Doctoral Thesis

Strain-induced insulator-to-metal transition in d¹ perovskite systems within density functional theory plus dynamical mean field theory

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Strain-induced insulator-to-metal transition in $d^1$ perovskite systems within density functional theory plus dynamical mean field theory

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Abstract

While density functional theory (DFT) has proven to be quite successful in describing many ground-state properties of solids, there is a growing list of materials which are not even described qualitatively correct within density functional theory. Here I describe some applications of density functional theory with dynamical mean field theory. This approach has been shown to give a significantly improved description, for many systems with strongly interacting electrons, where standard DFT fails.

A new code has been developed that allows to perform combined density functional theory plus dynamical mean-field theory (DFT+DMFT) calculations for a large variety of systems. This code has been applied to study strain dependence of the metal-insulator transition in certain transition metal oxides.

Results of DFT+DMFT calculations are presented here, assessing the effect of epitaxial strain on the electronic properties of the Mott insulator LaTiO$_3$ and the correlated metal SrVO$_3$. In particular, the effect of strain on the collective tilts and rotations of the oxygen octahedra in the orthorhombically distorted $Pbnm$ perovskite structure of LaTiO$_3$ has been taken into account. It is found that LaTiO$_3$ undergoes an insulator-to-metal transition under a compressive strain of about $-2\%$, consistent with recent experimental observations. It is shown here, that this transition is driven mainly by strain-induced changes in the hopping integrals between the Ti $t_{2g}$ orbitals, which in turn are related to changes in the octahedral tilt distortion and changes in the Ti-O bond lengths. This is compared with the case of SrVO$_3$ without octahedral tilts, where one finds a metal-to-insulator transition under the tensile epitaxial strain. Similar to LaTiO$_3$, this metal-insulator transition is also linked to the strain-induced changes in the hopping integrals within the $t_{2g}$ orbitals. It is demonstrated that a clear distinction between strain and interface effects is necessary for the understanding of emerging properties in oxide heterostructures.
Abstract


Im Rahmen dieser Arbeit wurde dazu ein neues Computer-Programm geschrieben, welches es ermöglicht, Rechnungen im Rahmen der Dichtefunktionaltheorie plus dynanischer Molekularfeldtheorie (DFT+DMFT) für eine Vielzahl verschiedener Materialien durchzuführen. Dieses Programm wurde dann für die Untersuchung der Verzerrungs-Abhängigkeit des Metall-Isolator-Übergangs in bestimmten Übergangsmetall-Oxiden eingesetzt.

Oxid-Heterostrukturen eine klare Unterscheidung zwischen Verzerrungs- und Grenzflächen-Effekten notwendig ist.
Chapter 1

Introduction

Transition metal perovskite systems have attracted the attention of the scientific community for over half a century for their electronic and magnetic properties arising from strongly correlated electrons which occupy their valence states. Such an abundance of the fascinating properties is due to the fact that in transition metal oxides the high polarizability of the metal cation competes with strong correlations which favour the insulating state. Because of this competition, transition metal oxides can exhibit abrupt changes in their electronic properties when exposed to small perturbations or external factors \textsuperscript{[1]}. Growth of perovskite oxides as thin films affords an additional parameter for controlling their delicate electronic balance. Indeed abrupt changes in properties of thin films of perovskite systems in comparison to their bulk forms, which have been reported, seem to offer the potential for possible future electronic devices \textsuperscript{[2]}. In particular, oxide thin films have the potential to revolutionize the electronic industry through so-called \textit{Mottronic devices} \textsuperscript{[3], [4], [5], [6]}.

Mottronic devices are an emerging generation of devices made of transition metal oxides with strongly correlated electrons. The functionality of Mottronic devices is based on the so-called Mott metal-insulator transition (more on that in chapter 3.3.1). This transition occurs for a material-dependent value of the Coulombic $U$ Hubbard parameter for which a system becomes insulating. It is named after Nobel laureate Nevill Francis Mott, who won the prize for his work on the electronic structure of magnetic and disordered systems. Especially, heterostructures of perovskite systems seem to be quite promising prototypes for future Mottronic devices. It has already been reported that conducting/insulating phases of thin films of perovskite systems, which are Mott materials, can be controlled by applying an epitaxial strain to the crystal lattice \textsuperscript{[7]}. It is believed that Mottronic devices can be useful as sensors, RAM-like memories in computers, and for
signal conversion devices.

At the same time, despite the experimental progress in growing high quality coherent perovskite oxide thin films [8] and heterostructures [9], [10], it is still challenging to predict the electronic or magnetic properties at heterointerfaces given the known properties of the bulk constituents. This is mainly caused by the experimental difficulties in determining the exact structure of the thin films. For example, determining the oxygen positions in a thin film is quite challenging. Simultaneously, properties of heterointerfaces are strongly dependent on small changes in the atomic structure. Moreover, many factors like an epitaxial strain, defects, and an interface effect between the thin film and the substrate occur concurrently under the condition of the experiment, and it is not possible based only on experimental data to point out which of these effects play the dominant role in the observed properties. Such experimental difficulties are a serious obstacle in manufacturing Mottronic devices, and this situation is unlikely to change unless a detailed understanding of the atomic and electronic structure in perovskite thin films is developed.

One way to address these difficulties in the interpretation of experimental results, is to employ electronic-structure calculations to model oxide thin films and heterostructures. By performing computational modelling, one can in principle, determine the exact atomic structure. Moreover, one can also focus on each factor, which occurs during the experiment, separately. In other words, one can investigate factors like interface effects, defects, an epitaxial strain, etc., not all at once, but also one by one.

In this project, I focus on the relation between structural and electronic properties in thin films of perovskite systems by means of computational methods. Within this project, a model for thin films is investigated by considering only one of the many factors which occur in the experiment: epitaxial strain. These types of calculation are called homoepitaxial strain calculations [11].

In particular, two transition metal (TM) oxide systems with a $d^1$ valence electron configuration, SrVO$_3$ and LaTiO$_3$, will be investigated within this project. SrVO$_3$ has a perfect cubic perovskite structure, with $Pm\bar{3}m$ symmetry, whereas LaTiO$_3$ has a lower symmetry, $Pbnm$, due to the slightly distorted perovskite structure. Even though structural differences seem to be rather small, those two materials have significantly different electronic properties: SrVO$_3$ is a so-called correlated metal and LaTiO$_3$ is a Mott insulator.

Both systems of interest, SrVO$_3$ and LaTiO$_3$, have only one valence
$d$ electron ($d^1$). According to simple band theories both systems should be metals. However, their electronic properties are much more complex. Because of their complexity, a standard ab-initio method like density functional theory (DFT) is not able to reproduce experimental results for these materials in their bulk forms [13]. It misses to describe properly the correlation effects between $d$ electrons. One way to give a better description is to use DFT together with dynamical mean field theory (DMFT) [13]. A combination of DFT+DMFT has already been successfully used to describe many correlated systems [13]. However, it is still not a widely used method as for example DFT, partly because there are no widely distributed software packages available, and what is available is often tailored for some specific problems.

Within this project I have developed a code capable of performing DFT+ DMFT calculations not only for SrVO$_3$ and LaTiO$_3$, but which is also applicable to a wider class of problems, for which a proper description of correlated electrons is essential.

It has already been reported that the structural differences in perovskite TM oxides may have a crucial influence on their electronic properties [13]. In the perfect perovskite system the TM-O-TM bond angle is 180°, but for the more distorted structure this angle has a smaller value, which reduces electron hopping between the TM and the O anion. Some perovskites have already lower symmetry in their bulk state, but it is also possible to decrease the TM-O-TM bond angle in thin films by applying for example an epitaxial strain. The epitaxial strain is caused by lattice mismatch between the film and the substrate. Depending on the substrate the strain will be different. In the case of perovskites, changes of lattice constants under the epitaxial strain have a crucial impact on the distortion of the TM-O-TM bonds.

In the cubic perovskite, due to the electrostatic field created by the oxygen ligands, the 5-fold degeneracy of $d$ states, from the atomic solution of the Schrödinger equation, is lifted, and those states can be grouped

![Figure 1.1: Splitting of three $t_{2g}$ orbitals in a tetragonal crystal field. Different effective fillings for the $d^1$ case are indicated.](image-url)
according to energy levels into two separate sets: three-fold degenerated \( t_{2g} \) states and energetically higher lying two-fold degenerated \( e_g \) states. In perovskite systems, which are distorted due to the epitaxial strain, the degeneracy of the \( d \) states is even further lifted. In figure 1.1 it is shown how the tetragonal distortion of the unit cell affects the crystal field splitting of the \( t_{2g} \) states. Even in the case of a simple strained perovskite without the distorted TM-O-TM bond angles in the structure, a compressive strain splits \( t_{2g} \) to \( E_{d_{xy}} > E_{d_{xz}}, E_{d_{yz}} \). Symbol ‘\( > \)’ indicates energetic order of orbitals. \( E_x \) denotes an orbital energy of the \( x \)-th orbital. A compressive strain means that the lattice constants parallel to the substrate plane (\( a = b \)) are shorter than in the unstrained case, a tensile strain means that \( a = b \) are longer then in the unstrained case. Because of the compressive strain \( d_{xy} \) is the lowest state and both \( d_{xz}, d_{yz} \) are degenerate and have higher energies. For the tensile strain, one obtains \( E_{d_{xz}}, E_{d_{yz}} > E_{d_{xy}} \). Such splittings change the occupancies of the lowest levels for \( d^1 \) from 1/6 for degenerate \( t_{2g} \) states in case of the unstrained case (1 electron per 6 degenerate spin-orbitals) to 1/4 for the compressive strain, and to 1/2 for the tensile strain. This can have a significant impact on the value of the critical \( U \) which opens the gap and creates a Mott insulator.

Even though the way strain affects the crystal field in a simple tetragonal case is well understood, when it comes to the applied strain in a more general case of systems, with symmetry lower than tetragonal, it is still unknown how changes of the crystal field splitting affect the physical properties of such perovskite systems. The fact, that a small perturbations of the TM-O-TM angles may modify a material significantly, invokes the question whether the application of epitaxial strain is enough to obtain a Mott metal-insulator transition. Furthermore, it is still an open question whether distortions induced by the strain, affect all valence orbitals in the same way or each in a different way leading to a so-called orbital selective Mott transition, in which some orbitals can be essentially metallic while other orbitals are already insulating (or vice versa) [14]. Finally, the contribution of hopping integrals to the electronic properties of a distorted system is in general not well understood. In principle, larger hopping integrals should make a material more metallic. Moreover, in a case of a strained system, the bond angles are also changing. Therefore, in principle it is unknown how big the weight of the hopping integrals’ contribution to the electronic properties is for strained \( d^1 \) perovskite systems: These are the problems which are addressed within this thesis.

In summary this project has two goals. First, the development of a code
that allows DFT+DMFT calculations to be performed for a large variety of complex oxides. Second, the developed code is then used to clarify the effect of strain on the electronic properties of \( d^1 \) perovskite systems, using SrVO\(_3\) and LaTiO\(_3\) as representative examples.

The remainder of this thesis is organised as follows. The second chapter is dedicated to a brief description of the perovskite structure, including Glazer notation, and an overview of the known facts about LaTiO\(_3\) and SrVO\(_3\). The third chapter focuses on the calculational methods used in this project. In particular, the most important aspects of DFT and DMFT, which are relevant to this project, are presented. The fourth chapter is a brief summary of all benchmarks used to validate the developed code. The fifth chapter presents the detailed analysis of DFT+DMFT calculations for strained SrVO\(_3\) and LaTiO\(_3\). Finally, in the last chapter the results obtained within this project are summarised.
2.1 Perovskite structure

Both systems investigated in this project—SrVO$_3$ and LaTiO$_3$—belong to the family of perovskites. The name perovskite comes from the mineral CaTiO$_3$ [18], which was the first representative of this large family of compounds to be found. The mineral was discovered in the Ural Mountains of Russia by Gustav Rose in 1839 and is named after the Russian mineralogist Lev Perovski.

A material has the perovskite structure if it has the same type of crystal structure as calcium titanium oxide [19]. The perovskite crystal structure was first methodically described by Victor Goldschmidt in 1926, in his work on tolerance factors [20]. The condition for the formation of the perovskite structure ($ABX_3$) is formulated in the form of the Goldschmidt tolerance factor $t$ [20]:

$$t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)}$$

Figure 2.1: SrVO$_3$: V atoms are dark blue, O atoms red, Sr are green. A perfect perovskite structure, without any distortions, can be observed. This system has $Pm\bar{3}m$ space group symmetry.
where:

\[ R_A - \text{ionic radius of A element,} \]

\[ R_X - \text{ionic radius of X element,} \]

\[ R_B - \text{ionic radius of B element.} \]

Figure 2.2: LaTiO$_3$: Ti atoms are light blue, O atoms are red, La atoms are green. Tilted octahedra are quite visible. This system has \( Pbnm \) space group symmetry.

In the formula above, \( A \) and \( B \) are cations and \( X \) is an anion. In the majority of compounds \( X \) is, as in the prototype material CaTiO$_3$, an oxygen onion, \( O^{2-} \), but in some cases it can also be a different anion, for example \( X = F^-, Cl^- , Br^- \) or \( I^- \). In the perovskite structure, each \( B \) cation is octahedrally coordinated with six \( X \) anions (Fig. 2.1). \( ABX_3 \) perovskite can be described as consisting of corner-sharing \( BX_6 \) octahedra with the \( A \) cation occupying the 12-fold coordinated site formed in the middle of the cube of eight such octahedra (Fig. 2.1). According to Gold-Schmidt’s theory, the ideal cubic perovskite, with \( Pm\bar{3}m \) space group symmetry, occurs for \( t = 1 \) (Fig. 2.1). In reality, cubic crystal structures for perovskites have been observed for tolerance factors between 1.0 and 0.9 [21], [22].

The cubic perovskite structure (see Fig. 2.1) occurs very rarely. Most perovskite systems, both natural and synthesised, consist of distorted octahedral patterns. An example of a distorted perovskite structure is presented in figure 2.2. The octahedral distortions, which modify the ideal cubic structure, are closely related to the size of the \( A \)-site cation. The octahedra in the crystal network start to rotate if the value of the \( t \) parameter
diverges considerably from values characteristic for the cubic forms ($t \simeq 1$) to values much lower than 1 ($t \ll 1$). In principle, the rotations can occur in all three dimensions, but for the cases relevant for this work (distorted perovskites with $Pbnm$ symmetry) it is possible to describe them completely by only two angles, $\phi$ and $\theta$ [11]. Since LaTiO$_3$ has $Pbnm$ group symmetry, the octahedral distortions in it can be described in this way. Both angles are presented in figure 2.3. An angle $\theta$ describes rotations in the $ab$ plane and an angle $\phi$ describes tilts along the $c$ axis. For the perfect cubic perovskite structure the angle $\theta$ is $90^\circ$ and the angle $\phi$ is $180^\circ$. In the case of distorted structures these angles have different values. When analysing distorted structures one usually monitors the deviation of these angles from their values which correspond to the perfect cubic case. The rotation of octahedra lowers the symmetry of the perovskite system to for example orthorhombic or rhombohedral. Usually in the case of perovskite systems with lower symmetries, $B-O$ bond lengths also change and they no longer have the same length in all crystallographic directions. For example in LaTiO$_3$, Ti-O bond lengths in different directions are different (for LaTiO$_3$: 2.057 Å, 2.031 Å, 2.0298 Å for T=293 K [12]).

Since perovskite systems are not truly ionic compounds, the tolerance factor $t$, which describes the stability of perovskite compounds, is only a rough estimate. For example, in the original paper, Goldschmidt proposed $t \in [0.9, 1.0]$ as the criterion of the formation of the stable perovskite structure. The parameter $t$ was originally defined for bulk perovskite compounds. Nevertheless, many of the structural characteristics mentioned for distorted bulk perovskites also hold in the case of strained perovskites, which can be found in perovskite heterostructures. In particular, in the majority of strained perovskite systems one can expect octahedral distortions which, in principle, can also be described by angles $\theta$ and $\phi$ (one has to keep in mind, however, that in some cases more angles for strained structures may be needed). Similarly, one should expect that in the strained perovskite systems, bond lengths will not be isotropic like in the cubic case.

2.2 Glazer notation

The angles $\theta$ and $\phi$, which are mentioned in the previous section, can be used only for some specific perovskite systems, e.g. for $Pbnm$-distorted structures. At the same time, most perovskite systems exhibit crystal structures with tilted octahedra. In order to group perovskite systems in a methodical way, a special notation was created, the so-called Glazer
Figure 2.3: Angles $\theta$, $\phi$ which are commonly used to describe octahedral tilts in $Pbnm$ perovskites [11]. $\theta$ describes rotations of octahedra in the $ab$ plane and $\phi$ describes octahedral tilts along the $c$ axis.

notation [15],[16].

In order to classify a tilted system according to Glazer notation one has to determine the rotations of octahedra around all pseudo-cubic axes [11]. The pseudo-cubic axes are presented in figure 2.4. The general formula is $a^\# b^\# c^\#$, where $a$, $b$, $c$ specify the rotations around each pseudo-cubic axis: $a$ around $x$, $b$ around $y$, $c$ around $z$. Superscripts indicate whether in the given direction adjacent octahedra rotate in phase or out-of-phase. “+” indicates that adjacent octahedra rotate in phase and “−” that they rotate out-of-phase. If two letters in the Glazer notation are the same, then the magnitude of the corresponding octahedral rotations, regardless of whether they are in- or out-of-phase, is the same. Each Glazer tilt system can be linked to a specific space group. For example SrVO$_3$, with $Pm\bar{3}m$ space group symmetry, corresponds to the $a^\circ a^\circ a^\circ$ Glazer system and LaTiO$_3$, with $Pbnm$ space group symmetry, to the $a^+b^-b^-$ Glazer system. Because of their connectivity the octahedra cannot rotate in all directions without any restrictions, therefore there exist 23 tilt systems which belong to 15 unique space groups [17].
2.3 LaTiO$_3$ and SrVO$_3$

Within this project two specific $d^1$ perovskites LaTiO$_3$ and SrVO$_3$ are investigated. Both LaTiO$_3$ and SrVO$_3$ are extensively described in the literature [23], [24], [25], [26], [27], [12]. Synthesis and examinations of their electronic properties in their bulk forms as well as in thin films are well documented. The corresponding bulk systems have also been studied theoretically using the DFT+DMFT method (see in particular Ref. [13]).

As already mentioned, bulk SrVO$_3$ is a perfect cubic perovskite with space group $Pm\bar{3}m$ (Fig. 2.1) and $a^\circ a^\circ a^\circ$ Glazer tilt pattern, all V-O-V angles are equal to 180$^\circ$, i.e the system is without tilts. It is therefore enough to consider only one formula unit of SrVO$_3$ in the unit cell to properly describe the system. The Goldschmidt tolerance factor for SrVO$_3$ is 1.02, which is consistent with the fact that it is a cubic perovskite [33], [34]. The Sr cation is located in the cavity created by eight VO$_6$ octahedra. Since the vanadium cation is in the 4-th oxidation state (V$^{4+}$), there is only one $d$ electron ($d^1$). It has been reported that photoemission spectra exhibit a lower Hubbard peak and a quasiparticle peak characteristic for a correlated metal [23], [24], [25]. Due to its simple structure, bulk SrVO$_3$ is an object of numerous theoretical investigations. Its spectral function obtained from local density approximation + DMFT is well documented in reference [13]. As a matter of fact, SrVO$_3$, is very often chosen as a benchmark material to test DMFT implementations [31], [32], because of its simple crystal structure as well as its simple band structure, in which V-$t_{2g}$ bands are well separated from other bands.
Recent technical advances in nano-scale synthesis have made it possible to also investigate thin films of SrVO$_3$, which behave differently than their bulk form [28]. In particular, ultra-thin films of SrVO$_3$ grown on SrTiO$_3$ have been investigated. It has been reported that for thin films of SrVO$_3$ the critical thickness for the Mott metal insulator transition is 2-3 monolayers [29], i.e. SrVO$_3$ becomes insulating if its thickness is reduced to less than 2 monolayers. If it is thicker than 3 monolayers, then it behaves similarly to its bulk form, i.e. it is metallic. This suggests that the effect of reduced dimension plays a crucial role here. Based only on results from the experiment, it is unclear what is the effect of the strain. Within this project we determine whether epitaxial strain may also have an influence on the observed MIT in thin films of SrVO$_3$. Recently it has also been reported that thin films of SrVO$_3$ grown by hybrid molecular beam epitaxy are excellent electrode materials, because they display low resistivity and superior chemical stability at room temperature [30].

Bulk LaTiO$_3$ is also a well documented system. Analyses of its crystal and magnetic structure are presented in [12]. The crystal structure of LaTiO$_3$ differs somewhat from the crystal structure of SrVO$_3$. The presence of octahedral tilts lowers the symmetry of the LaTiO$_3$ bulk structure to the so-called GdFeO$_3$-type structure with an $a^+b^-b^-$ octahedral tilt pattern (Fig. 2.2). In LaTiO$_3$, the minimal unit cell contains four formula unit. LaTiO$_3$ is a G-type antiferromagnet below $T_N = 146K$. Moreover, it is also believed to be a Mott insulator above $T_N$, due to the strongly correlated $d$ electrons on the Ti atoms [13].

Even though LaTiO$_3$ in its bulk state is insulating, when LaTiO$_3$ is grown on a SrTiO$_3$ substrate the thin film becomes metallic. In contrast, when LaTiO$_3$ is grown on DyScO$_3$ or GdScO$_3$ substrates, its films are insulating [35]. It has also been reported that systems which are built from alternating layers of LaTiO$_3$ and SrTiO$_3$ (superlattices of LaTiO$_3$ and SrTiO$_3$) are metallic [37], even though SrTiO$_3$ in its bulk state is also insulating. In fact, since the titanium atom is in its 4th oxidation state, Ti$^{4+}$ with zero $d$ electrons, SrTiO$_3$ is a band insulator. Several possible factors responsible for this phenomenon have been suggested. First, the Ti atoms in the LaTiO$_3$ film and in the substrate SrTiO$_3$ have different oxidation states, which may lead to charge transfer between layers (interface effect). As a matter of fact in [38], the observation of a two-dimensional electron gas at the LaTiO$_3$/SrTiO$_3$ interface, is mentioned as a main factor responsible for the MIT. Second, the perovskite structure, when grown on the substrate experiences a mismatch between the lattice constants of
the thin film and the lattice constants of the substrate. The thin film increases its elastic energy by adjusting its lattice constants to the those of the substrate. This additional energy gain is partially compensated by the chemical bonding of the atoms at the interface. Modifications of structure in the thin film in comparison to its bulk state may play a crucial role in the observed metallicity. In reference [35], the importance of epitaxial strain is mentioned. In particular, metallicity of LaTiO$_3$ grown on SrTiO$_3$ in the case of thin LaTiO$_3$ film with thickness varied from 15 nm to 45 nm, has been observed [35]. Moreover, in reference [35] measurements for the following layered system: LaTiO$_3$ 17 nm/EuTiO$_3$ 10 nm/SrTiO$_3$, are also reported. Despite presence of a buffering layer of EuTiO$_3$, which prevents diffusion of Ti ions at the film/substrate interface, the thin film of LaTiO$_3$ is still metallic. This suggests a strong contribution of epitaxial strain to the observed metallic properties. Lastly, even though thin films are grown with extraordinary quality, defects still occur (they can be induced by strain) and they may have a considerable contribution to the conducting properties of the whole system. Actually a considerable influence of defects on the electronic properties has already been observed for some heterostructures [39], [40]. From all considered factors, the effect of epitaxial strain seems to be quite intriguing, yet it is often considered in combination with other factors but very rarely as a separate factor in the analysis. Therefore, within this project the effect of epitaxial strain on the electronic properties of LaTiO$_3$ is studied in detail.

A theoretical investigation of structural and electronic properties of bulk LaTiO$_3$ using the LDA+DMFT approach has been presented in [13]. It has been shown how the electronic properties changes across the series: SrVO$_3$ – CaVO$_3$ – LaTiO$_3$ – YTiO$_3$, which exhibit increasing amplitude of octahedral tilts in the given order. The tolerance factor from Eq. (2.1) decreases by about 10 % across the series, although it is almost the same for LaTiO$_3$ and CaVO$_3$ [13]. Since the radii satisfy $R_{Sr^{2+}} \simeq R_{La^{3+}} > R_{Ca^{2+}} \simeq R_{Y^{3+}}$ and $R_{V^{4+}} < R_{Ti^{4+}}$, it can be concluded that the radii of the A cations decreases in relation to the size of the BO$_6$ octahedron across the series. It has been reported that the larger the tilts the lower the TM-O-TM bond angle and so the lower hopping amplitudes between neighbouring TM atoms [13]. As a result, while CaVO$_3$ is still metallic, LaTiO$_3$ and YTiO$_3$ are already Mott insulators.

In addition to the DFT+DMFT investigation of LaTiO$_3$ in the bulk form, theoretical investigations of LaTiO$_3$ with applied epitaxial strain in thin films as well as in superlattices have also been published. Thereby,
different authors have used different methods to model the LaTiO$_3$/SrTiO$_3$ systems. DFT+U is quite often used as a main tool for the analysis [42]. In particular, the magnetic properties of LaTiO$_3$/SrTiO$_3$ heterostructures have been studied by means of DFT+U [42]. Large ferroelectric-like distortions of the TiO$_6$ octahedra are reported from investigations in which DFT+U together with model Hamiltonians are used [43]. Density functional perturbation theory has also been used to explore the LaTiO$_3$/SrTiO$_3$ systems. In particular, the lattice polarization has been analysed in Ref. [45]. Studies by means of model Hamiltonians are also reported [46]. More general studies of heterostructures by means of model Hamiltonians are presented in [47].

The more sophisticated DFT+DMFT approach has also been used. First of all, DMFT calculations have been performed to study a generalised model of Mott-insulator band-insulator heterostructures [48]. Moreover, the impact of defects on LaTiO$_3$/SrTiO$_3$-like heterostructures have also been studied [44].

Both interface and strain effects are studied in [49]. Not only heterostructures are considered there, but also both structural and electronic conditions which can drive the Mott insulator-metal transition. Bulk orthorhombic LaTiO$_3$, is compared against tetragonal LaTiO$_3$ in the corresponding thin films. It is argued that both interface effects between LaTiO$_3$ and SrTiO$_3$ (where Ti atom has formally 0.5 electron on $d$ states) as well as the hypothetical tetragonal symmetry of strained LaTiO$_3$ (no octahedral distortions) in the thin film are responsible for the metallicity of LaTiO$_3$/SrTiO$_3$ superlattices. Furthermore, it is reported that enforcing the tetragonal symmetry on bulk LaTiO$_3$ is enough to invoke metallicity in its thin film form. However, in these calculations the assumption is made that there are only ideal tetragonal distortions without any tilting of the oxygen octahedra, in LaTiO$_3$ heterostructure. This is quite a big simplification and according to the results presented in Ref. [13] this seems to be too crude approximation. In more realistic calculations one should consider the correct orthorhombic or monoclinic symmetry of strained LaTiO$_3$. Therefore, in the present project DFT+DMFT calculations are performed for strained LaTiO$_3$ in which octahedral tilts are taken into account.

An even more advanced description of LaTiO$_3$/SrTiO$_3$ superlattices is presented in [50]. Full charge self-consistent DFT+DMFT computations for several coherent superlattices of LaTiO$_3$/SrTiO$_3$ with different thicknesses are described in that paper. Moreover, octahedral tilts in LaTiO$_3$ are taken into account. Even though [50] uses more sophisticated methods
than the earlier investigation in [49], it mainly focusses on the transition of the Ti oxidation states which occurs across the LaTiO$_3$/SrTiO$_3$ interface. Actually, flow of the charge from Ti in LaTiO$_3$ to Ti in SrTiO$_3$ is postulated as the dominating reason for metallicity in LaTiO$_3$/SrTiO$_3$ heterostructures by Lechermann and co-workers [50]. In reality, even for the ideal case, where no defects are incorporated into the heterostructure, two potential reasons for metallicity are always present: the interface between the film/substrate system and epitaxial strain, which the thin film experiences while grown on the substrate. The effect of epitaxial strain on LaTiO$_3$ is included in the calculations of Ref. [50], but no analysis of its contribution to the observed metallicity is presented. In contrast, within this project epitaxial strain is the only factor included in the calculations. One can therefore, say that both Ref. [50] and the present project are complementary when it comes to which factors are taken into account, and combined they should give a full picture of what happens if LaTiO$_3$ is grown on SrTiO$_3$. Furthermore, the work from Ref. [50] and this project can not only help to better understand LaTiO$_3$/SrTiO$_3$ heterostructures but also contribute to better insight into electronic properties of heterostructures at room temperature in general.
Chapter 3

Computational methods used in this work

3.1 Density functional theory

3.1.1 Theorems of Hohenberg and Kohn

Within the Born-Oppenheimer Approximation (fixed nuclear positions) any problem of electrons and nuclei interacting via the Coulomb interaction can be described by the Hamiltonian $H$:

$$ H = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_i V_{\text{ext}}(r_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|R_I - R_J|} \quad (3.1) $$

$$ V_{\text{ext}}(r_i) = -\sum_J \frac{Z_J e^2}{|R_J - r_i|} \quad (3.2) $$

where:
- $m_e$ – mass of an electron,
- $r_i$ – coordinate of i-th electron,
- $R_I$ – coordinate of I-th nucleus,
- $Z_I$ – atomic number of I-th nucleus,
- $V_{\text{ext}}$ – external potential, which describes the interaction between electrons and nuclei (external fields can in principle, also be included into $V_{\text{ext}}$).

A possible way to deal with such a problem is offered by Density Functional Theory (DFT), which is based on the two Hohenberg-Kohn theorems [51].

Theorem I

For any system of interacting particles in an external potential $V_{\text{ext}}(r)$, the potential $V_{\text{ext}}(r)$ is determined uniquely, except for a constant, by the ground state particle density $n_0(r)$. 
Proof:

Let’s suppose $V_{\text{ext}}$ is not uniquely determined by $n_0(r)$, then we have two or more external potentials which correspond to the same ground state density: $E_0 = \langle \Phi | \hat{H} | \Phi \rangle$, $E'_0 = \langle \Phi' | \hat{H}' | \Phi' \rangle$. According to Rayleigh-Ritz’s variational principle we have:

$$E_0 < \langle \Phi' | \hat{H} | \Phi' \rangle = \langle \Phi' | \hat{H}' | \Phi' \rangle + \langle \Phi' | \hat{H} - \hat{H}' | \Phi' \rangle =$$

$$E'_0 + \int n(r)[V_{\text{ext}} - V'_{\text{ext}}] dr.$$  \hspace{1cm} (3.3)

Using the same arguments we have:

$$E'_0 < \langle \Phi | \hat{H} | \Phi \rangle = \langle \Phi | \hat{H}' | \Phi \rangle + \langle \Phi | \hat{H} - \hat{H}' | \Phi \rangle =$$

$$E_0 - \int n(r)[V_{\text{ext}} - V'_{\text{ext}}] dr.$$ \hspace{1cm} (3.4)

If we add Eq. (3.3) and (3.4) we get $E_0 + E'_0 < E'_0 + E_0$ which is never fulfilled. Therefore, there cannot be $V_{\text{ext}} \neq V'_{\text{ext}}$ that correspond to the same electronic density for the ground state, unless they differ by a trivial additive constant.

**Theorem II**

A universal functional for the energy $E[n(r)]$ in terms of the density $n(r)$ can be defined:

$$E[n(r)] = F[n(r)] + \int n(r)V_{\text{ext}} dr,$$ \hspace{1cm} (3.5)

with

$$F[n(r)] = \langle \Phi[n(r)] | \hat{T} + \hat{U}_{ee} | \Phi[n(r)] \rangle.$$ \hspace{1cm} (3.6)

where:

- $\hat{T}$ – operator of kinetic energy,
- $\hat{U}_{ee}$ – electron-electron interaction.

$\Phi[n(r)]$ – ground state function which corresponds to $n(r)$

The density $n(r)$ that minimizes this functional is the exact ground state density $n_0(r)$.

Proof:
\[
\langle \Phi[n]|\hat{H}|\Phi[n]\rangle = F[n(r)] + \int n(r)V_{\text{ext}}d\mathbf{r} = E[n] \quad (3.7)
\]

\[
\geq E[n_0] = E_0 = \langle \Phi[n_0]|\hat{H}|\Phi[n_0]\rangle.
\]

The inequality follows from the Rayleigh-Ritz variational principle for the wave function, but applied to the electronic density.

According to the first theorem, the knowledge of the ground state density is in principle sufficient, to fully determine the system. The second theorem presents a way to obtain this ground state density.

### 3.1.2 Kohn-Sham equations

The Hohenberg-Kohn theorems rigorously prove that the density can be used as the basic variable in calculating properties of the system, but does not give a framework for doing so. Practical implementations of DFT are based on the Kohn-Sham ansatz [53].

According to this approach the many-body system is mapped onto a fictitious non-interacting system of electrons in an effective potential \(V_{\text{eff}}\). The potential \(V_{\text{eff}}\) is defined such that the ground state density of the original system \(n_0(r)\) is equal to that of the chosen non-interacting system \(n_{KS}(r)\) (KS stands for Kohn-Sham). The Hohenberg-Kohn theorems tell us that the total energy for the interacting system can be written:

\[
E[n] = T[n] + U_{ee}[n] + \int V_{\text{ext}}(\mathbf{r})n(\mathbf{r})d^3r + E_{N-N}, \quad (3.8)
\]

where:

- \(T[n]\) – interacting kinetic energy,
- \(U_{ee}[n]\) – Coulombic potential for the interacting system,
- \(V_{\text{ext}}(\mathbf{r})\) – external potential,
- \(E_{N-N}\) – nuclear-nuclear interaction (the Born-Oppenheimer approximation is used, so the nuclear kinetic contribution to the energy can be neglected.)

As was mentioned before, within the Kohn-Sham framework we assume the single particle system and the interacting system to have the same
density. So we can rewrite the equation for the total energy $E[n]$ in the following way:

$$E[n^{KS}] = T_s[n^{KS}] + E_H[n^{KS}] + T[n^{KS}]$$  \hspace{1cm} (3.9)

with the exchange-correlation energy $E_{xc}$ defined as:

$$E_{xc} = T[n^{KS}] - T_s[n^{KS}] + U_{ee}[n^{KS}] - E_H[n^{KS}]$$  \hspace{1cm} (3.10)

where:

$T_s$ – kinetic energy of the non-interacting auxiliary system.

Remarkably, $E_{xc}$ is a universal functional. It does not depend on the external potential. Unfortunately, the exact form of the exchange-correlation energy is not known. The most common approximations will be described further in Sec. 3.1.3. The kinetic energy difference $T[n^{KS}] - T_s[n^{KS}]$ is the kinetic contribution to correlation. The difference $V[n^{KS}] - E_H[n^{KS}]$ is the electrostatic contribution to correlation and exchange.

The Hartree energy $E_H[n^{KS}]$ is the classical electrostatic energy for a charge distribution $n(r)$:

$$E_H[n^{KS}] = \frac{1}{2} \int \int n^{KS}(r)n^{KS}(r') \frac{d^3r \cdot d^3r'}{|r - r'|}.$$  \hspace{1cm} (3.11)

The non-interacting energy $T_s$ is defined from the single particle wavefunctions $\{\psi_i^{KS}\}$ (also-called Kohn-Sham states):

$$T_s[n^{KS}] = \sum_{i,occ} \frac{1}{2} \int \psi_i^{KS} \nabla^2 \psi_i^{KS} d^3r.$$  \hspace{1cm} (3.12)

In practice, however, $T_s$ is calculated as a sum of all occupied KS eigenvalues minus the potential energy which corresponds to the effective KS potential $V_{eff}$. Within the auxiliary system, the electron density $n^{KS}$ is linked to the Kohn-Sham states by the following relation:

$$n^{KS} = \sum_{i} |\psi_i(r)|^2.$$  \hspace{1cm} (3.13)

where:
occ – indicates summation over all occupied orbitals; N electrons occupy the N states with the lowest energies.

The total number of electrons N in the auxiliary system can be obtained by the spatial integration over the electron density of the auxiliary system:

\[
N = \int n(r) d^3r.
\]  

(3.14)

In practice, the chemical composition of the system of interest is known. Therefore, the value of N is also known.

In order to use the Kohn-Sham framework one has to formulate a procedure for evaluating the total energy and the single particle wavefunctions. To do so we have to add constraints on the total number of particles (parameter \(\mu\)) and orthonormality of the wavefunctions \((\varepsilon_{ij})\). Then one has to minimise the following functional F:

\[
F = E - \mu N - \sum_{ij} \varepsilon_{ij} \langle \psi_i^{KS} | \psi_j^{KS} \rangle - \delta_{ij}
\]

(3.15)

with respect to \(\psi_i^{KS}(r)\). This yields:

\[
\frac{\delta E - \mu N}{\delta \psi_i^{KS}(r)} = \frac{\delta T_i[n]}{\delta \psi_i^{KS}(r)} + V_{\text{eff}}(r) \psi_i^{KS}(r) - \mu \psi_i^{KS}(r) - \sum_j \varepsilon_{ij} \psi_j^{KS}(r) = 0.
\]

(3.16)

With \(V_{\text{eff}}(r)\):

\[
V_{\text{eff}}(r) = e^2 \int \frac{n(r')}{|r - r'|} d^3r' + V_{xc}(r) + V_{\text{ext}}(r).
\]

(3.17)

where:

\(V_{xc}\) – exchange correlation potential (more about \(V_{xc}\) in Sec. 3.1.3).

In any practical application, one expands \(\psi^{KS}\) in basis functions. The choice of basis usually depends on the system of interest. If one wants to perform a calculation for isolated molecules (gas phase), one usually uses a basis with localised functions in which every vector of the basis is constructed from a polynomial multiplied by a Gaussian function [54]. In solid state physics, plane waves are often used. Within this project, plane waves are used in all calculations. The plane wave basis is described in more detail in Sec. 3.1.4

The density is then calculated through an iterative procedure:

1) Start with an initial guess for \(n^{KS}(r)\).
2) Calculate $V_{\text{eff}}[r, n^{KS}(r)]$:

$$V_{\text{eff}}[r, n^{KS}(r)] = V_{\text{ext}}[r] + V_{H}[n^{KS}(r)] + V_{xc}[n^{KS}(r)], \quad (3.18)$$

where:

$$V_{H}[n^{KS}(r)] = e^2 \int d^3 r' n^{KS}(r') \frac{1}{|r-r'|} \text{ (Hartree potential)}.$$  

3) Solve the set of Kohn-Sham one particle equations:

$$\left( - \frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}}[n^{KS}(r)] \right) \psi_j^{KS}(r) = \epsilon_j \psi_j^{KS}(r), \quad (3.19)$$

where:

$\psi_j^{KS}$ – one particle Kohn-Sham wave function which describes an electron in the j-th state of the fictitious system, $\epsilon_j$ – energy corresponding to $\psi_j^{KS}$. $\psi_j^{KS}$ is normalized:

$$\langle \psi_i^{KS} | \psi_j^{KS} \rangle = \delta_{ij}. \quad (3.20)$$

4) Calculate new $n^{KS}(r)$:

$$n^{KS}(r) = \sum_{j, \text{occ}}^N |\psi_j^{KS}(r)|^2. \quad (3.21)$$

5) Check whether new $n^{KS}(r)$ is equal (within some tolerance) to the one from the previous step. If this is not fulfilled return to point 2), otherwise calculate the required properties.

This scheme is usually applied for fixed positions of the nuclei. The optimal positions of the nuclei can then be found by minimization of the total energy of the system with respect to the nuclear coordinates.

In order to extend Kohn-Sham theory to spin-polarized systems it is sufficient to consider the electronic density as composed by two independent spin densities $n^{\uparrow}, n^{\downarrow}$, such that:

$$n = n^{\uparrow} + n^{\downarrow} \quad (3.22)$$

Each of these densities have its own self-consistent Kohn-Sham equations:

$$\left( - \frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}}[n^{KS\uparrow}, n^{KS\downarrow}(r)] \right) \psi_j^{KS\{\uparrow, \downarrow\}}(r) = \epsilon_j^{\{\uparrow, \downarrow\}} \psi_j^{KS\{\uparrow, \down\}}(r). \quad (3.23)$$
Even though each spin-density has its own KS equation, both of them are related to the same system and therefore they are coupled (during calculations a number of all electrons in a system is fixed).

The only input information required by DFT are the types and initial positions of the nuclei and N given by the neutrality condition. As seen, DFT is a "first principles" method. The following quantities (and many others) can be calculated:

- \( n_0 \) – ground state electron density
- \( E_{\text{tot}} \) – total energy of the ground state
- \( d(\epsilon) \) – density of states (DOS) which is defined in the following way:
  \[
  d(\epsilon) = \sum_j \delta(\epsilon - \epsilon_j). \tag{3.24}
  \]

### 3.1.3 Exchange-correlation potential

#### Local density approximation

DFT is in principle, exact, however, an exact expression for \( V_{xc} \) is not known. The most successful approximation is the Local Density Approximation (LDA) \[51, 53\]. In LDA the exchange-correlation energy in each point is taken as the exchange-correlation energy per electron from a uniform electron gas with a density equal to the density of the system in the same point and multiplied by this density:

\[
E_{xc}^{\text{LDA}}[n(r)] = \int d^3 \mathbf{r} \ n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r}))
\]

\[
V_{xc}^{\text{LDA}}[n(r)] = \frac{\delta [E_{xc}^{\text{LDA}}[n(\mathbf{r})]]}{\delta [n(\mathbf{r})]}, \tag{3.25}
\]

where:

\( \epsilon_{xc}(n(\mathbf{r})) \) – exchange-correlation energy density of a homogeneous electron gas with density \( n(\mathbf{r}) \).

Within LDA, exchange contribution to the energy can be calculated analytically \[53\]:

\[
E_x^{\text{LDA}}[n] = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int n(\mathbf{r})^{4/3} \, d\mathbf{r}. \tag{3.26}
\]

The correlation contribution has to be approximated. In order to obtain an approximate relation for \( E_c[n] \), a proper fitting has to be done to Monte
Carlo results for the homogeneous electron gas. Most of the modern functionals in use are based on Monte Carlo data published by Ceperley and Alder [55]. Commonly used LDA correlation functionals are Vosko-Wilk-Nusair [56], M. Teter-Pade [57], and Perdew-Zunger [58]. Since these fits are all based on the Ceperley-Alder data, there are only minor variations between them.

Several trends within LDA have been reported [59]. LDA favours electronic densities that are more homogeneous than the exact ones. It usually describes metallic systems correctly but gives an insufficient description for insulators or even correlated metals. In general, LDA tends to underestimate bond lengths.

**General gradient approximation**

The LDA can be extended to the Generalized Gradient Approximation (GGA) to include effects of (weak) spatial variations of the density [60]. In this method the energy density from Eq. (3.25) is replaced by a generalized expression that depends on both \( n(r) \) and \( \nabla n(r) \).

\[
E_{XC}^{GGA}[n] = \int n(r)\varepsilon_x(r)F_{xc}(n(r), \nabla n) d^3r, \tag{3.27}
\]

where:

\( F_{xc}(n(r), \nabla n) \) – is a complicated function of \( n \) and \( \nabla n \). Its exact form depends on which variant of GGA is used.

Common GGA functionals are Perdew-Wang92 [61] and Perdew-Burke-Ernzerhof (PBE) [62]. There exist several variations on PBE, such as revPBE [63] and PBEsol [64], which are obtained by changing the formula used in PBE. Modifications of PBE are based on data obtained from Monte Carlo simulations.

Usually GGA performs slightly better than LDA. Especially, it describes bond lengths better. However, sometimes it can overestimate bond lengths [59].

### 3.1.4 Plane wave basis

In the current project, only calculations for periodic systems are performed. In such calculations the Kohn-Sham orbitals become Bloch states:

\[
\psi_{nk}^{KS}(r) = \exp(i\mathbf{k}\mathbf{r})u_{nk}(\mathbf{r}), \tag{3.28}
\]
\[ u_{nk}(r + T_{l_1l_2l_3}) = u_{nk}(r), \]  
\[ T_{l_1l_2l_3} = l_1 \cdot a_1 + l_2 \cdot a_2 + l_3 \cdot a_3 \]  
(3.29)  
(3.30)

where: \( a_1, a_2, a_3 \) – primitive lattice vectors, \( l_1, l_2, l_3 \) – integer numbers, \( k \in \text{FBZ} \). FBZ stands for the First Brillouin Zone.

The set of \( \psi_{nk}^{KS}(r) \) is labelled by a band index \( n \) and the Bloch wave vector \( k \). In practice \( \psi_{nk}^{KS}(r) \) is expanded in a basis, which can be chosen according to a number of factors, such as accuracy, simplicity, and efficiency. In all calculations within this project, the KS orbitals are represented in a plane wave basis:

\[ u_{nk}(r) = \sum_{b_1b_2b_3} c_{nk}(G_{b_1b_2b_3}) \exp(iG_{b_1b_2b_3}r), \]  
(3.31)

\[ \psi_{nk}^{KS}(r) = \exp(ikr) \sum_{b_1b_2b_3} c_{nk}(G_{b_1b_2b_3}) \exp(iG_{b_1b_2b_3}r) \]  
\[ = \sum_{b_1b_2b_3} c_{nk}(G_{b_1b_2b_3}) \exp[i(k + G_{b_1b_2b_3})r], \]  
(3.32)

where:

\( k \in \text{FBZ} \), \( c_{nk}(G_{b_1b_2b_3}) \) – expansion coefficient, \( G_{b_1b_2b_3} \) is a reciprocal lattice vector: \( G_{b_1b_2b_3} = b_1 \cdot k_1 + b_2 \cdot k_2 + b_3 \cdot k_3 \), \( k_1, k_2, k_3 \) – primitive vectors of the reciprocal lattice.

The plane wave basis automatically fulfils the periodicity condition of electronic states in a crystalline solid. For a practical implementation, we use finite size of the basis. The size of the basis is controlled by the plane wave energy cutoff \( (E_{\text{cut}}) \):

\[ \frac{\hbar^2}{2m_e} |k + G_{b_1b_2b_3}|^2 \leq E_{\text{cut}}. \]  
(3.33)

### 3.1.5 Pseudopotential methods

Not every electron in the system contributes in the same way to its properties. Electrons which occupy energy levels close to the Fermi level – valence electrons – play a more important role than those occupying energy levels much lower than the Fermi level – core electrons. Core states are highly localized and not involved in chemical bonding, whereas valence states are extended and responsible for chemical bonding. At the same time, the corresponding wave functions oscillate very intensively in the vicinity of the
nuclei. Due to these oscillations, it is very challenging to describe electron states properly, since it requires a plane wave basis with a large kinetic energy cutoff and results in very CPU-power demanding calculations. One has to consider simplifications in the treatment of electrons in the vicinity of the nuclei. First one has to define a simplified treatment for core electrons. Luckily, from all-electron calculations it can be seen that the behaviour of core electrons for a specific element (La, Ti etc.) changes very little for different materials. One has to keep in mind, however, that in some cases a distinction between valence and core electrons according to the closed shell rule is too simplified, and one also has to treat higher lying core electrons on the same basis as valence electrons. Such core electrons are often called semicore electrons. They are localized and polarizable, but generally do not contribute directly to chemical bonding.

In order to simplify calculations, core electrons are often removed from the calculations, and the interaction of the valence electrons and semicore electrons with the nucleus plus the core states (including orthogonalization) is replaced by an effective potential, which is called a pseudopotential. Pseudopotentials were first used in the 1930s \[65]\, \[66]\; . Generally, each element is described by a different pseudopotential. In order to construct potentials, a realistic atomic reference configuration should be chosen. While constructing pseudopotentials, two factors are important: softness and transferability. Softness defines how many planewaves (how large cutoff) are needed to obtain accurate results while using a particular pseudopotential. The harder the pseudopotential, the larger basis is needed. Transferability defines how universal a pseudopotential is, i.e. whether a pseudopotential constructed for a specific reference system can be used for the same atomic species but in a different environment. Apart from this, a pseudopotential has to fulfil several other criteria. First of all, the pseudopotential is constructed in such a way that the pseudowavefunctions match the all-electron wavefunctions beyond the matching radius \(r_c\):

\[
\psi_{l}^{PS}(r, \epsilon) = \psi_{l}^{AE}(r, \epsilon) \quad \text{for} \quad r > r_c, \tag{3.34}
\]

where:

\[
\psi_{l}^{AE}(r, \epsilon) - \text{radial part of the atomic valence function with angular momentum } l \text{ at energy } \epsilon, \text{ which fulfils the radial Schrödinger equation:}
\]

\[
\left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_{ext}(r) \right\} r\psi_{l}^{AE}(r, \epsilon) = \epsilon r\psi_{l}^{AE}(r, \epsilon), \tag{3.35}
\]

\[24\]
\[ \psi^P_{l}(r, \epsilon) - \text{radial part of the pseudofunction with angular momentum } l, \text{ which is a solution of the Schrödinger equation with a pseudopotential:} \]

\[
\left\{-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_{ps}(r, l) \right\} r\psi^P_{l}(r, \epsilon) = \epsilon r\psi^P_{l}(r, \epsilon). \tag{3.36}
\]

The criterion described above is based on the observation that a good description of the valence wave functions inside of the core region is not strictly necessary. One doesn’t lose any crucial information if the inner solution (inside some cutoff radius) is replaced with a smooth nodeless pseudo-wave function, which is not a solution of the original atomic problem. Once \( \epsilon \) has been fixed (not necessarily to an eigenvalue), solution of the Schrödinger equation with a pseudopotential is uniquely determined by the value of the wave function \( \psi^P_{l}(r, \epsilon) \) and its derivative at any given point \( r_0 \). In practice, these two conditions are formulated in the form of the radial logarithmic derivative and \( r_c \):

\[
\left[ \frac{d}{dr} \ln \psi^AE_{l}(r, \epsilon) \right]_{r_c} = \frac{1}{\psi^AE_{l}(r_c, \epsilon)} \left[ \frac{d\psi^AE_{l}(r, \epsilon)}{dr} \right]_{r_c}, \tag{3.37}
\]

\[
\frac{1}{\psi^PS_{l}(r_c, \epsilon)} \left[ \frac{d\psi^PS_{l}(r, \epsilon)}{dr} \right]_{r_c}.
\]

Another criterion, which is usually used in the construction of pseudopotentials is based on norm preservation:

\[
\int_0^{r_c} r^2 \left[ \psi^AE_{l}(r, \epsilon) \right]^2 dr = \int_0^{r_c} r^2 \left[ \psi^PS_{l}(r, \epsilon) \right]^2 dr. \tag{3.38}
\]

This property is called a norm-conservation. It was first introduced by Hamann, Schlüter, and Chiang (1979) [67]. This criterion was derived from the Friedel sum rule [68], [69]. The norm conserving criterion can be presented as:

\[
-\frac{1}{2} \left\{ \left[ r\psi^AE_{l}(r, \epsilon) \right]^2 \frac{d}{d\epsilon} \frac{d}{dr} \ln \psi^AE_{l}(r, \epsilon) \right\}_{r_c} = \tag{3.39}
\]

\[
-\frac{1}{2} \left\{ \left[ r\psi^PS_{l}(r, \epsilon) \right]^2 \frac{d}{d\epsilon} \frac{d}{dr} \ln \psi^PS_{l}(r, \epsilon) \right\}_{r_c} = \int_0^{r_c} r^2 \left[ \psi^PS_{l}(r, \epsilon) \right]^2 dr.
\]

Based on Eq. (3.39) it can be concluded that the norm-conservation condition imposes that the logarithmic derivatives of the all-electron and the pseudo wavefunctions vary in the same way to the first order in the energy. It means that a small change in the energy, due to changes in the
external potential, produces only a second-order change in the logarithmic
derivative. Therefore, once $\epsilon$ is set for some reference structure (it is then
called the reference energy) $\psi^{AE} \simeq \psi^{PS}$ in a range of energies around the
reference energy. This criterion makes it possible to derive pseudopotentials from atomic reference structures and then use them for the system
in which this atom is part of a molecule or a solid. As a matter of fact, the
condition that, the energies of the pseudo-wave functions coincide with
those of the all-electron wave functions for a chosen electronic configuration
of the atom, was proposed by Hamann, Schlüter, and Chiang as one of the
conditions which should be fulfilled while constructing a norm-conserving pseudopotential. Norm-conservation is a crucial condition if one aims for
highly transferable pseudopotentials. However, the transferability is lim-
ited to systems which are similar to the reference atomic structure. In the
case of norm-conserving pseudopotentials, one can improve the transfer-
ability by reducing the radius $r_e$. This, however, has to be compensated by
an increase of the required kinetic energy cutoff. Pseudopotentials which
fulfil the norm-conservation condition are called norm-conserving pseu-
dopotentials. Since they don’t depend on empirical parameters they are
ab-initio pseudopotentials.

The norm-conservation is crucial for the transferability of the pseudopot-
tentials. However, such potentials are relatively hard. They require a rel-
atively large plane wave cutoff to obtain accurate results. In this project, ultrasoft pseudopotentials, invented by Vanderbilt, are used [70], which are
a generalisation of norm-conserving pseudopotentials, and require a smaller
plane wave basis (are softer). Vanderbilt obtained smoother pseudopoten-
tials by a redefinition of the condition from Eq. (3.39). In Vanderbilt’s
construction of pseudopotentials the first step is to decompose a pseudo-
potential into a local part $V_{loc}^{\text{ion}}(r)$ and a non-local part $V_{NL}$ (in principle, norm-conserving pseudopotentials can also be decomposed this way):

$$V^{Van} = V_{loc}^{\text{ion}}(r) + V_{NL}. \quad (3.40)$$

The non-local part has the following form:

$$V_{NL} = \sum_{nm} D_{nm}^{(0)} |\beta_n\rangle \langle \beta_m|. \quad (3.41)$$

Other quantities that are also used in the construction are:

$$D_{nm} = D_{nm}^{(0)} + \int d\mathbf{r} V_{eff}(\mathbf{r}) Q_{nm}(\mathbf{r}) \quad (3.42)$$

$$Q_{nm} = \psi_n^{AE*}(r, \epsilon) \psi_m^{AE}(r, \epsilon) - \psi_n^{PS*}(r, \epsilon) \psi_m^{PS}(r, \epsilon) \quad (3.43)$$
$D_{nm}^{(0)}$ characterise the pseudopotential and differ for different atomic species. These quantities have to be provided at the beginning of the calculations. The $\beta_m$ functions form a set of orthogonal basis functions which vanish outside $r_c$ and which form the complete basis for $r < r_c$. The matrix $Q$ defines the generalised norm-conserving condition. In the Vanderbilt approach the electron density $n(r)$ is defined as ($\psi^{PS} = \psi^{KS}$; here indices $n, m$ denote orbital states also on the different sites):

$$n(r) = \sum_{ok} \left[ |\psi^{KS}_{ok}(r)|^2 + \sum_{nm} Q_{nm} \langle \psi^{KS}_{ok}| \beta_n \rangle \langle \beta_m | \psi^{KS}_{ok} \rangle \right]. \quad (3.44)$$

In principle, the Vanderbilt pseudopotential is fully defined by means of $\beta, D^{(0)}_{nm}, V^{\text{ion}}, Q_{nm}$. The relaxation of the norm-conserving condition is realised in the following way:

$$\langle \psi^{KS}_{n k} | \hat{S} | \psi^{KS}_{m k} \rangle = \delta_{nm}. \quad (3.45)$$

$\hat{S}$ is the Hermitian overlap operator defined as:

$$\hat{S} = 1 + \sum_{nm} q_{nm} |\beta_n \rangle \langle \beta_m |, \quad (3.46)$$

with $q_{nm}$ as:

$$q_{nm} = \int dr Q_{nm}(r) = \langle \psi^{AE}_n (r, \epsilon) | \psi^{AE}_m (r, \epsilon) \rangle_{r_c} - \langle \psi^{PS}_n (r, \epsilon) | \psi^{PS}_m (r, \epsilon) \rangle_{r_c}. \quad (3.47)$$

The orthogonality from Eq. (3.45) is consistent with the conservation of charge:

$$\int n(r) = N_v, \quad (3.48)$$

where $N_v$ corresponds to all semicore and valence states included in the calculation. After some transformation, the Hamiltonian of the system can be represented in the following way [71]:

$$H = -\nabla^2 + V^{\text{eff}} + \sum_{nm} D_{nm} |\beta_n \rangle \langle \beta_m |, \quad (3.49)$$

The Vanderbilt pseudopotential construction allows to use quite a large $r_c$ and a smaller planewave basis without losing accuracy within the calculations. However, because norm-conservation is relaxed, even if the pseudo-
and all-electron wavefunctions become identical beyond the cutoff radius, the charge enclosed in the pseudized region is different. Nevertheless, as long as the electron density is calculated according to Eq. (3.44) it integrates exactly to the number of valence and semicore electrons in the system.

In general, both norm-conserving or ultrasoft pseudopotentials can be used exchangeably. However, ultrasoft pseudopotentials are more delicate to construct. They also carry additional technical difficulties at the implementation level. Moreover, they introduce a small computational overhead. In principle, ultrasoft and norm-conserving pseudopotentials can be used for different chemical species in the same system. For example, an ultrasoft pseudopotential can be used for O and a norm-conserving pseudopotential for Si in SiO₂. The size of a planewave basis which is used in a calculation is determined by the hardest pseudopotential in use.

Within this project, ultrasoft pseudopotentials with semicore states are used for all systems. Ultrasoft pseudopotentials are taken from the official site of Quantum Espresso [73] (QE). All DFT calculations are performed by means of QE.

3.2 DFT+U

The DFT+U approach was introduced by Anisimov and co-workers in [72], as a modifications of LDA, which combines an ab-initio method with the model Hubbard Hamiltonian, to treat correlated materials. Within DFT+U, the Coulomb interaction $U$ is applied only to so-called correlated states, for which electrons are strongly correlated (more on that in Sec. 3.3.1). It is assumed that non-correlated states are described sufficiently well within DFT.

The DFT+U method modifies the occupations of the correlated states with respect to DFT. DFT+U describes successfully the magnetic ground state of Mott insulators. This is because DFT+U opens a gap, by making a long-range order (magnetic or/and orbital).

In the DFT+U approach the Coulomb interaction is described within the static mean-field theory. This means that the true many-body effects are lost. Nevertheless, DFT+U still provides an enhancement in the description of strongly correlated electrons.

Within DFT+U one uses the Hamiltonian in the following form (sim-
plified version):

\[ H = H^{DFT} + \sum_{im\sigma} t_{im}^\sigma n_{im\sigma}, \text{ with } t_{im}^\sigma = U \left( \frac{1}{2} - \langle n_{im\sigma} \rangle \right). \] (3.50)

The total energy functional, which corresponds to the Hamiltonian above, has the following form:

\[ E_{DFT+U} = E_{DFT} + \sum_i \left[ \frac{1}{2} U \sum_{m\sigma \neq m'\sigma'} \langle n_{ima} \rangle \langle n_{im'\sigma'} \rangle - E_{DC} \right]. \] (3.51)

\( E_{DC} \) is the double counting correction to the total energy. \( E_{DC} \) contains all the correlations effects included already by the DFT term \( (E_{DFT}) \). \( E_{DC} \) has to be subtracted from the total energy to avoid including some correlation effects twice: from DFT and from the Coulomb interaction. More about \( E_{DC} \) is presented in Sec. 3.3.4. One has to keep in mind that in a more general case \( E_{DFT+U} \) has a more complex form [74].

### 3.3 Dynamical mean field theory

Recently, dynamical mean field theory (DMFT) has gained much popularity as a method for studying correlated electron systems. DMFT was developed as a method to numerically solve the Hubbard model. Later it was realised, that it can not only be used for the model calculations, but it can also be combined with various ab-initio methods [52]. In contrast to DFT+U, which is mostly applicable for insulating materials, especially those with a magnetic order, DMFT, combined with the ab-initio method like DFT, can be used for a wide range of materials: from metals to Mott insulators. In the case of the realistic value of the Hubbard Coulomb interaction \( U \) (will be explained later in Sec. 3.3.1), DFT+U usually opens a gap which may not be correct. At the same time for the realistic \( U \), DMFT most often gives a correct description. In particular DFT+DMFT gives a correct description of correlated metals and DFT+U may not.

In DMFT, one starts from the initial guess of the lattice problem given by the system of interest, usually with the lattice self energy set to zero. Then one constructs the corresponding impurity problem (in a general case there can be many impurity problems), and solves lattice and impurity problems self-consistently. In the impurity problem, the electrons interact with an effective bath, or a mean field, of conduction electrons determined by the lattice problem. The self energy from the impurity problem is then
used as an approximation for the self energy of the lattice problem. The impurity problem can be solved by a number of many-body techniques. In this project, the impurity problem is solved using a continuous time Quantum Monte Carlo solver [76].

3.3.1 Formulation of the many-body problem

Lattice problem described by Hubbard Hamiltonian

The problem of interacting electrons within a periodic system is often described using the so-called Hubbard Hamiltonian [77]:

\[
H = \sum_{i,j,n,m,\sigma} t_{ijnm}(c_{i\sigma}^\dagger c_{m\sigma} + c_{m\sigma}^\dagger c_{i\sigma}) + \sum_{pmoni\sigma\sigma'} U_{pmoni}c_{i\sigma}^\dagger c_{m\sigma'}^\dagger c_{n\sigma} c_{o\sigma}', \quad (3.52)
\]

where:

- \( t_{ijnm} \) – hopping amplitude between orbitals \( n \) and \( m \) located at sites \( i \) and \( j \),
- \( U_{pmoni} \) – interaction strength between \( n, m, p, o \) orbitals at site \( i \),
- \( c_{i\sigma}^\dagger, c_{i\sigma} \) – creation/annihilation operators for electron at site \( i/j \) and orbital \( n/m \) with spin \( \sigma \).

According to this model, electrons can hop between sites with a probability defined by \( t_{ijnm} \). This process leads to delocalization of electrons and is responsible for chemical bonding. In a perfect metal with non-interacting electrons, this is the only electronic factor responsible for the physical properties. In real materials, there are always some Coulomb interactions present between electrons. In particular, in the case of strongly correlated systems, such interactions have a big impact on the properties of the material. The Hubbard model describes interactions between electrons by means of the matrix \( U \) with elements \( U_{pmoni} \). In general, the elements of the matrix \( U \) are defined as the matrix elements of the Coulomb interaction, but if one limits the description to only a few bands around the Fermi level then the matrix \( U \) includes also implicitly the interaction of the chosen electrons with all other electrons in the system, which are not occupying the considered bands. In this case \( U \) becomes the screened interaction. The parameter \( U \) can be understood as a penalty energy, which electrons experience while being on the same site. If \( U_{pmoni} \) is small in comparison to the parameter \( t_{ijnm} \), electrons can easily move within the whole crystal. If \( U_{pmoni} \) is very large in comparison to \( t_{ijnm} \), the system
resembles a collection of isolated atoms. Then, every site has a certain number of electrons, depending on the specific chemical element on that site. Since in this case moving an electron to the site where all orbitals are already occupied, each by one electron is punished by a very large energy penalty, the system becomes an insulator. This kind of insulator is called a Mott insulator. In contrast to a so-called band insulator which is insulating because of completely filled bands, a Mott insulator occurs for partially filled bands.

In order to use the Hubbard Hamiltonian, one first has to calculate the hopping integrals $t_{ijmn}$ and the Coulomb interaction $U_{lmnoi}$. Within this project, $t_{ijmn}$ are calculated from DFT. Details are presented in Sec. 3.3.2. As it comes to $U$, it can in principle, be calculated from constrained DFT \cite{78}, \cite{79} or \cite{80}. Another approach would be, instead of calculating $U$ from ab-initio, start from a reasonable value of $U$ and perform a series of calculations for different values of $U$. Then the effect of $U$ on the physical properties can be studied in detail. In particular the critical $U$ for the Mott metal-insulator transition can easily be estimated (more on that in Sec. 3.3.5). Within this project the latter approach for $U$ is used, i.e. there has been no need for constrained calculations.

**Green’s function**

The central quantity within DMFT is the interacting imaginary time Green’s function: $G(\tau)$, by means of which the many body problem can be easily formulated. $G(\tau)$ is defined in the following way (spin index has been dropped for the simplicity):

$$G_{ijmn}(\tau_1 - \tau_2) = - \langle T c^\dagger_n(\tau_1) c^i_m(\tau_2) \rangle, \quad (3.53)$$

where:

$T$ – imaginary time ordering operator.

The one particle Green’s function describes the motion of one particle (or hole) between imaginary time Green’s function $\tau_2$ and $\tau_1$ within an interacting system. The Green’s function, which describes the motion of particles in the corresponding non-interacting system is called the non-interacting Green’s function $G^\circ_{ijmn}(\tau_1 - \tau_2)$.

The relation between $G(\tau_1 - \tau_2)$ and $G^\circ(\tau_1 - \tau_2)$ is given by the Dyson equation:

$$[G^\circ]^{-1} = [G]^{-1} + \Sigma, \quad (3.54)$$

where:
$\Sigma$ – self energy.

Both the lattice problem and the impurity problem can be expressed in terms of the Green’s function. In a periodic system we can make the Fourier transformation from the real space into the momentum space. After this transformation $c_n^\dagger(\tau) \rightarrow c_{kn}^\dagger(\tau)$ and $c_m^\dagger(\tau) \rightarrow c_{km}(\tau)$. This means that also the Green’s function is a function of $k$. In DMFT one considers a lattice system as a periodic system in the limit of infinite dimensions (an infinite number of neighbouring sites) \[52\]. In this limit the self energy of the lattice system becomes purely local, i.e it does not depend on $k$ any longer:

$$\Sigma(k) \rightarrow \Sigma. \quad (3.55)$$

In practical calculations DMFT is an approximation, since it is used to calculate properties of three dimensional periodic systems. A detailed definition of the lattice Green’s function will be presented in Sec. 3.3.2.

**Impurity problem solved by continuous time impurity solver**

In DMFT the lattice system is mapped onto one or more Anderson Impurity Models (AIM). In case all lattice sites are equivalent, the lattice problem is mapped only on one impurity problem. The Anderson impurity problem is usually solved in a Quantum Monte Carlo simulation by so-called impurity solver (please note that some impurity solvers use other methods than QMC). Within this project a continuous time Quantum Monte Carlo solver is used \[76\], \[82\]. In the case of a lattice problem, for which not all sites are equivalent, the lattice problem is mapped onto two or more impurity problems. In that case each Anderson impurity problem is solved separately. Once all impurity problems are solved, the lattice Green’s function is reconstructed using the Dyson equation (more on this reconstruction in Sec. 3.3.1).

Each Anderson impurity problem represents an atom or a molecule embedded in a host medium, which is called the bath. This bath has states which can be parametrized by ”momentum” $p$. Electrons can hop between the impurity and the bath via the hybridisation between the impurity and the bath states. The general Hamiltonian for the impurity system is:

$$H = H_{loc} + H_{bath} + H_{hyb}, \quad (3.56)$$

where:
$H_{loc}$ – is the so-called local Hamiltonian. Its particular form depends on the system of interest. In particular, it depends on how many correlated orbitals per site are taken into account. Within this project, only $d^1$ correlated systems which can be described by $t_{2g}$ orbitals are investigated, and the Kanamori Hamiltonian is used. The Kanamori Hamiltonian is only a special case of $H_{loc}$. A more general discussion about $H_{loc}$ is presented in Sec. 3.3.2.

$H_{bath} = \sum_p \varepsilon_p b_p^\dagger b_p$. $b_{p}^\dagger$, $b_{p}$ are creation and annihilation operators for electrons at p-th state in the bath.

$H_{hyb} = \sum_{p,\nu}(c_{\nu} V_{p\nu} b_{p}^\dagger + b_{p} V_{p\nu} c_{\nu}^\dagger)$ $H_{hyb}$ describes hopping between the bath and the impurity, $c_{\nu}^\dagger$ is the creation operator for the electron in level $\nu$ (and $c_{\nu}$ is the annihilation operator for the electron in level $\nu$). States on the impurity are discrete. $V$ is a hybridization matrix and is given by the problem in hand.

Once we define the Hamiltonian for the impurity model, we can also define the partition function $Z$ which corresponds to this Hamiltonian:

$$Z = Tr e^{\beta H}. \tag{3.57}$$

The partition function can be expanded into a series of diagrams. One way is to expand it in powers of the interaction $H_{loc}$, this approach is called the weak-coupling approach [81]. Within the weak-coupling approach one can simulate large clusters in a very efficient way, because it scales favourably with system size. Another possibility is to expand $Z$ in powers of the impurity-bath hybridization [76]. This is called the hybridisation expansion. The hybridisation expansion can handle impurity models like for example the Anderson impurity model with strong interactions. In both types of an expansion, the Hamiltonian is split into two parts, $H = H_1 + H_2$. The partition function $Z$ can be represented as:

$$Z = Tr \left[ e^{-\beta H_1} T e^{-\int_0^\beta d\tau H_2(\tau)} \right], \tag{3.58}$$

where:

$T$ – time ordering operator

$Z$ can be further expanded to:

$$Z = \sum_{n=0}^{\infty} \int_0^\beta d\tau_1 \ldots \int_{\tau_{n-1}}^\beta \text{Tr} \left[ e^{-(\beta-\tau_n)H_1(-H_2)} \ldots e^{-(\tau_2-\tau_1)H_1(-H_2)} e^{-\tau_1 H_1} \right], \tag{3.59}$$
which is of the form of Eq. (3.62).

In the hybridisation expansion, $H$ is decomposed as:

$$H_1 = H - H_2 = H_{\text{loc}} + H_{\text{bath}}, \quad (3.60)$$

$$H_2 = H_{\text{hyb}}. \quad (3.61)$$

When solving the Anderson impurity problem, the partition function $Z$ is calculated. Once one has expanded $Z$ in a series of diagrams, $Z$ can be re-presented as a sum of configurations with weight $w_c$, where each diagram represents one particular configuration:

$$Z = \sum_c w_c. \quad (3.62)$$

In a Quantum Monte Carlo simulation, a random walk in the configuration space $c_1 \to c_2...$ is implemented in such a way that each configuration can be reached from any other in a finite number of steps (ergodicity). Every configuration is visited with a probability proportional to $|w_c|$. In order to avoid the correlations between measurements not every visited configuration is recorded. This is an important strategy to avoid correlations between recorded configurations. Usually every x-th visited configuration is recorded and it is considered a measurement. Number x of skipped configurations is fixed during the simulation. The total number of measurements is called QMC cycles.

Both the Green’s function and the partition function share similar diagrams, so the measurements used to obtain $Z$ can in principle, be also used to evaluate imaginary time $G$. Moreover, the imaginary time Green’s function can be expressed as:

$$G_{ijnm}(\tau) = -\langle T c_i^\dagger(\tau)c_m^\dagger(0) \rangle = -\frac{1}{Z} Tr \left[ e^{-\beta H} c_i^\dagger e^{-\tau H} c_m^\dagger \right]. \quad (3.63)$$

The interacting Green’s functions $G(\tau)$ from the impurity solver are used to construct the self consistency cycle in DMFT (please look at other paragraphs of Sec. 3.3.1 for more details about the self consistency cycle).

When calculating $G$ by the impurity solver, one has to make sure that calculations are accurate enough. The main parameter to improve the quality of the results is the number of measurements during the Quantum Monte Carlo simulation. Additionally, there are various techniques to improve accuracy. First of all, in order to speed up calculations and improve their stability, one can use the conservation of various quantum numbers,
such as the particle number, the total spin, and the total momentum \[83]. In general, the accuracy of the results for a given amount of time depends also on whether the system is metallic or insulating. For metallic systems each Quantum Monte Carlo step lasts longer on average than for insulating systems, as the average perturbation order used in the expansion of \( Z \) is related to the kinetic energy, and increases as the interaction strength \( U \) decreases. At the same time, more Monte Carlo steps are needed for the insulating state than for a metallic case in order to properly sample the interval around \( \tau = \beta/2 \) where \( G(\tau) \) is almost zero.

Another technique used to improve the quality of the results, is to use orthogonal Legendre polynomials to expand \( G(\tau) \) \[84\]. First, it can be observed that the Green’s function in imaginary time can be defined in terms of Legendre polynomials \( P_l(x) \) on the interval \([-1, 1]\):

\[
G(\tau) = \sum_{l \geq 0} \frac{\sqrt{2l + 1}}{\beta} P_l[x(\tau)] G_l,
\]

where:

\( G_l \) – denotes the coefficients of \( G(\tau) \) in the Legendre basis,

\[
x(\tau) = \frac{2\tau}{\beta} - 1.
\]

The inverse transformation from \( G(\tau) \) to \( G_l \) is defined as:

\[
G_l = \sqrt{2l + 1} \int_0^\beta d\tau P_l[x(\tau)] G(\tau)
\]

Some basic properties of Legendre polynomials are summarised in appendix A of \[84\]. In principle, the Legendre coefficients \( G_l \) can be measured by the impurity solver instead of the imaginary time slices. It can be shown that the Legendre basis can be used to filter out a noise from the Quantum Monte Carlo (QMC) calculation provided that not too many expansion coefficients are used \[84\]. Usually when the basis is of size 200 or more then noise is no longer filtered out \[84\]. Because of that, the number of measured Legendre coefficients during the Quantum Monte Carlo simulation should be considered as one of the critical parameters by means of which one can tune accuracy of the calculations.

The impurity solver from the TRIQS library is used for this project. Legendre coefficients are measured directly in all cases.
Link between lattice system and impurity problems

In order to use the DMFT approximation in practical calculations one needs to map the lattice problem onto the Anderson impurity problem. It can be shown that the Green’s function which corresponds to the Anderson impurity model and the local Green’s function within DMFT share the same irreducible Feynman diagrams [85]. The same can be concluded about \( \Sigma \) for both models. Therefore it is possible to construct a self-consistent scheme for the calculation. In the simplest case, where there is only one atom with correlated states per unit cell, the lattice problem is defined by only one correlated site. In this case, there is also only one impurity problem to solve. The link between the lattice system and the Anderson system in such a case is as follows:

\[
\Sigma_{\text{lattice}} = \Sigma_{\text{imp}}, \tag{3.66}
\]

\[
G_{\text{lattice}} = G_{\text{imp}}. \tag{3.67}
\]

In cases, in the system there is more than one atom with correlated states per unit cell, the situation is more complicated. One has to consider more than one correlated site, which implies that the number of impurity problems to solve is also larger than one. In that case one has to reformulate previous conditions:

\[
\Sigma_{\text{lattice}}^n = \Sigma_{\text{imp}}^n, \tag{3.68}
\]

\[
G_{\text{lattice}}^n = G_{\text{imp}}^n. \tag{3.69}
\]

Index \( n \) denotes the number of the correlated shell. In the case of more than one correlated site, \( G_{\text{lattice}}^n \) denotes the block from the non-interacting lattice Green’s function which corresponds to the \( n \)-th correlated shell. In the case in the system are more than one correlated atoms, but some of them are related to each other by symmetry it is possible to reduce the number of impurity problems, that have to be solved independently, only to those, which are symmetry inequivalent, by using symmetry operations. More about inequivalent impurity problems is discussed in Sec. 4.1.

DMFT: Self-consistent scheme of the calculation

DMFT calculations are self consistent calculations. In each iteration we submit \( G_0 \) to the impurity solver and receive as an output the impurity self
energy, which is used as an approximation for the local self energy of the lattice problem. We iterate until the self energy is converged. The detailed self-consistency cycle is as follows:

1) Choose an initial self-energy $\Sigma$ (e.g. $\Sigma = 0$).

2) Calculate $G^{\text{loc}}(i\omega_n)$ by $k$-integration of the Dyson equation:

$$G^{\text{loc}}(i\omega_n) = \frac{1}{V_{BZ}} \int d^3k \left[ G^0(k, i\omega_n)^{-1} - \Sigma(i\omega_n) \right]^{-1}, \quad (3.70)$$

$$G^0(k, i\omega_n)^{-1} = i\omega_n + \mu 1 - H_0(k), \quad (3.71)$$

here:

$\omega_n = \frac{(2n+1)\pi}{\beta}$, $1$ – the unit matrix, $V_{BZ}$ – volume of the First Brillouin Zone FBZ, $G^0(k, \omega)$ – one particle Green’s function for the non-interacting case, $\mu$ – chemical potential, $H_0(k)$ – non-interacting part of the Hamiltonian.

3) Calculate $G^\circ$ from the Dyson equation:

$$G^\circ = (G^{-1} + \Sigma)^{-1}, \quad (3.72)$$

where:

$G^\circ$ – non-interacting Green’s function of the AIM. It is also called the Weiss field.

4) Calculate the Anderson impurity Green’s function $G_{\text{imp}}$ using $G^\circ$. The Anderson impurity problem is solved using continuous-time QMC solver for quantum impurity models \[76\]

5) Calculate the new impurity self energy $\Sigma_{\text{NEW}}$

$$\Sigma_{\text{NEW}} = (G^\circ)^{-1} - G_{\text{imp}}^{-1}, \quad (3.73)$$

6) Check conditions for convergence: $\| \Sigma - \Sigma_{\text{NEW}} \| < \epsilon$ (here some general formula for a norm is presented only as an example, but the criterion for convergence can be formulated arbitrarily provided it is possible to verify convergence by that criterion), where $\epsilon$ – tolerance. If conditions are not fulfilled return to point 2) using $\Sigma_{\text{NEW}}$ instead of $\Sigma$. 

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3.3.2 Calculational scheme for Density Functional Theory + Dynamical Mean Field Theory

Construction of Hamiltonian

The starting point for the combined DFT+DMFT approach is to separate electrons into two subsets: strongly correlated electrons, where the electron-electron interaction is important, and weakly correlated electrons. There is a different treatment of strongly correlated and weakly correlated electrons within DFT+DMFT. In contrast, to strongly correlated electrons, for weakly correlated electrons $\Sigma$ is set to zero. In DFT+DMFT the following Hamiltonian is solved:

$$ H_{DFT+DMFT} = H_{DFT} + H_{DC} + \sum_i H_{loc}^i, \quad (3.74) $$

$H_{DFT}$ is a part of the Hamiltonian constructed from DFT results:

$$ H_{DFT} = \sum_{ipjm} t_{ijpm} c_{ip}^{\sigma \dagger} c_{jm}^\sigma, \quad (3.75) $$

where:

- $c_{ip}^{\sigma \dagger}$ (or $c_{ip}^\sigma$) - creates (annihilates) an electron with spin $\sigma$ and an orbital index $p$ at site $i$,

- $t_{ijpm}$ - is a hopping parameter between site $i$ and $j$ and an orbital $p$ and $m$. The $t_{ijpm}$ elements are in principle, calculated from DFT results (this is how it is done in this project, but of course they can be evaluated also using different methods or even experimental data, however then it is not DFT+DMFT...). In order to do so, selected bands from DFT are used to construct a localized basis, in which $t_{ijpm}$ are expressed. More on the localized basis is presented in Sec. 3.3.3.

The $t_{ijpm}$ elements are used to construct $H_0(k)$ which is used in Eq. (3.71).

$H_0(k)$ is constructed according to the following formula:

$$ H_{0pm}(k) = \frac{1}{L} \sum_{ij} t_{ijpm} \exp[ik(R_i - R_j)], \quad (3.76) $$

$R_i$ - lattice vector, $L$ - number of lattice sites $i$.

$H_{DC}$ - describes the electron-electron interaction already included in $H_{DFT}$. To avoid double counting, this has to be subtracted from $H_{DFT}$. Various double counting terms are discussed in detail in Sec. 3.3.4.
\( \mathbf{H}(\mathbf{k}) - \mathbf{H}_{DC} \) is used to evaluate the lattice Green’s function \((\mathbf{H}_0(\mathbf{k}))\). \( H^i_{loc} \) is the interacting part of the Hamiltonian (Sec. 3.3.1). It is the local electron-electron interaction of the Hubbard model for the \( i \)-th inequivalent correlated site. In the approach used in this project the local Hamiltonian is defined separately for each inequivalent correlated site \( i \). An inequivalent site is defined here as the atom with correlated electrons in the unit cell which is symmetry inequivalent to other atoms in the same unit cell. Each inequivalent impurity problem is solved independently. The solution of the Anderson impurity problem – self energy, for all other sites is then reproduced using the fact that inequivalent sites are related to all other sites by symmetry operations (more details in Sec. 4.1).

In general \( \mathbf{H}_{loc} \) is a special, system dependent, form of (see also Eq. 3.52)

\[
\sum_{p\text{moni}\sigma \sigma'} U_{p\text{moni}} \hat{c}^\dagger_{p\sigma} \hat{c}^\dagger_{m\sigma'} \hat{c}_{n\sigma'} \hat{c}_{o\sigma}
\]

from the Hubbard Hamiltonian (Eq. (3.52)). The choice of the local Hamiltonian \( \mathbf{H}_{loc} \) depends on the system of interest. For a given inequivalent correlated shell, one of two types of the local Hamiltonian are used in this project: the Kanamori Hamiltonian [86] and the Slater Hamiltonian [87], [88], [89]. For most calculations within this project, the Kanamori Hamiltonian, which is suitable for the description of \( t_{2g} \) systems, is used:

\[
H^{Kanamori}_{loc} = \sum_{p\sigma} U_{p\sigma} n^\sigma_{p\sigma} n^\sigma_{p\sigma'} + \sum_{m\neq m', \sigma, \sigma'} (U' - \delta_{\sigma, \sigma'} J) n^\sigma_{m\sigma} n^\sigma_{m'\sigma'} - \sum_{p\neq m\sigma} \frac{J}{2} \hat{c}^\dagger_{p\sigma} \hat{c}_{p\sigma'} \hat{c}_{m\sigma} \hat{c}_{m\sigma'} - \sum_{p\neq m\sigma} \frac{J}{2} \hat{c}^\dagger_{p\sigma} \hat{c}_{p\sigma'} \hat{c}_{m\sigma} \hat{c}_{m\sigma'}
\]  

\((3.77)\)

\(U\) – defines the Coulomb repulsion between electrons in different spinorbitals but in the same orbital.

\(U'\) – defines the Coulomb repulsion between electrons in different orbitals.

\(J\) – the Hund exchange term.

The following relation is often used:

\[
U' = U - 2J.
\]  

\((3.78)\)

This relation is true for atomic orbitals (due to rotational invariance of the Hamiltonian). In periodic systems it is only an approximation. However, in all DMFT calculations reported here this relation is used.
Particular terms in the Hamiltonian have the following meaning:

\[ \sum p \sigma U n_p^\sigma n_p^\sigma' \] describes the situation in which electrons experience a repulsion of \( U \) while being in the same orbital \( p \).

\[ \sum m \neq m', \sigma, \sigma' (U' - \delta_{\sigma\sigma'} J) n_m^\sigma n_m'^{\sigma'} \] describes inter-orbital Coulomb interactions between electrons.

\[ \sum p \neq m \sigma \frac{J}{2} c_{pm}^{\sigma} c_{m\sigma} c_{pn}^{\sigma'} c_{n\sigma'} \] is called a spin flip term, electron with spin \( \sigma \) in orbital \( m \) is annihilated and in his place an electron, also in the same orbital \( m \), with the opposite spin is created. The same happens with electron at the orbital \( p \).

\[ \sum p \neq m \sigma \frac{J}{2} c_{pm}^{\sigma} c_{m\sigma} c_{pn}^{\sigma'} c_{n\sigma'} \] is called a pair hopping term. It describes an event in which a pair of electrons hops from orbital \( m \) to orbital \( p \).

In many previous, already published calculations, the Hirsch-Fye impurity solver was used (see [52]). Within this solver, spin flip and pair hopping terms are neglected in the Hamiltonian \( H_{loc} \).

The Slater Hamiltonian is more general than the Kanamori Hamiltonian, and it is defined in the following way:

\[ H_{loc}^{Slater} = \frac{1}{2} \sum_{pmon} n_{pm}^{\sigma} n_{pm}^{\sigma'} \]

(3.79)

In contrast to the Kanamori Hamiltonian, the interaction parameter \( U \) in the Slater Hamiltonian has the form of the matrix not a set of scalars (in the Kanamori Hamiltonian the matrix \( U \) is defined by three numbers: \( U \), \( U' \), \( J \)). The elements of the matrix \( U \) can be defined in the following way:

\[ U_{pmon} = \sum_k a_k(pmon) F_k, \]

(3.80)

where: and \( a_k \) are angular integrals (for \( d \) states \( l=2 \)):

\[ a_k(pmon) = \frac{4\pi}{2k + 1} \sum_{q=-k}^{k} \langle lp|Y_q^k|lo\rangle \langle lm|Y_q^k|ln\rangle. \]

(3.81)

\( Y_q^k \) – is a spherical harmonic function of degree \( q \) and order \( k \).

\( |lp\), |lm\), |ln\), |lo\) – \( p \), \( m \), \( n \), \( o \) states in the basis of spherical harmonics with angular momentum \( l \).
$F_k$ are called Slater integrals:

$$F_k = \int dr_1 r_1^2 \int dr_2 r_2^2 R_{nl}^2(r_1) \frac{r_{k-1}^k}{r_{k+1}^k} R_{nl}^2(r_2),$$  \hspace{1cm} (3.82)$$

where $r_{<}, r_{>}$ is the smaller (larger) of $r_1$ and $r_2$.

$U_{pmon}$ calculated from Eq. (3.80) will be very large (15-20 eV), but due to screening effects it is much smaller in real materials. To calculate the real $U_{pmon}$ means, in principle, to solve the many-body problem and in practice is not done in this work. Though some methods exist to estimate $U$. One has to keep in mind, however, that there is a possibility to directly compute the necessary screened Coulomb integrals for certain material systems from approximated first-principle schemes (constrained DFT [52]). They are mentioned in Sec. 3.3.1. In principle, one fixes $F_k$ to ”reasonable” values. $a_{k}(pmon)$ are system independent and can easily be calculated. Usually, one parametrizes the full $U$ matrix with only two free parameters $U_{int}$ and $J_{hund}$, where:

- $U_{int}$ is the average interaction $U$ over all correlated states of the impurity problem (for example in the case of $d$ states it is an average over $U$ for all 5 states),

- $J_{hund}$ average coupling over all correlated states of the impurity problem [90], [91], [92].

For example, for the impurity problem with all $d$ states included, one usually uses [89](exact relation $J_{hund} = \frac{F_2 + F_4}{14}$):

$$F_0 = U_{int}$$
$$F_2 = J_{hund} \times 8.6154$$
$$F_4 = F_2 \times 0.625$$

In the case of d-electrons, $F_1, F_3$ do not contribute to the Coulomb integrals (they vanish because of the symmetry).

**DFT+DMFT: Self-consistent scheme**

The DFT+DMFT scheme of calculation can be divided into the following steps:

1) Perform DFT calculation and obtain the ground state density $n^{KS}(r)$ and the corresponding band structure.
2) Construct orbitals, which describe the chosen localized electrons (Sec. 3.3.3).

3) Construct $H_{DFT+DMFT}$ and perform DMFT calculation.

4) Obtain a correction for $n^{KS}(r)$ and recalculate the DFT band structure; iterate until self-consistency is obtained.

In practice step 4) is often neglected and only a non-self-consistent DFT+DMFT calculations are performed. Also, one usually assumes that effects of strong correlations do not affect the positions of the nuclei.

3.3.3 Maximally localized Wannier functions

General algorithm

One difficulty in merging DFT with DMFT is the fact that one has to use a different, more localized, basis for the DMFT treatment. In DFT one usually uses Kohn-Sham orbitals expanded in a plane wave basis, which is suitable for the description of infinite periodic systems. A plane wave basis is, however, not suitable for the description of the localized correlated orbitals of the impurity atom. Within this project maximally localized Wannier functions are used to construct localized orbitals from Bloch states [93]. A Wannier orbital is defined as:

$$w_{\alpha}(r - T) = \frac{V}{(2\pi)^3} \int_{BZ} dk \exp (-i k T) \sum_{n \in W} U_{\alpha n}^{(k)} \psi_{nk}^{KS}(r),$$

(3.83)

where:

- $T$ – lattice vector (corresponds to a specific unit cell),
- $U_{\alpha n}^{(k)}$ – unitary transformation,
- $W$ – set of Bloch functions used to construct the Wannier orbital.

The Wannier functions form an orthogonal basis:

$$\langle w_{\alpha}(r - T) | w_{\alpha'}(r - T') \rangle = \delta_{TT'} \delta_{\alpha\alpha'}.$$  

(3.84)

The Wannier functions defined by Eq. (3.83) are not unique. This is due to the arbitrariness of the unitary transformation $U_{\alpha n}^{(k)}$, which is related to the arbitrary phase factor of Bloch states. Several approaches can be used to reduce the arbitrariness in $U_{\alpha n}^{(k)}$. One can for example explicitly
employ projection techniques on the occupied subspace spanned by the Bloch orbitals \([94],[95]\). Within this project, however, the criterion of maximal localization is used \([93],[96]\). According to this approach, in order to obtain uniquely defined so-called *maximally localised Wannier functions* (MLWFs), one uses the total quadratic spread \(\Omega\) defined as:

\[
\Omega = \sum_\alpha \left[ \langle 0\alpha | r^2 | 0\alpha \rangle - \langle 0\alpha | r | 0\alpha \rangle^2 \right] = \\
\sum_\alpha (\langle r^2 \rangle_\alpha - \langle r \rangle_\alpha^2)
\]

\[
\langle \hat{O} \rangle_\alpha = \langle w_{0\alpha}(r) | \hat{O} | w_{0\alpha}(r) \rangle,
\]

where:

\(w_{0\alpha}(r) = w(r)\) i.e. \(T = 0\).

When \(\Omega\) is minimized, one obtains MLWFs.

In order to use the localisation criterion in practice, it is convenient to transform it slightly by adding and subtracting the off-diagonal components: \(\tilde{\Omega}\). One then obtains:

\[
\Omega = \Omega_I + \tilde{\Omega},
\]

where:

\[
\Omega_I = \sum_\alpha \left[ \langle 0\alpha | r^2 | 0\alpha \rangle - \sum_\beta | \langle T\beta | r | 0\alpha \rangle |^2 \right]
\]

\[
\tilde{\Omega} = \sum_\alpha \sum_{\beta \neq 0\alpha} | \langle T\beta | r | 0\alpha \rangle |^2.
\]

It can be shown that both of these quantities are positive-definite \([108]\). Moreover, \(\Omega_I\) is invariant under any arbitrary unitary transformation of the Bloch orbitals. Therefore, during the localisation search only \(\tilde{\Omega}\) needs to be minimized. At the end of the search, the elements \(| \langle T\beta | r | 0\alpha \rangle |\) are as small as possible. To find the most localized Wannier orbitals is to find the unitary transformation which transforms the selected Bloch states to the most localized Wannier orbitals.

The central quantity in the minimization algorithm is the matrix \(M\), its elements are scalar products between Bloch orbitals at neighbouring \(k\)-points:

\[
M_{\beta \alpha}^{(k,b)} = \langle u_{\beta k} | u_{\alpha,k+b} \rangle.
\]
\( |u_{\alpha,k} \rangle \) is the periodic part of the Bloch state from Eq. (3.28). Both \( \Omega_I \) and \( \hat{\Omega} \) can be expressed as functions of the matrix \( M \) [96].

In order to obtain MLWFs, one first calculates matrix elements between a reference set of Bloch orbitals (KS eigenstates) at neighbouring k-points (Bloch states on a uniform k-mesh):

\[
M^{(0)(k,b)}_{\beta\alpha} = \langle u^{(0)}_{\beta k} | u^{(0)}_{\alpha,k+b} \rangle,
\]

where:

- \( b \) – vector connecting a k-point to one of its near neighbours
- \( u^{(0)}_{\beta k} \) – part of the reference Bloch state which has the periodicity of the Hamiltonian as defined in Eq. (3.28) and in Eq. (3.29).

In each iteration one calculates a new \( U \) according to the steepest-descent procedure [97]:

\[
U^k_z = U^k_{z-1} \exp \left[ \Delta W^{(k)} \right],
\]

where:

- \( z \) – number of iteration,
- \( \Delta W^{(k)} \) – defined by a user fixed finite step. One can easily evaluate \( \exp \left[ \Delta W^{(k)} \right] \), using the fact that \( i\Delta W^{(k)} \) is Hermitian [98].

Then, one evaluates the M matrix according to:

\[
M^{(k,b)} = U^{k\dagger} M^{(0)(k,b)} U^{k+b}.
\]

From the matrix M one evaluates the spread. Then the \( U \) matrix is evaluated again in the next iteration.

Using \( u^{(0)}_{\beta k} \) directly from DFT may lead the minimization process to a non-physical minima. Therefore one usually uses a rough estimation of MLWFs, like for example atomic d states or atomic p states. For this, one first projects the initial guess onto the Bloch manifold at wave vector \( k \):

\[
|\psi_{\alpha k} \rangle = \sum_\beta |\psi^{KS}_{\beta k} \rangle \langle \psi^{KS}_{\beta k} | g_\alpha \rangle,
\]

where:

- \( g_\alpha \) – rough estimate of MLWF for \( \alpha \)-th orbital
One also has to perform an orthogonalization of the obtained Bloch states. In the code wannier90 [99], which is used in this project, the orthogonalization is done through a Löwdin transformation:

\[
|\tilde{\psi}_{\alpha k}\rangle = \sum_{\beta} \frac{|\psi_{\beta k}\rangle}{\sqrt{\langle \psi_{\beta k} | \psi_{\alpha k} \rangle}}.
\]

This set is then used to construct \( M_{\beta \alpha}^{(0)(k,b)} \).

**Disentanglement**

The general algorithm, which is described in Sec. 3.3.3 is designed to deal with isolated groups of bands. The isolated groups of bands are defined as bands that may be degenerate at certain high-symmetry k-points, but are separated from all other bands by finite gaps throughout the entire Brillouin zone. Since the valence bands play the most important role for the properties of a material, they most often are used to construct MLWFs. In real materials valence bands are rather rarely isolated from other bands.

In the situation in which a group of bands selected for the construction of MLWFs are entangled with other bands, it is not clear which bands should be used in the general algorithm. One first has to obtain set of *smooth pseudo-Bloch states* to proceed. The process of building the smooth pseudo-Bloch states is called disentanglement [96]. Once the smooth pseudo-Bloch states are produced, one can follow the general algorithm described in Sec. 3.3.3.

In order to apply the disentanglement procedure, one has to first define an energy window, within which there are bands with the desired atomic character. Within that window, at least for one k-point, the number of bands is larger than the number of MLWFs one wants to construct. Otherwise we don’t have disentanglement. In order to find the transformation from Bloch states to the smooth pseudo-Bloch states, one then minimizes \( \Omega_I \) (Eq. (3.88)). By minimizing \( \Omega_I \) one is choosing self-consistently at every k-point the subspace of the smooth-pseudo Bloch states that changes as little as possible with k-points [96]. The number of the obtained pseudo-Bloch states is equal to the number of the final MLWFs. The next step is then to use the general algorithm in order to obtain MLWFs.

**Properties of maximally localized Wannier functions**

MLWF can be used in many applications. The main fields of application are as follows:
To describe the chemical bond.

To analyse global and local dielectric properties.

As a basis for constructing model Hamiltonians.

**Chemical Bond**

Once MLWFs are constructed, one can calculate their centres of charge. Those charges can be treated in the first approximation as "classical" electrons, which build the bond. By analysing the spatial distribution of centres of charges, one can determine the character of the corresponding bond. For example whether it is ionic or covalent. Moreover, for the given element, one can also calculate the coordination number (the number of its near neighbours) in an elegant way, which is equivalent of finding the oxidation state of the particular atom. An example of such an analysis for a disordered Si system is presented in [100]. By means of MLWFs one can also analyse bond angles [101]. Using MLWFs one can also analyse quite accurately hydrogen bonds [102]. Many more examples of MLWFs usage for the bond analysis are presented in [96].

**Local and global dielectric properties**

Centres of MLWF can be directly related to the macroscopic observables: polarisation [96]. This exact correspondence exists due to the fact that the sum of the Wannier centres is invariant with respect to a unitary transformation between the orbitals [103]. By means of MLWFs one can also calculate Born dynamical charges, which describe the change in the macroscopic polarization induced by the displacement of a given ion [96]. It is also possible to calculate contributions originating from individual MLWFs to Born charges [96]. There are many papers, in which MLWFs are used to analyse dielectric properties. Examples for the usage of MLWF as an analysis tool for the dielectric properties of perovskite ferroelectrics can be found in [104] and in [105].

**Basis for model Hamiltonians**

MLWFs are a convenient basis for tight binding (TB) methods. Such methods give a relatively good description of systems with localized strongly correlated electrons. Within the tight binding approximation one considers the basis orbitals localized on sites of the lattice system. Electrons, which occupy those orbitals, can jump with some probability to the neighbouring
atoms. A tight binding model can be described by the Hubbard Hamiltonian (Eq. (3.52)). Even though TB models were initially developed as an approximation, if one uses MLWFs obtained from DFT calculations, the TB model becomes exact (within the DFT approximation of course). Diagonal elements of the Hamiltonian in the MLWF basis can be interpreted as on-site energies and off-diagonal elements connecting different sites can be interpreted as hopping integrals. On-site energies are the exact energies of the Wannier orbitals. In principle, they give information about the crystal field splitting created by the ligands. The absolute values of the hopping integrals are a measure of the overlap of orbitals between neighbouring atoms. The larger hopping integrals the larger is the overlap. Hopping integrals define the probability of an electron for jumping from one site to another. Both hopping integrals and crystal field splitting play a crucial role for the electronic properties of $d^1$ perovskite systems, and are analysed in detail in chapter 5.

MLWFs are not only a great tool for analysing DFT results, they can also be used as a convenient basis to express the Hamiltonian ($H_{DFT+DMFT}$ from Eq. (3.74)), which is used in DMFT calculations. Within the MLWF framework it is possible to include states with correlated character like $t_{2g}$ and non-correlated character like O 2$p$ states in the Hamiltonian used in DMFT.

### 3.3.4 Double counting

In order to use DMFT on top of DFT one has to subtract the electron-electron interactions already included in the DFT calculations via the exchange-correlation potential. This is realized by $H_{DC}$ in $H_{DFT+DMFT}$ (Eq. (3.74)). The task is quite challenging. After all, we have to subtract effects included only in an approximate way in the DFT calculations, and how to subtract a term which is in general unknown? Because of that, there is no universal formula for $H_{DC}$, which would work in all cases. Nevertheless, various expressions, which work quite well for particular types of systems, have been proposed.

The general expression for the double counting term is as follows:

$$H_{DC} = \mu_{DC} \sum_{m\sigma} n_{m\sigma},$$

(3.96)

where:

$\mu_{DC}$ – is the double-counting potential.
The most often used approximations for $\mu_{DC}$ are as follows:

- Around mean field (AMF) [72]
- Fully localized limit (FLL) [107]
- Held formula [52]
- Lichtenstein formula [109]

**Around mean field limit**

The around mean field limit was designed as a correction to DFT. It was tailored to deal with spin-polarised, strongly correlated metals, for which DFT with, for example, LDA as an exchange-correlation potential fails. The starting point was the Hubbard Hamiltonian. As a matter of fact, it was one of the first attempts to merge the Hubbard model and ab-initio DFT. Within this approximation, the single particle potential is given by [72]:

$$H_{AMF}^{DC} = \frac{1}{2} U \sum_{\sigma} N_{\sigma} (N - n_{\sigma}^{\circ}) - \frac{1}{2} J \sum_{\sigma} N_{\sigma} (N_{\sigma} - n_{\sigma}^{\circ}).$$

where:

- $N$ – total number of electrons,
- $N_{\sigma}$ – total number of electrons for the given spin,
- $n_{\sigma}^{\circ}$ – average number of electrons for the given spin $\sigma$:

$$n_{\sigma}^{\circ} = \frac{1}{2l + 1} \sum_{m} n_{m\sigma}$$

where:

- $n_{m\sigma}$ – number of electrons for $m$-th orbital and spin $\sigma$.

This double counting correction is only nonzero if spin and/or orbital order develops. AMF approximation works rather well for moderately correlated metallic systems.
Fully localized limit

The fully localized limit was initially designed to reproduce correctly the insulating, antiferromagnetic ground state in transition-metal oxides with strongly correlated electrons, such as FeO, CoO, and NiO \[107\]. This double counting variant can be obtained by considering the energy of an isolated atomic shell with N electrons. Within this approximation the effective potential has the following form:

\[
H_{FLL}^{\sigma DC} = \frac{1}{2} U N (N - 1) - \frac{1}{2} J \sum_{\sigma} N_{\sigma} (N_{\sigma} - 1).
\]  

(3.99)

Held Formula

The first two approximations to double counting presented here, FFL and AMF, were initially created as a direct extension of DFT: DFT+U (please have a look at Sec. 3.2 for more details). When DFT+DMFT was developed they become often used double counting corrections also for that method. Since FFL and AMF were initially not designed for DFT+DMFT, they may not be optimal. In contrast, Held defined the double counting potential exclusively for the DFT+DMFT framework as:

\[
\mu_{H\text{E}LD}^{\sigma DC} = \hat{U} (N - \frac{1}{2}),
\]

(3.100)

where:

\( \hat{U} \) is an averaged Coulomb interaction. It is defined as:

\[
\hat{U} = \frac{U + (M - 1)(U - 2J) + (M - 1)(U - 3J)}{2M - 1},
\]

(3.101)

M – is the number of orbitals. The formula corresponds to the average Coulomb interaction in the Kanamori Hamiltonian.

In this formalism, the double counting correction is the same for both spins. Within this project, if not stated differently, Held’s formula is used for the calculations.

Lichtenstein formula

Another double counting formula, which was specially tailored for DFT+DMFT is, Lichtenstein formula. Lichtenstein defines the double counting potential as \[109\]:

\[
\mu_{\text{Licht}}^{DC} = \frac{1}{2} \sum_{\sigma} \Sigma_{\sigma mm} (\omega = 0)
\]

(3.102)
The double counting term is defined as the static part of the self energy \( \Sigma(\omega = 0) \), calculated in DMFT. It is argued that, the static correlation effects are already well described in density functional theory. In contrast to the previous definitions, Lichtenstein formula is orbitally dependent.

**General remarks**

In practice, the double counting contribution is calculated separately for each correlated site. The double counting term is necessary for systems which have more than one inequivalent correlated site or which have non-correlated orbitals in the local Hamiltonian. Inequivalent correlated sites are sites which are not related by symmetry operations. In all other cases, the double counting term only shifts the chemical potential and can be left out.

### 3.3.5 Green’s function: all you want to know about system?

In the calculations presented in this report, the AIM is solved by a continuous time Quantum Monte Carlo solver [76]. This solver gives as a result the one particle Green’s function in imaginary time \( G(\tau) \). \( G(\tau) \) itself is quite featureless. Its shape is quite similar for very different systems. Nevertheless, after some post-processing, one can extract various information from the Green’s function. In contrast, to standard DFT calculations, DFT+DMFT calculations are often performed for a temperature different from zero. The temperature is defined in terms of \( \beta \):

\[
\beta = \frac{1}{k_B T}.
\]

### Average density per spin and orbital

The thermal average occupation for spin \( \langle n_\sigma \rangle \) can be calculated in the following way:

\[
\lim_{\delta \to 0^+} G_\sigma(\beta + \delta) = -\langle n_\sigma \rangle.
\]

Using this property of the Green’s function, one can not only calculate spin dependent occupancies, but also orbitally resolved occupancies.

### Spectral function

From \( G(\tau) \) one can calculate the spectral function \( A(\omega) \), which can be directly compared with photoemission experiments. The spectral function
$A(\omega)$ is related to the retarded Green’s function $G^R(\omega)$\cite{[111]} in the following way:

$$A(\omega) = -\frac{1}{\pi} Im G^R(\omega).$$

(3.105)

Green’s function can be defined as general function of a complex variable $G(Z)$. If $G(Z)$ is evaluated on the real axis then one obtains $G^R$. $A(\omega)$ describes single particle excitations (addition/removal of an electron) in many-body systems. It has the following properties:

$$\forall \omega \ A(\omega) > 0,$$

(3.106)

$$\int_{-\infty}^{\infty} d\omega A(\omega) = 1.$$  

(3.107)

For the non-interacting system $A(\omega)$ has the following form:

$$A(\omega) = \sum_{n,k} \delta(\omega - \epsilon_{nk}),$$

(3.108)

where $\epsilon_{nk}$ are the energies of the one-particle levels, i.e. in this case $A(\omega)$ is identical to the DOS (see Eq. (3.24)).

$A(\omega)$ is related to $G(\tau)$ in the following way \cite{[111]}:

$$G(\tau) = \int d\omega \frac{A(\omega) \exp(-\tau \omega)}{1 + \exp(-\beta \omega)}.$$  

(3.109)

**Critical U**

Using the Green’s function obtained from calculations for various $U$ one can also estimate the critical $U$ of the Mott metal-insulator transition for a particular material (e.g. Ref. \cite{[110]}). First of all, one can estimate the critical $U$ by monitoring $G(\beta/2)$. $G(\beta/2)$ is linked with $A(\omega = 0)$ by the following relation \cite{[115],[110]}:

$$\lim_{\beta \to \infty} -\beta G(\beta/2) = \pi A(0).$$

(3.110)

If $A(0)$ is zero, then the system is an insulator, and in the opposite case it is a metal. Since $G(\beta/2)$ is exactly proportional to $A(\omega)$ only in the limit $\beta \to \infty$ (i.e. $T=0K$), the identification of the metal-insulator transition phase boundary requires the definition of a suitable threshold value for $G(\beta/2)$. In addition, $G(\beta/2)$ suffers from a significant statistical noise in
the insulating state, because this region is difficult to sample with standard continuous time hybridisation solver (CT-HYB solver). Nevertheless, $G(\beta/2)$ can still be used to monitor the metal-insulator transition.

Another quantity, which can be used to monitor the metal-insulator transition, is the effective quasiparticle mass \([115]\). The effective quasiparticle mass is a measure for electron localization in the system. For an ideal metal the effective mass is equal to the mass of a free electron. The more localized electrons are the larger are their effective masses. For the insulating state, the effective quasiparticle mass diverges. The effective mass can be defined as a function of the self energy:

$$\left\{ \frac{m'_{k}}{m} \right\} = 1 - \frac{\partial \text{Re} \Sigma_{\sigma k(\omega)}}{\partial \omega}{\bigg|}_{\omega=0}.$$  \hspace{1cm} (3.111)

This can be approximated to [110]:

$$\left\{ \frac{m'_{k}}{m} \right\} \simeq 1 - \frac{\text{Im} \Sigma(i\omega_0)}{\omega_0},$$  \hspace{1cm} (3.112)

where:

$$\omega_0 - \text{the lowest Matsubara frequency}$$

The slope $K$ of $G(i\omega \to 0)$ is another quantity, which can be used to measure metallic / insulating properties of a system [115]. Its positive value indicates that a system is a metal, whereas a negative value indicates an insulator. Moreover, it is quite insensitive to Quantum Monte Carlo noise. In practice, it can be approximated in the following way:

$$K = \frac{\text{Im}\{G(i\omega_1) - G(i\omega_0)\}}{\omega_1 - \omega_0},$$  \hspace{1cm} (3.113)

where:

$$\omega_1 - \text{second lowest Matsubara frequency}$$

### 3.4 Maximum entropy method

#### 3.4.1 Maximum Entropy method – Bayesian inference

One of the quantities which can be obtained from DFT+DMFT calculations is the spectral function $A(\omega)$. In order to obtain $A(\omega)$ from the $G(\tau)$ calculated within DFT+DMFT, Eq. (3.109) needs to be inverted. Even
though it seems that the inversion (Eq. (3.109)) should be rather straightforward, the mapping $G(\tau) \rightarrow A(\omega)$ is a numerically ill-posed problem, due to the numerical properties of the kernel $K(\tau, \omega) = \frac{\exp(-\tau \omega)}{1 + \exp(-\beta \omega)}$. For large values of $\tau$ and $\omega$, $K(\tau, \omega)$ becomes very small, which makes it difficult to invert (Eq. (3.109)). Moreover, one obtains $G(\tau)$ only for a finite grid of $\tau$, and one always obtains noisy data because of the error intrinsic to stochastic methods, which are used to solve the impurity problem. That is the main reason why an infinite number of possible solutions for $A(\omega)$ exist. One of the methods used to solve this problem is the Maximum Entropy Method (MEM) \[111\. It is based on Bayes theorem:

$$Pr[a, b] = Pr[a | b] Pr[b] = Pr[b | a] Pr[a], \quad (3.114)$$

where $Pr[a]$ – is the probability of an event $a$, $Pr[a | b]$ – is the conditional probability of an event $a$ given an event $b$ and $Pr[a, b]$ is the joint probability function for $a$ and $b$. In the analytic continuation problem our events are:

$\bar{G}_i = \bar{G}(\tau_i)$ – estimated (measured) value of $\bar{G}(\tau = \tau_i)$. This is an averaged value obtained from Quantum Monte Carlo simulation: $\bar{G}(\tau_i) = \bar{G}_i = \frac{1}{o} \sum_{j=0}^{o} \bar{G}(\tau_i)^j = \frac{1}{o} \sum_{j=0}^{o} \bar{G}_i^j$ ( $o$ - number of independent measurements, $j$ stands for $j$-th measurement and $i$ for $i$-th imaginary time slice $\tau_i$),

$A$ – spectral function, $A(\omega)$.

In MEM we are looking for the most probable $A(\omega)$ for a given $\bar{G}(\tau)$; i.e. we are maximizing the posterior probability $Pr[A | \bar{G}]$ which is given by:

$$Pr[A | \bar{G}] = \frac{Pr[\bar{G} | A] Pr[A]}{Pr[\bar{G}]} \quad (3.115)$$

here:

- $Pr[\bar{G} | A]$ is called the likelihood function. If there are many independent measurements of $\bar{G}(\tau_i)$ for every value $\tau_i$, then:

$$Pr[\bar{G} | A] \propto \exp(-\chi^2/2), \quad (3.116)$$

$$\chi^2 = \sum_{i,j} (\bar{G}_i - G_i) C_{ij}^{-1} (\bar{G}_j - G_j), \quad (3.117)$$

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\[ C_{ik} = \frac{1}{o(o + 1)} \sum_{j} (G_i - \bar{G}_i)(G_k - \bar{G}_k), \]  
\hspace{10cm} (3.118)

where:

\( G_i = G(\tau_i) \) – imaginary time Green’s function which corresponds to a given \( A(\omega) \) obtained from Eq. (3.109).

\( C_{ij} \) – covariance matrix element; represents the statistical relationship between different measurements,

\( M \) – number of values \( G_i = G(\tau_i) \), i.e. number of “time slices”,

- \( Pr[A] \) is called the prior probability. It is usually expressed as:

\[ Pr[A] \propto \exp[\alpha S] \]  
\hspace{10cm} (3.119)

\[ S = \int d\omega \left( A(\omega) - m(\omega) - A(\omega)\ln\left[ \frac{A(\omega)}{m(\omega)} \right] \right), \]  
\hspace{10cm} (3.120)

where:

\( m(\omega) \) – default model (more details in [111]).

\( \alpha \) – is called a regularization parameter.

The entropy \( S \) has a maximum value of 0 if \( A(\omega) = m(\omega) \). Otherwise it is negative. The negativeness is a measure of how much \( A(\omega) \) differs from \( m(\omega) \).

- \( Pr[\tilde{G}] \) – evidence. It is treated as a normalization constant.

\( Pr[A|\tilde{G}] \) can therefore be represented as follows:

\[ Pr[A|\tilde{G}] \rightarrow Pr[A|\tilde{G}, m, \alpha] \propto \exp \left[ - \frac{\chi^2}{2} + \alpha S \right] = \exp \left[ Q \right], \]  
\hspace{10cm} (3.121)

For a given \( \alpha \) and \( m(\omega) \) the goal is to find the \( A(\omega) \) that maximizes \( Q \) (and thus the posterior probability). In the limit of \( \alpha \to 0 \) MEM is reduced to the least-square fitting method. For \( \alpha > 0 \) the entropy term has a non-zero contribution which results in \( \alpha \) smoothing \( A(\omega) \).

For a given default model and fixed \( \alpha \) the following can be observed [111]:

\[ \forall_{A_i, A_m} \frac{\partial^2 S}{\partial A_i \partial A_j} < 0, \]  
\hspace{10cm} (3.122)
\[ \forall_{A_i, A_m} - \frac{\partial^2 \chi^2}{\partial A_j \partial A_m} < 0, \quad (3.123) \]

where:

\[ A_i = A(\omega_i) \Delta \omega_i, \]

This means that there exists at least one extremum of \( Q(A) \) and both calculated derivatives are concave functions for every \( A_i = A(\omega_i) \). Therefore \( Q \) has a unique maximum.

### 3.4.2 Types of the Maximum Entropy Method

For the chosen default model and fixed \( \alpha \) it is possible to calculate an optimal \( \hat{A}_\alpha(\omega) \). However, for each \( \alpha \) the resulting \( \hat{A}_\alpha(\omega) \) will be different. So the question arises: what is the appropriate value of \( \alpha \)?

**Historic MEM**

One of the first approaches was based on a determination of \( \alpha \) such that the following condition is fulfilled:

\[ \chi^2 = M. \quad (3.124) \]

If the search for an optimal \( A(\omega) \) is performed according to this criterion then this is called **historic MEM**.

**Classic MEM**

In **Classic MEM** one tries to find the most probable \( \alpha \). \( Pr[\alpha | \mathcal{G}] \) can be calculated in the following way [111]:

\[ Pr[\alpha | \mathcal{G}] = \frac{1}{\alpha} \frac{\exp(Q(\hat{A}_\alpha))}{Z_{LS}(\alpha)} \frac{(2\pi)^{N/2}}{\sqrt{det[\alpha I + \Lambda(\hat{A}_\alpha)]}}, \quad (3.125) \]

\[ \Lambda_{ij} = \sqrt{A_i} \frac{\partial^2 (\chi^2 / 2)}{\partial A_i \partial A_j} \sqrt{A_j}, \quad (3.126) \]

where:

\[ Z_{LS}(\alpha) - \text{normalisation constant [111].} \]

The \( A(\omega) \) which maximizes \( Q \) for the most probable \( \alpha \) is the solution of classic MEM.
Bryan MEM

In *Bryan’s MEM* the optimal $\bar{A}(\omega)$ is calculated by averaging over $\alpha$ according to its probability $[111]$:

$$\bar{A}(\omega) = \int d\alpha \hat{A}_\alpha(\omega) Pr[\alpha|\bar{G}].$$  \hfill (3.127)
Chapter 4

Wannier2TRIQS benchmarks

Within this project, a code for performing DFT+DMFT calculations has been developed, which is based on the TRIQS library [116] and wannier90 [99] output. The goal is to produce the general purpose code, which can be used for DFT+DMFT calculations for many different materials. This code has been called ”wannier2TRIQS”. After implementing the code, intensive benchmark calculations have been performed, to verify that all features work correctly. Details of the implementation and benchmarks are described in the following sections.

4.1 Closer look at the implementation

In order to use the developed code, one first has to perform a DFT calculation. As long as there exists an interface from any DFT program to the wannier90 [96] program, the DFT program can be used. One can in principle interface the code with many DFT programs like VASP ([117],[118],[119],[120]), Quantum Espresso ([73]), ABINIT [121], Wien2k ([122],[123]) (for Wien2k, however, there exist the full charge self consistency implementation, which uses the TRIQS library) or an alternative implementation that is interfaced with the wannier90 code. From the band structure obtained from DFT, one can then construct the Hamiltonian in the MLWF basis. In principle one has to generate the file ..._hr.dat which contains the real-space representation of the Hamiltonian expressed in MLWFs. The ..._hr.dat file is then used as input for the code developed within this thesis. In order to keep generality only one-shot, i.e., non charge self-consistent DFT+DMFT calculations are considered. This is because in general a self consistency DFT+DMFT interface has to depend on the specific DFT code in use. The developed code depends on the TRIQS library [84]. In particular, it uses the CT-QMC impurity solver contained in
The newly developed code requires two input files to perform calculations: "filename_hr.dat" and "PARAMETERS". The first file contains the real-space representation of the Hamiltonian in the MLWF basis obtained by the wannier90 program. The latter is the file which contains the user-defined parameters for the DMFT calculations, such as for example $U$, $J$ and $\beta$. The code consists mainly of two python files:

- `wan2DMFT.py`, which defines the self consistent scheme of the DMFT calculation, and
- `Wannier_to_TRIQS_interface.py`, which contains all required functions.

The similarity with the usual convention for DFT codes is kept: input ASCII file → executable → output files. In order to run the DMFT program one has to execute the `wan2DMFT.py` python script.

In `wan2DMFT.py`, first data from the input ASCII file PARAMETERS is read, then initial objects for the DMFT calculations are prepared by `Wannier_to_TRIQS_interface.py`. In particular, the initial non-interacting Green’s function is constructed as input for the impurity solver. In each iteration, after the impurity problems are solved, the lattice Green’s function...
is reconstructed. The lattice Green’s function is reconstructed from the self energies calculated by the impurity solver. Depending on the system, one or more impurity problems are solved independently by the impurity solver during DMFT calculations. The impurity solver from the TRIQS library is used to solve the impurity problems (version 1.1: cthyb_matrix).

In the general case, a material can contain more than one site per unit cell, which contains strongly correlated electrons. Some of those sites can be related by symmetry, but it often happens that there is more than one symmetry inequivalent site in a system. Within the code, symmetry inequivalent sites in a system are called \textit{inequivalent correlated shells}. In addition symmetry equivalent correlated sites are called \textit{equivalent correlated shells}.

It may happen that there are at least two symmetry equivalent impurity problems. One approach would be to solve all impurity problems by the impurity solver, regardless of symmetry. Such an approach, however, would duplicate the computational effort without any gain. A better way is to solve only one impurity problem, and then reconstruct the solutions of the impurity for the other sites from symmetry operations. This second approach is implemented in \texttt{Wannier\_to\_TRIQS\_interface.py}. In a case, there are symmetry equivalent sites in the system, Wannier function located on one site can be transformed into one of the Wannier functions located on a symmetry-equivalent site. The problem is to find these symmetry transformations. Using those transformations one can then transform the corresponding matrix elements (or matrix blocks) of $H$, $G$ and $\Sigma$.

One has to find the similarity transformation operators $R$, by means of which one can reproduce results for all symmetry equivalent sites, having just the result for one site. One can construct such a transformation from the part of the Hamiltonian expressed in the MLWF basis in real space at the origin. In this Hamiltonian, one can define blocks which correspond to correlated sites. For simplicity only case for the system with 2 correlated sites and only one inequivalent site is discussed but this simple construction will also hold for the more complex scenario. The Hamiltonian is defined as:

$$\textbf{H}(0) = \left( \begin{array}{c} H^I(0) \\ \cdots \\ H^{II}(0) \end{array} \right)$$ \hspace{1cm} (4.1)

The goal is to find a way to reproduce block $n$ ($n = \{II\}$) from block $I$

$$H^n(0) = R^\dagger_{I\rightarrow n} H^I(0) R_{I\rightarrow n}$$ \hspace{1cm} (4.2)
First, we diagonalize each block (in this example sites with three correlated states are considered):

\[
H^I(0) = V_I^\dagger \begin{pmatrix}
H_{11}^I(0) & 0 & 0 \\
0 & H_{22}^I(0) & 0 \\
0 & 0 & H_{33}^I(0)
\end{pmatrix} V_I \tag{4.3}
\]

and for the 2nd site:

\[
H^{II}(0) = V_{II}^\dagger \begin{pmatrix}
H_{11}^{II}(0) & 0 & 0 \\
0 & H_{33}^{II}(0) & 0 \\
0 & 0 & H_{22}^{II}(0)
\end{pmatrix} V_{II} \tag{4.4}
\]

The matrix \(V_{II}\) contains the eigenvectors of \(H^{II}(0)\). Eigenvalues \(\{H_{11}^I, H_{22}^I, H_{33}^I\}\) form a set, which uniquely defines inequivalent sites and sites related by symmetry (equivalence relation). Each site, which has the same eigenvalues as inequivalent site, is related to this site by symmetry. It belongs to the equivalence class of the element \(\{H_{11}^I, H_{22}^I, H_{33}^I\}\). \(V_I\) are unitary matrices so the following is true:

\[
V_I H^I(0) V_I^\dagger = \begin{pmatrix}
H_{11}^I(0) & 0 & 0 \\
0 & H_{22}^I(0) & 0 \\
0 & 0 & H_{33}^I(0)
\end{pmatrix} \tag{4.5}
\]

If one combines Eq. (4.5) with Eq. (4.4) then one obtains:

\[
V_{II} H^{II} V_{II}^\dagger = V_I H^I V_I^\dagger \tag{4.6}
\]

Using the fact that \(V\) are unitary operators one obtains that:

\[
H^{II} = V_{II}^\dagger V_I H^I V_I^\dagger V_{II} = R_{I\rightarrow II}^\dagger H^I R_{I\rightarrow II} \tag{4.7}
\]

Other equivalent sites, if present, can be treated analogously. The expressions above are valid as long as the eigenvalues are sorted. In the case of numpy python library this is unfortunately not a case. Moreover, the order of the eigenvalues is not uniquely defined (since it is stored in the hash table, the order is machine dependent). In order to make it possible to express the symmetry operators in terms of eigenvectors one has to apply "sorting" operator \(S\) to all operators \(V\):

\[
V_n \rightarrow S_n V_n \tag{4.8}
\]

The sorting operator guarantees that, for each symmetry equivalent site, the order of the eigenvalues in the diagonalised block of the Hamiltonian is the same.
Since $\mathbf{R}$ is a unitary transformation and it is translationally invariant, it can be applied to other quantities, such as the self energy $\Sigma$, the Weiss field $\mathcal{G}$, and local Green’s function $\mathbf{G}$:

$$\Sigma' = \mathbf{R}_{I \rightarrow n}^\dagger \Sigma' \mathbf{R}_{I \rightarrow n}$$

(4.9)

Thus one can use Eq. (4.9) to obtain $\Sigma$ for all equivalent sites from the solution of the impurity problem for only the first site. In cases where there is more than one inequivalent correlated shell, the procedure described above is applied to each set of equivalent sites separately. Once the self energy for the whole system is constructed, the lattice Green’s function can also be constructed, and the DMFT calculation proceeds according to the self-consistent scheme, which is described in chapter 3.3.2.

Within the implementation discussed here, only single-site DMFT calculations are possible. Within the single-site DMFT the self energy is purely local, i.e., $\Sigma$ off-block components between different sites are set to zero. However, off-diagonal elements occur in the Hamiltonian $\mathbf{H}_0(k)$, and because of that off-diagonal elements are also included in the lattice Green’s function (see also Eq (3.70) and (3.71)):

$$\mathbf{G}_{\text{latt}}(i\omega) = \frac{1}{(\mu + i\omega)\mathbf{I} - \mathbf{H}_0(k) - \mu_{\text{DC}}}. \quad (4.10)$$

By including symmetry of the correlated shells in the calculation one not only significantly speeds up the calculation, after all the DMFT calculation scales linearly with number of sites, but also improves accuracy of the calculation.

The developed code allows not only calculations for systems with more than one inequivalent correlated shell. It also allows to explicitly include additional non-correlated MLWF states in the DMFT calculations (the self energy, which corresponds to the non-correlated states is set to zero). While performing more advanced calculations, one has to keep in mind that a fixed format of the input $\mathbf{H}_0(\mathbf{R})$ is expected. The equivalent correlated shells have to be grouped together. Non-correlated shells are expected to be defined after all correlated states. The required format of the Hamiltonian is presented in figure 4.2.

The block structure of the lattice Green’s function is the same as the block structure of the full Hamiltonian $\mathbf{H}_0$ in the MLWF basis. Each of the equivalent correlated site, within the same equivalence class, is related to other sites by the equivalence relation of symmetry. Each of equivalent correlated site has to be grouped as one block. In figure 4.2 each of such
equivalence classes is represented by a color, for example a red color defines one of such classes. The first sub-block of each lattice Green’s function correlated block, for example first sub-block of red block from figure 4.2, is treated as the interacting Green’s function for the particular impurity problem according to the DMFT equations (Eq. (3.68) and in Eq. (3.69)). Each such the block of the interacting Green’s function is then used to evaluate the Weiss field from the Dyson equation (3.54), which gives the new input for the corresponding impurity problem (see chapter 3.3.1 for the DMFT scheme).

All data from the calculation performed by the implemented code is stored in one file with a hdf format [124]. Even though the structure of the hdf file seems to be quite complex with a comparison to the simple ASCII file, this choice of the output file format is quite beneficial. The language of implementation is Python (since most of TRIQS is written in Python this is the natural choice...). An output in the form of the ASCII file would make the implementation quite complex because Python writes everything to ASCII files as strings. Coding complex TRIQS objects to ASCII files
in the form of strings and then decoding them again for example in the
case of a rerun would be quite cumbersome and not give much of practical
gain in functionality. However, in order, to be able to work with ASCII
files, simple tools have been developed, which make extracting data from
the hdf file to ASCII files easy. The related components are listed below:

- `monitoring_function.py` – generic class with functions capable to plot
  TRIQS objects to figures with a desired format. It also contains a
  set of functions, which enable the user to extract data from TRIQS
  objects into ASCII files.

- `plotting_tools_interface.py` – defines all valid TRIQS objects, which
  can be analysed. Reads TRIQS objects from an hdf file.

- `Wannier_to_TRIQS_plotting_tools.py` – executable, which should be
  executed by the user, if there is a need to produce plots or ASCII files
  with data. Reads input parameters, which should be analysed, from
  the ASCII file:

  \[ \text{PARAMETERS\_ANALYSE} \]

- `PARAMETERS\_ANALYSE` – ASCII input file with the user defined
  objects to be analysed.

To sum up, extracting data from the hdf file to ASCII files, which then can
be used as input to various visualisation programs is realised in the follow-
ing way: `PARAMETERS\_ANALYSE` → `Wannier_to_TRIQS_plotting_tools.py` (executable) → ASCII files.

In principle, no programming knowledge is required to perform calcu-
lations with the developed code. This is with the analogy to many DFT
codes, for which scientists do not need to know Fortran, for example, to be
able to perform a DFT calculation. Once input files with valid input data
are provided, one can start calculations.

The developed code can be applied to systems, which have to be de-
scribed by the different interaction Hamiltonians than the Kanamori Hamil-
tonian (Eq. (3.77)). In particular, one can perform the DFT+DMFT cal-
culations for systems, for which one has to construct the Slater Hamiltonian
(Eq. (3.79)) with the full $U$ matrix. The code can also be used in the case
of a system with more than one inequivalent site. In particular, in can also
be applied to oxide heterostructures. A summary of the implementation is
presented in figure 4.3.
Figure 4.3: The summary of the implementation. Dark green labels ASCII input/output files or generated plots. Light green boxes are short descriptions. Blue color denotes python source files.
4.2 Benchmarks

In order to validate the implementation of the new code several tests for well-examined materials have been performed. The following systems are used for these benchmarks:

- SrVO$_3$,
- NiO.

All benchmarks are compared with literature data. Benchmarks are used to demonstrate, that the inclusion of both correlated and non-correlated states is valid. Moreover, these benchmarks also verify the correct treatment of equivalent and inequivalent correlated sites.

4.2.1 SrVO$_3$: one site versus many sites ($t_{2g} + O\, 2p$)

As the first benchmark system, SrVO$_3$ is considered. SrVO$_3$ itself is a well examined system [23]. In the case of this system, bands around the Fermi level, with predominant V-$t_{2g}$ character, are well separated from other bands. Moreover, in most of available published results V-$t_{2g}$ states alone are used as a correlated basis. Below bands with predominant V-$t_{2g}$ character, are bands with the predominant O-$2p$ character. Since these bands in principle correspond to the antibonding states resulting from the hybridization O-$2p$ with V-$t_{2g}$, they have also some V-$t_{2g}$ character. It is therefore reasonable to include these states in the description. Furthermore, in the bigger basis, resulting MLWFs with the V-$t_{2g}$ character become more localized and atomic like. Moreover, by considering the bigger basis, it becomes possible to verify if the implementation can handle properly systems with both correlated and non-correlated states. In addition, simple tests are performed to verify if the implementation of the symmetry treatment is valid.

Apart from the non-correlated sites, also the implementation of symmetry transformations is verified. For this purpose a supercell is used, which contains 4 simple unit cells of SrVO$_3$. Calculations for the supercell with four units of SrVO$_3$ versus a unit cell with only one unit of SrVO$_3$ are compared. Different scenarios of the multiplicity for the correlated shells are considered. The following hypothetical systems are considered in this benchmark:

- a simple perovskite unit cell, $B$: in the system there is only one correlated shell (so there is also only one inequivalent correlated shell),
- $\sqrt{2} \times \sqrt{2} \times 2$ supercell, $4 \times B$: all 4 V sites are symmetry equivalent, there is only one inequivalent correlated shell,

- $\sqrt{2} \times \sqrt{2} \times 2$ supercell 4 sites, $2 \times B \times B'$: the 4 V sites are grouped into two inequivalent correlated sites, each is with the the multiplicity 2,

- $\sqrt{2} \times \sqrt{2} \times 2$ supercell 4 sites, $3 \times B \times B'$: the 4 V sites are grouped into two inequivalent correlated sites, one with the multiplicity 1 and another one with the multiplicity 3,

- $\sqrt{2} \times \sqrt{2} \times 2$ supercell 4 sites: $BB'B''B'''$: the 4 V sites are grouped into four inequivalent correlated sites, each with the multiplicity one (there is no symmetry equivalent sites in the system). All 4 sites are treated separately.

These are all hypothetical cases because they are as a matter of fact all different descriptions of the same system: SrVO$_3$. Therefore all calculations are expected to give the same results.

**DFT setup**

In order to perform these DMFT benchmark calculations, first the corresponding DFT calculations using Quantum Espresso have been performed. Details of these calculations are listed below.

- **Simple unit cell (1 V site):**
  - k-point mesh: $8 \times 8 \times 8$
  - plane wave kinetic energy cutoff: 45 Ry (612 eV)
  - lattice constant $a=7.2605$ Bohr (SrVO$_3$ has cubic crystal structure)
  - Non-spin polarised calculations
  - The following pseudopotentials from the QE site are used in the calculations:
    - * Sr.pbe-nsp-van.UPF
    - * V.pbe-sp-van.UPF
    - * O.pbe-van_bm.UPF

- **Super cell containing 4 V sites**
  - k-point mesh: $9 \times 9 \times 6$
- plane wave kinetic energy cutoff: 60 Ry (816 eV)
- lattice constant $a = 10.2679$ Bohr, $b = 10.2679$ Bohr, $c = 14.5210$ Bohr
- Non-spin polarised calculations
- The following pseudopotentials from the QE site are used in the calculations:
  * Sr.pbe-nsp-van.UPF
  * V.pbe-sp-van.UPF
  * O.pbe-van_bm.UPF

In this benchmark the extended $V-t_{2g}+O-2p$ basis of MLWFs is considered. For both systems MLWF, which consist of $V-t_{2g}$-like and O 2$p$-like orbitals, are constructed and used later to build the local Hamiltonian for DMFT calculations (Fig. 4.4). Even though $V-t_{2g}$-like bands have the predominant $V-t_{2g}$ character, they are also hybridised with O-2$p$ bands. Similarly O-2$p$-like are hybridised with $V-t_{2g}$ bands. Nevertheless, resulting MLWFs are quite localised. This is because of the maximally localization criterion, which favours, if there is such a possibility, atomic shapes of orbitals. Moreover, one can observe that in the contrast to the smaller $V-t_{2g}$ basis MLWFs [13], in the larger basis MLWFs are more localised and have a more atomic character (Fig. 4.4 and 4.5).

The atomic character of bands for four sites is presented in figure 4.6. The atomic character is represented in the form of fatbands. In this representation each dot for the given k-point represents the particular atomic character. The size of the dot defines how much the particular data point for the given k-point has the particular atomic character. For example, a small dot of O 2$p$ character for the given k-point means that the band at that k-point has a very small O 2$p$ character, whereas a big dot indicates a considerable O 2$p$ character. As it is in the case of one site, also in case of the supercell system $V-t_{2g}$ and O-2$p$ bands are hybridised with each other. Moreover, the atomic character of bands is consistent with already published results for one site [106]. States with the oxygen character are well below the correlated states. Bands with the $V-t_{2g}$ character are quite well separated from the bands with predominant $e_g$ character.

**DMFT setup**

DMFT calculations have been performed after constructing the MLWFs. For both simple perovskite and supercell systems the same setup has been
Figure 4.4: MLWF orbitals – one site. First three MLWFs have a clear V-$t_{2g}$ atomic character and they are centered on the V atom. Two other MLWFs have clear O-2p character and are centered on O atom. All MLWFs are quite well localized.
Figure 4.5: MLWF orbitals – four sites. It can be observed that $t_{2g}$ states are well localized and resemble atomic states. As it comes to MLWFs with the oxygen character only small tails can be observed.

Figure 4.6: Atomic character of bands for the supercell of $4 \times \text{SrVO}_3$ (fatbands). It can be seen that bands with the predominant O character are visibly below the correlated states. Also in the case of the correlated states a clear distinction between bands with the $e_g$ and $t_{2g}$ character can be done. The dotted horizontal blue line marks the upper and lower limit of band width for the particular groups of bands.
used:

- Kanamori form of the local Hamiltonian
- $\beta = 10 \ 1/eV$,
- $U = 6.0 \ eV$,
- $J = 0.65 \ eV$,
- $40$ DMFT loops,
- $24 \times 10^6$ QMC cycles,
- $50$ Legendre coefficients, the Green’s function is expanded in the Legendre basis, in which only the first $50$ terms are non-zero ($l_{max} = 50$),
- Held’s formula to evaluate the DC term (see Eq. (3.100) and (3.101)),
- spin flip and pair hopping terms included in the Kanamori Hamiltonian (those terms are included in all calculations presented here).

A solution of the Anderson impurity problem is affected by a numerical noise from Quantum Monte Carlo calculations. Because of that, even in the case of DMFT paramagnetic calculations, results for both spins are different. This essentially leads to the deterioration of accuracy during a simulation. If one knows in advance, that Green’s functions and thus also self energies are spin independent, one can enforce averaging over spins into the self consistency DMFT cycle and this way improve the quality of results.

As a matter of fact, for this benchmark averaging over spins has been done. Moreover, also averaging over states for each inequivalent correlated shell has been done. In general, most of the measured quantities are quite consistent with already published results. The biggest differences are observed for the DC correction term. For one site it is $6.14 \ eV$, and for four sites without taking into account any symmetry it is $6.25 \ eV$. Nevertheless, this agrees reasonably well with the published results for the simple perovskite structure ($6.6 \ eV$ in [106]).

Even though, as has been mentioned before, in most published investigations of SrVO$_3$ only a minimal V-$t_{2g}$ basis is considered, there exists also published data using larger, V-$t_{2g}$+O-2p basis. In order to compare the benchmark results with already published data the spectral function has been calculated. $A(\omega)$ has been calculated directly from the imaginary time lattice Green’s function by means of the MEM method. The obtained
Figure 4.7: $A(\omega)$. In all cases the same shape of the spectral function can be observed. However, the intensity of the spectral function from a) differs from other spectral functions intensities in b)-d). One has to keep in mind that in a), there is the spectral function, which corresponds to the simple perovskite system and in other cases the spectral functions are calculated for the supercell, which essentially has 4 times more units of octahedra, than the simple perovskite structure. Nevertheless, the obtained spectral functions agree well with [106].
spectral functions (Fig. 4.7) agree well with available resources, which are presented in Fig. 4.8.

In all reported references as well as in the performed benchmarks $U=6.0$ eV and $J=0.65$ eV is used. Held formula is used in the benchmark, whereas in the main reference [106], the AMF formula is used. Furthermore, the different localized basis is used here then in [106]: in [106] PLO and MLWFs here.

4.2.2 SrVO$_3$: Test of the full Slater Hamiltonian.

After successful results of the benchmark, in which SrVO$_3$ has been treated within the V-$t_{2g}$+O-2p localized basis, another benchmark has been performed. Additional bands at higher energies with the predominant V-$e_g$ character have been included in the DMFT Hamiltonian. In this case, since we have all 5 $d$ orbitals in the system, the Kanamori Hamiltonian is not applicable. Therefore, the goal of this benchmark is to test the implementation of the Slater Hamiltonian containing the full matrix $U$. In this benchmark calculations have been performed, with the larger basis, only for the simple perovskite system.

Details of DFT calculations are as follows:

- k-mesh: $9 \times 9 \times 9$
- plane wave kinetic energy cutoff: 60 Ry (816 eV)
- lattice constant: $a = 7.2605$ Bohr
- non-spin polarised calculations

The MLWFs are shown in figure 4.9. It can be seen that, five MLWF orbitals have a clear $d$ atomic shape and are centered on the V site. Three other MLWFs have an atomic $p$ shape and are centered on O atoms (this is what we should expect). In case of O-2$p$ only three representants are shown. In the considered basis there are three O 2p-like MLWFs for each of the three O atoms.

DMFT setup

The DMFT calculations have been performed with the following input parameters:

- $\beta = 10$ 1/eV,
- $U = 6.0$ eV,
Figure 4.8: a) The spectral function for SrVO$_3$ within DFT+DMFT using the projected local orbitals (PLO) scheme (more about PLO in [106]). Since exactly the same DMFT parameters: $\beta$, $U$, $J$ are used in the reference and in the benchmark presented here, this is the main reference ([106] Fig. 6). Nevertheless, one has to keep in mind that in this reference the different localized basis is used (in [106] PLO, here MLWFs). Moreover, Held’s formula is used in the benchmark, whereas in the reference [106], the AMF formula is used. Copyright (2015) by The American Physical Society. b) The orbitally resolved spectral function for SrVO$_3$ obtained by DFT+DMFT and PLO ([125] Fig. 7). IOP Publishing. Reproduced with permission. All rights reserved. c) The total $A(\omega)$ for SrVO$_3$, $dp$ Hamiltonian, which is built from vanadium $t_{2g}$ and oxygen $p$ states ([126] Fig. 8). In all references, within DMFT, $U$=6.0 eV and $J$=0.65 eV are used. Copyright (2015) by The American Physical Society.
Figure 4.9: MLWF in V $d$+O $2p$ basis. Quite good localisation of the obtained MLWFs can be observed. The first 5 MLWFs (a)-(e) resemble the atomic $d$ orbitals. They are centered on the V atom. The other three MLWFs (f)-(h) can be easily related to the atomic oxygen $2p$ states. The oxygen $2p$-like MLWFs are centered on the oxygen atoms. Only MLWFs for one oxygen atom are shown.
Figure 4.10: $A(\omega)$ for the V-$d$+O-$2p$ local Hamiltonian. The spectral functions of O-$2p$, V-$t_{2g}$ and V-$e_g$ are shown. It can be observed that the $t_{2g}$ states are non-zero at the Fermi level, while the $e_g$ states are zero at the Fermi level.

- $J = 0.65$ eV,
- 50 DMFT loops,
- $10 \times 10^6$ QMC cycles (for all 5 $d$ orbitals calculations take much longer than for only three V-$t_{2g}$ orbitals),
- 50 Legendre coefficients ($l_{max} = 50$),
- Held’s formula to evaluate the DC term,
- Slater Hamiltonian
- Averaging over states for each subset of the inequivalent correlated shell V ($e_g, t_{2g}$) has been done, also averaging over spins has been done.

In order to compare with [106], the spectral function has been calculated for both the correlated and non-correlated states (Fig. 4.10). From all $d$ states only the V-$t_{2g}$ states are non-zero at the Fermi level, the V-$e_g$ states vanish at the Fermi level. For the V-$e_g$ states the lower Hubbard peak is occupied ($\langle n \rangle_{e_g} \simeq 0.8$) and for the V-$t_{2g}$ states the lower Hubbard peak and the part of the quasiparticle peak below the Fermi level ($\omega = 0$) are occupied ($\langle n \rangle_{t_{2g}} \simeq 1.9$). The fact that, for the spectral function, which corresponds to V-$e_g$ MLWFs, the lower Hubbard peak is occupied, is due to the hybridisation between the V-$e_g$ states and the O-$2p$ states. The hybridisation between the V-$e_g$ states and the O-$2p$ states can clearly be seen...
in Fig. 4.6, in which fatbands are presented. If one compares Fig. 4.10 with the literature [106] one can see a minor difference below -2 eV. Differences occur most likely due to the usage of the different basis for the local Hamiltonian (respectively Maximally localized Wannier Orbitals – MLWF and Projected Local Orbitals – PLO). Additionally the hybridisation between the V-$d$ and O-2$p$ has been removed in [106], but in this benchmark it hasn’t been removed from the spectral function. The occupation in V-$t_{2g}$ (1.9 electrons/formula unit) case is almost the same as it is in the case of the smaller basis V-$t_{2g}$+O 2$p$ (1.8 electrons/formula unit). Altogether the total $\langle n \rangle$ on the $d$ states is 2.7 electrons/formula unit.

In comparison to the calculations for the V-$t_{2g}$+O-2$p$ basis in case of V-$d$+O-2$p$ basis the larger charge on the impurity site is observed. Also values of the DC energy and its derivative over the electron density are different for the different cases. It can be concluded, that the effective charge on the impurity problem depends on the size of the MLWFs basis used in the calculations.

4.2.3 NiO

Next, calculations for NiO have been performed. Similarly to SrVO$_3$, NiO is also a quite well examined material [127], [128], [129], [130]. However, from figure 4.11 it can be seen that in contrast to SrVO$_3$, the energy gap between the O-2$p$ and the Ni-$t_{2g}$ and the Ni-$e_g$ bands is much smaller in NiO. Even though, the oxygen bands are not entangled with Ni-$d$ bands, the upper limit of oxygen bandwidth nearly coincides with the lower limit of the Ni-$t_{2g}$ band width. Because of that it is widely agreed that they should be explicitly included in the DMFT calculations to obtain proper physics of the system [130]. Also, in the case of NiO there are more correlated electrons per unit cell in the system then in the case of SrVO$_3$. With 8 $d$ electrons at the Ni site, both Ni-$t_{2g}$ and Ni-$e_g$ states are occupied. In contrast to SrVO$_3$, in order to properly describe NiO, one therefore has to use the Ni-$d$+O-2$p$ basis for the DMFT calculations.

The following setup has been used for the DFT calculations:

- NiO has rock salt structure. The primitive cell of the fcc structure with $a_0 = 4.12$ Å has been used
- The following pseudopotentials are used in the calculations:
  - Ni.pbesol-n-rrkjus.psl.0.1.UPF
  - O.pbesol-n-rrkjus.psl.0.1.UPF

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• k-mesh: $9 \times 9 \times 9$

• plane wave kinetic energy cutoff: 60 Ry (816 eV)

Similarly to the benchmarks performed previously, the non-spinpolarised calculations have been performed to obtain the band structure for the construction of MLWFs. The obtained MLWFs have quite similar shapes to those obtained for SrVO$_3$ for the same size of the basis ($V-d+O-2p$). They closely resemble atomic orbitals centered at the different sites.

The setup for the DMFT calculations is as follows:

• $\beta = 10 \ 1/eV$,
• $U = 8.0 \ eV$,
• $J = 1.0 \ eV$,
• 39 DMFT loops,
• $100 \times 10^6$ QMC cycles (insulating solution requires higher precision in the QMC),
• 30 Legendre coefficients ($l_{max} = 30$),
• Held’s formula to evaluate the DC term,
• Slater Hamiltonian is used to account for all 5 $d$ states (Eq. (3.79)).
• Averaging over states for each subset of inequivalent correlated shell Ni ($e_g, t_{2g}$), has been applied, also averaging over spins has been applied.

The comparison of the benchmark result is made with the following references:

• [127], [128], [129]: $\beta = 10 \ 1/eV$, $U=8.0 \ eV$, $J=1.0 \ eV$
• [130]: $\beta = 5 \ 1/eV$, $U=8.0 \ eV$, $J=1.0 \ eV$

In general, the DMFT settings in these references are quite similar to the one used here. The different $\beta$ used in [130] does not affect too much the spectral function, it is still comparable with the $A(\omega)$ from the other authors. The material is paramagnetic for both $\beta = 10 \ 1/eV$, and $\beta = 5 \ 1/eV$. Those references, however, differ in the used variant of the double counting correction. Within this benchmark FLL (Eq. 3.99) has been used. The biggest challenge in this calculations, is the fact that NiO is a Mott insulator. In order to obtain the meaningful results for the insulating
solution quite higher precision calculations, with $100 \times 10^6$ QMC cycles have been needed. Nevertheless, a good agreement with published results has been achieved. The spectral function for NiO is presented in figure 4.12 and it is in the good agreement with [127], [128], [129], [130].

Apart from proving that the code is working properly, the benchmark described above, has shown how much the results depend on the choice of the double counting approximation. The Held formula, which has given quite promising results in the case of the correlated metal SrVO$_3$, is totally unsuitable for the insulating material, like NiO. In the case of the Held formula the value of the double counting correction is 43.5 ($\mu_{DC}$) eV, while in the case of FLL one gets 57.6 eV ($\mu_{DC}$) (the reported values are directly taken from the DMFT calculations). In the case of the Held formula the DC approximation is too small to shift correctly the spectral function of O 2$p$ states with respect to the correlated $A(\omega)$. The rule of thumb for choosing the proper DC term is that one should always monitor a gap between the spectral function, which corresponds to the non-correlated states and the correlated states. If this gap becomes non-physically large, then one should change the DC variant. In validating the size of the energy gap one can, for example, use DFT data. The spectral function of the non-correlated and the correlated states should be shifted only up to few eV with respect to DOS from DFT. If the gap is larger than that then one should consider to use other DC approximation. One has to keep in mind though, that there is no universal strategy to choose DC variant and in some cases it can be the biggest challenge in calculations.
Figure 4.11: Atomic character of bands around the Fermi level for NiO (fatbands). It can be seen that all three groups of bands: O-2$p$, Ni-t$_{2g}$, Ni-e$_g$ are almost overlapping. The horizontal dotted blue line marks the upper and lower limit of band width for the particular groups of bands.
Figure 4.12: Orbitally resolved spectral function of NiO for the interacting Hamiltonian. Solid black line Ni-$e_g$ states, red dotted line Ni-$t_{2g}$ states, green solid line O-$2p$ states.
Chapter 5

Applications

5.1 LaTiO$_3$

5.1.1 Bulk LaTiO$_3$

The goal of this preliminary calculations is to find the optimal calculation parameters suitable for LaTiO$_3$ - like systems and check if it is justifiable to treat LaTiO$_3$ structure from DFT calculations as a good approximation to its structure in the paramagnetic state, which occurs in the elevated temperature.

Benchmark calculations have been performed to find optimal parameters. All optimal, crucial DFT parameters are listed below:

- plane wave kinetic energy cutoff: 40 Ry (544 eV),
- k-point mesh: $6 \times 6 \times 4$,
- $\text{degauss}$: 0.01 Ry,
- Gaussian smearing algorithm,
- energy convergence threshold is set to $10^{-5}$ (atomic units),
- force convergence threshold to $10^{-4}$ (atomic units).

Energy cutoff in principle, defines the size of plane wave basis used to express Kohn-Sham orbitals. The larger cutoff the larger the basis (see also 3.1.4). The used value of 544 eV is a sensible compromise between the size of basis and the computation effort. The k-point mesh together with the $\text{degauss}$ parameter and used smearing alghoritm define sampling of the First Brillouin Zone. In general one would like to use as much dense k-point grid as possible but too large k-point grid leads to very heavy calculations with very little or even no effective gain in accuracy. Even if one
uses reasonable number of k-points calculations still may be quite demand-
ing. In order to further simplify calculations one can use some techniques to lower necessary number of k-points. In the current calculations I use Gaussian smearing with a 0.01 Ry smearing parameter [131]. Smearing is generally used for metallic system but it has to be used for LaTiO$_3$ as well because DFT predicts it to be a metal. In metallic systems the bands near the Fermi level are partially occupied. One has to use a high-density of k-points to account for this partial occupation. In smearing technique one substitutes the step function which defines occupation for a given k-point and band index by a smeared function for which partial occupation is allowed. This allows in principle, to use a less dense k-point grid but introduces an artificial contribution of temperature (smearing can be viewed as an artificial temperature) so one should use as small smearing as possible. In the calculations in interest step function is replaced by a Gaussian function with width defined by degauss parameter.

DFT is a self-consistency, iterative calculation. In each iteration, for the given positions of atoms, a new total energy of the system is calculated (ionic relaxation). One of the criteria to finalize calculations is defined by the difference in the total energy between the previous iteration and the current iteration. Once this difference is smaller than the user defined energy convergence threshold, it is considered that the total energy of the system has converged.

Another criterion for finalizing calculation is the force convergence threshold. When crystal structure is properly optimized the system is in equilib-
rium and there is no effective force on any of atoms. Of course one can only define zero within some numerical accuracy. In the discussed calculations convergence with respect to forces is satisfied when all components of all forces are smaller than the user-defined force convergence threshold.

Optimal parameters have been used to perform a full structural relax-
ation of bulk LaTiO$_3$. A comparison of the DFT results with the experimental results is presented in the table 5.1:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>$a$ [Å]</td>
<td>5.53</td>
<td>5.64</td>
<td>5.63</td>
<td>5.62</td>
</tr>
<tr>
<td>$b$ [Å]</td>
<td>5.62</td>
<td>5.59</td>
<td>5.62</td>
<td>5.61</td>
</tr>
<tr>
<td>$c$ [Å]</td>
<td>7.87</td>
<td>7.90</td>
<td>7.91</td>
<td>7.92</td>
</tr>
<tr>
<td>$\frac{90 - \theta}{2}$ [°]</td>
<td>8.2</td>
<td>9.6</td>
<td>9.3</td>
<td>8.1</td>
</tr>
<tr>
<td>$\frac{180 - \phi}{2}$ [°]</td>
<td>12.2</td>
<td>13.1</td>
<td>12.9</td>
<td>11.3</td>
</tr>
</tbody>
</table>

Table 5.1: Bulk LaTiO$_3$ – comparison with the experiment

Two of the compared parameters in the table above are the angles $\theta$
and $\phi$ (Fig. 2.3 and also 5.4 b), c)). Both angles are used as a convenient tool to measure octahedral tilts [11]. Those angles are a measure of the distortion of the octahedral network from the hypothetical perfect cubic structure (eg., a structure like in SrVO$_3$). In the case of cubic structure $\theta = 90^\circ$ and $\phi = 180^\circ$. In the case of a structure with $Pbnm$ symmetry like for example LaTiO$_3$ those two angles provide a compact description of octahedral tilts. The angle $\theta$ is related to $c^\parallel$ pattern and the angle $\phi$ to $a^-a^-$ in $a^-a^-c^\parallel$ Glazer pattern which corresponds to the $Pbnm$ group symmetry.

The main difficulty in a comparison between the experimental structure and the theoretical structure is due to the fact that it is impossible to relax the paramagnetic Mott-insulating phase at room temperature using DFT, since within DFT one can only relax a structure which essentially corresponds to the ground state at 0K. One way to deal with this problem is to perform non-spinpolarised calculations for the ground state and then compare it with experimental structures above critical temperature. In the case calculated non-spinpolarised structure compares well with experimental results one can say that non-spinpolarised calculations can reproduce correctly structure of bulk LaTiO$_3$ for temperatures above critical temperature, In particular, room temperature. If such an agreement can be observed then one can also have confidence that in the case of strained LaTiO$_3$ calculated structures will also be realistic.

Considering that lattice parameters calculated within DFT are typically within $\sim 1\%$ of experimental data, overall agreement with reported results can be claimed. In particular, $b$ and $c$ deviate even less than 1% from reported measurements. Furthermore, both angles $\theta, \phi$ are within range of experimental data. The only noticeable disagreement is for $a$: between 1.6 \% and 2 \% deviation depending with what experimental value the comparison is made. According to the experimental evidence $a$ and $b$ change in an anomalous way ($a > b$) with temperature [12]. Assuming that only tilts of perfect octahedra affect lattice constants, one obtains $b > a$ which is also observed in DFT calculation. One should expect that angles will change more than bond lengths, and they should be a driving force for changes in the structure to accommodate strain. Discrepancy from this trend occurs due to the anomalous change of bonds in octahedra. The reason for these anomalous changes is unclear, however.

In order to construct MLWFs one has to first perform DFT calculations and calculate band structure and density of states (DOS). The method of construction is presented in 3.3.2, here it is explained in detailed for the
Figure 5.1: Electronic structure of bulk LaTiO$_3$ from DFT. a) Density of states (DOS), both total and projected density of states are presented b) Band structure along the high symmetry k-points within the First Brillouin Zone. Due to the disentanglement of bands used for the construction of MLWFs not perfect match between KS states and MLWF can be observed. Both band structure and DOS are presented in reference to the Fermi level $\varepsilon_F$.

In the case of bulk LaTiO$_3$. In figure 5.1 one can see the electronic structure of bulk LaTiO$_3$ from DFT calculations. One can clearly see that oxygen states are located mostly within $[-8, -4]$ eV interval. At the same time both La $d$ states are located slightly higher than the Fermi level, at [2, 5] eV from the Fermi level. Similarly Ti $e_g$ states are also located above the Fermi level at interval [1, 5] eV. Moreover, one can see that around the Fermi level the dominating states are Ti-$t_{2g}$ states. Furthermore, one can see that the obtained band structure agrees well with already published results [13], even though in the reference experimental structure is considered and in the benchmark presented here relaxed structure is examined. It can be seen that DFT within non-magnetic PBE predicts bulk LaTiO$_3$ to be a metal where in reality it is a Mott insulator [13]. It can be concluded that DFT alone doesn’t give a correct description of bulk LaTiO$_3$. It is shown in [13] that the combination of DFT+DMFT can describe properly insulating bulk LaTiO$_3$.

In the next step of the creation of the local Hamiltonian one has to choose from the DFT band structure bands which will be used for the construction of MLWFs. From figure 5.1 one can see that there is a large gap between peaks with O $2p$ states character and peaks around the Fermi level with mainly Ti-$t_{2g}$ states from Ti. The corresponding gap is approximately 3 eV. Even though DFT gives only very approximate description
of the electronic properties of LaTiO$_3$ one can say that even if many-body effects are included, the gap between O 2$p$ states and Ti-$t_{2g}$ is still quite large. One can see also that around the Fermi level states have some character of La $d$ and O 2$p$ states. In principle, this additional contribution from other states than Ti-$t_{2g}$ is not crucial and it will be automatically included in Wannier orbitals. Conclusions derived from this benchmark are consist with observations stated in [13] that physics of LaTiO$_3$ can be captured by only considering bands with Ti-$t_{2g}$ character so MLWFs should be constructed exclusively from bands with Ti-$t_{2g}$ character.

It is relatively simple to determine the minimal size of the basis for the construction of the local Hamiltonian in MLWFs which will be used by the DMFT method. However, while constructing this Hamiltonian one has to face some technical difficulties. In bulk LaTiO$_3$ correlated $t_{2g}$-like states (states with considerable Ti-$t_{2g}$ character) are entangled with other states. In that case the construction of MLWFs is done according to the procedure which is described earlier in 3.3.3: first smooth pseudo-Bloch states are found and only then from them MLWF are constructed. Because of the way smooth pseudo-Bloch states are calculated, there will never be a perfect match in resulting band structures in the case of disentanglement. Such a perfect match can only be obtained in the case bands used for the construction of MLWFs are isolated from other bands. The crucial parameter for the disentanglement procedure is the energy window. It has to be chosen large enough to include all bands with significant correlated character but in the case it is too large it may introduce some numerical artefacts into the constructed MLWFs leading to artificially small spread [96]. In the following benchmark the energy window is chosen to be $[-0.9, 2.0]$ around the Fermi level. From figure 5.1 b) one can see that the band structure expressed in KS states from DFT doesn’t match exactly the band structure expressed in the MLWFs basis. This mismatch is caused by the way MLWF orbitals for bulk LaTiO$_3$ are constructed.

On the top of DFT, DMFT calculations has been performed using the local Hamiltonian expressed in the MLWF basis and developed code. The critical parameters used in DMFT are as follows:

- $U$ is varied
- $J$ 0.64 eV
- k-point mesh: $9 \times 9 \times 7$
- 50 Legendre coefficients ($l_{\text{max}} = 50$)
Figure 5.2: Estimation of critical \( U \) and orbital occupancy from DMFT. a) \( G \) at \( \beta/2 \) versus \( U \), b) Orbital occupancy versus \( U \) Orbital occupancy is expressed per spin. c) spectral function for varied \( U \).

- \( \beta \) 10 \( 1/eV \) (1190 K)
- 14 DMFT loops cycles
- 4 M QMC cycles
- only Ti-\( t_{2g} \) orbitals included

Within this project \( d^1 \) systems: LaTiO\(_3\), SrVO\(_3\) are considered, for which a minimal basis with only \( t_{2g} \) is assumed to be enough. In such a case only correlated orbitals of one shell are present in calculations and the double counting term becomes just a mere shift of the chemical potential.

The search for the critical \( U \) is done. Results of this search are shown in figure 5.2. Off diagonal elements of the Green’s function and self energy are
included in DMFT calculations as they are, without any transformation. The diagonal elements of $G(\tau)$ are examined in detail. Basing on equation 3.110 one can say that $G(\beta/2)$ from figure 5.2 a) is an approximation to a spectral function at the Fermi level for finite temperatures. Relatively large values of $G(\beta/2)$ indicate that system is a metal whereas when $G(\beta/2)$ is close to zero, means that the system is already insulating. It can be seen that all Ti $t_{2g}$ states become insulating for the same value of critical $U \simeq 5$. In figure 5.2 b) orbitally resolved occupations per spin are presented. It can be observed that even for relatively small $U$ there is a difference in occupation between orbitals and for $U \simeq 5$ eV mostly one orbital is occupied. In figure 5.2 c) spectral function $A(\omega)$ is presented. For low $U=3.5$ eV one can see quasiparticle peak characteristic for a metal. With increase of $U$ to 4.0 eV three peak structure appears. Three peak structure is typical for correlated metals. Apart from quasiparticle peak which becomes narrower two other peaks evolve: lower and upper Hubbard peaks. With increase of $U$ quasiparticle peak slowly vanishes and two Hubbard peaks become larger. At $U=5.0$ eV quasi particle becomes basically negligible and for $U=6$ eV it is clear that there is no spectral weight any longer at the Fermi level which means that system is an insulator. All presented sub-figures give a consistent picture of the Mott insulator transition for LaTiO$_3$. From figure 5.2 it can be estimated that bulk LaTiO$_3$ becomes insulating for $U \simeq 5$ which is in a good agreement with the literature [13]. In particular, spectral function is well reproduced. From figure 5.2 b) one can see that two out of three Ti-$t_{2g}$ states in LaTiO$_3$ are almost degenerate, their orbital energies differ only 8 meV (diagonal elements of $H_R$ are considered). The third orbital is slightly more occupied, the gap between it and the second lowest orbital is 50 meV (diagonal element of $H_R$ is considered). Since there is only one electron at LaTiO$_3$ Ti-$t_{2g}$ states, all occupancies sum to one. Small differences in occupancies show that splitting of Ti-$t_{2g}$ in bulk LaTiO$_3$ is relatively small. The benchmark calculations presented here have shown that produced code for DMFT calculations can reproduce the literature results for bulk LaTiO$_3$ and it is also suitable for DMFT calculations of strained LaTiO$_3$. Therefore the developed code is used also for DMFT calculations for strained LaTiO$_3$. Details of these calculations will be presented in chapter 5.1.3.
5.1.2 DFT calculations for strained LaTiO$_3$

Optimal lattice parameters

Within this project the influence of strain on properties of thin films grown in the epitaxial way is investigated. Epitaxy is the oriented growth of one crystalline material on the surface of a single crystal of a different material [133]. The adjective epitaxial means that:

1) one particular crystal plane of the crystal film comes into contact with surface of the host which is usually called substrate,

2) one particular crystallographic direction in the contact plane of the film is parallel to some crystallographic direction in the contact plane of the substrate.

If a film is grown according to this scenario it is called an *epitaxially strained film*. The schematic process of epitaxial growth is presented in figure 5.3 a). In a vicinity of an interface between a film and a substrate a periodicity of the film and the substrate change due to the lattice mismatch between the film and the substrate. In order to react to this mismatch, the film and the substrate adjust their lattice constants. If the film is thin enough then lattice constant of the substrate stays essentially unchanged and only the thin film adjusts its lattice constant to that of the substrate. Atoms in the thin film have to adjust their positions to lower the energy of the whole system. As a result bond lengths and angles in the thin film are different then those in its bulk form. The effect of the substrate on the structure of the film is decreasing with thickness of the thin film. If thickness of the thin film reaches some critical value then the formation of defects become a more favourable way of lowering the energy of the system. Occurrence of the defects leads essentially to full recovery of the bulk structure in the film.

Our model for strained LaTiO$_3$ is based on thin films of LaTiO$_3$ grown on SrTiO$_3$ [35]. It is reported that in the case of LaTiO$_3$ / SrTiO$_3$ the effect of strain on LaTiO$_3$ film is present for films which are of thickness of 45 nm or less [35]. SrTiO substrate crystallizes in the ABO$_3$ cubic perovskite structure (space group $Pm\bar{3}m$). As discussed in 2.3 LaTiO$_3$ exhibits a distorted perovskite structure with the orthorhombic symmetry space group $Pbnm$. In principle, there are two possible orientations in which LaTiO$_3$ can grow on SrTiO$_3$:

1) the longest lattice constant $c$ in strained LaTiO$_3$ is perpendicular to the surface of substrate,
2) the longest lattice constant \( c \) in strained \( \text{LaTiO}_3 \) is parallel to the surface of substrate.

Only the first orientation is considered in this project. Since the substrate has a cubic symmetry in strained \( \text{LaTiO}_3 \) two of its shorter lattice constants: \( a, b \) are the same and \( c \) is such that the system as a whole has minimal energy. Both \( a \) and \( b \) are equal to \( \sqrt{2} \) multiplied by length of the substrate lattice constant. Within this project series of strained \( \text{LaTiO}_3 \) structures, all with \( a = b \) and in the form of infinite crystals are considered. The substrate is not included explicitly, only its effect on position of atoms is considered. One has to keep in mind, however, that the propagation of octahedral tilt pattern from the substrate to thin film is also neglected. Applied strain is within \( \pm 5\% \) interval. For the coherent structure \( a = b = a_0 = 5.60 \text{ Å} \). The coherent structure is the strained structure with the lowest energy and optimized \( c \) lattice constant from set of all considered \( a = b \) values. Strain \( \varepsilon \) of each structure is linked with the value of the coherent lattice constant by the equation:

\[
\varepsilon = \frac{(a - a_0)}{a_0}
\]

where:

\( a \) – lattice parameter of the strained structure \( (a = b) \).

If \( a < a_0 \) then applied strain is called compressive, \( a > a_0 \) then strain is called tensile. In the case \( a_0 = a \) the structure is unstrained. The unstrained structure is called coherent structure.

In section 5.1.1 it is described how parameters for the bulk structure, also suitable for the strained structures, are determined. Since applied strain is of order of few percent one can say that DFT should have similar difficulties in description of the strained structures as it has with the bulk form. Nevertheless, one can say that since DFT approach gives a correct description of bulk \( \text{LaTiO}_3 \) geometry, it should also produce proper structures of strained \( \text{LaTiO}_3 \).

For all structures lattice parameter \( c \) is found according to the so-called energetic criterion. For each value of \( a = b \) calculations are performed for the series of \( c \) lattice constants. In each of these calculations positions of atoms are relaxed. The symmetry of the strained \( \text{LaTiO}_3 \) structures is fixed to \( \text{Pbnm} \). \( \text{Pbnm} \) is the symmetry for some orthorhombic perovskite systems in their thin films when the longest lattice constant \( c \) is oriented perpendicular to the hypothetical substrate, hypothetical, because the homoepitaxial strain calculations are performed in this project. In particular,
such an orientation is observed to be more favourable for strained CaTiO$_3$ in [134]. Since it is a system in many ways similar to strained LaTiO$_3$ such an orientation is also quite probable in this case. After set of structures with the reasonable guess for $c$ parameters are obtained data is fitted to the 3rd order polynomial and the longest lattice parameter $c$, which corresponds to the most stable structure, is calculated. When an optimal $c$ lattice constant is found for given in-plane strain from fit an additional calculation at exactly this value of $c$ is performed where all internal positions are relaxed. The example of such calculations is presented in figure 5.3 b). This procedure is repeated for different values of the in-plane constraint within a certain range, and in the next section the resulting trends corresponding to these equilibrium structures under the epitaxial constraint are analysed.

Within this project the starting point is the consideration of films of LaTiO$_3$ grown on SrTiO$_3$ but since the goal is to analyse the effect of strain for $d^1$ TM oxides in general, different values of strain than those reported in experiments are also considered, the conditions considered in this project are not thus limited to only one experiment on which LaTiO$_3$/SrTiO$_3$ is examined but cover a wider family of cases where LaTiO$_3$ is grown on different substrates.

**Structural analysis of strained LaTiO$_3$**

The next step to get a better insight is to analyse structural differences between the strained structures. First, one can for example compare changes of the out-of plane lattice parameter $c$. Such a comparison is presented in the upper panel of figure 5.4 a). In general, one would expect that while $a = b$ lattice constants reduce their length, the lattice constant $c$ should elongate and vice versa. Such is also the trend observed from figure 5.4 a). Moreover, one can also observe that the changes in the $c/a$ ratio agree well with experimental data from Ref. [35], represented by the blue diamonds. This is one more argument that the method of choice for determining the structure, is very reliable in predicting the strained LaTiO$_3$ structure.

In the bottom panel of figure 5.4 a) it can be seen how epitaxial strain influences the change in bond lengths. The bond lengths in the $ab$ plane ($L_2$, $L_3$), which is the plane parallel to the hypothetical substrate, increase with strain, and the bond lengths perpendicular to the $ab$ plane ($L_3$) reduce their length with strain. In order to further describe the evolution of the structure under strain, one can analyse the octahedral tilts in the unit cell. The amplitude of the octahedral tilts can be described by means of angles
Polynomial Fit of dataset using function: \( a0 + a1*x + a2*x^2 + a3*x^3 \)

\[
a0 = 6.0105 \times 10^1 \pm 8.47 \times 10^{-1}
\]

\[
a1 = -1.1890 \times 10^2 \pm 1.87 \times 10^0
\]

\[
a2 = 7.7424 \times 10^1 \pm 1.37 \times 10^0
\]

\[
a3 = -1.6539 \times 10^1 \pm 3.36 \times 10^{-1}
\]

\[
\text{Chi}^2/\text{doF} = 2.3994 \times 10^{-9}
\]

\[
R^2 = 0.9999921
\]

\[
\text{Adjusted } R^2 = 0.999987
\]

\[
\text{RMSE (Root Mean Squared Error)} = 4.8984 \times 10^{-5}
\]

\[
\text{RSS (Residual Sum of Squares)} = 1.6796 \times 10^{-8}
\]

Figure 5.3: Schematic picture of epitaxial strain growth b) Example of search for the optimal \( c \) parameter using the energetic criterion. Search in the case of structure with 5% of strain is shown. Both \( \chi^2 \) and \( R^2 \) indicate that fitting to the 3rd order polynomial is quite effective.

\( \Theta \) and \( \Phi \) (Fig.: 5.4 b) and c) ). As has been mentioned before, the angle \( \Theta \) describes rotations in the \( ab \) plane and \( \Phi \) tilts in the direction \( c \). In the middle panel of Fig. 5.4 deviations of \( \Theta \), \( \Phi \) (\( \theta \), \( \phi \) respectively) from the perfect cubic perovskite structure are plotted versus strain:

\[
\theta = \frac{90^\circ - \Theta}{2}
\]

\[
\phi = \frac{180^\circ - \Phi}{2}
\]

One can observe that \( \theta \) reduces with strain: octahedra have more freedom to rotate in the \( ab \) plane and the angle \( \theta \) has a tendency to approach
Figure 5.4: a) Calculated c/a ratio (upper panel), octahedral tilt angles (middle panel), and Ti-O bond distances (lower panel) in LaTiO$_3$ as function of in-plane strain. The c/a ratio is calculated from the orthorhombic lattice parameters (c/a $\approx \sqrt{2}$ for zero strain), and is compared to experimental data from Ref. [35] (filled diamonds). b) and c) show projections of the orthorhombically distorted Pbnm perovskite structure. The three different Ti-O bond distances are denoted as L1-L3. The angles $\theta$ and $\phi$ measure in-plane “rotations” and out-of-plane “tilts”, respectively, and are related to the specific bond angles, which are indicated in b) and c) by capital letters $\Theta$ and $\Phi$. Figure taken with permission from [36]. Copyright (2015) by the American Physical Society.

its value for the perfect cubic structure, but saturates for strain $+4\%$ and decreases slightly for the larger strain. On the other hand, the angle $\phi$ increases with strain. With increase of strain, the c lattice parameter is shorter and the octahedra are forced to tilt more in this direction. No discontinuities in the angles as a function of strain can be observed. Therefore one can see that the $a^-a^-c^+$ tilt pattern from the bulk state is maintained for all the explored strain values. Similar trends, but for a dif-
ferent strained perovskite, SrRuO$_3$, which as LaTiO$_3$, is also orthorhombic in its bulk state, are reported in the literature [135].

Crystal field splitting

From the DFT band structure for the optimized strained structures one can construct the Hamiltonian in the MLWF basis using wannier90 (see chapter 3.3.3 for more details) [96]. In order to do so, one has to define an energy window, within which the bands with the correlated character are located. In the similar fashion as for bulk LaTiO$_3$ in section 5.1.1 one should also expect disentanglement in the case of strained LaTiO$_3$. In principle, for each strained structure the energy window for the construction of the MLWFs has to be chosen individually. In the case of strained LaTiO$_3$ one expects dependence of strain on DOS around the Fermi level, however, the main observed features of the states around the Fermi level shouldn’t change, so the minimal basis of Ti-$t_{2g}$ should be enough for the DFT+DMFT calculations also for the strained structures.

From figure 5.5 one can see that bands with the mainly O-2$p$ character are in the considerable distance from the bands with the mainly Ti-$t_{2g}$ character. At the same time, from figure 5.6 one can observe that there are well defined bands with the mainly Ti-$t_{2g}$ character. Furthermore, because in LaTiO$_3$ there is only one electron occupying the $d$ states (it is $d^1$ system), only Ti-$t_{2g}$ states are partially occupied. Therefore, one can easily see that in all cases the bands, which have the strongly correlated character relevant for the construction of the Hamiltonian for the DMFT calculations, are located approximately within ± 1.6 eV around the Fermi level. In all cases the disentanglement procedure is needed. The dashed blue lines, which are parallel to x-axis, indicate the upper bound of the energy window taken for the disentanglement procedure. Since bands with the oxygen character are well separated from Ti-$t_{2g}$ bands, it is straightforward to define the lower bound of the energy window. The upper bound of the energy window has to be defined separately for each structure. It should be chosen high enough to include all bands with correlated Ti-$t_{2g}$ character, but not larger than needed [136]. The MLWFs, constructed from the Ti-$t_{2g}$-like bands with a carefully chosen energy window for the nominally unstrained case, are depicted in figure 5.8. It can be seen that the resulting Wannier functions resemble the atomic $d$ states with the Ti $t_{2g}$ character centered on the Ti sites, but also exhibit strong O-$p$-like tails located at the surrounding oxygen sites. Overall, the orbital character is less obvious compared to the similar Ti-$t_{2g}$ Wannier functions for SrVO$_3$ (see e.g. [114] and Fig. 4.4).
Figure 5.5: A comparison between bands with the O-2p character and those with the Ti-$t_{2g}$ character for the structure with -3.76 % compressive strain. A large gap between O-2p-like bands and Ti-$t_{2g}$ -like bands can be seen.

This is due to the tilts and rotations of the oxygen octahedra surrounding the Ti sites. Nevertheless, there is a good agreement between obtained Wannier functions and the N’th order muffin-tin orbitals calculated for LaTiO$_3$ in Ref. [13].

Using the MLWF basis one can construct a real space representation of the Hamiltonian. From this real space representation one can then obtain information about the crystal field splitting for each of the strained LaTiO$_3$ structures. In order to do so, one has to take the matrix elements of the Hamiltonian, which correspond to the vector $\mathbf{R} = 0$, and diagonalize the
block, which corresponds to any of the Ti sites. The obtained eigenvalues represent the orbital energies of the Ti-\(t_{2g}\) states in the crystal field for the particular strained structure. It is enough to examine the eigenvalues, which correspond to only one Ti site, because all other sites are related by the symmetry, and the crystal field splitting is the same for all of them. The effect of strain on the crystal field splitting is presented in figure 5.7 a). It can be seen that for the coherent structure two orbitals are almost degenerate and the third orbital has a significantly lower energy. The orbital with the lowest energy is lower in the energy by 108 meV compared to the other two Ti-\(t_{2g}\) states, whereas the splitting between the two energetically higher orbitals is rather small (25 meV). This is consistent with the orbital splittings calculated in Ref. [13] for bulk LaTiO\(_3\). In the case of tensile strain, the small splitting between the two higher states is approximately conserved, but the gap between the lowest state and two other states is increased. In the case of 6 \% tensile strain, the gap between the two higher states increases only slightly to 28 meV, but the gap between the lowest state and the second lowest state increases to 305 meV. On the other hand, in the case of compressive strain, the gap between the two higher states significantly increases. Moreover, the gap between the lowest state and the second lowest state is decreasing with increasing compressive strain. For compressive strain of \(-3.76\ \%\) the gap between the two higher states increases to 189 meV and the gap between the two lower states decreases to 65 meV. Thus, applying strain does not simply increase the overall crystal-field splitting, but also leads to the qualitative changes in the relative energy differences between the three Ti-\(t_{2g}\) Wannier orbitals. This analysis of the crystal field splitting for the strained structures suggests that LaTiO\(_3\) under compressive strain, which reduces the gap between the two lowest states, should be less insulating. This happens because in case of \(d^1\) system this splitting increases the partial (non-integer) filling of the corresponding levels. A similar picture arises from the analysis of the effect of strain on Ti-\(t_{2g}\) bandwidth, which is presented in figure 5.7 b). For each strained structure bandwidth is calculated as the width of the energy window, within which bands have the Ti-\(t_{2g}\) character, which is above some fixed threshold. For the compressive strain bandwidth calculated this way is visibly larger than in the unstrained case. The wider bandwidth is another confirmation that the compressively strained system may be more metallic than the unstrained case. On the other hand tensile strain has little effect on width of Ti-\(t_{2g}\) bands. One can see thus a clear direction in changes under strain.
Hopping integrals

Apart from considering the direct influence of nearest oxygen ligands around Ti sites, which leads to the crystal field splitting, one can also analyse the influence of the nearest TiO$_6$ octahedra, which surround Ti sites. This can be done by analysing hopping parameters, which are defined in terms of matrix elements between the MLWFs (please see chapter 3.3.3 for more details).

Fig. 5.9 shows the hopping amplitudes between neighbouring Ti sites as a function of strain. No obvious trends can be observed. While a weak overall decrease is visible for the in-plane hopping integrals with increasing tensile strain, no clear trend can be recognized for the out-of-plane hopping integrals. Some hopping amplitudes indeed increase with strain, consistent with the smaller lattice constant along $c$, but other hopping amplitudes decrease. This is, partially due to the complicated changes in the orbital character of the MLWFs as a function of the octahedral tilts, but can also partially reflect the fact that the trends expected from the changes in bond distances are opposite to the trends expected from the bond angles. For compressive strain, the shorter in-plane bond distances would in principle, enhance the corresponding hopping amplitudes. On the other hand, the simultaneous increase of the angle $\theta$ leads to a stronger distortion of the in-plane Ti-O-Ti bond angle, which is detrimental to the hopping. Thus, the trends expected from the changes in bond distances and bond angles are opposite to each other and it is unclear how the hopping between the Ti-$t_{2g}$ states at neighbouring Ti sites will be affected by the structural changes.

Nevertheless, one can still say that DFT data shows a reasonable trend of changes in electronic properties under applied strain. In principle, basing only on the DFT results one can say that the changes in the crystal field splitting show the trend, which is also observed in the experiment: that compressive strain makes the material more metallic. One has to keep in mind however that DFT gives rather a poor description of the electronic properties. In particular, DFT predicts both the bulk structure and the strained structures of LaTiO$_3$ to be metallic. Moreover, the changes of the hopping integrals under strain, which have been calculated from DFT data, seem to be quite complex and does not give a clear answer whether hopping integrals are enforcing metallicity of LaTiO$_3$ under compressive strain or not. One has to use a better method to describe the electronic properties of strained LaTiO$_3$, e.g. DMFT, in order to really confirm a Mott insulator-metal transition under applied strain. A detailed description of results
from DMFT calculations for LaTiO$_3$ is presented in the following sections.

### 5.1.3 DMFT calculations for strained LaTiO$_3$

**Effect of epitaxial strain on critical U**

In order to obtain a correct description of the electronic properties of strained LaTiO$_3$, DMFT calculations have been performed. Calculations have been performed with the following parameters:

- $12 \times 10^6$ QMC cycles
- $\beta = 40.0$ [1/eV] (T=290 K)
- 15 DMFT cycles
- Legendre coefficients: 40 ($l_{max} = 40$)
- $U$ was varied between 4 eV and 5.9 eV
- $J = 0.64$ eV

Within these calculations, the off-diagonal elements between the different orbitals on the same site are taken into account both for the local Green’s functions and the self-energy. Such the off-diagonal elements appear due to the symmetry-lowering associated with the octahedral tilts. They are essentially zero in the case of cubic perovskites. In figure 5.10 a) the trace of the total Green’s function at the imaginary time $\tau = \beta/2$ as a function of $U$ is presented. A comparison between different strain values is made. Based on the relation from Eq. (3.110) this can be used as a measure of the total spectral function at the Fermi level. It can be seen, that there is a change from $TrG(\beta/2) \neq 0$ to $TrG(\beta/2) \simeq 0$ in the interval $4.0 \text{ eV} < U < 5.5 \text{ eV}$ for all compressive strain values, i.e. the system undergoes a metal-insulator transition with increasing $U$. Moreover, it can be seen, that epitaxial strain has a pronounced effect on the critical $U$ for this transition. While tensile strain strongly decreases the critical $U$ (to values smaller than 4 eV for $\varepsilon > 2.26 \%$ ), compressive strain has the opposite effect, and increases the critical $U$ to slightly above 5 eV at $-3.76 \%$ strain.

In other words, the trend, which is already noticeable from DFT calculations, is confirmed by data from DMFT calculations: compressive strain is capable to change LaTiO$_3$ into a metal, while tensile strain should essentially preserve an insulating properties of bulk LaTiO$_3$. Assuming a realistic $U$ for the Ti-$t_{2g}$ Wannier orbitals in the range of 4.5-5 eV, it
can be seen that a strain-induced insulator-to-metal transition occurs in LaTiO$_3$ for compressive strain of the order of $-2\%$. This is consistent with the experimental observation of metallic conductivity in thin films of compressively strained LaTiO$_3$ grown on SrTiO$_3$ ($-1.6\%$ strain) $[35]$. 

In order to better visualise discussed the insulator-to-metal transition, the orbitally-resolved spectral functions for different strain values have been calculated for $U = 4.88$ eV. They are presented in figure 5.11. The spectral functions are obtained from the imaginary time Green’s functions by the analytic continuation using the maximum entropy method $[111]$. The spectral functions obtained in the insulating state for zero strain agree well with those reported in Ref. $[13]$ for bulk LaTiO$_3$. All spectral weight below zero energy corresponds to the occupied orbital with lowest energy. For $-1.75\%$ strain, the gap is closed in the spectral function for all three occupied orbitals. Finally, at $-3.76\%$ strain, strong quasiparticle features appear around zero energy, consistent with $TrG(\beta/2) \approx 0$ shown in Fig.5.10.

In summary, calculations have are consistent with experimental results even with neglecting interface effects. It can be concluded that, in the case of LaTiO$_3$ which is a $d^1$ system, the changes of the lattice parameters followed by the changes of the atomic positions due to epitaxial strain are enough to make LaTiO$_3$ metallic. Taking into account the accuracy of the DFT method, it can be predicted that, if LaTiO$_3$ would be grown on hypothetical substrate for which it would experience compressive strain 1-2\% it should be metallic. Moreover, if the thin film would experience even larger compressive strain while grown on the substrate, than it should stay metallic and even show a better characteristic as a metal.

Even though it is clear that compressive strain alone is indeed enough to turn LaTiO$_3$ into a metal the reason why it occurs has to be clarified. From figure 5.10b, which shows the orbital occupancies as a function of $U$ for different strain values, one can observe that the changes in the crystal-field levels are mirrored in the orbital occupations calculated within DMFT. For large tensile strain, the energetically lowest orbital is essentially completely filled, whereas the other two orbitals remain empty. With increasing compressive strain, one of the two empty orbitals gains some occupation at the expense of the filled orbital. This trend can clearly be seen from the occupations for large $U$, i.e. where the system is insulating. The transition to the metallic phase is then accompanied by a strong charge transfer from the nearly filled into the nearly empty orbital, while the third orbital remains mostly unaffected. I have verified that the basis diagonalizing the local occupation matrix is very similar to the crystal field basis diagonalizing the
local Kohn-Sham Hamiltonian $H_0$. The scalar product between the eigenvector corresponding to the lowest crystal-field orbital and the eigenvector corresponding to the \textit{nearly-filled} orbital is larger than 0.96 for all strain values. It thus appears that the decrease of the splitting between the two lowest crystal-field levels under compressive strain is crucial to facilitate the electron exchange between these two states within the metallic state. In contrast, tensile strain strongly increases this crystal-field splitting and thus enforces the insulating state, i.e. the critical $U$ for the transition is strongly reduced (see Fig. 5.10). This suggests that the tendency towards the metallic phase under compressive strain is controlled by changes in the crystal-field energies. In other words, it seems that the changes in the crystal field splitting are the driving force for the observed metal-insulator transition. Further evidence for the strong effect of the crystal field splitting on induced metallicity is the resolved real part of the self-energy at zero frequency, which can be viewed as an additional \textit{effective} chemical potential shift [137], it is shown in figure 5.10 c). As can be seen from Fig. 5.10 c), where $\Sigma(0)$ has been approximated by its value at the lowest Matsubara frequency, the electron-electron interaction strongly enhances the splitting between the energetically lowest and the two higher lying orbitals in the insulating regime and effectively shifts the chemical potential beyond the boundaries of the noninteracting bands [137].

In order to verify this hypothesis, one can decompose strain into two components:

- strain with the fixed hopping integrals,
- strain with the fixed crystal field splitting,

and analyse each of those components separately. An analysis of strain with the fixed hopping integrals can be performed in the following way. One can substitute the hopping integrals from the original strained structure by the hopping integrals from the reference structure. As the reference structure one can use the unstrained, coherent structure. In the case of the fixed hopping integrals, I constructed the real space representation of the Hamiltonian for the artificial system, which corresponds to the given original strained structure, by putting on-site part of the Hamiltonian, which corresponds to the given original strained structure into the unstrained system. By on-site (for $R = 0$) I mean blocks which correspond to each correlated site:

- Site one $H_{1,1}, H_{1,2}... H_{3,3}$
- Site two $H_{4,4}, H_{4,5}...H_{6,6}$
- Site three $H_{7,7}, H_{7,8}...H_{9,9}$
- Site four $H_{10,10}, H_{10,11}...H_{12,12}$

In all systems created that way, the hopping integrals are from the reference structure and they are fixed. While the hopping integrals are fixed, one can easily analyse the effect of the changes of the crystal field splitting under applied strain in detail.

On the other hand in the case of the fixed crystal field splitting, one can create the fictitious systems by putting on-site part of the Hamiltonian, from the reference structure into the strained structure. This way for the different values of strain the crystal field splitting stay constant and only the hopping integrals are changing. In that situation one can easily analyse changes of the hopping integrals with strain.

Both components of strain are referred later in the text as fake strain. Results of the calculations for fake strain are discussed in detail in the next chapter.

Effect of crystal field and hopping parameters on the critical $U$

Fake strain calculations have been performed with the following parameters:

- $24 \times 10^6$ QMC cycles
- $\beta$ 40.0 [1/eV] ($T=290$ K)
- 20 DMFT cycles
- Legendre coefficients: 50 ($l_{\text{max}} = 50$)
- $U \in [4,5.9]$ eV
- $J=0.64$ eV

The effect of the fixed hopping integrals on the critical $U$ is presented in figure 5.13. It can be seen that in the case of compressive strain, the critical $U$ for the strained structures with the fixed hopping integrals is only slightly larger than that from the reference, unstrained structure. It means that if only the crystal field splitting is varied then the system is expected to be a closer to MIT, but only this effect may not be enough for the system, to undergo the transition to metal under compressive strain.
At the same, in the case, in which only the crystal field splitting is varied, system becomes insulating for the relatively low $U$, in comparison to the reference structure.

However, in the case where the fixed crystal field (Fig. 5.12), the critical $U$ is significantly increased with compressive strain. It means that in fact the hopping integrals plays the crucial role in observed metallicity under compressive strain for LaTiO$_3$. In case, only the hopping integrals are varied in the system, the critical $U$ for 4.26 % strain is only slightly smaller then that from the unstrained case.

Basing only on the fake strain calculations, one can say that the changes in the hopping integrals are the driving force for the observed MIT in strained LaTiO$_3$. 
Figure 5.6: Atomic Ti-$t_{2g}$ character of bands around the Fermi level. A comparison between different strained structures is shown: for $-3.76$ % strain (a), for the unstrained case (b), and for $+6.0$ % strain (c). The size of the green dots represents the Ti-$t_{2g}$ character in the corresponding Bloch function. The dashed blue lines mark the upper boundaries of the energy window used to obtain the maximally localized Wannier functions. All energies are expressed in reference to the Fermi level $E_F$. Figure taken with permission from [36]. Copyright (2015) by The American Physical Society.
Figure 5.7: a) Crystal field splitting calculated from the Hamiltonian expressed in ML-WFs. Zero energy denotes the Fermi level for each strain value. b) Width of bands with Ti-\(t_{2g}\) character. Figure taken with permission from [36]. Copyright (2015) by The American Physical Society.
Figure 5.8: The three maximally localized Wannier functions located on the same Ti site, calculated for the nominally unstrained structure. The corresponding Wannier functions are obtained by initial projection on $d_{xy}$ (a), $d_{yz}$ (b), and $d_{xz}$ (c) orbitals, respectively. Figure taken with permission from [36]. Copyright (2015) by The American Physical Society.
Figure 5.9: Nearest neighbour hopping amplitudes corresponding to hopping between effective Ti-t_{2g} Wannier functions, as function of epitaxial strain. a) hopping along the orthorhombic c direction. b) hopping within the a – b plane. The orbital character that are used to denote the various hopping amplitudes refers to the initial projections used to obtain the corresponding Wannier functions. As can be seen from Fig. 5.8, the actual orbital character of the resulting Wannier functions can exhibit significant deviations from this initial projection. Figure taken with permission from [36]. Copyright (2015) by The American Physical Society.
Figure 5.10: a) Trace of the local Green’s function at $\tau = \beta/2$ as function of the interaction parameter $U$, calculated for different values of epitaxial strain. b) Occupations as function of the interaction parameter $U$, calculated for different strain values. c) Effective chemical potential, $\mu - \text{Re}\Sigma(\omega_0)$, as a function of the interacting Hubbard parameter $U$, calculated for different strain values. The three different orbitals for each strain are indicated by solid, dotted, and dashed lines in b) and c), in order of decreasing occupation. The dashed and dot-dashed horizontal lines in (c) indicate the band-edges of the noninteracting system for 0% and 3.76 % strain, respectively. In a) and c), the Fermi level is used as the zero energy reference for each strain value. Figure taken with permission from [36]. Copyright (2015) by The American Physical Society.
Figure 5.11: Orbitally-resolved spectral functions for $U = 4.88$ eV and $\varepsilon = 0$ (upper panel), $\varepsilon = -1.75\%$ (middle panel), and $\varepsilon = -3.76\%$ (bottom panel). The inset shows the behaviour close to $\omega = 0$ for $\varepsilon = -1.75\%$. Orbitals 1, 2, and 3 correspond to the eigenfunctions of the occupation matrix and are ordered with decreasing occupation. Figure taken with permission from [36]. Copyright (2015) by The American Physical Society.
Figure 5.12: Fake strain: calculations with fixed crystal field. Three representative cases for fake strain are presented: tensile strain 4.26 %, unstrained case 0.0 %, compressive strain –3.76 %. A significant increase of the critical $U$ for compressive strain can be observed.

Figure 5.13: Fake strain: calculations with fixed hopping integrals. Three representative cases are presented: tensile strain 4.26 %, unstrained case 0.0 %, compressive strain –3.76 %. A large effect of the crystal field splitting in the case of tensile strain can be observed.
5.2 SrVO\textsubscript{3}

5.2.1 DFT calculations

Optimal lattice parameters

In order to gain more insights in the effect of epitaxial strain in \textit{d}\textsuperscript{1} systems strained SrVO\textsubscript{3} has been investigated. Within this project only the tetragonal form of SrVO\textsubscript{3} is considered. There are many implications of choosing the tetragonal form of strained SrVO\textsubscript{3}. In particular, the hopping integrals are expected to be much simpler than in the case of LaTiO\textsubscript{3}. Another aspect is the octahedral tilts in general. By comparing strained LaTiO\textsubscript{3}, in which the octahedral tilts are present with strained, tetragonal SrVO\textsubscript{3}, which has \textit{P4/mmm} symmetry, one can better see the effect of the octahedral tilts in the \textit{d}\textsuperscript{1} systems on their electronic properties. Moreover, in the case of tetragonal strained SrVO\textsubscript{3} there is only one possible orientation, in which it can grow on the hypothetical substrate. In other words the simple but quite realistic structure of strained SrVO\textsubscript{3} may be easier to interpret and compare with the experiment than strained LaTiO\textsubscript{3}.

In order to perform calculations for strained SrVO\textsubscript{3}, first the optimal lattice parameters for the strained structures have to be calculated in the similar manner as in the case of LaTiO\textsubscript{3}. Also bi-axial, epitaxial strain is applied to the SrVO\textsubscript{3} systems. In all calculations, lattice constants lengths are fixed and positions of the atoms are fixed by the symmetry. An energetic criterion for finding the optimal lattice constant is used, e.g both \textit{a} and \textit{b} lattice constants are set to equal value (epitaxial strain) and then for the fixed values of \textit{a} = \textit{b} the calculation for a set of the \textit{c} lattice parameters are performed. As before the optimal \textit{c} parameter is found from fitting to the 3rd order polynomial for structures with fixed \textit{a} = \textit{b}. An example of such calculations is presented in figure 5.14. The crucial accuracy parameters used in the calculations are as follow:

- plane wave kinetic energy cutoff: 40 Ry (544 eV),
- k-point mesh: \(7 \times 7 \times 7\),
- de gauss 0.01,
- default smearing algorithm (Gaussian smearing),
- energy convergence threshold is set to 1.d-5,
- force convergence threshold to 1.d-4.
The theoretical constant $a = b = a_0$ for the coherent structure is 1.0054 in units of 7.2605 a.u. The optimal lattice constant $c$, for such a value of $a = b = a_0$, is 1.0043 in units of 7.2605 a.u. The $c$ lattice constant differs from the $a$ lattice constant 0.1%. It can be concluded that within the numerical accuracy $a=b=c$ for the coherent structure, which has been obtained from the DFT method. This is consistent with experimental data, according to which bulk SrVO$_3$ is cubic [13].

In the case of the other structures, strain leads to the lowering of the symmetry to $P4/mmm$. In all calculations reported here the octahedral tilts are not considered i.e., it is assumed that strain of the order ±4% is small enough to conserve the octahedral pattern $a^\circ a^\circ a^\circ$ from bulk SrVO$_3$. One of course should expect that at some point epitaxial strain should introduce octahedral tilts to strained SrVO$_3$. However, it should happen for very high strain. With increasing strain, at some it will be energetically more favourable to change bond angles rather than continue to shorten (elongate) bonds. Such high strain, however, is very unlikely to be reproduced in the experiment.

**Structural analysis of strained SrVO$_3$**

A detailed structural analysis of strained SrVO$_3$ is presented in figure 5.15. In particular, in figure 5.15 a) it is shown how the volume of strained SrVO$_3$ changes with respect to the lattice parameter $a$. The data points obtained from experiments are shown as black dots, and the red line represents the polynomial fit to the data. The fit is given by the function $a_0 + a_1x + a_2x^2 + a_3x^3$ from $x = 0.9$ to $x = 1.1$. The coefficients of the fit are:

- $a_0 = 2.2771 \times 10^1 \pm 4.4 \times 10^{-1}$
- $a_1 = -6.2442 \times 10^1 \pm 1.325 \times 10^0$
- $a_2 = 5.6908 \times 10^1 \pm 1.327 \times 10^0$
- $a_3 = -1.7232 \times 10^1 \pm 4.42 \times 10^{-1}$

The goodness of the fit is quantified by the following metrics:

- $\chi^2$/dof = 1.2192e-07
- $R^2 = 0.99990$
- Adjusted $R^2 = 0.99987$
- RMSE (Root Mean Squared Error) = 0.0003492
- RSS (Residual Sum of Squares) = 2.07259e-06

Figure 5.14: Example of search for the optimal lattice parameter $c$ in the case of SrVO$_3$. An example of fitting to the third order polynomial is presented.
SrVO$_3$ changes with strain. One can clearly see that the volume of strained SrVO$_3$ is expanding with strain. The relation volume versus strain is approximately linear. It can be concluded that changes in two dimensions caused by epitaxial strain are not fully accommodated by changes in the third direction, changes of the lattice constant $c$.

Also in figure 5.15 b) a relation between changes in $a$, $b$ ($a=b$) versus $c$ lattice parameters is presented. One can observe the quite intuitive fact, that while $a$ and $b$ parameters elongate the $c$ parameter reduces and vice versa. In contrast to LaTiO$_3$, in the case of strained SrVO$_3$, since no octahedral distortions are present, the changes of the in-plane lattice constants parallel to the hypothetical substrate have to be fully accommodate by the changes of the lattice parameter $c$.

Finally, one can see in figure 5.15 c) that the coherent structure, which is quite close to bulk SrVO$_3$ is the most stable structure. Both structure under compressive and tensile strain have higher energies, they are less stable. The larger amplitude of strain is the bigger difference between the strained structure and the coherent structure.

Overall, the structural analysis of strained SrVO$_3$ leads to intuitively consistent conclusions. Thus, it can be confirmed that, for all strained structures well converged $c$ lattice parameters are obtained. Those properly converged strained structures can be used for further analysis of the electronic properties.

Crystal field splitting

A similar construction of MLWFs has been made as in the case of LaTiO$_3$. In figure 5.16 the bands relevant for the construction are presented for three representative structures. In the case of the unstrained coherent structure no entanglement with other bands is detected. This is consistent with data for the bulk structure from Ref. [13]. One can see that also in all other cases the bands with V-$t_{2g}$ character are quite well separated from other bands, and even if there is a need for applying the disentanglement procedure, the determination of the energy window is much easier than in the case of LaTiO$_3$ (please compare with chapter 5.1.2). This simplification in the construction of MLWFs is caused by the lack of octahedral tilts in strained SrVO$_3$.

Also, the MLWFs themselves look simpler than for the case of LaTiO$_3$. MLWFs for the unstrained structure are depicted in figure 5.17. As in the case of LaTiO$_3$, oxygen tails can be observed. Nevertheless, a clear character of d-orbitals can also be detected. Moreover, it is possible to directly
Figure 5.15: Structural analysis of strained SrVO$_3$. a) The volume dependence on strain. b) The optimal c versus a. c) The total energy for SrVO$_3$ under epitaxial strain.

link each of the obtained MLWFs with a particular d-atomic orbital, $d_{xy}$, $d_{yz}$ or $d_{xz}$. Therefore, the notation for the atomic V-$t_{2g}$ orbitals will be used as a label for each MLWF. Also, in the case of the unstrained structure, all three MLWFs are related to each other by means of symmetry operations. For each strained structure, the MLWFs have more or less the same shape. However, oxygen tails are changing their size with strain. For compressive strain oxygen tails, which are parallel to the $xy$ plane, are more pronounced than the tails parallel to the $z$ axis. For the equilibrium structure, the oxygen tails are comparable in all three dimensions. For tensile strain, the oxygen tails along the $c$ axis are larger than the oxygen tails parallel to the $xy$ plane (one has to keep in mind that the direction of the oxygen tails are relative to the central V where the tail is located).

Due to the tetragonal symmetry of SrVO$_3$, in which there is only one
Figure 5.16: Bands with V-t_{2g} character for strained SrVO_{3} structures. a) −4.5 % compressive strain, b) 0.0 % (coherent structure), c) 3.4 % tensile strain.
Figure 5.17: a), b), c) MLWFs for the unstrained structure of SrVO$_3$. Each MLWF can be related to one of the $t_{2g}$ orbitals. All MLWFs have oxygen tails.
Figure 5.18: Crystal field splitting for strained SrVO$_3$. Zero energy denotes the Fermi level for each strain value.

octahedron, both $d_{xz}$ and $d_{yz}$ are degenerate (see Fig. 5.18). For compressive strain $d_{xz}$ and $d_{yz}$ orbitals have lower energies than $d_{xy}$, but for tensile strain $d_{xy}$ has lower energy than the two other orbitals. In the case of compressive strain the V-O bond lengths in the $ab$-plane are reduced. Because of that, the $d_{xy}$ orbital, which is oriented in the $ab$-plane, has higher energy than in the unstrained case. At the same time for compressive strain, the V-O bond lengths, which are parallel to the $c$-axis elongate, the oxygen ligands interact weaker with the $d_{yz}$ and $d_{xz}$ orbitals, and because of that those orbitals have lower energies than in the unstrained case. In the case of tensile strain the situation is opposite. The V-O bond lengths in the $ab$-plane are longer than in the unstrained case. The oxygen ligands interact weaker with the $d_{xy}$ orbital and lower its energy in comparison to the unstrained case. At the same time, the bond lengths parallel to the $c$ axis reduce their length. Both orbitals $d_{xz}$ and $d_{yz}$ have higher energies than those for the unstrained structure. Considering changes of the distance between the oxygen ligands and the V-$t_{2g}$ orbitals under applied strain and the symmetry of the system under epitaxial strain, this is the expected behaviour (Ref. [11]).

**Hopping integrals**

Also the hopping integrals, obtained from the real space representation of the Hamiltonian in the MLWF basis, have been analysed. The hopping
Figure 5.19: Hopping integrals between $t_{2g}$ MLWFs of neighbouring V sites. a) Hopping integrals in $x$ direction, b) Hopping integrals in $y$ direction, c) Hopping integrals in $z$ direction. The absolute values $|t|$ of the hopping amplitudes are shown.
integrals between neighbouring cells in each direction have been calculated (Fig. 5.19). Due to the high symmetry, the off-diagonal hopping integrals are zero.

For the hopping integrals in the $x$ direction the absolute values of the hopping integrals between $d_{xy}$-$d_{xy}$ and $d_{xz}$-$d_{xz}$ orbitals from the neighbouring cells reduce with strain. With increasing strain, the distance between orbitals in the $xy$ plane is increasing, and so the overlap between these orbitals in this plane is reduced. At the same time, the overlap between $d_{yz}$-$d_{yz}$ orbitals from the neighbouring unit cells in the $x$ direction is very small and is almost not changing with strain. It is only slightly decreasing with increase of strain. This is due to the planar shape of the $t_{2g}$ orbitals.

The hopping integrals in the $x$ and $y$ directions are in principle, equivalent, due to the symmetry relation between $d_{xz}$ and $d_{yz}$ orbitals (one can be transformed into another by a $90^\circ$ rotation around the $z$ axis) and the tetragonal symmetry of the applied epitaxial strain. Due to the different orientations of the $d_{yz}$ and $d_{xy}$ orbitals their oxygen tails are changing in a different way with strain. Because of this, degeneracies of the $d_{xy}$-$d_{xy}$ and $d_{yz}$-$d_{yz}$ hopping integrals are lifted.

In the case of the hopping integrals in the $z$ direction, the hopping integrals $d_{xz}$-$d_{xz}$ and $d_{yz}$-$d_{yz}$ between neighbouring unit cells, are degenerate due to the tetragonal symmetry induced by epitaxial strain. Absolute values of both these integrals increase with strain, because the distance between these orbitals is reduced in the $z$ direction with strain. This is caused by the fact that because of strain the $c$ lattice parameter is reduced, while the lattice parameters $a$ and $b$ are elongated, and the only way those changes can be accommodated by the system are changes of the distance between the atoms. On the other hand, the overlap between $d_{xy}$-$d_{xy}$ orbitals between neighbouring unit cell along the $z$ direction is very small and it almost does not change with strain.

Analysis of the band structure in perovskites using the tight binding model

The following subsection is based on an undergraduate student’s project done by Klara Peininger, who has been supervised by the author.

So far, two cases have been studied: strained distorted LaTiO$_3$ with $Pbnm$ symmetry and strained SrVO$_3$ with much higher $P4/mmm$ symmetry. In the simple case of strained SrVO$_3$ only the bond lengths are changing under applied strain. On the other hand in the much more complex strained LaTiO$_3$, both the bond angles and bond lengths are changing with applied strain, and in particular the interpretation of the hopping in-
integrals becomes complicated. At the same time, the structural changes under strain in the case of strained SrVO$_3$ are easy to interpret. However, the conclusion derived from such an analysis are only applicable to the relatively narrow class of perovskite compounds without octahedral tilts. In contrast strained LaTiO$_3$ covers a much larger class of compounds. After all, many perovskite systems are distorted in their bulk form, and have $Pbnm$ symmetry [41],[138]. One of the possible ways to better understand what happens for such systems, is to continuously modify the crystal structure of the system from cubic SrVO$_3$ to the more complex tilted system with bond lengths kept constant, but with octahedral tilts. It can be done quite easily if one builds a model, in which one focuses only on rotations. One can use bulk SrVO$_3$ as the starting point and then introduce octahedral tilts but fix the bond lengths and analyse changes in the hopping integrals. That was the motivation for this student project. The following tilts pattern have been considered in this project:

- $a^0a^0c^+$ – in this tilt pattern octahedral tilts occur only along the pseudo cubic $c$ axis and adjacent octahedra along the pseudo-cubic $c$ axis rotate in the same direction.
- $a^0a^0c^-$ – as in the previous case the tilts occur only along the pseudo cubic $c$ axis but this time adjacent octahedra along the pseudo cubic $c$ axis rotate in opposite direction.
- $a^-a^-c^0$ – in this case rotations occur in the two pseudo cubic axes $a$ and $b$. The angle of the rotations for both axes are the same, but the adjacent octahedra rotate in opposite directions.

These Glazers tilt systems, are presented in figure 5.20.

The main results of the student project are presented in figure 5.21. For all considered cases the angle of the octahedral rotation is varied between 0° and 20°. In all cases the introduction of tilts to the model SrVO$_3$-like system lifts the degeneracy between the V-$t_{2g}$-like orbitals. The rotations split the $d_{xy}$ and $d_{yz}/d_{xz}$ orbitals. For $a^0a^0c^+$ and $a^0a^0c^-$, the $d_{yz}/d_{xz}$ orbital lowers its energy in comparison to the $d_{xy}$ orbital, once octahedral tilts are enabled. In case of $a^-a^-c^0$ $d_{yz}/d_{xz}$ orbital have higher energy than $d_{xy}$ with increase of the rotation amplitude.

The hopping integrals can be easily understood if one considers that in a first approximation, they can be treated as atomic $d$ orbitals. In principle, the overlap between the $d_{xy}$-like orbitals from neighbouring sites for both $a^0a^0c^+$ and $a^0a^0c^-$ configurations along the $x$ direction decreases...
with increase of the distortion angle. For the \( a^{-}a^{-}c^{0} \) configuration, the overlap between \( d_{xy} \)-like orbitals from the neighbouring sites and is not affected by the amplitude of the octahedral distortions. In contrast, for the overlap between the \( d_{yz} \)-like and the \( d_{xz} \)-like orbitals along the \( z \) direction the hopping, is only slightly changing for the \( a^{0}a^{0}c^{+} \) case but it changes more in the two other considered cases. On the other hand the \( d_{yz} \) and \( d_{xz} \) orbitals in the \( y \) direction almost don’t depend on the tilting angle.

To summarise, in the case of the hypothetical SrVO\(_{3}\) systems with different octahedral rotations, the changes in the case of the crystal field splitting and the hopping integrals have a rather simple geometric interpretation. The investigation started by the supervised student seems to be quite promising. The next step would be to explore hopping integrals in the bigger basis, including both V-\( t_{2g} \) and O-p orbitals.
Figure 5.21:  a) Crystal field splitting and hopping integrals for the hypothetical SrVO₃ systems with different octahedral rotations. Since the \( d_{xz} \) and \( d_{yz} \) orbitals are degenerate, only the difference between \( d_{xy} \) and \( d_{yz} \) is monitored. b) Only the largest hopping integrals are presented. On the left hopping between \( d_{xy}-d_{xy} \) along \( x \) axis, in the middle hopping \( d_{xz}-d_{yz} \) along \( z \) axis, on the right hopping \( d_{yz}-d_{xz} \) along \( y \) axis are shown.
5.2.2 DMFT calculations

Effect of epitaxial strain on critical U

![Graph showing TrG(β/2) vs U for different strains](image)

Figure 5.22: Electronic properties of strained SrVO\textsubscript{3} after the inclusion of the many-body effects. a) The estimation of the critical U using Eq. (3.110).

In order to analyse the electronic properties of strained SrVO\textsubscript{3}, DMFT calculations have been performed based on the DFT results. The DMFT parameters, used in the calculations, are as follows:

- \( \beta \): 40 1/eV
- DMFT loops cycles: 40
- k-grid: 9 × 9 × 9
- \( J \): 0.65 eV
- \( 24 \times 10^6 \) QMC cycles
- Legendre coefficients: 50 (\( l_{max} = 50 \))

In order to examine the effect of strain on the electronic properties of SrVO\textsubscript{3}, a search for the critical U has been done. The search for the critical U is done using the approximated formula from Eq. (3.110). The relation between \( G(\beta/2) \) and the Hubbard parameter U for each strain structures is explored. The comparison of the critical U between the different structures is presented in figure 5.22. One can observe that for 3.4 % tensile strain the system becomes insulating for about U 5-5.5 eV, whereas for other cases, it
becomes insulating for $U$ larger than 6 eV. One can say that tensile strain is lowering the critical $U$, which makes material more insulating. At the same time compressive strain seems to have a little effect on the material: critical $U$ for strain 0.0 %, −1.5 %, −4.5 % is almost the same: $\approx 6.5$ eV. Since for the bulk material the realistic value of $U$ is 3.5-4 eV, it is very unlikely that in the case of the strained structures the value of $U$ would be above 5 eV. This means that under applied tensile strain it may be possible to make SrVO$_3$ it closer to MIT than it is in its bulk form, but a metal-insulator transition is very unlikely. Nevertheless, similar trends like in the case of LaTiO$_3$ are observed. Tensile strain seems to favour the insulating phase.

Effect of ”fake strain” on critical $U$

In order to better understand the electronic properties of strained SrVO$_3$ ”fake strain” calculations have been performed in a similar way as in the case of strained LaTiO$_3$. Two cases are considered: fake strain with the fixed hopping integrals and fake strain with the fixed crystal field. As it comes to fake strain with the fixed hopping integrals I put the on-site part of $H$ into the unstrained system, by on-site I mean blocks, which correspond to the correlated site, since the system is cubic one has to focus only on the diagonal elements. In the case of fake strain with the fixed crystal field I have taken on-site block of $H$ ($H_{11}$, $H_{22}$, $H_{33}$) from the reference system, the unstrained system and put into the original system. Then with such a constructed real representation of the Hamiltonian, the DMFT calculations have been performed. The DMFT calculations have been performed with the following parameters:

- $\beta$: 40 1/eV
- DMFT loops cycles: 40
- k-point grid: $9 \times 9 \times 9$
- $J = 0.65$ eV
- QMC cycles: $24 \times 10^6$
- Legendre coefficients: 50 ($l_{max} = 50$)

The results from these fake strain calculations are presented in figure 5.23. By looking at fixed hopping integrals one can clearly see that the crystal field alone doesn’t increase critical $U$ of the compressively strained
Figure 5.23: Fake strain for SrVO$_3$. a) fixed hopping integrals, b) fixed crystal field. Unstrained structure (green color) is used as the reference structure for the construction of fake strain.

SrVO$_3$ but in the case of tensile strain it has significant effect in pushing it closer to MIT. At the same time from figure 5.23 b) one can see that hopping integrals in compressively strained structures seems to have some effect on increasing the critical $U$. In summary the trends observed in the analysis of strained SrVO$_3$ for tensile strain are in good agreement with those observed for strained LaTiO$_3$. In case of the compressive strain behaviour of SrVO$_3$ and in LaTiO$_3$ is rather different.

Based on the obtained results one can say that the changes in hopping integrals increase the critical $U$ in case of compressive strain. In the case of tensile strain changes in crystal field splitting play a crucial role in lowering the critical $U$. Since the observations above have been done for two representative compounds of $d^1$, the observed trends can be extended to $d^1$ systems in general.

**DMFT – $J$ dependence**

Next, I have also investigated the $J$ dependence on the Mott transition in SrVO$_3$. One can use the atomic approximation to rationalize the $J$ dependence on the MIT transition. For one band, in the atomic limit, the Hubbard peaks become Dirac delta functions. In that case the Mott insulator gap $\Delta$ is defined in the following way:

$$\Delta = U$$ (5.2)
For the multi-band case the relation between $\Delta$, $U$ and $J$ is as follows [139]:

$$\Delta = \begin{cases} 
U - 3J & \text{for off half-filling} \\
U + (N - 1)J & \text{for half-filling}
\end{cases},$$

(5.3)

where:

- $N$– number of orbitals.

The *half-filling* means that in the system the number of electrons is equal to $N/2$. In case there is no half-filling in the system then it is said that the system is *off half-filling*. For the off half-filling $J$ is decreasing $\Delta$ and for the half-filling, provided that there is more than one state, $\Delta$ is increasing with $J$. These equations are valid for the systems with degenerate orbitals and large enough $J$. If $J$ is very small then orbital fluctuations have a dominant role and the trend will be different. In the case of the non-degenerate states (for example split by crystal field) one can usually distinguish subsets separated energetically from each other with the half-filling or not (like for example $t_{2g}/e_g$). One can then apply the equations above to each particular subset.

![Figure 5.24: Tr$G(\beta/2)$ versus $\Delta = U' - J$. $\Delta$ is the energy gap in the atomic limit for the off half-filling case.](image)

DMFT calculations have been performed with the following setup:

- $U' = 5.85$ eV ($U=U'+2J$)
- $J$ is varied
- k-point mesh: $9 \times 9 \times 9$
- 50 Legendre coefficients ($l_{\text{max}} = 50$)
Figure 5.25: Evolution of $A(\omega)$ in case of $J$ varied and $U$ fixed. Since for the unstrained case all orbitals are degenerate, the corresponding spectral functions are all the same. The energy gap in the limit of atomic approximation is monitored ($\Delta = U' - J$ [eV]). a), b), c) are ordered with respect to the decreasing gap. It can be observed that the gap estimated this way, for which MIT occurs, has approximately 5 eV. The gap is the energy gap in the atomic limit for the off half-filling case.
• $\beta = 40 \, 1/eV \, (290K)$
• 20 DMFT loops cycles
• $24 \times 10^6$ QMC cycles
• calculations for unstrained SrVO$_3$
• only V-$t_{2g}$ orbitals included

For the fixed value of $U$, $J$ has been varied. Unstrained SrVO$_3$ is examined. Three $t_{2g}$ orbitals occupied by only one electron are investigated (off half-filling case). It can be observed in figures 5.24, 5.25 that an increase of $J$ invokes MIT. From figure 5.24 it can be seen that $TrG(\beta/2)$ is decreasing with $J$, which indicates that $A(0)$ is approaching zero for increasing $J$. This can be even better seen in figure 5.25 where a MIT transition for $\Delta \simeq 5 \, eV$ is clearly visible. This is what should be expected for off half-filling case within the atomic limit approximation. The gap estimated within the atomic limit is around $\Delta \simeq 5.0 \, [eV]$.

One has to keep in mind that in the atomic limit zero band width is considered, whereas in the investigated case of unstrained SrVO$_3$, the band width is not zero. The value of the band width increases the value of the observed gap. Nevertheless, the atomic limit approximation predicts correctly the trend how the electronic properties of SrVO$_3$ are modified with changes of $J$. The atomic limit approximation properly predicts that increasing $J$ moves SrVO$_3$ towards MIT.
Chapter 6

Summary

In summary, a code has been developed, which can be used to perform DFT+DMFT calculations for a wide range of compounds, including heterostructures. In principle, the developed code makes it possible to treat arbitrary number of symmetry equivalent and inequivalent correlated sites. Furthermore, if required, non-correlated MLWFs can also be used to construct the local Hamiltonian for DMFT calculations. The validity of the code has been checked by various benchmarks, and its usability has been demonstrated by the detailed analysis of electronic properties for two $d^1$ perovskite systems: LaTiO$_3$ and SrVO$_3$. Because of the differences in their structure: SrVO$_3$ has $Pm\bar{3}m$ and LaTiO$_3$ has $Pbnm$ group symmetry, which is quite common for perovskite systems, one can say that those two systems are good representants of $d^1$ perovskites.

The DFT+DMFT calculations performed within this project give a better understanding of the physics of $d^1$ perovskite systems. In particular, the DFT results of strained SrVO$_3$ and LaTiO$_3$ give more insight into structural changes of $d^1$ perovskites under applied strain, notably that the angles between the oxygen octahedra and the bond lengths change considerably when the constraint of epitaxial strain is considered. That, in return, affects the electronic properties which are mostly investigated by DMFT.

From the DMFT calculations a reliable description of the electronic properties of the studied systems is obtained. In particular, the calculations performed within this project demonstrate that an insulator-to-metal transition occurs under compressive epitaxial strain in the case of LaTiO$_3$, and suggest that SrVO$_3$ under tensile epitaxial strain should be closer to a MIT than its bulk form. The observed trend for LaTiO$_3$ is in good agreement with experiment [35]. A considerable effect of both crystal field splitting and hopping integrals can be concluded from the DMFT calcula-
The performed "fake strain" calculations give a better understanding of the role of each mentioned contributions. These calculations, for both SrVO\(_3\) and LaTiO\(_3\), show that the changes in hopping integrals under epitaxial strain are the main driving force for the observed changes in metallic properties. In particular, it is demonstrated that the hopping integrals are the crucial factors in making compressively strained LaTiO\(_3\) metallic. At the same time, the DMFT results suggest that also the crystal field splitting has a prominent effect on the electronic properties by enforcing insulating properties in the case of strained LaTiO\(_3\) under tensile strain. Also, it is observed that SrVO\(_3\) should be closer to a MIT under tensile strain because of changes in the crystal field splitting.

Even though additional interface effects or the presence of defects might further influence the properties of the real system, the results obtained within this project indicate that, if one applies compressive strain, LaTiO\(_3\) becomes metallic. This has to be taken into account even if other effects are also important. From the results presented in this document, it is clear that epitaxial strain is an important factor for the emerging properties observed in oxide heterostructures. Therefore, in order to understand the effect of the interface in these heterostructures, the properties of the corresponding strained material should be taken as reference, not the properties of the bulk material.

The fact that strain can alter the delicate balance between electron hopping and Coulomb interaction, and destroy the Mott insulating state in LaTiO\(_3\), has been previously suggested [49]. However, the corresponding calculations are performed for a simplified tetragonal crystal structure without octahedral tilts. The results presented here demonstrate the close interplay between the structure and electronic properties in LaTiO\(_3\) and also show that it is crucial to consider realistic crystal structures within the DMFT calculations. Within this work detailed analysis of epitaxial strain has been done. One has to keep in mind that other effects are important as well. At the same time in many projects so far all effects at the same time are studied like for example in [50]. Even if some separation of effects is considered by authors like for example in [49], still certain crude approximations about symmetry may call into question some of the final conclusions derived by authors. Therefore in future work in order to complete the bigger picture of electronic properties of strained \(d^1\) perovskites, one should also investigate separately interface effects and defects. One has to keep in mind that since only \(d^1\) perovskite systems are studied in this
project, derived conclusions can only be applied to them. In particular, trends for $d^2$ perovskite systems may be totally different.

Parts of this project have already been published as an article in Physical Review B, see Ref. [36].
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