UNIVERSIDADE FEDERAL DO PARANÁ

MATHEUS FRANCO RIBEIRO

EFFECTS OF DIMENSIONALITY ON THE ELECTRONIC STRUCTURE OF THE RUDDLESDEN-POPPER SERIES  $Sr_{n+1}(Fe/Ni/V)_nO_{3n+1}$ 

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Dissertação apresentada ao Curso de Pós-Graduação em Física do Setor de Ciências Exatas da Universidade Federal do Paraná, como requisito parcial para obtenção do grau de Mestre em Física.

Orientador: Prof. Dr. Rodrigo José Ochekoski Mossanek

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Viva a ciência brasileira!

"Highly organized research is guaranteed to produce nothing new." -Frank Herbert

#### RESUMO

Uma série de Ruddlesden-Popper consiste em empilhamentos de estruturas cristalinas básicas de maneira periódica, chamando atenção da comunidade científica devido à rica física que exibem e as promissoras aplicações, especialmente em dispositivos de energia verde e catálise industrial. De fórmula geral  $A_{n+1}B_nO_{3n+1}$ , estes materiais compõe-se de n camadas de perovskitas ABO<sub>3</sub> entre filme de óxidos AO. Conforme n é abaixado na série, o confinamento gradual das estruturas perovskitas leva a um caráter 2D mais pronunciado nas propriedades do material, ocasionando o surgimento de magnetorresistência gigante, estruturas magnéticas não colineares, transições metal-isolante e regimes de transferência de carga negativa. Neste trabalho, nos focamos na série  $Sr_{n+1}TM_nO_{3n+1}$ , para TM = Fe com  $n = \infty, 2, 1$  e também para TM = V para  $n = \infty, 1$ . O material Sr<sub>3</sub>FeNiO<sub>7</sub> também foi considerado, consistindo em uma dopagem de Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7</sub> com Ni na proporção 1:1. Realizamos cálculos no formalismo da Teoria do Funcional Densidade (DFT) utilizando os potenciais de troca e correlação PBEsol e mBJ-Jishi para estudar os efeitos da dimensionalidade na estrutura eletrônica dos materiais e identificar tendências gerais nas séries, tendo simulado diversas estruturas magnéticas fisicamente relevantes. Se determinou que a redução da dimensionalidade dos sistemas ou a introdução de um dopante leva diretamente a uma maior localização na estrutura de bandas e uma mudança no comportamento magnético e condutivo do material. O caráter de oxigênio 2p foi analizado, a partir do qual se pode ver que a presença das camadas de óxido de estrôncio causa a diferenciação dos tipos de oxigênio em relação a sua posição no cristal e leva a comportamentos químicos diferentes, com uma atividade mais expressiva ao longo do plano ab do que ao longo do eixo c. Isso foi interpretado como evidência do comportamento 2D-like de tais materiais, nos quais a interação entre as camadas de perovskita separadas pelo óxido são fortemente reduzidas. Para a série do ferro, uma comparação dos espectros de absorção de raios-x (XAS) calculados forneceu uma boa concordância com os espectros experimentais, melhorada quando se considerou uma abordagem variacional de função de Green para introduzir o efeito do potencial atrativo do buraco de caroço (que não é obtido diretamente da DFT). Considerando a série do vanádio, a comparação foi feita com espectros de condutividade ótica, também mostrando uma boa concordância para ambos os materiais, apesar de que para n = 1 uma translação rígida em energia foi necessária por causa do *qap* que não pode ser reproduzido em nossos cálculos. Concluímos portanto que mudanças na dimensionalidade são uma característica chave dessas séries, levando aos diversos comportamentos físicos que exibem em sua estrutura eletrônica.

**Palavras-chave**: Série de Ruddlesden-Popper; Teoria do Funcional Densidade; Estrutura Eletrônica.

#### ABSTRACT

Ruddlesden-Popper series consists on stacks of basic crystalline structures in a periodic fashion, drawing scientific attention due to the rich physics they exhibit and their promising applications, mainly in green energy devices and industrial catalysis. Of general formula  $A_{n+1}B_nO_{3n+1}$ , these materials consist on n layers of ABO<sub>3</sub> perovskites in between AO oxide films. As n is lowered in the series, the gradual confinement of the perovskite structures leads to a more pronounced 2D-character in the material's properties, originating for example giant magnetoresistance, non-collinear magnetic structures, metal-insulator transitions and negative charge-transfer regimes. In this work, we focused on the series  $Sr_{n+1}TM_nO_{3n+1}$ , for TM = Fe and  $n = \infty, 2, 1$  as well as TM = V for  $n = \infty, 1$ . The material Sr<sub>3</sub>FeNiO<sub>7</sub> was also considered, consisting of a 1:1 doping with Ni of  $Sr_3Fe_2O_7$ . We conducted calculations within the Density Functional Theory (DFT) framework using the PBEsol and mBJ-Jishi exchange-correlation potentials aiming to study the effects of dimensionality on the electronic structure of the materials and identify general trends in the series, having simulated several physically relevant magnetic structures. It was found that lowering the dimensionality of the systems or introducing a dopant leads directly to a greater localization of the band structure and a change in the material's conductive and magnetic behavior. The oxygen 2p character was analyzed, through which it could be seen that the presence of the strontium oxide layers causes the differentiation of oxygen species in regards to their position in the crystal and leads to different chemical behavior, with a more expressive activity along the ab plane than along the c axis. This was interpreted as evidence of the 2D-like behavior of such materials, in which the interaction between perovskite layers separated by the oxide is greatly reduced. For the iron series, experimental comparison with X-Ray absorption (XAS) data yielded a good agreement with the calculated spectra, enhanced when considering a Green's function variational approach in order to introduce the attractive core-hole potential effect that isn't obtained directly from DFT. Considering the vanadium series, the comparison was done with optical conductivity spectra, which also showed a good agreement for both materials, however for n = 1 a rigid shift in energy was needed to account for the band gap that couldn't be reproduced in our calculations. We conclude thus that dimensionality changes are a key characteristic of these series, driving the various physical behavior they exhibit by directly impacting their electronic structure.

Keywords: Ruddlesden-Popper Series; Density Functional Theory; Electronic Structure.

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# 1. Introduction

A great scientific effort is applied towards discovering, understanding and designing materials with specific properties, which can be then used to propose solutions to existing problems in society [1, 2, 3]. For this end, it is of utmost importance to understand how the electrons in a system organize themselves and interact with one another and with other degrees of freedom. It is this *electronic structure* that establishes the material's physical properties, so that many theories have been developed since the 19th century in the attempt to explain how these complex interactions take place and give rise to each system's behavior. One of the first successful steps was taken by Drude, who considered the already established at the time kinetic theory of gases to a electron gas in a metal [4]. Drude's theory assumes that valence electrons are free to wander in the material, thus behaving like a gas of weakly bound electrons [5]. Even considering its very rough simplifications, this approach gave satisfactory results for many systems, but failed to predict correctly for example the contribution of each electron to the metal's specific heat, largely due to the fact that the free-electron approximation is too drastic.

With the development of quantum mechanics some years later, a series of other theories were proposed in order to explain the discrepancies of Drude's. By taking into account the Coulomb repulsion between electrons and their fermionic nature (electronic correlation), the spin degree of freedom and the effects of a periodic potential on the electronic structure, more complicated physical behavior could be modelled and explained. Special attention is given to band theory and Mott-Hubbard theory [5, 6, 7], which will be explained in more detail in chapter 2.

Because the systems of interest involve many electrons, exact solutions to Schrödinger's equation can't be found and thus computational methods are widely used. Historically, Fock's extension of Hartree's method [8] became commonplace in the study of solids, molecules and clusters despite its computational costs, but other approaches such as Slater's linear combination of atomic orbitals (LCAO) [9] and linear muffin-tin orbitals (LMTO) [10] were also proposed. A breakthrough development was done by Pierre Hohenberg and Walter Kohn in 1964 [11] in the study of an uniform electron gas. They discovered that in the ground state of any multielectronic system, there is an univocal relation between the electronic density and the wave function <sup>1</sup>, so that efforts could be directed towards finding this electronic density by alternative means and the same information contained in the wave function could be obtained. This led directly to the development of the much acclaimed Density Functional Theory (DFT) <sup>2</sup>over the following years, one of the most successful methods for the calculation of electronic structure and widely used in fields that range from chemistry to physics, from geosciences to pharmacology [3]. A detailed explanation of DFT is given on chapter 2.

Considering the theoretical methods mentioned above and the different classes of studied materials, transition metal oxides (TMOs) have attracted great interest due to the wide range of physical properties they can exhibit and the often complicated physics behind them. These systems feature combinations of transition metals and oxygen, with the presence of pre-transition or post-transition elements being a common occurrence. A defining characteristic is the progressive filling of the *d* shells, which due to the more localized nature of these orbitals and the influence of the electronic correlation can lead to very distinct electronic and magnetic behavior. For example, TMOs can be insulating (BaTiO<sub>3</sub>), metallic (LaNiO<sub>3</sub>), semiconductors (Fe<sub>0.9</sub>O), ferromagnetic (CrO<sub>2</sub>), antiferromagnetic (LaCrO<sub>3</sub>) or even multiferroic (BiFeO<sub>3</sub>) [12, 7]. The discovery of high temperature superconductivity in cuprates in the 1980's sparked a renewed interest in the area and showed that a comprehensive understanding of the electronic structure of such materials is still lacking, although many important steps have been made since then [13].

The interplay between the different degrees of freedom in TMOs, such as charge, spin, orbital and lattice properties give rise to the highly-correlated nature of these materials. An illustration of these complex interactions is present in figure 1. When external influences are considered, such as pressure, magnetic or electric fields, it is not uncommon for TMOs to undergo transitions caused by changes in the nature of the kinetic hopping of charge carriers and orbital bandwidth, leading to charge-transfer or Mott-Hubbard regimes that can't be explained by conventional band structure theory [14]. The study of these correlated phases is thus vital for possible applications of TMOs in the most varied situations, often requiring innovative theoretical and experimental methods due to the complexity and specificity of each system considered.

One subclass of TMOs that has been extensively studied are the perovskite oxides, of general formula  $ABO_3$ , where A is usually a pre-transition metal and B can be a transition or post-transition element. These arrange themselves, ideally, in a perfect cubic unit cell, with the A cation occupying the vertices of a cube, inside of which a face-centered octahedron of oxygens is present. The B site cations are located on the center of this larger structure. [15, 16]. These systems can be considered prototypical highly-correlated oxides due to their tuneability and stability, their characteristics being discussed in more detail

<sup>&</sup>lt;sup>1</sup> The details of such relation will be discussed later on, on chapter 2.4.

 $<sup>^{2}</sup>$  Walter Kohn received the Nobel prize in Chemistry in 1998 for the devolpment of DFT.



Figure 1 – The interactions between the different degrees of freedom in TMOs give rise to highly-correlated phases. Taken from reference [14].

in chapter 3.

Ruddlesden and Popper synthesized in the late 1950s the material  $Sr_3Ti_2O_7$  [17], which can be understood as a bilayer of strontium titanate perovskites  $SrTiO_3$  stacked between strontium oxide SrO layers along the *c* axis. This layered perovskite structure became known as a Ruddlesden-Popper (RP) phase, of general formula  $A_{n+1}B_nO_{3n+1}$ , with several other materials organizing themselves in the same manner being discovered shortly after. Here, *n* refers to the number of perovskite layers in between the AO oxide layers, so that when  $n = \infty$  only the perovskites are present. These systems are of special importance as examples of TMOs with a 2D character [12, 18] due to the confinement of the perovskites in the *ab* plane. Because of the amount of possible combinations and the reduction in the dimensionality of the system, Ruddlesden-Popper materials have a wide range of physical behavior and possible applications. As of the last decade, a great interest has been directed towards applications in solar cells, optoelectronics and photocatalysis [19, 20, 21, 22, 23], where the oxygen is often partially replaced for some element like N, S or Cl. A more in depth explanation of the properties of a RP series is given in chapter 3.

### 1.1 Overview

In the present work, we focused our attention on two distinct RP series, namely  $Sr_{n+1}Fe_nO_{3n+1}$  for  $n = \infty, 2, 1$  and  $Sr_{n+1}V_nO_{3n+1}$  for  $n = \infty, 1$ . These present complicated electronic and magnetic behavior that is still not fully understood and will be detailed in the following chapters. Our main goal was to analyse the dependence of each material's electronic structure on the system's dimensionality. In order to do so, we conducted comprehensive DFT calculations in the collinear spin approximation, considering different magnetic arrangements. This approximation was employed aiming to greatly reduce the

computational costs associated with the calculations. The resultant density of states and band structure was studied differentiating the oxygen contributions by their positions, the O 2p character in the bands also being determined in relation to the projections along the *ab* plane and along the *c* axis. In the case of n = 2 for the iron series, the nickel-doped Sr<sub>3</sub>FeNiO<sub>7</sub> material was also considered. In order to validate our results, experimental comparisons involving oxygen X-Ray absorption spectra for the iron series and optical conductivity measurements for the vanadium series were conducted.

In chapter 2, basic concepts regarding the theory of electronic structure and DFT are introduced, which will be necessary for the following discussions. In chapter 3, general properties of Ruddelsden-Popper series are outlined and a review of the reported properties and characteristics of the materials of interest is detailed. The computational methods applied in this work and the experimental techniques used to drawn comparisons are explained in chapter 4, the results obtained and their analysis being conducted on chapter 5. Finally, concluding remarks are discussed in chapter 6. In appendices I and II (6,6) additional information regarding the computational methods and further tests are shown.

# 2. Theoretical Basis

### 2.1 Band Theory

Among the many theories proposed to explain the electronic structure of crystalline solids, band theory has been one of the most successful. The cornerstone of this approach lies on Bloch's theorem, which states that the eigenfunctions  $\Psi(\mathbf{r})$  of an electronic system under a periodic potential  $U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r})$ , where  $\mathbf{R}$  is the lattice vector of a Bravais lattice <sup>1</sup>, can be written as the product of a plane wave times a function with the same periodicity as that of the lattice [5]. This can be written as

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}), \qquad (2.1)$$

where **k** is a wave vector that characterises the translational symmetry of the periodic potential and  $u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}(\mathbf{r})}$ . To reproduce the crystal's periodicity, one considers unit cells, which are the basic structure that when replicated in all directions yields the lattice. One special type of unit cell is the Wigner-Seitz primitive cell, consisting on the region of space that is closer to one lattice point than to any other, containing exactly one of these points in its interior. By doing a Fourier transform of the lattice vectors, one obtains the unit cell in the reciprocal space, so that the same definitions can be applied to obtain its **k**-space equivalents <sup>2</sup>. The Wigner-Seitz cell in reciprocal space is known as the first Brillouin zone, being of vital importance in the study of many properties [5].

The evaluation of Schrödinger's equation considering Bloch's theorem and  $\mathbf{k}$  restricted to the first Brillouin zone yields an infinite family of solutions with discretely spaced eigenvalues. Much like the simple case of a particle in a box, one can define a quantum number n to distinguish between each family of solutions. Here, n is called the band index. Despite that, due to the nature of the Hamiltonian's dependence on  $\mathbf{k}$ , these solutions vary continuously with the wave vector.

<sup>&</sup>lt;sup>1</sup> A Bravais lattice is the collection of all points spanned by a lattice vector  $\mathbf{R} = n_1 \mathbf{a_1} + n_2 \mathbf{a_2} + n_3 \mathbf{a_3}$ , where  $\mathbf{a_i}$  are any three vectors not in the same plane and  $n_1$  take on any integer value. The result is a periodic spacing of points, which represent a crystalline system [5].

<sup>&</sup>lt;sup>2</sup> In k-space, the Bravais lattice vector **K** is given by  $\mathbf{K} = x_1 \mathbf{b_1} + x_2 \mathbf{b_2} + x_3 \mathbf{b_3}$ , provided that  $a_i \cdot b_j = 2\pi \delta_{ij}$ , representing the period in the reciprocal lattice.

By considering the lattice periodicity now on the **k**-space, we can use the band index to specify each family of infinite solutions of Schrödinger's equation by allowing **k** to range through all of the space. The periodic condition implies that, for each n, the eigenstates and eigenvalues are also periodic functions of **k** in the reciprocal lattice:

$$\Psi_{n,\mathbf{k}+\mathbf{K}}(\mathbf{r}) = \Psi_{n\mathbf{k}}(\mathbf{R}), \qquad (2.2)$$

$$\varepsilon_{n,\mathbf{k}+\mathbf{K}} = \varepsilon_{n\mathbf{k}}.\tag{2.3}$$

Here  $\varepsilon_{n\mathbf{k}}$  is called an energy band, a continuous function of  $\mathbf{k}$  that contains all of the information of a specific set of electronic levels, and  $\mathbf{K}$ , given by the relation  $\mathbf{K} = x_1\mathbf{b_1} + x_2\mathbf{b_2} + x_3\mathbf{b_3}$ , is the Bravais lattice vector in reciprocal space. The collection of these bands and the information they represent is called the band structure of the solid. The quantity of electronic states in a band in the energy interval [E, E + dE] is called the density of states (DOS), and is a very useful tool to analyze the material's characteristics.

In the ground state of any crystalline material, the filling of the bands dictates its electronic behavior. It is usual to consider the reference energy to be that of the Fermi level  $E_F$ , that is, the chemical potential as the temperature approaches zero. The energy difference between the top of the highest ocuppied band, called the valence band, and the bottom of the lowest unoccupied band, called the conduction band, is known as the band gap. The Fermi level can be shifted due to impurities in the crystal [5]. This shift can take place, for example, by the introduction of extra electrons in the conduction band or holes into the valence band, which increase the conductivity by increasing the carrier mobility [6].

When an energy gap is present, there is a cost associated to promoting an electron from the valence band to the conduction band. In this case, the material can be characterized as an insulator, when the gap is large compared to the thermal energy  $k_BT$ , or as a semiconductor, when it is of the order of  $k_BT$ . When no gap is present, the electrons in the valence band can easily be excited to the conduction band, where they can become delocalized and conduct electricity. Thus, in this case, the material is characterized as a conductor. One can also think about these classifications in terms of the DOS: when the density of states is non-zero around  $E_F$ , the material is an conductor. A schematic representation of this in terms of the density of states is represented in figure 2. Also depicted are the cases of semimetals, where the DOS approaches zero at the Fermi level, impacting conduction, and the p and n-type semiconductors, which have the valence band top or conduction band bottom at  $E_F$ , respectively.

The determination of the periodic eigenfunctions  $\Psi_{n,\mathbf{k}}$  is in general quite complicated, thus approximations are made, the simplest of which consists of considering



Figure 2 – Schematic representation of electronic density of states around the Fermi level for different electronic behavior. Image taken from Nanite, CC0, via Wikimedia Commons.

that the total wavefunctions can be written in terms of a linear combination of atomic orbitals (LCAO). This method is called tight binding, as it considers that the orbitals are "tightly bound" to the atoms themselves and the only appreciable overlap comes from first neighbors [7]. For a transition metal oxide system, usually the most important orbitals to consider as basis sets are the transition metal d and the oxygen 2p orbitals.

The mixing of the orbitals give rise to bonding and anti-bonding contributions, meaning that for different  $\mathbf{k}$  one obtains different energies associated. Due to this general fact, it is common to represent the band structure on a band diagram as depending on the wave vector along specific high-symmetry directions <sup>3</sup>, highlighting the energy dispersion along the (first) Brillouin zone. Such an example is given on figure 3. There one can see that each band changes its energy level depending on the position  $\mathbf{k}$  in reciprocal space that is being considered, which are represented by letters like  $\Gamma$  and Z that represent highsymmetry points following standard nomenclature, which can be found on any textbook of the area such as the one by Ashcroft and Mermin [5].

Because the tight binding (or LCAO) method is very simplified, several other methods for obtaining the band structure exist. One of such was derived directly from this first method by Slater and Koster in 1954 [9], aptly called simplified LCAO. The basic idea is to consider base functions with orbital-specific symmetries and replace the integrals of the energy matrix elements by constants, which are fitted to accurate experimental data. These constants refer to specific combinations of orbitals written in terms of cubic harmonics, for example the combination of an s orbital with a  $p_x$  one. This allows the

<sup>&</sup>lt;sup>3</sup> Because the full band structure is tridimensional, it is impossible to plot it against the energy or wave-vector dependency.



Figure 3 – Example of a band structure for the  $RuO_2$  oxide in the tetragonal structure, calculated using the augmented plane wave method. Adapted from reference [7].

energy terms to be greatly simplified and calculated more directly, yielding a reasonable agreement with experimental values.

Another method of great success is the augmented plane wave method (APW), also proposed by Slater and outlined by himself in reference [24]. This consists on numerically integrating the radial Schrödinger's equation on a spheric region centered around each atom, averaging over the angular dependence written in spherical harmonics, yielding a potential that depends on radial distance alone, called the muffin tin approximation. The system's wavefunction is then expanded in terms of plane waves in the space between non-overlaping spheres and made continuous by appropriate boundary conditions (augmentation). A derived method called the linearized augmented plane wave with local orbitals (LAPW+lo) is of special importance to this work, being outlined in the methodology chapter 4.1.

## 2.2 Effects of Electronic Localization

The approach of building a basis set of molecular orbitals, as described in the previous section, and the usual band theory that follows breaks down when the interaction between orbitals is weak enough. This can happen when there is not enough inter atomic orbital overlap, which results in the electrons being much more localized [6]. In this case, the bands that are generated do not show great dispersion and become quite narrow. As a consequence, the mutual electronic repulsion needs to be treated more carefully and not just as an averaged potential. As expected, this is no easy task, and many different

approximations were proposed along the years. One model that proved itself to be quite useful is known as the Hubbard model [25], being used to tackle many different problems. A thorough review is outside the scope of this work, but can be found on the work by Imada and collaborators [26].

The basic idea of the model lies on assuming that the most important contribution in energy arising from the electronic repulsion is that between electrons of the same atom. Considering an isolated atom, the energy associated with repulsion U can be interpreted as the energy required to remove an electron from somewhere else, the ionization energy I, minus the lowering in energy by the reorganization of the electronic cloud of the receiving atom, the electronic affinity A. This is simply written as

$$U = I - A, \tag{2.4}$$

Where the repulsion U is also known as Hubbard's U and can be considered a form of electronic correlation, in the sense that the presence of an electron in an orbital alters the probability density of electrons that are nearby.

As an example, a one dimensional chain of atoms with s valence orbitals as in figure 4. When there is little overlap between the orbitals, i.e. the electrons are localized and atoms are almost isolated, the ground state of the system consists of singly occupied valence shells. Thus, if one electron is to jump to a neighboring atom, the Coulomb repulsion between them implies an energy cost U as given by the equation above. In this sense, the effect of electronic repulsion is to make the band of half-filled s orbitals insulating if the interaction between adjacent orbitals is small enough. If this interaction were to increase, that is, the overlap between the orbitals become greater, a delocalization of the electrons would be favored and thus a conductive behavior would arise, turning the band metallic. This kind of electronic behavior is know as metal-insulator transition, and materials where the main cause of insulating nature is due to electronic localization are known as Mott-Hubbard insulators [26].

A way of quantifying how much overlap is present is through a parameter known as bandwidth W, the energy interval occupied by a given band. The presence of the electronic repulsion U causes a separation known as Hubbard splitting into sub-bands between the configuration of a single electron per orbital and the doubly occupied one, which is schematically represented in figure 5, where the energy is plotted as a function of the bandwidth W. For W = 0, the case of isolated atoms, the gap that separates the two sub-bands is exactly the repulsion given by equation 4, but as the bandwidth increases and more overlap between the orbitals happen, it becomes easier to delocalize the electrons and thus the gap decreases. When the two bands meet at the Fermi level, that is, when the bandwidth is of the same magnitude of the repulsion, there is no energy cost associated with the delocalization and thus the material becomes metallic, as predicted by usual band theory. Thus, one can argue that the electronic repulsion can only be overlooked when the



Figure 4 – A linear chain of valence s electrons with little overlap. The ground state (a) has half-filled orbitals with one electron on each atom, where any excitation (b) implies an energetic cost due to electronic repulsion. Figure taken from reference [6].

condition W > U is satisfied.

Naturally, the approximation proposed doesn't take into account a series of other phenomena that take place in real solids, such as the polarization of the electronic clouds due to the presence of holes, which reduce the energy needed to excite the electrons in the material. This polarization causes the Hubbard splitting to decrease faster in a non-trivial manner, rendering direct calculations of U quite challenging, although it can be determined by experimental comparison, at least approximately. The problem usually lies on the very nature of the highly idealized model, with the assumption of localized repulsion and single-band models [7]. Even with these difficulties, the model is effective on the study of magnetic insulators and magnetic transitions, and several generalized models have been proposed for specific problems, often with good success [26, 7].

When considering the effects of the repulsion U on transition metals, a wide array of behavior can take place. For example, in the case of metallic elements, the dorbitals bandwidth is usually enough to satisfy the condition W > U, so that band theory shows a good agreement with experimental data, although U directly influences the magnetic structure of the materials. It is in compounds of these transition metals however that the rich behavior really manifests, with many examples of Mott-Hubbard induced metal-insulator transitions [26, 6, 7].

Although dependence of the material's properties is highly characteristic on the material itself, some general properties can be outlined for transition metal compounds [6]. Firstly, any kind of characteristic or interaction that increases the bandwidth of the d orbitals or decreases the repulsion U will favor delocalization, which in turn favors (but does not assure) metallicity. Thus, the larger the d orbital, the broader the band and the smaller the U. It is also worthy of note that mixed stoichiometry compounds, such as



Figure 5 – Schematic dependence of the Hubbard splitting on the bandwidth W. When W equals the Hubbard U, the sub-bands fuse together and the predictions of band theory, which do not take into account electronic repulsion, agree with those of the model. The decrease of the splitting as W increases is not equal for both sub-bands due to polarization effects. Figure adapted from reference [6].

 $Fe_3O_4$  featuring  $Fe^{2+}$  and  $Fe^{3+}$ , can favor metallic behavior despite electronic repulsion due to the different oxidation states. This is represented in figure 6, where there is no energy cost associated on the electron or hole motion through the lattice because of the non-equal sites.

It is also worthy of note the influence of local symmetry on the d orbital characteristics [6]. As these orbitals interact with those of other atoms, the ligands, molecular orbitals are formed. When the metal-ligand orbitals point directly towards each other, the bond is of  $\sigma$  type, otherwise being of  $\pi$  type. The ligand electrons occupy the bonding orbitals, leaving the metal d electrons to occupy the antibonding ones. Because electronic repulsion is greater in the  $\sigma$  bond, as there is a greater wavefunction overlap, the molecular orbitals that derive from it have a higher energy than those of  $\pi$  bond origin. In a octahedral symmetry  $(O_h)$ , the d orbital degeneracy is broken and  $d_{z^2}$  and  $d_{x^2-y^2}$ , which are  $\sigma$  antibonding and labeled as  $e_g$ , become higher in energy than  $d_{xz}, d_{xy}, d_{yz}$ , which are  $\pi$  antibonding and labeled as  $t_{2g}$ . The shapes of these orbitals are depicted in figure 7.

The separation between  $e_g$  and  $t_{2g}$  levels depends on the intensity of the interaction between metal and ligand, being quantified in a parameter 10Dq known as ligand field splitting, and also on the intra-atomic exchange j, representing the energy cost associated with two electrons occupying the same orbital <sup>4</sup>. When 10Dq is sufficiently large, it is

 $<sup>^4</sup>$  A more in-depth explanation of exchange and its effects will be given in the following section, focusing however on *inter*-atomic exchange.



Figure 6 – For mixed valence compounds, metallic character can arise due to no cost in electron (a) or hole (b) delocalization. Figure taken from reference [6].



Figure 7 – Spatial shapes of metal  $e_g$  and  $t_{2g}$  orbitals under octahedral symmetry. The black dots along each direction represent the ligands, whose orbitals are not depicted for visual clarity. Figure taken from reference [7].



Figure 8 – Schematic representation of a  $d^5$  configuration in low, intermediate and high spin states. The choice of ground state depends on the ligand field splitting 10Dq and the intra-atomic exchange j.

more energetically favorable to fully occupy the  $t_{2g}$  orbitals even though there is electronic repulsion and the energy cost due to j, which leads to a smaller total spin magnetic moment. This is known as a low-spin configuration, in opposition to when 10Dq is small, which favors the occupation of levels with spins in the same orientation to minimize j, called high-spin configuration. When 10Dq and j are of the same order of magnitude, the electronic configuration depends more on each specific case, being named intermediate spin (see figure 8) [6].

As a consequence of the uneven occupation of the  $e_g$  and  $t_{2g}$  orbitals, that is, a different number of electrons occupy each orbital, an asymmetrical charge density is generated. This in turn yields a resultant force that tends to distort the local geometry. This effect is known as Jahn-Teller distortion [6] and is responsible for a lowering of the local symmetry from octahedral  $O_h$  towards tetragonal  $D4_h$  and breaking the degeneracy of either (or both) orbitals. It is more pronounced when the uneven occupation happens in the  $e_g$  orbitals due to their spatial dispersion, that is, when there are one or three electrons in these orbitals. In the case of octahedral symmetry, this distortion often leads to the elongation of the bonds along one of the axis, yielding a tetragonal structure. A schematic depiction of this phenomenon is present in figure 9.



Figure 9 – Schematic of the Jahn-Teller effect from an octahedral  $O_h$  symmetry towards a tetragonal  $D_{4h}$  symmetry, with degeneracy breaking of the  $e_g$  and  $t_{2g}$  orbitals. Figure taken from reference [27].

### 2.3 Electronic Structure and Magnetism

As the electronic structure of a material defines what macroscopic and microscopic physical behavior it can exhibit, the study of the specific interactions that lead to magnetic ordering or the lack thereof are of great practical importance. These arise from the quantum-mechanical nature of the electrons in the material, rendering full *ab initio* descriptions quite difficult in some cases. In order to tackle this difficulty, several models have been proposed over the years, with various degrees of applications and accuracy.

First off, one needs to take into account the fermionic nature of electrons. Pauli's exclusion principle forbids two fermions of occupying the same quantum state, or more formally, requires that the wavefunctions of two fermions must be antisymmetric when they are interchanged [28]. This constrains the number of electrons that can occupy the same orbital and is fundamental to understand what drives magnetic ordering. In the following sections, some specific interactions will be discussed.

### 2.3.1 Exchange

As a direct consequence of Pauli's exclusion principle, an energy contribution due to the indistinguishability of the electrons appears naturally in multi-electronic systems because of the wavefunction's antissymmetric nature. As an example, consider the simple case of only two electrons interacting, which can represent for example a localized interaction or an He atom. The total wave function needs to be antisymmetric, what can be realized by the combination of a symmetric spatial state with an antisymmetric singlet spin state  $\chi_S$  (s = 0), or a antisymmetric spatial state with a symmetric triplet spin state  $\chi_T$  (s = 1), written as

$$\Psi_S = \frac{1}{\sqrt{2}} [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)]\chi_S$$
(2.5)

$$\Psi_T = \frac{1}{\sqrt{2}} [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) - \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)]\chi_T$$
(2.6)

Here,  $\psi_{a,b}$  refer to the single wave functions of both electrons [29]. Calling  $E_S$  and  $E_T$  the energies of both states, given by

$$E_S = \int \Psi_S^* \mathcal{H} \Psi_S d\mathbf{r}_1 d\mathbf{r}_2 \tag{2.7}$$

$$E_T = \int \Psi_T^* \mathcal{H} \Psi_T d\mathbf{r}_1 d\mathbf{r}_2, \qquad (2.8)$$

and  $\mathcal{H}$  the interaction Hamiltonian, the difference in energy between both states is

$$E_S - E_T = 2 \int \psi_a^*(\mathbf{r}_1) \psi_b^*(\mathbf{r}_2) \mathcal{H} \psi_a(\mathbf{r}_2) \psi_b(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2, \qquad (2.9)$$

where it was assumed that the spin states are normalized. If the Hamiltonian for this two electron system is given by a very general expression of the type

$$\mathcal{H} = A\mathbf{S}_1 \cdot \mathbf{S}_2,\tag{2.10}$$

where A is some constant and  $\mathbf{S}_{1,2}$  are the spin operators of each electron, it is easy to show that the total spin quantum number s will take on only two values, namely s = 0 or 1. The former is associated with a singlet (i.e. antiparallel spins) state and the latter with a triplet (i.e. parallel spins) state. The dot product is given by [29]

$$\mathbf{S}_{1} \cdot \mathbf{S}_{2} = \begin{cases} \frac{1}{4} & \text{if } s = 1\\ -\frac{3}{4} & \text{if } s = 0 \end{cases}$$
(2.11)

The difference between the singlet and triplet states can be parametrized using this result, leading to an effective Hamiltonian written as

$$\mathcal{H} = \frac{1}{4} (E_S + 3E_T) - (E_S - E_T) \mathbf{S}_1 \cdot \mathbf{S}_2.$$
(2.12)

Direct substitution for each case returns the corresponding energy. In this effective expression, the first term is a constant that can be grouped in other constant energy terms, leaving the second term which holds the spin dependency. The *exchange integral* J is defined by

$$J = \frac{E_S - E_T}{2} = \int \psi_a^*(\mathbf{r}_1) \psi_b^*(\mathbf{r}_2) \ \mathcal{H} \ \psi_a(\mathbf{r}_2) \psi_b(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2, \qquad (2.13)$$

leading the effective spin Hamiltonian to be written as

$$\mathcal{H} = -2J\mathbf{S}_1 \cdot \mathbf{S}_2. \tag{2.14}$$

Here, the relative spin orientation is governed by the sign of J. In the case of J > 0,  $E_S > E_T$  and the triplet state (parallel) is favoured. On the other hand, if J < 0, the singlet state (antiparallel) is favored as  $E_S < E_T$ .

Although this Hamiltonian was derived for a two electron system, it inspired a generalization known as Heisenberg model

$$\mathcal{H} = -\sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \qquad (2.15)$$

where  $J_{ij}$  is the exchange constant between an electron pair, which can be located on the same atom or different atoms. The direct evaluation of  $J_{ij}$  is quite complicated in general, but the same interpretation of the favoured spin alignment can be done as in the two electron case. This simple expression can be used to study many complex interactions and is widely employed in the magnetism literature, either in form above or with additional terms to account for more general cases. For example, a model with the same format, called Anderson's model, is used in the study of spin glasses. In this case, the complication lies on assuming that  $J_{ij}$  is no longer a constant, but a gaussian distribution of values to tackle complexity [30].

In a nutshell, the exchange interaction arises as a consequence of Pauli's exclusion principle and has no classical analog. The energy associated with this interaction depends on the relative orientation of any spin pair, thus driving magnetic ordering by lowering or increasing the total energy of the magnetic system. In general, if the electron pair belongs to the same atom, the exchange integral is usually positive and favoring triplet states. This is due to the fact that an antisymmetric spatial state minimizes the Coulomb repulsion and lowers the total energy of the system, being the physical origin of Hund's first rule [29].

In real materials, more complicated interactions may take place. One of such is called the superexchange, which can be understood as the exchange interaction between two magnetic atoms, mediated by a non-magnetic third. This is often the case for magnetic oxides, such as MnO [28, 31]. In this situation, the magnetic ions are too far apart, so that there is no significant overlap of the d orbitals. Instead, the exchange mechanism happens, for example, through the hybridization of the metal d (e.g. Mn) electrons with the p orbitals of the intermediary atom (e.g. O). This favors the delocalization of the p electrons, which in turn lowers their kinetic energy. Additionally, due to Pauli's exclusion principle, this intermediary interaction can drive magnetic ordering by favoring the parallel or antiparallel orientation of the spins of the metal atoms.



Figure 10 – Schematic representation of superexchange interaction driving antiferromagnetic ordering considering a situation with a half-filled (a) and a less than half-filled shell (b). Adapted from reference [28]

A schematic example considering MnO is shown in figure 10. The covalent bonding between one  $Mn^{2+}$  and  $O^{2-}$  atoms leads to only the opposite spin being available for another Mn-O bond, which requires by Pauli's exclusion principle that the second Mn atom orders itself antiferromagnetically in relation to the first, as is depicted in (a). When the metal's *d* orbitals are empty, the superexchange interaction also leads to antiferromagnetic coupling as can be seen on (b). If the metals involved have different valences or impurities are present, then the same mechanism can lead to ferromagnetism, although this interaction is weaker and less common, being also referred to as double exchange [29].

Besides exchange and superexchange, other exchange-like interactions may take place in specific situations. By considering the spin-orbit effect in a non-centrossymetric crystal environment, the ground state of one magnetically active ion and the excited state of another present an interaction called anisotropic exchange or Dzyaloshinskii-Moriya (DM). This is modelled by a simple hamiltonian like  $H_{DM} = \mathbf{D} \cdot (\mathbf{S_1} \times \mathbf{S_2})$ , where  $\mathbf{D}$  is a vector that has a non-zero value only when the two spin sites are not equivalent [31]. This favors the canting of the spins away from a collinear orientation, which can yield a weak ferromagnetic behavior, while also being key in driving the material's magnetic structure towards more complicated spin textures such as spin helices [32]. A schematic representation of this interaction is displayed on figure 11.

For materials that are based on rare earths, elements with semi-filled 4f shells, yet another interaction can result in magnetic behavior. This is called the RKKY interaction,



Figure 11 – The Dzyaloshinskii-Moriya interaction (DM) depends on the D vector, which is only non-zero when inversion symmetry is not present in the material considered. In this case, a canting of the spins happens and a weak magnetization can be generated. Image adapted from reference [32].

named after the discoverers of the effect, and is the result of an indirect exchange between magnetic ions, mediated by conduction electrons. As the 4f orbitals are very localized, there is no overlap between these orbitals for adjacent atoms, but their presence magnetically polarizes conduction electrons in the vicinity, which in turn interact with the other atoms, propagating through the lattice. This coupling has an oscillatory nature and may cause both ferromagnetism or antiferromagnetism, depending on the distance between magnetic moments [29, 31].

### 2.4 Density Functional Theory

Among the many methods developed over the years for the calculation of physical properties of multi electronic systems, those based on Density Functional Theory (DFT) have proven themselves to be quite powerful and with a wide range of applications. The cornerstone of the theory lies on two theorems named after Pierre Hohenberg (1934-2017) and Walter Kohn (1923-2016, Nobel Prize in Chemistry 1998), which can be summarized as:

- 1. In the ground state of a multielectronic system, the total energy is a *unique* functional of the electronic density  $E[n(\mathbf{r})]$ ;
- 2. The true electronic density, that corresponds to the solution of the Schrödinger's equation, is the one that minimizes the energy of  $E[n(\mathbf{r})]$ .

These theorems assure us that the electronic density  $n(\mathbf{r})$  carries all the information that can be derived from the multielectronic wave function  $\Psi(\mathbf{r}_1, \mathbf{r}_2, ... \mathbf{r}_n)$ . Thus, determining the electronic density is completely equivalent to solving the Schrödinger's equation for any multielectronic system, granted that it finds itself in the ground state. In the words of Kohn himself [33], the advantages of focusing on the electronic density is that it is a real, three dimensional quantity that depends only on the spatial region of interest, and is *physical*. In contrast,  $\Psi(\mathbf{r}_1, \mathbf{r}_2, ... \mathbf{r}_n)$  is a 3*N*-dimensional complex quantity, thus not measurable, which depends on all of the electronic coordinates.

The proof of the first theorem is quite ingenious, although simple, relying on a *reductio ad absurdum* strategy [33, 3]. Consider the following Hamiltonian:

$$H(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = T + U + \sum_i V_N(\mathbf{r}_i), \qquad (2.16)$$

where T and U are respectively the kinetic energy and interaction energy operators and  $V(\mathbf{r}_i)$  is an external potential. The energy of this system can be written as

$$E = \langle \Psi | H | \Psi \rangle = \int V_N(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \langle \Psi | (T+U) | \Psi \rangle, \qquad (2.17)$$

where  $n(\mathbf{r})$  is the electronic density. Now assume that  $\Psi$  is the ground-state corresponding to  $V_N$ , with energy E. Suppose that the same density can be generated by a different potential  $V'_n$ , with corresponding H',  $\Psi'$  and E'. Because  $\Psi$  is not the ground state for this other potential, we have that

$$\langle \Psi | H' | \Psi \rangle = \langle \Psi | (T+U) | \Psi \rangle + \int d\mathbf{r} \, n(\mathbf{r}) \, V'_n(\mathbf{r}) > E'.$$
(2.18)

Thus we can conclude that

$$E - E' > \int d\mathbf{r} \, n(\mathbf{r}) \left[ V_N(\mathbf{r}) - V'_N(\mathbf{r}) \right]$$
(2.19)

as no assumptions were made on the nature of the external potentials, the same analysis can be done considering  $\Psi'$  on equation 2.18, yielding

$$\langle \Psi' | H | \Psi' \rangle = E' - E > \int d\mathbf{r} \, n(\mathbf{r}) [V_n(\mathbf{r}) - V'_n(\mathbf{r})].$$
(2.20)

By adding the two equations, one obtains 0 > 0. Thus, the initial assumption that two different potentials can lead to the same electronic density in the ground state is false, proving the first theorem.

With this in mind, Hohenberg and Kohn considered an extension of the Hartree-Fock method for independent electrons. The Hamiltonian for this case can be written as

$$\left[-\sum_{i}\frac{\hbar}{2m_{e}}\nabla_{i}^{2}-\sum_{I}\frac{\hbar}{2M_{I}}\nabla_{I}^{2}+\frac{1}{2}\sum_{i\neq j}\frac{e^{2}}{4\pi\epsilon_{0}}\frac{1}{|\mathbf{r}_{i}-\mathbf{r}_{j}|}+\frac{1}{2}\sum_{I\neq J}\frac{e^{2}}{4\pi\epsilon_{0}}\frac{Z_{I}Z_{J}}{|\mathbf{R}_{I}-\mathbf{R}_{J}|}-\sum_{i,I}\frac{e^{2}}{4\pi\epsilon_{0}}\frac{Z_{I}}{|\mathbf{r}_{i}-\mathbf{R}_{I}|}\right]\Psi=E_{tot}\Psi\quad(2.21)$$

In this expression, the first two terms are the kinetic energy of the electrons and the nuclei, followed by the Coulomb repulsion of electron-electron pairs, nucleus-nucleus and lastly the attraction between electrons and nuclei. This last term is very problematic to treat mathematically due to the number of interactions it encodes and their complexity.

Naturally, this problem becomes very difficult to solve for all but the simplest systems, thus several steps aimed at simplifying this expression can be done. They are listed in detail in reference [3], but an outline of the process can be discussed. First off, one can adopt atomic units <sup>5</sup> to get rid of the constants and also consider the Born-Oppenheimer approximation, so that the nuclear coulomb interaction becomes a constant. By defining single electron Hamiltonians and considering them as independent, one arrives at the Hartree problem. The next step consists of satisfying the exclusion principle by means of Slater determinants and averaging the electron-electron interactions as a mean field.

When one also considers the exchange potential between electrons explicitly, that is, the energy associated with the indistinguishability of electrons (and all quantum particles for that matter), one arrives at the Hartree-Fock theory. The last step is to consider another potential *ad hoc* to take into account the *correlation* of electrons <sup>6</sup>. The basic idea is that, due to the Coulomb repulsion, the probability distribution of finding an electron at a given point is influenced by the presence of another in the vicinity. In other words,  $|\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 < |\phi(\mathbf{r}_1)\phi(\mathbf{r})_2|^2$ , meaning that the probability distribution of the multielectronic wave function  $\Psi$  is different than the one obtained by the product of the (independent) single electron wavefunctions  $\phi$ .

In the end, one arrives at the system known as Kohn-Sham equations (in atomic units) [34]

$$\left[-\frac{\nabla^2}{2} + V_n(\mathbf{r}) + V_H(\mathbf{r}) + V_x(\mathbf{r}) + V_c(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$
(2.22)

where  $-\nabla^2/2$  is the kinetic energy operator,  $V_n$  the constant nuclear potential,  $V_H$  the Hartree potential,  $V_x$  the exchange potential and lastly  $V_c$  the correlation potential. Here,  $\phi_i$  and  $\epsilon_i$  correspond respectively to single electron wavefunctions and eigenvalues.

Taking a look back at the Hohenberg-Kohn theorem, one can express the energy as a functional of the electronic density by using the Kohn-Sham Hamiltonian in 2.22 as

$$E = F[n]$$

$$= \int d\mathbf{r} \, n(\mathbf{r}) \, V_n(\mathbf{r}) - \sum_i \int d\mathbf{r} \, \phi_i^*(\mathbf{r}) \frac{\nabla^2}{2} \phi_i(\mathbf{r}) + \frac{1}{2} \int \int d\mathbf{r} \, d\mathbf{r}' \frac{n(\mathbf{r}) \, n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{XC}[n]$$
(2.23)

<sup>&</sup>lt;sup>5</sup>  $\hbar = e = m_e = 4\pi\epsilon_0 = 1$ , where  $\hbar$  is Planck's reduced constant,  $e(m_e)$  the electron charge (mass) and  $\epsilon_0$  the vacuum's permittivity.

<sup>&</sup>lt;sup>6</sup> This choice is highly dependent on the system under study. For DFT, possibilities will be discussed in the following subsections.



Figure 12 – Outline of a self-consistent algorithm.

where the first term relates to the external potential and the following to the kinetic energy, the Hartree energy and lastly the exchange-correlation energy, which has been bundled up in a single unknown functional  $E_{XC}[n]$ . In order to find the electron density at the ground state (as this is only valid for this situation), one utilizes the so called Kohn-Sham variational principle [34] in regards to the electronic density, which can be written as a functional derivative of the exchange-correlation energy,

$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}(\mathbf{r})}{\delta n(\mathbf{r})},\tag{2.24}$$

and arrives at the same set of equations obtained before, aptly called Kohn-Sham equations 2.22. This means that, in the ground state, the correct electronic density is that which minimizes the energy functional, precisely the statement of the second Hohenberg-Kohn theorem stated before.

The problem now lies elsewhere: how does one determine the electronic exchange and correlation potential, the only unknown in equation 2.23? If this were known, one would have exact solutions for the ground state of any multi-electronic system (barring computational errors). Alas, that is not the case, so useful approximations must be considered for specific cases. Also worthy of note is the recursiveness in the above equation:  $n(\mathbf{r})$  is needed to calculate E, but in order to calculate E one needs the electronic densitY to write the Hartree potential [2]. This can be solved using a self-consistent algorithm which is explained in the following and summarized in figure 12.

Starting from an initial external potential, which can be derived from other methods such as a Hartree-Fock calculation, one obtains the initial density as per the Hohenberg-Kohn theorem. This initial density is used in the definition of the Hartree and exchange-correlation potentials, which are then used to generate the Kohn-Sham equations. Solving them yields a new electronic density, which is compared to the initial. If the difference between them is lower than a given threshold, the calculation has converged



### Hartree World

Figure 13 – Different degrees of complexity for the treatment of the exchange-correlation potential, from the simplest at the bottom (equivalent to Hartree theory) towards the chemically exact at the top (extracted from reference [35]).

and thus the physical properties can be obtained. If that is not the case, then this new density is used as input for another iteration and so on.

As mentioned before, the *crux* of the theory lies on the definition of the exchangecorrelation potential  $V_{XC}$ , or equivalently, the exchange-correlation energy  $E_{XC}$ . Although its general form is unknown, several useful properties of the exact functional have been discovered and thus serve as constraints to proposed functionals, such as the electronic hole density and low/high density limits. Perdew [35] coined the term "Jacob's ladder" in reference to the increasingly more complex approximations one can consider, which are summarized in the figure 13.

The exchange-correlation energy functional can be written generally as

$$E_{XC}[n_{\uparrow}, n_{\downarrow}] = \int d\mathbf{r} \, n(\mathbf{r}) \, \varepsilon_{XC}([n_{\uparrow}, n_{\downarrow}]; \mathbf{r}) \,, \qquad (2.25)$$

where the integrand is the exchange-correlation energy density and  $\varepsilon_{XC}$  is the exchangecorrelation energy per electron. The different steps on the ladder refer to what kind of ingredients one uses to define  $\varepsilon_{XC}[n_{\uparrow}, n_{\downarrow}]$ . The basic approximation is called the local spin density approximation (LSD) or just local density approximation (LDA), that considers the exchange-correlation energy of an homogeneous electron gas. In this case, the space is separated in small units inside of which n is constant or near constant. The reason for such an assumption is that the exchange energy of this system is known exactly and the correlation can be determined through numerical techniques [3].

As more ingredients are considered in the construction of  $\varepsilon_{XC}$ , such as the gradient of the electronic densities  $\nabla n(\mathbf{r})$  and the kinetic energy densities  $\tau(\mathbf{r})$ , taking care to satisfy some constraints, one expects better descriptions of physical properties. For the lower and higher steps in this hierarchy of functionals, no empirical fitting is used, but for intermediate steps those can be quite handy. In summary, the choice of functional to use depends on the system under study and available computational resources. Some lists of types of functionals can be found in the paper by Perdew and Schmidt [35] and in the open-source functional library LibXC [36]. We will focus our attention on a more in-depth description of the two functionals used for this work, which are the solid adapted Perdew-Burke-Ernzerhof (PBEsol) [37] and the modified Becke-Johnson potential parametrized by Jishi *et al.* (Jishi - mBJ) [38]. The reasoning behind this choice will be explained in the following subsections.

As can be seen in equation 2.25, the spin polarization can be taken into account in the definition of the exchange correlation potential. The treatment of the spin degree of freedom in the density functional theory framework is called spin-DFT and follows more or less the same idea of non-relativistic DFT, only more mathematically involved. This generalization can be done by starting not from the (non-relativistic) Schrödinger's equation but from Dirac's equation, written for a one electron system as

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left[c\alpha\cdot(\mathbf{p}+e\mathbf{A}) - e\phi + \beta m_e c^2\right]\Psi(\mathbf{r},t), \qquad (2.26)$$

where  $\Psi(\mathbf{r}, t)$  is a column matrix of four different wave functions called the 4-spinor, which can also be written as the array of two 2-spinors,  $\Psi$  and  $\psi$ , as

$$\Psi(\mathbf{r},t) = \begin{bmatrix} \Psi(\mathbf{r},t) \\ \psi(\mathbf{r},t) \end{bmatrix}, \text{ with } \Psi(\mathbf{r},t) = \begin{bmatrix} \psi(\mathbf{r},t;1) \\ \psi(\mathbf{r},t;2) \end{bmatrix} \text{ and } \psi(\mathbf{r},t) = \begin{bmatrix} \psi(\mathbf{r},t;3) \\ \psi(\mathbf{r},t;4) \end{bmatrix}.$$
(2.27)

In the above equation, the quantities  $\alpha$  and  $\beta$  are  $4 \times 4$  matrices involving the Pauli matrices  $\sigma_i$ . After some extensive calculations [3] it can be shown that the  $\psi$  spinor, called the small component of the Dirac 4-spinor, is much smaller than  $\Psi$ , the large component, and is usually ignored. The equation for the large component recovers Schrödinger's equation but with an extra term, the spin term, which depends on the spin operator **S** given by

$$\mathbf{S} = \frac{\hbar}{2}\boldsymbol{\sigma}.$$
 (2.28)

Because by construction Dirac's equation is in agreement with special relativity, the spin property shows up naturally and must not be postulated as in the case of the Schrödinger's quantum mechanical treatment. By applying the same logic that yields the Hohenberg-Kohn theorem 2.4 for the non-relativistic case, it was shown that the total energy is a unique functional of not only the electronic density  $n(\mathbf{r})$ , but also of the so called spin density  $\mathbf{s}(\mathbf{r})$  [3]. Both of these quantities are now built considering independent 2-spinors, whose components are related to up or down spin, as

$$n(\mathbf{r}) = \sum_{i} \Psi_{i}^{\dagger}(\mathbf{r}) \Psi_{i}(\mathbf{r}), \qquad (2.29)$$

$$\mathbf{s}(\mathbf{r}) = \sum_{i} \boldsymbol{\Psi}_{i}^{\dagger} \mathbf{S}(\mathbf{r}) \boldsymbol{\Psi}_{i}(\mathbf{r}), \qquad (2.30)$$

$$\Psi_i(\mathbf{r}) = \begin{bmatrix} \phi_i(\mathbf{r}; 1) \\ \phi_i(\mathbf{r}; 2) \end{bmatrix}$$
(2.31)

where the sum runs over the N lowest-energy spinors and  $\phi_i$  are the independent electron wave functions. In this sense, to every point in space with non-zero electron density, an element of magnetic dipole moment  $\mathbf{s}(\mathbf{r})d\mathbf{r}$  is associated. It is also very common to define another object called the density matrix  $n_{\alpha\beta}(\mathbf{r})$ , which allows the densities above to be written in a more compact manner, where  $\alpha$  and  $\beta$  have values 1 or 2, referring to the spinor up or down components, yielding

$$n(\mathbf{r}) = \sum_{\alpha} n_{\alpha\alpha}(\mathbf{r}), \ \mathbf{s}(\mathbf{r}) = \frac{\hbar}{2} \sum_{\alpha\beta} n_{\alpha\beta}(\mathbf{r}) \boldsymbol{\sigma}_{\alpha\beta}.$$
(2.32)

This allows to cast the Hohenberg-Kohn theorem into a single object, namely the density matrix. That is, the total energy of the ground state of a multielectronic system is a unique functional of the density matrix  $E = G[n_{\alpha\beta}(\mathbf{r})]$ . In analogy to equation 2.24, now the exchange correlation potential  $V_{\alpha\beta}^{XC}$  is written as the functional derivative in regards to the density matrix as

$$V_{\alpha\beta}^{XC} = \left. \frac{\delta E_{XC}}{\delta n_{\alpha\beta}} \right|_{n_{\alpha\beta}(\mathbf{r})}.$$
(2.33)

Finally, the Kohn-Sham equations 2.22 are now written with the subscripts  $\alpha$  and  $\beta$  as

$$\left[-\frac{1}{2}\nabla^2 + V_n(\mathbf{r}) + V_H(\mathbf{r})\right]\phi_i(\mathbf{r};\alpha) + \sum_{\beta} V_{\alpha\beta}^{XC}(\mathbf{r})\phi_i(\mathbf{r};\beta) = \epsilon_i\phi_i(\mathbf{r};\alpha).$$
(2.34)

Through an apt manipulation [39], this equation can be recast as

$$\left[-\frac{1}{2}\nabla^2 + V_n(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) + \mu_B \boldsymbol{\sigma} \cdot \mathbf{B}_{XC}(\mathbf{r})\right] \boldsymbol{\Psi}_i(\mathbf{r}) = \epsilon_i \boldsymbol{\Psi}_i(\mathbf{r}), \qquad (2.35)$$

which is the basically the same as the non-spin-polarized version (2.22) with an additional term  $\mathbf{B}_{XC}$ , called the "exchange and correlation magnetic field". This can be understood

as the effective magnetic field generated by the many electrons and can be the source of magnetic ordering. In summary, the electronic spin degree of freedom can be taken into account in DFT calculations through a new formulation based on Dirac's equation and spinors, resulting in equation 2.34, or equivalently 2.35.

One final remark must be made about spin-DFT in regards to how the spins can be oriented in the material: *collinear* or *non-collinear*. For collinear calculations, one considers that the spins can only orient themselves in a single direction (Ising spins). Naturally, this approximation can simulate only ferromagnetic, antiferromagnetic and ferrimagnetic materials. In this case, the spinors can be chosen to have only one non-zero component and calculations are greatly simplified. For the non-collinear case, the spinors have two non zero components and the spin density can oriented, in principle, along any direction in the Bloch sphere. This approach is more versatile and can be used to study more exotic spin arrangements such as spin helices and domain walls. Unfortunately, the doubling of the functions needed to describe each electron causes an increase of about 64 times the computational cost [3].

### 2.4.1 PBEsol

Belonging to the class of generalized gradient approximations (GGA), the original Perdew-Burke-Ernzerhof [40] is one of the most successful functionals proposed, combining both computational efficiency and reliability. It uses not only the local electronic density  $n(\mathbf{r})$  in the construction of the exchange and correlation energy per electron but also how it varies spatially through its gradient  $\nabla n(\mathbf{r})$ . The main motivation behind the proposal of this functional was, at the time, the necessity of improving another functional of the same class, the Perdew-Wang 1991 or PW91 [41]. Among the problems that PW91 presented were a complicated and overparametrized expression for the exchange-correlation energy per electron, spurious variations for small and large density gradients and also a worse description of the linear response of the density for a uniform electron gas than LDA [40].

In contrast to PW91, PBE focuses on satisfying only the constraints that are "energetically relevant". So, the solution proposed by the authors consists on writing  $\varepsilon_{XC}$  in 2.25 as the product of the electronic density n by the exchange energy of the uniform electron gas  $\varepsilon_X^{unif}(n)$  and a non-local enhancement factor for exchange and correlation  $F_{XC}$ , which depends on a dimensionless density gradient s, the local Seitz radius  $r_s$  and on the relative spin polarization  $\zeta = (n_{\uparrow} - n_{\downarrow})/n$  as :

$$E_{XC}^{GGA}[n_{\uparrow}, n_{\downarrow}] = \int d\mathbf{r} \, n \, \varepsilon_X^{unif}(n) \, F_{XC}(r_s, \zeta, s).$$
(2.36)

This approach is very interesting as it retains the correct features of the LSD potentials while also addressing the most energetically important electronic density gradient non-local aspects, yielding a potential that is relatively simple to study, implement and

improve, justifying its enormous success <sup>7</sup>. That being said, one of the key aspects that PBE does not take into account is the correct second-order gradient coefficients for  $E_X$  and  $E_C$  in the slow density varying limit.

Eleven years after the first paper, Perdew, Burke and other collaborators (but not Ernzerhof), proposed an improvement on the PBE potential specially aimed at improving results for solids [37]. Over the years, several studies showed that PBE overestimates physical properties such as bulk moduli, phonon frequencies, magnetic and ferroelectric ordering, while surface energies are underestimated. The authors show that a fundamental dilemma is presented by GGA-type approximations. When the gradient dependence is enhanced, atomization and total energies are improved at the cost of bond leghts, whereas usual solid oriented GGAs, having reduced gradient dependence, improve lattice parameters while worsening total energies. This is due to an intrinsic characteristic of these functionals, where determining accurate exchange energies requires violating the validity of the functional for slowly varying electronic densities, such as are found in solids.

The proposed solution was to compromise the value of the effective gradient coefficient for exchange  $\mu$  and consequently of a second coefficient  $\beta$ , related to the limit correlation of an uniform electron gas, in order to improve surface energies by not restoring completely the gradient expansion. In other words, a new parametrization of the already existing parameters in the original PBE, dubbed PBEsol. The authors also point out that such a solution becomes exact when the solids are placed under intense pressures, which result in truly slow varying electronic densities  $n(\mathbf{r})$  in real solids and surfaces. The cost comes as expected in the predictions of atomization energies, which are more relevant to molecules than to solids

### 2.4.2 Jishi - mBJ

Another approach in building appropriate exchange-correlation potentials is starting from the Hartree-Fock equation and adapting the exchange potential  $V_{X\sigma}$ :

$$-\frac{1}{2}\nabla^2\psi_{i\sigma} + [V_{\rm nuc} + V_{\rm el} + V_{X\sigma}^{(i)}]\psi_{i\sigma} = \epsilon_{i\sigma}\psi_{i\sigma}.$$
(2.37)

In this equation,  $V_{\text{nuc}}$  is the attractive Coulomb potential from the nucleus,  $V_{\text{el}}$  is the repulsive Coulomb potential due to the electrons. The  $\sigma$  index refers to spin component (up or down) and *i* to the orbital considered. The exchange potential is written as

$$V_{X\sigma}^{(i)}(\mathbf{r}_1) = -\frac{1}{\psi_{i\sigma}^*(\mathbf{r}_1)\psi_{i\sigma}(\mathbf{r}_1)} \sum_j \int \frac{\psi_{i\sigma}^*(\mathbf{r}_1)\psi_{j\sigma}^*(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_1)\psi_{i\sigma}\mathbf{r}_2}{r_{12}} d^3\mathbf{r}_2, \qquad (2.38)$$

<sup>&</sup>lt;sup>7</sup> To illustrate this, the original paper has been cited over 175.000 times as of 09/2023 according to Google Scholar, ranking as the 16th most cited paper of all time according to Nature (https://www.nature.com/news/the-top-100-papers-1.16224)

which is manifestly spin and orbital dependent. This causes a series of difficulties for the implementation and interpretation of the results. One of the ways this was treated was by Slater in 1951 [42] through an orbital averaged exchange potential

$$V_{X\sigma}^{\text{Slater}} = \sum_{i} \frac{\rho_{i\sigma}}{\rho_{\sigma}} V_{X\sigma}^{(i)}, \qquad (2.39)$$

where  $\rho_{i\sigma}$  is the density of the *i*th spin-orbital. Effectively, this means considering a local potential. Also of importance is the concept of exchange-hole  $\rho_{X\sigma}(\mathbf{r}_1\mathbf{r}_2)$ , that is, the smaller electronic density of a given spin component (up or down) in the vicinity of an electron of the same spin type, and defined as

$$\rho_{X\sigma(\mathbf{r}_1\mathbf{r}_2)} = \frac{1}{\rho_{\sigma}(\mathbf{r}_1)} \left| \sum_{i} \psi_{i\sigma}^*(\mathbf{r}_1) \psi_{i\sigma}(\mathbf{r}_2) \right|^2.$$
(2.40)

Thus, one can write 2.39 as

$$V_{X\sigma}^{\text{Slater}} = -\int \frac{\rho_{X\sigma(\mathbf{r}_1\mathbf{r}_2)}}{r_{12}} d^3\mathbf{r}_2.$$
(2.41)

As exchange potentials can be optimized to minimize the total energy of the Slater determinants of the respective orbitals, and for spherically symmetrical atoms can be solved exactly, a comparison between these exact exchange optimized effective potentials (OEP) and the Slater potential was made by several groups [43]. The problem with OEPs is that they require the same two electron integrals present in the Hartree-Fock method and have numerical instabilities. With the goal of obtaining a simpler effective potential to model exchange for DFT calculations, Becke and Johnson proposed in 2006 [43] an exchange potential  $V_{X\sigma}^{\rm BJ}$  that respects several interesting properties such as invariance to unitary orbital transformations and exact treatment of any ground state hydrogenic atom. It is given in terms of the kinetic energy density  $\tau_{\sigma} = \sum_{i} |\nabla \psi_{i\sigma}|^2$ , the total electronic density  $\rho_{\sigma} = \sum_{i} |\psi_{i\sigma}|^2$  and the Slater potential as

$$V_{X\sigma}^{\rm BJ} = V_{X\sigma}^{\rm Slater} + \frac{1}{\pi} \sqrt{\frac{5}{12}} \sqrt{\frac{\tau_{\sigma}}{\rho_{\sigma}}}.$$
 (2.42)

This is a purely density dependent exchange potential that has a simple form and is also able to reproduce at lesser cost the properties of the more costly OEPs.

Focusing specifically at improving band gaps, a chronic problem in DFT, Tran and Blaha proposed in 2009 [44] a modification of Becke-Johnson's exchange potential with a correlation term from LDA (TB-mBJ), which has a small effect. Their idea was to develop a semi-local potential  $V_{X,\sigma}^{\text{mBJ}}$  that mimics the behavior of orbital-dependent potentials at a smaller computational cost when compared to methods such as hybrid functionals or Green's function + screened Coulomb's interaction (*GW*). This functional is given by the expression
$$V_{X,\sigma}^{\text{MBJ}}(\mathbf{r}) = c V_{X,\sigma}^{\text{BR}}(\mathbf{r}) + (3c-2)\sqrt{\frac{5}{12}}\sqrt{\frac{\tau_{\sigma}(\mathbf{r})}{\rho_{\sigma}(\mathbf{r})}},$$
(2.43)

where  $V_{X,\sigma}^{\text{BR}}$  is the Becke-Roussel potential [45], given by

$$V_{X,\sigma}^{\mathrm{BR}} = -\frac{1}{b_{\sigma}} \left( 1 - e^{-\rho_{X\sigma}(\mathbf{r}_{1}\mathbf{r}_{2})} - \frac{1}{2}\rho_{X\sigma}(\mathbf{r}_{1}\mathbf{r}_{2})e^{-\rho_{X\sigma}(\mathbf{r}_{1}\mathbf{r}_{2})} \right), \qquad (2.44)$$

and c acts as a mixing parameter of "exact" exchange (considering the restrictions of  $V_{X,\sigma}^{\text{BJ}}$ [43]). The term  $b_{\sigma} = [\rho_{X\sigma}(\mathbf{r}_{1}\mathbf{r}_{2})^{3}e^{\rho_{X\sigma}(\mathbf{r}_{1}\mathbf{r}_{2})}/((8\pi\rho_{\sigma}))]^{1/3}$  takes into account the exchange hole from equation 2.40 but calculates it in another manner, adding the correlation term from LDA [46]. It's important to notice that, contrary to the original approach from Becke and Johnson, Tran and Blaha used the Becke-Roussel potential instead of the Slater potential (see eq. 2.42), but it was shown that these potentials are quasi-identical for atoms. Thus, for c = 1 the original Becke-Johnson potential is recovered. The mixing parameter c was chosen to incorporate the semi-local dependence on the density  $\rho$  and its gradient  $\nabla \rho$ through

$$c = \alpha + \beta \left[ \frac{1}{V_{\text{cell}}} \int_{\text{cell}} \frac{|\nabla \rho(\mathbf{r}')|}{\rho(\mathbf{r}')} d^3 r' \right]^{1/2}.$$
 (2.45)

Here,  $\alpha$  and  $\beta$  are free parameters that were fitted to several experimental and theoretical band gap data, aiming to minimize mean absolute relative error, and  $V_{\text{cell}}$  is the unit cell volume. This means that this potential adds two "empirical" quantities that, in principle, depend on the choice of systems to fit. As mentioned before, semi empirical approaches to DFT have shown to be successful for specific objectives and thus shouldn't be discarded on the basis of full *ab initio* only calculations. Of major importance are the values of these parameters, given by

$$\alpha = -0.012$$
,  $\beta = 1.023 \,\mathrm{bohr}^{1/2}$ . (2.46)

Although well suited for a range of solids and molecules, the TB-mBJ potential yield less satisfactory results for transition metal oxides. In order to fix this issue, Jishi *et al.* [38] proposed a simple reparametrization of the modified Becke-Johnson potential specifically tailored to improve the band gap of perovskite systems. The new parameters were chosen (i.e. not fitted through error minimization) to be

$$\alpha = 0.4 , \ \beta = 1.0 \,\mathrm{bohr}^{1/2} .$$
 (2.47)

so as to better reproduce the experimental band gap of a series of halide perovskites. Thus, the biggest change was done on the free parameter  $\alpha$ , decreasing the relative influence of the  $|\nabla \rho|/\rho$  dependence on the total exchange-correlation potential. It must be noted that improving the band gap predictions is very relevant for the discussion of magnetic structures and their effect on the electronic structure of a material, thus the usage of a very system specific functional is justified.

# 3. Review of the Literature

### 3.1 General Properties

The perovskite oxide crystal structure is represented by the chemical formula ABO<sub>3</sub>, where A is usually a pre-transition metal such as K, Sr or La, and B a transition or post-transition metal [7]. It consists of a cube with A cations on the vertices, a face-centered octahedra of oxygens and the B metal on the centre, as depicted in figure 14. The versatility and stability of this structure is remarkable, exhibiting a very wide range of phenomena depending on the combination of elements, dopings and vacancies, a few of which are ferroelectricity and multiferroicity, magnetoresistance and very high dielectric constants [15, 28].

The description of the structure of the  $Sr_3Ti_2O_7$  compound was first done by Ruddlesden and Popper in 1958 [17], who noted that this material could be considered



Figure 14 – The simple perovskite structure, with the BO<sub>6</sub> octahedra highlighted.

n	Ideal Structure	Space group (number)
$\infty$	cubic	$Pm/\bar{3}m$ (221)
2	tetragonal	I4/mmm (139)
1	tetragonal	I4/mmm (139)

Table 1 – Structural information of ideal Ruddlesden-Popper unit cells.

an intermediate between  $SrTiO_3$  and  $Sr_2TiO_4$ . It consists on a double strontium titanate perovskite ( $SrTiO_3$ ) layer, interweaved with strontium oxide (SrO) layers. The discovery of other materials that share the same structure, such as  $Sr_3Fe_2O_7$  shortly after [47] drew interest on the possible combinations of elements and the properties that these materials could exhibit.

These systems became known as Ruddlesden-Popper (RP) compounds, of general formula  $A_{n+1}B_nO_{3n+1}$  or alternatively  $AO(ABO_3)_n$ , where *n* refers to the number of perovskite layers stacked in-between the AO rock-salt layers. The perovskite-only case can be understood as  $n \to \infty$ . The A site usually corresponds to a rare or alkaline earth element, whereas the B site can be occupied by transition or post transition metals [18]. The unit cells of the ideal structures (i.e. non-distorted) crystallize in the space groups described in table 1, depending basically on the Goldschimdt tolerance factor *t* [48] of Shannon's ionic radii [49], given by

$$t = \frac{r_A + r_O}{\sqrt{2(r_A + r_B)}}.$$
 (3.1)

Here,  $r_A$  and  $r_B$  refer to the radii of the A and B cations while  $r_O$  oxygen's. For  $n = \infty$ , the ideal cubic structure is obtained for  $t \approx 1$  and becomes distorted as t decreases, with a stability interval of 0.75 < t < 1.00. For the n = 1 materials, the same relation leads to the ideal tetragonal structure, also featuring distortions for smaller t, but the stability interval is decreased to about 0.85 < t < 1.02 [23]. As n increases beyond three perovskite layers, the RP stacking becomes thermodynamically less favorable and phase transitions are expected. In the rare cases where higher n phases are stabilized, they are usually present as defects on the bulk of the lower and more stable n compounds [50].

The defining characteristic of a Ruddlesden-Popper series is the progressive confinement of the perovskite layers as n is lowered. In this sense, one can say that the system's dimensionality decreases with n, going from an isotropic (i.e. only perovskite) 3D material for  $n = \infty$  towards a 2D-like slab stacking of rock salt and perovskites [23]. In the ideal  $n = \infty$  structure, there is fundamentally no difference between the oxygen crystallographic positions, but the introduction of the rock-salt layers is enough to break this symmetry and separate the oxygens by their chemical neighborhood, as is graphically represented in figure 15. Considering the oxygen octahedra, the oxygen ions that lie along the *ab* plane will henceforward be referred to as basal, in contrast to the apical ones, which lie along the c axis. As a further distinction, for n = 2, the apical oxygen that is shared



Figure 15 – Example of the ideal structures for a given Ruddlesden-Popper series  $A_{n+1}B_nX_{3n+1}$  for different n. As n increases (left to right), the material goes from a 2D-like confined structure towards an isotropic perovskite only structure. It is important to note the different oxygen crystallographic sites, here denoted as  $X_i$ , for the different n in the series. Figure taken from reference [23].

between perovskites will be called apical prime.

In terms of electrical conductivity, metal-insulator transitions are common in RP series. These stem from the different nature of the perovskites, usually metallic, and the rock-salt, usually insulating. Thus, as n grows, so does the conductivity due to the increased interaction between oxygen and the B cation along the c direction [23]. Interesting to note is also that this conductivity is of mixed ionic-electronic origin, the ionic conduction originating both from the apical oxygens as well as basal vacancies, and the electronic conduction from the perovskite oxygen octahedra proper [51]. These characteristics can be enhanced by controlled non-stoichiometric synthesis, where the lack or excess of oxygens may lead also to a more stable structure [18, 23].

In the following, a more in depth review of the properties reported in the literature for the specific materials we are focused in this study will be given.

### 3.2 SrFeO<sub>3</sub>

The  $n = \infty$  member of the strontium-iron series consists of a tetragonal perovskite structure with a small distortion along the *c* axis, deviating from the ideal cubic structure and belonging to the space group P4/mmm, with cell parameters a = b = 3.857 Å and c = 3.869 Å [52]. As this distortion is small, hard to detect and doesn't have a Jahn-Teller origin, previous studies usually reported a perfect cubic perovskite structure [53, 54, 55]. Due to the plethora of stable phases, non-stoichiometric SrFeO<sub>3± $\delta$ </sub> is also heavily studied and can feature very different physical properties such as ferroelectricity and semiconductivity [56].

In this compound, the unusual formal oxidation Fe<sup>+4</sup> contrasts with the usual Fe<sup>4+</sup> that is expected of a B-site metal of perovskites, but can be better explained in a more covalent picture. The compound is an example of a negative charge-transfer metal, where the ground state is dominated by holes in the ligand, which are directly responsible for electric conduction. This kind of regime takes place when the charge transfer energy  $\Delta$ , the cost associated with the localization of a ligand electron on the metal, is smaller than on-site Coulomb correlation energy U (see section 2.2)<sup>1</sup>. This makes it energetically more favorable to have a ground state where the metal "steals" electrons from the ligand, creating n holes denoted as  $\underline{L}^n$ . In this sense, XAS studies coupled with cluster model calculations showed that the ground state of SrFeO<sub>3</sub> is best described by

$$|3d^4\rangle \to 0.36 |3d^4\rangle + 0.58 |3d^5\underline{L}\rangle + 0.06 |3d^6\underline{L}^2\rangle, \qquad (3.2)$$

where the coefficients refer to the percentage occupation of this configuration [55]. It is interesting to notice that the occupation of the configuration with a ligand hole is greater than the purely ionic one, meaning that the covalency in this compound is extremely important and dominates the ground state character. As the Jahn-Teller effect is caused by an asymmetric charge distribution in the  $t_{2g}$  and  $e_g$  orbitals, it would be energetically favorable for the Fe<sup>4+</sup> ions in the high  $t_{2g}^3 e_g^1$  (<sup>5</sup>E) configuration to undergo the geometrical distortion away from  $O_h$  symmetry. This is suppressed due to the main contribution of the  $|3d^5\underline{L}\rangle$  configuration, the dominant contribution to the ground state, being in the high-spin state  $t_{2g}^3 e_g^2$  (<sup>6</sup>A<sub>1</sub>) which can't exhibit the effect as a result to the symmetric charge distribution. Thus, the highly covalent (i.e. highly correlated) nature of the ground state quenches the expected Jahn-Teller effect and maintains octahedral symmetry [55, 54].

The material's magnetic structure is still yet to be fully understood as a consequence of its great complexity. Neutron diffraction studies showed that the material presents a helical spin structure, where long range magnetic interactions are important and lead to spin-canting, the magnetically active iron atom having a magnetic moment of about 2.7  $\mu_B$  [57]. The propagation wave vector of the spin wave is parallel to the  $\langle 111 \rangle$ direction and the exchange integrals between *n*-th neighbors in the Heisenberg spin  $J_n$ Hamiltonian are  $J_1 = 1.2$ ,  $J_2 = -0.2$  and  $J_4 = -0.3$  meV [58]. The changing signs mean that the strongest exchange interaction is of ferromagnetic nature between first neighbors, whereas between second and fourth neighbors it tends to order antiferromagnetically. This long ranged ( $J_4 > J_2$ ) interaction suffices to stabilize the screw spin structure with a Néel

<sup>&</sup>lt;sup>1</sup> When  $\Delta > U$ , one has the Mott-Hubbard regime.

temperature of about 134 K [59]. The magnitude of the wave vector is relatively small, yielding a large wavelength for the helical structure, with an angle between adjacent spins of about 40°, suggesting that the material is close in energy to a ferromagnetic phase [55].

More recently, thin films of  $SrFeO_3$  have also drawn the attention of the spintronics community due to the topological magnetic structure it presents. As temperature and external field are varied, it was shown that the material undergoes complex magnetic transitions that allow it to exhibit a superposition of noncollinear orderings, called a multi-q spin structure. This takes place even in the absence of the Dzyaloshinskii-Moriya, as the crystal is centrosymmetric, being the simplest system known to exhibit this behavior [60, 61]. Further research is needed to ascertain the conditions and characteristics of these exotic magnetic phases. Besides spintronics, the material and its oxygen rich/deficient phases have shown remarkable applications in the field of green energy in technologies such as solar cells, oxide fuel cells and decontamination processes [62].

# 3.3 $Sr_3Fe_2O_7$

First proposed in the 60s as a hypothetical material [47] and successfully synthesized in stoichiometric form in the 90s [63],  $Sr_3Fe_2O_7$  is a small gap semiconductor in the negative charge transfer regime, whose gap is of p - p type [64, 65]. X-ray diffraction shows that the material has the ideal structure corresponding to the I4/mmm space group and no signs of Jahn-Teller distortion, with cell parameters a = b = 3.848 Å and c = 20.140 Å [64, 66]. An interesting characteristic that this system exhibits is charge disproportionation. Even at room temperature, the Fe<sup>4+</sup> sites can be separated into Fe<sup>+3</sup> and Fe<sup>+5</sup> contributions, which can be studied by means of Mössbauer spectroscopy for example, even though it seems that this characteristic has no structural implications. The temperature  $T_D$  for this disproportionation to happen is at about 343 K, being closely followed by a metal-insulator transition at above 350 K [67, 68].

Much like the  $n = \infty$  case, the ground state is dominated by holes in the ligand due to the charge transfer effect. XAS studies show that the occupation of configurations with ligand holes, mainly  $|3d^5\underline{L}\rangle$ , is greater than the fully ionic  $|3d^4\rangle$ , being given (surprisingly) by the same ratio as in equation 3.2 [65]. Thus, the same mechanism for suppressing the Jahn-Teller distortion is present. The main difference between the two systems is the confinement in a more 2D-like environment as mentioned, which is responsible for increasing the localization of the electronic structure [18]. Because of this, even though the expected behavior is metallic for a negative charge transfer regime like for  $n = \infty$ , the reduction in the bandwidth W due to the change in dimensionality is enough to make it smaller than the hybridization  $T_{\sigma}$ , generating a gap that involves O 2p holes and is thus of the p - p type [69, 65].

The material orders itself antiferromagnetically at the Néel temperature of  $T_N \approx$ 

115 K within a complex modulated helical spin structure [67, 63]. Detailed neutron scattering measurements have shown a best fit for an elliptical modulation, yielding magnetic moments on the c axis equal to 3.19  $\mu_B$  and along the ab plane  $3.58\mu_B$  for single crystals [70]. This structure has a propagation vector in the direction (0.1416, 0.1416, 1), showing a rotation axis of  $\langle 111 \rangle$ . This means that all spins lie in a plane perpendicular to the  $\langle 111 \rangle$  direction and, along the c axis, the spins of neighboring iron atoms are antiparallel, fully analogous to the  $n = \infty$  situation [70]. An analysis of the exchange constants within the Heisenberg spin Hamiltonian between first, second and third neighbors based on this data yielded  $J_1 = -7.2$  meV,  $J_2 = 1.05$  meV and  $J_3 = 2.1$  meV respectively. The negative value of  $J_1$  implies that predominant interaction is ferromagnetic <sup>2</sup>, although long ranged antiferromagnetic exchange is also significant and is, in fact, what stabilizes the helical spin structure [70]. The competing exchange interactions near a metal-insulator transition also indicate that the system has magnetic orderings that are relatively close in energy.

The presence of a helical spin order in a quasi-2D system is rare, thus could be of use for spintronics applications, specially taking into account the rich magnetic phase diagram of a more general structure with oxygen vacancies  $Sr_3Fe_2O_{7-\delta}$  [68]. More recently, studies on this general structure and various dopants have also found promising applications in solid fuel cells, catalysis and environmental applications [71, 72, 73].

## 3.4 Sr<sub>3</sub>FeNiO<sub>7</sub>

There is plenty of evidence that the Ruddlesden-Popper series materials are highly sensitive to doping and excess or lack of oxygen, as was argued in the previous sections. Thus, it is expected that the substitution of an iron atom for a less magnetically active ion can greatly alter the physical properties the system exhibits. The double perovskite structure  $Sr_3FeNiO_7$  crystallizes in a tetragonal structure, corresponding to the ideal I4/mmm space group, a = b = 3.8415 Å and c = 20.040 Å, with highly regular stackings along the c-axis and no signs extra long-range ordering [74]. The thermodynamical conditions of growth favor a disposition in a tridimensional checkerboard pattern, such as depicted in figure 16.

An important consequence of the doping is the reduction in many orders of magnitude of the electrical resistivity, specially at low temperatures [74]. Theoretical calculations could reproduce the experimental X-ray photoelectron spectra when considering the occupations of the different  $Fe^{4+}$  electronic configurations as given by 3.2. In the case of Ni<sup>3+</sup>, the ground state configuration obtained was

<sup>&</sup>lt;sup>2</sup> In the paper, the authors define the Heisenberg Hamiltonian without the usual - sign we considered in section 2.3, so that the negative (positive) values of J imply ferromagnetism (antiferromagnetism).



Figure 16 – Unit cell of the double perovskite structure  $Sr_3FeNiO_7$ . Each perovskite has neighbors of the opposing type, forming a tridimensional checkerboard pattern.

$$|3d^{7}\rangle \to 0.28 \,|3d^{7}\rangle + 0.60 \,|3d^{8}\underline{L}\rangle + 0.10 \,|3d^{9}\underline{L}^{2}\rangle \,. \tag{3.3}$$

The occupation of the configuration with a hole in the ligand being higher than the purely ionic one both for iron and nickel is evidence of a negative charge transfer regime. The band gap is of p - p type, in the same manner as the non-doped n = 2 compound, showing that the nickel substitution isn't enough to change the nature of the material's semiconductive behavior [74]. Also worthy of note is that the p - d charge transfer parameter is lowered for the doped material while the bandwidth remains basically unchanged, which decreases the band gap and thus leads to the much higher conductivity in comparison with Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7</sub> [75, 76].

When it comes to the magnetic structure, a linear response to applied field was obtained at temperatures equal to 100K and 200K, a characteristic of a paramagnetic material. There is evidence of a transition towards a spin-glass material for temperatures lower than  $T_{SG} = 40$  K, with small hysteresis loops, whereas for temperatures over 300 K the material behaves as a ferromagnet [74].

### 3.5 $Sr_2FeO_4$

Crystallizing in the ideal K<sub>2</sub>NiF<sub>4</sub> structure, belonging to space group I4/mmm, the n = 1 compound was first synthesized in the 90s following unsuccessful attempts at growing single Sr<sub>2</sub>FeO<sub>4</sub> crystals, with cell parameters given by a = b = 3.8642 Å and c = 12.3968 Å [77]. This is due to the previously mentioned stability of several intermediate compounds, which tend to show up as parasitic phases in the growing process. This might also be one of the reasons why this material is less studied than the other members of the series.

As argued before for a Fe<sup>4+</sup> system, the ground state of the material must be dominated by holes in the ligand, characteristic of a negative charge transfer  $\Delta < 0$  regime. Analysis of slightly oxygen deficient samples, general behavior of strongly correlated systems, comparison with the properties of the n = 2 system, which are not expected to change drastically, and pressure analysis support this claim [63, 78, 79]. In this sense, Sr<sub>2</sub>FeO<sub>4</sub> is characterized as a strongly correlated insulator in the negative charge transfer regime, but studies that elucidate the contributions of each ligand-hole configuration to the ground state are still lacking. The high-spin ground state appears to be stabilized by some unidentified hidden distortion, which is invisible to standard diffraction techniques [80].

The magnetic structure of the material is also markedly complex, with an antiferromagnetic ordering at  $T_N = 56$  K. The nature of this ordering has been the subject of many studies [63, 78, 79], which indicated a helical spin ordering. More recently, Adler *et al.* [80] showed that the best fit for the magnetic structure is an elliptical cycloidal spin structure that is confined to the tetragonal *ab* plane, described by an incommensurate wave vector  $\mathbf{k} = (0.137, 0.137, 0)$  with minor and major magnetic moments of 1.9 and 3.46  $\mu_B$  respectively, which are tilted away from the *c* axis by an angle of about 70°. The action of an external magnetic field between 3 and 6 T is enough to drive a spin flop transition, confining the spins in a plane perpendicular to the field direction, reorientating the ellipses but without changing the magnetic moments, showing a robust structure.

Much like the n = 2 case, the combination of helical magnetism in a 2D system might be of interest for spintronics applications, but the presence of a gap in the n = 1system may be a complicating factor. In another direction, the study of oxygen vacancies and doping is pointed as being of potential relevance for applications in anionic conductors below 700°C and various catalysis reactions [81].

# 3.6 SrVO<sub>3</sub>

The discovery of superconductivity in cuprates [82] led to interest in systems that are similar and could be used as models to explain high- $T_c$  behavior. One of these systems is the strontium vanadate SrVO<sub>3</sub> due to the electronic configuration  $3d^1$  of the V<sup>4+</sup> ion, with a single electron in the valence band, which is analogous to the  $3d^9$  configuration of the cuprates, with a single hole in the valence band [83]. Thus, many efforts were directed towards understanding this material and also its Ruddlesden-Popper phases.

 $SrVO_3$   $(n = \infty)$  crystallizes in the perfect cubic perovskite structure, belonging

to the  $Pm/\bar{3}m$  space group, with cell parameter a = 3.840 - 3.849 Å [84]. The singlephase compound is of difficult growth due to instabilities in the Sr/V stoichiometry and oxygen content, being only successfully synthesized in the late 90s [85]. It is characterized as a highly-correlated system near a Mott-Hubbard transition, the  $d^1$  electron partially occupying orbitals of the  $t_{2g}$  class and thus exhibiting a metallic behavior, which due to effects of electronic correlation might lead to the appearance of a Mott gap [86]. Among these effects are modifications of bond topology, charge distribution and effective mass of charge carriers, which might arise from the reduced bandwidth this material exhibits [87]. In this sense, even though there is electron delocalization in the occupied bands, the size of their bandwidth is small enough to render correlation effects very significant. The metallicity of the single crystal compound was observed for a variety of growth conditions and seems to be unaffected by oxygen excess or vacancies, but no superconductivity was observed [84, 83].

The magnetic susceptibility of the compound increases slightly with decreasing temperature and saturates below 100 K, which is evident of paramagnetic behavior, with deviations typically attributed to impurities or parasitic phases[84, 88].

As of lately, applications of  $SrVO_3$  in transparent conductors have been proposed due to the material's rare combination of both high electrical conductivity and acceptable optical transparency, which can be further altered by tuning the correlation through film thickness and external fields [87]. Doped species were also reported to be potentially useful in fluorescence applications and high-performance anodes in lithium-ion batteries [89, 90].

# $3.7 Sr_2VO_4$

 $Sr_2VO_4$  is the layered perovskite phase of  $SrVO_3$  with  $n = \infty$ , crystallizing in a tetragonal unit cell within the I4/mmm space group, with cell parameters a = b = 3.837 Å and c = 12.576 Å [91]. Much like in the case of the iron series, the presence of the insulating SrO layers decouples the perovskite layers and turns the material an insulator along the c axis, but conductivity may still take place in the ab plane [18, 83]. Being the electronic equivalent of La<sub>2</sub>CuO<sub>4</sub>, an important compound in the family of high-T<sub>c</sub> superconductors,  $Sr_2VO_4$  exhibits a similar layered two dimensional spin-1/2 lattice, but the material in its bulk form has a very persistent insulating nature [92]. Thin-films studies show that a Mott-Hubbard gap lower than 0.2 eV is present and may be removed by doping with La [93].

A very unique property of this material, which gathered a lot of attention, is the prediction of a complex ground state due to several competing interactions. Detailed theoretical calculations showed that the material is simultaneously on the verge of a Mott transition, a ferromagnetic-antiferromagnetic transition and an orbital-ordering transition at about 100 K[94]. Because the vanadium  $d_{yz}$  and  $d_{zx}$  orbitals remain degenerate and the crystal field splitting of  $d_{xy}$  is small, the material would arrange itself in a long period 2x4 structure where the valence orbitals are organized in a stripe-like structure, called orbital ordering, stabilized also by long range exchange. [94]. This rare combination of phenomena was reported experimentally not long after, happening only for samples close to the nominal stoichiometry [95, 92]. At low temperatures below 10 K, a magnetic transition signature was found corresponding to weak ferromagnetism or canted antiferromagnetism, evolving towards an antiferromagnetic character in the orbital ordered state [95]. For temperatures above 127 K the material becomes paramagnetic [92].

# 4. Methodology

#### 4.1 WIEN2K

All calculations were done using the WIEN2K [96] distribution, a comprehensive DFT code developed by Peter Blaha and collaborators at TU-Wien in the 1980s and constantly updated. It is based on a linearized augmented plane wave (LAPW) method, which expands on Slater's APW method [24] and includes local orbitals (lo) for improvement of radial basis functions, thus being also dubbed as APW+lo. A more detailed explanation is given in the following.

First off, as proposed by Slater, one divides the space in a system into two regions, where different basis expansions are used for the Schrödinger's equation. Around each atom, a sphere is defined with some atom-dependent spherical potential V and the basis set consists of the solutions of the radial equation for each type of atom. These spheres are non-overlapping, which leaves some interstitial space of separation, where the wavefunctions take on the form of planewaves that depend on the lattice wave-vectors. Mathematically, one has

$$\phi(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\omega}} \sum_{n} C_{n} e^{i\mathbf{k_{n}}\cdot\mathbf{r}} &, \text{ inside interstitial} \\ \sum_{lm} A_{lm} u_{l}(r) Y_{lm}(\mathbf{r}) &, \text{ inside spheres.} \end{cases}$$
(4.1)

Here,  $\phi$  is the wavefunction,  $\omega$  is the cell volume,  $\mathbf{k_n} = \mathbf{k} + \mathbf{K_n}$  where  $\mathbf{K_n}$  is the lattice wave vector,  $\mathbf{k}$  is the wave vector inside the first Brillouin zone,  $u_l$  is the solution to the radial Schrödinger equation and  $Y_{lm}$  are the spherical harmonics. This approximation is often called the "muffin-tin" approximation, being very apt for describing close packed materials and losing reliability as coordination and symmetry decreases [97]. In order to maintain the kinetic energy well defined, constraints at the boundary between the two regions are needed. This yields after some calculations a relationship between the coefficients  $A_{lm}$ , the planewave coefficients  $C_n$  and an energy parameter  $E_l$ , which are the variational coefficients of the APW method. The functions that satisfy the boundary condition are called the augmented plane waves.



Figure 17 – Schematic representation of the LAPW method, considering two types of atoms in a given crystal system. The muffin-tin spheres are not overlapping.

The linearization process to turn the APW method to LAPW refers to a change in the basis functions inside the spheres. Now, they are written in terms of a linear combination of the radial functions, as previously, but also their derivatives with respect to energy. Because of this change, equation 4.1 can be rewritten as

$$\phi(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\omega}} \sum_{n} C_{n} e^{i\mathbf{k_{n}}\cdot\mathbf{r}} &, \text{ inside interstitial} \\ \sum_{lm} [A_{lm}u_{l}(r) + B_{lm}\dot{u}_{l}(r)]Y_{lm}(\mathbf{r}) &, \text{ inside spheres} \end{cases}$$
(4.2)

In this equation,  $B_m$  is just a coefficient for the energy derivative of the radial function  $\dot{u}(r)$ , fully analogous to  $A_{lm}$ . The reason to make this change is because the linearized augmented plane waves have more variational freedom inside the sphere, reducing the size of the basis required for a good convergence in comparison with the previous definition [97]. A schematic representation of the method is present in figure 17.

An improvement on the method relies on increasing the efficiency of the linearization by adding inside the spheres some local orbitals  $\phi_{lm}^{lo}$  given by

$$\phi_{lm}^{lo} = [A_{lm}u_l(r, E_{1,l}) + B_{lm}(u)_l(r, E_{1,l})]Y_{lm}(\mathbf{r}), \qquad (4.3)$$

which have the same general form of the orbitals on 4.2 but whose coefficients do not depend on the  $\mathbf{k_n}$  wavevectors and are additionally under the constraint of being normalized and going to zero at the boundary [96]. With this optimized basis set of functions, standard DFT calculations can be conducted as detailed in section 4. In this scheme, the convergence of the basis set is determined by a cutoff parameter given by  $R_{mt}K_{max}$ , where  $R_{mt}$  refers to the smallest atomic sphere radius in the unit cell of the system and  $K_{max}$  is the modulus of the largest reciprocal lattice vector in the plane wave expansion.

## 4.2 X-ray Spectroscopy

When radiation interacts with matter, several excitation and decay processes take place. At specific incident photon energies called absorption edges, an electron from a low-lying energy level (called core electron) can be promoted to a higher energy level. As these core states are tightly bound to the atomic nucleus, the energy required for this absorption to take place is on the X-ray region of the electromagnetic spectra, being able to reach up to 30 keV [98]. Thus, X-ray absorption spectroscopy (XAS) refers to a first order optical process (i.e. one photon only), where a core electron is excited to the empty portion of the electronic structure and later decays to more internal levels following two main distinct mechanisms: (i) the fluorescence process, emitting radiation equal to difference in energy levels between the core hole and excited state, and (ii) Auger process, where the energy emitted by the decay to the core hole excites a third electron, which is then released from the sample.

A distinction is made for the cases where the excited electron reaches the conduction band, yielding the X-ray absorption near edge structure (XANES), and when it reaches the continuum with energy just above that of XANES, yielding the extended X-ray absorption fine structure (EXAFS). The radiation emitted via fluorescence or the emitted Auger electrons are collected, resulting in the XAS spectrum. This is characteristic of each element and contains important information regarding for example the chemical environment, oxidation states, symmetry and structure of the compounds [99]. The signal can also be obtained by the total electron yield (TEY) method, in which the current that flows to the sample to neutralize the excess of positive charge is detected, being under certain conditions proportional to the absorption cross section [98].

For relatively lower energies, the Auger mechanism is dominant whereas for higher energies fluorescence becomes the main decay channel. It is important to note that the decay leads to other core holes, which trigger subsequent emissions by fluorescence, Auger and also low-energy decay processes such as luminescence until all core holes are filled, a phenomenon known as electron cascade [98]. A schematic representation of XAS is present in figure 18. A core electron is excited to the empty portion of the DOS by the absorption of an incident photon with energy  $\hbar\Omega$ , reaching a state with energy  $\varepsilon_w$ . Also represented is the X-ray photoelectron spectroscopy (XPS), a closely related technique where the core-electron is ejected as a photoelectron with energy  $\varepsilon_k$ .

Due to historical reasons, the spectroscopy notation to identify specific electronic states differs from the usual atomic orbitals notation. The correspondence is done in the table 2. Instead of using the numbers (1,2,3,..) for the principal quantum number n, the



Figure 18 – Schematic representation of XAS and XPS in terms of the density of states (DOS). Figure taken from reference [98].

Orbital	Spectroscopy
1s	K
2s	$L_1$
$2p_{1/2}$	$L_2$
$2p_{3/2}$	$L_3$
3s	$M_1$
$3p_{1/2}$	$M_2$
:	:

Table 2 – Correspondence between usual orbital notation and spectroscopical notation.

letters (K, L, M, ...) are used, and the orbital angular momentum labels (s, p, d, f) are exchanged for (1,2,3,4,...), going from high to low energy. This takes into account the possibility of spin-orbit coupling, so that the  $2p_{1/2}$  state is labeled as  $L_2$  and the  $2p_{3/2}$  state as  $L_3$  and so on. Because of this, the presence of spin-orbit coupling splits the absorption edges (when possible) into two peaks close in energy.

The interaction of X-rays with matter is best described by the so-called Fermi's Golden Rule, given by

$$W_{fi} = \frac{2\pi}{\hbar} |\langle \Phi_f | T | \Phi_i \rangle|^2 \delta(E_f - E_i - \hbar\Omega), \qquad (4.4)$$

in which the probability of a transition  $W_{fi}$  between the initial state  $\Phi_i$  and final state  $\Phi_f$ depends on a transition operator T and is proportional to a delta function, which states that the transition only takes place when the energy of the final state  $E_f$  is equal to the sum of the energies of the initial state  $E_i$  and the incident photon  $\hbar\Omega$ . The operator T is obtained by solving the Lippman-Schwinger equation, and considering only the first order perturbation on the interaction Hamiltonian  $\mathbf{p} \cdot \mathbf{A}$  due to the one-photon nature of XAS one obtains [98]

$$W_{fi} \propto |\langle \Phi_f | \mathbf{r} | \Phi_i \rangle|^2 \delta(E_f - E_i - \hbar\Omega).$$
(4.5)

In equation 4.5,  $\mathbf{r}$  is the electric dipole operator, which is the leading term of the interaction. By expanding the wavefunctions of the initial and final states into radial and angular parts according to Wigner-Eckart's theorem, one obtains the following selection rules regarding the respective quantum numbers:

$$\Delta J = \pm 1,0\tag{4.6}$$

$$\Delta s = 0 \tag{4.7}$$

$$\Delta l = \pm 1 \tag{4.8}$$

For example, considering these rules a 1s core electron can only be excited to p states, whereas a p electron can never transition to another p state. The forbidden transitions can in fact take place, but with a very reduced probability, being the result of higher order terms in the transition operator such as the electric quadrupole. An estimate of the magnitude of the matrix element associated with this term yields a value smaller than  $10^{-4}$  that of the electric dipole, justifying the dipolar approximation [98].

As mentioned, a characteristic of XAS spectra is that, although being an element specific technique, it is also sensitive to the chemical environment. In this sense, considering for example a transition metal oxide, the analysis of the oxygen K (1s) edge can also give information regarding the metal, such as valence charges and covalent behavior [100, 101].

### 4.3 Optical Conductivity Spectrum

Considering Drude's model for the electronic conduction in a metal, one obtains the following equation of motion for the weakly bound electrons subjected to a spatially uniform force field  $\mathbf{f}(t)$  [5]:

$$\frac{d\mathbf{p}(t)}{dt} = -\frac{\mathbf{p}(t)}{\tau} + \mathbf{f}(t).$$
(4.9)

Here,  $\mathbf{p}(t)$  is the electron's linear momentum and  $\tau$  is known as the relaxation time, the average interval between scattering events with ions in the solid. Although derived from a very simplified model, this equation is quite useful when considering several applications that have general validity, such as the current induced in a metal by a timedependent electric field, which can be due to an electromagnetic wave interacting with the material. In this case, the electric field is written in terms of its complex extension as  $\mathbf{E}(t) = \text{Re} \{\mathbf{E}(\omega)e^{-i\omega t}\}$  to account for the oscillatory nature of the field and the force field is simply  $\mathbf{f}(t) = -e\mathbf{E}$ , *e* being the electronic charge. By writing the moment in terms of the current density  $\mathbf{j}$  as  $\mathbf{j} = -ne\mathbf{p}/m$ , with *n* being the number of charge carriers and *m* their mass, and taking into account that both the real and imaginary parts of the solution must obey equation (4.9), one promptly arrives at the following results:

$$\mathbf{j}(\omega) = \sigma(\omega)\mathbf{E}(\omega), \qquad (4.10)$$

$$\sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau},\tag{4.11}$$

$$\sigma_0 = \frac{ne^2\tau}{m}.\tag{4.12}$$

The quantity  $\sigma(\omega)$  is the conductivity of the material, which makes the connection between the time-varying electric field and the current density it causes on the metal. For  $\omega = 0$  one obtains  $\sigma = \sigma_0$ , which is known as the direct current Drude conductivity [5]. These equations are valid when the wavelength of the field is far larger than the electronic mean free path, the average distance between scattering events, so that the electric field does not vary appreciably over small distances. This condition is usually satisfied by the interaction of a metal with light in the visible part of the electromagnetic spectrum, whose wavelengths are of about 10<sup>3</sup> to 10<sup>4</sup> Å, so that  $\sigma$  is also called optical conductivity. By considering the wave's magnetic field, one arrives at a correction that is about 10<sup>-10</sup> times smaller than the leading electric field term, being thus usually ignored [5]. Taking the real and imaginary parts of  $\sigma$ , one obtains

$$\operatorname{Re}\{\sigma(\omega)\} = \frac{\sigma_0}{1 + \omega^2 \tau^2},\tag{4.13}$$

$$\operatorname{Im}\{\sigma(\omega)\} = \frac{\sigma_0 \omega \tau}{1 + \omega^2 \tau^2}.$$
(4.14)

The real part is associated with transmission of the wave through the medium, whereas the imaginary part is related to absorption. This can be more readily seen by analyzing the complex dielectric constant  $\epsilon(\omega)$  that is derived from this theory [5]

$$\epsilon(\omega) = 1 + \frac{4\pi i \sigma(\omega)}{\omega}.$$
(4.15)

If  $\omega \tau \gg 1$ , this can be expressed in a first approximation by

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}; \quad \omega_p^2 = \frac{4\pi n e^2}{m}, \tag{4.16}$$

where  $\omega_p$  is a quantity known as the plasma frequency of the material. For  $\omega < \omega_p$ ,  $\epsilon$  is negative and thus the solutions to the wave equation decay exponentially, meaning the material reflects the majority of the incoming wave. If  $\omega = \omega_p$ , then most of the wave is absorbed, whereas for  $\omega > \omega_p$  the solutions become oscillatory and the wave can penetrate the metal. Thus, even in this simple model one can study how light (with high enough frequency) interacts with a metal, leading to the dispersion relation  $\omega^2 = \omega_p^2 + c^2 k^2$ , where ck is the wave number [102].

Naturally, Drude's theory is limited and thus more complex theories taking into account the electron's quantum nature have been proposed to explain the behavior of the electronic conductivity and dielectric constant in various media. In the review by Dagotto [103] some possibilities are discussed. When considering models that take into account lattice behavior explicitly, such as Hubbard's model, the optical conductivity is defined as a correlation function between the Fourier transforms of current density operators at two different sites, yielding in the linear-response approximation an expression for the real part of the optical conductivity  $\sigma_1(\omega)$  given by

$$\sigma_1(\omega) = \operatorname{Re}\left\{\sigma_{xx}(\omega)\right\} = D\delta(\omega) + \frac{e^2\pi}{N} \sum_{n\neq 0} \frac{|\langle \phi_0 | \hat{j}_x | \phi_n \rangle|^2}{E_n - E_0} \delta(\omega - (E_n - E_0)).$$
(4.17)

This is, as expected, a much more complicated relation for  $\sigma_1$ . Here the first term refers to the Drude part of the conductivity, D being known as Drude weight, yielding exactly  $\sigma_0$ defined in equation (4.12) for constant frequency. The second part expresses a relation similar to Fermi's Golden Rule of equation (4.4), with the transition rate between lattice states being given by the current operator. The main consequence of this expression is that the real part of the conductivity shows a delta function at zero frequency, showing that the majority of the weight of the conductivity is located at this point in frequency-space. It can be shown [103] that with increasing lattice size, D converges to a non-zero constant if the material is a metal and to zero if it is an insulator, thus can be used to characterize metal-insulator transitions. For a metallic system, the Drude term causes the appearance of a structure at frequencies close to zero in the optical conductivity spectrum which are associated with intraband transitions.

#### 4.4 Computational Details

We conducted DFT calculations as implemented in the WIEN2K distribution, based on the linearized augmented plane wave method. The materials studied are part of the Ruddlesden-Popper series  $Sr_{n+1}TM_nO_{3n+1}$ , the transition metals TM considered being Fe and V. We analyzed for the iron series the compounds  $SrFeO_3$ ,  $Sr_3Fe_2O_7$ ,  $Sr_2FeO_4$ , corresponding respectively to  $n = \infty$ , 2, 1. Also for n = 2, the compound  $Sr_3Fe_NiO_7$  representing a 50-50% doping was considered. In the case of the vanadium series, only  $SrVO_3$  and  $Sr_2VO_4$  were considered, corresponding to  $n = \infty$ , 1.

All calculations were done using a two-step process: first, converged results were obtained considering the Perdew-Burke-Ernzerhof potential adapted for solids (PBEsol) [37]. These were then used as input for a second calculation, now with the modified Becke-Johnson potential as parameterized by Jishi *et. al.* [38], which requires a previous converged result as detailed in section 2.4. A minimization of internal parameters was also conducted for the unit cells that have free parameters, aiming to obtain the relaxed structure.

A convergence criterion of  $R_{mt}K_{max} = 7$  was used, where  $R_{mt}$  is the radius of the smallest atomic sphere in the unit cell and  $K_{max}$  the largest wave vector in the basis set. These in turn are given by  $\mathbf{k}_n = \mathbf{k} + \mathbf{K}_n$ , where  $\mathbf{K}_n$  are the reciprocal lattice vectors and  $\mathbf{k}$ the wave vector in the first Brillouin zone. For all calculations, except when determining optical properties, a sampling of k-points was chosen as to have a difference between adjacent points  $\Delta k$  equal to 0.1. For the optical a finer k-point mesh is needed, thus we considered  $\Delta k = 0.05$ . The resulting mesh is then optimized by the program itself, yielding different values for each material. The core hole cutoff was chosen to be equal to -7.0 Ry, meaning that states whose energy are lower than this parameter have no core leakage beyond the atomic sphere. All other parameters involved in the calculations were chosen to be the default values.

Several physically relevant magnetic structures in the collinear approximation were considered for each material and compared in order to better reproduce experimentally observed ground-state ordering. This approximation was chosen in order to reduce computational costs which were already significative due to the number of different structures and systems being considered. As argued in section 2.4, when spins are allowed to take on any direction in space and thus simulate helical magnetism, the computational costs associated increase *at least* 64 times due to the theoretical constraints of DFT.

The magnetic structures considered are listed in table 3, as well as the supercell size chosen for the antiferromagnetic (AFM) states. A supercell is composed of multiples of the original cell along the directions of the crystal  $a \times b \times c$ , being needed to reproduce the AFM states due to the differentiation between transition metal atoms with respect to up/down spin. We chose the supercell sizes as the smallest that could replicate the desired magnetic orderings.

A schematic depiction of the antiferromagnetic configurations in the n = 2structure is shown in figure 19, with the ferromagnetic (FM) phase as comparison. The antiferromagnetic type A structure (AFMA) consists on ferromagnetic orderings in each perovskite bilayer and antiferromagnetic between bilayers <sup>1</sup>. Type C (AFMC) on the other

<sup>&</sup>lt;sup>1</sup> There is no physical reason for each single layer to align itself in its entirety antiferromagnetically to the next.



Figure 19 – Antiferromagnetic orderings considered in the calculations. Represented are only the n = 2 structures, but for  $n = \infty, 1$  the same logic applies.

Material	Magnetic structures	Supercell size
$SrFeO_3$	PM, FM, AFMA, AFMC, AFMG	2x2x2
$\mathrm{Sr}_{2}\mathrm{FeO}_{4}$	PM, FM, AFMA	2x2x1
$\mathrm{Sr}_3\mathrm{Fe}_2\mathrm{O}_7$	PM, FM, AFMA, AFMC, AFMG	2x2x1
$\mathrm{Sr}_3\mathrm{FeNiO}_7$	PM, FM, AFMA, AFMC, AFMG	2x2x1
$SrVO_3$	PM, FM	non-applicable
$\mathrm{Sr}_{2}\mathrm{VO}_{4}$	PM, FM, AFMA, AFMG	1x1x2 (AFMA), $2x2x4$ (AFMG)

Table 3 – Calculated structures and supercells considered.

hand consists on antiferromagnetic orderings between first neighbors in each layer, but ferromagnetic between layers. Finally, type G (AFMG) consists on antiferromagnetic first neighbor orderings both inter and intralayers. The same idea is applied to the  $n = \infty, 1$ materials.

For calculations which are set as paramagnetic initially (i.e. that did not converge to a paramagnetic solution), the magnetic moment of each atom is artificially turned off so that there is a lower amount of degrees of freedom being considered. For the ferroand antiferromagnetic structures, the spin directions are fixed but their values can vary, allowing also spin flip transitions, where an atom with spin initially pointing downwards can converge to a solution where it's pointing upwards.

The positions of each atom on the unit cell are detailed in table 4, as reported in experimental work. The structures for the iron series are depicted in figure 20, where the different positions of oxygen are highlighted. For  $Sr_3FeNiO_7$ , the original unit cell of the non-doped material was used to create the supercell, where the iron atoms were replaced

Material	Atomic Positions				
$SrFeO_{2}$ [52]	Sr(0,0,0)	$F_{0}(050505)$	O Basal $(0, 0.5, 0.5)$		
511003 [52]	51 (0,0,0)	10 (0.5,0.5,0.5)	O Apical $(0.5, 0.5, 0)$		
	$S_{r}$ (0.0.0.5)		O Basal $(0, 0.5, 0.09432)$		
$Sr_{3}Fe_{2}O_{7}$ [66]	$SI_1(0,0,0.3)$	Fe $(0,0,0.09741)$	O Apical $(0,0,0.19329)$		
	$Sr_2(0,0,0.51720)$		O Apical' $(0,0,0)$		
$S_{\rm T} = C [77]$	$S_{m}(0, 0, 2570)$	$\mathbf{F}_{\mathbf{a}}$ $(0, 0, 0)$	O Basal $(0,0.5,0)$		
$SI_2 FeO_4 [11]$	51 (0,0.5570)	re (0,0,0)	O Apical $(0,0,0.1573)$		
$SrVO_3$ [84]	Sr $(0,0,0)$	V $(0.5, 0.5, 0.5)$	O $(0.5, 0.0, 0.5)$		
$S_{n} VO [01]$	Sr (0,0,0.35438)	V (0,0,0)	O Basal $(0,0.5,0)$		
$51_2 \vee O_4 [91]$			O Apical $(0,0,0.15778)$		

Table 4 – Atomic positions for each material studied.



Figure 20 – Structures considered for the iron Ruddlesden-Popper series with different n. In the case of vanadium, the structures are basically the same, with Fe  $\rightarrow$  V.

by nickel in a tridimensional checkerboard pattern. A schematic can be seen in figure 16. In the case of the vanadium series, the only difference is that the  $n = \infty$  material is perfectly cubic, so the series can be represented in the same manner just by substituting the iron ions for vanadium.

In order to obtain the oxygen K-edge XAS spectrum, the density of states obtained from these calculations was then treated using a core-hole potential approach to simulate the effects of an excitation process on a ground state result. For that end, the real part of the Green's function was obtained by means of a Hilbert transform, as implemented in the SciPy library through analytical signal methods. Considering a variational approach, a new Green's function was obtained, corresponding to the effect of the potential V on the original density of states. Because the excited electron must be attracted to the hole on the internal level, V must be negative. This leads the new density of states, calculated from the new Green's function, to be shifted towards smaller energy values and also change its structure. Finally, a gaussian broadening of width = 0.4 eV was considered, and the resultant density of states can be directly compared to the usual XAS spectrum. Further details and justification of this method, as well as the computational implementation can be found on appendix I.

# 5. Results and Discussion

### 5.1 Iron Series

Considering the magnetic orderings for each material as defined in chapter 4, the total energy, total and atomic magnetic moments were obtained. For SrFeO<sub>3</sub>  $(n = \infty)$ , this data is listed in table 5<sup>1</sup>. Likewise, the data for n = 2 and n = 1 can be found on tables 6 and 8. Contributions for different atom types are discriminated, with special attention towards oxygen. For some materials there are two strontium types, which refer to atoms that are more perovskite-like (Sr1) or oxide-like (Sr2). These results will be discussed in more detail in the following.

For  $SrFeO_3$ , the magnetic configuration with the lowest total energy, the ground state, is the ferromagnetic ordering. In this case, iron is the most magnetically active atom as is expected, with a magnetic moment of about 4  $\mu_B$ . The strontium and oxygen atoms also exhibit some magnetic moment but a lot less expressive than the transition metal. One thing to notice is that the basal and apical oxygens contribute differently to the total magnetic moment of the material, a pattern which was found to be persistent throughout the whole RP series. The experimental magnetic moments of iron and oxygen are reported to be 2.7-3.1  $\mu_B$  and 0.1  $\mu_B$  respectively [104, 57], but the calculated values described in the literature range from 2.5 to 3.7  $\mu_B$  for iron and 0.08 to 0.16  $\mu_B$  for oxygen [105, 104, 106]. Considering that the experimental values are obtained in the true magnetic ground state which is helical antiferromagnetic, the difference between both values is not surprising. When subjected to extremely high magnetic fields ( $\approx 40$  T), the AFM state changes to a FM state with a total magnetic moment of about 3.5  $\mu_B$  [60], closer to our calculation. Also worthy of note is that the strongest interaction between adjacent iron atoms is of ferromagnetic nature [57], which agrees with our finding that FM ordering is the most stable of the collinear magnetic structures.

It can also be seen for this material that the ground state magnetic ordering lies close in energy to the paramagnetic and antiferromagnetic phases, which is a sign of

<sup>&</sup>lt;sup>1</sup> In these tables, energy is given in Rydberg units as is customary, where 1 Ry = 0.5 Ha = 13.6 eV. The magnetic moment due to atomic multiplicities was also averaged for easier comparison.

Table 5 – Results obtained for SrFeO<sub>3</sub>. It can be seen that although the FM configuration is the lowest in energy and thus is the calculated ground state, there is appreciable competition with other magnetic structures. The magnetic moment of the iron atom in this configuration is close to the experimentally reported 3.5  $\mu_B$  of a ferromagnetic ordering [60]. Different contributions to the total magnetic moment by each oxygen type were also observed.

$\mathrm{SrFeO}_3$	Total Energy (Ry)	Total Magnetic Moment $(\mu_B)$	Sr $(\mu_B)$	Fe $(\mu_B)$	O $(\mu_B)$
PARA	-9340.3348	-	-	-	-
FM	0340 4188	3 0000	0.0047	4 0068	Basal = -0.0075
F IVI	-9340.4100	5.9999	-0.0047	4.0000	Apical = 0.0308
	0340 2806	0.0000	0.0000	Fe1 = 3.9573	Basal = 0.0000
AFMA	-9340.2890	0.0000	0.0000	Fe2 = -3.9573	Apical = 0.0000
AFMC	0340 1046	0.0000	0.0000	Fe1 = 4.0990	Basal = 0.0000
AFMO	-9340.1040	0.0000	0.0000	Fe2 = -4.0990	Apical = 0.0000
AFMG	-9340.1660	0.0879	-0.0003	Fe1 = 1.6491	Basal = 0.0145
				Fe2 = -1.6352	Apical = 0.0145

Table 6 – Obtained results for  $Sr_3Fe_2O_7$ . The calculated ground state magnetic structure is the AFMA configuration, corresponding to ferromagnetic alignments along the plane and antiferromagnetic between the perovskite double-layers, predicted to be much more stable than the others. There is a significant decrease on the Fe magnetic moment when compared to the FM phase, however it is still the magnetically active ion in the material.

$\mathrm{Sr}_3\mathrm{Fe}_2\mathrm{O}_7$	Total Energy (Ry)	Total Magnetic Moment $(\mu_B)$	Sr $(\mu_B)$	Fe $(\mu_B)$	O $(\mu_B)$
PARA	-25182.0024	-	-	-	-
FM	-25182.0276	7.9998	Sr1 = 0.0013 Sr2 = -0.0019	3.8304	Basal = 0.0286 Apical = 0.36041 Apical' = -0.50581
AFMA	-25205.3271	-0.0008	${ m Sr1} = 0.0000 { m Sr2} = 0.0000$	Fe1 = 2.7147 Fe2 = -2.7143	$\begin{array}{l} \text{Basal} = 0.0000\\ \text{Apical} = 0.0008\\ \text{Apical'} = -0.0000 \end{array}$
AFMC	-25182.0775	-0.0185	${ m Sr1} = 0.0001 { m Sr2} = 0.0011$	Fe1 = 3.65763 Fe2 = -3.65903	$\begin{array}{l} \text{Basal} = -0.0386\\ \text{Apical} = 0.0217\\ \text{Apical'} = -0.0060 \end{array}$
AFMG	-25180.8386	0.0000	Sr1 = 0.0086 Sr2 = 0.0081	Fe1 = 1.2006 Fe2 = -1.2515	Basal = -0.0587 Apical = 1.7119 Apical' = -1.5556

competing magnetic interactions in a highly correlated compound [58]. It's interesting to notice that there is a very sharp decrease in the magnetic moments for the AFMG structure, yielding in fact a weak ferromagnet. It could be argued that this phase combined with the paramagnetic one represents interactions that contribute to a decrease in the magnetic moment of the real material, which might be a mechanism towards driving the onset of the helical spin structure.

As the dimensionality n is lowered in the series, a change in behavior is observed. As can be seen on table 6, the ground state structure for n = 2 is that with antiferromagnetic ordering of the A type, being much more stable than the other structures analyzed. A calculation reported on the literature based on a GGA + U approach, with U = 5 eV and J = 1 eV, obtained the same arrangement very close to a FM ground state, the difference between the two being about 0.01 eV [71]. This is consistent with other calculations that Table 7 – Obtained results for Sr<sub>3</sub>FeNiO<sub>7</sub>. Notice that the most stable phase is now a paramagnetic configuration, hinting that breaking the potential's periodicity through the nickel doping is enough to break magnetic order. The initially FM and AFMG converge to different ferrimagnetic orderings, with very distinct iron and oxygen magnetic contributions.

$\mathrm{Sr}_3\mathrm{FeNiO}_7$	Total Energy (Ry)	Total Magnetic Moment $(\mu_B)$	Sr $(\mu_B)$	Fe $(\mu_B)$	Ni $(\mu_B)$	O $(\mu_B)$
PARA	-25677.2831	-	-	-	-	-
FM	-25677.0245	8.0001	Sr1 = -0.0092 Sr2 = -0.0331	Fe1 = 1.5063 Fe2 = 1.5053	Ni1 = 1.3414 Ni2 = 1.3445	Basal = 2.0667 Apical = -0.0739 Apical' = -0.0399
AFMG	-25677.0677	8.0001	${ m Sr1}=0.0091 \ { m Sr2}=-0.0029$	Fe1 = 4.1088 Fe2 = 4.1081	Ni1 = 1.4914 Ni2 = 1.4911	Basal = -0.6833 Apical = -1.1975 Apical' = -1.4173

showed that, for  $Sr_3Fe_2O_7$ , the first neighbor interactions are of ferromagnetic ordering but the longer ranged are antiferromagnetic, with smaller values [70]. The magnetic moment of the iron atoms is experimentally reported at 3.1 and 3.5  $\mu_B$  due to the elliptical modulation, with antiparallel ordering between Fe atoms at different double perovskite layers [70, 107], not too distant from the calculated moments.

Considering that the true ferromagnetic state is non-collinear, meaning antiferromagnetic contributions are important, and that the strontium oxide layers effectively cuts the connection between adjacent perovskite layers' magnetic structures along the *c* axis, we argue that the large difference obtained between the energy of the AFMA and the other arrangements is significative and a result of an exchange-correlation potential that is highly tailored to perovskites. Moreover, the only difference between the AFMA and FM structures is, as can be seen on figure 19, exactly the opposing ferromagnetic ordering between the double perovskite layers which is experimentally reported.

When the n = 2 system is doped with nickel in a 1:1 proportion, we obtained different properties as can be seen on table 7. The lowest energy magnetic configuration obtained was a paramagnetic phase, in agreement with the reported behavior of the system [74]. Thus, we conclude that the introduction of Ni in the systems seems to be enough to break the complex magnetic ordering of  $Sr_3Fe_2O_7$  and stabilize a simpler, paramagnetic structure. The "ferromagnetic" and "antiferromagnetic-G" phases, which lie a bit higher in energy than the ground state, are actually two distinct ferromagnetic orderings with two magnetic sublattices. When considering an initially ferromagnetic (FM) configuration, the magnetic moments of Fe and Ni converge to being quite close in magnitude (nickel's being slightly smaller) and a very significant resultant magnetic moment of the basal oxygens is present. This would imply that the magnetically active sites in the lattice become more distributed than in comparison to the other materials in the series.

The originally AFMG ordering converges to a different ferromagnetic ordering, in which even though Fe and Ni point in the same direction, the iron magnetic moment is much greater than nickel's. Analysing the oxygens' magnetic momenta, it can be seen that this is accompanied by a significant shift in the contributions of each oxygen type, even though the total magnetic moment remains the same. The great lack of studies on this material do not allow us to obtain much more intuition regarding its properties.

The second ferrimagnetic phase is closer to the ferromagnetic phase of the nondoped material and is characterized by a very dominant Fe moment, having now apical and apical prime oxygens with significant magnetic activity. These different scenarios could be associated with the onset of spin-glass behavior at very low temperatures as argued by Mogni et al. [74], which is a consequence of a highly frustated magnetic system. At a temperature range of 350 to 570 K, the effective (i.e. resultant) magnetic moment of the material was found to be of about 4.1  $\mu_B$ , close to the 8  $\mu_B$  we obtained with the doubled unit-cell, which has double the magnetic moment of the single cell and thus is also close to 4  $\mu_B$  [74].

Table 8 – Obtained results for  $Sr_2FeO_4$ . The calculated ground state obtained was the FM arrangement, although the energy difference to the AFMA configuration is small. This antiferromagnetic ordering was considered as the ground state for following analysis, as it is closer to the experimentally reported elliptical spin structure than the FM ordering.

$\mathrm{Sr}_{2}\mathrm{FeO}_{4}$	Total Energy (Ry)	Total Magnetic Moment $(\mu_B)$	Sr $(\mu_B)$	Fe $(\mu_B)$	O $(\mu_B)$
PARA	-15841.6702	-	-	-	-
FМ	15841 7840	3 0006	0.0008	3 8574	Basal = 0.1087
1, 1/1	-10041,7040 -10041	-0.0008	0.0014	Apical = -0.0299	
	15841 4021	0.0000	0.0000	Fe1 = 3.0012	Basal = -0.0001
AFMA	-10041.4001	0.0000	0.0000	Fe2 = -3.0008	Apical = -0.0001

When the perovskites are confined in the 2D structure of  $Sr_2FeO_4$  (n = 1), we obtained the FM phase as the phase with the lowest total energy. The experimentally determined magnetic structure is an elliptical helix only slightly tilted away from the *ab* plane with a relatively small angle between adjacent iron spins of 70° [80]. Taking into account the same argument of the n = 2 material that the SrO do not allow for strong interactions that tend to align the spins ferromagnetically along c, effect that should be even more pronounced for n = 1, we considered the AFMA structure to be the magnetic ground state in the collinear spins approximation. This is justified by taking into account the (relatively) small energy differences between the structures analyzed.

Table 9 compiles the magnetic ground states considered for all materials that were used for further calculations.

Table 9 – Resultant magnetic ground states for each material.

Material	SrFeO <sub>3</sub>	$\mathrm{Sr}_3\mathrm{Fe}_2\mathrm{O}_7$	$\mathrm{Sr}_3\mathrm{FeNiO}_7$	$\mathrm{Sr}_{2}\mathrm{FeO}_{4}$
Magnetic Ground State	FM	AFMA	PARA	AFMA

#### 5.1.1 Density of States and Band Structure

By studying the density of states (DOS) and the projected density of states (PDOS) on the valence orbitals of each atom, we can obtain the behavior of the electronic structure of the entire series and more directly analyze the effects of dimensionality. The comparison between all the materials is present in figure 21, where the Fermi level is taken as zero energy, meaning states with negative energy are all occupied, forming the valence band, and states with positive energy are all unoccupied, forming the conduction band. It is also important to point that in this type of graph, positive (negative) values of the DOS represent the states associated with up (down) spin. Some general characteristics can be noted, such as that for all materials there is a large overlap between the energy intervals with large oxygen and transition metals contributions, some between the oxygen and strontium and little to none between the transition metals and strontium. This is a measurement of covalency between the atoms, which indicates that the bond between the transition metals and oxygen has a highly covalent nature, in agreement with the negative charge-transfer regime characteristics highlighted on chapter 3.

One can observe that, due to the little covalency between strontium and transition metals, the strontium bands are not as highly affected by the changes in the dimensionality of the series as the other bands. Most notably, it can be seen that as n is lowered, the density of states becomes more localized, that is, the energy intervals occupied by the bands become smaller and the number of states becomes higher, with sharper peaks. This is in agreement with the expected behavior of a Ruddlesden-Popper series and leads to the progressive distinction between the material's characteristics in the ab plane and the c axis as dimensionality is reduced. Considering specifically n = 2, it can be seen that doping can also be a mechanism to drive localization, which is expected as the local periodicity of the crystal's potential with only iron atoms is broken by the introduction of nickel, increasing the effective bond distances between iron atoms.

In figures 22 to 26, the PDOS of figure 21 are plotted separately for each atom, highlighting the different oxygen species. It can be seen that  $SrFeO_3$  shows a half-metallic behavior, in which the density of states is highly sensible to spin orientation. This leads to a energy gap of about 2.3 eV for the down spin component and no gap for the up spin, meaning that the material behaves as a conductor for an up-polarized spin current and as a semi-conductor for a down-polarized spin current. This behavior was also observed in a study with a GGA + U formalism [108] and other calculations reported in the literature, although not displaying half-metallicity exactly, point towards this behavior with a much more pronounced density of iron states for one spin than the other [104, 109]. To the best of our knowledge, no experimental study exploring this predicted property have been reported. It can also be seen that the structures of basal and apical oxygen are very similar to one another, showing a great degree of covalence only with the iron atom. The slight differences are attributed to the small apical distortion in the crystal unit cell.



Figure 21 – Comparison between the total density of states (DOS) and its projections onto valence orbitals (PDOS) for each material of the iron series, with the ground state magnetic structures indicated. For all members of the series, a great overlap between oxygen and transition metal states was observed, an indicator of highly covalent interactions, which are also present in a lesser degree between oxygen and strontium. The transition from a half-metallic material with  $n = \infty$  to a semiconductor for n = 1 showcases the effects of 2D confinement on the materials' electronic structure. The presence of mostly p - d levels near the Fermi level are indicators of the negative charge-transfer the systems exhibit.



Figure 22 – PDOS of SrFeO<sub>3</sub>, showcasing the different oxygen species and semi-metallic character. It can be seen that there is almost no difference between the basal and apical oxygen structures besides the intensity due to atom multiplicity, even considering the slight apical elongation of the material's structure. This is due to the isotropic nature of the material, composed of only identical perovskites in every direction.

The DOS for n = 2 (figure 23) obtained does not show the expected semiconductive behavior as is reported in the literature through thermodynamical studies [110, 72]. This difficulty on reproducing the electronic behavior is also observed on other studies that report the density of states using methods such as GGA+U [71, 111]. As these calculations do not take into account the experimentally observed charge disproportionation of the iron sites [67], it can be argued that it constitutes a key mechanism to turn the material into a semiconductor. That being said, our results point towards a separation of the iron structures close to the Fermi level, which could be improved by considering a non-collinear magnetic structure that is closer to the material's real arrangement.

One key difference between  $n = \infty$  and n = 2 is that, due to the reduction in dimensionality, the different oxygen species now have a quite distinct density of states and thus must exhibit different physical behavior. The basal oxygens show a very covalent 2p - 3d bond when projected both in the ab plane and along the c axis, now with a larger interaction with the strontium atoms, although still small. The apical oxygens on the other hand show a much more localized structure that is more strongly covalent with the iron atoms through the x and y projections of the 2p valence orbital than with z projection. The same is observed with the apical prime species, the oxygens shared between each perovskite layer in the bilayered structure, which has a smaller contribution to the overall DOS due to having a smaller multiplicity. This change in behavior is evidence of the relative independence between adjacent bilayers due to the presence of the strontium oxide layer, which greatly reduces the available states associated with the  $2p_z$  orbitals, which lie along the c axis. As a consequence, the material's main characteristics (electronic, magnetic, thermodynamical...) must be more pronounced in the plane and thus be of 2D-like nature.

The semiconductive behavior of the n = 2 phase is realized for the Ni substitution, as presented in figure 24. It can be seen that a small gap of about 1.2 eV appears when the less magnetically active nickel atom is introduced, which is concomitant with the transition to a paramagnetic ordering as observed experimentally [74]. The local symmetry breaking caused by this greatly localizes the structures of all atoms while at the same time seemingly reducing slightly the covalency between the transition metals and oxygen types. Regarding the different characteristics of basal and apical oxygens, the same logic of the non-doped n = 2 material can be applied. Thus, apical oxygens exhibit a limited interaction through the  $2p_z$  orbital due to the presence of the insulating SrO layers, with apical prime oxygens showing a similar behavior but more influenced by the basal oxygens close to the Fermi level. A comparison between the changes is the transition metals' PDOS is shown in figure 25, where it can be more clearly seen how the Ni doping creates sharper peaks within narrower energy intervals in the Fe states.

When the perovskite layer is maximally confined in the n = 1 phase, the trend of localization in the structures is followed, as can be seen on figure 26. Most notably, the Fe



Figure 23 – PDOS of Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7</sub>. It can be seen that the introduction of the SrO layers has a profound effect on the structures of all atoms, especially the oxygens', which behave differently from another. The apical oxygen's PDOS shows a more localized structure and predominant character along the plane, direct consequence of the presence of the oxide layers, whereas the basal and apical prime species display more covalence with the transition metal. A metallic character was observed, in contrast to the known semiconductive nature of the material. This points towards the true non-collinear magnetic structure, not considered in this calculation, playing an important role in its conductivity.



Figure 24 – PDOS of Sr<sub>3</sub>FeNiO<sub>7</sub>. The introduction of Ni, which showcases a similar structure to the Fe atoms, causes an expressive localization of the density of states in comparison to the non-doped case. This is also enough to open the expected gap that couldn't be reproduced for the Fe-only material while also destroying its complicated magnetic structure.



Figure 25 – Comparison between the transition metals PDOS calculated for n = 2, featuring the system with only Fe on the upper panel and the Ni doped on the lower panel. Localization of the structures becomes very evident, even causing a separation that is enough to originate a small bandgap and thus semiconductive behavior.

states become less abundant near the Fermi level at the same time that a small gap of about 1 eV appears, close to the 1.8 eV gap reported in a very recent theoretical study within the hybrid DFT framework [112]. It can also be seen that the apical oxygens have a stronger interaction with the strontium structure at E = 7 eV than the basal species, as expected due to the proximity to the SrO layer.

In order to allow a more direct comparison of the different oxygen structures in the series, the evolution of the DOS as n is lowered is depicted in figure 27, with only the basal oxygens on the upper panels and the apical and apical' oxygens on the lower panels. The localization effects can be seen very clearly throughout the series. As the chemical environment around each oxygen species changes with different n, the bands associated with the 2p orbital and its components become increasingly more distinct, leading to the different physical characteristics of each material.

Another way of visualizing the evolution of the electronic structure is through the band structure, considered along points of high symmetry in the first Brillouin zone. It is also possible to showcase, given the material's bands, which have a higher contribution due to each atom or specific orbitals, represented by smalls circles whose radius are weighted by this contribution. Figures 28 to 31 showcase the character of oxygen 2p orbitals present in the bands of each material, with the graphs on the left considering specifically the character of  $p_x$  and  $p_y$  orbitals, and on the right the  $p_z$  contribution. The more O 2p states are available at a given energy interval, the higher is the character that the bands in these intervals are going to have, which can be used to evaluate covalence effects. The obtained plots are then compared with the material's total DOS as presented before, in which covalence is represented by the overlap in electronic states.

In figure 28, one can see that the projection's characters for SrFeO<sub>3</sub> change depending on the majority or minority spin being considered, a consequence of the halfmetallic character of the  $n = \infty$  material. In blue are depicted the spin down channel contributions, which have a much more intense  $p_x + p_y$  character than the spin up channel, but this behavior is flipped when considering the  $p_z$  character. It is important to note here that the distinction between apical and basal oxygens is not being considered, only the difference between contributions on the plane and on the axis for all the oxygen species. Also worthy of note is that near the Fermi level, the bands which have more  $p_x + p_y$ character are flatter than the ones with  $p_z$  character, which is yet another way to measure localization, in this case not due to dimensionality but to the different conductive behavior for different spin channels. This measurement of localization is based on the fact that the band's dependence on **k** is given by some dispersion relation which depends on the material, as mentioned in chapter 2. So, bands which show less dispersion (i.e. more localized) won't have a significative dependence on **k** and thus be represented by straight horizontal lines in band plots.

In figure 29 are the O 2p band characters for  $Sr_3Fe_2O_7$ . Because half-metallicity is



Figure 26 – PDOS of  $Sr_2FeO_4$ . In comparison to the other *n* materials, here a much more pronounced localization of the structures can be seen, even for the Fe atom. The confinement of the perovskite layers leads to projections along the plane to be enhanced, showcasing its 2D nature. This also leads to the appearance of a small gap of about 1 eV.


Figure 27 - Evolution of the oxygen PDOS in the Ruddlesden-Popper series, separated between apical and basal oxygen types and 2pprojections along the plane and along the vertical axis. The progressive localization and sharpening of the structures with lower n and doping can be easily seen, evidence of the different chemical behaviors exhibited by the oxygens according to their positions in the crystal, justifying the need to analyse them separately.



Figure 28 – Band structure of  $SrFeO_3$  with corresponding O 2*p* character weights. Due to the material's half-metallic nature, a further distinction was made between down (blue) and up (red) spin. It can be seen that for the character along the plane, there is a larger contribution from the the down spin, the opposite being true for character along the axis. For both cases, a large dispersion is observed along the high-symmetry path.

only present in the  $n = \infty$  material, the up and down contributions to the band character are the same. Thus we adopt blue circles to indicate only the  $p_x + p_y$  character and red circles for  $p_z$ , this convention being followed for all other materials. It can be seen that the oxygen 2p contributions are quite similar when considering both characters, as can be seen by the great overlap between oxygen and iron states on a large energy range. The biggest difference between the two lies on the bands that are located at about -5 eV, whose character is mainly  $p_x + p_y$ . This can be explained by looking at figure 27, in which it can be seen that most occupied electronic states are due to the  $p_x + p_y$  contribution of the basal oxygens. The presence of a higher number of bands overall, when compared to  $n = \infty$ , can be attributed to the higher number of atoms in this material's unit cell, which renders a more complicated band structure. That being said, these bands have a flatter behavior, which is expected due to the increased localization of electronic structure of Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7</sub>.

As could be seen with the DOS alone, in the case of the nickel-substituted n = 2 system, this localization is greatly increased. On figure 30 are the band structures, which



Figure 29 – Band structure of  $Sr_3Fe_2O_7$  with corresponding O 2*p* character weights. In comparison to the  $n = \infty$  case, a much more complicated band structure can be seen, where the oxygen character is noticeably smaller but also more distributed. That being said, for the bands at about -5 eV the  $p_x + p_y$  character is noticeably greater, a consequence of mainly basal oxygens states in this range. The main feature to be observed is that the bands become, in general, much flatter and thus less dispersion is observed, a direct effect of localization by the lowering of *n* in the series.

are markedly flatter than the non-doped system, with a very intense  $p_x + p_y$  O 2p character close to the Fermi level, whereas the  $p_z$  character is more distributed and less pronounced. In the case of Sr<sub>2</sub>FeO<sub>4</sub>, depicted in figure 31, a very strong  $p_x + p_y$  character is present at about -1 eV, with lesser contributions distributed at other energy intervals. The  $p_z$ character is more concentrated below the Fermi level, also at about -1 eV, being less evident for other intervals. One interesting characteristic is that just below the Fermi level, the bands have basically only  $p_x + p_y$  character and have a relatively high dispersion, which can be attributed to the mixed ionic and electronic conduction along the plane for the n = 1 phase [18].

#### 5.1.2 X-Ray Absorption

In order to validate our results, we conducted comparisons between our theoretical results and experimental X-ray absorption (XAS) spectra. These were collected by the



Figure 30 – Band structure of Sr<sub>3</sub>FeNiO<sub>7</sub> with corresponding O 2*p* character weights. A very significant localization can be seen, with nearly flat bands overall. A strong  $p_x + p_y$  character is observed close to the Fermi level and crossing it, with  $p_z$  character being less predominant. In comparison with the iron-only n = 2 material, it can be seen that doping can also lead to a great degree of localization in the system.

group on the SGM beamline of the old brazilian synchrotron LNLS. The measurements were made for the  $n = \infty, 2, 1$  materials at room temperature using polycrystalline samples that were scraped at pressures below  $10^{-10}$  mbar aiming to remove superficial contamination. The overall experimental resolution of the beamline was 0.5 eV.

As explained on chapter 2, XAS is a technique that probes the unnocupied part of the density of states, identifying the conduction band near the Fermi level. Thus, one can use DFT to estimate the spectra by treating the calculated DOS only beyond the Fermi level. This can be done by summing up (in modulus) the contributions of up and down spin densities and doing a rigid translation of the structure by a given energy corresponding to the first absorption edge [98]. Such procedure should yield a rough estimate of the true spectrum as DFT gives only the ground state density, whereas X-ray absorption is an excited process. This approximation can be improved using the core-hole potential procedure that was mentioned in chapter 4 and that is detailed in appendix I.

By analyzing the O 1s X-ray absorption spectrum, which corresponds to transitions from the O 1s occupied band to the O 2p unoccupied states, one can indirectly obtain



Figure 31 – Band structure of  $Sr_2FeO_4$  with corresponding O 2*p* character weights. A great degree of localization is also observed for this material. It is interesting to notice that the  $p_z$  character is very limited to narrow ranges in energy in comparison with the dominant  $p_x + p_y$  character, especially close to the Fermi level. This is a marked feature of a two-dimensional system, as is expected considering the confinement it is subjected to due to presence of the strontium oxide layers.

information regarding the transition metal due to hybridization effects [113]. This is specially justified when considering systems with very strong covalent nature between ligand and metal, such as the iron RP series considered, in which all materials are in a negative charge-transfer regime. In figure 32 are the calculated XAS spectra for all the materials and the respective experimental data. Cluster model calculations allow to elucidate the main components of each structure [55, 75, 65]. Looking initially at the experimental results, we see that at about 520 eV there is a steep increase in the intensity detected, which is characteristic of the oxygen K-edge. This first structure is soon followed by a satellite structure just a few eV after. These two initial peaks have the influence of mainly the iron 3d orbital, the first corresponding to the Fe  $t_{2g}$  band and the latter to the  $e_g$  band [65]. The peak around 533 eV corresponds to a Sr 4d band, whereas the smaller structures after 540 eV are attributed to the transition metals 4sp bands. Naturally absorption isn't the only process that takes place when the sample is irradiated, the result of all the other complicated interactions between matter and x-ray accounting for the rising background energy along the spectrum.

It can be seen that, as expected, the spectra derived from our theoretical calculations gives an approximation to the experimental data, with different degrees of accuracy. In general, the correct structures are present, but their position and separation in energy as well as relative intensities don't correspond perfectly to the data. That being said, taking into account the limitations of DFT, the agreement is already surprisingly good for a first estimate. As n is lowered in the series, the evolution of the structures as a function of dimensionality become evident, with a lowering of the first peak's relative intensity with the exception of the Ni doped n = 2. Most importantly, the contribution of the Sr 4dbands become the more relevant the more the perovskite layers become confined, an effect that can be attributed to the influence of the SrO layers and local symmetry breaking on the electronic localization. This also allows us to explain why this peak becomes more defined when comparing the spectra of Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7</sub> and Sr<sub>3</sub>FeNiO<sub>7</sub>.

As an additional analysis, we also studied how the band structure and its O 2p character relates to the calculated and experimental XAS spectra. For  $n = \infty$ , given on figure 33, it can be seen that the Fe 3d peaks have a strong oxygen character, as is expected due to the great covalency between the two atom types observed. These peaks are also associated with bands that have a relatively high dispersion, which is related to the conductive nature of the material. It is also interesting to note that the Fe 4sp bands have basically only  $p_x + p_y$  character, which indicate that these more internal iron orbitals bond strongly with the oxygen atoms only along the plane. For Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7</sub> (figure 34), the diffuse O 2p character is present throught the spectrum, with similar contributions of  $p_x + p_y$  and  $p_z$  orbitals, but the band structure becomes a lot more complicated to interpret.

When the Ni atoms are introduced, there is a great change in the band structure compared to the iron-only system. It can be seen on figure 35 that the Fe/Ni 3d peaks correspond to strongly localized (i.e. flat) bands, the same happening for the Sr 4d structure, whereas the bumps on the spectra due to Fe/Ni 4sp orbitals are related to more dispersed bands. As expected, this behavior is not homogeneous for the in plane and out of plane O 2p characters, being the  $p_z$  character more present only for the 3d peaks. For the n = 1material, we see that the first peaks are associated with bands that are very localized and simultaneously with others that show a greater dispersion. Considering that the first peak relates to the  $t_{2g}$  and the second to the  $e_g$  orbitals of iron, we can argue that our calculations predict a very localized  $e_g$  band that contrasts to the less localized  $e_g$  one. The O 2p character is also distinct for  $p_x + p_y$  and  $p_z$  orbitals, the first having a more general presence throught the spectrum, and the latter being only more pronounced for the 4dpeak. The qualitative similarities on the O 2p character between Sr<sub>3</sub>FeNiO<sub>7</sub> and Sr<sub>2</sub>FeO<sub>4</sub>, the materials with the most localized electronic structures, also support the conclusion that local symmetry breaking greatly alters the covalent nature of the oxygen bonds in a non-isotropical manner.



Figure 32 – First approximation to the experimental X-ray absorption spectra as calculated by Density Functional Theory. It can already be seen that there is a relatively good agreement, with the right structures being present in the spectrum but shifted in energy or with mismatched relative intensities. The differences are expected considering that DFT gives the material's ground state properties whereas XAS is an excited state process.



Figure 33 – Comparison between the band structure of SrFeO3 and its XAS spectrum. It can be readily seen that the first peak, corresponding to the oxygen K-edge, has a very strong oxygen character as expected, with the difference in spin up and down contributions accounting for the secondary peak.



Figure 34 – Comparison between the band structure of  $Sr_3Fe_2O_7$  and its XAS spectrum. The oxygen character is more diffuse throughout the bands, with a slightly stronger  $p_x + p_y$  character being present closer to the peak corresponding to the influence of the Sr 4d bands.



Figure 35 – Comparison between the band structure of  $Sr_3FeNiO_7$  and its XAS spectrum. It can be readily seen that the first peaks in the XAS spectrum correspond to a mixed  $p_x + p_y$  and  $p_z$  character, whereas the following structures have mostly  $p_x + p_y$  character.



Figure 36 – Comparison between the band structure of  $Sr_2FeO_4$  and its XAS spectrum. Like in the case of the Ni doping, the first peak associated with the Fe 3*d* levels show a mixed  $p_x + p_y$  and  $p_z$  character, while the rest of the structures having a more dominant  $p_x + p_y$  character. This indicated that both doping and dimensional-lowering tend to privilege interactions along the plane, fully in agreement with our DOS analysis and reported behavior.

In order to improve the theoretical predictions, further calculations using the ground state DOS obtained from DFT and taking into account the attractive potential V of the core-hole left by the promotion of an oxygen 1s electron to a higher state were conducted. As mentioned, the theoretical details are left as an appendix to the interested reader. An example of the results obtained is depicted in figure 37 for the maximally confined n = 1 system. Several different V values are considered (in eV units), which change not only the relative intensities of the structures but also their energy separations, the resultant spectra being subjected to a gaussian broadening of 0.4 eV to smoothen out the curves. When V = 0.0, one has the original spectrum from DFT but broadened, and as V becomes more negative it becomes clear how the Fe 3d and Sr 4d peaks become more pronounced at the cost of the reduction in intensity of the Fe 3sp peaks, closer to the experimental data.

As the core-hole potential is inserted in a more or less *ad hoc* manner, its correct value is not known. Thus, we determined the best fit by visually comparing the corrected spectrum with the experimental data. This must be done carefully, as higher values of V although reducing the energy separation between structures to values closer to the experimental ones, tend to privilege one of the peaks and greatly reduce the intensity of the others. It must be noted that the sensitivity to this potential is also not linear, meaning that after some threshold that depends on the material, slight changes in the value ( $\sim 0.1$  eV) can result in very large changes to the resultant spectrum.

Finally, the comparison between core-hole adjusted theoretical XAS spectrum of the iron series and experimental data is portrayed in figure 38, considering the best fit Vs determined individually. For  $n = \infty$  we now see a very good agreement for the iron 3d peaks, the others being slightly shifted to higher energies by about 2 eV but with a good relative intensity. For n = 2 (FeFe), the energy positions of the structures are in excellent agreement to the data, but the relative intensities of the first peaks are swapped. The nickel-doped system shows a behavior similar to  $n = \infty$  in the sense that the relative intensities are mostly correct but the structures themselves show a small energy shift towards higher energies. For n = 1 the comparison between theoretical and experimental data is stellar, with only a slight swap in the predicted intensities of the iron 3d peaks.

### 5.2 Vanadium Series

As in the iron series, the resultant total energies, total and atomic magnetic moments obtained for the different magnetic orderings considered are listed in tables 10 and 11. For SrVO<sub>3</sub> ( $n = \infty$ ), it can be seen that even if the system is initialized in the ferromagnetic state, it converges to an essentially paramagnetic solution, very close in energy to the calculation that is initialized as paramagnetic. Thus, we can conclude that the system's ground state shows in fact no magnetic ordering, which is consistent with



Sr<sub>2</sub>FeO<sub>4</sub> O 1s X-Ray Absorption Spectroscopy

Figure 37 – Evolution of the calculated XAS spectra for  $Sr_2FeO_4$  with the introduction of the core-hole potential V, considering different values (in eV) with a gaussian broadening of 0.4 eV. As V increases, the structures are shifted towards lower energies and their relative intensities change, a consequence of the attractive nature of the potential.



O 1s X-Ray Absorption Spectroscopy

Figure 38 – Comparison between core-hole adjusted XAS spectra as derived from DFT and the experimentally measured curves. For  $n = \infty, 2$  (FeNi), a great agreement in the relative intensities is obtained but the structures themselves are slightly shifted for higher energies. For n = 2, 1 (FeFe), the positions of the peaks are in excellent agreement with the data but the relative intensities of the first two peaks are swapped.

data reported in the literature [86, 85, 83].

In the case of  $Sr_2VO_4$ , the calculated ground state magnetic structure is the antiferromagnetic of type A. which lies very close in energy to the paramagnetic and type G antiferromagnetic orderings. Reported theoretical predictions using an LDA+U, GW and path-integral renormalization group approach predicted that the competition is instead mainly between the FM and AFM arrangements, with a coexistence of both phases at temperatures around 100 K [94]. Measurements of the temperature dependence of the magnetic susceptibility  $\chi$  however show a behavior typical of weak ferromagnetism and strongly enhanced Pauli paramagnetism, common for strongly correlated 3d systems close to a metal-insulator transition [95]. Considering this, we argue that the paramagnetic contribution to the orbitally-ordered ground state is more important than the contribution associated with the ferromagnetic arrangement, which also agrees with the expected diminished interaction along c due to the SrO layers. As can also be seen on table 11, the atomic magnetic moments for both FM and AFM configurations are similar, with the largest moment on the transition metal, in agreement with experimental measurements that indicated a moment  $< 1\mu_B$  [114]. In comparison to the iron series, we see that these values are much smaller, which is expected considering that vanadium is not a very magnetically active atom.

Table 10 - Obtained results for SrVO<sub>3</sub>. The FM calculation converged to an essentially paramagnetic phase, with very similar energies. Thus, the ground state of the system is undoubtedly paramagnetic, in agreement with the literature.

$\mathrm{SrVO}_3$	Total Energy (Ry)	Total Magnetic Moment $(\mu_B)$	Sr $(\mu_B)$	$V(\mu_B)$	O $(\mu_B)$
PARA	-8694.6644	-	-	-	-
$\mathbf{FM}$	-8694.6678	0.0902	0.0002	0.0637	0.0063

Table 11 – Obtained results for  $Sr_2VO_4$ . The close competition in energy between paramagnetic, AFMA and AFMG phases is an indicator of a highly frustrated magnetic system. The magnetic ground state considered for following analyses was the AFMA ordering based on the reported properties of the material. A much smaller magnetic moment is exhibited by the vanadium ion in comparison to the iron series, as is expected due to V being less magnetically active. Different contributions to the magnetic moment by basal and apical oxygens were also determined.

$\mathrm{Sr}_{2}\mathrm{VO}_{4}$	Total Energy (Ry)	Total Magnetic Moment $(\mu_B)$	Sr $(\mu_B)$	$V(\mu_B)$	O $(\mu_B)$
PARA	-15195.8792	-	-	-	-
FM	-15169.5119	1.0000	0.0016	0.8793	Basal = -0.0457
					Apical = 0.0518
AFMA	-15195.8672	-0,0370	$\mathrm{Sr1} = 0.0002$	V1 = 0.8307	Basal = 0.0383
			Sr2 = -0.0007	V2 = -0.9266	Apical = 0.0200
AFMG	-15195.7842	0.0000	Sr1 = -0.0008	V1 = -0.8378	Basal = -0.0335
			$\mathrm{Sr2}=0.0010$	V2 = 0.7396	Apical = 0.1299

#### 5.2.1 Density of States and Band Structure

Following the analysis, the DOS and PDOS of both materials were obtained and are displayed on figure 39 as comparisons. Similar to the iron series, a large covalence is observed between the oxygen and transition metals, the main difference lying on the behavior close to the Fermi level. For the iron series, all materials are on the negative charge transfer regime, thus the states around the Fermi level should be of p - p type, with predominance of oxygen 2p. The vanadium series on the other hand is closer to the Mott-Hubbard regime, and should have states around the Fermi level of d - d type, with a predominance of vanadium 3d states [69]. Both statements agree with our results. The general trend of localization with lower n is also observed for this series. A more detailed analysis of each material is given on the following.

The PDOS of  $n = \infty$  is depicted in figure 40. As SrVO<sub>3</sub> crystallizes in the perfect cubic perovskite structure, there is no chemical difference between the basal and apical oxygens, thus the difference in the density of states is due solely to the multiplicity of each oxygen species (2:1). The strontium states are located in pretty much the same energy region as for SrFeO<sub>3</sub>, showing that the little covalent character between the strontium and transition metals seem to be a general feature of the strontium perovskites. As expected, the large density of vanadium states at the Fermi level yield the conductive nature of the material.

Considering now the n = 1 material, as can be seen on figure 41, there is a substantial difference that can be attributed to the introduction of the SrO layers. The large vanadium structure present for  $n = \infty$  at the Fermi level is separated into two distinct structures with a small gap between them. As the first one is still located at the Fermi level, our calculation yields a metallic behavior that contrasts to the known semiconductor nature of the material, with an optical gap of about 2 eV [115]. This false prediction turns out to be very persistent for many different initial magnetic structures and calculation conditions, and reported DOS in an GGA+U scheme also exhibit the same problem [116]. We conducted several other tests by changing the supercell size of the antiferromagnetic calculations and also the exchange-correlation functional for a GGA+U approach and none were able to correctly predict a small gap or fail in comparison to experimental data of optical conductivity. These are detailed in appendix II. This intrinsic difficulty can be attributed to the DFT calculations not taking into account explicitly the known orbital-ordering behavior of the material, which greatly impacts the physical properties it exhibits [92, 95].

Also worthy of note is the expected change in oxygen states according to their basal or apical position. The basal oxygens have states associated with the projections of the 2p orbitals on the plane distributed over a wider energy interval than the projection along the axis, which show more narrow peaks and are shifted closer to the Fermi level when compared to the  $n = \infty$  case. The apical oxygens on the other hand show a more



Figure 39 – Comparison between the DOS of  $n = \infty, 1$  of the vanadium series. Close to the fermi level there is a more pronounced d band influence, consistent with materials close to a Mott-Hubbard transition. Great covalence is observed between the oxygen and vanadium atoms, and to a lesser extent between oxygen and strontium. For both materials a metallic character was predicted, in contrast to the semiconductive nature expected for n = 1.



Figure 40 – PDOS of SrVO<sub>3</sub>. The metallic nature of the material is attributed to the large number of V 3d states near the Fermi level. No difference besides absolute number of states is observed between the oxygen types, as expected considering the material crystallizes in a perfectly cubic unit cell and is composed of only perovskites, being equivalent in all directions.



Figure 41 – PDOS of  $Sr_2VO_4$ . As in the case of the iron series, by lowering n a difference between the structures of each oxygen type is observed, with the apical oxygens showcasing more prevalent character along the plane as a consequence to the proximity of oxide layers. The metallic character predicted contrasts with the known semiconductive nature of the material.

localized structure both for the projections along the plane and along the axis, with a higher density for the  $p_x + p_y$  states. A comparison between the oxygen states for  $n = \infty, 1$  is highlighted in figure 42, in which the evolution of the oxygens' density of states can be more readily analyzed.

The band structures of both materials were obtained and their O 2p character characterized, following analyses that are similar to the ones conducted for the iron series. In figure 43 are the bands corresponding to SrVO<sub>3</sub>, showing relatively high dispersion considering the highly-correlated nature of the material. It is interesting to notice that, below the Fermi level, the bands with the lowest energy have a strong  $p_z$  character, whereas the ones with slightly higher energy show a strong  $p_x + p_y$ . Moreover, the bands that cross the Fermi level and thus are directly related to the conduction in the material exhibit have basically only  $p_x + p_y$  character, pointing to a preference in conduction along the abplane even in the absence of the strontium oxide layers. For Sr<sub>2</sub>VO<sub>4</sub> (figure 44), it can be seen that the O 2p character is greatly increased, especially for the bands related to the occupied states, the  $p_x + p_y$  being relatively more present also in the conduction band. The confinement in a 2D environment also produces for this material much flatter bands, which are a consequence of the localization of the electronic structure, although the states at around -6 eV still retain the more delocalized behavior of the  $n = \infty$  material.

#### 5.2.2 Optical Conductivity

Aiming at validating our calculations, we conducted experimental comparisons of the optical conductivity behavior for both materials, as data regarding this property has been widely reported. Our results were obtained following the method that is already implemented in the WIEN2K package [117], and are displayed on figure 45. For  $n = \infty$ , the experimental data was taken from the work of Makino et. al [118] and for n = 1 from the work of Matsuno et. al [115]. Considering firstly the  $SrVO_3$  system, we see a very good agreement between our calculations and the reported behavior. There is no difference between the xx and zz components of the real part of the optical conductivity, as expected for an isotropic system. For low energies it can also be seen that there is a feature called a Drude tail, that happens for metallic states and is due to intraband transitions d - dtransitions in the occupied states [118, 100]. The width of this structure is directly related to the plasma frequency  $\omega_p$ , the typical oscillation of the electronic motion in the absence of external field, which is turn directly proportional to the density of electrons in the conduction band. Thus, the more states that cross the Fermi level, which characterizes a metal, the wider in energy will this tail be. There is a small bump in the values of the conductivity at about 2 eV, which is associated with transitions to unoccupied V  $t_{2g}$  states, the transitions to the  $e_q$  states being hidden by the more pronounced structure starting at 4 eV and associated with p - d charge-transfer transitions [100].



Figure 42 – Evolution of the oxygen 2p PDOS for the vanadium series, separated by the contributions of basal and apical oxygens and the projections along the ab plane and along the c axis. The differences between the structures caused by the reduction in dimensionality become evident, with a greater localization of states associated with the apical oxygens.



Figure 43 – Band structure of SrVO<sub>3</sub> with highlighted O 2p character. A lot of dispersion is observed, with different bands exhibiting markedly single-type character, either  $p_x + p_y$  or  $p_z$ .

The case of n = 1 is more complicated due to the non-isotropic environment along ab plane and the c axis. This leads to a difference between the components of the real part of the optical conductivity, showing a smaller optical gap of about 1 eV for transitions on the plane in comparison to the 3 eV gap along the axis. As our calculation did not render a semiconductor, a rigid shift of the theoretical obtained conductivity by about 1.4 eV yielded a good agreement with the available data in relation to the energy positions, but less so in terms of the relative intensities. Our calculations also predict the behavior of this property for values beyond the experimentally measured. The first peak is associated with intersite d - d transitions [115], called Mott-Hubbard transitions, whereas the peak at about 3 eV is of charge-transfer nature and is attributed to the transitions from the oxygen 2p bands to empty  $d_{xz+yz}$  orbitals [116].



Figure 44 – Band structure of SrVO<sub>3</sub> with highlighted O 2p character. Features similar to those observed in the iron series are also present, namely the flattening of the band structures, evidence of localization, and the more evident  $p_x + p_y$  character in a larger energy range.



Figure 45 – Comparison between calculated and experimentally reported real parts of the optical conductivity for SrVO<sub>3</sub> and Sr<sub>2</sub>VO<sub>4</sub>. Data for  $n = \infty$  taken from reference [118] and for n = 1 taken from [115]. Good agreement with experimental data is shown for both systems, n = 1 requiring a rigid shift of 1.4 eV in the spectrum to account for the gap that wasn't reproduced in our calculations. It can be seen that while for  $n = \infty$  the optical conductivity is isotropic, for n = 1 there are large differences between the components along the x and z directions.

## 6. Conclusions

In the present work, a comprehensive theoretical study on the electronic structure of two highly-correlated Ruddlesden-Popper series (RP) was conducted, namely  $Sr_{n+1}Fe_nO_{3n+1}$  for  $n = \infty, 2, 1$  and  $Sr_{n+1}V_nO_{3n+1}$  for  $n = \infty, 1$ . These can be understood as the insertion of intergrown layers of strontium oxide SrO between the *n* strontium ferrite/vanadate  $Sr(Fe/V)O_3$  perovskite layers. As *n* is lowered from infinity to one, representing the gradual change from an isotropic perovskite only system to a 2D-like stacking of insulated perovskite layers, non-trivial transitions in the magnetic structure and conductive nature of these materials are observed experimentally. Due to the complexity of these systems, open questions regarding these properties and their underlying causes still remain. Our goal with this work was to help shine light on the dependence of the physical properties of these materials on the dimensionality of the system.

Our approach consisted on calculations based on Density Functional Theory (DFT), which are standard in condensed matter physics in great part due of its *ab initio* bottom-up nature and accuracy. For that end, we considered a two-step process for obtaining the ground state properties, where first a converged calculation with the PBEsol exchange-correlation potential was done and then used as the input for a second calculation, now considering the mBJ potential, as parametrized by Jishi and collaborators. The reasoning for this is that Jishi's mBJ is specifically tailored to perovskite systems and thus should yield better results, but requires a previous calculation as input. All of the calculations were done using the WIEN2K distribution.

We managed to reproduce known general properties of the RP series, specially the localization of the electronic structure with lower dimensionality, which indicates that the interactions along the ab plane become dominant once the connection between adjacent perovskite layers along c is made more difficult through the insertion of the SrO layers. This localization is what drives the changes in the magnetic structure and conductivity of the materials, being reflected on the several analyses that were conducted. Also observed was the high degree of covalence between the transition metals and the oxygen, and to a lesser degree between oxygen and strontium, typical of highly-correlated transition metal systems.

Considering specifically the iron series, it is characterized by complex magnetic structures due to competing ferromagnetic-antiferromagnetic interactions and frustration, while also exhibiting for all materials negative charge-transfer regimes, with a ground state electronic configuration dominated by holes in the ligand. We obtained the experimentally determined magnetic structures, in the collinear approximation, as the arrangements of lowest energy, the exception being for n = 1, whose energy difference to the calculated ground state configuration is of only about 5 eV. Thus, our calculations support the reported degree of importance of the competing magnetic interactions even in a simplified model with all spins lying along the same direction.

By analyzing the density of states projected onto the valence orbitals (PDOS) of each atomic species, we were able to directly determine the effect of localization for lower n. It could be seen that the band structure of the materials become progressively more concentrated in smaller energy intervals, exhibiting sharper features and also less dispersion along the high-symmetry points in the first Brillouin zone. The presence of the strontium oxide layers provokes a differentiation between basal and apical oxygens, which in turn leads to different chemical activity between them. The apical oxygens tend to show structures that are more localized and more pronounced when projected along the plane due to the presence of the oxide layers. This effect was also studied by considering the oxygen 2p character on the band structures, where different behavior is observed for the  $p_x + p_y$  and  $p_z$  components. The influence of doping was also considered for the case n = 2, where it was noticed that by breaking the periodicity of the potential with the introduction of Ni atoms, the band structure can also become more localized, leading to a disruption of the material's magnetic ordering.

An experimental comparison was done considering X-Ray absorption spectrum (XAS) data. For this end, we obtained approximate spectra directly from DFT, which were then treated using a variational approach to the systems' Green's functions in order to simulate the attractive potential of the core-hole. A significant improvement was observed in comparison to the untreated spectra, leading to a good agreement with experimental data considering the limitations of DFT to the ground state properties of a system.

In the case of the vanadium series, similar results were obtained. As n is lowered the band structure also becomes more localized and a difference between the oxygen types is observed. The n = 1 material turned out to be resistant to several attempts to reproduce the semiconductor behavior observed experimentally. This is credited to the calculations not taking into account the complicated orbital ordering it exhibits in the ground state, reinforcing the importance attributed to the influence of this characteristic on the material's properties by other studies. The experimental comparison was conducted using measurements of optical conductivity reported in the literature. Our calculations show a very good agreement for the  $n = \infty$  system, reproducing even small features of the spectrum, whereas for n = 1 an agreement was observed only by doing a rigid shift of 1.4 eV, close to the reported gap that wasn't predicted by our calculation.

Thus, we conclude that the present study was successful in highlighting the effects of the gradual 2D confinement as n in lowered in a Ruddlesden-Popper series, more specifically the consequences on the electronic structure and the differentiation of the oxygen species due to their position in the crystal. We were able to reproduce experimental data both regarding XAS and optical conductivity spectra with a good accuracy, what supports our calculations even in the collinear spin approximation. Possible future steps consist on taking into account non-collinear DFT approaches, which should yield even better results due to the known helical spin ordering several of the materials considered exhibit. Another possibility is to consider the effects of non-stoichiometry on the electronic structure, as these materials often show oxygen vacancies or excess which are known to highly impact the physical properties such as electrical conductivity and magnetic ordering.

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# APPENDIX
## I. Core-Hole Potential

### Green's Function Theory

<sup>1</sup> Considering z to be a complex variable and  $L(\mathbf{r})$  a time-independent, linear and hermitian differential operator, the Green's function  $G(\mathbf{r}, \mathbf{r}'; z)$  is defined as the solution to the inhomogeneous differential equation:

$$[z - L(\mathbf{r})]G(\mathbf{r}, \mathbf{r}'; z) = \delta(\mathbf{r} - \mathbf{r}').$$
(1)

*G* is subjected to boundary conditions for **r** or **r'** on the surface of the domain  $\Omega$ . Define  $\lambda \equiv \operatorname{Re}\{z\}$  and  $s \equiv \operatorname{Im}\{z\}$  such that L possesses a complete set of eigenfunctions  $\{\phi_n(\mathbf{r})\}$  so that

$$L(\mathbf{r})\phi_n(\mathbf{r}) = \lambda_n \phi_n(\mathbf{r}). \tag{2}$$

One can represent these quantities in the bra-ket notation by projecting, for exemple, in the position basis  $|\mathbf{r}\rangle$ , leading to  $G(\mathbf{r}, \mathbf{r}'; z) \equiv \langle \mathbf{r} | G(z) | \mathbf{r}' \rangle$  and  $\delta(\mathbf{r} - \mathbf{r}' L(\mathbf{r})) \equiv \langle \mathbf{r} | L | \mathbf{r}' \rangle$ . This allows us to rewrite 1 as

$$(z-L)G(z) = 1, (3)$$

where now L and G are representation independent. If all eigenvalues of (z - L) are nonzero, condition satisfied for z not belonging to the spectra of eigenvalues  $\{\lambda_n\}$  of L, then this equation can be written formally as

$$G(z) = \frac{1}{z - L},\tag{4}$$

which is to be understood when projected unto a basis. for example considering the complete basis of eigenstates  $|\phi_n\rangle$ 

$$G(z) = \frac{1}{z - L} \sum_{n} |\phi_n\rangle \langle \phi_n| = \sum_{n} \frac{|\phi_n\rangle \langle \phi_n|}{z - \lambda_n}.$$
(5)

<sup>&</sup>lt;sup>1</sup> This section is based entirely on the book *Green's Functions in Quantum Physics*, by E. N. Economou [119].

Because L is hermitian, all of its eigenvalues are real and thus G(z) is analytic in the whole complex plane except the points or intervals on the real axis that correspond to its eigenvalues, that is, the poles of G(z) are the discrete eigenvalues of the operator. If z on the other hand is part of the continuous spectrum of L, then the Green's function is not well defined and one has to resort to limiting procedures. Thus, the branch cuts of G(z) are associated with the continuous spectrum of the operator. In this sense, all of the information regarding eigenvalues and therefore eigenstates of an arbitrary operator L that respects the properties defined in the beginning of this section is present in the Green's function G(z).

Defining the limiting Green's functions  $G^+$  and  $G^-$  as

$$G^{+}(\mathbf{r}, \mathbf{r}'; \lambda) \equiv \lim_{s \to 0^{+}} G(\mathbf{r}, \mathbf{r}'; \lambda + is)$$
(6)

$$G^{-}(\mathbf{r}, \mathbf{r}'; \lambda) \equiv \lim_{s \to 0^{+}} G(\mathbf{r}, \mathbf{r}'; \lambda - is),$$
(7)

it can be shown that these quantities are directly associated with the density of states (DOS) per unit volume  $\rho(\mathbf{r}; \lambda)$  by the relation

$$\rho(\mathbf{r};\lambda) = \mp \frac{1}{\pi} \operatorname{Im} \{ G^{\pm}(\mathbf{r},\mathbf{r}';\lambda) \}.$$
(8)

That is, given an operator L, which can be the hermitian operator of the time-independent Schrödinger equation or Kohn-Sham equation 2.22, the density of states can be found considering the operator's associated Green's function or vice-versa. This is key to the next step, that is to consider a perturbation to this operator.

Let's define the one-particle Hamiltonian  $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$ , where  $\mathcal{H}_0$  is the original Hamiltonian, whose eigenvalues and eigenfunctions are already known or are easy to obtain, and  $\mathcal{H}_1$  is a perturbation. Considering equation 4, one can define the Green's functions  $G_0$ and G(z) associated with these operators as

$$G_0(z) = (z - \mathcal{H}_0)^{-1} \tag{9}$$

$$G(z) = (z - \mathcal{H})^{-1}.$$
 (10)

Thus, one can write  $\mathcal{H}$  as

$$G(z) = (z - \mathcal{H}_0 - \mathcal{H}_1)^{-1} = \{(z - \mathcal{H}_0 \left[1 - (z - \mathcal{H}_0)^{-1} \mathcal{H}_1\right])\}^{-1}$$
(11)

$$= \left[1 - (z - \mathcal{H}_0)\mathcal{H}_1\right]^{-1} (z - \mathcal{H}_0)^{-1}$$
(12)

$$= [1 - G_0(z)\mathcal{H}_1]^{-1}G_0(z).$$
(13)

The operator  $(1 - G_0 \mathcal{H}_1)^{-1}$  can be written as a power series, justified as the matrix element involving the perturbation must be small, yielding

$$(1 - G_0 \mathcal{H}_1)^{-1} = 1 + G_0 \mathcal{H}_1 + (G_0 \mathcal{H}_1)^2 + (G_0 \mathcal{H}_1)^3 + \dots$$
(14)

$$= 1 + G_0 \mathcal{H}_1 + G_0 \mathcal{H}_1 G_0 \mathcal{H}_1 + G_0 \mathcal{H}_1 G_0 \mathcal{H}_1 G_0 \mathcal{H}_1 + \dots$$
(15)

$$= 1 + G_0 \mathcal{H}_1 + G_0^2 \mathcal{H}_1 + G_0^2 \mathcal{H}_1 G_0 \mathcal{H}_1 + \dots$$
(16)

Here the fact that  $[G_0, \mathcal{H}_1] = 0$  was used. Plugging (14) in (11), we have

$$G(z) = G_0 + G_0 \mathcal{H}_1 G_0 + G_0 \mathcal{H}_1 G_0 \mathcal{H}_1 G_0 + \dots$$
(17)

$$= G_0 + G_0 \mathcal{H}_1 (G_0 + G_0 \mathcal{H}_1 G_0 + ...)$$
(18)

$$=G_0 + G_0 \mathcal{H}_1 G \tag{19}$$

This is a Dyson series for the unknown G(z), which becomes solvable once projected into a basis. Thus, the procedure for the analysis of a perturbed Hamiltonian can be summed up in the following:

- 1. First, one must determine the Green's function associated with the unperturbed Hamiltonian  $\mathcal{H}_0$  through, for example, equation 5;
- 2. Write the perturbed Hamiltonian's Green's function G in terms of the  $G_0$  and  $\mathcal{H}_1$  as in equation (17);
- 3. Obtain information regarding the eigenvalues and eigenfunctions of the perturbed Hamiltonian, for example the density of states (8).

This is the basis of the method to simulate the core-hole potential of chapter 4, where the core-hole is to be taken as the perturbation and the density of states is the one calculated from DFT.

#### Computational Implementation

To calculate the XAS spectra from DFT, we set the values of the DOS below the Fermi level (E = 0) to zero and sum up the absolute values of up and down DOS for energies above it. This is done because XAS gives information regarding the conduction band near the Fermi level. Thus, because this density of states is already given per unit cell volume, we must simply normalize by the number of unit cells considered in each specific calculation and equation (8) can be applied. As the discontinuity lies at the Fermi level due to the setting the values before it to zero, we consider  $G^+$ , yielding

$$Im\{G^{+}(E)\} = Im\{G_{0}(E)\} = -\pi\rho_{0}(E).$$
(20)

The same relation can be applied for the perturbed function G and the corresponding density of states  $\rho$ 

$$\operatorname{Im}\{G(E)\} = -\pi\rho(E). \tag{21}$$

The idea of the method can be summed up in the following:

- 1. With the original density of states that represents the XAS spectrum  $\rho_0$ , the imaginary part of the  $G_0$  is obtained. As a result of causality [119], these Green's functions respect the Kramers-Kronig relations, so that  $\operatorname{Re}\{G_0\}$  can be obtained by a Hilbert transform;
- 2. With the numerical  $G_0$  resulting from the above procedure, we obtain G from equation (17) considering that  $\mathcal{H}_1 = V$ . Because these operators are already acted upon a basis, the equation is algebraic and thus  $G = G_0(1 VG_0)^{-1}$ ;
- 3. The core-hole corrected density of states  $\rho$  is then given by taking the imaginary part of the determined G(E) as in equation (21);
- 4. Finally, a gaussian broadening of 0.4 eV is applied to the entire DOS in order to smooth its behavior and better compare to the experimental data.

In step 1, the integration was made using the *scipy.signal.hilbert* package of the SciPy library [120]. The Hilbert transform of a function u(t) is given by the following equation

$$H\{u(t)\} = \frac{1}{\pi} \operatorname{P} \int_{-\infty}^{+\infty} \frac{u(\tau)}{t-\tau} d\tau, \qquad (22)$$

where P indicates Cauchy's principal value [121]. This transform is exactly the imaginary term of the Kramers-Kronig relation for u(t), the real term being just -1 times this value. The *hilbert* function of the SciPy library computes the analytical signal  $u_a(t)$  of a given signal u(t), defined by

$$u_a(t) = u(t) + iH\{u(t)\},$$
(23)

where  $\text{Im}\{u_a(t)\}\$  is the Hilbert transform of u(t). Thus, for our specific case, since we obtain the imaginary part of  $G_0$  by equation (21), we can write

$$\operatorname{Re}\{G_0(E)\} = -H\{\operatorname{Im}\{G_0(E)\}\}$$
(24)

$$= +\pi H\{\rho_0(E)\}$$
 (25)

$$= \pi \operatorname{Im}\{\rho_{0,a}(E)\}.$$
 (26)

Here,  $\rho_{0,a}$  is the analytical signal of  $\rho_0$ , which is calculated by the *hilbert* function as mentioned.

### II. Additional Results for $Sr_2VO_4$

As mentioned in chapter 5, several attempts to produce a density of states (DOS) for  $Sr_2VO_4$  which displayed the expected semiconductive behavior were done without success. This reinforces the argument of the importance of considering the known orbital-ordering state this material presents in its ground state, which is not taken into account by usual density functional theory (DFT) calculations. These results are reproduced in the following.

First off, we observe that there is a sensible difference of the results with the size of the supercell considered. Because the system is highly correlated and also magnetically frustrated, a larger supercell can stabilize longer ranged interactions that may be spurious. An example of this is depicted in figure 46, where the same type A antiferromagnetic ordering (AFMA) of chapter 5 was considered but with an unit cell that is doubled only along the *ab* plane (2x2x1) instead of only along the axis (1x1x2). It can be seen that the predicted gap is of about 3.5 eV, over three times larger than the experimental gap of about 1 eV [115]. The lack of significant *d* character close to the energy level that the material must present considering it lies close to a Mott-Hubbard transition and the much more pronounced overlap between metal and strontium levels show that this result, consequence of a simple change in the supercell dimensions, is inconsistent with the known properties of the material.

This inconsistency can also be analyzed when considering the optical conductivity results (figure 47), which yield a completely different curve than the experimental data [115], and most importantly show an isotropic behavior that is far from reality.

Among the tentative approaches to reveal the expected gap in the DOS, we also conducted LDA+U studies initialized in an AFMA ordering for different values of U, considering an effective exchange parameter J = 0.6 eV obtained by Hartree-Fock calculations. The results for U = 0.2 eV and U = 1.0 eV are in figures 48 and 49 respectively, where it can be seen that a metallic behavior similar to the one we reported on chapter 5 was obtained. Also worthy of note is that changes in the value of U have almost no effect on this structure, so the problem in the comparison with the experimental data still remains.

Additionally, due to the reported close competition in energy between the antiferromagnetic and ferromagnetic states (FM) reported in other works [116] which we did



Figure 46 – Density of States of the A-type antiferromagnetic structure for a 2x2x1 supercell. The calculated gap is far higher than the  $\sim 1$  eV gap that is reported [115].

not observe, we also investigated the FM state prediction. The DOS obtained is depicted on figure 50, where a very similar structure to 41 is observed at the Fermi level but with a half-metallic character. Even though interesting, it is known that this material is a semiconductor and has an antiferromagnetic-like behavior for low temperatures [94], therefore this prediction has no basis in experimental data.

That being said, the obtained optical conductivity results for this configuration show an agreement similar to the one we report in chapter 5 and can be seen on figure 51. A shift of 1.2 eV was necessary to better compare the calculation and the experimental data, which can be attributed to the energy gap that was not predicted by DFT. Considering that both FM and AFMA (with a 1x1x2 supercell) yielded similar comparisons with the optical conductivity but the material is definitely not in a ferromagnetic state according to experiments, we believe that the AFMA results are more significative.

As a test to see if the FM state could predict a gap within the LDA+U scheme, we considered several values of U and even for extreme and unrealistic values the gap is still not observed. These results are depicted in figures 52 to 54, where it can be seen that the higher the U utilized, the more the DOS tends towards the one calculated using the Jishi-mBJ potential of figure 50.



Figure 47 – Optical conductivity for the AFMA configuration with a 2x2x1 supercell, deviating completely from the experimental curve [115].



Figure 48 – DOS obtained for AFMA calculation with U = 0.2 eV.



Figure 49 – DOS obtained for AFMA calculation with U = 1.0 eV.



Figure 50 – DOS obtained for the ferromagnetic configuration of  $Sr_2VO_4$ , displaying half-metallic character.



Figure 51 – Optical conductivity obtained for the FM system. A good agreement is found between the experimental data and calculated results when forcefully taking into account the gap that wasn't predicted.



Figure 52 – DOS obtained considering U = 0.4 eV.



Figure 53 – DOS obtained considering U = 1.0 eV.



Figure 54 – DOS obtained considering U = 5.0 eV.

# ANNEX

### Curricular Data

#### Participation in Events:

- V Workshop of the Graduate Program in Physics UFPR. Curitiba, Brazil. Poster presentation: "Effects of Dimensionality on the Electronic Structure of the Ruddlesden-Popper series  $Sr_{n+1}Fe_nO_{3n+1}$ " (2023).
- XVIII Escola Brasileira de Estrutura Eletrônica. Campinas, Brazil. Poster presentation: "Effects of Dimensionality on the Electronic Structure of the Ruddlesden-Popper series  $Sr_{n+1}V_nO_{3n+1}$ " (2023).
- 41<sup>st</sup> Intenational Conference on Vacuum, Ultraviolet and X-Ray Physics (VUVX). Campinas, Brazil. Contributed Talk: "Effects of Dimensionality on the Electronic Structure of the Ruddlesden-Popper series Sr<sub>n+1</sub>(Fe/Ni/V)<sub>n</sub>O<sub>3n+1</sub>" (2023).
- Autumn Meeting of the Brazilian Physical Society. Ouro Preto, Brazil. Poster presentation: "Effects of Dimensionality on the Electronic Struture of the Ruddlesden-Popper Series  $Sr_{n+1}Fe_nO_{3n+1}$  and  $Sr_3FeNiO_7$ ." (2023).
- IV Workshop of the Graduate Program in Physics UFPR. Curitiba, Brazil. Contributed talk: "Effects of Dimensionality on the Electronic Structure of the Ruddlesden-Popper series  $Sr_{n+1}Fe_nO_{3n+1}$ " (2022).
- 7º Escola de Química Computacional. Ribeirão Preto, Brazil. Virtual event. Contributed talk: "Effects of Dimensionality on the Electronic Structure of the Ruddlesden-Popper series  $Sr_{n+1}Fe_nO_{3n+1}$ " (2022).
- Semana Acadêmica de Física UFPR. Curitiba, Brazil. Poster presentation: "Effects of Dimensionality on the Electronic Structure of the Ruddlesden-Popper series  $Sr_{n+1}Fe_nO_{3n+1}$ " (2022).