Orbital ordering in frustrated Jahn-Teller systems

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We consider the superexchange in ‘frustrated’ Jahn-Teller systems, such as the transition metal oxides NaNiO$_2$, LiNiO$_2$, and ZnMn$_2$O$_4$, in which transition metal ions with doubly degenerate orbitals form a triangular or pyrochlore lattice and are connected by the 90°-metal-oxygen-metal bonds. We show that this interaction is much different from a more familiar exchange in systems with the 180°-bonds, e.g. perovskites. In contrast to the strong interplay between the orbital and spin degrees of freedom in perovskites, in the 90°-exchange systems spins and orbitals are decoupled: the spin exchange is much weaker than the orbital one and it is ferromagnetic for all orbital states. Due to frustration, the mean-field orbital ground state is strongly degenerate. Quantum orbital fluctuations select particular ferro-orbital states, such as the one observed in NaNiO$_2$. We also discuss why LiNiO$_2$ may still behave as an orbital liquid.

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There is a large class of compounds containing transition metal (TM) ions with orbital degeneracy - the so-called Jahn-Teller (JT) systems. Orbital degrees of freedom and, in particular, their ordering or the cooperative Jahn-Teller effect, give rise to a very rich physics. The interplay between orbitals and spins often leads to rather peculiar magnetic structures, turning e.g. cubic perovskites like KCuF$_3$ into quasi-one-dimensional spin-chain materials. It was recently suggested that in some JT systems orbitals remain disordered at all temperatures, forming an orbital liquid state. The suppression of an orbital ordering was discussed for materials with a simple cubic structure, e.g. the perovskite LaTiO$_3$, and was attributed to a strong anisotropy of orbital interactions and a strong coupling between orbital and spin excitations. One would expect to find an even stronger tendency to form an orbital liquid in JT compounds with more complicated crystal structures, especially, in ‘geometrically frustrated’ systems, e.g. the spinel ZnMn$_2$O$_4$, in which Mn$^{3+}$ ions with the configuration $(t_{2g}^3e_g^1)$ form a pyrochlore lattice of corner sharing tetrahedra, or the layered materials LiNiO$_2$ and NaNiO$_2$ with a triangular lattice of low-spin Ni$^{3+}$ ion in the $(t_{2g}^2e_g^1)$ configuration. Orbital ordering in such systems is an open issue, interesting from both theoretical and practical points of view, as some of these compounds (LiNiO$_2$, NaNiO$_2$) are now studied as promising materials for rechargeable batteries, and their performance may be significantly affected by the JT effect.

An important difference between the TM oxides with ‘frustrated lattices’ and perovskites is the angle between the oxygen-metal bonds connecting two neighboring TM ions. While in perovskites this angle is close to 180°, in the geometrically frustrated JT systems it is typically 90°. Though usually ignored, this difference has important consequences for orbital and magnetic orderings. In this Letter we derive the Hamiltonian of the 90°-exchange and show that, unlike in perovskites, in frustrated JT systems orbitals and spins are essentially decoupled and that orbital and magnetic orderings can be considered separately from each other. Considering in particular layered materials with a triangular lattice, we show that the orbital interactions are strongly frustrated, which results in a large number of disordered mean-field ground states. However, we argue that this frustration is lifted by quantum orbital fluctuations that stabilize a ferro-orbital state and induce a gap in the spectrum of orbital excitations. We also show that the ordering of spins in the layers is ferromagnetic. These results agree with experimental properties of NaNiO$_2$ and lead us to a conclusion that the puzzling absence of both spin and orbital ordering in LiNiO$_2$ results from disorder rather than from the superexchange.

We first obtain the exchange Hamiltonian describing interactions between TM ions with one electron or hole on doubly degenerate $e_g$-levels. In this case orbital states are conveniently described by introducing isospins (or pseudospins) $T_j$ on each TM site $j$, which act on the up and down states, $|T^\pm = \pm \frac{1}{2}\rangle$ identified with, respectively, $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbitals. Quite generally, an effective interaction between the orbitals and spins on pairs of neighboring TM sites $i$ and $j$ has the form

$$H_{ST} = \sum_{ij} [J_S(S_iS_j) + J_FT_iT_j + J_{ST}(S_iS_j)T_iT_j]$$  \hspace{1cm} (1)

(for simplicity, we do not show here the full structure of the orbital interactions, which are strongly anisotropic both in real and isospin space). In perovskites with the 180°-bonds the spin- and orbital-exchange constants $J_S$ and $J_T$, as well as the constant $J_{ST}$, describing the coupling between orbitals and spins, are all of the same order of magnitude. This makes the spin and orbital orderings dependent on each other. The strong interplay between orbitals and spins is also crucial for the mechanisms of suppression of these orderings used in...
ions from two neighboring planes (separated by a plane 
= 0 for the state and 0 for the states of the plaquette energy in powers of the hopping amplitude
Fig. 1(b). shows a plaquette in the αβ-plane (α, β = x, y, z) formed by two neighboring Ni sites 1 and 2 and the two oxygens shared by the oxygen octahedra surrounding the TM ions. An effective exchange Hamiltonian for two \( e_g \) nickel electrons is obtained by expanding the plaquette energy in powers of the hopping amplitude
\( t \), which is assumed to be much smaller than the energy \( \Delta \) of the electron transfer from O to Ni and the Hubbard repulsion on oxygen \( U_p \). The orbital and spin exchange appears in the fourth order of the perturbative expansion and the higher-order terms are neglected here.

We first neglect also the Hund’s rule coupling between the spins of two holes on oxygens. In that case the 90°-exchange is independent of a spin configuration and only involves orbitals. The orbital exchange Hamiltonian of the plaquette in the αβ-plane has the form
\[
H_T = J_T \mathcal{I}^{αβ} + \text{const},
\]
where
\[
\mathcal{I}^{αβ} = \left( \frac{3}{2} - I_1^α \right) \left( \frac{3}{2} - I_2^β \right) + \left( \frac{3}{2} - I_1^β \right) \left( \frac{3}{2} - I_2^α \right)
\]
and \( J_T \) is the coupling constant specified below. The factor \( \frac{3}{2} - I_1^α \) counts the number of the oxygen electrons that can hop to the Ni site 1 along the bond in the α-direction. This number equals 1, if the \( e_g \)-electron is in the state \( |I_1^α = +\frac{1}{2}\rangle \), and 2, if the electron occupies the state \( |I_1^α = -\frac{1}{2}\rangle \). (For one hole on \( e_g \)-level, as in Cu2+ \( t \)-bonding, the exchange interaction corresponding to Eq. (4) involves combinations \( (\frac{3}{2} + I_1^α) \) instead of \( (\frac{3}{2} - I_1^α) \).) The two terms in Eq. (3) correspond to the two exchange paths on the plaquette through the oxygens \( O_1 \) and \( O_2 \).

The orbital coupling
\[
J_T = -\frac{4t^2}{\Delta^2(2\Delta + U_p)} + \frac{2t^4}{\Delta^4} = \frac{2t^4 U_p}{\Delta^2(2\Delta + U_p)}
\]
is the sum of the contributions of two different mechanisms of the orbital exchange. The first term in Eq. (5) is due to the exchange via the intermediate states with two holes on one of the oxygens from the plaquette. The mechanism resulting in the second term in Eq. (5) works even for infinite \( U_p \), when the two-hole oxygen states are forbidden. To understand its origin consider first a single Ni site inside the oxygen octahedron. The hopping of electrons from the 6 oxygens to nickel results in the energy decrease \( δE \). For two neighboring Ni sites this decrease is smaller than \( 2δE \), as the surrounding octahedra share two oxygens and the two-hole oxygen states are forbidden for infinite \( U_p \). The effect of the blocking of the two-hole states on common oxygens depends on orbital states of the \( e_g \)-electrons, which gives rise to the orbital exchange with the coupling constant \( \frac{2t^4}{\Delta^4} \).

The intermediate states with two holes on one oxygen also result in a spin exchange. As in such states the holes occupy two mutually orthogonal orbitals \( p_α \) and \( p_β \), the spin exchange is only possible due to the Hund’s rule coupling \( J_H \) between the spins of the holes (in systems with the 180°-bonds the spin exchange occurs even for \( J_H = 0 \)). The corresponding exchange Hamiltonian involves both spin and isospin operators and to the lowest-
order in powers of $J _ { H }$ it has the form

$$H _ { T S } = - J _ { T S } T _ { \alpha \beta } \left[ \frac{3}{4} + (S _ { 1 } S _ { 2 } ) \right] ,$$

(6)

where $J _ { T S } = \frac{4 t ^ { 2 } J _ { H } }{3 ( 2 \Delta + U _ { p } )}$ and $T _ { \alpha \beta }$ is given by Eq. (3).

The interaction described by Eq. (6) is different the $180 ^ { \circ }$-exchange in two important respects. First, since for any orbital state the expectation value $\langle T _ { \alpha \beta } \rangle > 0$, the spin exchange is effectively ferromagnetic independent of an orbital state (the average spin-exchange coupling $-J _ { T S } \langle T _ { \alpha \beta } \rangle < 0$ is negative). Second, since $J _ { H } \ll U _ { p }$, the spin-isospin coupling in the $90 ^ { \circ }$-systems is weaker than the pure orbital exchange, described by Eq. (3):

$$J _ { T S } \frac{J _ { T S } - J _ { H } }{U _ { p } } \frac{2 \Delta }{2 \Delta + U _ { p } } \alpha \beta .$$

Thus, in $90 ^ { \circ }$-exchange systems spins and orbitals cannot strongly influence each other, i.e. they are essentially decoupled. (A similar conclusion was reached by Reitsma and Feiner (unpublished). We are grateful to L. F. Feiner for informing us about their results.)

We can now obtain the Hamiltonian describing the orbital interactions in the Ni layers of NaNiO$_2$ (see Fig. 1). In each layer Ni ions form a triangular lattice, the sites of which lie on intersections of the three sets of lines parallel to the unit vectors $e _ { x y }$, $e _ { y z }$, and $e _ { z x }$, as shown in Fig. 2. It will be convenient to identify $e _ { \alpha \beta }$ with the three unit vectors in the isospace (see Eq. 1) by $n ^ { x } = e _ { y z }$, $n ^ { y } = e _ { z x }$, and $n ^ { z } = e _ { x y }$. The bonds between the nearest-neighbor sites $j$ and $j + e _ { \alpha \beta }$ of the triangular lattice (the lattice constant is put to 1) are diagonals of the Ni-O plaquettes lying in the $\alpha \beta$ plane (cf. Fig. 1b). Hence, the Hamiltonian, describing orbital interactions on the triangular lattice has the form:

$$H _ { T } = J _ { T } \sum _ { j } \sum _ { \alpha \beta } I _ { j } ^ { \alpha } I _ { j + e _ { \alpha \beta } } ^ { \beta } ,$$

(7)

The terms linear in the operators $I _ { j } ^ { \alpha }$ (see Eq. 3) are canceled in (6), since $\sum _ { \alpha } I _ { j } ^ { \alpha } = 0$.

The Hamiltonian Eq. (6) is invariant under the global rotation of the isospin operators $T ^ { \alpha }$ over the angle $\frac{2 \pi}{3}$ around the $y$-axis combined with the rotation of the triangular lattice over the same angle. This transformation is equivalent to a cyclic permutation of the indices $x$, $y$, and $z$ of the vectors $e _ { \alpha \beta }$ and the isospin operators $I ^ { \alpha }$.

Thus the Hamiltonian Eq. (6) has the same symmetry as the so-called ‘compass’ model, describing exchange interactions between TM ions on a cubic lattice (13) (note, however, that in our case the three operators $T ^ { x }$, $I ^ { x }$, and $T ^ { z }$ are not independent).

The orbital exchange on a triangular lattice turns out to be strongly frustrated and the mean-field ground state is not unique. The simplest states with the minimal energy $E _ { 0 } = - \frac{3}{2} J$ per site are ferro-orbital states, in which $\langle T _ { j } \rangle = T m$ on all lattice sites, where $m$ is an arbitrary unit vector in the $(T ^ { x } , T ^ { y } )$-plane and $T = \frac{1}{2}$. The energy of these states is independent of orientation of $m$, even though the Hamiltonian (6) is not invariant under arbitrary rotations in the $(T ^ { x } , T ^ { y } )$-plane (this continuous ground-state degeneracy is similar to the one of the ‘compass’ model 13). Furthermore, there exist also disordered mean-field ground states, which can be obtained from the ferro-orbital states by inverting the sign of $\langle T _ { j } \rangle$ on an arbitrarily selected set of lines parallel to $e _ { x y }$ (see Fig. 2). Such states are ordered along the $x y$-lines, but there are no long-range correlations between the $x$-projections of isospins in the transverse direction. By circular permutations of the $x$, $y$, and $z$ indices one can obtain similar states, which are only ordered along the lines parallel to the $e _ { y z }$ and $e _ { x z }$ vectors.

This large ground-state degeneracy is lifted by quantum orbital fluctuations (the so-called ‘order-from-disorder’ mechanism 14, 15). First, we have checked numerically that disordered states (see Fig. 2) have a higher energy of the zero-point fluctuations than the corresponding uniform states. Second, the zero-point energy of uniform states has 6 minima at the isospin orientations $m = \pm n ^ { x } , \pm n ^ { y } , \pm n ^ { z }$. In the original notation these are the ferro-orbital states with one of the orbitals $d _ { 3 z ^ { 2 } - r ^ { 2 } }$, $d _ { 3 z ^ { 2 } - r ^ { 2 } }$, $d _ { 3 y ^ { 2 } - r ^ { 2 } }$, $d _ { 3 y ^ { 2 } - r ^ { 2 } }$, $d _ { 3 y ^ { 2 } - r ^ { 2 } }$, and $d _ { 3 y ^ { 2 } - r ^ { 2 } }$ occupied at each site. Furthermore, the anharmonicity effects 14 usually stabilize elongated octahedra, i.e. the orbitals $d _ { 3 z ^ { 2 } - r ^ { 2 } }$, $d _ { 3 z ^ { 2 } - r ^ { 2 } }$, or $d _ { 3 y ^ { 2 } - r ^ { 2 } }$. As was mentioned above, spins in layers order ferromagnetically.

We would like to point out that the standard description of orbital excitations with non-interacting bosons (‘isospin-wave approximation’) is insufficient for the cal-

![FIG. 2: The triangular lattice formed by Ni ions in the [111]-plane. Shown also is a disordered mean-field ground state, in which the isospins form lines parallel to the unit vector $e _ { x y }$, such that $\langle T _ { j } \rangle$ is the same on all lattice sites, while the sign of $\langle T _ { j } \rangle$ varies arbitrary from line to line.](image)

![FIG. 3: The self-energy diagrams due to the cubic (a) and the quartic (b) interactions that result in a gap opening and a two-dimensional dispersion.](image)
calculation of quantum corrections to the ground-state energy of the frustrated Hamiltonian Eq.(3). In this approximation the orbital excitation spectrum for the six ground states is one-dimensional

$$\omega_q = 3\sqrt{2T} J_T \sin \left( \frac{q \cdot m}{2} \right), \quad (8)$$

which is a direct consequence of the absence of long-range correlations between chains in disordered mean-field ground states. The gapless one-dimensional spectrum leads to infrared-divergent fluctuations. To get rid of them, one has to take into account interactions between the bosons, which can be consistently done in the large isospin limit, $T \gg 1$. The interactions suppress quantum fluctuations by opening a gap and inducing a dispersion in the direction transverse to $m$. This can be understood from the fact that the self-energy diagrams, shown in Fig. 3 (a) and (b), diverge unless a gap is introduced (in field theory a similar mechanism is known as a ‘dynamical mass generation’ [17]). The physical origin of the gap is the breaking of the continuous ground-state degeneracy by quantum fluctuations [13]. In the large-$T$ limit the quantum fluctuations are relatively small and the gap $\Delta \propto J_T \sqrt{T}$ is much smaller than the band width $W \sim 3\sqrt{2J_T}T$ of the orbital excitations. The dispersion in the transverse direction is of the order of $\Delta$ [13].

The main conclusions of our theory of the exchange in frustrated systems (spins are coupled much weaker than orbitals, the ground state is ordered both ferro-orbitally and ferromagnetically) are in agreement with the orbital and magnetic structure of the layered compound NaNiO$_2$, which undergoes two transitions: At $T_o = 480$K the oxygen octahedra become elongated, which corresponds to the ferro-orbital ordering of the $d_{3z^2-r^2}$-type, and at the much lower temperature, $T_s = 20$K, the Ni spins in the [111] layers order ferromagnetically [8].

It is, therefore, very puzzling that the structurally identical material LiNiO$_2$ shows neither orbital nor spin ordering. In principle, we cannot exclude that the quantum orbital fluctuations, which for $T = \frac{1}{2}$ are relatively large, destroy the long-range ferro-orbital ordering and stabilize an orbital liquid (such quantum melting of the ‘order-from-disorder’ was discussed in the context of another frustrated system in Ref. [9]). Since for $T = \frac{1}{2}$ there is no small parameter in the problem, the question whether the ground state of the orbital Hamiltonian Eq.(3) is ordered or disordered, can only be resolved by numerical calculations that are beyond the scope of this Letter. In any case, this possible explanation of the absence of orbital ordering in LiNiO$_2$ is fundamentally different from those based on a strong interplay between orbitals and spins [4, 11, 12]. Actually, due to the decoupling of spins from orbitals in frustrated systems, an orbital liquid should still have a ferromagnetic order.

We think that the puzzles surrounding LiNiO$_2$ indicate an importance of electron-lattice interactions and disorder, not included in the present theory. As was argued in Refs. [8, 20], the ‘intrinsic’ disorder caused by the presence of magnetic Ni ions in the Li [111] planes, results in a strong interlayer coupling that frustrates the ferromagnetic spin ordering in Ni layers. In NaNiO$_2$ such disorder should be weaker: as the size difference of Na and Ni ions is larger than that of Li and Ni ions, the alternating stacking of the Na and Ni [111] layers is more perfect than that of Li and Ni in LiNiO$_2$. The larger charge radius of the Na ion also implies stronger electron-lattice interactions in NaNiO$_2$. In general, such interactions suppress quantum orbital fluctuations and stabilize a ferro-orbital ordering [21, 22]. This may explain why NaNiO$_2$ is orbitally ordered, while LiNiO$_2$ is not.

In conclusion, we developed a theory of the orbital and spin exchange in JT systems with doubly degenerate electronic orbitals and 90° metal-oxygen-metal bonds. We showed that in these systems spins and orbitals are essentially decoupled: spins interact much weaker than orbitals and the spin exchange is ferromagnetic for any orbital state. The orbital exchange between TM ions on a triangular lattice is strongly frustrated, resulting in infinite number of disordered classical ground states. An even stronger frustration can be shown to occur in spinels, in which TM ions form a pyrochlore lattice (to be published elsewhere). We showed, however, that small quantum orbital fluctuations remove the frustration and induce a ferro-orbital ordering. Our theory is an agreement with the orbital and magnetic structure observed in NaNiO$_2$. We also argued that large quantum fluctuations and ‘intrinsic’ disorder may, in principle, turn a frustrated system into an orbital liquid, which may explain the absence of orbital ordering in LiNiO$_2$.

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