Orbital Ordering and Orbital Fluctuations in Transition Metal Oxides

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Abstract

We summarize some characteristic features of the frustrated magnetic interactions in spin-orbital models adequate for cubic transition metal oxides with orbital degeneracy. A generic tendency towards dimerization, found already in the degenerate Hubbard model, is confirmed for $t_{2g}$ but not for $e_g$ systems. In the $t_{2g}$ case the quantum orbital fluctuations are more pronounced and contribute to a stronger competition between different magnetic and orbital states. Therefore the orbital liquid states exist in some undoped $t_{2g}$ systems, while in the manganites such states can be triggered only by doping.

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The physical properties of transition metal oxides are dominated by large on-site Coulomb interactions $\propto U$ which suppress charge fluctuations. Therefore, such systems are either Mott or charge-transfer insulators, and the metallic behavior might occur only as a consequence of doping. Here we will discuss first the undoped systems with localized $d$ electrons which interact by effective superexchange (SE) interactions. An interesting situation occurs when $d$ electrons occupy partly degenerate orbital states, and one has to consider orbital degrees of freedom in the SE at equal footing with electron spins [1]. Competition between different states is then possible, holes may couple to orbital excitations [2], and the quantum effects are enhanced already in undoped systems [3]. The first models of SE in such situations were proposed almost three decades ago [4], either by considering the degenerate Hubbard model [5, 6], or for realistic situations encountered in cuprates (KCuF$_3$ and K$_2$CuF$_4$) and in V$_2$O$_3$ [7]. Then it was realized that the SE which is usually antiferromagnetic (AF) might become ferromagnetic (FM) when Hund’s exchange interaction $J_H$ is finite, but only in recent years the phenomena which originate from the orbital physics are investigated in a more systematic way.

The SE which involves the orbital degrees of freedom is described by the so-called spin-orbital models [8], and is typically highly frustrated on a cubic lattice where it might even lead to the collapse of magnetic long-range order by strong spin or orbital fluctuations [3]. However, in real $e_g$ systems such quantum phenomena are usually quenched by finite $J_H$ which induces a structural phase transition and thus helps to stabilize a particular ordering of occupied orbitals which supports $A$-type AF order, as observed when degenerate orbitals are filled either by one hole (KCuF$_3$) [9], or by one electron (LaMnO$_3$) [10]. The coupling to the lattice due to the Jahn-Teller (JT) effect also helps to stabilize the orbital ordering, and quantitative models of the structural transition have to include both these effects [10].

The essential feature of the SE described by spin-orbital models is the frustration of magnetic interactions: the FM terms occur next to the AF ones, and it depends on the physical

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The simplest spin-orbital model which illustrates this physics may be derived for the density of one electron per site ($n = 1$) in a doubly degenerate Hubbard model. We assume that the hopping is isotropic and diagonal between two orbitals $\alpha$ and $\beta$ at sites $i$ and $j$, and include only the on-site interaction elements: Coulomb $U$ and Hund’s exchange $J_H$, 

$$H = -t \sum_{\langle ij \rangle \mu \sigma} a_{i \mu \sigma}^\dagger a_{j \mu \sigma} + U \sum_{i \mu} n_{i \mu \uparrow} n_{i \mu \downarrow} + \left( U - \frac{5}{2} J_H \right) \sum_i n_{i \alpha} n_{i \beta} - 2J_H \sum_i \langle S_i \rangle_{i \beta} \epsilon_{i \beta} + J_H \sum_i \left( a_{i \sigma \uparrow}^\dagger a_{i \sigma \downarrow}^\dagger a_{i \beta \uparrow} a_{i \beta \downarrow} + a_{i \beta \downarrow}^\dagger a_{i \beta \uparrow}^\dagger a_{i \alpha \uparrow} a_{i \alpha \downarrow} \right),$$

with the spin, $\{ S_{i \mu \sigma}^\dagger, S_{i \mu \sigma}, S_{i \mu \sigma}^\dagger \} = a_{i \mu \sigma}^\dagger a_{i \mu \sigma}, a_{i \mu \sigma}^\dagger a_{i \mu \sigma}, (n_{i \mu \uparrow} - n_{i \mu \downarrow})/2$, and density operators, $n_{i \mu} = n_{i \mu \uparrow} + n_{i \mu \downarrow}$, at orbital $\mu = \alpha, \beta$ defined in the usual way. The interactions are rotationally invariant in the orbital space [11]. If $U \gg t$, the electrons localize and the low-energy physics is described by the SE interactions which follow from the virtual $d^5$ processes on the bonds $\langle ij \rangle$. They lead either a high-spin $3A_2$ state, or to a double occupancy in either orbital which has to be subsequently projected onto two low-spin $^1E$ and $^1A_1$ states. The excitation spectrum is equidistant, as for $d^8$ ions in the cuprates [Fig. 1(a)], with the excitation energies derived from Eq. (1): $\varepsilon(3A_2) = U - 3J_H$, $\varepsilon(1E) = U - J_H$, and $\varepsilon(1A_1) = U + J_H$ [9]. The SE Hamiltonian derived from Eq. (2) takes the form,

$$H_I = J r_1 \sum_{\langle ij \rangle} \left( \frac{\langle \vec{S}_i \cdot \vec{S}_j \rangle + \frac{3}{4}}{4} \right) \left( \frac{\langle \vec{T}_i \cdot \vec{T}_j \rangle - \frac{1}{4}}{4} \right) + \frac{1}{2} J \sum_{\langle ij \rangle} \left( \frac{\langle \vec{S}_i \cdot \vec{S}_j \rangle - \frac{1}{4}}{4} \right) \times \left[ r_2 (1 + T_i^+ T_j^- + T_i^- T_j^+) + r_3 (2T_i^+ T_j^+ + T_i^- T_j^-) \right],$$

where $J = 4t^4/U$ is the energy unit for the SE interaction, and the coefficients $r_1 = 1/(1 - 3\eta)$, $r_2 = 1/(1 - \eta)$, $r_3 = 1/(1 + \eta)$ follow from the above charge excitations, where $\eta = J_H/U$. Similar to spin, the pseudospin operators are: $\{ T_i^+, T_i^-, T_i^\pm \} = \{ \sum_\sigma a_{i \alpha \sigma}^\dagger a_{i \beta \sigma}, \sum_\sigma a_{i \beta \sigma}^\dagger a_{i \alpha \sigma}, (n_{i \sigma} - n_{i \bar{\sigma}})/2 \}$. It is important to use the accurate form of the electron-electron interactions [5, 9], and for this reason some early work led to inaccurate expressions [4, 6]. Note that spin interactions have SU(2) symmetry, while the orbital interactions are anisotropic. The first term is simple and follows from the excitations of spin triplet and interorbital singlet state.

Figure 1: Excitation spectra in cubic transition metal oxides for: (a) $e_g$ systems: Cu$^{3+}$ ($d^9$) and Mn$^{3+}$ ($d^5$) ions; (b) $t_{2g}$ systems: Ti$^{2+}$ ($d^5$) and V$^{2+}$ ($d^3$) ions [8].
The low-spin terms $\propto r_2(\mathbf{r})^3$ are more involved and include not only orbital-flip processes, but also pair hopping terms $\propto (\mathbf{T}_i^x \mathbf{T}_j^y + \mathbf{T}_i^y \mathbf{T}_j^x + \mathbf{T}_i^z \mathbf{T}_j^z - \mathbf{T}_i^z \mathbf{T}_j^z)$. This demonstrates that the anisotropy in the orbital sector is a feature which follows from the multiplet spectra of transition metal ions [12], where the orbital triplet state never occurs at $J_H > 0$.

The model (2) simplifies in the limit of $J_H \to 0$, and represents a superposition of excitations which involve either spin triplet and orbital singlet, or spin singlet and orbital triplet, $\mathbf{H}_I = J \sum_{\langle ij \rangle} \left[ (\mathbf{S}_i \cdot \mathbf{S}_j + \frac{3}{4}) (\mathbf{T}_i \cdot \mathbf{T}_j - \frac{1}{4}) + (\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4}) (\mathbf{T}_i \cdot \mathbf{T}_j + \frac{3}{4}) \right]$, (3) which is just a different way of writing the SU(4) symmetric spin-orbital model [13]. In this case the spin and orbital correlations obey full SU(4) symmetry, and the correlations functions: $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$, $\langle \mathbf{T}_i \cdot \mathbf{T}_j \rangle$, $\frac{1}{4} \langle (\mathbf{S}_i \cdot \mathbf{S}_j)(\mathbf{T}_i \cdot \mathbf{T}_j) \rangle$, are all identical [14]. This condition is violated when the mean-field approximation (MFA) is used and the spin and orbital variables are decoupled, so the results of the MFA might be unreliable.

Although some qualitative arguments were given, the classical phase diagram of the spin-orbital model (2) was not investigated before. We include the orbital splitting at every site, $\sim E_0(n_{i\alpha} - n_{i\beta})/2$, and compare the energies of four different three-dimensional (3D) phases: (i) AF long-range order (LRO) with either $\alpha$ or $\beta$ orbital occupied at every site, (ii) FM phase with alternating $\alpha/\beta$ orbitals on two sublattices, and (iii) a dimer phase (DIM) characterized by orbital valence bond (OVB) states, with orbital singlets at every second bond along c axis (or any other, as the present problem is isotropic). When the orbital singlet is formed on a single bond, the energy gain due to the first term in Eq. (2) is maximized and the FM interaction follows. This leads at small $J_H$ to a DIM state in the model for vanadates [15], as we will discuss below. On the contrary, the orbitals are uncorrelated at all other bonds, the AF terms win as long as the Hund’s interaction is weak (Fig. 2). The AF states: AF1 and AF2 are stabilized by the orbital splitting $E_0$ which has to counterbalance the energy gains on the FM bonds. Of course, it is hard to imagine that the DIM state with ordered orbital singlets might be realized as such, but the alternation of FM/AF bonds is plausible, so the present phase diagram should rather be viewed as demonstrating a generic competition between different signs of the SE interactions. It shows that one may indeed expect enhanced quantum fluctuations close to the orbital degeneracy when $J_H$ is small [3].

The simplest realistic spin-orbital model describes $d^9$ ions interacting on a cubic lattice,
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as in KCuF₃. The interactions are the same as in Eq. (1), but the hopping term is now nondiagonal and allows for orbital excitations [2]. In the limit of \( U \gg t \) the charge excitations \( dₚdₚ^\dagger \leftrightarrow dₜdₜ^\dagger \) lead again to the same excited states as above, with their energies [Fig. 1(a)] reproducing the exact spectrum of \( d^9 \) ions [12]. We define the SE \( J = 4t^2/U \) by the largest hopping element \( t \) between two \( |z⟩ = |3z^2-r^2⟩ \) orbitals along the \( c \) axis, and one finds,

\[
\mathcal{H}(d^9) = \frac{1}{4} J \sum_\gamma \sum_{\langle ij \rangle | | |} \left[ \left( \vec{S}_i \cdot \vec{S}_j + \frac{1}{4} \right) \tilde{J}^{(\gamma)} (d^9) + \tilde{K}^{(\gamma)} (d^9) \right],
\]

(4)

where \( \gamma = a,b,c \) and \( \vec{S}_i \) are spin \( S = 1/2 \) operators. The operator expressions:

\[
\tilde{J}^{(\gamma)} (d^9) = (2 + \eta r_2 - \eta r_3) \mathcal{P}^{(\gamma)}_{\langle ij \rangle} - \eta (3r_1 - r_2) \mathcal{P}^{(\gamma)}_{\langle ij \rangle},
\]

(5)

\[
\tilde{K}^{(\gamma)} (d^9) = -[1 + \eta (3r_1 + r_2)/2] \mathcal{P}^{(\gamma)}_{\langle ij \rangle} - [1 + \eta (r_2 - r_3)/2] \mathcal{P}^{(\gamma)}_{\langle ij \rangle},
\]

(6)

describe spin and orbital SE, and the coefficients \( \eta \) are defined as in Eq. (2). The operators:

\[
\mathcal{P}^{(\gamma)}_{\langle ij \rangle} = \left( \frac{1}{2} + \tau_i^\gamma \right) \left( \frac{1}{2} - \tau_j^\gamma \right) + \left( \frac{1}{2} - \tau_i^\gamma \right) \left( \frac{1}{2} + \tau_j^\gamma \right),
\]

(7)

\[
\mathcal{P}^{(\gamma)}_{\langle ij \rangle} = 2 \left( \frac{1}{2} - \tau_i^\gamma \right) \left( \frac{1}{2} - \tau_j^\gamma \right),
\]

(8)

project on the orbital states, being either parallel to the bond \( \langle ij \rangle \) direction on one site \( (P_\perp = 1/2 - \tau_i^\gamma) \) and perpendicular on the other \( (P_\parallel = 1/2 + \tau_j^\gamma) \) one, or parallel on both sites. They are represented by the orbital operators \( \tau_i^\gamma \) for the three cubic axes:

\[
\tau_i^{a(b)} = (-\sigma_i^a \pm \sqrt{3} \sigma_i^b)/4, \quad \tau_i^c = \sigma_i^c/2,
\]

(9)

where the \( \sigma \)'s are Pauli matrices acting on: \( |x⟩ = \left( \begin{array}{c} 1 \\ 0 \end{array} \right) \), \( |y⟩ = \left( \begin{array}{c} 0 \\ 1 \end{array} \right) \), which transform as \( |x⟩ \propto x^2 - y^2 \) and \( |z⟩ \propto (3z^2 - r^2)/\sqrt{3} \).

In LaMnO₃ the SE is more involved and couples total spins \( S = 2 \) at the Mn⁺⁺ ions. It originates from the charge excitations, \( d_4^i d_4^j \leftrightarrow d_5^i d_5^j \) [10]. The \( e_g \) part, following from \( d_4^i d_4^j \leftrightarrow d_5^i (t_{2g}^i)^\dagger d_5^j (t_{2g}^j)^\dagger \) processes, involves again FM terms due to the high-spin \( ^{4}A_1 \) state, and three AF terms due to the low-spin states: \( ^{4}A_1, ^{4}E, \) and \( ^{4}A_2 \) [Fig. 1(a)], and has analogous orbital dependence as in the cuprate case. In contrast, the \( t_{2g} \) part follows only from low-spin excitations \( d_5^i d_5^j \leftrightarrow d_5^i (t_{2g}^i)^\dagger d_5^j (t_{2g}^j)^\dagger \) and is therefore AF and almost orbital independent. Both terms are given explicitly in Ref. [10].

Both the cuprate model (4) and the \( e_g \) term in the manganite model describe strongly frustrated SE interactions, which take a universal form in the limit of \( J_H \to 0 \),

\[
\mathcal{H}^{(0)}_c = \frac{1}{4} J \sum_\gamma \sum_{\langle ij \rangle | | |} \left[ \left( \frac{1}{2} \vec{S}_i \cdot \vec{S}_j + 1 \right) \left( \frac{1}{2} - \tau_i^c \right) \left( \frac{1}{2} - \tau_j^c \right) - 1 \right].
\]

(10)

Several classical phases have the same energy of \(-3J/4\) per site [3]: the G-AF phases with arbitrary occupation of orbitals, and A-AF phases with \( \langle (1/2-\tau_i^c)(1/2-\tau_j^c) \rangle = 0 \), as obtained for staggered planar orbitals, e.g. for \( x^2 - y^2/z^2 \) orbitals staggered in \( (a,b) \) planes. We emphasize that the model (10) is qualitatively different from the idealized SU(4) symmetric case (3) due to the directionality of \( e_g \) orbitals. In fact, the \( e_g \) orbitals order easier, may couple to the lattice and thus appear to be more classical than the isotropic case described by Eq. (2). Their ordering supports magnetic phases with coexisting FM [in \( (a,b) \) planes] and AF (along \( c \) axis) interactions.

The classical phase diagram of the cuprate model (4) is shown in Fig. 3(a). Quantum corrections to this phase diagram were discussed in Ref. [3]. They suggest that a spin liquid,
supported by particular OVB correlations, might be realized near the degeneracy of classical phases. Finite $J_H$ stabilizes the $A$-AF phase, with staggered two-sublattice orbital order, $|i\mu\sigma\rangle = \cos \theta_i |i\sigma\rangle + \sin \theta_i |i\pi\rangle$, where $i \in A(B)$ sublattice. The AF interactions decrease with increasing $J_H/U$ and dominate at realistic $J_H/U \approx 0.12$ [18]. However, the FM interactions within the $(a,b)$ planes predicted by the model [8] are considerably stronger than measured [16], showing that the quantitative understanding requires also Goodenough processes which would provide additional AF interactions. In contrast, the FM interactions are stronger than AF ones in the $A$-AF phase realized in LaMnO$_3$ [17], and are much better reproduced by the SE terms derived in Ref. [10] with $\eta = 0.117$ [18].

The transition metal oxides with partly filled $t_{2g}$ orbitals exhibit different and even more interesting phenomena. In this case the JT coupling is much weaker, and (unlike for the $e_g$ orbitals) the orbital quantum number is conserved in the hopping processes. This leads to qualitatively different physics realized in $t_{2g}$ systems, somewhat more similar to the isotropic case, Eq. (2). Each $t_{2g}$ orbital is orthogonal to one of the cubic axes, so we label them as $a$, $b$, and $c$ (for instance, $xy$ orbitals are labelled as $c$). The models for titanates and vanadates follow from the $d_{ij}^0 d_{ij}^0 + d_{ij}^{-1} d_{ij}^{n+1}$ processes [19, 20], and may be written in a general form:

$$\mathcal{H}(d^n) = J \sum_{\gamma} \sum_{(i,j) \in \gamma} \left[ (\vec{S}_i \cdot \vec{S}_j + S^2) \hat{J}_{ij}^{(\gamma)}(d^n) + \hat{K}_{ij}^{(\gamma)}(d^n) \right]$$

(11)

with the exchange constants $\hat{J}_{ij}^{(\gamma)}(d^n)$ between $S = 1/2$ spins for titanates ($n = 1$) and $S = 1$ spins for vanadates ($n = 2$), and purely orbital interactions $\hat{K}_{ij}^{(\gamma)}(d^n)$. In titanates these interactions depend on the Hund’s rule splittings of $d^9$ ions [12] [Fig. 1(b)] via the coefficients: $r_1 = 1 - 3\eta$, $r_2 = 1 - \eta$, $r_3 = 1 + 2\eta$, and were given in Refs. [8, 21]. They are faithfully reproduced with a model Hamiltonian containing $U$ and $J_H$ for $t_{2g}$ orbitals. A priori, the magnetic interactions are anisotropic, and may be either AF or FM, depending on the orbital correlations.

In the limit of $J_H/U = 0$ the Hamiltonian (11) takes the form,

$$\mathcal{H}^{(0)} = \frac{1}{2} J \sum_{\gamma} \sum_{(i,j) \in \gamma} \left[ 2 \left( \frac{1}{\sqrt{2}} \vec{S}_i \cdot \vec{S}_j + 1 \right) (\tau_i \cdot \tau_j + \frac{1}{4} n_i n_j) - \frac{4}{3} S \right],$$

(12)

and shows again a strong frustration of SE interactions [19]. Although it resembles formally the SU(4)-symmetric spin-orbital models [13] even more than Eq. (10), the pseudospin oper-
The pseudospin operators are: \( \tau_i = \{ \tau_i^x, \tau_i^y, \tau_i^z \} \) have here a different meaning and refer to a pair of orbital flavors for each cubic direction \( \gamma \), given by two active \( t_{2g} \) orbitals which contribute to the SE [19, 20]. Thus, the model is again different from the idealized SU(4) symmetry Eq. (3).

At finite \( \eta \) the magnetic interactions are \textit{a priori} anisotropic, and may be either AF or FM, depending on the orbital correlations. In order to get some qualitative insight into the competition between these terms, one may include an anisotropy term \( \sim E_c [n_{ic} - (n_{ia} + n_{ib})/2] \), and evaluate the energy of a DIM phase with fluctuating \( a \) and \( b \) orbitals along \( c \) axis \((n_{ia} + n_{ib} = 1)\), a FM phase with equally and randomly occupied orbitals \((n_{ic} = 1/3)\), and a two-dimensional (2D) AF phase with only \( c \) orbitals occupied \((n_{ic} = 1)\). Unlike for \( d^9 \) case, the FM phase is stable in a broad regime of parameters [Fig. 3(b)], and the DIM phase is stabilized by \( E_c \approx 0.2J \). Of course, this analysis is oversimplified and large corrections due to quantum effects are expected. Indeed, a FM isotropic phase is realized in YTiO\(_3\), but a closer inspection shows that the orbitals do order, but this ordering does not break the cubic symmetry [22]. A completely different state is realized in LaTiO\(_3\), however, with isotropic AF interactions [23]; such interactions are explained by quantum resonance realized simultaneously in spin and orbital sector [19]. This shows that a particular type of magnetic ordering may be triggered by quantum fluctuations in the orbital liquid.

The magnetic ordering realized in vanadates is different: C-type of AF order is observed both in LaVO\(_3\) [24] and in YVO\(_3\) at intermediate temperatures \( 77 < T < 116 \) K, and G-type AF order is stable in YVO\(_3\) for \( T < 77 \) [25]. As in \( V_2\)O\(_3\) [26], the SE interactions between \( S = 1 \) spins follow from the \( d_i^xd_j^x = d_i^yd_j^y \) processes, leading to the effective spin-orbital model given by Eq. (11) with \( n = 2 \). When the electrons condense in \( c \) orbitals \((n_{ic} = 1)\) due to the orbital splitting caused by the JT effect, the second electron occupies either \( a \) or \( b \) orbital at every site \((n_{ia} + n_{ib} = 1)\), allowing for a resonance on the bonds \((ij)\) along \( c \) axis. In this case the pseudospin operators are: \( \tau_i^+ = a_i^\dagger b_i, \tau_i^- = b_i^\dagger a_i, \tau_i^z = \frac{1}{2}(n_{ia} - n_{ib}) \), and \( n_i^{(c)} = n_{ia} + n_{ib} \), where \( \{a_i^\dagger, b_i^\dagger\} \) are Schwinger bosons for \( a \) and \( b \) orbitals at site \( i \).

The vanadate model has again an interesting classical phase diagram which unifies certain features we have already seen for degenerate isotropic orbitals, and in the \( t_{2g}^2 \) model [Fig. 4(a)]. At \( \eta = 0 \) and \( E_c = 0 \) one finds again the frustrated SE (12) between \( S = 1 \) spins. While the orbital liquid cannot stabilize in this case, orbital singlets may form along the \( c \) direction when \( c \) orbitals have condensed \((n_{ic} = 1)\) and the \( a \) and \( b \) orbitals fluctuate. This favors the OVB state, with strong FM interactions alternating with weak AF ones along the one-dimensional (1D) chains [15]. At large \( J_H \) this state is unstable, however, and the orbital

Figure 4: (a) Mean-field phase diagram in \((J_H, E_c)\) plane as obtained for the vanadate model of Ref. [20]. (b) Exchange constants for increasing \( J_H \) at \( E_c = 0 \) for the DIM \((J_{c1}, J_{c2}, J_{ab})\) and for C-AF \((J_c)\) and \( J_{ab} \) phase [27].
fluctuations support FM interactions along c axis and stabilize the C-AF phase [20]. By considering the energy in the MFA one finds a phase transition from the DIM to C-AF phase at $n_c \simeq 0.09$ [27], as long as $n_{ic} = 1$. At large uniform orbital splitting $E_c > 0$, the charge gets redistributed to $n_{ia} = n_{ib} = 1$, and an anisotropic G-AF state with the strong AF bonds along c axis, and weaker ones within (a, b) planes, follows. To our knowledge, such a state has not been observed so far. The G-AF phase found in YVO$_3$ at $T < T_{N1}$ is characterized by large JT distortions, and thus can be explained by a staggered field which favors C-type orbital ordering [20], in agreement with recent experiments [25].

The SE interactions in transition metal oxides depend on the multiplet splittings $\propto J_H$. For example, if $n_{ic} = 1$ and $n_{ia} + n_{ib} = 1$ in cubic vanadates, the exchange constants within the (a, b) planes ($J_{ab}$) and along the c axis ($J_c$) in the C-AF phase are given by [20]:

$$J_{ab} = \frac{1}{4} \left[ 1 - \eta (R + r) + (1 + 2\eta R - \eta r) (n_{ia} n_{ib}) \right] / 4, \quad (13)$$

$$J_c = \frac{1}{2} \left[ (1 + 2\eta R) (\tau_i \cdot \tau_j + 1/4) - \eta r (\tau_i^z \tau_j^z + 1/4) - \eta R \right], \quad (14)$$

where $R = 1/(1 - 3\eta)$ and $r = 1/(1 + 2\eta)$. Similar expressions can be derived in the DIM phase at $\eta < \eta_c$. Assuming orbital singlets in the DIM phase, and strong 1D orbital fluctuations, described by a pseudospin 1D Heisenberg model in the C-AF phase, one finds that the FM/AF exchange constants coexist and increase/decrease with increasing $J_H$ [Fig. 4(b)]. It is interesting to observe that the values of $J_{ab}$ and $\left| J_c \right|$ are similar for a realistic value of $\eta \approx 0.116 [18]$, as the orbital fluctuations enhance the FM interactions $\propto J_c$.

Let us come back to the question why the orbital liquid state cannot stabilize in LaMnO$_3$. In this case the orbitals do order, and the orbital interactions are so strong that their ordering would occur well above $T_N$ even in the absence of the JT interaction [10]. However, the splitting between the high-spin $^6A_1$ state and low-spin states is $5J_H$ (Fig. 1a), which explains the proximity to the FM ordering. The manganites at $x < 0.15$ are insulating [17], and are orbital ordered, with either A-AF or FM insulating (FI) phase due to polaronic effects [Fig. 5(a)]. Therefore, a single hole does not propagate freely but scatters on orbital [28] and spin [29] excitations. We discussed elsewhere that doping $x > 0.15$ stabilizes the FM metallic state due to the double exchange (DE) for strongly correlated $e_g$ orbitals [30]. This FM metallic state is nothing else than the realization of the orbital liquid in an $e_g$ system. By considering the DE and SE together one arrives at a quantitative explanation of: (i) the spin-wave stiffness $D$ increasing with $x$ [31], which just reflects the gradual release of the kinetic
energy by hole doping [Fig. 5(b)]; (ii) the isotropic spin waves observed around $x = 0.3$ in a system being so susceptible towards the orbital ordering. The spin-wave stiffness $D_{\text{eff}} = 7.45$ meV obtained at $x = 0.3$ without any fitting parameters agrees well with $D_{\text{exp}} = 8.79$ meV measured in La$_{0.7}$Pb$_{0.3}$MnO$_3$ [32] and explains the observed dispersion $\omega_q$ [Fig. 5(b)]. A transition from the FM to A-AF phase observed in bilayer manganites La$_{2-x}$Sr$_{1+2x}$Mn$_2$O$_7$ [33] can also be explained within the same approach.

In summary, the transition metal oxides with orbital degrees of freedom show a very fascinating behavior, with various types of magnetic and orbital order. While $e_g$ orbitals usually order and explain A-AF phases, further stabilized by the JT effect, the $t_{2g}$ orbitals have a generic tendency towards disorder, which leads to the isotropic orbital liquid in the G-AF phase in LaTiO$_3$, and to a 1D anisotropic orbital liquid in the C-AF phase in LaVO$_3$ and YVO$_3$. So strong orbital fluctuations in $e_g$ systems and the orbital liquid state are triggered only by large doping in the manganites. Very interesting quantum effects might also soon be discovered in the orbital liquid states in doped titanates and vanadates.

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