Spin-Orbital Entanglement and Violation of the Goodenough-Kanamori Rules

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We point out that large composite spin-orbital fluctuations in Mott insulators with t_{2g} orbital degeneracy are a manifestation of quantum entanglement of spin and orbital variables. This results in a dynamical nature of the spin superexchange interactions, which fluctuate over positive and negative values, and leads to an apparent violation of the Goodenough-Kanamori rules.

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Since the 1960's the magnetism of correlated Mott insulators like transition-metal oxides has been understood by means of the Goodenough-Kanamori (GK) rules [1,2]. These state that if there is large overlap between partly occupied orbitals at two magnetic ions, the superexchange interaction between them is strongly antiferromagnetic (AF) because of the Pauli principle, whereas overlap between partly occupied and unoccupied orbitals gives weakly ferromagnetic (FM) interaction due to Hund's exchange [3]. In the archetypical case of 180° bonds through a single ligand ion this translates into a complementary interdependence between spin order and orbital order [4]: ferro-orbital (FO) order supports strong AF spin order, while alternating orbital (AO) order supports weak FM spin order. The canonical example of this behavior is $KCuF_3$, where weak FM (positive) spin correlations in the ab planes and strong AF (negative) correlations along the c axis are accompanied by AO order in the ab planes and FO order along the c axis.

The GK rules (and extensions thereof [5]) have been extremely successful in explaining the magnetic structure in a wide range of materials. This may seem surprising because they presuppose that the orbital occupation is static, whereas in recent years it has become clear that if partly filled orbitals are degenerate, both spin and orbital degrees of freedom should be considered as dynamic quantum variables and be described by so-called spin-orbital models [6,7]. The GK rules work that well because in many compounds a structural phase transition, driven by the Jahn-Teller (JT) coupling of degenerate orbitals to the lattice, lifts the degeneracy and fixes the orbital occupation well above the magnetic transition. This happens typically for electrons in e_g orbitals where large JT distortions favor C-type orbital order, as in $KCuF_3$. However, for t_{2g} orbitals the JT coupling is rather weak, and recent experiments in pseudocubic perovskite titanates [8] and vanadates [9] indeed indicate that the relevant orbitals *fluctuate*, and the conditions for applying the GK rules are not satisfied.

In this Letter we investigate the magnetism of correlated insulators in the case where classical static orbital order is absent. We will show that spins and orbitals then get entangled due to composite spin-orbital quantum fluctuations and that the familiar static GK rules are violated to the extent that even the signs of the magnetic interactions may fluctuate in time. To demonstrate this general feature in the most transparent way, we consider three different spin-orbital models for correlated insulators with 180° perovskite bonds between d^1, d^2, and d^9 ionic configurations, respectively, where the GK rules definitely predict complementary signs of spin and orbital intersite correlations. The first two models are derived for t_{2g} electrons as in $LaTiO_3$ (d^1) and $LaVO_3$ (d^2), where we demonstrate the violation of the GK rules, while the third one is for e_g holes as in $KCuF_3$ (d^9), in which the GK rules are perfectly obeyed. This qualitative difference results from the quantum nature of t_{2g} orbitals which may form singlets, while e_g orbitals behave more Ising-like and orbital singlets cannot form.

Superexchange may be regarded to arise from virtual excitations into upper Hubbard bands, due to hopping with amplitude t, while low-energy charge excitations are quenched by strong on-site Coulomb interaction U. The resulting spin-orbital models take the generic form

$$\mathcal{H} = J \sum_{\gamma} \sum_{\langle ij \rangle \| \gamma} [(\vec{S}_i \cdot \vec{S}_j + S^2)\hat{J}_{ij}^{(\gamma)} + \hat{K}_{ij}^{(\gamma)}] + \mathcal{H}_{\rm orb}, \quad (1)$$

where $\gamma = a, b, c$ labels the cubic axes. The first term describes the superexchange interactions ($J = 4t^2/U$ is the superexchange constant) between transition-metal ions in the d^n configuration with spin S. The orbital operators $\hat{J}_{ij}^{(\gamma)}$ and $\hat{K}_{ij}^{(\gamma)}$ depend on Hund's exchange parameter $\eta = J_H/U$, which determines the spectra of the virtual $d_i^n d_j^n \rightarrow d_i^{n+1} d_j^{n-1}$ charge excitations. In all three models considered here, for each axis γ only two orbital flavors are relevant, and $\hat{J}_{ij}^{(\gamma)}$ and $\hat{K}_{ij}^{(\gamma)}$ can be expressed in terms of pseudospin $T = 1/2$ operators $\vec{T}_i$ and $\vec{T}_j$. Finally, $\mathcal{H}_{\rm orb}$ stands for the orbital interactions (of strength V) induced by the coupling to the lattice—its form depends on the type of orbitals (t_{2g} or e_g).

For the t_{2g} systems we will consider chains along the c axis, where only two (yz and zx) orbital flavors are active, i.e., participate in the hopping. We assume the idealized case where these two orbitals contain one electron per site, which implies that the third (xy) orbital is empty in the d^1 model and filled by one electron in the d^2 model. The orbital operators, $\hat{J}_{ij}^{(c)}(d^1)$ [10,11] and $\hat{J}_{ij}^{(c)}(d^2)$ [12], describing the coupling between the $S = 1/2$ spins of the Ti^{3+} (d^1) ions in cubic titanates and that between the $S = 1$ spins of the V^{3+} (d^2) ions in cubic vanadates, respectively, reduce in the absence of Hund's coupling to an SU(2)-symmetric expression $\propto (\vec{T}_i \cdot \vec{T}_j + \frac{1}{4})$, which may take both positive and negative values. Note also that the superexchange [see Eq. (1)] thus contains interactions like $(S_i^+ T_i^-)(S_j^- T_j^+) + (S_i^- T_i^+)(S_j^+ T_j^-)$, which generate *simultaneous* fluctuations of spins and orbitals described by the composite operators $Q_i^+ \equiv S_i^+ T_i^-$ etc. At finite η both $\hat{J}_{ij}^{(c)}(d^1)$ and $\hat{J}_{ij}^{(c)}(d^2)$ also contain

$$\vec{T}_i \otimes \vec{T}_j = \frac{1}{2}(T_i^+ T_j^+ + T_i^- T_j^-) + T_i^z T_j^z. \tag{2}$$

This operator appears because double occupancy of either active (yz or zx) orbital is not an eigenstate of the on-site Coulomb interaction. Consequently, the total T and T^z quantum numbers are not conserved and orbital fluctuations are amplified. Finally, $GdFeO_3$-type distortions induce orbital interactions $\propto -VT_i^z T_j^z$ favoring FO order along the c axis [13].

In the e_g system there are two orbital flavors ($3z^2 - r^2$ and $x^2 - y^2$), and for each axis a different linear combination of them is active ($3x^2 - r^2$ along a, $3y^2 - r^2$ along b, and $3z^2 - r^2$ along c). Thus the superexchange $\hat{J}_{ij}^{(\gamma)}(d^9)$ between the $S = 1/2$ spins at the Cu^{2+} (d^9) ions in $KCuF_3$ is expressed [14] in terms of axis-dependent orbital operators $T_i^{(a,b)} = -\frac{1}{4}(\sigma_i^z \mp \sqrt{3}\sigma_i^x)$ and $T_i^{(c)} = \frac{1}{2}\sigma_i^z$, given by Pauli matrices σ_i^x and σ_i^z. In the absence of Hund's coupling $\hat{J}_{ij}^{(\gamma)}(d^9) = (T_i^{(\gamma)} - \frac{1}{2})(T_j^{(\gamma)} - \frac{1}{2})$, which, in sharp contrast to the t_{2g} case above, is never negative owing to only a single orbital being active along each axis. In formal terms, $\hat{J}_{ij}^{(\gamma)}(d^9)$ is not SU(2) symmetric, and thus orbital singlets are not formed. The Ising-like form of $\hat{J}_{ij}^{(\gamma)}(d^9)$ makes the d^9 model look more classical than the t_{2g} models, but spin-orbital dynamics is still promoted as the orbital flavor is not conserved [15]. Finally, the JT ligand distortions around Cu^{2+} ions lead to orbital interactions $\propto VT_i^{(\gamma)} T_j^{(\gamma)}$ that favor AO order.

We investigated intersite spin, orbital and composite spin-orbital correlations in the above spin-orbital models. To make the results comparable in all cases, we use

$$S_{ij} = \langle \vec{S}_i \cdot \vec{S}_j \rangle / (2S)^2 \tag{3}$$

for the spin correlations. The orbital and spin-orbital correlations are defined for the t_{2g} (d^1 and d^2) models as

$$T_{ij}^{(t)} = \langle \vec{T}_i \cdot \vec{T}_j \rangle, \tag{4}$$

$$C_{ij}^{(t)} = [\langle (\vec{S}_i \cdot \vec{S}_j)(\vec{T}_i \cdot \vec{T}_j) \rangle - \langle \vec{S}_i \cdot \vec{S}_j \rangle \langle \vec{T}_i \cdot \vec{T}_j \rangle]/(2S)^2, \tag{5}$$

while for the e_g (d^9) model

$$T_{ij}^{(e)} = \langle T_i T_j - \tfrac{1}{2}(T_i + T_j) \rangle^{(\gamma)}, \tag{6}$$

$$C_{ij}^{(e)} = \langle (\vec{S}_i \cdot \vec{S}_j)[T_i T_j - \tfrac{1}{2}(T_i + T_j)] \rangle^{(\gamma)} - S_{ij} T_{ij}^{(e)}. \tag{7}$$

These definitions of $C_{ij}^{(t,e)}$ are dictated by the structure of the spin-orbital superexchange in the $J_H \to 0$ limit.

We have solved both t_{2g} models, d^1 and d^2, on four-site chains along the c axis using periodic boundary conditions, and we find that nontrivial spin-orbital dynamics strongly influences the intersite correlations. First we consider $V = 0$, i.e., the purely electronic (superexchange) spin-orbital models. In the titanate d^1 case one recovers the SU(4) model [16] in the limit of $\eta = 0$, with robust SU(4) singlet correlations [17]. Indeed, in the four-site chain all intersite correlations are *identical and negative*, $S_{ij} = T_{ij}^{(t)} = C_{ij}^{(t)} = -0.25$ [Fig. 1(a)]. As expected, this value is somewhat lower than -0.215 obtained for the infinite SU(4) chain [18]. At finite η one finds $T_{ij}^{(t)} < C_{ij}^{(t)} < S_{ij} < 0$ as long as the spin-singlet ($S = 0$) ground state persists, i.e., for $\eta \lesssim 0.21$, and the GK rules, which imply that the signs of S_{ij} and $T_{ij}^{(t)}$ are different (spin and orbital correlations are complementary), are violated. Apparently the composite spin-orbital correlations $C_{ij}^{(t)} < 0$ dominate and cannot be determined from S_{ij} and $T_{ij}^{(t)}$ by mean-field (MF) decoupling, so the spin and orbital variables are *entangled*, similar to entanglement in pure spin models [19]. In fact, the values of the correlations indicate that the wave function on a bond $\langle ij \rangle$ is close to a singlet of the (total) composite quasispin $\vec{Q}_i + \vec{Q}_j$, equivalent to a linear combination of (spin-singlet/orbital-triplet) and (spin-triplet/orbital-singlet).

The vanadate d^2 model behaves similarly, with all three S_{ij}, $T_{ij}^{(t)}$, and $C_{ij}^{(t)}$ correlations being negative in the spin-singlet ($S = 0$) orbital-disordered phase, stable for $\eta \lesssim 0.07$ [Fig. 1(b)]. Here the spin correlations are weakly AF ($S_{ij} \simeq -0.05$), and AF and FM bonds compete, promoting a dimerized state [20]. For both (d^1 and d^2) models the conventional picture is restored at large Hund's coupling, which stabilizes the FM ground states (at $\eta \gtrsim 0.21$ for d^1, and at $\eta \gtrsim 0.07$ for d^2). Here the spin-orbital correlations decouple ($C_{ij}^{(t)} = 0$) and the GK rules are perfectly obeyed, with positive $S_{ij} = 0.25$ (FM) and negative $T_{ij}^{(t)} = -0.5$ (AO) correlations.

The d^9 model shows completely different behavior. Considering a four-site plaquette in the ab plane, one finds that the conventional spin-orbital interrelation (AF/FO or FM/AO) is a robust property of the model at any value of Hund's coupling. For small $\eta \lesssim 0.25$, FO correlations $T_{ij}^{(e)} > 0$ are accompanied by strong AF spin correlations,

$S_{ij} < 0$, and this changes into the opposite at large η [Fig. 1(c)], just as one would expect from the GK rules. Reflecting this situation, the composite spin-orbital correlations $C_{ij}^{(e)}$ are weaker than the spin correlations S_{ij} and the orbital correlations $T_{ij}^{(e)}$. This permits spin-orbital separation in the ground state, and corrections to this picture are only perturbative [21].

Next we consider finite V, where one expects that the coupling to the lattice could suppress the orbital fluctuations and cure the apparent violation of the GK rules in the t_{2g} models. Indeed, at small η finite V induces orbital order and so stabilizes the AF/FO phase [Figs. 1(d) and 1(e)], composite spin-orbital fluctuations are suppressed and the GK rules are restored. Already infinitesimal interaction $V > 0$ removes the SU(4) symmetry of the d^1 model at $\eta = 0$ by an Ising-like orbital anisotropy. However, for sufficiently large Hund's exchange η the spin-singlet phase survives (unless $V \gg J$, i.e., orbital interactions much stronger than the superexchange). At $V = J$ one thus finds three magnetic phases in the d^1 (d^2) model [Figs. 1(d) and 1(e)]: (i) AF/FO order [22] in the range of $\eta \lesssim 0.04$ ($\eta \lesssim 0.06$); (ii) an intermediate orbital-disordered phase with negative spin, orbital and composite spin-orbital correlations of about equal strength, and (iii) FM/AO order for $\eta \gtrsim 0.22$ ($\eta \gtrsim 0.11$). The first two are separated by an orbital transition within the spin-singlet phase. Notably, the GK rules are perfectly obeyed in phases (i) and (iii) [23], while again they do not apply in the intermediate phase (ii), which is moved now to a more realistic regime of larger ηS.

In the d^9 case finite V only stabilizes the large-η phase with FM/AO order at the expense of the small-η AF/FO phase, but the behavior of the model is not changed qualitatively [compare Figs. 1(c) and 1(f)]. We emphasize that the different behavior of t_{2g} and e_g systems is intrinsic, i.e., has its origin in different spin-orbital physics generated by the electronic superexchange interactions. In particular, it is not caused by being affected differently by coupling to the lattice (i.e., by finite V).

Further evidence that the GK rules do not directly apply in t_{2g} systems follows from the spin exchange constants $J_{ij} \equiv \langle \hat{J}_{ij}^{(\gamma)} \rangle$, the expectation value being taken over the orbital variables. One finds that in the orbital-disordered phase formally FM interaction $J_{ij} < 0$ is in fact, both for $V = 0$ and for finite V, accompanied by AF spin correlations [Figs. 2(a), 2(d), 2(b), and 2(e)], whereas in the e_g case the spin correlations follow the sign of J_{ij} for all values of η [Figs. 2(c) and 2(f)]. This remarkable difference between t_{2g} and e_g systems is due to composite spin-orbital fluctuations, which are responsible for "*dynamical*" exchange constants $\hat{J}_{ij}^{(\gamma)}$ in the former case, which exhibit large fluctuations, measured by $\delta J = (\langle (\hat{J}_{ij}^{(\gamma)})^2 \rangle - J_{ij}^2)^{1/2}$ [11], as we illustrate here at $\eta = 0$. While the average spin exchange constant is small in both t_{2g} models ($J_{ij} \simeq 0$ for d^1, $J_{ij} \simeq -0.04$ for d^2), $\hat{J}_{ij}^{(\gamma)}$ fluctuates widely over both positive and negative values. In the d^1 case the fluctuations between $(S = 0/T = 1)$ and $(S = 1/T = 0)$ bond states are so large that $\delta J = 1$. They survive even quite far from the high-symmetry SU(4) point (at $\eta > 0.1$). Also in the d^2

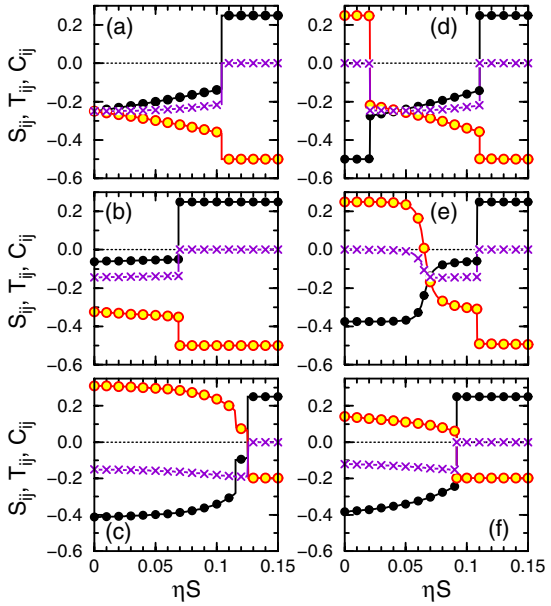

FIG. 1 (color online). Intersite spin S_{ij} (filled circles), orbital $T_{ij}^{(t,e)}$ (empty circles), and composite spin-orbital $C_{ij}^{(t,e)}$ (crosses) correlations as functions of Hund's exchange ηS, for $V = 0$ (left) and for $V = J$ (right) for: (a), (d) d^1 model, (b), (e) d^2 model, and (c), (f) d^9 model.

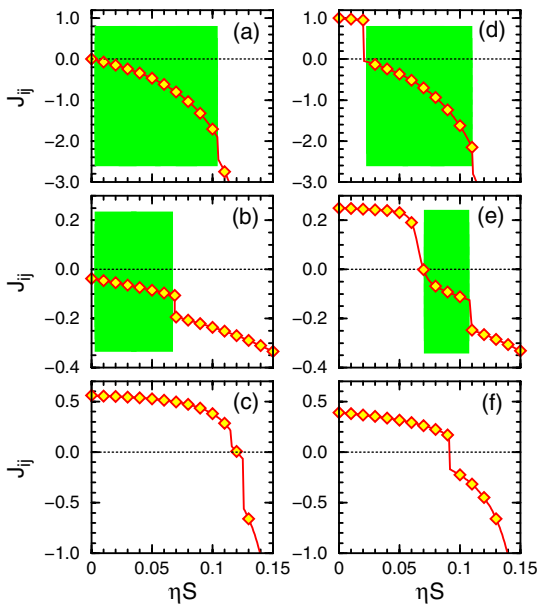

FIG. 2 (color online). Spin exchange constants J_{ij} at $V = 0$ (left) and at $V = J$ (right) as functions of Hund's exchange ηS for (a), (d) d^1 model; (b), (e) d^2 model; (c), (f) d^9 model. In the shaded regions in (a), (b), (d), and (e), J_{ij} is negative (FM) and yet the spin correlations are AF, $S_{ij} < 0$ (see Fig. 1).

TABLE I. Energies per site: exact E_0 and MF E_{MF} for the spin-singlet phases in the three spin-orbital models, obtained with four-site clusters. All energies and V in units of J.

		d^1 model		d^2 model		d^9 model	
ηS	V	E_0	E_{MF}	E_0	E_{MF}	E_0	E_{MF}
0.0	0.0	−0.500	0.0	−0.316	−0.028	−0.594	−0.443
0.06	0.0	−0.655	−0.006	−0.388	−0.112	−0.634	−0.472
0.07	1.0	−0.607	0.097	−0.311	−0.027	−0.633	−0.487

model the orbital bond correlations change dynamically from singlet to triplet [12], resulting in $\delta J > |J_{ij}|$, with $\delta J = \frac{1}{4}\{1 - (2T_{ij} + \frac{1}{2})^2\}^{1/2} \simeq 0.247$. In contrast, the more classical behavior in the d^9 case is confirmed by $\delta J < J_{ij}$, as $J_{ij} \simeq 0.56$ and $\delta J = \frac{1}{2}\{1 - (2T_{ij} - \frac{1}{2})^2\}^{1/2} \simeq 0.50$.

When quantum entanglement occurs, the ground state energy E_0 cannot be estimated reliably by MF decoupling of composite correlations (i.e., with the assumption $C_{ij}^{(t,e)} = 0$). The corrections beyond the MF energy E_{MF} are largest in the d^1 case and remain significant in the d^2 model (Table I), but are much less pronounced in the d^9 model, even at $V = 0$. Only when such corrections disappear, orbitals disentangle from spins and can be analyzed separately [24], or spin states can be treated for fixed orbital order according to the (static) GK rules.

We further notice that the d^2 model exhibits an interesting property related to the nature of transitions between different phases. Namely, the ground state at $V = J$ is a nondegenerate spin singlet for $0 < \eta \lesssim 0.11$, while the orbital quantum numbers change gradually from $\langle T \rangle \simeq 2$ and $\langle T^z \rangle \simeq \pm 2$ to $\langle T \rangle \simeq 0$ and $\langle T^z \rangle \simeq 0$ in the crossover regime of $\eta \simeq 0.06$ [see Fig. 1(e)]. We have verified that when the orbital terms $\propto T_i^+ T_j^+$ are neglected, i.e., if Eq. (2) is replaced by an Ising-like term $T_i^z T_j^z$, a sharp transition occurs instead (from the doubly degenerate FO state with $T^z = \pm 2$ to a disordered state with $T = 1$, $T^z = 0$), consistent with abrupt transitions found before for an infinite chain [25]. Therefore, we anticipate that the $T_i^+ T_j^+$ terms induce a continuous orbital phase transition in the thermodynamic limit.

We emphasize that composite spin-orbital fluctuations and dynamical exchange constants will control, for realistic parameters, the behavior of titanates and vanadates. In fact, the idea that SU(4)-like fluctuations dominate in the ground state has been put forward to understand the unusual properties of $LaTiO_3$ [10] and the possible quantum critical point in the titanate phase diagram [11,26]. Such fluctuations also drive C-AF spin order in $LaVO_3$ [12] and spin-orbital dimerization in YVO_3 [9,25].

Summarizing, in correlated insulators with partly filled t_{2g} shells, orbitals and spins are entangled, and average spin and orbital correlations are typically in conflict with the (static) GK rules. These rules should then instead be understood in terms of dynamical spin and orbital correlations that are complementary to each other, and both configurations—(orbital-singlet/spin-triplet) and (orbital-triplet/spin-singlet)—are entangled in the ground state. It remains both an experimental and theoretical challenge to investigate the physical consequences of spin-orbital entanglement in real systems.

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