

Orbital Ordering in Charge Transfer Insulators

M.V. Mostovoy¹ and D.I. Khomskii^{1,2}

¹*Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

²*II Physicalisches Institut, Universität zu Köln, Zùlplicher Strasse 77, 50937 Köln, Germany*

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We discuss a new mechanism of orbital ordering, which in charge transfer insulators is more important than the usual exchange interactions and which can make the very type of the ground state of a charge transfer insulator, i.e., its orbital and magnetic ordering, different from that of a Mott-Hubbard insulator. This purely electronic mechanism allows us to explain why orbitals in Jahn-Teller materials typically order at higher temperatures than spins, and to understand the type of orbital ordering in a number of materials, e.g., K_2CuF_4 , without invoking the electron-lattice interaction.

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Since the seminal Zaanen, Sawatzky, and Allen paper [1], it is widely accepted that strongly correlated insulators can be divided into two classes according to the nature of their gap. The Mott-Hubbard insulators (MHI) are characterized by the lowest-energy excitations of the type $d^n + d^n \rightarrow d^{n-1} + d^{n+1}$, obtained by transferring a d electron from one transition metal (TM) ion to another, whereas in charge transfer insulators (CTI) the corresponding excitations are holes on ligand sites (oxygen ions in the case of TM oxides): $d^n + p^6 \rightarrow d^{n+1} + p^5$. MHI are usually described by an effective Hubbard model, in which only the d -electron states are considered explicitly. On the other hand, (doped) CTI are described by models that include also the relevant oxygen p states, such as the dp (or three-band Hubbard) model of high- T_c superconductors [2]. The value of the gap is determined by the smallest of the two parameters: the energy of electron transfer from ligand to TM sites Δ and the Hubbard repulsion on TM sites U_d . For CTI (usually, the oxides of heavier $3d$ metals) $\Delta < U_d$, while for MHI $U_d < \Delta$.

The distinction between these two types of insulators becomes apparent upon doping, while in the absence of doping both CTI and MHI with one electron or hole per TM site are $S = \frac{1}{2}$ Heisenberg antiferromagnets. In this respect Jahn-Teller materials, in which d electrons, in addition to spins, have also orbital degrees of freedom, are much more interesting. In this Letter we show that in insulators with orbital degeneracy not only the excitation spectrum, but also an orbital and magnetic ordering in the ground state may strongly depend on the ratio Δ/U_d . The difference between the ground states of CTI and MHI results from a peculiar interaction between orbitals on nearest-neighbor d sites, which may be called “the orbital Casimir force,” as it originates from the vacuum energy of charge fluctuations due to the hopping of electrons between the ligand and TM ions (whereas the usual exchange involves the electron transfer from one TM site to another). We recently noted the importance of such an interaction in geometrically frustrated systems with the 90° metal-oxygen-metal bonds, e.g., $NaNiO_2$, where it

determines the type of orbital ordering [3]. Here we show that this interaction of electronic origin is generally present in all TM oxides and, in particular, in materials with the 180° metal-oxygen-metal bonds, like perovskites ABO_3 and their layered analogs A_2BO_4 , and it is not included in the widely used exchange model [4] [sometimes called the Kugel-Khomskii (KK) model]. That model is derived from an effective Hubbard model describing only the degenerate d -electron orbitals and, strictly speaking, applies only to MHI with $\Delta \gg U_d$. The new orbital interaction obtained below helps to resolve the difficulty of the KK model, in which an orbital ordering is strongly coupled to a magnetic one, implying close temperatures of orbital and magnetic orderings, whereas usually orbitals order at higher temperatures than spins.

We first calculate an exchange Hamiltonian for two TM ions with one hole on the doubly degenerate e_g level, e.g., Cu^{2+} ($t_{2g}^6 e_g^3$). The two orthogonal e_g orbitals $|3z^2 - r^2\rangle$ and $|x^2 - y^2\rangle$ may be described by, respectively, the up and down states of the isospin- $\frac{1}{2}$ operator T^z [4]. It is convenient to introduce an overcomplete set of operators $d_{i\alpha\sigma}$ on each TM site i annihilating a hole in the state $|3\alpha^2 - r^2\rangle$ ($\alpha = x, y, z$) with the spin projection σ . These states are hybridized with the p_α orbitals on two neighboring oxygen sites $i \pm \frac{\alpha}{2}$ (the corresponding oxygen hole operators are denoted by $p_{i \pm \frac{\alpha}{2}, \sigma}$). The hole states on TM sites are described by the standard atomic Hamiltonian, which includes the on-site repulsion U_d and the Hund’s rule exchange coupling J_d for holes on two orthogonal orbitals. The Hamiltonian of oxygen holes hybridized with the d states is

$$H_p = H_{\text{kin}} + U_p \sum_{i,\alpha} p_{i+\frac{\alpha}{2}}^\dagger p_{i+\frac{\alpha}{2}} p_{i+\frac{\alpha}{2}}^\dagger p_{i+\frac{\alpha}{2}} - t_{pd} \sum_{i,\alpha,\sigma} [d_{i\alpha\sigma}^\dagger (p_{i+\frac{\alpha}{2},\sigma} + p_{i-\frac{\alpha}{2},\sigma}) + \text{H.c.}], \quad (1)$$

where the first term is the kinetic energy of holes in the oxygen p band, the second term is the Hubbard repulsion on oxygen sites, and the last term describes the hopping between oxygen and TM sites.

Integrating the oxygen degrees of freedom out, one obtains an effective interaction between d electrons in the form of an expansion in powers of $(t_{pd}/\Delta)^2$. The lowest order term provides a hopping between TM sites, which together with the Coulomb and Hund's rule interactions between d electrons gives an effective dd model. For dispersionless oxygen holes, $H_{\text{kin}} = \Delta \sum_{i,\alpha,\sigma} P_{i+\frac{\alpha}{2}\sigma}^\dagger P_{i+\frac{\alpha}{2}\sigma}$, the effective dd hopping occurs between nearest-neighbor TM sites, and its amplitude is $t_{dd} = t_{pd}^2/\Delta$.

The next term in this expansion ($\propto t_{pd}^4$) gives an orbital and spin exchange mediated by two oxygen holes. The corresponding diagrams are shown in Fig. 1, where in the diagrams 1(a) and 1(b) two holes do not interact with each other in the virtual state, while the black squares in diagrams 1(c) and 1(d) correspond to one or more Hubbard interactions on oxygen sites. Each diagram gives rise to a particular form of spin and orbital exchange. Thus, if the holes on the TM sites i and j exchange places [Fig. 1(a)], the spin exchange is described by operator $P_{\text{ex}} = +1$ if the total spin of the two holes $S = 1$, and -1 for $S = 0$. This operator can also be written in the form $P_{\text{ex}} = 1 - 2P_0$, where $P_0 = 1/4 - (\mathbf{S}_i \mathbf{S}_j)$ is the projector on the $S = 0$ state. If, on the other hand, the holes return to their starting points, the corresponding "spin factor" is -1 . The interacting holes in the diagrams 1(c) and 1(d) must have opposite spin projections, so the spin exchange in that case is described by $S_i^+ S_j^- + S_i^- S_j^+$ [see Fig. 1(c)], while if the spin projections remain unchanged [see Fig. 1(d)], the spin operator is $-2(1/4 - S_i^z S_j^z)$. Since the diagrams 1(c) and 1(d) differ only by the spin factors, their sum is proportional to $-2P_0$, corresponding to the fact that the on-site Hubbard interaction between two holes is nonzero only when their spins add to the total spin 0.

While the spin dependence of the exchange interactions, discussed above, is very general, the orbital structure depends on the dispersion of holes and on relative positions of the sites i and j . In particular, for dispersionless holes the orbital interaction in the order t_{pd}^4 occurs only between two nearest-neighbor TM sites, e.g., i and

$i + \alpha$, and is proportional to $J_{i\alpha} = (\frac{1}{2} + I_i^\alpha)(\frac{1}{2} + I_{i+\alpha}^\alpha)$, where

$$\begin{aligned} I^x &= -\frac{1}{2}T^z - \frac{\sqrt{3}}{2}T^x, & I^y &= -\frac{1}{2}T^z + \frac{\sqrt{3}}{2}T^x, \\ I^z &= T^z, \end{aligned} \quad (2)$$

and the operator $(\frac{1}{2} + I_i^\alpha) = d_{i\alpha}^\dagger d_{i\alpha}$ is the projector on the state $|3\alpha^2 - r^2\rangle$ on the site i .

Combining the exchange interactions in the dd model with those resulting from the processes shown in Figs. 1(c) and 1(d), we obtain in the order t_{pd}^4

$$\begin{aligned} H_{ST} &= -\frac{4t_{pd}^4}{\Delta^2} \sum_{i,\alpha} \left[\left(\frac{1}{U_d} + \frac{2}{2\Delta + U_p} \right) I_{i\alpha} P_0 \right. \\ &\quad \left. + \frac{J_d}{2U_d^2} \left(\frac{1}{4} - I_i^\alpha I_{i+\alpha}^\alpha \right) P_1 \right], \end{aligned} \quad (3)$$

where the first and the second terms describe, respectively, the antiferromagnetic (AFM) and the ferromagnetic (FM) spin exchange coupled to orbital interactions. Here $P_1 = 1 - P_0 = 3/4 + (\mathbf{S}_i \mathbf{S}_j)$ is the projector on the $S = 1$ state.

In addition to the coupled spin and orbital interactions, there exists also a spin-independent orbital Hamiltonian

$$\begin{aligned} H_T^{(h)} &= \frac{2t_{pd}^4}{\Delta^2} \sum_{i,\alpha} \left[\frac{1}{\Delta} \left(\frac{1}{2} + I_i^\alpha \right) \left(\frac{1}{2} + I_{i+\alpha}^\alpha \right) \right. \\ &\quad \left. - \frac{1}{U_d} \left(\frac{1}{4} - I_i^\alpha I_{i+\alpha}^\alpha \right) \right]. \end{aligned} \quad (4)$$

In MHI the orbital interaction is of the same order as H_{ST} described by Eq. (3). On the other hand, in CTI with $\Delta \ll U_d, U_p$ the first term in Eq. (4) is the strongest interaction between holes on TM sites. The term $\propto \Delta^{-3}$ is not really an exchange interaction, since in the order t_{pd}^4 it is impossible to exchange two holes in such a way that they never occupy the same oxygen or TM ion [the process shown in Fig. 1(a) does not contribute in that order]. This term comes from the virtual hopping of holes to all neighboring oxygen sites [Fig. 1(b)], except for the oxygen bridging the two neighboring TM ions.

The term in $H_T^{(h)}$ containing only Δ in the denominator is similar to the purely orbital interaction for the 90° metal-oxygen-metal bonds [3], and its origin can be better understood by noting that it is the only term that does not vanish in the limit of infinite on-site Hubbard repulsion U_p and U_d . It represents the energy of the delocalization of holes over the octahedra of the ligand ions, surrounding TM sites, or, more correctly, the increase of that energy due to the fact that the neighboring octahedra share one ligand ion and for infinite U_p the intermediate two-hole states on the shared ion are forbidden. This energy increase depends on orbital states of the neighboring holes, which gives rise to the orbital interaction. Thus the origin of this interaction is similar

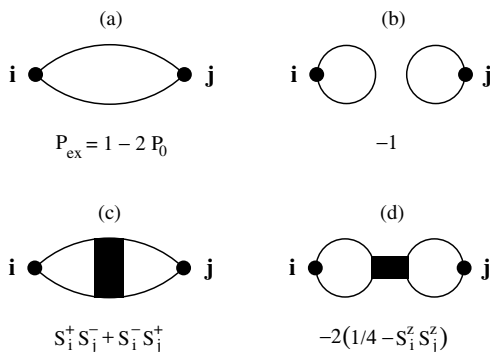


FIG. 1. Diagrams describing interactions mediated by two virtual oxygen holes.

to that of the Casimir effect [5], resulting from the dependence of the energy of zero-point fluctuations of electromagnetic field on positions of two metallic plates. Note that the sign of this orbital interaction is positive, while all other terms in Eqs. (3) and (4) are negative (since they describe the second-order corrections to the ground state energy in the effective dd hopping). The result of this new orbital interaction can be formulated as the following “rule of thumb” (applied also to materials with one-electron per TM site): to avoid the energetically unfavorable occupation of the bridging oxygen by two holes, the d holes should occupy orbitals directed away from the common oxygen either on both neighboring TM sites [see Fig. 2(b)] or, at least, on one site [see Fig. 2(a)].

The importance of the orbital exchange Eq. (4) for an orbital ordering may be understood already by considering the minimal-energy states of a pair of holes on the neighboring TM sites i and $i+z$. In MHI ($\Delta > U_d$) the exchange is dominated by H_{ST} (3) and the last term in Eq. (4). The AFM exchange between spins of the holes is the strongest for $I^z = \frac{1}{2}$ on both sites; i.e., the lowest energy is achieved if both holes occupy the $|3z^2 - r^2\rangle$ state, as shown in Fig. 2(c). The ground state of the pair is a spin singlet. On the other hand, in CTI ($\Delta < U_d$) the strongest interaction is the orbital Hamiltonian H_T [see Eq. (4)], and the state shown in Fig. 2(c) has the highest orbital energy, since both hole orbitals are oriented towards the common ligand ion. The more energetically favorable states in CTI will be those in which at least one hole is in the $|x^2 - y^2\rangle$ state [see Figs. 2(a) and 2(b)]. Furthermore, both the last term in Eq. (4) and the relatively weak FM spin exchange due to the Hund’s rule coupling select the state shown in Fig. 2(a) with the total spin of the pair $S = 1$. Thus, the ground state of the pair in the CT regime is different from that in the MH regime.

Consider now two neighboring TM sites with one e_g electron, as, e.g., Mn^{3+} ($t_{2g}^3 e_g^1$), Cr^{2+} ($t_{2g}^3 e_g^1$), and the low-spin Ni^{3+} ($t_{2g}^6 e_g^1$). In the KK model the systems with one electron/site and one hole/site order in exactly the same way, since the Hubbard model, from which the KK ex-

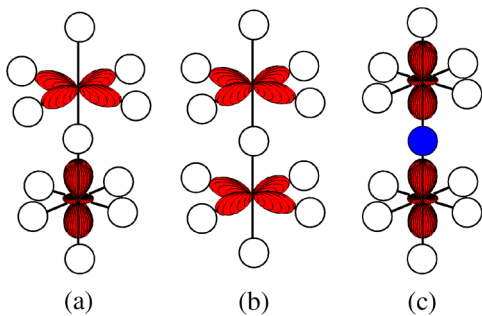


FIG. 2 (color online). Favorable [(a) and (b)] and unfavorable (c) occupations of hole orbitals of neighboring TM ions in CTI, in which the exchange is dominated by Eq. (4).

change Hamiltonian is derived, has the electron-hole symmetry [4]; consequently, the term H_{ST} (3) has the same form for both electrons and holes. On the other hand, in the dp model this symmetry is lost: the new orbital interaction for a one-electron case has the form [cf. Eq. (4)]

$$H_T^{(e)} = + \frac{2t_{pd}^4}{\Delta^2} \sum_{i,\alpha} \left[\frac{1}{\Delta} \left(\frac{3}{2} - I_i^\alpha \right) \left(\frac{3}{2} - I_{i+\alpha}^\alpha \right) - \frac{1}{U_d} \left(\frac{1}{4} - I_i^\alpha I_{i+\alpha}^\alpha \right) \right]. \quad (5)$$

In this case for both MHI and CTI the energy of a pair of TM electrons on the sites i and $i+z$ is minimal if both electrons occupy the $d_{3z^2-r^2}$ orbital, Fig. 2(c), and their spins form the singlet state.

Interestingly, the electron-lattice [Jahn-Teller (JT)] coupling also gives rise to an effective orbital interaction [6]

$$H_{JT} = J_{JT} \sum_{i,\alpha} I_i^\alpha I_{i+\alpha}^\alpha, \quad (6)$$

which is similar to Eq. (4), but lacks terms linear in isospin operators and has the same form for electrons and holes. In general, orbital and magnetic ground states of a pair of JT ions in CTI, MHI, and materials with strong JT interactions differ from each other (see Fig. 3), which gives a possibility to experimentally discriminate between these mechanisms of orbital ordering. Thus, Cu^{2+} pairs (one hole) in K_2ZnF_4 were found to have a triplet ground state [7], showing that the orbital exchange Eq. (4) and/or JT interaction are in this case stronger than the KK exchange. We are not aware of similar data for pairs of one-electron ions.

Next we consider layered perovskites with one hole per TM site, e.g., K_2CuF_4 and $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{CuCl}_4$. The JT interaction Eq. (6) for $\alpha = x, y$ favors an antiparallel orientation of neighboring isospins: holes on the $A(B)$

	MHI	CTI	JT
One hole	$S=0$	$S=1$	$S=1$
One electron	$S=0$	$S=0$	$S=1$

FIG. 3. The orbital ground state and the total spin S of a pair of JT ions with one hole/electron per site in MHI, CTI, and materials with the strong JT interaction.

sublattice occupy the $\cos\frac{\theta}{2}|3z^2 - r^2\rangle + \sin\frac{\theta}{2}|x^2 - y^2\rangle$ state with $\theta = +\frac{\pi}{2}(-\frac{\pi}{2})$. Experimentally one finds a “canted” antiferro-orbital ordering with $\theta = \pm\frac{\pi}{3}$, corresponding to alternating $d_{x^2-z^2}/d_{y^2-z^2}$ orbitals [8,9]. To explain the canting in the electron-lattice approach, one has to invoke a considerable lattice anharmonicity, which favors elongated oxygen octahedra [6]. On the other hand, the orbital interaction in two-dimensional CTI ($U_d \rightarrow \infty$),

$$H_T = +\frac{2t_{pd}^4}{\Delta^3} \sum_i (I_i^x I_{i+x}^x + I_i^y I_{i+y}^y - I_i^z), \quad (7)$$

contains, in addition, the linear term ($\propto I^z$), which plays the role of an “orbital field” and immediately gives the canted state with $\theta = \pm\frac{\pi}{3}$. Since these two neighboring orbitals do not overlap, the Hund’s rule coupling [the last term in Eq. (3)] results in the FM exchange between the spins of the holes, in agreement with experiments. For MHI we get from Eq. (3) a different ground state: ferro-orbital ordering with $I^z = -\frac{1}{2}(d_{x^2-y^2}$ orbitals) occupied on all sites and AFM spin ordering. Previously, the KK model was successfully used to predict the orbital structure of that compound [10], *assuming* that spins order ferromagnetically, but as we mentioned above, such a state is not the ground state of the KK model.

In layered perovskites with one e_g electron per TM ion the electron exchange interaction favors the $d_{x^2-y^2}$ -ferro-orbital ordering both for CTI and MHI, in disagreement with the ferro-orbital ordering of the $d_{3z^2-r^2}$ type found in LaSrMnO₄ [11]. The observed elongation of oxygen octahedra in the z direction (transverse to the MnO₂ layers) can, however, be a steric effect, which in the layered systems gives rise to an additional term $H' = -\lambda \sum_i I_i^z$ in the orbital Hamiltonian.

In CTI with a cubic perovskite structure orbital interactions for both one hole and one electron per TM site [Eqs. (4) and (5)] have the same form as the lattice-mediated interaction Eq. (6):

$$H_T = \frac{2t_{pd}^4}{\Delta^2} \left(\frac{1}{\Delta} + \frac{1}{U_d} \right) \sum_i (I_i^x I_{i+x}^x + I_i^y I_{i+y}^y + I_i^z I_{i+z}^z), \quad (8)$$

making it difficult to infer the relative importance of these two mechanisms from an orbital ordering. Moreover, since the ordering in the model Eq. (8) is frustrated, in realistic materials it can be influenced by a number of (weaker) interactions and frustration-lifting mechanisms [12,13]. An indirect argument in favor of importance of the exchange interactions in the cubic perovskites KCuF₃ and LaMnO₃ comes from recent LDA + U calculations, which give the correct orbital and magnetic ordering for an undistorted lattice [14].

In conclusion, we showed that the description and properties of orbital ordering in charge transfer insulators are much different from those in Mott-Hubbard insulators. In particular, even in perovskite CTI with the 180°-exchange path orbital interactions are stronger than the spin exchange, so that an orbital ordering, in general, occurs at higher temperatures. In this respect the mechanism of orbital ordering in CTI is similar (but not identical) to the ordering due to the electron-phonon interaction. Another difference between MHI and CTI is that the electron-hole symmetry in the latter is lost, so that orbital and magnetic orderings in materials with one-electron and one hole per TM site are in general different. The effective orbital Hamiltonian for CTI allows us to describe the ordering in a number of such materials, without invoking any extra factors. Most importantly, in orbitally degenerate insulators not only the excitation spectrum but also *the very type of the ground state* may be different in Mott-Hubbard and charge transfer regimes, in contrast to the nondegenerate case, in which it is the same.

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