



# Orbital physics in transition-metal oxides from first-principles



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## ABSTRACT

Transition-metal oxides often possess charge, spin, and orbital degrees of freedom, and they are a platform for many functional materials. It is the interplay among those degrees of freedom which gives rise to the diverse properties, typically associated with the orbital physics. In this article, we will provide an overview of our first-principles studies on the orbital physics in transition-metal oxides, which include (1) orbital ordering in the layered manganite  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$  due to an anisotropic crystal field, (2) orbital ordering in the ferromagnetic insulator  $\text{Cs}_2\text{AgF}_4$ , (3) spin–orbital state transition and varying electronic and magnetic properties in the cobaltate series  $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ , and (4) spin–orbit coupling and Ising magnetism in  $\text{Ca}_3\text{Co}_2\text{O}_6$ ,  $\text{Ca}_3\text{CoMnO}_6$ , and  $\text{Sr}_3\text{NiIrO}_6$ . Apparently, orbital physics spans 3d–4d–5d transition-metal oxides.

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## 1. Introduction

Transition-metal oxides (TMOs) are a great platform for functional materials, and they are a strongly correlated electron system. The charge, spin and orbital states of the TM atoms are often coupled to one another due to their multiple degrees of freedom and the electron correlation. These states are closely related to diverse material properties and functionalities, e.g., charge ordering, orbital ordering, spin-state and magnetic transitions, metal–insulator transition, superconductivity, colossal magnetoresistance, and multiferroicity. It is therefore very important to study those charge–spin–orbital states and their fascinating coupling for modeling and understanding of the abundant properties. This has formed a research stream in condensed matter physics over past decades, and orbital physics has been termed [1,2].

Orbital physics has been extensively studied for 3d TMOs and some 4d ones like ruthenates. For example,  $\text{LaTiO}_3$  was studied for its spin dynamics and possible orbital liquid state [3–5].  $\text{VO}_2$  was proposed to be an orbital-assisted metal–insulator transition system where electron correlation and spin–Peierls distortion are both effective [6].  $\text{LaMnO}_3$  is a model system of the  $e_g$  orbital ordering. The Verwey transition of  $\text{Fe}_3\text{O}_4$  (insulator-to-metal transition) is associated with melting of a complex charge–orbital order.  $\text{LaCoO}_3$  has a thermally excited spin–orbital state transition,

which may be a low-spin to high-spin type [7].  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  is an orbitally selective insulator–metal transition system [8,9]. Very recently, research interest has been extended to 5d TMOs, which probably possess a significant spin–orbit coupling and provide an avenue to novel magnetic and electronic properties due to an entangled spin–orbital state [10,11].

In this paper, we will summarize our first-principles studies on the orbital physics. We will address (1) the type of orbital order in the layered manganite  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$  and its origin, (2) orbital ordering in the ferromagnetic (FM) insulator  $\text{Cs}_2\text{AgF}_4$ , (3) spin–orbital state transitions and exotic electronic/magnetic properties of  $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ , and (4) spin–orbit coupling and significant Ising magnetism in  $\text{Ca}_3\text{Co}_2\text{O}_6$ ,  $\text{Ca}_3\text{CoMnO}_6$ , and  $\text{Sr}_3\text{NiIrO}_6$ . Apparently, orbital physics spans the 3d–4d–5d TMOs and it is quite common.

## 2. Results and discussion

### 2.1. Orbital ordering in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$

Manganites are well known for their colossal magnetoresistance effect, which arises from a competition between a FM metallic state due to a double exchange, and an antiferromagnetic (AF) insulating state associated with charge–orbital ordering. Layered manganite  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$  is one of the prototype charge–orbital ordered systems, and the pattern of its orbital ordering was subject to a debate: either the cross-type  $x^2 - z^2/y^2 - z^2$  or the rod-like  $3x^2 - r^2/3y^2 - r^2$  orbital ordering was proposed. An orbital ordering can have an electronic origin, e.g., via a superexchange interaction of Kugel–Khomskii model [12], or its occurrence is due to a

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common Jahn–Teller (JT) distortion, namely, an electron–phonon coupling [13]. Even if an orbital ordering is of an electronic origin, a local lattice distortion (JT like) would always follow. Then, it is not a straightforward task to identify the origin of an orbital order.

Fortunately, normally there is a one-to-one correspondence between the orbital ordering pattern and the local distortion. Taking a transition metal with a half-filled  $e_g$  orbital in a  $\text{TMO}_6$  octahedron as example (such as  $\text{Mn}^{3+}$ ), the rod-like  $3z^2 - r^2$  orbital is stabilized (destabilized) if the octahedron is uniaxially elongated (compressed). Therefore, it seems reasonable that  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$  has a cross-type  $x^2 - z^2/y^2 - z^2$  orbital order as the manganite has compressed Mn–O bonds which alternate in the  $\text{MnO}_6$  octahedra along the  $y$  and  $x$  directions [14], see Fig. 1(a).

However, it was a surprise that recently we have identified the orbital order to be the rod-like  $3x^2 - r^2/3y^2 - r^2$  [15], in sharp contrast to the prediction based on the local lattice distortions. Using the most recent neutron diffraction data [14], our first-principles calculations find that while the  $x^2 - z^2$  is not at all an occupied eigen orbital for the nominal  $\text{Mn}^{3+}$  ion, the  $3x^2 - r^2$  is an occupied eigen orbital instead and it has a lower crystal-field level than the  $x^2 - z^2$  by 90 meV, see Fig. 1(b). This finding is contrary to the common view that the crystal-field level sequence and orbital state can be determined by the local distortions. Our finding is rationalized by taking into account the fact that a crystal field is a long range effect and in a layered (or chain like) material, anisotropic long-range part of the crystal field (beyond the local Jahn–Teller effect) could play a leading role in determining the level sequence. By referring to the experimental structural data [14], we find that the further neighbors of the  $\text{Mn}^{3+}$  ion are very different between

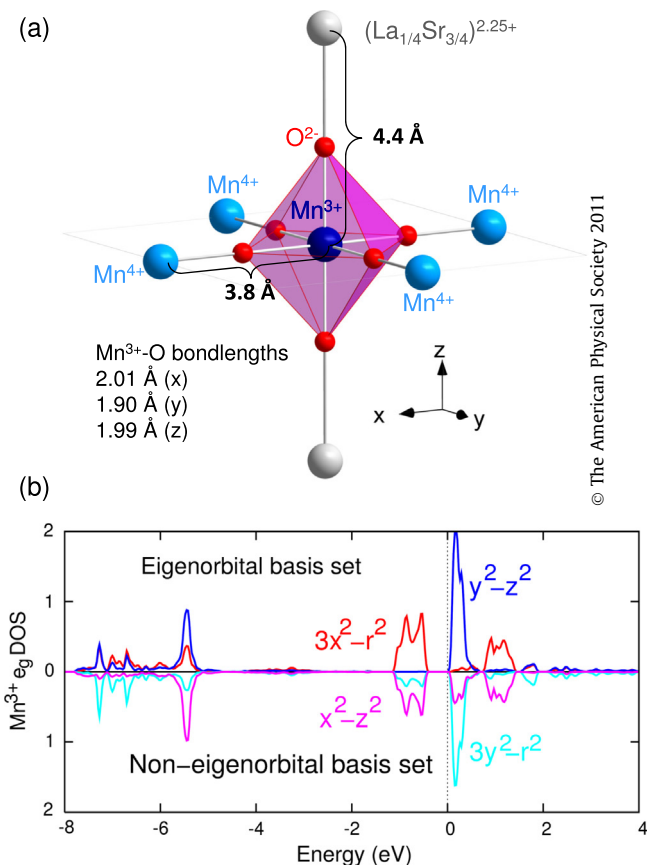
the in-plane and the out-of-plane. It is the stronger in-plane attractive interactions [higher valence states ( $4+$  vs  $2.25+$ ) and shorter distances ( $3.8 \text{ \AA}$  vs  $4.4 \text{ \AA}$ )], in addition to the local JT effect, which stabilizes the  $3x^2 - r^2/3y^2 - r^2$  orbital order, see Fig. 2. This orbital order naturally explains, via the Goodenough–Kanamori–Anderson (GKA) superexchange rules, the experimental AF structure of the CE type. The present orbital order pattern had been confirmed by an X-ray adsorption linear dichroism study [15].

Therefore, this work has demonstrated that the standard way—finding the orbital occupation of JT ions using the local distortion data—can be incorrect. For the layered materials (or more generally, for anisotropic ones), the usually ignored long-range crystal field effect and anisotropic hopping integrals could become crucial in determining the orbital occupation and the orbital order. Indeed, this anisotropic long-range crystal field effect has also been highlighted in other layered or chain-like materials [16], for understanding their intriguing orbital physics.

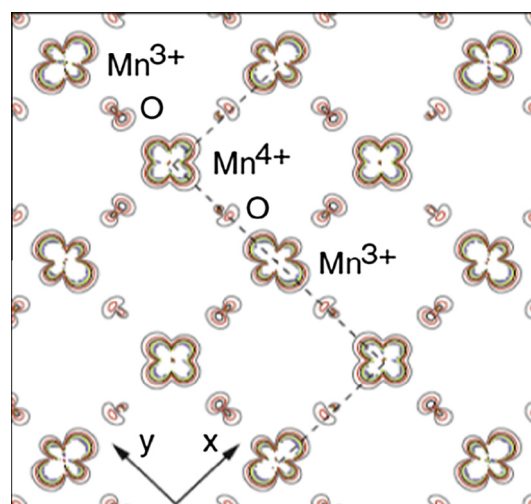
## 2.2. Orbital ordering in the ferromagnetic insulator $\text{Cs}_2\text{AgF}_4$

It is quite often that 3d TMOs with orbital degeneracy display an orbital ordering associated with lattice distortions (of the Jahn–Teller type). In contrast, 4d or 5d TMOs rarely show this, mainly due to the delocalized character of their 4d or 5d valence electrons. It is therefore a surprise when 4d or 5d TMOs show an orbital order. In this respect, the layered silver fluoride  $\text{Cs}_2\text{AgF}_4$  was of concern [17]. It has the same  $\text{K}_2\text{NiF}_4$  structure as the cuprate  $\text{La}_2\text{CuO}_4$ . While  $\text{La}_2\text{CuO}_4$  is a well known AF Mott insulator,  $\text{Cs}_2\text{AgF}_4$  is a FM insulator.

As an itinerant magnetism of the Ag 4d electrons is not the case for this insulator, what is the origin of the FM order? By referring to the orthorhombic structure of  $\text{Cs}_2\text{AgF}_4$  with the in-plane Ag–F bonds alternately elongated along the  $x$  and  $y$  axes, one could infer a  $y^2 - z^2/x^2 - z^2$  orbital order for the single holes on the  $\text{Ag}^{2+}$  ions ( $4d^9$ ), simply using the crystal field level diagram. The experimentally observed lattice distortion of the  $\text{AgF}_6$  octahedra (here defined as the Ag–F bond length difference of  $0.33 \text{ \AA}$ ) was well reproduced by our density functional calculations [18] (giving the value of  $0.30 \text{ \AA}$ ) within the generalized gradient approximation. This big distortion yields an  $e_g$  crystal-field splitting of about 1 eV. The lower  $3x^2 - r^2$  orbital is doubly occupied, and the higher  $y^2 - z^2$  orbital is singly occupied and its exchange splitting of about 0.5 eV opens an insulating gap. The spin density is plotted in Fig. 3, and the  $y^2 - z^2/x^2 - z^2$  orbital order is apparent. As the



**Fig. 1.** (a) Local structure of the nominal  $\text{Mn}^{3+}$  ion in  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ , and (b) density of states (DOS) of the  $\text{Mn}^{3+}$   $e_g$  orbitals projected onto the  $(3x^2 - r^2, y^2 - z^2)$  basis set or onto  $(x^2 - z^2, 3y^2 - r^2)$ . Fermi level is set at zero. [Reproduced from Ref. [15]].



**Fig. 2.** In-plane orbital ordering pattern in  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ .

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