Charge disproportionation in transition metal oxides
Sadoc, Aymeric Gaël Jocelyn

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1.1 Scientific interest

Transition metal oxides form a large class of compounds that show intriguing and often technologically useful electronic and magnetic properties. Magnetic phenomena and temperature induced or pressure induced phase transitions are extensively studied in transition metal (TM) oxides, but full understanding and control of such properties of the materials has not yet been achieved. In general, the electron motion in these materials cannot be described correctly by simple quantum chemical one-electron theories such as the local density approximation (LDA) of density functional theory (DFT) or Hartree-Fock (HF) theory. This is due to the neglect of electron-electron correlation, which is especially important for electrons in the TM valence d shells. NiO constitutes one example where the simple LDA-DFT approximation fails to predict the insulating character. On the other hand HF theory predicts a fundamental gap that is much too large. The strong local electron correlation can explain the experimentally observed band gap. Materials with strong local electron correlation are sometimes denoted "strongly correlated materials".

The interplay between local distortions of the TM environment, magnetic and electric properties has not only been investigated with many different experimental techniques, but also computational studies play an important role in the elucidation of the physics of these materials. Although no computational method has been developed yet that can explain all the intriguing properties, the different schemes can give complementary in-
formation. The embedded cluster approach treating a small part of the crystal enables the use of configuration interaction (CI) methods, and hence, a rigorous way to describe the strong electron correlation effects. Band calculations realized in reciprocal space applying translational symmetry have until recently been limited to the use of one-electron models but give valuable descriptions of the limiting physical situations of what can be expected. Periodic Hartree-Fock tends to overestimate the localization of the electrons, while LDA leads to rather delocalized electrons. Hybrid density functionals that mix a certain amount of the Hartree-Fock exchange interaction with the DFT expression of this interaction interpolate between the two limiting situations. LDA+U recovers the electron correlation effects by extending the standard LDA scheme with a semi-empirical parameter that describes on-site electron repulsion. A new method has been recently presented by Stoyanova et al. for generating correlated many-electron bands for localized excited states, hole states and added-electron states in extended systems with strong electron correlation effects. The method allows for a rigorous treatment of the electronic response that accompanies excitation processes [1, 2].

1.2 Mixed valence compounds

Mixed valency is frequently associated with semiconducting or metallic properties and appears to be an essential feature of the copper oxide superconductors [3]. It can be defined as a co-existence of different oxidation states of an element in a molecule or crystal. A famous example is magnetite Fe$_3$O$_4$, known to be a natural magnet and assumed to contain Fe$^{2+}$ and Fe$^{3+}$ ions. In the spinel structure of Fe$_3$O$_4$, the Fe ions are stabilized in octahedral and tetrahedral environments, respectively. The two different oxidation states, i.e. charge states in the fully ionic model are often denoted Fe(II) for the Fe$^{2+}$ ions and Fe(III) for the Fe$^{3+}$ ions. The common oxidation states for Fe in crystals, Fe(II) with electron configuration $[1s^22s^22p^63s^23p^63d^n]$ n=6, d$^6$, and Fe(III) with n=5, d$^5$ result in different chemical bonding schemes. Fe(II) is in general more weakly bound to its ligands than Fe(III).
1.3 Perovskite oxides

On the other hand, it is often difficult to determine the electronic configuration of these TM ions, which determine most of the intriguing but unexplained physics. How are the electrons arranged around each metal site? How are they coupled between metal sites? What is the influence of temperature and pressure? What are the resulting electrical and magnetic properties?

The effective atomic charge of these ions is not a direct experimental observable and form a theoretical point of view various valid definitions are possible. Once proper definition has been chosen, effective charges can be investigated using quantum chemical tools. This dissertation discusses the definitions of the charge and gives some insight on perovskite oxide crystals. In the perovskite oxides type the TM ions are generally assumed to be in high oxidation states, e.g. Fe(IV) \((d^4)\) in CaFeO\(_3\) crystals and Ni(III) \((d^7)\) in YNiO\(_3\) crystals. In addition to this high valent character, it has been proposed that some perovskites undergo a charge disproportionation with decreasing temperature. The resulting oxidation states would lead to controversially highly valent TM ions such as Fe\(^{5+}\) \((d^3)\) in CaFeO\(_3\) [4].

1.3 Perovskite oxides

The general formula of perovskite oxides is ABO\(_3\), where A and B are cations of different sizes. X-ray and/or neutron diffraction studies establish that the B centers in the 3d-perovskites are coordinated by six ligands in a quasi-octahedral site. The idealized structure is cubic face centered (see Figure 1.1), but differences in ratio between the A and B cations can distort the structure in a number of ways, of which tilting is the most common one. Although the local site symmetry is usually lowered to C\(_i\) due to Jahn-Teller (JT) distortions and tilting of the BO\(_6\) octahedra, it is common practice to maintain the \(e_g\) and \(t_{2g}\) terminology to describe the TM-3d orbitals. This is also done in simple crystal field theory, which is treated in more detail in section 2.

The well-known JT effect distorts the lattice below a particular temperature in 3d perovskites with TM-3d\(^4\) \((t_{2g}^3 e_g^1)\), TM-3d\(^7\) \((t_{2g}^6 e_g^1)\) or TM-3d\(^9\) \((t_{2g}^6 e_g^3)\) electronic configurations.
1. General introduction

**Figure 1.1:** (a) ABO$_3$ crystal structure made of (b) a cubic lattice of A$^{n+}$ ions containing (c) [BO$_6$]$^{n-}$ octahedra

The lifting of the degeneracy of states of E$_g$ symmetry causes an energetically favorable distortion of the octahedron and can give rise to orbital ordering and complex magnetic coupling along the lattice. The partial substitution of the A ions by differently charged ions introduces electron holes in the TM–O octahedra and affects the electron distribution of the TM ions. The interplay between the charge, orbital and spin degrees of freedom is one of the central themes in current research on perovskite oxides. Many efforts are also devoted to the relation between the tilting of the BO$_6$ octahedra and the metal to insulator transition temperature ($T_{MI}$). The so-called charge disproportionation [4, 5] discussed in section 1.2 is a complementary interesting phenomenon found in some 3d perovskite oxides.

### 1.4 Experimental data

High-energy electron spectroscopies, and more recently resonant inelastic (hard and soft) x-ray scattering and neutron spectroscopy have been used to study the electronic and magnetic structure of strongly correlated materials. Spectral signatures seen by these techniques that are not explained by one-electron band theories are often related to strong electron correlation effects. The experimental spectra can be compared to predictions of
1.4. Experimental data

certain models or may be used to establish constraints to the parameter sets. Mössbauer spectroscopy can also give valuable information on these systems, but only for a limited number of TM ions among which the $^{57}$Fe Mössbauer spectroscopy is one of the most used.

1.4.1 X-ray diffraction

The crystalline structures can be investigated using x-ray and neutron diffraction. The use of a synchrotron source enables the determination of very accurate lattice parameters of the unit cell and the nucleus position of all heavy atoms. The unit cell can be defined as a region of space (see Fig. 1.2) that when repeated in three dimensions fills all space and reproduces the crystal structure. If one adds the information from neutron diffraction, which is more sensitive to lighter atoms like oxygens, the structure of the crystal can be determined with high accuracy. These data are used as input to model the motion of the electrons in a field of clamped nuclei, which corresponds to the Born-Oppenheimer approximation that is applied in this thesis.

Table 1.1: Bond distances in Å obtained from X-ray/neutron diffraction for $\text{LaMnO}_3$, $\text{CaFeO}_3$ and $\text{YNiO}_3$.

<table>
<thead>
<tr>
<th>Bond distances (Å)</th>
<th>$\text{LaMnO}_3$</th>
<th>$\text{CaFeO}_3$</th>
<th>$\text{YNiO}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>space group</td>
<td>$P_{bnm}$</td>
<td>$P_{bnm}$</td>
<td>$P_{2_1/n}$</td>
</tr>
<tr>
<td>TM–O$_{(x)}$</td>
<td>1.968</td>
<td>2.010</td>
<td>1.853</td>
</tr>
<tr>
<td></td>
<td>/ 1.997</td>
<td>/ 1.920</td>
<td>/ 1.927</td>
</tr>
<tr>
<td>TM–O$_{(y)}$</td>
<td>1.907</td>
<td>1.998</td>
<td>1.870</td>
</tr>
<tr>
<td></td>
<td>/ 1.971</td>
<td>/ 1.927</td>
<td>/ 2.014</td>
</tr>
<tr>
<td>TM–O$_{(z)}$</td>
<td>2.178</td>
<td>2.035</td>
<td>1.894</td>
</tr>
<tr>
<td></td>
<td>/ 1.953</td>
<td>/ 1.918</td>
<td>/ 2.018</td>
</tr>
</tbody>
</table>

Table 1.1 reports the TM–O distances in three different perovskite structures below and above their respective structural phase transition temperature (JT and CD). In the high temperature regime of each of the three perovskites the three TM–O distances in the crystal are almost equivalent, with a maximum difference of 0.059 Å. In $\text{LaMnO}_3$ at 300 K, the Mn–O distances are decreased in two directions x (-0.042 Å) and y (-0.091 Å) and increase along the z (0.143 Å) direction with respect to the high temperature phase.
Figure 1.2: Unit cell of an ABO$_3$ compound that crystallizes in the P$_{bnm}$ space group.

The distortion along x is in the order of temperature effect variations and also the same order as the distortions observed in the high temperature phase. But the decrease and increase along the y and z directions can be associated to Jahn-Teller distortions that are explained by particular electronic configurations. While in the LaMnO$_3$ crystal, the Mn–O distances effectively agree with a JT type distortion, the isoelectronic compound CaFeO$_3$ adopts a different type of local distortion. Using powder diffraction techniques, the room temperature and low temperature crystal structure of CaFeO$_3$ have been determined by Woodward et al. [4] and Takeda [6]. At 300 K the crystal structure is distorted from the ideal perovskite structure by tilting of the octahedra. Below 290 K two distinct Fe sites develop, lowering the symmetry. This corresponds to an expansion and a compression of the octahedra in the two different crystallographic sites (see Table 1.1). The same kind of distortion has been reported in RNiO$_3$ crystals (R = Ho, Y, Er and Lu) [7]. We focus in this dissertation on the YNiO$_3$ for which we also report the TM–O bond distances in Table 1.1.
1.4.2 Mössbauer spectroscopy

Fifty years ago, Rudolf L. Mössbauer discovered the "recoil free" nuclear resonance absorption of $\gamma$-rays, which is now known as the Mössbauer effect [8–10]. During emission or absorption of a $\gamma$-ray, a free nucleus recoils due to conservation of momentum, with a recoil energy ($E_R$). An analogy of the emission can be made with gun recoil when firing a bullet. As the nuclei are moving due to random thermal motion, the $\gamma$-ray energy has a spread of values $E_D$ explained by the Doppler effect. Mössbauer realized that the atoms within a solid matrix have a very large effective mass. The recoiling mass is now effectively the mass of the whole system, making $E_R$ and $E_D$ very small. If the $\gamma$-ray energy is small enough, the recoil of the nucleus is too low to be transmitted as a phonon (vibration in the crystal lattice) and so the whole system recoils, making the recoil energy practically zero: a "recoil-free" event. The resonant emission and absorption is used to probe the tiny hyperfine interactions between an atom’s nucleus and its environment.

This spectroscopic effect has been observed for about 100 nuclear transitions in some 80 nuclides in nearly fifty elements. Unfortunately, not all transitions are suitable for exploitation but the $^{57}\text{Fe}$ has become a very important tool to characterize this particular transition metal. Iron enters in the composition of many interesting materials in solid state science and also in several protein systems in chemistry and biochemistry.

The measurement of variations of the original $\gamma$-ray, which depends on nuclear and electronic properties, is achieved by the use of the Doppler effect. The energy levels in the absorbing nuclei can be modified by their environment in three main ways: by the Isomer Shift, Quadrupole Splitting and Magnetic Splitting. The energy changes caused by the hyperfine magnetic splitting due to Zeeman effect are very small, of the order of a $10^{-7}$ eV for $^{57}\text{Fe}$. The isomer shift is usually approximated by the following expression [11,12]:

$$\delta = E_A - E_S = \frac{4\pi}{5} Ze^2 S(Z) R^2 \left(\frac{\delta R}{R}\right) (\rho(0)^A - \rho(0)^S)$$ (1.1)

where $Z$ is the nuclear charge of the absorber ($Z=26$ for iron), $e$ is the elementary charge and $S(Z)$ the relativistic correction factor ($S(Z)=1.32$ for iron). $\delta R$ is equal to $(R_g - R_e)$
where $R_g$ and $R_e$ are the nuclear radii in the nuclear ground and excited state. Finally, $ho(0)$ is the electron density at the nucleus of the absorber A or the source S. If emitting and absorbing nuclei are in identical environments then the transition energies are identical and this produces a spectrum for which the absorption peak occurs at 0mm/s. The isomer shift depends mainly on the s-electron densities (as sum of all s-electron shells) of the absorber, but may be influenced indirectly via shielding effects of p-, d- and f-electrons, which are not capable (if neglecting relativistic effects) of penetrating the nuclear field.

Temperature dependence of the $^{57}$Fe Mössbauer spectrum of CaFeO$_3$ powder specimen at atmospheric pressure 0.1 MPa from 5 K to 300 K [13] showed that with decreasing temperature, the single line spectrum becomes a doublet below $\sim$ 200 K as shown in Figure 1.3. Isomer shift of each single line in the doublet is interpreted as showing the presence of Fe$^{3+}$ and Fe$^{5+}$ states suggesting a disproportionation reaction from Fe$^{4+}$ into Fe$^{3+}$ and Fe$^{5+}$ with the decreasing temperature ($T_{CD}=298$ K). Below 100K, the spectrum consists of two magnetically split sextets ($T_{Neel}=127$ K).

Moreover, high pressure Mössbauer spectroscopy [14] and XRD have demonstrated the existence of a first-order phase change at a critical pressure $P=30$ GPa from a high spin to low spin state at the Fe$^{4+}$ cations of CaFeO$_3$. The low spin phase represents a third electronic state in CaFeO$_3$.

An overview of the different magnetic phases is given in the pressure temperature magnetic phase diagram of CaFeO$_3$ reported by Nasu et al. [9] (see Figure 1.4). In CaFeO$_3$ the magnetic ordering temperature increases with the increase of pressure, but $T_{CD}$ does not show any significant change up to 17 GPa and is suddenly suppressed above 20 GPa.

### 1.4.3 Additional experimental information

Based on the presence of a specific mode in the Raman spectra Ghosh et al. [15] suggested that some JT distortion is present at room temperature in CaFeO$_3$, indicating the existence of a JT Fe$^{4+}$ ($d^4$) ionic state along with the non-JT Fe$^{3+}$ state ($d^5L^{-1}$ where $L^{-1}$ denotes a hole on the oxygens ligands).
1.4. Experimental data

**Figure 1.3**: Temperature dependence of the $^{57}$Fe Mössbauer spectrum of CaFeO$_3$ powder specimen at atmospheric pressure 0.1 MPa from 5 K to 300 K. [13]

The isoelectronic compound SrFeO$_3$ has an almost ideal perovskite crystal structure, the Fe–O–Fe angle = 180° compared to the 155° for CaFeO$_3$. This compound does not show any indication of CD by decreasing the temperature down to 4 K. [16] Only one iron site
Figure 1.4: Pressure-temperature (p, T) magnetic phase diagram for CaFeO$_3$. The low-pressure phases are a non-charge disproportionated paramagnetic phase (NCD P), a charge disproportionated paramagnetic phase (CD P) and a charge disproportionated antiferromagnetic phase (CD AF) depending on temperature and pressure. The high-pressure phase is a non-charge disproportionated, magnetically ordered phase (NCD MO). Each boundary determined by the experiments is shown as squares, triangles and circles. [14]

is observed among all temperature and pressure variations. Bocquet et al. [17] concluded from X-ray and UV photoemission spectroscopy that the ground state of SrFeO$_3$ consists of heavily mixed d$^4$ and d$^5$L$^{-1}$ states in agreement with more recent XAS measurements combined with semi-empirical cluster calculations [18]. These authors emphasize a ground state containing considerable O-2p hole character.
1.5 Outline

This dissertation presents the results from first principles quantum chemical electronic structure calculations on TM perovskite oxides and analyzes carefully the wave functions and their properties. Chapter 2 shortly describes the computational methods and gives a detailed description of the material models. The description of the crystal is realized with the embedded cluster approach. A small fragment of the crystal surrounded by a Madelung field is used to calculate some properties of the material. The size of the considered clusters and the choice made to approximate the exact wave function are discussed to estimate the influence on interpretations that are proposed. For comparison we also performed some calculations using a periodic approach and determined the density of states for these crystals. The chosen methodology is then applied in the following chapters on several systems and more specifically on perovskite materials. The major aim is to study particular local distortions that have traditionally be explained by charge disproportionation, which is proposed as an alternative to so-called Jahn-Teller distortions.

Since Mössbauer spectroscopy is at the origin of the assumption of charge disproportionation, we first investigate in chapter 3 the way to obtain information about the Mössbauer parameters from wave function based electronic structure calculations of bare clusters. The results, which relate the measured isomer shift from Mössbauer spectroscopy with the calculated electron density at the Fe nucleus, the so-called contact density, are compared with previous studies. We present the application of the simple tool based on the rotation of pairs of orbitals presented in Chapter 2. It enables a simple counting of electrons in the TM 3d shell. We also investigate in more details the charge distribution around the TM ions in various TM compounds.

Chapter 4 presents the results obtained for embedded cluster calculations to represent perovskite oxides. We analyze the ground state of the Fe ions in a CaFeO₃ crystal. The influence of the material model and cluster wave function is studied for different approximations used in the following chapters. The ground state and first excited states are calculated at room temperature and normal pressure. We further treat the influence of an
increasing pressure on the different computed states.

Chapter 5 reports on the influence of charge transfer configurations in several perovkites oxides and compares isoelectronic crystals that present different type of distortions. Particular attention is paid to the influence of charge transfer in LaMnO$_3$, CaMnO$_3$ and CaFeO$_3$, which show either Jahn-Teller distortion or charge disproportionation.

In the last chapter 6, we explicitly address the problem of charge disproportionation in CaFeO$_3$ and YNiO$_3$ with decreasing temperature. The application of periodic and embedded cluster approaches on both crystals has been performed. The combined analysis leads to a rather complete description of the electronic properties that are compared to experiment. We finally give some general conclusions.