains in AF and MO phases of the order of 0.6J [19]. We therefore believe that RPA is here as accurate as in the pure-spin HAF and conclude that the classical order is destroyed by quantum fluctuations in the small \( |E_z| \) and small \( \eta \) region between dashed and dotted lines in Fig. 1.

Although the above theory is known to perform quite well in the simplest systems [20] it might be misleading in more complicated situations. For instance, the “finite mass mode softening” occurs also in the \( J_1-J_2-J_3 \) model where it is shown to be inconsequential in the large \( S \) limit because of an “order out of disorder” phenomenon [4]. In contrast, low order spin-wave theory is blind for the quantum transition occurring in the bilayer model [4]. In all these cases, including ours, the quantum melting is promoted by the drastic enhancement of local fluctuations. It is then instructive to consider valence bond (VB) states [21] with the individual spins paired into singlets and the orbitals optimized variationally. As the energy of a singlet is lowest when the orbitals along the bond, the optimal states with all singlets lined up in parallel (see Fig. 3) are: (i) for \( E_z > 0 \), singlets along the \( a \)-axis with orbitals close to \( 2z^2 - 1 \) (VBA), and (ii) for \( E_z < 0 \), singlets along the \( c \)-axis with orbitals \( \sim |z| \) (VBc). Both optimize spin and orbital energy on every second bond, and have lower energy than the classical states close to the classical degeneracy [22].

Further, we included the leading quantum fluctuations in the VB states. The energy of the resonating VBc (RVBc) state was obtained using the Bethe ansatz result for the 1D HAF. We attempted to improve the VBa state by constructing the PRVB states, \( |\Psi_{\text{C}}\rangle \sim (|\Psi_a\rangle + e^{i\phi}|\Psi_b\rangle) \), from the singlet pairs along \( a \) and \( b \), \( |\Psi_a\rangle \) and \( |\Psi_b\rangle \). Surprisingly, more energy is gained instead in the plaquette VB (PVB) states in which the wave functions \( |\Psi_a\rangle \) and \( |\Psi_b\rangle \) alternate and form a superlattice. The exceptional stability of these (nonresonating) PVB states is due to a unique mechanism involving the orbital sector. Unlike in the HAF, the bonds not occupied by the singlets contribute orbital energy and this is optimized when singlets in orthogonal directions are connected [22]. If \( \eta < 0.30 \), this PVB alternating (PVBA) state (Fig. 3) is stable at \( E_z > 0 \), while a similar PVB interlayered state with alternating layers of \( (a,b) \)-plane/c-axis bonds (PVBIc), and the RVBc state are stable at \( E_z < 0 \). Finally, a state interlayered along \( a \), but in the same pattern as in PVBIc, occurs in between the PVBA and PVBIc states. Thus, a spin liquid is stabilized by the orbital degeneracy over the MO phases with RPA fluctuations in a broad regime (Fig. 4). This resembles the situation in a 2D 1/5-depleted lattice [8], but the present instability is much stronger and happens in three dimensions.

Summarizing, we find strong theoretical arguments supporting the conjecture that quantum-melting might occur in orbital degenerate Mott-Hubbard insulators. Why does it not occur always (e.g., in KCuF\(_3\))? Next to the Hund’s rule coupling, the electron-phonon coupling \( \lambda \) is dangerous. The lattice will react to the orbital fluctuations, dressing them up in analogy with polaron physics, and thereby reducing the coupling constant. In order to quantum melt KCuF\(_3\)-like states, one should therefore look for ways to reduce both the effective \( J_H \) and \( \lambda \). We believe that this situation is encountered in LiNiO\(_2\): although the spin-spin interactions in the (111) planes should be very weakly FM according to the Goodenough-Kanamori rules, magnetic LRO is absent [23] and the system might represent the spin-orbital liquid. More strikingly, LiNiO\(_2\) is cubic and should undergo a collective JT transition, which absence is actually an old chemistry mystery! Upon electron-hole transformation, \( d^7 \) low-spin Ni\(^{3+} \) maps on \( d^9 \) Cu\(^{2+} \) in KCuF\(_3\), but with a difference in chemistry. While the \( e_g \) hole in KCuF\(_3\) is nearly entirely localized on the Cu, the \( e_g \) electron in LiNiO\(_2\) is rather strongly delocalized over the Ni and surrounding O ions which reduces both \( J_H \) and \( \lambda \), and explains the absence of classical ordering. A more precise experimental characterization of LiNiO\(_2\) is needed.

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FIG. 1. Mean-field phase diagram of the spin-orbital model (1-4) in the $(E_z, J_H)$ plane. Full lines indicate transitions between the classical states, while LRO is destroyed above the dashed (below the dotted) lines for the AF (MO) phases.

FIG. 2. Renormalization of AF LRO $\langle S_z^i \rangle$ in AFzz (left) and AFxx (right) phases as functions of $E_z/J$.

FIG. 3. Schematic representation of spin singlets (double lines) in the disordered states: VBa, VBc, and PVBA. In the PVBA state the plaquettes with singlets $\parallel a$ and $\parallel b$ alternate both in the $(a, b)$ planes and in the c direction, while the PVBa state is obtained by interleaving successive PVBA $(a, b)$ planes with one VBc double layer.

FIG. 4. The same as in Fig. 1, but including quantum fluctuations. The spin liquid (RVBc, PVBlc, PVBla, and PVBA) takes over in the shaded crossover regime.
