

Orbital-only models: ordering and excitations

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Abstract. We consider orbital-only models in Mott insulators, where the orbital-orbital interactions are either due to Jahn–Teller distortions or due to the Kugel–Khomskii superexchange. This leads to highly anisotropic and frustrated orbital Hamiltonians. For two-fold degenerate e_g systems, both types of orbital interactions lead to the same form of the Hamiltonian—the 120° model. In both cases, the predicted symmetry of the orbital ordering is the same, although different from the one observed experimentally. The orbital operators that appear in the two kinds of orbital-only Hamiltonians are different. In the case of superexchange, the orbital degrees of freedom are represented by quantum pseudo-spin 1/2 operators. But when the interactions are Jahn–Teller mediated and the coupling with the lattice is strong, the orbital operators are essentially classical pseudospins. Thus as a function of the relative coupling strengths, a quantum-to-classical crossover is expected. For three-fold degenerate t_{2g} orbitals, the Jahn–Teller coupling gives rise to a particular type of orbital compass models. We point out that fluctuations—whether due to quantum effects or finite temperature—are of prime importance for ordering in the 120° and orbital compass models. The fluctuations generally generate a gap in the orbital excitation spectrum. These orbital excitations—orbitons—are hybrid excitations that carry both a lattice Jahn–Teller and a magnetic Kugel–Khomskii character.

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1. Introduction

Physical properties of the transition-metal oxide (TMO) systems of interacting electrons are determined not only by the electronic charge and spin, but in many cases also by the orbital degrees of freedom. In TMOs, the 3d shell of the TM ion is only partially filled. In many of these compounds, this leaves room for an extra electronic degree of freedom: an electron can occupy one of the different (almost) degenerate 3d orbitals.

In TMOs with degenerate orbitals, there are essentially two possible mechanisms that can lead to orbital ordering. The first mechanism is related to the Jahn–Teller interaction of degenerate orbitals with the lattice distortions, see e.g. [1, 2]. Another mechanism was proposed in 1972 [3] and is a direct generalization of the usual superexchange [4]–[6] to the case of orbital degeneracy and thus provides an immediate link between magnetism and orbital ordering. See [7]–[9] for reviews on this subject.

In this paper, I focus on orbital-only models and neglect, e.g., spin degrees of freedom. A number of observations motivated this choice. Firstly, in the full electron correlation problem—as it occurs in many transition metal compounds—several strongly interacting degrees of freedom play a role: orbital, spin, lattice and charge. This intricate problem is far from understood. Thus we concentrate on a single aspect and investigate orbital degrees of freedom in detail. Secondly, orbital-only models are non-trivial and interesting in themselves. On the one hand, they are similar to quantum spin systems, as orbital operators obey a spin algebra. On the other, in orbital models, orbital frustration is always present, which makes them quite distinct from canonical spin models. This distinction is related to the underlying symmetry of the Hamiltonian. Orbital degrees of freedom represent quadrupolar charge distributions in real space. Thus the symmetry of real space—the point group symmetry in the lattice—is reflected in orbital models. Spins, in contrast, are essentially decoupled from the lattice as long as relativistic spin–orbit coupling is small, so that general spin Hamiltonians are Heisenberg-like and have a very high symmetry (continuous spin rotation symmetry). In any realistic orbital Hamiltonian, continuous orbital rotation symmetry is manifestly broken. Finally, in many compounds, the orbital ordering

temperature is higher than the magnetic ordering temperature. In LaMnO_3 , for instance, the Néel temperature is about $T_N \approx 130$ K, while orbital ordering already occurs below $T_{OO} \approx 750$ K. This implies that there is a large temperature range in which the system is orbital-ordered while the spin is disordered. In this case, the spin structure is featureless, allowing the spin degrees of freedom to be integrated out. This justifies a description of the system in terms of an orbital-only Hamiltonian.

1.1. Orbital degrees of freedom

The orbital part of the electronic wavefunction gives, by definition, the angular distribution of electronic charge around the nucleus. For a free 3d ion, the orbital part of the wavefunction is given by the spherical harmonics $Y_{2,m}$, which are five-fold degenerate, with $|m| \leq 2$. The spherical harmonic wavefunctions constitute a complete and orthonormal basis for the d-states and the same energy is associated with all five orbital wavefunctions, if relativistic spin-orbit coupling is neglected. A partial filling of the 3d shell therefore implies that there is a certain number of ways in which electrons can be distributed over the available degenerate orbitals—this constitutes the orbital degree of freedom.

The famous Jahn–Teller theorem [1] states that, in the ground state, a local degeneracy cannot occur: a degenerate state is unstable with respect to external perturbations. In any physical system, this orbital degeneracy will therefore always be lifted and the ground state will be characterized by one particular set of orbitals being occupied and the other orbitals being empty. Note, however, that it is not *a priori* clear which orbitals will be occupied; moreover, both thermal and quantum fluctuations oppose long-range ordering of orbital degrees of freedom [10, 11, 13]. Also, in a solid, the orbital configuration need not be the same for all TM ions in the lattice. In the latter case or when, more generally, in the solid a translation-symmetric orbital superstructure is formed, we speak of orbital ordering. In order to answer questions related to the occurrence of orbital ordering, we need to specify, firstly, the exact symmetry of the degenerate orbitals that are involved and, secondly, how the orbitals on neighbouring lattice sites interact.

1.2. Local interactions: Jahn–Teller

In a TMO, the TM ion is surrounded by oxygen ions. Therefore, in a solid, the spherical symmetry of a TM ion in free space is lowered to a certain discrete point symmetry: the surrounding oxygen ions produce a non-spherical electrical potential at the locus of the TM ion. This crystal-field potential changes the electronic orbital eigenstates (wavefunctions) and energies. The lower symmetry can, therefore, give rise to a lifting of orbital degeneracy. Whether a particular orbital degeneracy is lifted by the crystal-field depends on the actual symmetry of both the orbital wavefunctions and the crystal-field potential.

To describe the crystal-field splitting of d orbitals, it is convenient to choose an alternative basis (which is an orthonormal basis consisting of linear combinations of spherical harmonics) for the electronic wavefunctions. The linear combinations are chosen in such a way that each basis state corresponds to an electron density distribution with a certain local electrical quadrupole moment. In this basis, the e_g states are $x^2 - y^2 = (Y_{2,-2} + Y_{2,2})/\sqrt{2}$ and $3z^2 - r^2 = Y_{2,0}$ and the t_{2g} states $xy = (Y_{2,-2} - Y_{2,2})/\sqrt{2}$, $yz = (Y_{2,-1} + Y_{2,1})/\sqrt{2}$ and $zx = (Y_{2,-1} - Y_{2,1})/\sqrt{2}$ (figure 1). In the case of orbital degeneracy, 3d states with different local quadrupole moments have the same energy (figure 2).

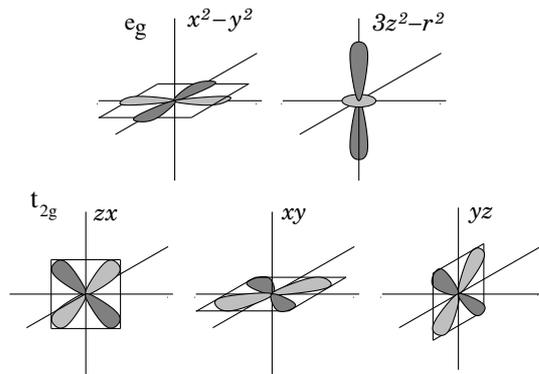


Figure 1. Orbitals corresponding to the angular part of atomic d-wavefunctions. Upper row: the two e_g orbitals $x^2 - y^2$ and $3z^2 - r^2$; lower row: the three t_{2g} orbitals zx , xy and yz .

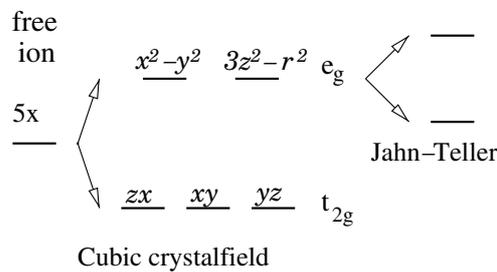


Figure 2. Crystal-field splitting and Jahn–Teller splitting of the five-fold degenerate atomic d-states.

As mentioned above, the electrical field of oxygen ions can lift the orbital degeneracy of the TM ion. Let us first consider the case where the oxygen ions form a perfect octahedron with the TM ion at its centre. (In this case, all six TM–oxygen bonds have equal length and all O–TM–O bonds are 90° .) The lobes of wavefunctions with e_g symmetry point towards the negative oxygen ions (see figure) and the lobes of the t_{2g} orbitals point just in between two oxygen atoms. Therefore the Coulomb energy for an electron in a t_{2g} state is less than that for an electron in an e_g state. The electronic 3d states of a transition metal ion at the centre of a perfect octahedron are therefore split into three-fold degenerate (triplet) t_{2g} states and two-fold degenerate (doublet) e_g states. The t_{2g} orbitals are lower in energy than the e_g orbitals, see figure 2.

Depending on the total number of electrons and their spin, the t_{2g} triplet or e_g doublet can be partially occupied and a degeneracy of the system remains. This is the case for t_{2g} orbitals when, for instance, one d electron is present (d^1 , corresponding to Ti^{3+} (in e.g. $LaTiO_3$) or V^{4+} ions), or for d^2 (V^{3+} in e.g. $LiVO_2$), but not for d^3 —at least when all three electrons have the same spin because then all three t_{2g} orbitals will be occupied: the Pauli principle forbids electrons with the same spin to occupy the same orbital. If, however, in the d^3 case one of the electrons would reverse its spin, there is again an orbital degree of freedom as this electron could occupy either of the three orbitals.

Orbital degeneracy in the doublet e_g is also quite common for d^9 (Cu^{2+} in e.g. $KCuF_3$; Ni^{3+} in e.g. $LiNiO_2$), which correspond to one hole in the doublet e_g . The e_g degeneracy is also present

for high spin d^4 , where the t_{2g} orbitals are filled and one electron in the doublet remains (Mn^{3+} in, e.g., $LaMnO_3$ and other manganites; Cr^{2+} in, e.g., Rb_2CrCl_4). For other partial fillings of the d shell, the orbital degeneracy can be present in either the t_{2g} or e_g sector, depending on the exact spin state of the ion.

According to the Jahn–Teller theorem, again, in a physical system the remaining degeneracy in the doublet or triplet will be lifted. A distortion of the oxygen octahedron that surrounds the central TM ion—a Jahn–Teller distortion—is very effective in doing so.

When an octahedron Jahn–Teller distorts, an additional crystal field is generated at the central TM site. The symmetry of this additional crystal field reflects the symmetry of the Jahn–Teller distortion. The different electric quadrupole moments—orbitals—that are present on the central TM ion interact, in general, differently from the additional crystal-field potential. Therefore, a local Jahn–Teller distortion induces a splitting of the local degenerate states, which leads to a particular orbital to be occupied and others to be empty (figure 2).

Still, however, the system is locally degenerate. Distortions of different symmetry induce different orbital occupations and vice versa, but the total energy of the system does not depend on which particular orbital is stabilized, as long as a particular orbital occupation is combined with a lattice distortion with the appropriate symmetry.

2. Orbital-only model: e_g doublet

Let us put things in a more formal way. We first consider an orbital degenerate doublet. The doublet is spanned by the states/orbitals $|1\rangle$ and $|2\rangle$ (so that $|1\rangle = |3z^2 - r^2\rangle$ and $|2\rangle = |x^2 - y^2\rangle$). In general, the occupied state is a linear combination of the two orbitals: $|\psi\rangle = \cos(\theta/2)|1\rangle + \sin(\theta/2)|2\rangle$. The ground-state wavefunction is thus uniquely defined by the angle θ . Note that the coefficients of the wavefunction can, in principle, be complex numbers: $|\psi\rangle = e^{i\phi} \cos(\theta/2)|1\rangle + e^{-i\phi} \sin(\theta/2)|2\rangle$, which introduces a second angle ϕ . However, in theoretical considerations only rarely complex wavefunctions are considered, although they are found to be important in some cases, for instance in doped metallic e_g systems [12]. In the following, for simplicity, we assume the wavefunction to be real. We associate a vector $\mathbf{T} = (T_z, T_x)$ with this wavefunction in the following manner: the first component of the vector is equal to the difference between the density of electrons in orbitals $|1\rangle$ and $|2\rangle$: $T_z = \langle\psi|1\rangle\langle 1|\psi\rangle - \langle\psi|2\rangle\langle 2|\psi\rangle = \cos\theta$ and the second component is a measure of the entanglement (mixing) between both orbitals in the ground state: $T_x = \langle\psi|1\rangle\langle 2|\psi\rangle + \langle\psi|2\rangle\langle 1|\psi\rangle = \sin\theta$. So the vector $\mathbf{T} = (1, 0)$ on the unit circle ($\theta = 0$) corresponds to orbital $|1\rangle$ being occupied and $\mathbf{T} = (-1, 0)$ on ($\theta = \pi$) corresponds to orbital $|2\rangle$ being occupied. Any other orbital can be obtained by rotating \mathbf{T} on the unit circle. For the moment, we neglect the fact that orbital degrees of freedom are quantized, a consequence of the fact that orbital degrees of freedom correspond to electrons that occupy particular states. Thus, in principle, the orbital operator \mathbf{T} obeys the spin-half angular momentum algebra, so that $T_z = \pm\frac{1}{2}$, but we will see that this fact becomes irrelevant when the coupling of the orbital degree of freedom to (essentially classical) lattice degrees of freedom is strong.

If state $|1\rangle$ is occupied, a certain Jahn–Teller distortion Q_3 is induced and when $|2\rangle$ is occupied, the opposite distortion $-Q_3$ is induced, see figure 3. A general lattice distortion is given by $Q_3 \cos\phi + Q_2 \sin\phi$. The elastic energy depends on the lattice distortion as $E_{elas} = \omega(Q_3^2 + Q_2^2)$, or in vector notation: $\mathbf{Q} = (Q_3, Q_2) = |Q|(\cos\phi, \sin\phi)$ and $E_{elas} = \omega|\mathbf{Q}|^2$. The coupling between a lattice and an orbital is linear, so that we find for the total local

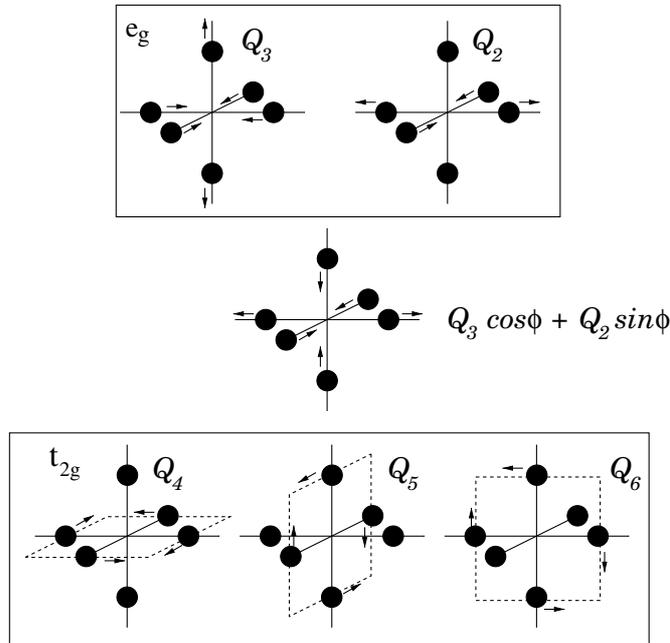


Figure 3. Jahn–Teller distortions of different symmetry. Top: the Q_3 and Q_2 distortions of e_g symmetry; middle: a linear combination of these two distortions (with $\theta = 2\pi/3$); and bottom: the three distortions of t_{2g} symmetry.

energy: $E_{local} = -g\mathbf{T} \cdot \mathbf{Q} + \omega|Q|^2$, where g is the electron–phonon coupling constant. The local energy is clearly minimal when \mathbf{T} and \mathbf{Q} are parallel, so that $\theta = \phi$ in the ground state. But after fixing θ the local energy is independent of ϕ , so that the system is, in fact, still infinitely degenerate.

A way to lift the local degeneracy is provided by the interactions between neighbouring quadrupole moments in the lattice. Such interactions naturally occur in TMOs as oxygen octahedra are connected: each oxygen ion belongs to more than one octahedron (e.g. in the perovskite structure, the octahedra are corner sharing, see figure). Therefore, if a particular octahedron is distorted, automatically all octahedra connected to it distort as well. In this way, the orbital degeneracy can, in principle, be lifted globally. Such a global lifting of the degeneracy implies that a long-range ordering of orbitals emerges from the effective orbital–orbital interactions, which are mediated by the lattice distortions.

2.1. Classical 120° model

On the basis of symmetry considerations of the relevant orbitals and of the lattice point group alone, one can now derive the Hamiltonian that describes the orbital degrees of freedom and the interaction between them, see e.g. [14]. As stated above, the symmetry of the degenerate orbitals determines the symmetry of the local distortions. On the other hand, the translational symmetry of the lattice determines how the local lattice distortions are inter-related. We denote the unit crystallographic axes of the solid by \hat{e}_a , \hat{e}_b and \hat{e}_c . If the orbital $3z^2 - r^2$ is occupied on site \mathbf{r} , the octahedron elongates with a Q_3 distortion and therefore the octahedron connected to it along the \hat{e}_c -axis is automatically compressed: a distortion $-Q_3$ is induced on site $\mathbf{r} + \hat{e}_c$. Thus, along the \hat{e}_c -axis, the interaction between the distortions is $Q_{3,r} Q_{3,r+\hat{e}_c}$. We can, however, rotate the orbitals

in any direction: by choosing $\theta = 2\pi/3$, we obtain an orbital that is elongated along the \hat{e}_a -axis: the $3x^2 - r^2$ orbital which is, explicitly, the linear combination $-\frac{1}{2}|3z^2 - r^2\rangle + \frac{1}{2}\sqrt{3}|x^2 - y^2\rangle$. The distortion that goes along with it is $-\frac{1}{2}Q_3 + \frac{1}{2}\sqrt{3}Q_2$. Therefore it is this linear combination of distortions that determines the interaction along the \hat{e}_a -axis. Along the \hat{e}_b -axis, the situation is analogous with $\theta = -2\pi/3$.

So our model is defined on a cubic lattice where, at each site \mathbf{r} , there is a unit-length two-component distortion vector (associated with the two-dimensional e_g subspace) denoted by \mathbf{Q}_r . Let now \hat{a} , \hat{b} and \hat{c} denote three evenly spaced vectors on the unit circle separated by 120° . To be specific, let us have \hat{c} point at 0° with \hat{a} and \hat{b} pointing at $\pm 120^\circ$, respectively. We define the projection $q_r^a = \mathbf{Q}_r \cdot \hat{a}$, and similarly for Q_r^b and Q_r^c . We have, explicitly, $q_r^c = Q_{3,r}$, $q_r^b = \frac{1}{2}(Q_{3,r} - \sqrt{3}Q_{2,r})$ and $q_r^a = \frac{1}{2}(Q_{3,r} + \sqrt{3}Q_{2,r})$. The Hamiltonian for e_g orbitals on a cubic lattice with corner sharing octahedra is

$$H_{120} = \sum_{\mathbf{r}} (q_r^a q_{\mathbf{r}+\hat{e}_a}^a + q_r^b q_{\mathbf{r}+\hat{e}_b}^b + q_r^c q_{\mathbf{r}+\hat{e}_c}^c). \quad (1)$$

We choose \mathbf{Q} on the unit circle so that E_{local} reduces to a constant. Thus we consider only transversal degrees of freedom (related to a rotation of the vectors \mathbf{Q}_r). The longitudinal degree of freedom corresponding to the modulus of \mathbf{Q} is neglected. Transversal fluctuations are more relevant to the orbital-ordering transition than longitudinal fluctuations. Physically, this is evident, as orbital order melts not because the Jahn–Teller distortions disappear locally (corresponding to a vanishing $|Q|$), but rather because the correlations between distortions on different sites vanish on a lengthscale that is larger than the correlation length (corresponding to vanishing correlations between directions of vectors \mathbf{Q}_r and $\mathbf{Q}_{r'}$ at distances $|\mathbf{r} - \mathbf{r}'|$ longer than the correlation length). We refer to this Hamiltonian as the 120° model because, on the unit circle, the three vectors \mathbf{Q} that appear in the Hamiltonian make an angle of 120° ($2\pi/3$).

Note that the model is essentially classical: the zero point quantum oscillations of the heavy oxygen ions that mediate the orbital–orbital interactions (or equivalently, the interactions between Jahn–Teller centres) are negligible.

As the orbital vector $\mathbf{T} = (T_z, T_x)$ is parallel to the distortion \mathbf{Q} , we can trivially rewrite the Hamiltonian above in terms of the orbital operators T . In terms of the projected operators $\tau_r^a = \frac{1}{2}(T_r^z + \sqrt{3}T_r^x)$, $\tau_r^b = \frac{1}{2}(T_r^z - \sqrt{3}T_r^x)$ and $\tau_r^c = T_r^z$, we obtain [15]

$$H_{120}^{clas} = \sum_{\mathbf{r}} (\tau_r^a \tau_{\mathbf{r}+\hat{e}_a}^a + \tau_r^b \tau_{\mathbf{r}+\hat{e}_b}^b + \tau_r^c \tau_{\mathbf{r}+\hat{e}_c}^c) = \sum_{\mathbf{r}, \alpha} \tau_r^\alpha \tau_{\mathbf{r}+\hat{e}_\alpha}^\alpha. \quad (2)$$

The question now is whether this 120° model can explain the experimental observation that orbital ordering occurs in cubic e_g systems at low enough temperatures. *A priori* it cannot be excluded that, in the 120° model, orbitals are disordered at any non-zero temperature. If this were the case, then this would lead to the far reaching conclusion that the actual ordering of orbitals is driven by an additional physical orbital ordering mechanism that is beyond the symmetry considerations on which the 120° Hamiltonian is based. To determine whether or not the classical 120° model for the Jahn–Teller distortions displays an orbital order–disorder phase transition is highly non-trivial. In [15, 16], it is proved that there is an orbital phase transition for the 120° model. The cooperative Jahn–Teller ordering occurs through a mechanism called ‘entropic stabilization’.

2.2. Entropic stabilization

The discerning feature of many orbital-only models is the presence of an infinite degeneracy of the ground state. To illustrate this point, we first perform a canonical transformation—a global rotation of all the orbital vectors on one sublattice by 180° about the T_y axis. This transforms the ‘antiferromagnetic’ orbital Hamiltonian onto its ‘ferromagnetic’ counterpart (and vice versa): the sign of the interaction changes. The equivalence of these two Hamiltonians holds for the classical and quantum models.

After the rotation, it can be easily established that any constant orbital ordering field $\vec{\tau}_r = \vec{\tau}_0$ is a ground state by noting that $\sum_\alpha [\tau_r^\alpha]^2$ is constant in this problem. Thus, up to an irrelevant constant, the Hamiltonian of equation 2 is

$$H_{120} = -\frac{1}{2} \sum_{r,\alpha} (\tau_r^\alpha - \tau_{r+\hat{e}_\alpha}^\alpha)^2, \quad (3)$$

which is obviously minimized when $\vec{\tau}$ is constant. Here we should emphasize that the continuous symmetries which underscore these ground states are just symmetries of the states and not of the Hamiltonian itself. Therefore we are not in a setting where a Mermin–Wagner argument can be applied.

Results are further complicated because, as it turns out, the constant orbital fields are not the only ground states. Indeed, in the 120° model, starting from some constant-field ground state, another ground state may be obtained, e.g., by reflecting all orbitals in the xy -plane through the vector \hat{c} . This new state can be further mutated by introducing more flips of this type in other planes parallel to the xy -plane. Obviously, similar alterations of the ‘pristine’ states can take place in the other two coordinate directions. What is not so obvious, but nevertheless true, is that the above-mentioned procedure exhausts all possible ground states for the 120° model [15].

Let us now consider the effects of finite temperature. Here, in general, we will see that there is a tendency to fluctuation-driven stabilization—sometimes known as ‘order-by-disorder’ [17]–[19]—that selects only a few of the ground states. We start by parametrizing each orbital \mathbf{T}_r by the angle θ_r with the x -axis. In this language, let us consider the finite-temperature fluctuations about the ‘pristine’, homogeneous ground states where each $\theta_r = \theta_0$. A change in θ_0 thus corresponds to a global rotation of the homogeneous orbital-ordering field. At low temperatures, nearby orbital vectors will tend to be aligned, so we can work with the variables $\phi_r = \theta_r - \theta_0$. Neglecting those terms of order higher than quadratic in ϕ_r , the Hamiltonian for the small amplitude fluctuations of the orbital ordering field becomes

$$H_{fluc} = \frac{1}{2} \sum_{r,\alpha} J_\alpha(\theta_0) (\phi_r - \phi_{r+\hat{e}_\alpha})^2, \quad (4)$$

where $\alpha = x, y, z$ while $J_x(\theta_0) = \sin^2(\theta_0)$, $J_y(\theta_0) = \sin^2(\theta_0 + 120^\circ)$ and $J_z(\theta_0) = \sin^2(\theta_0 - 120^\circ)$. The important point is that the stiffness of the system—the resistance of the system against deviations from perfect order—depends on the angle θ_0 . Thus depending on the global orientation of the ordering field, the system is more or less susceptible to orbital fluctuations. Therefore the free energy of the system depends on θ_0 . A more detailed analysis [15] now shows that the free energy $F(\theta_0)$ actually has strict minima at $\theta_0 = 0^\circ, 60^\circ, 120^\circ, 180^\circ, 240^\circ$ and 300° .

Thus, at the level of Gaussian fluctuations, which in spin models is referred to as spin-wave approximation, it is clear that finite-temperature effects will select six ground states above all

others. Of course, this is only the beginning of a complete mathematical analysis: one must account for all other possible thermal disturbances and their interactions, the interactions of the said additional disturbances with the orbital waves, and the interaction of orbital waves with one another. For this, one has to go beyond the level of perturbation theory, which, as can be readily verified, is plagued by divergences even at the lowest non-vanishing order.

The approach that is used to prove that there is orbital order in the classical 120° model at finite temperatures is to block the lattice [15]. One can then tabulate—with controllable tolerance—whether or not each block mimics the harmonic behaviour of a favoured ground state embellished with orbital-wave excitations. The key is to show that, with high probability, such regions are indeed heavily favoured and, of equal importance, distinct regions of this type corresponding to different favoured ground states are separated by domain walls which exhibit a positive stiffness. The resulting orbital ordering pattern is shown in figure 4.

2.3. Quantum 120° model

Whereas the orbital-lattice Hamiltonian is essentially classical, the interaction between orbital degrees of freedom and the electronic spin brings in quantum mechanics [7]. This coupling is via the magnetic superexchange interaction: orbital degeneracy can also be lifted by coupling to the spins. It turns out that both kinds of interaction mechanisms bring about very similar orbital-only models [20]–[24], [26]. Such orbital-only Hamiltonians correspond to superexchange-based Kugel–Khomskii Hamiltonians, where the spin variables are integrated out: the spin degrees of freedom are assumed to be homogeneously ordered and static. The Kugel–Khomskii spin–orbital models are quantum mechanical in nature as only electronic degrees of freedom enter the Hamiltonian. The similarity of orbital–lattice and orbital–spin Hamiltonians is due to the fact that in deriving these Hamiltonians one can rely on symmetry considerations.

A convenient mathematical procedure to describe orbital ordering is to introduce operators T_i of the pseudospin $\frac{1}{2}$, describing the orbital occupation, so that, e.g., the state $|T^z = \frac{1}{2}\rangle$ corresponds to the occupied orbital $|3z^2 - r^2\rangle$, and $|T^z = -\frac{1}{2}\rangle$ to $|x^2 - y^2\rangle$, the direct consequence of quantizing the angle θ . These orbital operators do not commute: they obey the canonical spin commutation relations.

For two-fold e_g orbitals, the quantum orbital-only Hamiltonian is

$$H_{120}^{quant} = \sum_{r,\alpha} \tau_r^\alpha \tau_{r+\hat{e}_\alpha}^\alpha, \quad (5)$$

i.e. the Hamiltonian is identical to its classical counterpart H_{120}^{clas} , with the only difference that the orbital operators are quantized. Orbital ordering and orbital excitations of this model are considered in, e.g. [21]–[23]. The Hamiltonian can be diagonalized in a semi-classical large T expansion, which is the equivalent of the large S expansion in spin-wave theory, for orbital degrees of freedom. In the leading, linear approximation, one finds that the excitation spectrum is gapless and that the dispersion of the orbital waves is two-dimensional and linear for small values of k . As a consequence, there can be no orbital ordering at any finite temperature at this level of approximation. At zero temperature, however, the system is stable against quantum fluctuations and ordering is possible in principle.

The fact that excitations are gapless is due to the same degeneracy of the classical ground state that we encountered in the classical 120° Hamiltonian. Excited states, however, break this degeneracy: the Hamiltonian itself is not rotationally invariant. Quantum fluctuations pick up

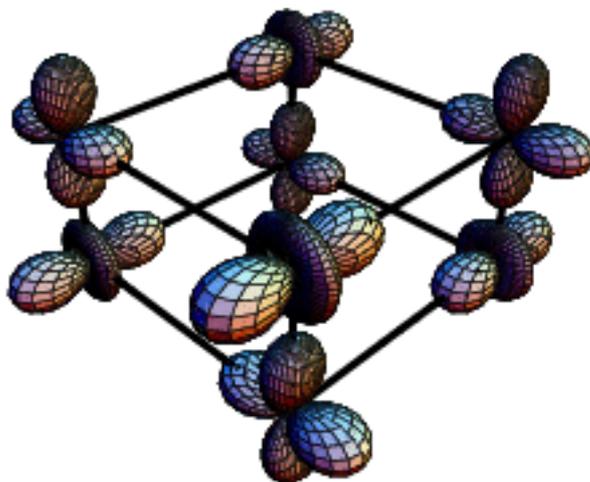


Figure 4. Orbital ordering pattern that is stable in the 120° orbital-only Hamiltonian, both classical and quantized.

these excited states. Therefore, higher-order terms in the semi-classical $1/T$ expansion lead to a ground-state wavefunction that does not have a continuous rotational invariance anymore, even at zero temperature. Hence higher-order corrections to linear orbital wave theory lead to a gap in the orbital excitation spectrum [23]. The gap stabilizes the orbital ordering also at finite temperatures and one thus expects the orbital-ordering phase transition to take place at finite (non-zero) temperature.

Interestingly, fluctuations, be it due to finite temperature or due to quantum-zero-point motion, seem to lead to the same orbital-ordered state with $\theta = 0$ (or an equivalent state, rotated by a multiple of 60°). Note, however, that only in the classical model we have an actual proof that such an ordering is stable. The results for the quantum model are less rigorous as the calculations rely on large T perturbation theory and Hartree–Fock decoupling. Especially for $T = \frac{1}{2}$ and in low dimensions, quantum melting in orbital-like models is known to occur, e.g., in the two-dimensional orbital compass model [25].

2.4. Experimentally observed orbital ordering

The 120° orbital model contains the bare bones for the description of orbital ordering in cubic perovskites with e_g Jahn–Teller ions, such as KCuF_3 and LaMnO_3 . At low temperatures, these materials are magnetically ordered and in such a case the orbital-only model has to be extended by consideration of the spin degrees of freedom: the Kugel–Khomskii model tells us that the ordering of these two degrees of freedom cannot be independent. But at higher temperatures, in the paramagnetic phase, the spin degrees of freedom form a homogeneous, fluctuating background and we only need to consider the orbital degrees of freedom and how they are coupled to each other via Jahn–Teller distortions and superexchange. In LaMnO_3 , the magnetic ordering takes place at 120 K and the orbital ordering temperature is about 750 K. For KCuF_3 , two distinct crystal structures exist, the so-called *a*-type and *d*-type. The two phases support different orbital ordering patterns, see figure 5 and are stable to a very high temperature. Magnetic ordering takes place at $T_c = 38$ K (*a*-type) and 22 K (*d*-type). At temperatures above T_c , anisotropic magnetic fluctuations do exist; however, these will hardly have a decisive impact on the orbital ordering [27].

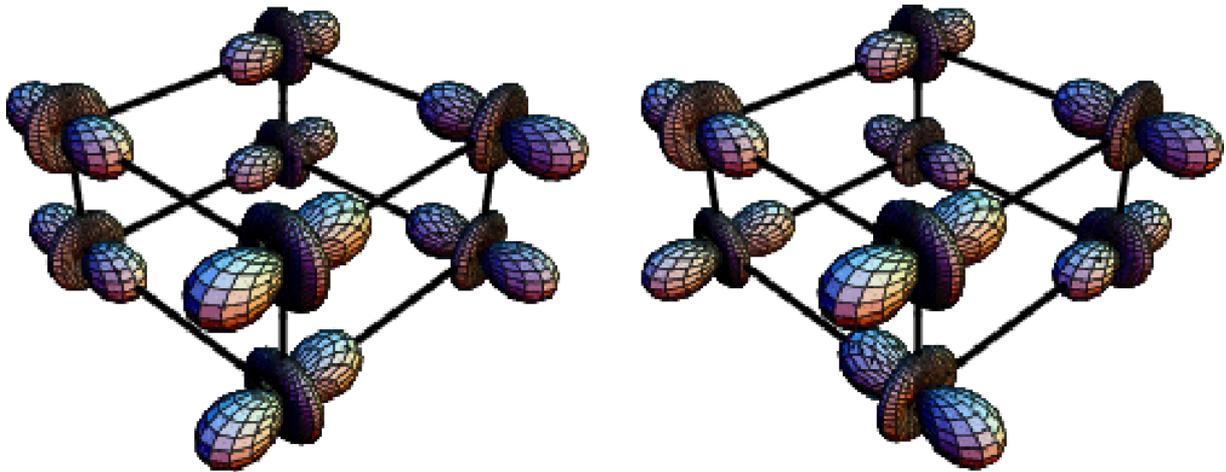


Figure 5. Schematic picture of the orbital ordering pattern that is observed in Jahn–Teller distorted LaMnO_3 and d -type KCuF_3 (left) and a -type KCuF_3 (right). The occupied orbitals are shown.

These observations leave us with an apparent paradox: the orbital ordering pattern predicted from the 120° orbital-only model is not the one observed in experiments. The orbital model needs to be extended. It is important to have a correct model for the orbital degrees of freedom, as these become important when charge carriers are introduced and the compound becomes conducting. Upon doping LaMnO_3 , the orbital-order temperature decreases and orbital degrees of freedom thus become relevant for the colossal magnetoresistance manganites.

For the resolution of the paradox, we have at least one proposal: anharmonic lattice effects [28]. Of the many (insulating) orbital-ordered e_g systems, none has a local compression of octahedra, i.e. an $x^2 - y^2$ distortion. It seems to be the rule that octahedra are elongated and the $3z^2 - r^2$ orbital is occupied. The reason for this is rather simple. When the octahedron is elongated along the c -axis, the oxygen atoms on that axis shift outward by 2δ ($\delta > 0$), whereas, at the same time, the other four oxygen atoms in the basal plane shift towards the central Jahn–Teller ion by a length $-\delta$. A compression of the octahedra corresponds to distortion of the octahedron with $\delta < 0$. The elastic energy associated with the distortion is

$$\sum_l \left(\frac{B}{2} \delta_l^2 - \frac{\xi}{3} \delta_l^3 \right),$$

where the sum is over all three directions and the coefficients $B, \xi > 0$. One sees immediately that the harmonic term does not depend on the sign of δ , i.e. on the distortion being an elongation or contraction of the octahedron. However, the anharmonic term favours $\delta > 0$ and thus elongation of the octahedra. This anharmonicity can be modelled by adding the term $E_{anh} = -\xi \cos 3\theta$ to the energy [6]. The corresponding Hamiltonian in terms of the orbital operators is

$$H_{anh} = -\xi \sum_r \prod_\alpha \tau_r^\alpha. \quad (6)$$

A systematic investigation of the orbital Hamiltonian $H_{120} + H_{anh}$ is still lacking. When the anharmonicity is very strong, one only has to consider distortions that are elongated along one of the three crystallographic directions, in leading approximation. When long-range elastic interactions between these elongated distortions are considered, it can be shown that, for the experimentally observed orbital-ordering patterns, the total energy is minimized [29].

It should be noted that the model above is derived under the assumption that the manganese atoms form a rigid cubic lattice [30]. In reality, the Mn lattice is elastic so that it can—and does—distort. A bondlength change in one (or two) spatial direction(s) leads to a uniform Q_2/Q_3 type local distortion of the MnO_6 octahedra. This effect should be taken into account when comparing theoretically obtained orbital-ordering patterns with the experimentally observed ones.

3. Orbital-only model: t_{2g} triplet

For the Jahn–Teller systems with an open t_{2g} shell, the situation is somewhat more complicated. The modification with respect to the previous discussion is that, because we have three degrees of freedom and $\mathbf{T} = (T_z, T_y, T_x)$ is a three-vector, we need two angles to fix the distortion. Thus \mathbf{T} lies on the unit sphere.

3.1. Classical compass models

The first observation is that the distortions of e_g kind (Q_3 and Q_2 in the figure) also couple to the three t_{2g} orbitals. An elongation of the octahedron along the z -axis (Q_3 in the figure) will clearly lower the energy of the yz and zx orbitals that have lobes along the z -axis, whereas it will lead to an increase of the energy of the xy orbital that lies in the plane. So the first contribution to the total energy for t_{2g} Jahn–Teller systems is simply given by our 120° model that we derived above, with the proviso that now τ^a , τ^b and τ^c are the three Cartesian components of a orbital (distortion) vector that lies on the unit sphere. We therefore refer to this model as the 90° orbital model. This model was introduced by Kugel and Khomskii in their seminal paper as a heuristic model for orbital–orbital interactions and is widely known as the orbital compass model. The orbital compass Hamiltonian is

$$H_{90}^{comp} = \sum_{r,\alpha} \tau_r^\alpha \tau_{r+\hat{e}_\alpha}^\alpha, \quad (7)$$

with τ on the unit sphere. This model is one-dimensional in the sense that each vector component interacts with its counterpart along one crystallographic axis. One expects, for example, that due to its one-dimensional features this Hamiltonian is very susceptible to disorder.

Naturally, there are also three Jahn–Teller distortions that couple exclusively to the t_{2g} orbitals, as shown in the figure. It is easy to see that a t_{2g} distortion in the xy -plane only couples to distortions of the same symmetry on neighbouring octahedra in the xy -plane. The situation for the other two types of distortions is analogous. We immediately arrive at the Hamiltonian for t_{2g} orbitals on a cubic lattice with corner-sharing octahedra where the interactions are due to t_{2g} Jahn–Teller distortions:

$$H_{90}^{2D} = \sum_r (\tau_r^a \tau_{r+\hat{e}_a}^a + \tau_r^a \tau_{r+\hat{e}_b}^a + \tau_r^b \tau_{r+\hat{e}_b}^b + \tau_r^b \tau_{r+\hat{e}_c}^b + \tau_r^c \tau_{r+\hat{e}_a}^c + \tau_r^c \tau_{r+\hat{e}_c}^c). \quad (8)$$

Again H_{90}^{2D} is a 90° model because the Cartesian components of $\boldsymbol{\tau}$ appear in the Hamiltonian. Every vector component couples with its counterparts in two spatial directions, so that the model in that sense is two-dimensional.

Adding the two contributions, we finally obtain the Hamiltonian for the t_{2g} orbital–orbital interaction mediated by Jahn–Teller distortions:

$$H_{t_{2g}} = (g + \Delta g)H_{90}^{comp} + gH_{90}^{2D}. \quad (9)$$

The coupling constants g and Δg depend on microscopic details of the solid under consideration and can, in principle, be derived from, e.g., experimental observations or *ab initio* calculations. The Hamiltonian can now be simplified to

$$H_{t_{2g}} = gH_{Heis}^{3D} + \Delta gH_{90}^{comp}, \quad (10)$$

where the isotropic Heisenberg Hamiltonian is, by definition, $H_{Heis} = \sum_{\langle ij \rangle} \boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j$, where $\langle ij \rangle$ are neighbouring sites and we used that $H_{90}^{comp} + H_{90}^{2D} = H_{Heis}^{3D}$. Thus the Hamiltonian $H_{t_{2g}}$ consists of a spatial isotropic part and an anisotropic part, where the latter is given by the one-dimensional 90° orbital compass model.

For the classical compass model, it is proved that there is long-range order at finite temperature again due to an order-from-disorder mechanism, both for the model in three [15] and two [31] spatial dimensions. This is in spite of the fact that, in this case, the degeneracies of the ground state are much larger than even the 120° model. This fact reflects itself in a nematic orbital-ordered phase.

3.2. Quantum compass models

Superexchange interactions between two sites with partially filled t_{2g} orbitals bring quantum mechanics into the t_{2g} orbital-only models. Whereas for e_g orbitals, lattice-mediated Jahn–Teller interactions and Kugel–Khomskii superexchange give precisely the same orbital Hamiltonian (when the isotropic spin ordering is integrated out), the situation for t_{2g} orbitals is quite different. This becomes already evident when the hopping integrals between e_g and t_{2g} orbitals on edge sharing octahedra are considered: these are zero by symmetry so that the superexchange interaction completely vanishes—contrary to the case of a Jahn–Teller distortion, where we did find an elastic interaction between e_g and t_{2g} orbitals on neighbouring sites.

The quantum orbital Hamiltonian for the t_{2g} subsector is given by [32] and is rather complicated, as along each crystallographic direction a particular pair of orbitals is active, so that on each bond one has a Heisenberg-like superexchange Hamiltonian. It is noteworthy that, for the full Kugel–Khomskii Hamiltonian that includes spin degrees of freedom, there is an exact proof that there is no spin ordering at any finite temperature [13].

The quantum compass model H_{90}^{comp} where the vector components of $\boldsymbol{\tau}$ are the Pauli matrices does appear in a very different context. It is the spin anisotropy Hamiltonian in the orbital liquid phase of LaTiO_3 [33] and it is shown that, in a spin-wave expansion, one can find a stable orbital-ordered state for the model in three spatial dimensions. Most remarkably, however, there is an exact proof that its counterpart in two spatial dimensions is quantum disordered [25].

4. Orbital excitations

Each time we have a certain ordering in solids, the corresponding excitations should appear. The quadrupolar charge ordering—orbital ordering—should give rise to elementary excitations with orbital signature, as this order causes a breaking of symmetry in the orbital sector. These excitations—we may call them orbitons—were first briefly discussed in [7] and were recently studied theoretically in several papers, e.g. [21]–[23], [34]–[36]. One of the problems that could complicate an experimental observation of these excitations is the usually rather strong Jahn–Teller coupling of orbital degrees of freedom to the lattice distortions. This could make it very difficult, if not impossible, to ‘decouple’ orbitons from phonons. And indeed the experimental efforts to observe orbitons were unsuccessful for many years. A breakthrough came when Tokura and co-workers managed to observe manifestations of orbital excitations in Raman scattering on untwinned single crystals of LaMnO_3 [37], followed by recent measurements in [38]–[40].

The observed orbitons were interpreted by the authors as being due to electron correlations [37], but in the comment that accompanied the publication it was immediately mentioned that here the coupling to phonons can also be very important [41]. Let us briefly discuss the question of the origin of orbitons.

Since there is no continuous symmetry that underlies the orbital Hamiltonians, the orbital excitations in orbital-ordered states are, in general, gapped. In the case of order-from-disorder, this orbital excitation gap is, as it were, dynamically generated by the finite-temperature (or quantum) fluctuations. In classical models, such a gap is thus temperature-dependent and vanishing when $T \rightarrow 0$.

The physical aspects of the coupling between the orbital excitation and Jahn–Teller phonons can be illustrated by considering the orbital and phonon excitations as dispersionless. We can view this as a reasonable first approximation because orbital excitations are gapped and Jahn–Teller lattice excitations are thus optical phonons. Applying this simplification leads to the single-site Hamiltonian [35]

$$H_{loc} = [\bar{J} + 2g(q_3^\dagger + q_3)]b^\dagger b + \omega_0(q_3^\dagger q_3 + q_2^\dagger q_2) + g(b^\dagger + b)(q_2^\dagger + q_2), \quad (11)$$

where the b operator describes an orbiton excitation, $q_{2,3}$ are the $Q_{2,3}$ phonon modes and $\bar{J} = 3J + 4g^2/\omega_0$, where g is the electron–phonon coupling constant, ω_0 the JT phonon frequency and J the superexchange energy. Let us discuss three important consequences of the orbiton–phonon coupling in equation (11). Firstly, the coupling to the lattice moves the orbiton to higher energy, an amount $4g^2/\omega_0$. This shift has a straightforward physical meaning: it is the phonon contribution to the crystal-field splitting of the e_g -states is caused by the static Jahn–Teller lattice deformation. The effective orbital-excitation energy is the sum of the local orbital exchange energy and static phonon contribution to the crystal-field splitting.

If, however, an orbital excitation is made, it strongly interacts with the Q_3 phonon, so that the orbital excitation can be dynamically screened by the Jahn–Teller phonons and lowered in energy. The crystal-field splitting and screening are strongly competing as both are governed by the energy scale set by the electron–phonon coupling. Finally, the orbital and Q_2 phonon modes mix, as is clear from the last term of H_{loc} . This implies that the true eigenmodes of the coupled orbital–phonon system have both an orbital and a phonon character.

In general, the mixing of orbital and phonon mode gives rise to extra phonon satellites in the orbiton spectral function at energy intervals of ω_0 . Vice versa, due to this mixing, a low intensity orbital satellite at $\approx 3J$ will be present in the Q_2 phonon spectral function. A plausible

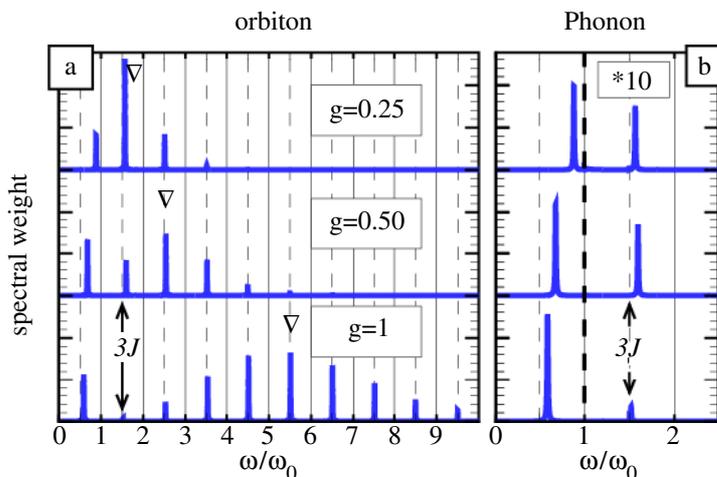


Figure 6. (a) Orbiton spectral function at the Γ and X points, $g = \omega_0/2$. (b) Spectrum of the Raman-active A_g and B_{1g} phonon modes for $g/\omega_0 = 0.35$. The experimental peak positions are indicated by ∇ . For $\omega > \omega_0$, the spectral weight is multiplied by 10; see [35].

estimate of the Jahn–Teller energy in LaMnO_3 ($E_{JT} = 4g^2/\omega_0$) is $E_{JT} \approx 200\text{--}300$ meV, and for the superexchange $J \approx 40$ meV. With these estimates, keeping in mind the results described above, namely the strong mixing of the orbital excitation and the phonons, one comes to the conclusion that the features at 150 meV observed in the Raman experiment [37], interpreted there as pure orbital excitations, are rather the orbiton-derived satellites in the phonon spectral function, see figure 6 [35]. A framework beyond the toy model described above is needed to establish the relevance of such an interpretation and to establish the exact nature of the satellites in the Raman spectra: this is still an open issue, both experimentally and theoretically. But it is clear that the elementary excitations of an orbital-ordered system are mixed modes with both an orbital and a phonon character or, in other words, are determined by both electron correlation effects and the electron–lattice interaction.

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