Orbital ordering and frustrations

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Abstract
Orbital ordering occurs in many transition metal compounds with Jahn–Teller
ions (Cu^{2+}, Mn^{3+}, low-spin Ni^{3+}, Ti^{3+} etc). It plays an important role in these
materials. At the same time, exchange interactions in orbitally degenerate
systems are inherently frustrated, even in materials with simple crystal lattices.
We discuss the origin of this frustration, considering in detail materials with
cubic and triangular lattices of transition metal ions. We also discuss possible
types of ground states of such systems, e.g., disordered orbital liquids and
ordering due to the order-from-disorder mechanism.

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1. Introduction

Many transition metal (TM) compounds show orbital ordering [1–3]. Typical examples are TM
oxides with so-called strong Jahn–Teller (JT) ions, e.g. $Cu^{2+}(d^9)$, $Mn^{3+}(d^4)$, low-spin $Ni^{3+}(d^7)$
etc, which in the cubic crystal field of a regular oxygen octahedron have one electron or one hole
on the doubly degenerate e_g-level. According to the well-known Jahn–Teller theorem, such
states are inherently unstable, and at low temperatures a distortion of the local coordination
lifts this orbital degeneracy. In concentrated systems it leads to a phase transition—the so-
called cooperative Jahn–Teller effect or orbital ordering [1]. Orbital ordering is also observed
in materials with partially filled three-fold degenerate t_{2g}-levels of TM ions, e.g. $Ti^{3+}(d^1)$
or V^{3+} (d^2). Some of these materials have very unusual properties [4–6]. However, the JT
effect for t_{2g}-electrons is usually weaker than for e_g-electrons and can be strongly affected
by the spin–orbital interaction $\lambda \mathbf{L} \cdot \mathbf{S}$, which for e_g-electrons is essentially quenched. This
complicates the discussion of orbital ordering in t_{2g}-systems and in this paper we concentrate
on materials with e_g-electrons, though many of our conclusions can be applied to t_{2g}-systems
too.

An orbital ordering can be described similarly to a magnetic (spin) ordering. In the
case of one electron or hole on a doubly degenerate orbital, one can describe the orbital
occupation introducing a pseudospin (or isospin) $T = \frac{1}{2}$, so that, e.g., the $d_{3z^2-r^2}$ or $d_{x^2-y^2}$
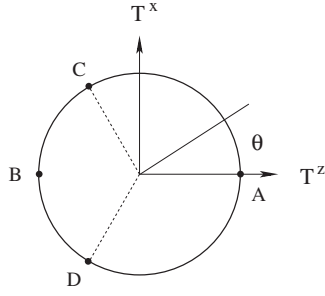
Figure 1. The (T^z, T^x) pseudospin plane. The points A, B, C and D on the circle correspond, respectively, to the $d_{3z^2-r^2}$, $d_{x^2-y^2}$, $d_{3x^2-r^2}$ and $d_{3y^2-r^2}$ orbitals.

orbital corresponds to the state with $T^z = +\frac{1}{2}$ or $T^z = -\frac{1}{2}$. A superposition of these two orbital states

$$|\theta\rangle = \cos\frac{\theta}{2}|3z^2 - r^2\rangle + \sin\frac{\theta}{2}|x^2 - y^2\rangle \tag{1}$$

is associated with a particular point on a circle in the (T^z, T^x)-plane, see figure 1. We only consider here linear combinations with real coefficients. In principle, one can also consider states with complex coefficients, e.g.,

$$|\pm\rangle = \frac{1}{\sqrt{2}}(|3z^2 - r^2\rangle \pm i|x^2 - y^2\rangle)$$

but they are rather special: they do not couple to the lattice, but break the time-reversal symmetry and have a nonzero magnetic octupole moment [7]. Such states are eigenstates of the $\mathbf{T}^y$ operator that usually does not appear in the exchange Hamiltonian of doubly degenerate JT systems.

The pseudospin operators can be used to describe interactions between orbitals on different TM sites in the same way as one describes the spin exchange. An orbital ordering corresponds then to a nonvanishing average pseudospin $\langle T_i \rangle$. However, the orbital exchange usually has a more complicated form than the spin exchange, due to the directional nature of orbitals. The strong anisotropy gives rise to a frustration of orbital ordering even in materials with simple bipartite lattices.

2. Phonon-mediated orbital exchange

We illustrate this point by considering effective orbital interactions in a perovskite lattice—a simple cubic lattice of TM ions with oxygen ions located on the edges between them (we ignore here for simplicity the tilting of $(TM)O_6$-octahedra present in many materials, which lowers the symmetry from cubic to orthorombic). There are two mechanisms of orbital ordering: a lattice instability due to the JT coupling of electrons to lattice [1, 8, 9] and a purely electronic mechanism resulting from the virtual hopping of TM electrons between neighbouring sites [1, 10]. Both lead to essentially the same type of effective exchange interactions. We first discuss the lattice-mediated orbital exchange.
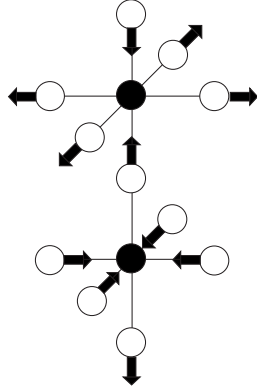
Figure 2. A pair of TM ions (black circles) along the z axis in the perovskite lattice. Arrows indicate the shifts of oxygen ions (white circles) resulting in lifting of the double degeneracy present for a regular O_6-octahedron.

Consider a pair of neighbouring TM sites j and $j + z$ along the z axis (see figure 2). For this pair the electron–lattice interaction responsible for lifting the double degeneracy of the e_g-states has the form

$$H_{JT} = -g \sum_{i=j,j+z} \left(d^\dagger_{i1\sigma} d_{i1\sigma} - d^\dagger_{i2\sigma} d_{i2\sigma} \right) Q_{3i} + \frac{K Q^2_{3i}}{2} \tag{2}$$

where $d^\dagger_{i1\sigma}$ creates the state $|3z^2 - r^2\rangle$ at the site i with the spin projection σ and $d^\dagger_{i2\sigma}$ is the creation operator of the other e_g-state $|x^2 - y^2\rangle$. The Q_{3i} phonon coordinate is the linear combination of the shifts of oxygen ions (from the O_6-octahedron containing the TM site j) along the corresponding TM–TM bonds (see figure 2):

$$Q_{3i} = \frac{1}{\sqrt{6}} [2(u_{j+z/2} - u_{j-z/2}) - (u_{j+x/2} - u_{j-x/2}) - (u_{j+y/2} - u_{j-y/2})].$$

In the subspace of states with one electron per TM site the combination of the electron operators $d^\dagger_{i\alpha\sigma}$ and $d_{i\alpha\sigma}$ in equation (2) is equivalent to the pseudospin operator:

$$\sum_\sigma \left(d^\dagger_{i1\sigma} d_{i1\sigma} - d^\dagger_{i2\sigma} d_{i2\sigma} \right) \equiv 2T^z_i. \tag{3}$$

Excluding the coordinate $u_{j+z/2}$ of the oxygen located between the two TM ions, we obtain for an effective orbital interaction for the pair

$$H_{j,j+z} = J T^z_j T^z_{j+z} \qquad J = \frac{2g^2}{3K} \tag{4}$$

which has the (antiferroorbital) Ising form favouring the antiparallel alignment of neighbouring pseudospins, e.g. $T^j_1 = +\frac{1}{2}$ (the $d_{3z^2-r^2}$ orbital on the site j) and $T^z_{j+z} = -\frac{1}{2}$ (the $d_{x^2-y^2}$ orbital on site $j + z$).

However, complications arise when we consider effective orbital interactions in the whole cubic lattice of TM ions. Since in the cubic lattice the three directions x, y, and z are equivalent, we can describe the exchange along the x direction by replacing the basis of states $(|3z^2 - r^2\rangle, |x^2 - y^2\rangle)$ by $(|3x^2 - r^2\rangle, |y^2 - z^2\rangle)$ and similarly for the y direction. The symmetry of the cubic lattice under circular permutations of the x, y and z axes is reflected in the three-fold symmetry of the (T^z, T^x)-plane (see figure 1), where the states $d_{3z^2-r^2}$, $d_{3x^2-r^2}$,

and $d_{3y^2-r^2}$ correspond, respectively, to $\theta = 0$ (point A in figure 1), $\theta = +\frac{2\pi}{3}$ (point C) and $\theta = -\frac{2\pi}{3}$ (point D), where

$$\left| \theta = \pm\frac{2\pi}{3} \right\rangle = -\frac{1}{2}|3z^2 - r^2\rangle \pm \frac{\sqrt{3}}{2}|x^2 - y^2\rangle.$$

One can also introduce the corresponding symmetric notation for pseudospin operators

$$I^z = T^z \qquad I^{x,y} = -\frac{1}{2}T^z \mp \frac{\sqrt{3}}{2}T^x \tag{5}$$

so that $I^\gamma|3\gamma^2 - r^2\rangle = +\frac{1}{2}|3\gamma^2 - r^2\rangle$, where $\gamma = x, y, z$. Using the symmetry of the cubic lattice and equation (4), we can then immediately write the Hamiltonian of the exchange along the x axis,

$$H_{j,j+x} = JI_j^x I_{j+x}^x = J\left(\frac{1}{2}T_i^z + \frac{\sqrt{3}}{2}T_i^x\right)\left(\frac{1}{2}T_j^z + \frac{\sqrt{3}}{2}T_j^x\right) \tag{6}$$

and similarly for a pair along the y axis:

$$H_{j,j+y} = JI_j^y I_{j+y}^y = J\left(-\frac{1}{2}T_i^z + \frac{\sqrt{3}}{2}T_i^x\right)\left(-\frac{1}{2}T_j^z + \frac{\sqrt{3}}{2}T_j^x\right). \tag{7}$$

The full Hamiltonian of lattice-mediated effective orbital interactions has the form

$$H = J\sum_i\left(I_i^x I_{i+x}^x + I_i^y I_{i+y}^y + I_i^z I_{i+z}^z\right) - \frac{3}{2}J\sum_i\left(\left(T_i^z\right)^2 + \left(T_i^x\right)^2\right). \tag{8}$$

It includes also the on-site term (the second sum in equation (8)), which suppresses complex orbitals discussed above by favouring alignments of pseudospins in the (T^x, T^z)-plane.

We can now see the source of the frustration in the orbital sector: while the exchange along the z direction stabilizes alternating $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbitals, the equivalent couplings along the x and y directions favour other pairs of orbitals, i.e. $(d_{3x^2-r^2}, d_{y^2-z^2})$ and $(d_{3y^2-r^2}, d_{z^2-x^2})$.

3. Compass model

A simple-looking spin model with similar properties (sometimes called the 'compass' model) was introduced in [1]:

$$H_{\text{comp}} = J\sum_i\left(S_i^x S_{i+x}^x + S_i^y S_{i+y}^y + S_i^z S_{i+z}^z\right). \tag{9}$$

It is very similar to the model (8), but while the three components of the pseudospin, I^x, I^y and I^z (see equation (5)), obey the condition $I^x + I^y + I^z = 0$, the spin projections S^γ, $\gamma = x, y, z$ are independent operators.

Consider the model (9) with $J < 0$ (ferromagnetic interactions), in which case the angular dependence of the spin exchange is similar to that of the conventional dipole–dipole interaction, and indeed, its properties can be qualitatively understood by considering the lattice of 'compasses' (or magnetic needles). The complications arising in this model are immediately clear from this analogy. If, instead of the square lattice, we consider a one-dimensional row of such compasses in the z direction, it is clear that the magnetic needles would order 'head to tail' parallel to the z axis. However, in a row along the x axis, spins would prefer to order in the x direction. In a square and in a cubic lattice this leads to a strong frustration, which in principle can destroy order altogether. Such a claim was indeed made by Glass and Lawson for a similar model with real dipole–dipole (long-range) interactions [11]: using the

Bogolyubov inequality they proved the absence of long-range magnetic ordering at nonzero temperatures in two and three dimensions. Interestingly enough, the situation here is in a sense opposite to that in conventional systems: while in standard models with a continuous symmetry, such as the Heisenberg model, the order is destroyed by fluctuations in one- and two-dimensional cases, but can exist in three-dimensional systems, here the order survives in one dimension, but is broken for $d = 2$ and $d = 3$. This can be traced back to different symmetry properties of the two types of models: in contrast to the Heisenberg model, which has a continuous symmetry and, correspondingly, Goldstone modes, in equations (8) and (9) the interaction for each pair has an Ising character. However, while in Heisenberg-like models the spin and coordinate spaces are largely independent, in the model (9) a rotation in the spin space is inherently related to the corresponding rotation in the coordinate space. This seems to 'restore' the symmetry of the system: if we assume a ferromagnetic ordering for $d = 2, 3$ and calculate the spin-wave excitation spectrum, we find that the spectrum is gapless despite the discrete Ising type of interactions for each pair. Moreover, this spectrum turns out to be one dimensional for a square lattice and two dimensional for a cubic lattice,

$$\omega_{2d}^2 = J^2 S^2 (1 - \cos k_x) \tag{10}$$

and

$$\omega_{3d}^2 = J^2 S^2 (1 - \cos k_x)(1 - \cos k_y) \tag{11}$$

so that the corresponding fluctuations diverge at all temperatures for $d = 2$, and at any $T > 0$ for the $d = 3$ case. This agrees with the fact that on the mean-field level there are many equivalent degenerate ground states in our system: apart from ferromagnetic states with an arbitrary orientation of spins $\mathbf{S}$, there are also states with ferromagnetic chains, e.g. along the z axis, with spins either parallel or antiparallel to the z direction and no correlations between orientations of spins in different chains.

What is the true ground state of this model, is still an open problem. One possibility is that beyond the mean-field approximation the order-from-disorder scenario [14, 15] selects a particular ordered state [16]. Another alternative is that the spin fluctuations are so strong that they destroy long-range order, leading to a (spin- or orbital-)liquid state [17]. In any case, we see that the properties of the models (8) and (9) are rather unusual.

4. Exchange interactions in the degenerate Hubbard model

We would like now to return to JT systems and discuss the purely electronic contribution to exchange interactions in these materials. The calculation of the exchange Hamiltonian, resulting from the virtual hopping of electrons on neighbouring sites, is usually done using the Hubbard model describing electrons on degenerate d-levels [1, 10],

$$H = -\sum_{ij\alpha\beta\sigma} t_{ij}^{\alpha\beta} d_{i\alpha\sigma}^\dagger d_{j\beta\sigma} + \sum_{i,\alpha\neq\beta} U_{\alpha\beta} n_{i\alpha\sigma} n_{i\beta\sigma} - J_H \sum_i \mathbf{S}_{i1} \cdot \mathbf{S}_{i2}. \tag{12}$$

Here i, j are site indices, σ denotes spin projection, and $\alpha, \beta = 1, 2$ are orbital indices. The second term in equation (12) describes the on-site Coulomb repulsion between electrons, which depends on the orbital occupation, and the last term is the Hund's rule exchange interaction between electrons occupying two different orbitals on the same site. For an isolated ion, we have $U_{11} - U_{22} = 2J_H$. However, in crystals the direct Coulomb interactions $U_{\alpha\beta}$ are modified by the screening, while the Hund's rule exchange coupling J_H remains unscreened. Therefore, $U_{\alpha\beta}$ and J_H should be considered as independent parameters.

For one electron or one hole per TM site, and in the strong coupling limit $U \gg J_H \gg W$, where W is the electron bandwidth, an effective Hamiltonian describing the coupled spin and

(a)   (b)   (c)
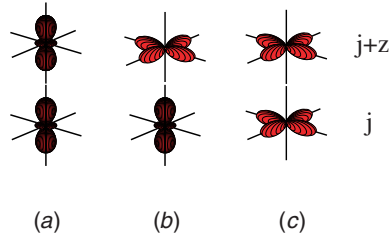
**Figure 3.** The overlap between d-orbitals of TM ions in the $180°$-exchange.

orbital degrees of freedom can be obtained using the perturbation theory in $t/(U, J_H)$ [10]. The hopping matrix elements $t_{ij}^{\alpha\beta}$ are spin independent (spin is conserved in the process of virtual electron hopping). As a result, the spin part of the exchange operator is rotationally invariant and has the standard Heisenberg form $\mathbf{S}_i \cdot \mathbf{S}_j$. In contrast, the hopping amplitudes depend on the type of initial and final orbitals, as well as on the spatial orientation of the pair of TM ions (see, e.g., figure 3), as a result of which the orbital part of the exchange Hamiltonian is strongly anisotropic.

For the pair of TM sites j and $j + z$, hopping only occurs between the two $d_{3z^2-r^2}$ orbitals (see figure 3(a)): hopping between the $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbitals is zero by symmetry (see figure 3(b)), and the overlap between the two $d_{x^2-y^2}$ orbitals in the z direction is very small (see figure 3(c)). Therefore, the usual type of exchange for this pair only occurs when the $d_{3z^2-r^2}$ orbitals $\left(T^z = \frac{1}{2}\right)$ are occupied on both sites. By the well-known Goodenough–Kanamori–Anderson (GKA) rules, such an exchange is antiferromagnetic, favouring the spin-singlet state of the two electrons (holes). This consideration allows us to immediately write an effective exchange Hamiltonian for this pair,

$$H_{j,j+z} = -\frac{4t^2}{U_{11}} \left(\frac{1}{2} + T_j^z\right) \left(\frac{1}{2} + T_{j+z}^z\right) \left(\frac{1}{4} - \mathbf{S}_j \cdot \mathbf{S}_{j+z}\right) \qquad (13)$$

where t is the hopping amplitude between the two $d_{3z^2-r^2}$ orbitals. The exchange Hamiltonian is proportional to the product of the projection operators on the orbital states $|3z^2 - r^2\rangle$ on the two TM sites and the projection operator on the spin-singlet state with $\mathbf{S}_j \cdot \mathbf{S}_{j+z} = -\frac{3}{4}$. The ground state of such a pair is a spin singlet with the orbital configuration shown in figure 3(a), in contrast to the (spin-triplet) state shown in figure 2, JT stabilized by the electron–lattice interaction. Due to the electron–hole symmetry of the orbitally degenerate Hubbard Hamiltonian (12), the effective Hamiltonians for one hole and one electron per TM site have the same form. There is also another mechanism of orbital exchange due to the hopping of electrons on empty orbitals of neighbouring sites and the Hund's rule ferromagnetic spin coupling [1], but it is usually weaker than the antiferromagnetic interaction (13) and we shall not discuss it here.

As in the derivation of equations (6) and (7), the exchange interaction for pairs of TM ions along the x and y directions can be obtained from equation (13) by the corresponding rotation in orbital space, i.e., by substituting the operators T^z in that equation by, respectively, the I^x and I^y operators. The resulting exchange Hamiltonian for the cubic lattice is sometimes called the Kugel–Khomskii (KK) model. The coupled orbital and spin exchange, described by equation (13) and the corresponding expressions for $H_{j,j+x}$ and $H_{j,j+y}$, has the same spatial anisotropy as the lattice-mediated orbital interactions (8), and we face again the problem of frustrated orbital ordering. It was even suggested that the coupling between orbitals and spins in equation (13) only makes it worse: it gives anomalously soft mixed spin–orbital excitations, resulting in a spin–orbital-liquid ground state [12, 13]. Other authors, however, argued that this
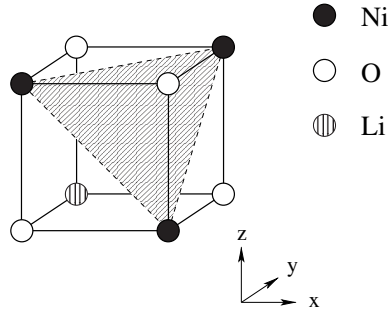
Figure 4. The crystal structure of LiNiO$_2$. The sublattice of Ni ions consists of triangular [111] layers (shaded).

coupling actually helps to lift the frustration, resulting in orbitally and magnetically ordered states, in which spins form antiferromagnetic chains (as in the cubic perovskite KCuF$_3$), stabilized by large quantum spin fluctuations [16]. It seems that the only way to clarify this controversy is to perform a direct numerical simulation of the model (13), but the latter is complicated by the sign problem (which again is a consequence of frustration).

5. 90°-exchange

So far, we only discussed a simple cubic lattice of TM ions and showed that even in that case orbital interactions are frustrated. There are also many Jahn–Teller materials with lattices that cannot be naturally subdivided into two sublattices of TM ions, e.g. a two-dimensional triangular and Kagome lattice or a pyrochlore lattice of corner-shared tetrahedra, e.g. the B-sublattice of spinels. Antiferromagnetic spin ordering in materials with such lattices is known to be strongly frustrated [18] and it is interesting to see if such 'geometric' effects can enhance the frustration of orbital interactions.

A typical example of such a material is LiNiO$_2$, in which the low-spin Ni^{3+} $\left(t_{2g}^6 e_g^1\right)$ ions, with spin $S = \frac{1}{2}$ and doubly degenerate orbitals $\left(T = \frac{1}{2}\right)$, occupy two-dimensional triangular [111] layers (see figure 4). While in perovskites the angle between metal–oxygen bonds connecting neighbouring TM ions is 180°, in LiNiO$_2$ this angle is 90°. This difference has important consequences for the spin and orbital exchange [19].

The actual exchange in TM oxides occurs not due to direct d–d-hopping, as described by equation (12), but involves hopping from oxygen ions to TM sites and intermediate states with holes on oxygen 2p-orbitals. Thus we have to start from the d–p model:

$$H_{\mathrm{dp}} = \sum_{im\sigma} \varepsilon_{\mathrm{p}} p_{im\sigma}^{\dagger} p_{im\sigma} + \sum_{jm\sigma} \varepsilon_{\mathrm{d}} d_{j\alpha\sigma}^{\dagger} d_{j\alpha\sigma} - \sum_{m\alpha ij\sigma} t_{ij}^{m\alpha} \left(p_{im\sigma}^{\dagger} d_{j\alpha\sigma} + d_{j\alpha\sigma}^{\dagger} p_{im\sigma} \right)$$

$$+ \sum_{imm'} U_{mm'} n_{im\sigma} n_{im'\sigma} + \sum_{j\alpha\beta} U_{\alpha\beta} n_{j\alpha\sigma} n_{j\beta\sigma}$$

$$- J_H^p \sum_{i,m\neq m'} \mathbf{S}_{im} \cdot \mathbf{S}_{im'} - J_H^d \sum_{j,\alpha\neq\beta} \mathbf{S}_{j\alpha} \cdot \mathbf{S}_{j\beta}. \tag{14}$$

Here $m = x, y, z$ and α are the orbital indices of, respectively, oxygen 2p-orbitals and TM d-orbitals, and the Hamiltonian of the model includes the direct (Hubbard) and the exchange (Hund's rule) Coulomb interactions on both the oxygen and TM ions.
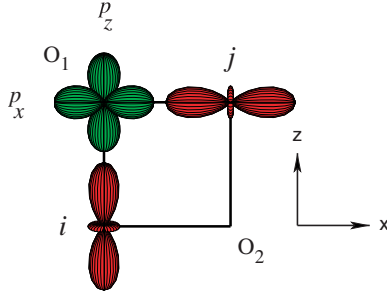
Figure 5. The overlap between the d-orbitals of the TM sites i and j with two different p-orbitals of oxygen O_1 for the 90°-exchange.

In the Mott–Hubbard (MH) region of the general Zaanen–Sawatzky–Allen diagram [20] (see also [21]), i.e. when the charge transfer gap $\Delta \gg U \gg W$ (Δ is $\varepsilon_p - \varepsilon_d$ for one hole and $\varepsilon_d + U_{dd} - \varepsilon_p$ for one electron per TM site, and W is the bandwidth), the model (14) can be reduced to the effective Hubbard model for d-electrons equation (12) with $t_{dd} = \frac{t_{pd}^2}{\Delta}$. On the other hand, in the charge transfer (CT) insulator regime, $U_d \gg \Delta \gg W$, one finds new orbital exchange terms that turn out to be more important than those obtained within the Hubbard model (12) (see the discussion below).

In any case, exchange interactions for the 90°-angle between the metal–oxygen bonds (see figure 4) are very different from equation (13) for the 180°-angle. In the 90°-geometry the orbitals of one TM (e.g. site i in figure 5) overlap with the p_z-orbital of the oxygen O_1 (see figure 5), whereas the d-orbitals of the ion j overlap with the orthogonal p_x-orbital of the same oxygen. Due to the orthogonality of these two oxygen orbitals, it is impossible to transfer a d-electron from one TM ion to another via oxygen ions, and this is the principal difference from the 180°-exchange. The only processes allowed are the transfers of oxygen electrons to the site i (from the p_z-orbital) followed by the transfer of another electron from the p_x-orbital of this oxygen to the the TM site j. If we first ignore the Hund's rule coupling on oxygen ions, these processes are independent of the spins of d-electrons, i.e. they do not result in a spin exchange. However, they do depend on the orbital occupation of the two TM ions, resulting in an orbital exchange. Therefore, for this geometry, the spin and orbital interactions are decoupled, the orbital exchange being much stronger than the spin one (the latter $\propto J_H/\Delta \ll 1$). On the other hand, in the KK model (13) the strongly coupled spin and orbital exchanges are of the same order. Thus, the KK model, obtained for the specific case of MH insulators with 180° metal–oxygen–metal bonds, should not be used uncritically for other situations.

These general considerations are confirmed by detailed calculations [19]. For instance, for the plaquette formed by two oxygen ions and two TM ions on the sites i and j in the zx-plane (see figure 5) the orbital exchange interaction is given by

$$H_T = J_T \left[\left(\tfrac{3}{2} - I_i^x \right)\left(\tfrac{3}{2} - I_j^z \right) + \left(\tfrac{3}{2} - I_i^z \right)\left(\tfrac{3}{2} - I_j^x \right) \right] \tag{15}$$

where

$$J_T = -\frac{4t_{pd}^4}{\Delta^2(2\Delta + U_p)} + \frac{2t_{pd}^4}{\Delta^3} = \frac{2t_{pd}^4 U_p}{\Delta^3(2\Delta + U_p)} \tag{16}$$

and the coupled spin-dependent exchange is

$$H_{TS} = -\frac{2J_H^p}{(2\Delta + U_p)} H_T \left(\frac{3}{4} + (\mathbf{S}_1 \mathbf{S}_2) \right). \tag{17}$$

Several points have to be stressed here. First of all, we indeed see that the orbital exchange is stronger than the spin one (usually $J_H^p \sim 0.6$–0.8 eV and both U_p and Δ are approximately 4–6 eV, so that $J_H^p < U_p, \Delta$). The spin exchange only appears due to the Hund's rule coupling (in this case on oxygen) and is always *ferromagnetic*, independent of the orbital occupation. Therefore, the spin ordering on this triangular lattice is not frustrated. This, in particular, invalidates the attempts to describe LiNiO$_2$ as a spin liquid of the RVB type [22].

The second point is the presence of two terms with opposite signs in the expression for orbital exchange (15). The origin of these terms is rather interesting. The negative term resembles those obtained in the Hubbard model: it describes the virtual process with two holes on one oxygen in the intermediate state, which is why it contains $2\Delta + U_p$ in the denominator. The positive term, however, is of a different nature—it remains nonzero even when $U_p \to \infty$. Its origin can be understood as follows: the virtual hopping of d-electrons from a TM site to six surrounding oxygen ions results in an energy decrease. However, each oxygen belongs to two different octahedra. For infinite U_p this leads to the blocking of some of these charge fluctuations: when, e.g., the oxygen O$_1$ in figure 5 is occupied by the hole from the site i, it blocks the virtual hole transfer from the site j. This blocking reduces the total energy gain due to the charge fluctuations and gives rise to an effective orbital exchange interaction, since the amount by which the energy is reduced depends on orbital occupations on the sites i and j. This mechanism of exchange is similar to the Casimir interaction between two metallic plates in vacuum.

While the Hubbard model gives an effective interaction, which respects the electron–hole symmetry, in the d–p model this symmetry is lost. In particular, for one hole per TM site the effective orbital interaction is of the form

$$H_T^{(\text{hole})} = J_T \left[\left(\tfrac{3}{2} - I_i^x \right)\left(\tfrac{3}{2} - I_j^z \right) + \left(\tfrac{3}{2} - I_i^z \right)\left(\tfrac{3}{2} - I_j^x \right) \right]$$ (18)

(cf equation (15) for one electron per site). In this case, the effect of blocking is minimized when the d-hole orbital on at least one site is not directed towards the common oxygen, e.g. the d$_{3z^2-r^2}$-orbital on the site j in figure 3(b) and the d$_{x^2-y^2}$-orbital on the site $j+z$. Therefore, the orbital interaction (18) favours hole orbitals directed away from the common oxygen ions, in contrast to the situation in MH insulators (see equation (13)), for which the energetically most favourable occupation is shown in figure 3(a).

If we now consider the exchange Hamiltonian for the whole triangular lattice, we find out that here also the interactions in different directions compete. The outcome is again that in the mean-field approximation the ground state is strongly degenerate. The orbital exchange on a triangular lattice is strongly frustrated and has a large number of mean-field ground states, including ferroorbital states, in which $\langle \mathbf{T}_j \rangle = T\mathbf{m}$ on all lattice sites, where $\mathbf{m}$ is an arbitrary unit vector in the (T^x, T^z)-plane. Furthermore, there are disordered ground states, which can be obtained from the ferroorbital states by, e.g., inverting the sign of $\langle T_j^x \rangle$ on an arbitrarily selected set of lines parallel to the lines with the $I^x I^y$-type of exchange (see figure 6). Such states are ordered along the lines, but there are no long-range correlations between the x-projections of pseudospins in the transverse direction (as in the compass model discussed in section 3). By circular permutations of the x, y and z indices one can obtain similar states, which are only ordered along the two other sets of lines in the triangular lattice.

The spectrum of orbital excitations for, e.g., $\langle \mathbf{T} \rangle = T\hat{z}$, calculated in the (pseudo)spin-wave approximation for $T \gg 1$, is given by

$$\omega_{\mathbf{q}} = 3\sqrt{2} T J_T \left| \sin \frac{q_z}{2} \right|.$$ (19)

As in the case of the compass model discussed in section 3, the excitation spectrum is gapless and it is independent of one of the projections of momentum (q_x). This
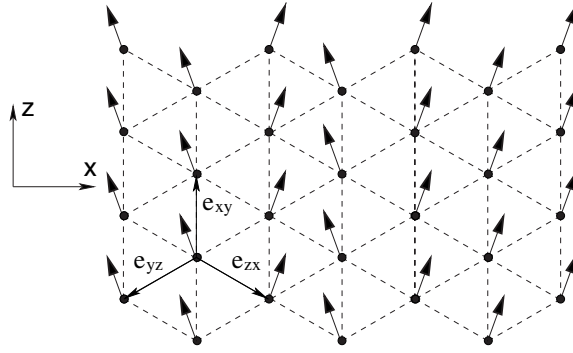
Figure 6. A disordered mean-field ground state, in which the pseudospins form lines parallel to the unit vector $\mathbf{e}_{xy}$, such that $\langle T_j^z \rangle$ is the same on all lattice sites, while the sign of $\langle T_j^x \rangle$ varies arbitrarily from line to line.

one-dimensional spectrum leads to divergent fluctuations, to remove which, one has to go beyond the (pseudo)spin-wave approximation and take into account interactions between the orbital excitations. One then obtains that the order-from-disorder mechanism chooses six particular ferroorbital ground states, e.g. $|3z^2 - r^2\rangle$ (all $\langle T_i^z \rangle = +\frac{1}{2}$) [19] and that the spectrum of elementary excitations acquires a gap $\propto J_T \sqrt{T}$, making the orbital fluctuations finite.

We note that the 'geometric' frustration of the triangular lattice plays an important role in this story. One can show [23] that, in contrast to the 'compass' model, an ordering of e_g orbitals on a square lattice is not frustrated. Thus in two dimensions, both the anisotropy of the orbital exchange and the special geometry of the triangular lattice are necessary for frustration. In a similar way one can treat other types of 'frustrated' lattices. For instance, effective interactions (15) and (17) can be used to describe exchange on the pyrochlore lattice of TM ions, since the local geometry of metal–oxygen–metal bonds is the same as in $LiNiO_2$. Also the orbital excitations for the $d_{3z^2-r^2}$ ferroorbital state on the pyrochlore lattice only propagate along two disconnected sets of bonds with the $I^x I^y$-type of exchange, similar to the case of the triangular lattice.

Applying the d–p model to systems with the 180°-exchange path, one can show that the 'orbital Casimir' interactions also exist in these systems [23]. They have a form similar to the phonon-mediated interactions (8) and modify the standard KK description. In charge transfer insulators these terms dominate the exchange, resulting in the decoupling of orbital and spin orderings and forcing orbitals to order at higher temperatures than spins, provided that the frustration of the orbital interactions is somehow lifted.

6. Summary

Summarizing, we have discussed orbital interactions and frustration of orbital ordering in different physical situations. We showed that due to the directional nature of the hopping amplitudes the orbital exchange is frustrated even for simple (perovskite) lattices. Frustration is therefore a generic property of orbital degrees of freedom. If in addition we deal with the systems with 'geometric' frustration, the ground state degeneracy becomes even stronger. The resulting type of orbital, and spin, structure of the ground state can then be determined either by small corrections to the exchange interactions lifting this degeneracy, e.g. the Hund's rule coupling or small 'external' splitting of degenerate e_g-levels due to deviations from the perfect cubic symmetry. Another possibility is an ordering due to the order-from-disorder

mechanism, discussed above. We note, however, that this semiclassical mechanism, strictly speaking, works for large values of pseudospin $T \gg 1$, when quantum fluctuations are relatively small. Since in reality $T = \frac{1}{2}$, strong quantum fluctuations may still result in a disordered ground state. Such a quantum orbital liquid remains an intriguing possibility.

The situation with other types of orbitally degenerate systems, e.g. materials with three-fold degenerate t_{2g}-orbitals, may have its own peculiarities [24]. First of all, due to a larger degeneracy and a weaker coupling to the lattice, one may expect stronger frustration and stronger quantum effects, which could result in an orbital-liquid ground state [6]. On the other hand, as we already mentioned in the introduction, in t_{2g}-systems the spin–orbital interaction may play an important role, which may remove the orbital degeneracy [24]. Furthermore, in frustrated lattices (of the type considered in section 5) of t_{2g}-ions, one has to take into account not only the exchange between the ions via oxygen ions, but also direct the t_{2g}–t_{2g} overlaps across the TM-oxygen plaquettes (see figure 5). What the resulting orbital structure would be with all these effects taken into account, is still an open problem. We see that the orbital physics, especially in materials with complex lattices, is very rich and can still produce many surprises.

Acknowledgment

References

[1] Kugel K I and Khomskii D I 1982 *Sov. Phys.–Usp.* **25** 231
[2] Tokura Y and Nagaosa N 2000 *Science* **288** 462
[3] van der Brink J, Khaliullin G and Khomskii D 2002 *Preprint* cond-mat/0206053 (*Colossal Magnetoresistance Manganites* ed T Chatterjie (Dordrecht: Kluwer) at press)
[4] Ren Y *et al* 1998 *Nature* **396** 441
    Ren Y *et al* 2000 *Phys. Rev.* B **62** 6577
[5] Keimer B *et al* 2000 *Phys. Rev. Lett.* **85** 3946
[6] Khalliullin G and Maekawa S 2000 *Phys. Rev. Lett.* **85** 3950
[7] Khomskii D 2000 *Preprint* cond-mat/0004034
    van der Brink J and Khomskii D 2001 *Phys. Rev.* B **63** 140416(R)
[8] Gehring G A and Gehring K A 1975 *Rep. Prog. Phys.* **38** 1
[9] Engleman R and Halperin B 1970 *Phys. Rev.* B **2** 75
[10] Kugel K I and Khomskii D I 1973 *Sov. Phys.–JETP* **37** 725
[11] Glass S J and Lawson J D 1973 *Phys. Lett.* A **46** 234
[12] Feiner L F, Oles A M and Zaanen J 1997 *Phys. Rev. Lett.* **78** 2799
[13] Oles A M, Feiner L F and Zaanen J 2000 *Phys. Rev.* B **61** 6257
    Feiner L F, Oles A M and Zaanen J 1998 *J. Phys.: Condens. Mat.* **10** L555
[14] Villain J *et al* 1980 *J. Phys. (Paris)* **41** 1263
[15] Shender E F 1982 *Sov. Phys.–JETP* **56** 178
[16] Khaliullin G and Oudovenko V 1997 *Phys. Rev.* B **56** 14243
    Khaliullin G 2001 *Phys. Rev.* B **64** 212405
[17] Nussinov Z and van der Brink J Private communication
[18] See, e.g., Ramirez A P, Broholm C L, Cava R J and Kowach G R 2000 *Physica* B **280** 290
[19] Mostovoy M V and Khomskii D I 2002 *Phys. Rev. Lett.* **89** 227203
[20] Zaanen J, Sawatzky G A and Allen J W 1985 *Phys. Rev. Lett.* **55** 418
[21] Khomskii D I and Sawatzky G A 1997 *Solid State Commun.* **102** 87
[22] Hirakawa K *et al* 1985 *J. Phys. Soc. Japan* **54** 3526
    Hirakawa K *et al* 1990 *J. Phys. Soc. Japan* **59** 3081
[23] Mostovoy M and Khomskii D 2003 at press
[24] Kugel K I and Khomskii D I 1975 *Sov. Phys. Solid State* **17** 454