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Quantum fluctuations in d^9 model

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Abstract

We study the phase diagram and excitations of an effective spin-orbital model derived for d^9 transition metal ions in the neighbourhood of an orbital degeneracy. RPA indicates a very strong renormalisation of the classical order parameters near the zero temperature multicritical point, suggesting the existence of a novel quantum liquid.

Transition metal oxides are perhaps the best known examples of charge transfer insulators [1]. As the electronic correlations are typically strong, the multiband models relevant for the doped systems may be replaced by effective models of the t–J variety. Examples are the effective strong-coupling models for NiO [2], CuO_2 planes in high-T_c superconductors [3], and the t–J model itself. In general the carrier propagation in such models may be more complex than in the usual t–J model due to excitonic excitations [4].

This raises the question whether already in the *undoped* systems the (often neglected) orbital degrees of freedom, responsible for the excitons, could lead to a behaviour different from that of a Heisenberg anti-ferromagnet. The urgent questions are of course: (i) to what extent the properties of the antiferromagnetic (AF) phases are modified by the orbital degrees of freedom, and (ii) whether some qualitatively new physics could be realised in this enlarged space. We will address these issues by considering the spin-orbital model describing d^9 transition metal ions like Cu^{2+}.

We start with the multiband model realised in CuO_2 planes of high-T_c superconductors [5]. In the limit where the Coulomb interaction U and charge-transfer energy are large compared to the d–p hybridisation, one first integrates out the oxygen orbitals to derive subsequently the superexchange interactions by considering the virtual fluctuations to high-energy configurations, $d_i^9 d_j^9 \rightleftharpoons d_i^8 d_j^{10}$. The excited d_i^8 configuration may be either one of the three singlets, or a triplet. The latter high-spin state has the lowest energy in this manifold, if the Hund's rule exchange interaction $J_H > 0$ is present. Thus, a part of the derived superexchange interactions is ferromagnetic (FM) and frustrates the usual AF interactions. As a result one finds a rather complex Hamiltonian [5,6], called in what follows the d^9 model. The leading part is the superexchange interaction between two $3d_{x^2-y^2} \sim x$ orbitals, $J = 4t_{xx}^2/U$. The remaining interactions, x–z and z–z ($3d_{3z^2-r} \sim z$), are reduced by factors of α_0^{-1} and α_0^{-2}, respectively, with $\alpha_0 \simeq 3$, due to the large differences between the involved hybridisation elements. In addition to the on-orbital spin operators, like $\mathbf{S}_{ixx} = \{d_{ix\uparrow}^\dagger d_{ix\downarrow}, d_{ix\downarrow}^\dagger d_{ix\uparrow}, (n_{ix\uparrow} - n_{ix\downarrow})/2\}$, one finds as well the interorbital ones, S_{ixz}, with their transverse parts, $S_{ixz}^+ = d_{ix\uparrow}^\dagger d_{iz\downarrow} + d_{iz\uparrow}^\dagger d_{ix\downarrow}$, describing spin flips with orbital flips. The second part of the Hamiltonian is Ising-like and describes the interaction between the orbital degrees of freedom, with possible orbital (excitonic) excitations. Finally, the crystal-field term represents the difference between the hole energies in the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals, $E_z = \epsilon_z - \epsilon_x$. The characteristic feature is that, although the spins are still SU(2) invariant, the rotational invariance in the orbital sector is explicitly broken by the lattice.

First we solve the classical problem using mean-field theory (MFT). It is usually assumed that the spin and orbital degrees of freedom decouple,

$$c_{i\sigma}^\dagger = \cos\theta_i \, d_{ix,\sigma}^\dagger + \sin\theta_i \, d_{iz,\sigma}^\dagger \tag{1}$$

We considered uniform phases with two sublattices, i.e. $\theta_i = \theta_A$ if $i \in A$, and $\theta_i = \theta_B$ if $i \in B$. As expected, due to the exclusively AF character of the (super) exchange at $J_H = 0$, one finds pure AF phases if $|E_z|$ is large, i.e. $\theta_A = \theta_B$, with either $d_{x^2-y^2}$ (AFxx), or $d_{3z^2-r^2}$ (AFzz) orbitals occupied for $E_z > 0$ and $E_z < 0$, respectively. A trivial consequence of the explicit symmetry breaking in the orbital sector is that the transition moves from $E_z = 0$ to $E_z = -E_z^0 = -((\alpha_0^2 - 1)/\alpha_0^2)J$. Note that the orbital mixing is totally suppressed in the AF phases ($\theta_i = 0$ or

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$\theta_i = \pi/2$). In contrast, for $J_{\mathrm{H}} > 0$ a FM phase with orbital ordering, $\theta_{\mathrm{A}} = -\theta_{\mathrm{B}}$, is stabilised close to the transition line between the above AF states, as shown in Fig. 1. However, the above transition point $\mathrm{M} = (E_z, J_H) = (-E_z^0, 0)$ appears to be unusual, because it is a zero temperature *multicritical* point on the classical level. The underlying reason is that one gains at this point the same amount of energy by mixing of two orbitals due to their alternating phases, as one loses by reversing the spins from the AF to the FM configuration, and close to M the system is classically frustrated. We have identified two more magnetic phases having the same energy at M, one of which is defined by

$$\phi_{i\sigma}^{\dagger} = \cos\theta_i \, d_{ix,\sigma}^{\dagger} + \sin\theta_i \, d_{iz,-\sigma}^{\dagger}, \qquad (2)$$

with $\phi_{i\uparrow}^{\dagger}$ ($\phi_{i\downarrow}^{\dagger}$) for A (B) sublattice, which has no classical analogon. This phase is stable against the AF phases near the dot-dashed line in Fig. 1, but has still higher energy than the FM phase on the MF level.

We studied the elementary excitations of different classical ground states in the random phase approximation (RPA) by solving the equations of motion for the Green functions ($\langle\langle S_{i,xx}^{+} | S_{j,xx}^{-} \rangle\rangle$, etc.) [7]. Furthermore, using an extension of the RPA [8], we evaluated the renormalisation of the order parameters and ground state energies. Because of the coupling between pure spin and mixed spin–orbital excitations, *two* transverse modes occur in the AF phases, which could be observed by neutron scattering. As usual, the renormalisation of the FM phase is insignificant. The renormalisations in the AF phases are mostly coming from the acoustic transverse mode. We find that the (near) degeneracy in the orbital channel strongly *enhances the quantum spin fluctuations* in the AF states (Fig. 2), overwhelming the classical order already well before the multicritical point is reached. Thus, we conclude that in the vicinity of the M point quantum mechanics takes over, as indicated in Fig. 1, and might stabilise a *quantum spin liquid.*

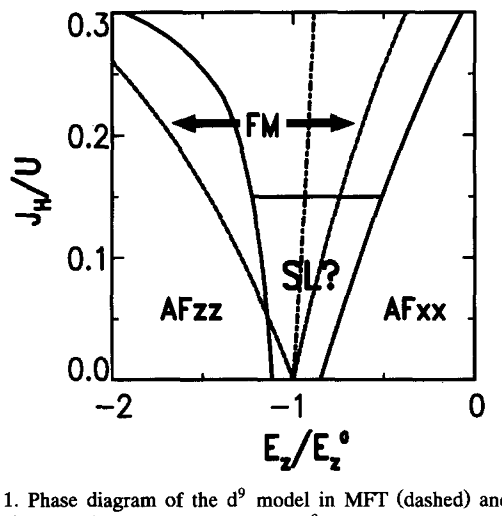

Fig. 1. Phase diagram of the d^9 model in MFT (dashed) and in RPA (full lines) as a function of E_z/E_z^0 and J_{H}/U for $\alpha_0 = 3$. The expected region of the spin liquid (SL) phase is indicated.

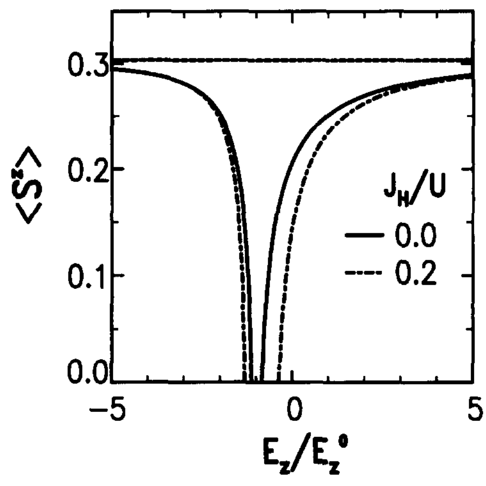

Fig. 2. Renormalisation of $\langle S_i^z \rangle$ for AFxx and AFzz phase, as functions of E_z/E_z^0 for $J_{\mathrm{H}}/U = 0$ and 0.2, and $\alpha_0 = 3$.

The states (2) involve rotation both in orbital and in spin space, indicating that the multicritical point is controlled by a higher symmetry than SU(2), namely a subgroup of SU(2) × SO(4). The coupled rotators of SO(4) can be rewritten in terms of two independent (on the level of the algebra) su(2) systems, which appears as a doubling of the spin system. In this language the multicriticality at M corresponds to these two spin systems exactly frustrating each other on the classical level. This frustration is of course lifted by quantum mechanics and elsewhere we will argue that the directionality inherent to d_x and d_z orbitals stabilises resonating-valence-bond-like spin–orbital states.

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