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Johan Jönsson

Electronic transitions and correlation effects

From pure elements to
complex materials

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POPULÄRVETENSKAPLIG SAMMANFATTNING

Ett materials makroskopiska egenskaper, såsom ledningsförmåga, magnetiska egenskaper, kristallstrukturparametrar, etc. är relaterade till, eller till och med bestämda av elektronernas konfiguration, vilken karakteriseras av elektronstrukturen. Genom att ändra förhållandena, till exempel via tryck, temperatur, magnetiska och/eller elektriska fält, dopning, etc. är det möjligt att modifiera elektronstrukturen hos ett material, och därigenom inducera fasövergångar mellan olika magnetiska och elektron-tillstånd. Mott metall-till-isolator övergången är ett berömt exempel på en fasövergång, då ett material genomgår en omfattande, ofta flera tiopotenser, förändring i ledningsförmåga, orsakad av samspelet mellan ambulerande och lokaliserade laddningsbärare.

Vid en elektronisk-topologisk övergång (eng. electronic topological transition, ETT) sker förändringar i elektronernas energifördelning vilket modifierar materialets Fermi-yta. I den här avhandlingen undersöks dylika övergångar i olika material, från rena grundämnen till komplicerade föreningar.

Flera olika toppmoderna beräkningsmetoder används för att redogöra för samspelet mellan elektroniska fasövergångar och egenskaper hos riktiga material. Täthetsfunktionalteori (eng. density functional theory, DFT), samt DFT + U, har används för att beräkna strukturella egenskaper. Lämplighetsgraden i att använda nyligen publicerade exchange-correlation-funktionaler, såsom SCAN (eng. strongly constrained and appropriately normed), för att beskriva magnetiska grundämnen undersöks även. För att inkludera dynamiska elektronkorrelationer använder vi metoden DFT + dynamisk medelfältteori (eng. dynamical mean field theory, DMFT).

Experiment utförda på hcp-Os vid högt tryck visar underliga hopp i kvoten mellan gitterparametrar. Tidigare beräkningar har indikerat att dessa övergångar kan vara relaterade till elektronisk-topologiska övergångar och korsande av kärntillstånd. I den här avhandlingen visas också att korsning av kärntillstånden är en generell egenskap hos tunga övergångsmetaller. Därför utförs röntgenabsorptionsexperiment på Ir för att leta efter tecken på denna typ av övergång. Övergångsmetalloxiden NiO har sedan länge förutspåtts genomgå en isolator till metall Mott-övergång. Det har föreslagits att denna övergång sker vid höga tryck i samband med att materialets magnetiska ordning försvinner och en strukturell övergång sker. I samarbete med experimenter letar vi efter denna övergång genom att studera röntgenabsorptionsspektra och det magnetiska hyperfina fältet. Vi ser inga indikationer på en Mott-övergång, upp till ett tryck på 280 GPa. Det har föreslagits att Mott-isolatorn TiPO_4 genomgår en så kallad spin-Peierls-övergång, vid rumstemperatur, när tryck appliceras. Vi undersöker dimeriseringen och den magnetiska strukturen i TiPO_4 som funktion av tryck. Vid höga tryck genomgår TiPO_4 ytterligare övergångar, från en isolerande till en metallisk fas för att slutligen genomgå en strukturell övergång. De nya högtrycksfaserna visar sig anmärkningsvärt vara Mott-isolatorer.

MAX-faser är en grupp material med specifik kristallstruktur, som kombinerar egenskaper från keramiska material och metaller. En MAX-fas består av lager av M –metall-atomer – och X – kol- eller kväveatomer – vilka sammanbinds av atomer från grupp A. Magnetiska MAX-faser som visar magnetiska egenskaper, liknande de för lågdimensionella material, är lovande kandidater för applikation inom exempelvis spinntronik. Den här avhandlingen undersöker lämplighetsgraden i att använda diverse teoretiska metoder för att beskriva magnetiska MAX-faser. Med hjälp av DFT och DFT + DMFT undersöker vi den paramagnetiska högttemperaturfasen och huruvida de magnetiska momenten bildas av lokaliserade eller ambulerande elektroner.

ABSTRACT

Macroscopic properties of real materials, such as conductivity, magnetic properties, crystal structure parameters, etc. are closely related to or even determined by the configuration of their electrons, characterized by the electronic structure. By changing the conditions, e.g., pressure, temperature, magnetic/ electric field, chemical doping, etc. one can modify the electronic structure of solids and therefore induce a phase transition(s) between different electronic and magnetic states. One famous example is the Mott metal-to-insulator phase transition, in which a material undergoes a significant, often many orders of magnitude, change of conductivity caused by the interplay between itinerancy and localization of the carriers.

Electronic topological transitions (ETT) involve changes in the topology of a metal's Fermi surface. This thesis investigates the effect of such electronic transitions in various materials, ranging from pure elements to complex compounds.

To describe the interplay between electronic transitions and properties of real materials, different state-of-the-art computational methods are used. The density functional theory (DFT), as well as the DFT + U method, are used to calculate structural properties. The validity of recently introduced exchange-correlation functionals, such as the strongly constrained and appropriately normed (SCAN) functional, is also assessed for magnetic elements. In order to include dynamical effects of electron interactions we use the DFT + dynamical mean field theory (DFT + DMFT) method.

Experiments in hcp-Os have reported peculiarities in the ratio between lattice parameters at high pressure. Previous calculations have suggested these transitions may be related to ETTs and even crossings of core levels at ultra high pressure. In this thesis it is shown that the crossing of core levels is a general feature of heavy transition metals. Experiments have therefore been performed to look for indications of this transition in Ir using X-ray absorption spectroscopy. In NiO, strong repulsion between electrons leads to a Mott insulating state at ambient conditions. It has long been predicted that high pressure will lead to an insulator-to-metal transition. This has been suggested to be accompanied by a loss of magnetic order, and a structural phase transition. In collaboration with experimentalists we look for this transition by investigating the X-ray absorption spectra as well as the magnetic hyperfine field. We find no evidence of a Mott transition up to 280 GPa. In the Mott insulator TiPO_4 , application of external pressure has been suggested to lead to a spin-Peierls transition at room temperature. We investigate the dimerisation and the magnetic structure of TiPO_4 at high pressure. As pressure is increased further, TiPO_4 goes through a metal to insulator transition before an eventual crystallographic phase transition. Remarkably, the new high pressure phases are found to be insulators; the Mott insulating state is restored.

MAX phases are layered materials that combine metallic and ceramic properties and feature layers of M-metal and X-C or N atoms interconnected by A-group atoms. Magnetic MAX-phases with their low dimensional magnetism are promising candidates for applications in e.g., spintronics. The validity of various theoretical approaches are discussed in connection to the magnetic MAX-phase Mn_2GaC . Using DFT and DFT + DMFT we consider the high temperature paramagnetic state, and whether the magnetic moments are formed by localized or itinerant electrons.

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Introduction

1.1 Computational materials science

Materials science has historically been an integral part of the development of human civilization. Entire historical periods have been named after advances in materials science that have lead to fundamental changes in society, such as the stone age, the bronze age, and the iron age. Today is no exception. Advances in materials science during the last century have lead to several technological revolutions, such as the development of the transistor. Today, there is a need to understand complex materials for possible applications in the technology of tomorrow. Setting up and carrying out experiments in order to identify all candidate materials is both time consuming and expensive. Instead, we need theoretical tools that are able to identify likely candidates that can then be investigated experimentally, saving both time and money. Sometimes, it may be very difficult or expensive to investigate some property in an experiment. In such cases simulations can act as useful replacements.

Computational materials science is a large and complicated field. There are several different methods developed in order to investigate the properties of a material using computers. The goal of the computational methods is to correctly predict macroscopic properties based on as few approximations as possible, but also to improve our understanding of the fundamental microscopic properties. Considerable effort is spent developing methods for furthering these two goals. Over the past three decades many new methods have been developed that are now mature enough for usage in computational materials science.

In this thesis, I will investigate the effects of changes in the electronic structure at high pressure. For this I will employ both computational methods

that have been widely used for several decades and newer methods that have been developed in the last two or three decades.

1.2 The many body problem

In quantum mechanics, the wave function of a system, Ψ , plays a very important role. In the non-relativistic limit, this wave function, can be obtained by solving the Schrödinger equation:

$$\begin{aligned} & -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 \Psi(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_N) + V(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_N) \Psi(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_N) \\ & = i\hbar \frac{\partial}{\partial t} \Psi(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_N), \end{aligned} \quad (1.1)$$

where $\hbar$ is the reduced Planck constant, N is the number of particles in the system, and m is the mass of the particle. Equation 1.1 is a partial differential equation that can be solved analytically only for a small number of problems. What characterises a certain problem is the interactions it includes. In equation 1.1 all interactions are included in the potential V .

In the case of a single particle, the only interactions possible are those involving an external potential. The same is true if we have many particles that do not interact with each other. If we have a system of $N > 1$ electrons, that do interact with each other, they can no longer be treated individually. The position, $\bar{r}_i$, of any one electron will depend on all $N - 1$ other electrons in the system. We say that the electrons are *correlated* with each other. For $N \geq 3$ no analytical solution to equation 1.1 exists. Instead, numerical methods are required.

Since the wave function must depend explicitly on each electron in the system, it quickly becomes a very complicated object, requiring massive computational effort to calculate and store [1]. One strategy is therefore to use simplified models that can be solved analytically, or numerically, with great accuracy, but only include certain types of interactions.

Any property can in principle be obtained from the wave function, but in many calculations we are interested in a rather small number of properties. We then need not calculate the full wave function of a system, but rather some other, simpler, quantity that can be used to obtain the properties we are interested in. One such method, discussed in section 2.1, is density functional theory (DFT)[2, 3], where the fundamental quantity is the electron density, $n(\bar{r})$. The electron density requires only one parameter: the position $\bar{r}$, where we want to evaluate the density. There are other approaches that instead use the so called Green's function, $G(\bar{r}, t, \bar{r}', t')$, which contains all information for describing how one particle propagates in the system. The Greens function is the probability amplitude that an electron starts at position $\bar{r}'$ at time t' , and ends up at the position $\bar{r}$ at time t . The Green's function depends on

two parameters, the starting position and time of the electron and its end position and time. This is the basis of dynamical mean field theory (DMFT) [4], which is discussed in chapter 2.4.

1.3 Electron correlation effects

The electron is an electrically charged particle and has an intrinsic magnetic moment, spin. Therefore, in a system with more than one electron they will interact via Coulomb and Pauli repulsions. Pauli repulsion is responsible for ensuring the Pauli principle, i.e., no two electrons may occupy the same state. This means that the wave function must be antisymmetric under exchange of two electrons, i.e.,

$$\Psi(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_i, \dots, \bar{r}_j, \dots, \bar{r}_N) = -\Psi(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_j, \dots, \bar{r}_i, \dots, \bar{r}_N). \quad (1.2)$$

This mechanism is called *exchange*.

An important example of a method including this anti-symmetry of the wave function is the Hartree-Fock method. It assumes that the many-body wave function can be constructed as a Slater determinant of non-interacting, single particle, wave functions [5] i.e.,

$$\Psi(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\bar{r}_1) & \phi_2(\bar{r}_1) & \dots & \phi_N(\bar{r}_1) \\ \phi_1(\bar{r}_2) & \phi_2(\bar{r}_2) & \dots & \phi_N(\bar{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\bar{r}_N) & \phi_2(\bar{r}_N) & \dots & \phi_N(\bar{r}_N) \end{vmatrix}. \quad (1.3)$$

By construction, this wave function is antisymmetric under exchange of two electrons. The remaining electron interactions are then included in a mean field. The individual electrons interact with the mean field generated by all electrons, and experience the same potential. Since the Hartree-Fock method includes electron exchange by construction, one can define electron Coulomb *correlations* to be the additional electron-electron interactions not included in Hartree-Fock.

1.4 From single atoms to crystals

Many solid materials are composed of atoms arranged in a regular pattern. This is what is called a *crystal* (see fig. 1.1). A 3D-crystal can be constructed by placing atoms in a unit cell; then copies of this cell are repeated in such a way as to cover the entire 3D space. Mathematically, a crystal can be described by a combination of translations (steps) that leave the crystal unchanged, and a basis that describes where the atoms are located within the unit cell. The set of translations form a so called Bravais lattice, which is the collection of all points reachable by applying one or more of the underlying translations. In three dimensions there are 14 different Bravais lattices.

Figure 1.1: (a) Schematic picture of a 2D crystal. (b) The crystal structure of hcp-Os, a hexagonal lattice with two atoms in the unit cell. (c) The crystal structure of Mn_2GaC , a hexagonal lattice with 8 atoms in the unit cell. In both (b) and (c) the unit cell is outlined with solid black lines.

At each lattice point one then superimposes the basis in order to obtain the crystal.

Any translation that leaves the crystal unchanged, $\bar{R}$, can be written as a linear combination of primitive vectors:

$$\bar{R} = n_a \bar{a} + n_b \bar{b} + n_c \bar{c}, \quad (1.4)$$

where the primitive translation vectors $\bar{a}, \bar{b}, \bar{c}$ are called the lattice vectors, and n_a, n_b, n_c are integers.

Every atom consists of a positively charged core which is surrounded by electrons. The atomic cores in a crystal are repeated periodically, giving rise to a periodic electronic potential which affects all electrons in the crystal. This external potential, V_{ext} , is included in the term V in equation 1.1. Accurately describing the behaviour of electrons in a periodic potential is one of the most fundamental parts of computational materials science.

1.4.1 Reciprocal lattice

The reciprocal lattice is the Fourier transform of the real space lattice. Where the real space lattice represents position, $\bar{r}$, the reciprocal lattice represents momentum, $\frac{1}{\hbar} \bar{k}$. Being the Fourier transform of the real space lattice, the reciprocal lattice of the reciprocal lattice is again the real space lattice.

Figure 1.2: First Brillouin zone of a hexagonal lattice, adapted from [6].

In three dimensions, the reciprocal lattice vectors can be calculated from the real space lattice vectors as follows:

$$\bar{a}^* = 2\pi \frac{\bar{b} \times \bar{c}}{\bar{a} \cdot (\bar{b} \times \bar{c})} \quad (1.5)$$

$$\bar{b}^* = 2\pi \frac{\bar{c} \times \bar{a}}{\bar{a} \cdot (\bar{b} \times \bar{c})} \quad (1.6)$$

$$\bar{c}^* = 2\pi \frac{\bar{a} \times \bar{b}}{\bar{a} \cdot (\bar{b} \times \bar{c})} \quad (1.7)$$

Just as for the real space lattice, any reciprocal lattice translation vector can be written $\bar{K} = n_{a^*}\bar{a}^* + n_{b^*}\bar{b}^* + n_{c^*}\bar{c}^*$, where $n_{a^*}, n_{b^*}, n_{c^*}$ are integers.

The unit cell of the reciprocal lattice is referred to as the first Brillouin zone. Some points in the Brillouin zone have special names. For a hexagonal lattice $\Gamma = (0, 0, 0)$, $A = \frac{2\pi}{a}(0, 0, \frac{a}{2c})$, $M = \frac{2\pi}{a}(\frac{1}{\sqrt{3}}, 0, 0)$, $K = \frac{2\pi}{a}(\frac{1}{\sqrt{3}}, \frac{1}{3}, 0)$, $L = \frac{2\pi}{a}(\frac{1}{\sqrt{3}}, 0, \frac{a}{2c})$, $H = \frac{2\pi}{a}(\frac{1}{\sqrt{3}}, \frac{1}{3}, \frac{a}{2c})$. By convention, points inside the Brillouin zone are denoted by Greek letters, and points on the boundary are denoted using Latin letters. The first Brillouin zone for a hexagonal lattice, along with some special points, is illustrated in figure 1.2.

1.5 Electronic band structure theory

For isolated atoms, there are only certain discrete energy levels that the electrons can occupy, such as $1s$, $2p$, or $3d$. When two atoms are brought close together these atomic energy levels will shift, and, because of Pauli repulsion, combine to form bonding and anti-bonding molecular orbitals. If a huge

Figure 1.3: Schematic illustration of the allowed energy values of an insulator (left) and a metal (right). Occupied states are shown in a darker colour and unoccupied states in a lighter. As can be seen in the figure, both insulators and metals have gaps of forbidden energy values. For an insulator the Fermi energy lies inside such a gap.

number of atoms, say $1 \text{ mol} \approx 10^{23}$, are brought close together in a crystal, the atomic energy levels will form quasi-continuous bands of allowed energy values and gaps of forbidden values. Figure 1.3 shows a sketch of the density of states (DOS) of an insulator and a metal. The y-axis shows energy, and the x-axis represents the number of states with that energy. In an insulator, there is a gap of forbidden energy values that separates the occupied states from the unoccupied states. This gap is called the band gap, or sometimes the fundamental gap, of the insulator. By contrast, in a metal there is no gap separating the occupied states from the unoccupied ones. Instead, there is a specific energy below which, at 0 K, all states are occupied and above which no states are occupied. This energy is called the Fermi energy, E_F .

The theory describing electronic bands is called electronic band structure theory, and is the result of work done by Felix Bloch [7] on the behaviour of the electronic wave function in a periodic potential. Electronic band structure theory is an approximation, it assumes that the crystal is infinite, homogeneous, and that the electrons are well described using single particle states, i.e., they are non-interacting except for Pauli repulsion. Electronic band structure theory is very successful and can describe many properties of materials correctly. This may be because the negatively charged electrons in a crystal will

Figure 1.4: Band structure plot of hcp-Os (see paper II). By treating all bands of a crystal as linear combinations of atomic orbitals one can assign to each band how much of its character comes from different atomic states. The thickness of the symbols show the degree of "atomic d-stateness" the band has.

screen the Coulomb potential generated by the atomic cores. The electrons may be surrounded by a bubble of positive charge, the electron and its bubble are called a *quasi-particle*. The Coulomb correlations between quasi-particles should be weak, meaning that the quasi-particles could be well described as non-interacting. In some materials, such as the alkaline metals e.g., fcc-Na, the electron-electron correlations are so weak that even a free electron model calculation might give accurate results for such the system. The Bloch theorem [7] states that the electronic wave function for an electron in a periodic potential can be written

$$\psi_{n\bar{k}}(\bar{r}) = e^{i\bar{k}\cdot\bar{r}} u_{n\bar{k}}(\bar{r}), \quad (1.8)$$

where $u_{n\bar{k}}(\bar{r})$ is a periodic function with the same periodicity as the potential function. For a crystal, this is the periodicity of the crystal. The vector $\bar{k}$ denotes the so-called crystal momentum. The energy eigenstates of the wave function will depend of the value of $\bar{k}$. Since $\psi_{n\bar{k}+\bar{K}} = \psi_{n\bar{k}}$, for any reciprocal lattice vector $\bar{K}$, all distinct values of $\psi_{n\bar{k}}$ will appear inside the first Brillouin zone of the crystal. Figure 1.4 shows the calculated band structure of hcp-Os. In chapter 2 I describe methods for performing calculations that include interactions beyond those in electronic band structure theory.

Figure 1.5: Fermi surface of Os, calculated in paper II. Note that the coordinate system has been shifted in order to clearly show the Γ point.

1.6 Fermi surface

The Fermi surface is the surface in reciprocal space which, at zero temperature, separates the occupied electronic states from the unoccupied. The shape of the Fermi surface is a result of the underlying crystal structure and electron interactions.

By definition only metallic materials can have a well defined Fermi surface. The simplest example of a Fermi surface is that of a free electron gas. Since the electrons are non interacting, the Fermi energy is simply given by the Fermi wave number, $\bar{k}_F$, as $\epsilon_F = \frac{\hbar^2}{2m} \bar{k}_F^2$. This is the equation for a sphere in 3-dimensional $\bar{k}$ -space, centred at the origin and with radius $|\bar{k}_F|$. In the case of a crystal, the periodic potential and the electron-electron interactions distort the Fermi surface from a sphere and can consist of several disconnected parts. Because of the periodicity of the crystal, the Fermi surface itself is also periodic and just like the band structure it is enough to calculate it inside the first Brillouin zone. Even if the band structure theory fails when electron correlations are included, the Fermi surface of a metal is still a well defined entity [8]. Figure 1.5 shows the Fermi surface of hcp-Os, obtained from calculations using the LDA+DMFT method (see section 2.4).

Figure 1.6: Illustration of ordered magnetic moments. In a) the moments are said to be ferromagnetically ordered, in b) the moments are antiferromagnetically ordered.

1.7 Magnetism

Understanding the magnetic properties of a material is of high importance in materials science. Magnetism is thus a direct consequence of the fact that electrons have spin, and therefore an intrinsic magnetic moment. Magnetism is a consequence of quantum mechanics; the Bohr-van Leuven theorem states that in a classical system, where magnetism comes only from moving charges, there can be no net magnetic moment at thermal equilibrium [9]. The electrons may align their spin moments, and their orbital motion, in the vicinity of lattice sites. This forms magnetic moments that can be associated with each site [10]. Due to electronic interactions between different sites, the magnetic moments are not independent. Such magnetic interactions do not require direct interactions between magnetic atoms, the interactions can be mediated by non-magnetic sites. Magnetic moments may arrange themselves, e.g., as shown in figure 5.2, showing both ferromagnetic (FM) and antiferromagnetic (AFM) order. In a FM state the magnetic moments of the atoms all align in the same direction. In AFM compounds the moments are ordered so that the unit cell has zero net magnetisation. A system can also exhibit zero net magnetisation without local moments, or with disordered local moments, which is called the paramagnetic state.

In systems studied in this thesis, the magnetic moments are formed by $3d$ -electrons of transition metal elements. These electrons can also take part in the bonding between atoms. This is known as itinerant electron magnetism, and usually makes the magnetic moments in a material sensitive to their chemical environments.

1.8 Mott insulators

In electronic band theory, the Bloch wave of any electron in the crystal will have an infinite range, leading to a non-zero probability to find the electron in any region of the infinitely large crystal. Therefore, if the unit cell contains unpaired electrons, the material should be a metal.

In 1937 it was pointed out by de Boer and Verwey that some materials, most famously the transition metal oxides, feature unpaired electrons, but are insulators and not metals [11]. It was suggested by Mott that the Coulomb repulsion between electrons could explain this insulating state [12]; the electrons become localized to a certain region or atom in the crystal. This type of material is known as a Mott insulator.

1.9 Models of many-body interactions

Full treatment of the interacting many-body problem is impossible. Investigating the many-body interacting problem using simplified models, with parameters of clear, physical meaning, can lead to great insights into the physics of interacting electrons.

1.9.1 The Hubbard model

The Hubbard model [13] is a simple model of the many body problem to explicitly consider interactions between electrons. The model consists of electrons on a lattice, which can jump from one site to another, and that only electrons on the same site interact with each other, (see figure 1.7). The electron-electron interaction is determined by the parameter U , often called the Hubbard U . The probability of an electron hopping from one site to another is described by the hopping matrix t_{ij} , where i, j enumerate the lattice sites. The parameter t is related to the kinetic energy of the electrons. The Hubbard model also takes into account Pauli repulsion, as there can be no more than one electrons of same spin on a site. The single band Hubbard model Hamiltonian can be written:

$$\hat{H} = - \sum_{\substack{i,j,\sigma \\ j>i}} t_{ij} \left(\hat{c}_{i,\sigma}^\dagger \hat{c}_{j,\sigma} + \hat{c}_{j,\sigma}^\dagger \hat{c}_{i,\sigma} \right) + U \sum_i \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow}, \quad (1.9)$$

where $\hat{c}_{i,\sigma}^\dagger$, and $\hat{c}_{i,\sigma}$ are the creation and annihilation operators, creating or destroying an electron with spin σ on site i , respectively. The operator $\hat{n}_{i,\sigma} = \hat{c}_{i,\sigma}^\dagger \hat{c}_{i,\sigma}$ is the spin density operator, counting the number of electrons of spin σ on site i .

Within the Hubbard model, Mott insulators can then be modelled by varying the ratio U/t . If $U \ll t$, the on-site interactions are not strong enough to prevent electrons from jumping between sites, and the system becomes

Figure 1.7: Schematic picture of the 2D-Hubbard model. Showing electrons with spin up or down jumping between sites.

metallic. When $U \gg t$, the electron electron interactions will dominate the inter-site hopping and the electrons will remain localized on their sites. In this way we end up with an insulating system, even with half filled bands, i.e., a Mott insulator, with AFM order. In case $U \sim t$ there is a transition from metal to insulator where the on-site interactions prevent two electrons from being on the same site.

Strong on-site interactions can also lead to ferromagnetism in the Hubbard model. This can be shown by treating the electron-electron interactions within a mean field approximation, i.e. (following [14]),

$$\hat{n}_{i,\sigma} = \langle n_{i,\sigma} \rangle + \delta n_{i,\sigma}, \quad (1.10)$$

where $\langle n_{i,\sigma} \rangle$ is the average number of electrons of spin σ on site i , and $\delta n_{i,\sigma}$ denotes the fluctuations around the average value. With this approximation the Hubbard Hamiltonian can be written (discarding terms of second order in fluctuations, or higher),

$$\hat{H}_{Hub}^{MF} = - \sum_{\substack{i,j,\sigma \\ j>i}} t_{ij} \left(\hat{c}_{i,\sigma}^\dagger \hat{c}_{j,\sigma} + \hat{c}_{j,\sigma}^\dagger \hat{c}_{i,\sigma} \right) + U \sum_i \left(\hat{n}_{i\uparrow} \langle n_{i\downarrow} \rangle + \hat{n}_{i\downarrow} \langle n_{i\uparrow} \rangle - \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle \right). \quad (1.11)$$

With this approximation the Hamiltonian becomes a single particle operator, and by transforming it into $\vec{k}$ -space it becomes diagonal. By exploiting the translational invariance of the system we get that the average number of electrons with spin σ must be the same for all sites, i.e.,

$$\langle n_{i\sigma} \rangle = n_\sigma. \quad (1.12)$$

We define the so called magnetisation density, $m = n_\uparrow - n_\downarrow$, and total density $n = n_\uparrow + n_\downarrow$. From this we define the dimensionless quantity

$$\zeta = \frac{m}{n}. \quad (1.13)$$

As shown in [14, 15], depending on the value of U we can get three different values of the spin polarisation: $\zeta = 0$, corresponding to an unpolarised system, $0 < \zeta < 1$, corresponding to partial polarisation, and $\zeta = 1$, corresponding to

Figure 1.8: Schematic picture of the Anderson impurity model. An impurity (circle) is embedded in an effective bath (wavy background) electrons with spin up or down can jump between the bath and the impurity.

full polarisation. If U is large, it becomes favourable to align the spins in the system. Pauli repulsion ensures that no two electrons on the same site have the same spin. However, by aligning all the spins the kinetic energy of the system is increased. This is the mechanism proposed by Stoner to explain why ferromagnetism appears in Fe and Ni [16, 17].

1.9.2 The Anderson impurity model

The Anderson impurity model [18] (AIM) is another approach to explicitly include interactions between electrons, including spin. Instead of taking into account interactions on all sites of the lattice, it considers one site embedded in an effective bath. Electrons are free to jump onto the site from the bath and from the site into the bath, as illustrated in figure 1.8. The Hamiltonian for the Anderson impurity model, for a single impurity, can be written:

$$\hat{H} = \sum_{\sigma} \epsilon \hat{d}_{\sigma}^{\dagger} \hat{d}_{\sigma} + \sum_{\substack{i,j,\sigma \\ j>i}} t_{ij} \hat{c}_{i,\sigma}^{\dagger} \hat{c}_{j,\sigma} + \sum_{i,\sigma} (V_i \hat{d}_{i,\sigma}^{\dagger} \hat{c}_{i,\sigma} + V_i^* \hat{c}_{i,\sigma}^{\dagger} \hat{d}_{i,\sigma}) + U \hat{d}_{\uparrow}^{\dagger} \hat{d}_{\uparrow} \hat{d}_{\downarrow}^{\dagger} \hat{d}_{\downarrow}, \quad (1.14)$$

where $\hat{c}, \hat{c}^{\dagger}$ are the annihilation and creation operators for the bath states. $\hat{d}, \hat{d}^{\dagger}$ are the annihilation and creation operators for the impurity states. ϵ is the impurity energy level, V is the hybridisation, which couples the impurity to the bath. The on-site interactions are described by U .

This model can be extended to the periodic AIM by placing the impurity in a periodic lattice. Combining the lattice problem of the Hubbard model with the Anderson impurity problem allows solving the Hubbard model in a mean field fashion. This is the basic idea used in the DMFT method, which is discussed in section 2.4.

1.10 Ab initio calculations

In computational materials science we want to investigate various properties of a material, such as magnetism, electronic structure (density of states, electron energy spectrum), the lattice vectors (discussed in section 1.4), the position of the atoms inside the unit cell (figures 1.1b and 1.1c), and mechanical properties (such as compressibility), from equation 1.1.

For a real material solving the many-body Schrödinger equation (equation 1.1) exactly is impossible, instead we must rely on other approaches. Models, with parameters of clear, physical, meaning, such as the Hubbard and Anderson impurity models are very useful e.g., for systematically investigating many-body effects. However the simplified nature of them means that they can only reliably describe a limited set of properties, and not all parameters are known, which reduces their predictive power. Instead, methods without adjustable parameters may predict properties for a wide range of materials. This is the so-called *ab-initio* approach, which is typically based on replacing the complicated many-body wave function with simpler objects, such as the Slater determinants used in the Hartree-Fock method, mentioned in section 1.3, or the electronic density used in DFT, which will be discussed in sections 2.1-2.3. Such calculations must rely on approximations in order to be feasible, even for modern computers. Designing appropriate approximations, which offer high accuracy without too high computational cost, is a challenging task. In practice it can sometimes be hard to determine how certain properties are affected by these approximations. Of considerable interest are methods that are capable of combining ab-initio methods with models, such as DFT + DMFT which is discussed in section 2.4.

Computational methods

2.1 Hohenberg-Kohn density functional theory

In 1964, DFT was suggested by Pierre Hohenberg and Walter Kohn [2]. They showed that the particle density of the ground state of a system of electrons can be uniquely determined from the external potential of the system. This is the first Hohenberg-Kohn theorem. They also showed that there is a universal, i.e. not depending on the system under consideration, functional of the particle density to determine the total energy of the system, which is minimized by the ground state density. This is the second Hohenberg-Kohn theorem.

In the Born-Oppenheimer approximation [19], the Hamiltonian for the problem can be written

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_i V_{ext}(\bar{r}_i) + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\bar{r}_i - \bar{r}_j|} + V_{II} \quad (2.1)$$

$$= \sum_i \hat{T}_i + \sum_i V_{ext}(\bar{r}_i) + \sum_{\substack{i,j \\ i \neq j}} V_{ee}(\bar{r}_i, \bar{r}_j) + V_{II}, \quad (2.2)$$

where $\hat{T}_i = -\frac{\hbar^2}{2m} \nabla_i^2$ is the kinetic energy operator operating on particle i , $V_{ext}(\bar{r})$ is the external potential e.g., the electrostatic potential generated by the nuclei of the system, $V_{ee}(\bar{r}_i, \bar{r}_j) = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\bar{r}_i - \bar{r}_j|}$ is the electron-electron interaction, the factor of $\frac{1}{2}$ takes care of the double counting of interactions, and V_{II} is the constant electrostatic interaction between nuclei. For a given V_{ext} , solving the Schrödinger equation produces the ground state wave function, Ψ_0 , as well as the wave functions for all excited states $\Psi_1, \Psi_2, \dots$. The electron density, $n(\bar{r})$, can be calculated as the expectation value of the density

operator $\hat{n}(\bar{r}) = \sum_{i=1}^N \delta(\bar{r} - \bar{r}_i)$ i.e.,

$$n(\bar{r}) = \frac{\langle \Psi | \hat{n}(\bar{r}) | \Psi \rangle}{\langle \Psi | \Psi \rangle} = N \frac{\int |\Psi(\bar{r}, \bar{r}_2, \dots, \bar{r}_N)|^2 d^3 r_2 \dots d^3 r_N}{\int |\Psi(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_N)|^2 d^3 r_1 d^3 r_2 \dots d^3 r_N} \quad (2.3)$$

The total energy as a functional of the particle density can be written

$$E[n] = F[n] + \int V_{ext}(\bar{r}) n(\bar{r}) d^3 r, \quad (2.4)$$

where $F[n]$ is the universal functional of the particle density and the angle brackets are there to emphasise that the functional depends on the electron density function, not the electron density in a particular point, $n(\bar{r})$.

A big advantage of DFT is that we do not need to calculate or store the complicated many-body wave-function of the system. The particle density is a much less complicated quantity, e.g., the full many-body wave function depends on the positions of all the electrons in the system, but the electron density only depends on one position coordinate. The second Hohenberg-Kohn theorem allows us to minimize the total energy with regards to the electron density, in order to find the ground state density. Thus we can numerically calculate and store the electron density, and by minimising the total energy with regards to the electron density we can obtain the ground state electron density. This, in principle, allows us to calculate any property using the ground state electron density, even for systems where doing so using the many-body wave function would be practically impossible [1]. However, how to perform these calculations in practice is not explained by the Hohenberg-Kohn theorems.

2.2 Kohn-Sham density functional theory

The original formulation of DFT by Hohenberg and Kohn did not include any suggestions for how to use the electron density in order to calculate any property. Therefore, in 1965 Walter Kohn and Lu Jeu Sham introduced a method for simplifying the calculation of the density, and approximating the universal functional [3]. The basic idea in Kohn-Sham DFT (KS-DFT) is to map the complex problem of many interacting particles onto a problem of non-interacting particles, Kohn-Sham particles, that move in an effective potential. The Hamiltonian for the Kohn-Sham approach can be written

$$\begin{aligned} \hat{H}_{KS} &= -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_i V_{ext}(\bar{r}_i) + \sum_i V_{eff}(\bar{r}_i) \\ &= \sum_i \left(\hat{T}_i + V_{ext}(\bar{r}_i) + V_{eff}(\bar{r}_i) \right), \end{aligned} \quad (2.5)$$

where V_{eff} is the effective potential. We can further subdivide $V_{eff} = V_H(\bar{r}) + V_{xc}(\bar{r})$, where $V_H(\bar{r}) = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\bar{r}')}{|\bar{r} - \bar{r}'|} d^3 r'$ is known as the Hartree potential,

and V_{xc} is called the exchange-correlation potential. The Hamiltonian can now be split into N independent parts that we sum in order to get the full Hamiltonian. This gives us N equations that look similar to the Schrödinger equation

$$\begin{aligned} -\frac{\hbar^2}{2m}\nabla^2\phi(\bar{r}) + (V_{ext}(\bar{r}) + V_{eff}(\bar{r}))\phi(\bar{r}) = \\ -\frac{\hbar^2}{2m}\nabla^2\phi(\bar{r}) + (V_{ext}(\bar{r}) + V_H(\bar{r}) + V_{xc}(\bar{r}))\phi(\bar{r}) = \epsilon\phi(\bar{r}). \end{aligned} \quad (2.6)$$

The particles described by the non-interacting single particle wave functions, $\phi_i(\bar{r}_i)$, are known as Kohn-Sham particles. We construct $V_{eff}(\bar{r})$ in such a way that the ground state density of the Kohn-Sham particles is identical to the ground state density of the original electrons.

The universal functional, F , can be rewritten using the Kohn-Sham scheme,

$$F[n] = T[n] + J[n] + E_{xc}[n]. \quad (2.7)$$

Where T is now the kinetic energy of the non-interacting Kohn-Sham particles, $J[n] = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\bar{r})n(\bar{r}')}{|\bar{r}-\bar{r}'|} d^3r d^3r'$ represents the electrostatic interaction of the electron density with itself. The term E_{xc} is called the exchange-correlation energy, and contains the energy contribution of the non-classical electron contributions. The energy functional now becomes:

$$E_{KS}[n] = T[n] + J[n] + E_{xc}[n] + \int V_{ext}(\bar{r})n(\bar{r})d^3r, \quad (2.8)$$

we note that $V_H(\bar{r}) = \frac{\delta J[n]}{\delta n(\bar{r})}$ and $V_{xc}(\bar{r}) = \frac{\delta E_{xc}[n]}{\delta n(\bar{r})}$, where $\frac{\delta}{\delta n(\bar{r})}$ denotes the functional derivative with regards to $n(\bar{r})$. The exchange-correlation term is universal i.e., it does not depend on the system under consideration. The exact form of E_{xc} is not known. Therefore, constructing accurate and efficient approximations of it is a very important and active field of research within KS-DFT, this is discussed in section 2.2.1.

From KS-DFT one obtains single particle wave functions, ϕ_α , and the corresponding single particle energies, ϵ_α . In a system with translational symmetry, these functions will depend on the crystal momentum vector, $\bar{k}$. Thus, the single particle wave functions become $\phi_{\bar{k}\alpha}$ and the single particle energies become $\epsilon_{\bar{k}\alpha}$. The electron density can then (in principle) be obtained by summing up the square modulus of the single particle wave functions of all occupied states, i.e.

$$n(\bar{r}) = \sum_{occ.} |\phi_{\bar{k}\alpha}|^2, \quad (2.9)$$

where the sum extends only over occupied states, α . From the single particle energies, $\epsilon_{\bar{k}\alpha}$ one obtains the Kohn-Sham band structure.

One can introduce spin into KS-DFT by introducing the spin polarized electron densities $n^\uparrow(\bar{r})$ and $n^\downarrow(\bar{r})$, corresponding to the density of spin up and

Figure 2.1: Flowchart of the self-consistent KS-DFT method.

down respectively. Each obtained as a sum over the corresponding occupied Kohn-Sham orbitals,

$$n^\sigma = \sum_{occ.} |\phi_{k\alpha}^\sigma|^2, \quad (2.10)$$

where σ can be either $\uparrow$ or $\downarrow$. Using these two densities we then define the total electron density, $n(\vec{r}) = n^\uparrow(\vec{r}) + n^\downarrow(\vec{r})$, and the magnetisation density, $m(\vec{r}) = n^\uparrow(\vec{r}) - n^\downarrow(\vec{r})$. This allows for the formulation of Kohn-Sham spin DFT [20]. In order to simplify notation we will omit the spin indices in the rest of this discussion and stick to the non spin polarised formulation of KS-DFT.

The self-consistent method of generating the ground state density is outlined in figure 2.1. Starting with an initial guess for the Kohn-Sham orbitals, or the electron density, one can solve the Kohn-Sham equations, equation 2.6, and obtain a new set of Kohn-Sham orbitals that generate a new electron density. By repeating this process until the density used in the Kohn-Sham

equations differs from the density obtained from the new Kohn-Sham orbitals by no more than a predetermined numerical convergence limit, one can obtain the ground state density generated by the external potential. There are several different methods developed for solving the Kohn-Sham equations, using different basis sets for expanding the KS-orbitals. In this thesis I have used the projector augmented wave [21] (PAW) method, as implemented in the Vienna ab-initio simulation package [22, 23], as well as the linear augmented plane wave [24, 25] (LAPW) method and augmented plane wave + local orbitals [26] (APW + lo) method, as implemented in the Wien2k [27] code.

2.2.1 Exchange-correlation functionals

Local Density Approximation

The so called local density approximation (LDA), was suggested by Kohn and Sham [3]. The exchange-correlation energy density per particle, $\epsilon_{xc}(\bar{r})$, is at every point equal to that of a homogeneous electron gas with the same density. The exchange-correlation energy is obtained by integrating the exchange-correlation energy density, multiplied by the electron density, over all space:

$$E_{xc}^{LDA}[n] = \int \epsilon_{xc}^{hom}(n(\bar{r}))n(\bar{r}) d^3r. \quad (2.11)$$

The extension of the LDA to the spin polarised case is known as the local spin density functional approximation (LSDA) [20].

Generalized Gradient Approximation

A step beyond the LDA functional was obtained with the so called generalized gradient approximation (GGA). The central idea is to not only include the electron density at every point, but also gradients of it:

$$E_{xc}^{GGA}[n] = \int \epsilon_{xc}(n(\bar{r}), \nabla n(\bar{r}), \dots) n(\bar{r}) d^3r. \quad (2.12)$$

Many forms of GGA functionals exist. For solid state applications the most common one is the one proposed by Perdew, Burke and Enzerhof (PBE) [28].

Meta-GGA

One way of going beyond the GGA approximation is to include the kinetic energy density of the occupied Kohn-Sham orbitals, usually defined as

$$\tau(\bar{r}) = \sum_i^{occ.} \frac{1}{2} |\nabla \psi_i(\bar{r})|^2. \quad (2.13)$$

There is currently no formulation of the kinetic energy density as an explicit functional of the density, $n(\bar{r})$. In this way one obtains the so called meta GGA (mGGA) family of exchange-correlation functionals.

The exchange-correlation energy of a mGGA functional is then calculated as

$$E_{xc}^{mGGA}[n] = \int \epsilon_{xc}(n(\bar{r}), \nabla n(\bar{r}), \dots, \tau(\bar{r})) n(\bar{r}) d^3r. \quad (2.14)$$

Several meta-GGAs have been suggested, one recent and very popular is the so called strongly constrained and appropriately normed (SCAN) functional. Developed by Sun et. al [29]. The SCAN functional is able to better interpolate between a system of finite size, such as a molecule, to a system that is effectively infinite, such as a crystal. Previously, there was a need for very different functionals for calculations of molecules and solids, but with the SCAN functional the same functional can be used for the two types of systems.

2.2.2 Performance for itinerant magnetic elements

In order to find the equilibrium volume V_0 of a system one can minimize the total energy with regards to the volume. By calculating the total energy as a function of volume it also becomes possible to determine the bulk modulus

$$B_0 = \left. \frac{dP}{dV} \right|_{V=V_0} = V_0 \left. \frac{\partial^2 E}{\partial V^2} \right|_{V=V_0}, \quad (2.15)$$

where P is the external pressure, as well as its pressure derivative B' . This is usually done by fitting the calculated $E(V)$ to an equations of state (EOS), such as the third order Birch-Murnaghan (BM) EOS [30]. The calculated energy, and therefore also V_0 , B_0 , and B' , will depend on the exchange-correlation functional used. This is illustrated in figure 2.2, table 2.2 shows the equilibrium parameters obtained. A well known shortcoming of the LDA and LSDA is that it tends to overbind. This can lead to incorrect results when magnetism is involved. For example, using LSDA one finds that non-magnetic fcc-Fe is lower in energy than ferromagnetic bcc-Fe [6]. This is obviously not correct since it is well known that, in the ground state, Fe is a ferromagnet, and has a bcc structure. GGA improves the equilibrium volume, and also the magnetic state [6]. Studies investigating the performance of the SCAN functional for BiFeO₃ [31] show that SCAN gives magnetic moments, of the Fe atoms, that agree better with experiments than PBE. In Paper I we investigated the functional for the ferromagnetic pure elements, Fe, Co, and Ni. Table 2.1 shows the calculated values of equilibrium volume, V_0 , bulk modulus, B_0 , and its pressure derivative, B' , obtained using the PBE, LSDA, and SCAN functionals.

Our results show that for hcp-Co and fcc-Ni SCAN tends to give too small equilibrium volume and too large bulk modulus. In bcc-Fe however, the equilibrium volume is only slightly overestimated and the bulk modulus is slightly underestimated. For all three systems the magnetic moments are overestimated, due to a larger exchange splitting compared to LSDA and PBE.

Table 2.1: Ground state parameters of bcc-Fe, fcc-Ni, and hcp-Co, from paper I. Calculated using the VASP code, employing the PBE, LSDA and SCAN functionals. Experimental values from [32].

		Volume ($\text{\AA}^3/\text{atom}$)	B_0 (GPa)	B'	mag. moment (μ_B)
bcc-Fe	PBE	11.35	197.7	4.45	2.20
	LSDA	10.36	253.3	4.39	1.95
	SCAN	11.58	157.5	5.05	2.66
	Exp.	11.64	175.1	4.6	1.98[33], 2.08[34], 2.13[35]
fcc-Ni	PBE	10.90	199.8	4.76	0.63
	LSDA	10.06	253.6	4.77	0.58
	SCAN	10.38	230.5	4.79	0.73
	Exp.	10.81	192.5	4	0.52[34], 0.55[36], 0.57[35]
hcp-Co	PBE	10.45	262.5	4.61	1.61
	LSDA	9.99	237.6	4.95	1.49
	SCAN	10.45	262.5	4.15	1.73
	Exp.	10.96	198.4	4.26	1.52[34], 1.55[33], 1.58[37]

Figure 2.2: Calculated total energy for fcc-Ni using the SCAN and PBE functionals, fitted to a 3rd order BM EOS. The dashed vertical line corresponds to the experimental volume given in table 2.2.

Table 2.2: Equilibrium parameters for fcc-Ni, calculated using the Wien2k code. Experimental values from [32]

	Volume ($\text{\AA}^3/\text{atom}$)	B_0 (GPa)	B'
SCAN	10.34	230.0	4.87
PBE	10.89	200.9	4.76
LSDA	10.03	256.2	4.80
Exp.	11.64	175.1	4.6

2.3 DFT + U

Since KS-DFT only uses the electron density to calculate the Coulomb interactions between particles, a delocalised electron may interact with itself. The exchange-correlation functional used is supposed to remove this contribution to the total energy, however since only approximate exchange-correlation functionals exist there is currently no way of exactly removing the self interaction in KS-DFT. The so called DFT + U method was originally proposed as a way to remove this self-interaction problem in DFT [38]. In the DFT + U method, a Hubbard-like interaction (see section 1.9.1) is introduced for certain orbitals of the Kohn-Sham particles, typically partially filled d - or f -orbitals. This pushes the Kohn-Sham particles towards a more localized behaviour, thus reducing the self interactions. In general the total energy functional of the DFT + U method can be written [38, 39]

$$E_{DFT+U}[n, \{n^\sigma\}] = E_{DFT}[n] + E_U[\{n^\sigma\}] - E_{DC}[\{n^\sigma\}], \quad (2.16)$$

where E_{DFT} is the energy obtained from DFT-calculations using a semi-local functional, such as LDA or PBE, E_U is the energy contribution of the Hubbard like interactions in the correlated orbitals, and E_{DC} is the energy contribution of the correlated orbitals from E_{DFT} . n is the electron density and $\{n^\sigma\}$ denotes the occupation matrix of the correlated orbitals with spin σ .

In general the energy of the Hubbard like interactions can be written

$$E_U[\bar{n}] = \frac{1}{2} \sum_{\{m\}, \sigma} \langle mm'' | V_{ee} | m' m''' \rangle \{n^\sigma\}_{mm'} \{n^{-\sigma}\}_{m'' m'''} + \\ (\langle mm'' | V_{ee} | m' m''' \rangle - \langle mm'' | V_{ee} | m''' m' \rangle) \{n^\sigma\}_{mm'} \{n^\sigma\}_{m'' m'''} \quad (2.17)$$

where m, m', m'' , and m''' denote the correlated orbitals. As shown in reference [39], the matrix elements of the Coulomb interaction, V_{ee} , can be determined using the Slater integrals F^k , $0 \leq k \leq 2l$. For d -electrons one needs F^0, F^2 and F^4 , these can be linked to the screened Coulomb parameters U and J [40, 41] e.g., for d -electrons, $U = F^0$, $J = (F^2 + F^4)/14$, $F^2 = \frac{14}{1.625}J$, and $F^4/F^2 = 0.625$.

The double counting term is needed to remove the semi-local DFT treatment of the correlated electrons, there are several approximations for doing this but the two most common are the around mean field (AMF) [42] and the fully localised limit (FLL) approximations [39]. The double counting energies from these two approximations can be written [43]

$$E_{DC}^{AMF} = \frac{1}{2}UN^2 - \frac{U+2lJ}{2l+1} \frac{1}{2} \sum_{\sigma} N^{\sigma^2} \quad (2.18)$$

$$E_{DC}^{FLL} = \frac{U}{2}N(N-1) - \frac{J}{2} \sum_{\sigma} N^{\sigma}(N^{\sigma}-1), \quad (2.19)$$

where l denotes the orbital quantum number of the orbital.

A simpler formulation of DFT + U was proposed by Dudarev et al.[44], it uses an effective on-site interaction $U_{eff} = \bar{U} - \bar{J}$, where $\bar{U}$ and $\bar{J}$ are the spherically averaged matrix elements of the screened Coulomb interaction matrix,

$$\bar{U} = \langle mm'' | V_{ee} | m'm''' \rangle \quad (2.20)$$

$$\bar{J} = \langle mm'' | V_{ee} | m'''m' \rangle. \quad (2.21)$$

The energy functional obtained from this approach can be written

$$E_{LSDA+U} = E_{LSDA} + \frac{\bar{U} - \bar{J}}{2} \sum_{m,\sigma} (n_m^{\sigma} - n_m^{2\sigma}), \quad (2.22)$$

where $n_m^{\sigma} = \{n^{\sigma}\}_{mm}$ is the occupation number of the correlated orbital m .

2.4 DFT + DMFT

A different approach to explicitly include electronic correlations in DFT calculations, beyond those already included in semi-local functionals, is to combine them with DMFT [45]. Like in the DFT + U method, only a certain subset of orbitals is treated as correlated, usually partially filled d - or f -states. For this subset, interactions can be handled explicitly via many-body calculation. In a very similar way to what is done for DFT + U the Hamiltonian for the DFT + DMFT method can be written

$$\hat{H}_{DFT+DMFT} = \hat{H}_{DFT} + \hat{H}_{DMFT} - \hat{H}_{DC}, \quad (2.23)$$

where the interactions of the correlated orbitals are included in $\hat{H}_{DMFT}$. The purpose of the double counting term, $\hat{H}_{DC}$, is to remove the DFT contribution of the correlated orbitals, therefore there is no difference between the expressions for the double counting energy in DFT + DMFT and DFT + U [46].

The Green's function $G(\bar{r}, \bar{r}', t, t')$, introduced in chapter 1, can be Fourier transformed into momentum and frequency representation, i.e.,

Figure 2.3: Schematic illustration of the DMFT problem. A lattice site (circle) is treated as an impurity embedded in an effective bath of non-interacting particles (wavy background).

$G(\bar{r}, \bar{r}', t, t') \rightarrow G_{\bar{k}}(\omega)$, where $\bar{k}$ is a wave vector, and ω frequency. From the Green's function we can obtain the distribution of the electron energies, the so called spectral function,

$$A(\bar{k}, \omega) = -\frac{1}{\pi} \text{Im}[G_{\bar{k}}(\omega)]. \quad (2.24)$$

For weakly interacting particles, the electron energies will be well defined and sharp, similar to bands. However, for strongly interacting particles the energies will be smeared out.

To calculate G , following the scheme outlined in [8], we start with the single particle Green's function for the crystal,

$$G_{\bar{k}}(\omega) = [\omega - \epsilon_{\bar{k}} - \Sigma_{\bar{k}}(\omega)]^{-1}, \quad (2.25)$$

where $\epsilon_{\bar{k}}$ are the single particle energies, and $\Sigma_{\bar{k}}(\omega)$ is the self energy, which includes all interactions. Using these we can define the Green's function of the impurity site as the single particle Green's functions, averaged over the Brillouin zone.

$$G(\omega) = \frac{1}{N_{\bar{k}}} \sum_{\bar{k}} G_{\bar{k}}(\omega), \quad (2.26)$$

where $N_{\bar{k}}$ is the number of $\bar{k}$ -points inside the Brillouin zone.

The main approximation in DMFT is that we only include local interactions, which for a single site means that

$$\Sigma_{\bar{k}}(\omega) \rightarrow \Sigma(\omega). \quad (2.27)$$

Determining the self energy is the main goal of the DMFT method. This is done by treating the correlated electrons as sitting on an impurity site,

embedded in an effective bath of non-interacting electrons, illustrated in figure 2.3. As in the Anderson impurity model. However, in the DFT + DMFT method, the bath is described using KS-DFT, usually with LDA or PBE. In the single site approximation all impurity sites are equivalent and we only need to find the solution for one to get the solution for the entire crystal.

2.4.1 The impurity problem

The Hamiltonian of the impurity problem can be written:

$$\begin{aligned}
 H = & \sum_{\bar{k},\alpha} \epsilon_{\bar{k},\alpha} c_{\bar{k},\alpha}^\dagger c_{\bar{k},\alpha} \\
 & + \sum_{\bar{k},\alpha} \left[V_{\bar{k},\alpha} c_{\bar{k},\alpha}^\dagger d_\alpha + V_{\bar{k},\alpha}^* d_\alpha^\dagger c_{\bar{k},\alpha} \right] \\
 & + \mu \sum_{\alpha} d_\alpha^\dagger d_\alpha + \frac{1}{2} \sum_{\mu_1, \mu_2, \mu_3, \mu_4} U_{\mu_1 \mu_2 \mu_3 \mu_4} d_{\mu_3}^\dagger d_{\mu_4}^\dagger d_{\mu_2} d_{\mu_1} \\
 = & H_{bath} + H_{hyb} + H_{loc},
 \end{aligned} \tag{2.28}$$

where the operators $c, c^\dagger$ and $d, d^\dagger$ destroy and create states in the bath and on the impurity respectively, and V is the hybridization function, connecting the impurity with the bath.

$$H_{bath} = \sum_{\bar{k},\alpha} \epsilon_{\bar{k},\alpha} c_{\bar{k},\alpha}^\dagger c_{\bar{k},\alpha} \tag{2.29}$$

is the term describing the bath states.

$$H_{hyb} = \sum_{\bar{k},\alpha} \left[V_{\bar{k},\alpha} c_{\bar{k},\alpha}^\dagger d_\alpha + V_{\bar{k},\alpha}^* d_\alpha^\dagger c_{\bar{k},\alpha} \right] \tag{2.30}$$

describes the hopping between the bath and the impurity site, and

$$H_{loc} = \mu \sum_{\alpha} d_\alpha^\dagger d_\alpha + \frac{1}{2} \sum_{\mu_1, \mu_2, \mu_3, \mu_4} U_{\mu_1 \mu_2 \mu_3 \mu_4} d_{\mu_3}^\dagger d_{\mu_4}^\dagger d_{\mu_2} d_{\mu_1} \tag{2.31}$$

describes the (local) interactions on the impurity site. The four index Coulomb interaction vertex,

$$U_{\mu_1 \mu_2 \mu_3 \mu_4} = \langle \mu_1 \mu_2 | V_{ee} | \mu_3 \mu_4 \rangle \tag{2.32}$$

can be fully specified using the two parameters U and J , as was discussed in section 2.3.

The hybridisation function matrix

$$\Delta_{\alpha\beta}(\omega) = \sum_{\bar{k}} \frac{V_{\bar{k},\alpha}^* V_{\bar{k},\beta}}{\omega - \epsilon_{\bar{k},\alpha}}, \tag{2.33}$$

is related to the hybridization function $\Delta(\omega)$, which in turn is related to the non-interacting Green's function, describing the bath

$$G^0(\omega) = [\omega - \epsilon - \Delta(\omega)]^{-1}. \quad (2.34)$$

By providing the non-interacting Green's function of the impurity, $G^0(\omega)$, as well as the parameters U and J , the impurity problem can be solved. There are many numerical methods available for solving the problem. In this thesis I have used the continuous time quantum Monte Carlo method (CT-QMC) as implemented in the TRIQS package, [47–53]. From the solution, the self energy and the interacting Green's function of the impurity are extracted.

2.4.2 Self-consistency cycle

The self energy of the impurity $\Sigma^{imp}(\omega)$ links the Green's function of the non-interacting bath, $G^0(\omega)$, to the interacting Green's function of the impurity $G^{imp}(\omega)$,

$$G^{imp}(\omega) = \left[(G^0)^{-1}(\omega) - \Sigma^{imp}(\omega) \right]^{-1}. \quad (2.35)$$

We require that $\Sigma^{imp}(\omega) = \Sigma(\omega)$ i.e., the impurity self-energy is equal to the self energy of the site. This gives us a self-consistent way of calculating the Green's function of the correlated orbitals, G^{imp} . We start with a guess for the non-interacting bath Green's function, G^0 , we then solve the impurity problem and obtain the impurity self energy, Σ^{imp} . With this we calculate the single particle Green's functions, and the full Green's function of the site, G . From the site Green's function we obtain a new non-interacting Green's function, G^0 , that we can use to restart the process. We continue doing this until the site Green's function, G , and the impurity Green's function, G^{imp} , differ by no more than a predetermined numerical convergence threshold.

Once the Green's function of the correlated orbitals has been found one can extract the electron density of these orbitals

$$n_{DMFT}(\bar{r}) = \lim_{h \rightarrow 0^+} -iG(\bar{r}, \bar{r}, t, t+h). \quad (2.36)$$

We can use the charge density obtained for the correlated orbitals to create a new effective potential to use the KS-DFT iterations. Thus closing the DFT + DMFT self consistent loop. The self-consistent cycle is outlined in figure 2.4. In this thesis I have used the DFT + DMFT method as implemented in Wien2k, with the toolbox for research in interacting quantum systems [47] (TRIQS) library application DFTTools [54–56].

Figure 2.4: Flowchart demonstrating the DFT + DMFT self consistency cycle.

Electronic transitions in pure elements at high pressure

The electronic properties of a material can greatly influence its macroscopic properties, such as thermal and electric conductivity.

This chapter will show examples of how increasing pressure may affect the electronic band structure of a material. Special emphasis will be put on electronic topological transitions (ETT) in Os and core level crossings (CLC) in Os and Ir at high pressure. The effects on the lattice parameters of these kinds of transitions is small, however they can lead to noticeable peculiarities in the ratios of lattice parameters at non-zero temperatures.

3.1 Electronic topological transition

An electronic topological transition (ETT) is a transition in which the topology of the Fermi surface changes e.g., new pockets might appear.

As was shown by Lifshitz in [57], an ETT occurs when the Fermi energy, ϵ_F , reaches a critical point, ϵ_c . At such a critical point, if the quasi-particle energy $\epsilon(\vec{p})$ has a local extrema (either a local maxima or a local minima) then a new pocket will either open or close in the Fermi surface, and if it has a saddle point two parts of the Fermi surface may either be connected or disconnected by the formation or destruction of a "neck". Figure 3.1 shows an ETT occurring in hcp-Os as a band maxima at the L-point crosses the Fermi energy.

Lifshitz also showed that, at 0 K, close to an ETT there appears an additional term in the thermodynamic potential,

$$\Omega = \Omega_0 + \delta\Omega \quad (3.1)$$

$$\delta\Omega \sim |\epsilon - \epsilon_c|^{5/2}. \quad (3.2)$$

Due to this additional term, $\delta\Omega$, at the point of the ETT, $\epsilon = \epsilon_c$, there appears a kink in the second derivative of the thermodynamic potential, $\sim |E - E_F|^{1/2}$, and an infinite jump in the third derivative, $\sim |E - E_F|^{-1/2}$. As temperature is increased these anomalies become smeared. The fact that the kink occurs in the second derivative, but in the third derivative there is an infinite jump motivated Lifshitz to call this transition a $2\frac{1}{2}$ order transition, according to the classification scheme introduced by Ehrenfest in 1933 [58].

In order to examine ETTs it becomes necessary to modify the Fermi surface of a material. Convenient ways of achieving this has been varying the concentration of different metals in an alloy [59], or by applying external pressure. For instance in hcp-Zn [60–63], an ETT occurs at the L-point upon compression. An ETT does not involve any structural transition but it can still result in observable effects on the crystal structure. The kink in the second derivative of the thermodynamic potential leads to kinks in the thermal expansion coefficient, and at non-zero temperatures this can lead to anomalies in the c/a -ratio of a material. As was shown in [64] for hcp-Fe, the elastic constants of a material are proportional to the second derivative of the thermodynamic potential and therefore have a kink at the ETT. The lattice constants, however, are proportional to the first derivative of the thermodynamic potential and therefore the effect of the ETT is much less noticeable. The fact that the effect on the c/a -ratio is stronger for non-zero temperatures, due to thermal expansion, means that it is hard to see in calculations performed at 0 K, such as KS-DFT, or that only include electronic temperature, such as DMFT.

3.2 Osmium at high pressure

In experiments investigating hcp-Os an ETT was suggested at 150 GPa, to explain peculiarities in the c/a -ratio at high pressures [65]. Os is a material with only weak electron interactions. However, it has been shown in other weakly correlated systems that the inclusion of electron correlations can lead to the appearance of new features in the electronic structure, such is the case for hcp-Fe [64] for instance. Calculations using LDA + DMFT confirmed that the anomaly in the c/a -ratio could be related to an ETT, but no investigation of the Fermi surface of Os was performed. In paper II calculations using the DFT+DMFT method were performed in order to carefully investigate the effect of pressure on the Fermi surface of Os. Two ETTs were observed, one at around 100 GPa in which an electron pocket appears around the Γ point, so far this ETT has not been observed in experiments. The second ETT occurs around a pressure of 180 GPa and involves the appearance of a neck as well as

(a)

(b)

Figure 3.1: a) Band structure of hcp-Os calculated with the Wien2k code. Note the band maxima at the L-point. (b) A pocket (blue) appears at the L-point in the Fermi-surface of hcp-Os as the band extrema in (a) crosses the Fermi energy. The Fermi surface has been calculated using the DFT + DMFT method. Images from paper II

Table 3.1: Comparison of equilibrium parameters obtained from EOS for Os.

	V_0 (a.u. ³ /atom)	B_0 (GPa)	B'
DFT + DMFT ($U = 3.0$ eV, my work)	96.11	396.5	4.61
Experiment[65]	94.54	398.5	4.94
GGA[65]	94.48	448	4.29
LDA[65]	93.33	447	4.41

a hole pocket at the L point. Paper II also includes calculations employing the LDA method. Using LDA only one ETT is observed as pressure is increased, a neck and a hole pocket appears at the L -point at 125 GPa. In fact the ETT at the Γ -point has occurred already at ambient pressure. The reason the ETT at the L -point occurs at a higher pressure in LDA + DMFT than in LDA is that by including electron correlations for the d -electrons these states are pushed towards higher energies, and so is the Fermi energy.

I calculated the fat bands of Os at ambient pressure (shown in fig. 1.4), showing that the states involved in the ETTs are of sp -character and thus not strongly affected by the LDA + DMFT treatment. I performed calculations of the EOS for Os using the DFT + DMFT method, employing a simplified workflow in which the c/a -ratio was kept fixed to the experimental value for all volumes. I found that using a U -value of 3.0 eV best reproduced the experimental EOS, this value of U is close to the value used for the calculations in paper II. Since Os is a weakly correlated system the effect of a small change in U should have negligible effect. In table 3.1 is shown the EOS I obtained as well as those obtained in experiments and DFT calculations [65]. With DFT + DMFT the equilibrium volume is overestimated, whereas the Bulk modulus, B_0 , and its pressure derivative, B' , are well reproduced. Plotting the $P - V$ curves for the different the EOS, figure 3.2, we see that the DFT + DMFT curve lies very close to the GGA curve. In order to fully assess the accuracy of the LDA + DMFT method calculations should be performed where the c/a -ratio is not kept fixed, but instead one should find the value at each volume that minimises the total energy.

3.3 Core level crossing

It is known that as pressure increases the core levels of electrons in the material gets shifted to lower energies, usually this shift is equal for all core levels.

In Os at around 440 GPa a peculiarity in the c/a -ratio is observed. This peculiarity has been attributed to the crossing of core levels [65]. In ref. [65] it was found by calculations that the $4f$ and $5p$ core levels shift at different rates as a function of pressure and eventually cross. This crossing occurs at the pressure where the peculiarity in the c/a ratio was observed. This type of transition was named a core level crossing (CLC). In [65] it is argued that this

Figure 3.2: Pressure - Volume curves for various EOS for Os.

transition can only affect the valence electrons indirectly. The authors of [65] suggest, using the pseudopotential transform, that large shifts in core states will affect the valence electrons, by modifying the non-local part of the effective potential and that this might be the mechanism by which CLCs affect the valence electrons. The effect of these transitions on macroscopic quantities, such as lattice parameters, must be very small. It is possible that they could result in peculiarities of the c/a -ratio [65] at non-zero temperature, through a mechanism similar to that of ETTs e.g., anisotropic thermal expansion.

That this type of transition is observed in Os raises the question, do CLC transitions only appear in Os? Paper III provides a systematic investigation of the $5d$ metals and shows that for heavier elements, different core levels can be shifted at different rates as pressure increases. This can possibly lead to a CLC transition. Paper III shows that CLCs are a general feature of those elements. For example in Re the CLC is predicted to occur already at ambient pressure, I calculated the density of states (DOS) for Re using DFT with LDA and including the effects of spin orbit coupling both at ambient pressure and at high pressure, see fig. 3.3. Already at ambient pressure the $5p$ -levels of Re have begun to broaden and they overlap the $4f$ -levels, indicating that the CLC has already occurred. This trend only continues at higher pressures as we see that the $5p$ -states continue to broaden.

Figure 3.3: Calculated DOS for Re at ambient pressure (left) and high pressure (> 270 GPa, right). Adapted from data from paper III

In paper IV experiments were performed to find the CLC in Ir by means of X-ray absorption spectroscopy. The transition is predicted in paper III to occur at 80 GPa.

Since the effect of the CLC on the crystal structure is expected to be very small, we observe no indication of any transition in either the calculated or the experimentally measured EOS, see figure 3.4. Moreover, since the X-ray spectroscopy used in paper IV does not directly probe the states involved in the CLC, the effect on the measured spectra is expected to be very weak. Indeed there is no indication of any electronic transition in either the calculated or experimentally measured X-ray absorption (XAS) spectra. However, there is good agreement between both the calculated XAS spectra and EOS with experiments. This indicates that our calculations are capable of properly describing the structural and electronic properties of Ir under pressure. It is possible that the CLC in Ir exists, and experiments capable of probing the $4f$ and $5p$ states directly are required.

Figure 3.4: Calculated EOS used as a reference for simulated XAS-spectra of Ir under pressure, compared to EOS measured experimentally in paper IV.

Electronic transitions in compounds

Several types of electronic transitions can occur in a real material. In this chapter I will discuss three particular transitions, the Mott transition; the Peierls transition and the closely related spin-Peierls transition.

4.1 Mott transitions

The Mott transition is a transition between a metallic and insulating state in which the valence electrons go from being delocalised and capable of conducting a current, to being highly localized around the atomic sites and incapable of conducting a current [66]. A simple model able to describe this type of transition is the Hubbard model, that was discussed in chapter 1. In the Hubbard model, the strength of the electron interactions, U , and the hopping between sites, t , determine the electronic and magnetic properties of the system. If the on-site interaction is strong enough to dominate the kinetic energy, the electrons will be unable to jump between sites and the material cannot conduct a current. If the interatomic hopping was to increase, however, the situation could arise when it becomes large enough to overcome the repulsive on-site interactions. In this case the electrons would begin to jump from site to site, and the material would become metallic.

In practice, a straightforward way of increasing the inter-site hopping in a material is by increasing the external pressure. Moving the atoms closer together, allowing for greater overlap of the wave functions of neighbouring electrons. Thereby increasing the kinetic energy of the electrons. One would expect that this could eventually lead to a transition from an insulating to a metallic state. In fact, this transition was predicted in 1949 [66] to occur in NiO. Since the first prediction by Mott several other materials have been predicted to undergo a Mott transition [67]. In experiments the Mott transi-

tion has been observed in MnO [68] and NiI₂ [69, 70] among other compounds [71], at high pressure. When the Mott transition has been observed, it has been accompanied by other phenomena, e.g., a collapse in volume, the disappearance of magnetic moments and a collapse of the hyperfine magnetic field [71].

4.2 The Mott transition in NiO

NiO is considered one of the most well known examples of a Mott insulator, it was suggested to undergo an insulator to metal transition by Mott in 1949 [66]. Still, there is a debate over at what pressure this transition occurs. There are reports of an insulator to metal transition in NiO occurring at 240 GPa [72]. However, in paper V we perform calculations and experimental measurements of the hyperfine field and calculate the DOS of NiO at pressures up to 300 GPa. Our results show that NiO remains insulating throughout the pressure range. We also find evidence of antiferromagnetic order in NiO, up to at least 280 GPa. Making us question the existence of a Mott transition even further, as it is believed that the insulator to metal Mott transition is closely related to the collapse of magnetic order [71].

4.2.1 Calculated X-ray absorption spectra

At high pressures there is a severe limitation on what experiments can be carried out. Fortunately, X-ray spectroscopy can still be performed, enabling experimental investigation of the electronic structure of a material.

In XAS, a core electron is excited to the unoccupied states by an X-ray photon, see figure 4.1. Because the core states have very narrow energy bands, there is a sharp increase in the absorption spectra as the photon energy reaches the binding energy of such a state. This is called an edge. Edges are classified according to the principal quantum number, n , of the core state that is excited; K, L, and M edges involve states with $n = 1, 2$, and 3 respectively.

The probability of a transition from a core state into the unoccupied valence states is given, in the non-interacting electrons approximation, by Fermi's golden rule:

$$p_{if} \sim \sum_f \left| \langle \phi_f | \hat{p} \cdot \bar{A}(\bar{r}) | \phi_i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega), \quad (4.1)$$

where $\hat{p}$ is the momentum operator and $\bar{A}(\bar{r})$ is the vector potential of the electromagnetic field. ϕ_i and ϕ_f are the initial and final single electron states with energies E_i and E_f , respectively, and ω is the angular frequency of the incoming radiation. The vector potential is often approximated as $\bar{A} \approx \bar{\epsilon} e^{i\vec{k} \cdot \bar{r}}$, where $\bar{\epsilon}$ is the polarisation vector of the light. For core states, the dipole

Figure 4.1: Schematic picture of the XAS process. A core electron is excited by an X-ray photon, promoting it into the unoccupied states.

approximation is often used: $e^{i\vec{k}\cdot\vec{r}} \approx 1$, which gives the transition probability

$$p_{if} \sim \sum_f \left| \langle \phi_f | \vec{\epsilon} \cdot \hat{p} | \phi_i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega). \quad (4.2)$$

From the non-zero transition probabilities one obtains the dipole allowed selection rules, $\Delta L = \pm 1$ and $\Delta S = 0$, i.e., transitions between s and p , p and d , etc., and conservation of spin.

It could be expected that NiO undergoes a structural transition at high pressures. Such a transition is observed in MnO [73, 74]. In paper V we measured the XAS spectra and X-ray diffraction (XRD) pattern of NiO at ambient pressure, and at 280 GPa and see no indication of any structural transitions. The measured XAS spectra is well reproduced by calculations the LDA + U method, see fig. 4.2. Indicating that LDA + U can be used to describe NiO both at ambient and high pressures.

Figure 4.2: Simulated Ni K-edge XAS spectra of NiO at (a) ambient pressure and (b) 280 GPa. Thick black lines are experimental spectra and red lines my calculations. Images from paper V

Figure 4.3: Schematic illustrations of the 1D (a) Peierls and (b) spin-Peierls transitions.

4.3 Peierls and spin-Peierls transition

The Peierls and spin-Peierls transitions refer to when a quasi-1D chain of ions form pairs (dimerise), see figure 4.3. If the chain has antiferromagnetic order and the pairs formed have a net magnetic moment of 0, it is called a spin-Peierls transition. Both phenomena should occur at very low temperatures, and the result is to open up a gap in the electronic structure around the Fermi energy, making the material an insulator.

The first inorganic compound found to exhibit the spin-Peierls transition was CuGeO_3 [75]. Another compound suggested to undergo the spin-Peierls transition is TiOCl [76].

4.4 Electronic transitions in TiPO_4

TiPO_4 is a Mott insulator that has been suggested to undergo a spin-Peierls transition at low temperatures [77]. Recent high pressure experiments [78] suggested that under compression TiPO_4 might undergo a spin-Peierls transition even at room temperature. At even higher pressures, 46 GPa, TiPO_4 was seen to undergo a structural transition into two new phases. One of these two phases feature the first occurrence of fivefold O-coordinated P, in an inorganic compound.

At ambient conditions, TiPO_4 crystallizes in what is called phase I, figure 4.4a. This phase is characterised by 1D chains of Ti atoms along the $\bar{c}$ lattice-vector, interconnected by PO_4 tetrahedra. The Ti atoms are situated inside edge sharing octahedra formed by O atoms. As pressure is increased phase I transforms into phase II, where the Ti-Ti distances along the chains are all different and incommensurately modulated. As pressure is further increased phase II turns into phase III, which is a doubling of the phase I unit cell along the $\bar{a}$ lattice vector, where the Ti-Ti distances along the chains alternate between a long and a short distance which we can describe as $d_{\text{Ti-Ti}} = c/2 \pm \delta$. For $\delta = 0$ we have an undimerised chain. Since phase I is antiferromagnetic it has been suggested that phase III is a spin-Peierls, at room temperature [78]. Indeed, calculations using the LDA + U method give magnetic moments of the Ti atoms in this proposed AFM structure, see figure 4.5. As can be seen in figure 4.6a, it also gives an insulator. Nevertheless, LDA + U does not reproduce the dimerisation of the Ti-chains, see figure 4.7.

Compressing phase III the dimerisation of the chains increases. Also in calculations the dimerisation increases, leading to better agreement with experiments. At the same time the magnetic moments decrease, see figure 4.5, and the fundamental gap shrinks continuously until it closes, see figures 4.6a and 4.6b. As this occurs however, there is a transition into two new phases, called phase IV and V. In paper VI, we investigate the structural and electronic properties of these two phases. By calculating the enthalpy of phase III, IV, and V we see that phase IV is metastable, see figure 4.8. Phase V is the first occurrence of an inorganic compound featuring fivefold coordinated phosphorous [78].

Figure 4.6 shows the DOS of TiPO_4 at different pressures. Note that with the transition into phases IV and V the fundamental gap opens up and remains open as pressure is increased further. For phase IV the gap shrinks as pressure is increased, see figures 4.6c and 4.6d, whereas for phase V the gap does not change, see figures 4.6e and 4.6f. The magnetic moments of

Figure 4.4: Crystal structures observed in TiPO_4 under increasing compression (a) phase I, (b) phase III, (c) phase IV and (d) phase V. Ti atoms are shown in blue, P are purple and O are red. Also shown in blue are the Ti-O polyhedra and the P-O polyhedra are purple. Images from paper VI

phase IV, shown in figure 4.5, continue to decrease with pressure; whereas in phase V, the magnetic moments are large and stable. It thus seems that the transition from phase III to phase V is a case of an inverse Mott transition occurring at high pressure.

Our calculations show that phase III is an insulator, with a fundamental gap formed by the Ti d-electrons, figure 4.6. Using LDA + U and assuming AFM order we find that the magnetic moments of the Ti atoms continuously decrease as pressure is increased, at the same time the fundamental gap of

Figure 4.5: Calculated magnetic moments of TiPO_4 phases III, IV, and V as a function of pressure. For phase III the magnetic moments vary between chains. Adapted from paper VI.

phase III shrinks. Eventually, the gap closes completely and the magnetic moments vanish, indicating a possible insulator to metal Mott transition.

As we discuss in paper VII the Ti dimers in phase III might form singlet states, meaning there should be no magnetic order in phase III at low temperatures. Such a dimer can be investigated using a simple Hubbard model with only two sites, see figure 4.9. Following [14], the Hamiltonian of such a model is:

$$\hat{H} = -t \sum_{\sigma} c_{1\sigma}^{\dagger} c_{2\sigma} + c_{2\sigma}^{\dagger} c_{1\sigma} + U \sum_{i=1}^2 n_{i\uparrow} n_{i\downarrow}, \quad (4.3)$$

where σ denotes the different spin directions $\uparrow$ and $\downarrow$. We investigate this system at half filling, meaning we have two electrons in the dimer. The possible states of the system are

$$|\uparrow, \downarrow\rangle, |\downarrow, \uparrow\rangle, |\uparrow\downarrow, 0\rangle, |0, \uparrow\downarrow\rangle, |\uparrow, \uparrow\rangle, |\downarrow, \downarrow\rangle, \quad (4.4)$$

where we denote the sites as $|1, 2\rangle$, with site 1 being the left one and site 2 the right one. The occupancy of each site is denoted with 0 if there is no electron on the site, $\uparrow$ or $\downarrow$ if there is one electron of spin up or down on the site and $\uparrow\downarrow$

Figure 4.6: Calculated DOS for TiPO_4 phases III, IV and V. Black line refers to the total DOS of the unit cell. Blue and red refer to the site and orbital-projected DOS. Energy given relative to the Fermi energy, E_F . Images from paper VI

if there are two electrons on the site. The Hamiltonian matrix of this system becomes:

$$\begin{bmatrix}
 & |\uparrow, \downarrow\rangle & |\downarrow, \uparrow\rangle & |\uparrow\downarrow, 0\rangle & |0, \uparrow\downarrow\rangle & |\uparrow, \uparrow\rangle & |\downarrow, \downarrow\rangle \\
 \langle\uparrow, \downarrow| & 0 & 0 & -t & -t & 0 & 0 \\
 \langle\downarrow, \uparrow| & 0 & 0 & -t & -t & 0 & 0 \\
 \langle\uparrow\downarrow, 0| & -t & -t & U & 0 & 0 & 0 \\
 \langle 0, \uparrow\downarrow| & -t & -t & 0 & U & 0 & 0 \\
 \langle\uparrow, \uparrow| & 0 & 0 & 0 & 0 & 0 & 0 \\
 \langle\downarrow, \downarrow| & 0 & 0 & 0 & 0 & 0 & 0
 \end{bmatrix}. \quad (4.5)$$

The eigenstates and eigenvalues of this matrix are (in order of increasing eigenvalues):

Figure 4.7: Dimerisation of Ti-chains in TiPO_4 phase III. Ti-Ti distances are shown as $d_{\text{Ti-Ti}} = c/2 + \delta$. Image from paper VII.

Eigenvalue	Eigenstate (not normalised)
$\frac{U}{2} - \frac{1}{2}\sqrt{U^2 + 16t^2}$	$\frac{-4t}{-U+\sqrt{U^2+16t^2}} \uparrow, \downarrow\rangle + \frac{4t}{-U+\sqrt{U^2+16t^2}} \downarrow, \uparrow\rangle + \uparrow\downarrow, 0\rangle + 0, \uparrow\downarrow\rangle$
0	$ \uparrow, \uparrow\rangle$
0	$ \downarrow, \downarrow\rangle$
0	$- \uparrow, \downarrow\rangle + \downarrow, \uparrow\rangle$
U	$- \uparrow\downarrow, 0\rangle + 0, \uparrow\downarrow\rangle$
$\frac{U}{2} + \frac{1}{2}\sqrt{U^2 + 16t^2}$	$\frac{-4t}{U+\sqrt{U^2+16t^2}} \uparrow, \downarrow\rangle + \frac{-4t}{U+\sqrt{U^2+16t^2}} \downarrow, \uparrow\rangle + \uparrow\downarrow, 0\rangle + 0, \uparrow\downarrow\rangle$

Figure 4.8: Calculated enthalpy of TiPO_4 , phase III, IV and V. All values are plotted relative to phase III. Image from VI

Figure 4.9: Schematic picture of the Hubbard dimer.

The spin singlet ground state and the ground state energy of the Hubbard dimer at half filling is;

$$|\psi_0\rangle = \frac{4t}{-U + \sqrt{U^2 + 16t^2}} |\uparrow, \downarrow\rangle + \frac{4t}{-U + \sqrt{U^2 + 16t^2}} |\downarrow, \uparrow\rangle + |\uparrow\downarrow, 0\rangle + |0, \uparrow\downarrow\rangle, \quad (4.6)$$

$$E_0 = \frac{U}{2} - \frac{1}{2} \sqrt{U^2 + 16t^2}. \quad (4.7)$$

To investigate the dimers further it would be necessary to go beyond the single site DMFT method and instead use a cluster DMFT (cDMFT) method [45, 79].

Modelling the paramagnetic state

5.1 The paramagnetic state

The paramagnetic state of a material is characterized by a net zero magnetization in the absence of an applied magnetic field. However, when an external magnetic field is applied, a net magnetisation is obtained. By performing measurements of the magnetization, M , as a function of applied magnetic field, $\vec{H} = H\vec{z}$, one can calculate the uniform spin susceptibility,

$$\chi_{\vec{q} \rightarrow \vec{0}} = \frac{dM}{dH}. \quad (5.1)$$

For localized robust magnetic moments, the uniform spin susceptibility will follow a Curie-Weiss law, i.e.,

$$\chi_{\vec{q} \rightarrow \vec{0}}(T) \propto \frac{\mu_{eff}^2}{T - T_c}, \quad (5.2)$$

for temperatures greater than the critical temperature T_c .

5.2 Disordered local moments

In order to simulate the paramagnetic state of a system with well described magnetic moments, a cell with the local magnetic moments randomly oriented can be used. It is practically impossible to simulate a truly random distribution of atoms. A random structure can potentially be approximated by increasing the size of the simulation cell, however this increases the computational cost of the calculation, and for a system of N atoms there are a total of $N!$ structures to average over. This problem was encountered in alloy theory, where the need to simulate a random configuration of different elements is

Figure 5.1: SQS structure for magnetic moments of spin up (blue) and down (red).

the basis of the entire field. In order to circumvent this problem the special quasi-random structures (SQS) method was invented [80]. The SQS method utilises the fact that in order to simulate a truly random structure one can achieve very good results even with a relatively small simulation cell, as long as the cell is set up in such a way that the average short range order parameters for the first few coordination shells vanish. Though the SQS method was originally developed for modelling alloys, it can be adapted to simulate magnetic disorder by treating atoms with magnetic moments pointing in different directions as belonging to different elements [81]. These magnetic atoms can then be placed in a SQS.

To model the paramagnetic state of a material using DFT, following [81, 82], we start with a Heisenberg Hamiltonian

$$\hat{H} = \sum_{ij} J_{ij} \bar{S}_i \bar{S}_j \quad (5.3)$$

where $\bar{S}_i$ is the spin vector on site i and J_{ij} is the exchange parameter for site i and j , describing the magnetic interaction between site i and j . We assume that all spins have the same magnitude i.e., $\bar{S}_i = S \bar{e}_i$, where $\bar{e}_i$ is a unit vector. In the paramagnetic state the average spin-spin correlation function, $\langle \Phi \rangle$, for

magnetic atoms in any nearest neighbour shell, must vanish, i.e.,

$$\langle \Phi \rangle = \frac{1}{N} \sum_{ij} \bar{e}_i \bar{e}_j = 0, \quad (5.4)$$

for any nearest neighbour shell, containing N magnetic sites, i and j are indices of sites within the shell. In order to fulfil equation 5.4 it is sufficient to simulate disorder in the neighbour shells with non-zero J_{ij} . The exchange interaction parameters are decaying with distance, so it is enough to set up an SQS with a limited number of short range parameters set to zero. An example of a SQS cell where the first three short range order parameters vanish is shown in figure 5.1. The electronic structure of this supercell can then be calculated using DFT. This method is known as the *SQS disordered local moments* (DLM) method. The temporal disorder of the paramagnetic state is replaced by spatial disorder, and the paramagnetic state is modelled as a symmetry broken state.

5.3 A quantum impurity

Another way to simulate the paramagnetic state of a material is by using the DMFT method. With DMFT, all excited states of the single impurity can be probed using QMC. This includes many-electron excitations, not just single particle excitations. DFT calculations are performed at 0 K, but in DMFT the electronic temperature is included.

Within DMFT one can investigate the properties of the correlated electrons, such as the average spin state and the spin-spin autocorrelation function, by probing the impurity state. From the average value of the $\hat{S}^2$ operator one can obtain an effective magnetic moment as,

$$\mu_{eff} = g_e \mu_B \sqrt{\langle S^2 \rangle}, \quad (5.5)$$

where $g_e \approx 2$ is the electron g-factor, and μ_B is the Bohr magneton. The z-component of the spin vector can be calculated using the operator

$$\hat{S}_z = \sum_i (n_{i,\uparrow} - n_{i,\downarrow}), \quad (5.6)$$

where $n_{i,\sigma}$ is the occupation number of electrons with spin σ , in orbital i .

Whether the magnetic moment of an atom is localized or itinerant can be understood from the spin-spin autocorrelation function, $\langle S_z(\tau) S(0) \rangle$ [83], measured in imaginary time, $\tau = it$. At $\tau = 0$ the spin-spin autocorrelation function equals $\langle S_z^2 \rangle$. If the value of the autocorrelation function remains close to its initial value, the magnetic moment is robust. If it decreases sharply the magnetic moment is instead itinerant. By integrating the spin autocorrelation function one obtains the local spin susceptibility

$$\chi_{loc} = \mu_B^2 \int_0^\beta \langle S_z(\tau) S_z(0) \rangle d\tau. \quad (5.7)$$

Figure 5.2: Volume dependence of the ground state magnetic structure of Mn_2GaC as a function of unit cell volume, calculated with LDA and PBE. (a) Net moment of lowest energy configurations as a function of volume. (b) Selected lowest energy spin spirals, corresponding to different volumes, as indicated in (a). Figure from [84], reused with the authors permission.

For localized magnetic moments, the local spin susceptibility will follow a Curie-Weiss law, see equation 5.2.

5.4 The paramagnetic state of Mn_2GaC

The compound Mn_2GaC was predicted and synthesised in 2014 [85]. It is an example of a magnetic compound among the so-called MAX-phase materials [86]. They are layered compounds composed of layers of M - metal - and X - C or N - ions interconnected by A group elements. MAX-phases were first discovered in the 1960s [87], and later rediscovered in 1996 [88]. Their combination of ceramic and metallic properties, as well as the fact that they are easily machined, makes them interesting for a diverse range of applications, such as hard coatings, and coatings for electrical contacts.

Whether the magnetic moments of the MAX-phases are robust local moments, or itinerant in nature is an open question. For Mn_2GaC , DFT calculations using LDA and PBE indicate strong local moments [84], with a complicated magnetic structure that is strongly dependent on the crystal structure, see figure 5.2. For small volumes the ground state is FM. As volume is in-

Figure 5.3: (a) Calculated spin-autocorrelation function for paramagnetic Mn_2GaC . Image from paper VIII. (b) Calculated inverse of uniform spin susceptibility and local spin susceptibility as a function of temperature. Adapted from data from paper VIII.

creased the system assumes a non-collinear AFM structure, and finally it assumes a collinear AFM structure. However, experiments of $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{GaC}$ indicate that the magnetic moments are itinerant in nature, and the undoped ground state is non-magnetic [89].

In paper VIII we investigate the nature of the magnetic moments in the high temperature, paramagnetic phase of Mn_2GaC , using the DFT + DMFT as well as the supercell DLM method.

Figure 5.3a shows the calculated spin autocorrelation function for $\beta = 9 \text{ eV}^{-1}$, and figure 5.3b shows the inverse local spin susceptibility, χ_{loc}^{-1} , as a function of temperature. The local spin autocorrelation function shows a strong dependence on τ , and the local spin susceptibility shows almost no temperature dependence, indicating that the magnetic moments are not robust.

Further indication that the magnetic moments are itinerant is seen in the inverse of the uniform spin susceptibility, $\chi_{\vec{q} \rightarrow 0}^{-1}$, figure 5.3b, showing no temperature dependence.

In a system with interacting electrons, the electronic bands become smeared. In figure 5.4a we see the $\vec{k}$ -dependent spectral function, $A(\vec{k}, \omega)$, calculated at $\beta = 9 \text{ eV}^{-1}$. Around the Fermi energy there are clearly defined bands. Furthermore, the band structure calculated with non-magnetic LDA, figure 5.4b, is very similar, indicating that the effect of dynamic interactions in Mn_2GaC is weak.

For the supercell DLM calculations we set up a $2 \times 2 \times 2$ supercell, and distribute the magnetic moments as in figure 5.1. After calculating the electronic structure, using the PBE functional, we obtain the distribution of magnetic moments shown in figure 5.5a. The wide distribution of moments is further

Figure 5.4: Calculated $\bar{k}$ -resolved spectral function of Mn d-electrons obtained from (a) paramagnetic LDA + DMFT, and (b) nonmagnetic LDA. Images from paper VIII.

Figure 5.5: (a) Distribution of Mn magnetic moments obtained from supercell DLM calculations using PBE. Image from paper VIII. (b) Calculated density of states using nonmagnetic LDA, DLM, and DFT + DMFT. Image from paper VIII.

indication that they are not robust. The average of the magnetic moments is $0.93 \mu_B$, which is lower than the calculated moment of the FM phase [84]. It is important to note that after electronic relaxation, some of the magnetic moments have flipped, meaning we have lost the initial SQS. We can also compare the DOS for the supercell DLM, DFT + DMFT, and non-magnetic LDA calculations, figure 5.5b. The DOS obtained from DFT + DMFT is very similar to that obtained with the supercell DLM method, indicating that the supercell DLM method is capable of describing the electronic properties of the paramagnetic phase of Mn_2GaC , despite the fact that the magnetic moments are not robust. We also see that the DOS of non-magnetic LDA and DFT + DMFT are very similar, indicating that dynamic electron interactions do not play a large role in determining the electronic structure.

By estimating the magnetic moment using equation 5.5 we get $\mu_{eff} \approx 1.89 \mu_B$, larger than what we get from the supercell DLM calculations. However, if we look at the z-component of the magnetic moment we get $\mu_{eff,z} \approx 1.1 \mu_B$, which agrees well with the DLM results.

To conclude, our calculations indicate that in the high temperature, paramagnetic state, Mn_2GaC shows itinerant electron magnetism, and that this state can be accurately described using both DFT + DMFT and supercell DLM. On short time scales DMFT gives local moments that agree with those obtained using DLM. This indicates that, despite the itinerancy DLM can be used to describe this compound.

Conclusions and outlook

In this thesis I have presented investigations of electronic transitions in various compounds based on methods ranging from KS-DFT to DFT + U, and DFT + DMFT.

Electronic transitions, such as ETTs, may be induced by external pressure. This is the case for hcp-Os, at pressures of about 150 GPa. We find that even for a weakly correlated material such as Os, the description of the electronic structure is improved by including dynamic correlation effects. At even higher pressures, around 440 GPa, it has been suggested that a CLC occurs. We investigate the CLC transition, and find that it should be a general feature of the heavy transition elements. Currently, there exists no theoretical description of the CLC, or what effects it might have on thermodynamic or structural properties. Together with experimentalists we search for the CLC in Ir, which is predicted to occur at around 80 GPa. Unfortunately, the XAS-edge investigated does not directly probe the states involved in the CLC. Therefore the effect of the CLC on the observed XAS spectra should be weak, and indeed we see no indication of the CLC in the measured spectra. Future experiments that can directly probe the states involved in the CLC are needed. Unfortunately, the CLC occurs at different pressures in different materials, and involves different states. It therefore becomes necessary to match the spectroscopic method used not only to the states involved in the transition, but also to what measurements can be performed at the synchrotron.

In transition metals, the balance between kinetic and Coulomb correlation energy leads to magnetism, which must be described in terms of itinerant electrons. A proper description of this phenomena is still challenging for electronic structure theory. Reasonable results are obtained using KS-DFT with the PBE functional, for the elemental ferromagnets Fe, Co, Ni. The

SCAN functional is said to represent a significant step towards a truly universal exchange-correlation functional. However, its performance for itinerant electron magnets is not an improvement over PBE.

At high temperatures magnetic materials undergo a transition to the magnetically disordered PM state. We present an investigation of the paramagnetic state of Mn_2GaC . Using DFT + DMFT and SQS DLM we investigate the Mn d-electrons, which are responsible for the magnetism. The quantum impurity description of the PM state indicates weak correlations, with itinerant nature. This result is supported by the SQS DLM calculations. It is worth noting that this investigation only concerned the high temperature PM state, the low temperature magnetically ordered states of Mn_2GaC need to be investigated in order to fully establish the nature of the magnetic moments.

If the Coulomb interactions are dominating, a system may become a Mott insulator, with AFM ordered local moments, such as NiO. Application of pressure is expected to cause a Mott insulator-to-metal transition, in combination with a structural transition. We investigate the Mott transition in a study combining DFT + U calculations and experiments. Although the Mott transition is best described by including dynamical effects, such as in the DFT + DMFT method, our results indicate that DFT + U is capable of describing the structural and electronic properties of NiO at high pressure. We see no indication of a Mott transition occurring in NiO at 280 GPa.

Another example of a Mott insulator is the high pressure phase III of TiPO_4 . Here, we find that the pressure induced closing of the Mott gap is connected to a structural phase transition. Astonishingly, these novel high pressure phases, called IV and V, both feature a Mott gap and reemerging magnetic order. In addition, the detailed crystallography of phase III seems to reveal a spin-Peierls state, with dimerised Ti chains. However, the dimerisation of spin-Peierls phase III is not satisfactorily reproduced with DFT + U, which does not describe the singlet state of the dimers. In order to further investigate the spin-Peierls state, calculations should include non-local dynamical correlations within the Ti dimers, e.g., using the cluster extension of DFT + DMFT.

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- [I] M. Ekholm, D. Gambino, H. J. M. Jönsson, F. Tasnádi, B. Alling, and I. A. Abrikosov. “Assessing the SCAN functional for itinerant electron ferromagnets”. In: *Phys. Rev. B* 98 (9 Sept. 2018).
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I calculated the NiO XAS spectra and contributed to the manuscript.

- [VI] H. J. M. Jönsson, M. Ekholm, S. Biermann, M. Bykov, and I. A. Abrikosov. “Mott and spin-Peierls physics in TiPO_4 under high pressure”. In: (Submitted).

I participated in planning, and performed the calculations and analysed the data. I was responsible for writing the manuscript.

- [VII] H. Johan M. Jönsson, Marcus Ekholm, Maxim Bykov, Leonid Dubrovinsky, Sander van Smaalen, and Igor A. Abrikosov. “Inverse pressure-induced Mott transition in TiPO_4 ”. In: *Phys. Rev. B* 99 (24 June 2019).

I participated in planning, and performed the calculations and analysed the data. I was responsible for writing the manuscript.

- [VIII] H. Johan M. Jönsson, Marcus Ekholm, Ivan Leonov, and Igor A. Abrikosov. “High temperature magnetic properties of the MAX phase Mn_2GaC ”. In: (In manuscript).

I participated in planning, and performed the calculations and analysed the data. I was responsible for writing the manuscript.

Papers

The papers associated with this thesis have been removed for copyright reasons. For more details about these see:

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-164314>

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