Charge disproportionation in transition metal oxides
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Chapter 5

Charge transfer in perovskites

Abstract

The procedure that analyzes the N-electron wave function obtained in embedded cluster calculations in valence bond terms such as ligand-to-metal charge transfer, double transfer and non charge transfer determinants, is applied to explain the existence or absence of Jahn-Teller distortions in LaMnO$_3$, CaMnO$_3$ and CaFeO$_3$. We find that the ground state of LaMnO$_3$ is dominated by non charge transfer configurations, whereas the charge transfer configurations dominate the ground state wave function in the other two perovskites.

5.1 Introduction

This chapter presents the application of the simple procedure presented in Section 2.5 to translate the quantum chemical results in concepts common to solid-state physics for LaMnO$_3$, CaFeO$_3$ and CaMnO$_3$ crystals. The electronic structure of ionic transition metal compounds with strong electron correlation effects is intensively studied by solid-state scientists as well as quantum chemists. In solid-state physics and chemistry the electronic structure is most often described in terms of atom-centered orbitals, enabling an interpretation of the wave functions in Valence Bond (VB) terms, such as ionic and covalent structures and charge transfer (CT) between different sites. On the other hand, quantum chemistry commonly makes use of optimized orbitals, which normally have important contributions from different centers. Consequently, in quantum chemical approaches the
importance of CT between different centers is not easily recognized in the $N$-electron wave function.

We investigate the importance of CT configurations for the presence or absence of distortions of the TMO$_6$ octahedra found in LaMnO$_3$, CaMnO$_3$ and CaFeO$_3$. The first compound has strongly distorted octahedra with three different metal–oxygen distances. [125, 131] CaMnO$_3$ and CaFeO$_3$ show important tilting effects of the octahedra, but the TM–O distances are equal. [4, 132] The ionic model predicts LaMnO$_3$ as well as CaFeO$_3$ to have a transition metal 3d$^4$ configuration and hence to be susceptible to Jahn-Teller distortions. The high formal charges of the metals in these three perovskites (Mn$^{3+,4+}$, Fe$^{4+}$) put serious doubts on the applicability of the ionic model as starting point for the study of the electronic structure of these materials. The computational scheme applied in this study employs the embedded cluster approximation and provides a balanced, unbiased description of all important electronic configurations.

5.2 Details of calculations

The embedded cluster approximation is used to represent the materials. The crystal is divided into a cluster and an outer region. In the present study the clusters comprise one transition metal and its six oxygen neighbors as performed in previous Chapters. The ionic model is used to assign electrons to the ions present in the cluster. All cluster electrons are treated quantum mechanically, using the CASSCF approximation outlined in Chapter 2. The outer region provides an appropriate representation for the rest of the crystal. The Coulomb and exchange interactions between the cluster electrons and those of the nearest ions in the crystal surrounding are represented by $\textit{ab initio}$ embedding model potentials (AIEMP’s) centered at these nearest ions. The electrostatic interactions of crystal ions further away from the cluster are represented by a large but limited set of point charges at lattice positions around the cluster. The value of the charges is optimized to accurately reproduce the Madelung potential (of the ionic crystal) on a fine grid in the whole cluster region.
The choice for a CAS expansion of the wave function implies the inclusion of highly excited configurations, which in general turn out to have negligible coefficients in the wave function expansion. The choice for a CAS expansion has, however, important advantages over a selected CSF expansion of the wave function. One advantage is that the orbital rotations among different active orbitals do not affect the energy of the system.

In this Chapter, we discuss simple two-by-two rotations of selected pairs of active orbitals as described in Section 2.5. We used the following material model: [TM O₆]²⁻-TM₆O₂₄A₈ for LaMnO₃ (x=9, A=La), CaMnO₃ (x=8, A=Ca) and CaFeO₃ (x=9, A=Ca). The cluster is in brackets, the other ions are represented by AIEMP’s. The AIEMP’s for all systems were developed in the course of this study following the procedure described in Ref. [45]. The high formal cluster charge is stabilized by the Madelung potential represented by a set of optimized point charges.

The basis set used to expand the one-electron orbitals is of atomic natural orbital (ANO) type. A primitive set of (21s,15p,10d,6f) functions centered on the TM centers is contracted to a (6s,5p,4d,2f) basis set. [77] For the oxygen centered basis functions, we apply a (14s,9p,4d) primitive set contracted to (4s,3p,2d) basis functions. [78] In addition, we add (1s,1p) orthogonalization functions on the model potentials that represent TM ions in the cluster surrounding. These orthogonalization functions enable approximate strong-orthogonality between cluster electrons and electrons represented by AIEMP’s. [79]

For most of the calculations we used the same active space as presented before, which is formed by twelve orbitals and 4+n electrons. n is the number of d-electrons associated to the TM in the ionic model. The number of active electrons is equal to 8 for CaFeO₃ (Fe⁴⁺-3d⁴), LaMnO₃ (Mn³⁺-3d⁴) and to 7 for CaMnO₃ (Mn⁴⁺-3d³). The twelve active orbitals include the mainly O-2p orbitals of e₉ character, formally doubly occupied in the ionic model, the five mainly TM-3d orbitals and five metal centered orbitals of the same symmetry character as the 3d-orbitals with an extra radial node, the so-called 3d' orbitals. [80] An active space without TM-3d' orbitals largely underestimates the importance of the charge transfer excitations, since these excitations can only become important when the wave function is flexible enough to account for the orbital relaxations that accompany
charge transfer excitations in the CI expansion. Accounting for these relaxations requires at least the inclusion of ligand-2$p$ to TM-$3d$ replacements, coupled with single replacements to orbitals that are not occupied in the leading configuration [33,81–83].

Although in $O_h$ symmetry the TM-$3d$ ($t_{2g}$) orbitals interact only weakly with ligand orbital combinations of $t_{2g}$ symmetry, the calculations on CaMnO$_3$ were repeated with a larger active space, including not only the (mainly) O-$2p$ orbitals of $e_g$ character but also those of $t_{2g}$ character, in order to investigate the effect of excitations from mainly O-$2p$ orbitals of $t_{2g}$ symmetry.

The orbitals were optimized for an average of states. For LaMnO$_3$ and CaFeO$_3$, we considered the two lowest quintet states corresponding to the two components of the $5E_g$ ($d^4$) state of an undistorted octahedron. In the case of CaMnO$_3$, we considered not only the $4A_{2g}$ but also the excited $4T_{2g}$ state in the orbital optimization. This ensures that all five TM-$3d$ orbitals have an average natural occupation different from zero, avoids convergence problems associated to the correlating TM-$3d^r$ orbitals and allows us to use the same number of active orbitals in all the systems studied here. The analysis of the wave function was done with root specific natural orbitals, namely those of the ground state. State specific orbital optimization performed for LaMnO$_3$ gives virtually identical results. All calculations performed for this study were done with the MOLCAS program suite developed in Lund by Roos and co-workers [116].

5.3 Jahn-Teller distortions in LaMnO$_3$, CaMnO$_3$ and CaFeO$_3$

The observation of phenomena as the superconductivity in cuprates and ruthenates, colossal magnetoresistance in manganites and charge ordering in many different perovskites, placed the transition metal perovskites at the center of present investigations in condensed matter physics. The coupling of the electronic structure to lattice deformations is an essential ingredient in the theoretical description of these phenomena [133]. Lattice defor-
5.3. Jahn-Teller distortions in $\text{LaMnO}_3$, $\text{CaMnO}_3$ and $\text{CaFeO}_3$

Table 5.1: Formal charge and number of TM-$d$ electrons ($n_d$) in the three perovskites considered. The prediction based on the ionic model for the local geometry around the TM is also given and compared to experimental findings.

<table>
<thead>
<tr>
<th>Material</th>
<th>Formal Charge</th>
<th>$n_d$</th>
<th>Ionic Model</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{LaMnO}_3$</td>
<td>+3</td>
<td>4</td>
<td>JT distortion</td>
<td>JT distortion</td>
</tr>
<tr>
<td>$\text{CaMnO}_3$</td>
<td>+4</td>
<td>3</td>
<td>octahedral</td>
<td>octahedral</td>
</tr>
<tr>
<td>$\text{CaFeO}_3$</td>
<td>+4</td>
<td>4</td>
<td>JT distortion</td>
<td>octahedral</td>
</tr>
</tbody>
</table>

Dynamations can either be dynamical in the form of polarons or static in the form of collective Jahn-Teller type distortions. The description of Jahn-Teller distortions around impurities in ionic solids with embedded cluster models has shown to be very versatile leading to a detailed understanding of the interplay between the electronic structure and the deformations around the impurity \cite{29, 134}. Here, we approach the problem of Jahn-Teller distortions in three different perovskites from a local point of view. The central question is whether the appearance or absence of static distortions can be understood with the analysis of the wave function in terms of optimal atomic-like orbitals as presented in previous chapters.

For the simple cubic oxides, NiO and MnO, treated in Section 2.5, the ionic model gives a reasonable starting point for the interpretation of the electronic structure. Nevertheless, important additional contributions appear in the wave function even for MnO, which has been considered as a prototype ionic material in many cases. In NiO and MnO the deviations from the ionic model can be caught quite well in the form of small orbital changes that occur in the CASSCF orbital optimization. Even with a small active space of five TM-$3d$ orbitals a reasonable representation of the charge distribution is obtained. Increase of the active space with the five $3d'$ correlating orbitals and the occupied O-$2p$ ($e_g$) orbitals does not change the electron distribution significantly, because CT configurations are not very important. On the other hand, the validity of the ionic model as starting point for the three distorted perovskite structures considered here is doubtful, because the model predicts high formal charges on the TM-sites. These charges constitute a large attractive potential for the electrons associated with the O$^{2-}$ ligands and CT or screening effects are expected to be quite important.
Table 5.2: Schematic representation of the wave function expansion expressed in natural and optimal atomic-like orbitals for LaMnO$_3$, CaMnO$_3$ and CaFeO$_3$. The weights of the different contributions are given in %

<table>
<thead>
<tr>
<th>material</th>
<th>MO-set</th>
<th>NCT</th>
<th>CT</th>
<th>DCT</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaMnO$_3$</td>
<td>natural</td>
<td>98.0</td>
<td>0.9</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>atomic</td>
<td>58.0</td>
<td>38.8</td>
<td>3.2</td>
</tr>
<tr>
<td>CaMnO$_3$</td>
<td>natural</td>
<td>96.3</td>
<td>2.0</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>atomic</td>
<td>20.9</td>
<td>55.9</td>
<td>20.4</td>
</tr>
<tr>
<td>CaFeO$_3$</td>
<td>natural</td>
<td>85.5</td>
<td>7.2</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>atomic</td>
<td>18.1</td>
<td>66.1</td>
<td>13.6</td>
</tr>
</tbody>
</table>

5.3.1 LaMnO$_3$

One-electron band structure calculations on the undoped compound LaMnO$_3$ show that the top of the valence band is a strong mixture of Mn-3$d$ and O-2$p$ states [30, 135, 136]. Although the top of the valence band can, of course, not directly be compared to the lowest $N$-electron state of an embedded cluster representing LaMnO$_3$, it is to be expected that the cluster calculation reflects this mixing by important covalent contributions to the wave function. Similar to the observations made for MnO and NiO, we find that the ground state CASSCF wave function has practically all its covalent interactions concentrated in the molecular orbitals. Firstly, there is one type of CSF that dominates the CI expansion, see first row of Table 5.2. Secondly, the Mulliken populations of the active orbitals indeed show some degree of mixing between the 2$p$ basis functions centered at the oxygens and the Mn-3$d$ basis functions (see Table 5.3). The $t^*_{2g}$ active orbitals are all occupied with one electron and highly localized on the Mn-ion. For LaMnO$_3$ they are not further considered in the analysis of the electronic structure, but we will discuss excitations amongst orbitals of $t^*_{2g}$ symmetry in some detail for CaMnO$_3$.

The leading determinant of the CASSCF wave function expressed in natural orbitals is $|\text{core} \ e^4_g \ t^*_{2g} \ e^{*1}_g|$. Following the character of the orbitals given in Table 5.3, this leading determinant corresponds (approximately) to the Mn-3$d^4$ (or NCT) configuration. The Mn-3$d^4$ ion in a weak octahedral crystal field has $^5E_g$ symmetry and is hence Jahn-Teller active.
Table 5.3: Mulliken population analysis (in %) and occupation number \( n \) of the natural \( e_g \)-like active orbitals in the ground state wave functions of the embedded TMO\(_6\) clusters representing LaMnO\(_3\), CaMnO\(_3\) and CaFeO\(_3\).

<table>
<thead>
<tr>
<th>Orbital</th>
<th>LaMnO(_3)</th>
<th>CaMnO(_3)</th>
<th>CaFeO(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n )</td>
<td>Mn-3d</td>
<td>O-2p</td>
</tr>
<tr>
<td>( e_g )</td>
<td>1.996</td>
<td>9.0</td>
<td>92.2</td>
</tr>
<tr>
<td></td>
<td>1.971</td>
<td>15.6</td>
<td>87.8</td>
</tr>
<tr>
<td>( e_g^* )</td>
<td>1.000</td>
<td>86.0</td>
<td>13.8</td>
</tr>
<tr>
<td></td>
<td>0.029</td>
<td>89.9</td>
<td>9.8</td>
</tr>
</tbody>
</table>

The dominant character of the NCT configuration is in agreement with the large distortion experimentally found in LaMnO\(_3\). On the other hand, the present representation of the electron distribution does not clearly reflect the strong mixture of O-2\(p\) and Mn-3\(d\) found in the one-electron valence band. A more transparent analysis of the charge distribution can be made after the transformation to optimal atomic-like orbitals. The covalent interactions disappear from the orbitals and are transferred to the CI expansion of the wave function. Consequently, the weight of the NCT configuration with 4 Mn-3\(d\) electrons is strongly reduced, but it remains dominant, which makes the appearance of Jahn-Teller distortions in LaMnO\(_3\) not unlikely. The importance of CT interactions is evident. The sum of all possible CT configurations gives 38.8%. Even DCT configurations show up with significant weights in the wave function. The number of Mn-3\(d\) electrons is easily extracted from the wave function expressed in atomic orbitals.

5.3.2 CaMnO\(_3\)

The formal charge of Mn in CaMnO\(_3\) is 4+, leading to a Mn 3\(d^3\) 4\(A_2g\) ground state. The higher formal Mn charge compared to LaMnO\(_3\) makes it not unexpected that the contribution of covalent interactions to the Mn–O bond increases with respect to the previous compound. The natural orbitals show a rather large mixing, the two orbitals \( e_g \) now have 30% contribution from the Mn-3\(d\) centered basis functions. There is also a stronger mixing in the \( e_g^* \) orbitals, but this is less relevant since these orbitals are practically empty in the
5. Charge transfer in perovskites

The transformation to atomic orbitals has dramatic consequences for the interpretation of the wave function. The weight of the NCT configuration is only 20% and CT configurations dominate the wave function. Furthermore, we observe that the DCT configurations are as important as the NCT configurations. The calculated number of Mn-3d electrons is far away from the formal d³ situation predicted by the ionic model. The dominance of the CT configuration leads to 3.88 d-electrons for Mn in CaMnO₃.

The high formal charge of Mn in CaMnO₃ may give rise to CT not only from O-2p \( e_g \) orbitals, but also to CT from O-2p orbitals of \( t_{2g} \) symmetry. Although the Mn-3d O-2p interaction is much smaller, the active \( t^*_{2g} \) orbitals are essentially non-bonding 3d orbitals and the inactive \( t_{2g} \) orbitals are essentially O-2p orbitals that are non-bonding (with respect to Mn–O bonding), some effect of O-2p to Mn-3d excitations within \( t_{2g} \) symmetry may be expected [118]. To investigate this, we repeated the CASSCF calculations with a larger active space that also includes the bonding \( t_{2g} \) orbitals. The effect on the total energy is, contrary to MnO, significant: the energy lowering is 1.7 eV. The weight of the NCT configuration decreases slightly, to 17.1%, and the weight of CT configurations is 53.5 %, of which 46.3% is associated with transfer from \( e_g \) and 7.1% is associated with transfer from \( t^*_{2g} \) orbitals to Mn-3d.

Having established that Mn in CaMnO₃ is closer to a Mn-3d⁴ ion than to the ionic assumption of Mn-3d³, the question should be answered why this ion is not Jahn-Teller active, or in other words, why the ground state has \( A_{2g} \) symmetry and not \( E_g \) as for other d⁴ systems. The key to the answer lies in the interaction between the NCT and CT determinants. In \( O_h \) terminology and expressed in the atomic orbitals, the lowest CT CSF’s are characterized by the \([O-2p (e^3_g) \text{ Mn-3d} (e^{11}_g) \text{ Mn-3d} (t^{3}_{2g})]\) electronic configuration, coupled to \( E_g \otimes E_g \otimes A_{2g} = A_{1g}, A_{2g}, E_g \) spatial symmetry. It is, however, only the \( ^4A_{2g} \) CSF that interacts with the lowest NCT CSF, which has \( ^4A_{2g} \) symmetry. This interaction between CT and NCT CSF’s will make the \( ^4A_{2g} \) state the lowest N-electron state in the cluster. This ground state, although dominated by a Mn-3d⁴L⁻¹ configuration, is not Jahn-Teller active in agreement with experiment.
5.3.3 CaFeO₃

The ground state of a TM-3d⁴ ion in a not too strong octahedral ligand field is ⁵E₉. The tilting and rotation of the FeO₆ units in the high temperature phase of CaFeO₃ reduce the Fe site symmetry to C₁. The distortions of the Fe–O distances are however so small that the lowest two quintet states of the cluster (a, b⁵A₂) are still almost degenerate. The CASSCF energies of the two states differ by less than 0.05 eV and the inclusion of dynamical electron correlation effects does not increase the splitting between the two quintet states.

As reported in Chapter 4, the analysis of the wave function gives a rather similar picture as for CaMnO₃. The natural orbitals are 30/70 mixtures of O and Fe and the CI expansion of the wave function in these orbitals is strongly dominated by the configurations with double occupied e_g orbitals. Because of the dominant oxygen character orbitals these configurations could be labeled as NCT, but this leads to an incorrect picture of the electronic structure. The wave function expressed in optimal atomic orbitals is dominated by the CT (Fe-3d⁵L⁻¹) configuration and has smaller contributions from the NCT and DCT configurations, see Table 5.2. The remainder is due to TCT configurations and configurations with weights smaller than 0.01%.

The calculated number of Fe-3d electrons is 4.85. Consequently, the iron ions in the high temperature phase of CaFeO₃ are best described as Fe³⁺ with 5 d-electrons. These ions are not Jahn-Teller active. We should however also account for the possible distortions due to the hole in the oxygen orbitals. In the leading determinant of the ground state wave function, there are three electrons in e_g orbitals, which are e_g-like linear combinations of O-2p basis functions. Such electronic configuration can in principle be Jahn-Teller active. Recently Garcia-Lastra and collaborators presented an appealing way to interpret Jahn-Teller distortions in terms of forces acting on the ligands by the charge distribution on the central ion [137]. Applying this concept to the present case, it is easily seen that the hole on the oxygens bridging two Fe-3d⁵ ions exerts a symmetric force and no Jahn-Teller distortion is expected.
Figure 5.1: Oxygen displacements in the ab plane as observed in LaMnO$_3$. Mn ions (not shown) are situated at the crossing points of the grey lines. This collective distortion leads to two short and two long TM–O distances in the ab plane. The TM–O distance along the c-axis is not affected. The inset shows the oxygen displacements in the TMO$_6$ cluster considered in the computational experiment.

5.3.4 Cluster energy versus Jahn-Teller distortion

To further explore the possibilities of the cluster model approach to predict Jahn-Teller distortions in perovskites, we performed a computational experiment. Starting from a cluster with equal TM–O distances in the ab-plane, we gradually switch on the Jahn-Teller distortion by moving two oxygens inward and two oxygens outward (see Fig. 5.1). The TM–O distance in the c-direction is maintained at the experimental value and the initial TM–O distances in the ab-plane are taken as the average of the corresponding experimental distances. This distortion mimics the collective movement of the oxygens in the ab-plane observed in LaMnO$_3$. Figure 5.2 depicts the results of this series of calculations. The total CASPT2 energy in the undistorted cluster is taken as zero of energy and the index on the x-axis is defined as the difference of the long and short TM–O bonds divided by the sum of them. We opt here for CASPT2 calculation in order to obtain as accurate as possible relative energies.

The continuous increase of the energy with the Jahn-Teller distortion for CaMnO$_3$
Figure 5.2: Relative CASPT2 energy of the ground state wave function as function of the distortion in embedded TMO₆ cluster representing LaMnO₃ (squares and triangles), CaMnO₃ (circles), and CaFeO₃ (diamonds). The lines are a guide to the eye. The dotted lines represent the CASSCF relative energies.

(circles) confirms the tendency toward a perfect octahedral oxygen coordination of Mn in this compound. The situation is quite different for LaMnO₃. We first discuss the curve with the squares, which corresponds to a MnO₆ cluster embedded in model potentials and point charges at the experimental lattice positions. The cluster energy is strongly reduced by applying the Jahn-Teller distortion and a minimum is observed at approximately 4.5%. The long and short Mn–O distances of 2.13 Å and 1.95 Å are not more than 0.05 Å shorter than the experimental distances. It can, however, be argued that the distortion is not solely caused by the coupling of the local electronic charge distribution with the lattice but induced by the embedding based on the experimental LaMnO₃ structure with long and
short Mn–O distances in the \(ab\)-plane. We, therefore, repeated the same computational experiment but now with an embedding that only reflects the tilting of the MnO\(_6\) octahedra and not the Jahn-Teller distortion. Results are depicted by the curve with the triangles. Although the minimum is less deep and located at smaller Jahn-Teller distortion, we clearly observe a tendency toward Jahn-Teller distortion which now can only be ascribed to the coupling of the cluster charge distribution with the lattice. The fact that all collective effects are missing explains the shallowness of the curve. Finally, we observe a minimum at small distortions for CaFeO\(_3\) (diamonds). This weak tendency to deform the perfect octahedral oxygen coordination of Fe can be ascribed to the appearance of the Jahn-Teller active NCT determinant in the cluster wave function, cf. Table 5.2. Actually, the experimental X-ray structure reflects a small Jahn-Teller distortion of the FeO\(_6\) octahedron [4]. Raman spectroscopy measurements [15] confirm the existence of Jahn-Teller distortions in CaFeO\(_3\), which were also explained by the admixture of Fe\(^{4+}\)L configurations to the wave function.

5.4 Conclusions

The transformation of the commonly used natural orbitals to optimal atomic orbitals provides us a practical scheme to interpret the CASSCF wave function in terms of valence bond terms as NCT, CT and DCT configurations. It may be useful to remark that relative small mixing in the natural orbitals lead to rather large CT contributions to the wave function expressed in atomic orbitals. This means that the delocalization tails of the natural orbitals onto neighboring centers are a very efficient way to account for CT, DCT or even higher excitations. The disadvantage of expressing the wave function with these delocalized orbitals is the difficulty to quantify the relative importance of the different types of excitations.

The ionic model is too simple a starting point to explain the existence or absence of Jahn-Teller distortions in the here considered perovskites. The high formal charges of the TM ions induce large CT effects such that the CT configuration can become the leading
determinant in the wave function expansion.

The embedded cluster model gives of course only a partial view of Jahn-Teller distortions in perovskites. Only local distortions can be addressed and there is no account of the collective nature. The present analysis of the cluster wave function and the dependence of the ground state energy as function of the distortion still gives useful insights in terms of local electronic configurations which can be at the origin of the collective effects.