## Electronic Correlation Effects in Transition Metal Systems: From Bulk Crystals to Nanostructures

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I suppose it is tempting, if the only tool you have is a hammer, to treat everything as if it were a nail.

Abraham H. Maslow [279]

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## Abstract

Condensed matter systems containing transition metals, be it single molecules or crystalline solids, exhibit many complex physical phenomena that warrant the constant interest of the scientific community. Their complex behavior emerges as a feature of the strongly correlated electrons occupying the partially filled d or f shells. From the technological point of view such systems are of interest, because they often show a complex phase diagram and, furthermore, their properties can be controlled by external handles, like temperature, pressure etc. Such systems pose a challenge to theoretical physics, since the multitude of phases exhibited by them indicates many competing degrees of freedom at work. The present thesis is concerned with a successful general methodology that can be applied for the realistic description and in some cases even prediction of the properties of systems containing strongly correlated electrons. The framework that we refer to as DFT++ is a general scheme to combine realistic density functional theory calculations with model Hamiltonian approaches to produce a unified ab initio description.

In the first part of this work we are concerned with the development of the general DFT++ methodology within the formalism of the projector augmented-wave method. We outline the general structure of the approach and show the specifics of an implementation involving only an Anderson impurity model and also self-consistent dynamical mean-field theory. Certain intricacies occurring at the interface between density functional and model Hamiltonian methods are also discussed in detail, with special focus on the so-called double counting of interaction terms.

Subsequently, we apply the DFT++ method to different systems ranging from bulk crystals to single atoms adsorbed on a surface. We begin by examining the spin state transitions in  $LaCoO_3$ , which have been under debate for over 50 years. We find corroborating evidence for one of the two major scenarios discussed in this context, namely the low-spin to high-spin transition, not involving the so-called intermediate-spin state.

As a second application we study the impact of dynamical correlations on the electronic structure of different transition metal-benzene sandwich molecules trapped between the tips of copper nanowires as examples of molecular magnetic devices. We find that, depending on the chemical valence of the transition metal center and in particular the geometry of the molecule the unusual orbital Kondo effect can be observed and, to some extend, controlled.

Finally, we consider the series of isolated manganese, iron, cobalt and nickel atoms adsorbed on a silver surface and explain their excitation spectra. We report on valence electron photoemission experiments revealing the complex evolution of the electronic spectra through this series: we find a monotonous decrease in the splitting of higher energy features and a non-monotonous variation of low energy spectral weight. By means of calculations using the DFT++ formalism we explain the photoemission results and show that both observations can be traced back to Hund's exchange. vi

# Zusammenfassung

Festkörpersysteme, die Übergangsmetalle entahlten, seien es einzelne Moleküle oder kristalline Festkörper, weisen viele komplexe physikalische Phänomene auf, die das konstante Interesse an Ihnen rechtfertigen. Das komplexe Verhalten dieser Systeme kann auf die stark korrelierten Elektronen in den teilweise gefüllten d oder f-Schalen zurückgeführt werden. Solche Systeme stellen eine Herausforderung für die Theorie dar, da die Vielzahl der möglichen Phasen auf viele konkurrierende Freiheitsgrade hinweist. Die vorliegende Arbeit beschäftigt sich mit einer allgemeinen Methode, die für die realistische Beschreibung und Vorhersage der Eigenschaften von Systemen mit stark korrelierten Elektronen angewendet werden kann. Die Methodik, die wir als DFT++ bezeichnen, stellt eine allgemeine Vorschrift zur kombination realistischer Dichtefunktional-Rechnungen mit Modellansätzen dar, um eine ab initio Beschreibung zu realisieren.

Im ersten Teil dieser Arbeit sind wir mit der Entwicklung der allgemeinen DFT++ Methodik, innerhalb des Formalismus der Projektor Augmentierten Ebenen Wellen-Methode, befasst. Wir skizzieren die Struktur des Ansatzes und zeigen die Besonderheiten einer Implementierung, die ein Störstellenmodell oder auch eine selbstkonsistente dynamische Molekularfeldtheorie beinhaltet. Bestimmte Feinheiten an der Schnittstelle zwischen der Dichtefunktionaltheorie und dem Modellansatz werden ebenfalls ausführlich diskutiert.

Anschließend wenden wir obige Methode auf verschiedene Systeme an, die sowohl kristalline Festkörper, als auch einzelne Atome auf einer Oberfläche beinhalten. Wir beginnen mit der Untersuchung der Spin-Übergänge in LaCoO<sub>3</sub>. Wir finden Hinweise für eines der beiden Szenarien, die in diesem Zusammenhang diskutiert werden, nämlich den "low-spin" zu "high-spin"- Übergang, der nicht den sogenannten "intermediate-spin"-Zustand beinhaltet.

Als zweite Anwendung untersuchen wir die Auswirkungen der dynamischen Korrelationen auf die elektronische Struktur von verschiedenen Übergangsmetall-Benzol Sandwich Molekülen zwischen den Spitzen eines Kupfernanodrahtes als Beispiele für eine molekulare magnetische Nanostruktur. Wir finden, dass, beeinflusst durch die chemische Valenz des Übergangsmetallzentrums und insbesondere die Geometrie des Moleküls, der ungewöhnliche orbitale Kondoeffekt beobachtet und kontrolliert werden kann.

Schließlich betrachten wir isolierte Atome von Mangan, Eisen, Kobalt und Nickel auf einer Silberoberfläche und erklären ihre Anregungsspektren. Wir berichten über Photoemissionsexperimente, die die komplexe Entwicklung der elektronischen Spektren zeigen: wir finden eine monotone Abnahme der Aufspaltung von Charakteristika bei höheren Energien und eine nicht-monotone Variation des spektralen Gewichts bei niedrigen Anregungsenergien. Durch Berechnungen mit Hilfe des DFT++ Formalismus erklären wir die Messungen und zeigen, dass das beobachtete Verhalten zum Hundschen Austausch zurückverfolgt werden kann. viii

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## Introduction

The understanding of the properties of transition metal systems is key to the three main branches of the natural sciences, physics, chemistry, and biology. Transition metals play a leading role in e.g. high temperature superconductivity [246], organometallic molecules [82], important in various areas of chemistry like catalysis, and biologically relevant molecules, like haemoglobin, or cobalamine (known also as Vitamin B12), to name only a few. Transition metals are furthermore used by certain anaerobic bacteria in their respiratory cycles, see e.g. [75]. It has even been put forward that transition metals were critical ingredients in the prebiotic soup that facilitated the formation of the first biological molecules as catalysts or electron donors that were later to become lifeforms [292].

Compounds containing transition metals can also be employed in energy production technologies, like catalytic oxidation of volatile organic contaminants [253], hydrocarbons [7], carbon oxide and lean nitrogen oxide trapping that could lead to new diesel engines [202], oxygen membranes to operate at high temperatures in oxyfuel power plants [65], fuel cells technology [29, 9, 247] and thermoelectric power generation [410].

In addition, transition metal compounds exhibit many fascinating effects that are of fundamental interest and, at the same time, pose great challenges for physicists. The iron series 3d transition metals contain the prototypical ferromagnets, iron, cobalt, and nickel, that are to this day subject of intensive research [256, 249, 250, 219, 24]. Transition metal alloys, like Ba<sub>x</sub>La<sub>5-x</sub>Cu<sub>5</sub>O<sub>5(3-y)</sub> or YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>, referred to as *cuprates*, were also the first high temperature superconductors [36]. Recently, the iron based *pnictides*, LaO<sub>1-x</sub>F<sub>x</sub>FeAs, emerged as another series of high temperature superconducting compounds containing a 3d transition metal [190]. Cuprates, however, remain the materials with the highest critical temperatures available, reaching over 130K in HgBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>8+ $\delta$ </sub> [377, 87].

Also other intrinsic many-body effects, like the Kondo effect [156] or the Mott metal insulator transition [170] occur in transition metals and their compounds. Recently, topologically nontrivial phases, relevant, inter alia, in the context of quantum hall effects [299] were realized on certain surfaces of transition metal perovskite materials [459].

It is thus of interest to many fields of science to understand the fundamental forces and interactions governing the behavior of such systems. Unfortunately, compounds exhibiting so many different effects and phases on the electronic level tend to be complicated to de-

#### 2 Introduction

scribe theoretically. On the other hand that is exactly what makes them so interesting. This is where transition metals touch one of the main challenges in solid state physics, which is the theoretical understanding of materials exhibiting electronic correlation effects. Correlation means in this case, that the valence electrons in the system cannot be described as independent particles, but instead have to be described as interacting constituents of a many-body state. Functioning theories exist for the description of simple metals where correlation effects are negligible and also for insulators where strong electron localization is prevalent. The intermediate region between those two extremes, however, shows unusual physical phenomena and turns out to be most difficult to describe, since perturbative approaches are not applicable. Transition metal compounds often tend to fall into latter category and make the use of sophisticated theoretical methods necessary.

The naïve ansatz for the solution of the many-body problem would be writing down the many-body Hamiltonian and then solving the Schrödinger equation. This approach of course runs into problems very quickly as the number of particles increases. A description of a solid typically would require the solution of a differential equation containing the often-cited  $10^{23}$  variables. It is evident that a direct solution, despite being impossible, also would produce an enormous amount of data that would probably defy interpretation. The solution would contain all effects on all energy scales and would possibly obfuscate the view on any underlying simpler structure. As a consequence, methods have to be developed to be able to cope with the complex electronic structure problem on a different footing than just solving the Schrödinger equation in a straight forward manner. One of the most prominent approaches to electronic structure is density functional theory (DFT) that earned Walter Kohn, one of the main contributors, the Nobel prize [215]. This theory uses the electronic density as its basic variable thereby reducing the amount of variables from the enormous number quoted above to just three in principle. Density functional theory has earned merits by reproducing the electronic properties of many weakly correlated systems, like simple metals, semiconductors or band insulating materials, to an astounding accuracy, yet it is not applicable to systems where electronic correlations are strong. In such systems the Coulomb interaction between electrons is large and the electrons become more localized, which leads to a physical behavior that cannot be described by DFT. Prominent examples are, again, transition metal systems like NiO, which experimentally is an insulator with a gap of 4.3eV [375], but is predicted to be a metal by DFT [21], or single transition metal atoms on surfaces that exhibit the Kondo effect [208, 443], which cannot be captured by DFT alone. Many other systems exist for which DFT fails qualitatively for different reasons. This is no surprise, since the theory involves certain approximations, like the Kohn-Sham mapping onto a system of non-interacting particles, or the local density approximation (LDA) to the exchange-correlation functional, that make it best suitable for itinerant systems [216]. Correlated electron systems, however, are most often quite the opposite. The electrons in such a system often occupy open shells with a high angular momentum, like d of f shells, and by virtue of their strong mutual interaction via Coulomb forces remain localized close to their respective ion. It is not surprising that a theory that at its heart is based on an electron gas model has difficulties in their description. On the other hand, there exist other approaches that have the capability to describe the effects of strong correlations, but are limited in other ways often due to the sheer complexity of the many-body problem.

Model Hamiltonian approaches can be used to take account of electronic correlations and to describe the complex physical behavior of correlated electron systems including the Mott metal-insulator transition, superconductivity, localization etc. As the name indicates, *realistic* systems are beyond the scope of applicability of such approaches. In general, a model Hamiltonian is devised to be as simple as possible, but still to show real world behavior. For a few years now a variety of methods exist, in general referred to as the DFT++ or LDA++ method following Ref. [255], that combine the material specific capabilities of DFT with a model Hamiltonian. With this approach it is possible to perform first principles calculations for realistic materials using realistic geometries and including local quantum correlations via a model Hamiltonian. The deficiencies of the density functional description of correlated systems are in part remedied by adding another layer to the computations. In this second layer the system is divided into a weakly correlated part and a strongly correlated one. The former is assumed to be correctly described by density functional theory. The latter, however, is additionally treated in a lattice or impurity model, that includes the Coulomb interactions of the correlated electrons as exactly as possible. This division into correlated and uncorrelated parts is somewhat arbitrary and in principle dictated by the labour of computation that only allows at most on the order of ten correlated orbitals depending on the approximations involved. Of course, approximations have to be applied to make this second layer solvable in the first place. One very prominent approximation for lattice models is the dynamical mean-field theory (DMFT) [124]. It neglects spatial fluctuations and thereby the momentum dependence of the electron self-energy, which allows for the lattice problem to be mapped onto the problem of an impurity coupled to an electron reservoir. This impurity problem is still a complicated many-body problem that has to be solved self-consistently. The combination of DFT and DMFT results in the so-called DFT+DMFT approach (often called LDA+DMFT, because of the almost synonymous usage LDA and DFT), a method that is capable of the description of both itinerant and correlated behavior on the same footing. Also extensions exist that take into account spatial fluctuations, like cluster extensions of DMFT [275] or the dual fermion approach [366]. The DFT+DMFT methodology has been applied in recent years to many condensed matter problems generating an enormous amount of research output<sup>1</sup>.

<sup>1</sup>The google scholar database (on September 10th, 2013) reports about 7500 papers containing "dynamical mean-field" in the title or abstract since the year 2000 alone. Most of these relate to condensed matter, although the term "dynamical mean-field" is not exclusive to this field.

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In this work we will be concerned with the DFT++ methodology on different levels. The first half of this work focusses on the interface between the density functional part of the calculation and the subsequent impurity solver treatment. Part of this will be devoted to the technical problem of the double counting of interaction terms that is an obstacle to finding a parameter free DFT++. The second half will consist of applications of the DFT++ in various flavors to systems ranging from bulk crystals to single molecules and atoms.

### **Structure and Scope**

The present work is organized as follows: In chapter 1 the applied methodology is presented in detail. We begin by introducing density functional theory in general and present specific implementations of the method relevant for this work, focussing on the projector augmented method (PAW) by Blöchl. We then move on to introduce elements of manybody theory relevant for later developments and present different model Hamiltonians suited for lattices (Hubbard model) and magnetic impurities (Anderson impurity model) as well as the theory connecting the two in certain limits: the dynamical mean-field theory (DMFT). Finally the combination of the DFT and the many-body model Hamiltonian approaches (DFT++, DFT+DMFT) is presented and elaborated on. Since the DFT++ methodology requires the (repeated) solution of impurity models we discuss different approaches for tackling such problems, referred to as *impurity solvers* in an own section. Here we briefly review the solvers that have been used in this work, these include quantum Monte Carlo, the non-/one-crossing approximations and exact diagonalization, and point out their respective merits and deficiencies. A discussion of the problem of analytic continuation of quantum Monte Carlo data concludes the methodology chapter.

The following chapters are in part based on published work, that is indicated in the respective chapter title. They are mostly self contained since they cover different topics: In chapter 2 we elaborate on the intricacies of the DFT++ methodology implemented in the PAW framework. We show how the method is implemented using a projection on local orbitals and show different possible ways to use DFT++ for bulk systems or single/multiple impurities. Since the Coulomb interaction is included in the DFT to some degree, the model Hamiltonian treatment leads to a double counting of some interaction terms. The double counting correction is meant to compensate this. As we will see in chapter 3 it is not uniquely defined and different approaches exist to determine it.

We then move on to applications of the methodology in the subsequent three chapters. We begin with the bulk system  $LaCoO_3$  that has been a matter of controversy in the scientific community for decades. We add to the discussion by presenting DFT++ results for the material obtained within DFT+DMFT with an exact diagonalization solver in chapter 4.

From three dimensional bulk systems we move on to one dimensional nanocontacts hosting transition metal-benzene sandwich molecules in chapter 5. These systems are shown to exhibit a Kondo effect for certain central atoms and parameter regimes. Finally, we focus on *zero* dimensional single transition metal atoms on a surface of silver in chapter 6 that are a testing ground for experimental and theoretical methodologies. We find that the effective Coulomb interaction in 3d transition metal atoms on noble metal surfaces is strongly influenced by the filling of the shell, in accordance with theoretical predictions for simple models.

## Chapter 1

## **Theory and Methodology**

### **1.1** Ab initio theory of condensed matter systems

In sciences concerned with condensed matter, typically these would include physics, chemistry and to some extend biology, one is typically faced with systems containing a large number of atoms. Examples are, large molecules, nano devices or crystalline solids.

The task of an ab initio theory of condensed matter systems would now be to compute properties of these systems without using adjustable parameters, using ideally only the atom numbers and the geometry of the problem as inputs.<sup>1</sup>

In quantum mechanical terms any condensed matter problem can be formulated using the Hamiltonian of the system. For a system containing M nuclei and N electrons the Hamiltonian can be written down as

$$\hat{H} = - \sum_{A=1}^{M} \frac{\hbar^2}{2M_A} \Delta_A - \frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \Delta_i + \sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ + \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A e^2}{|\mathbf{r}_i - \mathbf{R}_A|} + \sum_{A < B}^{M} \frac{Z_A Z_B e^2}{|\mathbf{R}_A - \mathbf{R}_B|}$$

where capital indices run over the nuclei and  $\mathbf{R}_{A/B}$ ,  $\mathbf{r}_{i/j}$  and  $M_A$ ,  $m_e$  denote the positions and masses of nuclei and electrons respectively. The unit of electronic charge is denoted by e, while  $Z_{A/B}$  denotes the atomic number.

To compute ground state properties one would try to find solutions of the non-relativistic

<sup>1</sup>In general so-called ab initio theories, like density functional theory, can contain very many parameters. They can still be called *ab initio* ("from the beginning", or in this context "from first principles"), because these parameters have been fixed once and for all and are not adjustable.

time-independent Schrödinger equation<sup>2</sup>

$$\hat{H} \Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{R}_1,\ldots,\mathbf{R}_M) = E \Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{R}_1,\ldots,\mathbf{R}_M),$$

which quickly becomes unfeasible as the particle numbers N and M exceed 1. In addition to the impossibility of the task there is also the sheer amount of data that would be produced if a solution, hypothetically, could be obtained. The amount of storage needed would surpass the storage capabilities of mankind by far and would not provide much insight into the systems most important properties. Controllable approximations also provide a good way of finding the most important energy scales or degrees of freedom of a system when faced with a specific problem. In this way the behavior of a physical system can be reduced to include only few, most important, characteristics that are necessary to correctly describe the phenomenon at hand. Such an approach also facilitates the understanding of physical phenomena, while the complete solution of a problem, in our case the full wavefunction of the system  $\Psi$ , might obscure the underlying, often simple, mechanisms. It is thus both inevitable and desirable to introduce approximations to the full problem.

First, one observes, that nuclei and electrons have very different masses and therefore their motion is expected to take place on different time scales. This observation can be cast in a more precise form via the adiabatic or, in this case called, Born-Oppenheimer approximation [58]. It is assumed that the electrons are in a stationary state for every instantaneous configuration of the nuclear lattice and that the nuclei can be assumed to move in an instantaneously adjusted electronic background potential. This means, that the solution of the full problem in the presence of fixed ion cores will depend on the positions of the ions only parametrically facilitating a product ansatz for the wave function

$$\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{R}_1,\ldots,\mathbf{R}_M)=\Phi(\mathbf{R}_1,\ldots,\mathbf{R}_M)\psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)$$

One can thus reduce the problem to the electronic problem only described by the *electronic* Hamiltonian

$$\hat{H}_{\rm el} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \Delta_i + \sum_{i< j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A e^2}{|\mathbf{r}_i - \mathbf{R}_A|},$$
(1.1.1)

which contains only the terms shown and depends only parametrically on the nuclear coordinates  $\mathbf{R}_A$ .

This problem, while considerably less complex than the original one is still not solvable exactly for more than a few particles, since the Hilbert space of the problem grows exponentially, like  $4^N$  for a system with N sites or orbitals, see e.g. Ref. [264]. Consequently,

<sup>2</sup>Relativistic effects like spin-orbit coupling can of course also be incorporated into the theory on different levels, see e.g. [277].

further approximations have to be introduced.

In general, there are two complementary approaches to the problem, that can be called the ab initio and model Hamiltonian approaches. The former tries to solve the problem for real systems in nature by applying methods and approximations to the real Hamiltonian of molecules or crystals, while the latter tries to reduce nature to the most important interactions and to cast these most important terms into a model Hamiltonian, that is a simplified model for the real system. An example of an ab initio method is density functional theory, while the model Hamiltonian approach can be identified with lattice or impurity models like the Hubbard or Anderson models. We will briefly outline and discuss both approaches below and also the successful combinations of both, like the combination of density-functional-theory with the dynamical mean-field theory DFT+DMFT [124]. We will begin with DFT and discuss its various flavors and implementations, afterwards the Hubbard and Anderson models will be introduced, before we dwell on the combination of DFT with model Hamiltonians, which we will refer to as the DFT++ method, following the work of Lichtenstein and Katsnelson [255].

### **1.2 Density Functional Theory**

Density Functional Theory (DFT) relies on the Hohenberg-Kohn theorems [159] which establish the electronic density  $n(\mathbf{r})$  as the basic variable instead of the electronic wave function  $\psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ . These theorems substantiate that a formally exact formulation of the many-body problem based on the electronic density is possible. This basic idea behind density functional theory can be traced back to Thomas-Fermi theory, which was proposed in 1927 [414, 105]. In their work Thomas and Fermi introduced the notion of the electronic density as the basic variable of the electronic problem. One could compute the ground state energy of a system without knowledge of the full many-body wavefunction. This implies a tremendous reduction of complexity, since the sought function reduces to a three dimensional density instead of a 3N dimensional wave function. Later, Slater introduced the so called  $X_{\alpha}$  method, a basic version of what we know today as density functional theory [395]. Both predecessors of DFT can be obtained from their *modern* counterpart as certain limits, see, e.g., [188].

We will briefly present the Hohenberg-Kohn theorems, the reasoning behind them and their most important implications. The derivations presented are standard and can be found in the original papers [159, 216, 251], review articles, e.g., by Jones and Gunnarsson [188] or in the many books on DFT, for example, by Parr and Yang [324], Martin [277] or Kübler [233]. A brief description can also be found in my Diploma Thesis [192]. We follow the original line of reasoning provided by Hohenberg and Kohn; for the more general derivation by Levy we refer to his original work [251] or for reviews to Refs. [188, 324].

The method is aimed at providing a solution of the electronic many-body problem described in Eq. (1.1.1). It is, however, not limited to the specific case of electrons interacting with nuclei, but can describe interacting particles moving in some external potential. The Hamiltonian thus takes the very general form

.

$$\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{ee}}, \qquad (1.2.1)$$

where

$$\hat{T} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \Delta_i, \qquad \hat{V}_{\text{ext}} = \sum_i^N v(\mathbf{r}_i), \qquad \text{and} \qquad \hat{V}_{\text{ee}} = \sum_{i$$

are the kinetic energy, the external potential and a two-body interaction, respectively. The two body interaction  $w(|\mathbf{r}_i - \mathbf{r}_j|)$  depends only on the distance of the particles. The external potential  $v(\mathbf{r}_i)$  can, but again need not, be an ionic Coulomb potential. The specific form of the Hamiltonian for electrons interacting via the Coulomb interaction among each other and with surrounding nuclei is then just Eq. (1.1.1).

Let us furthermore define the density operator

$$\hat{n}(\mathbf{r}) = \sum_{i}^{N} \delta(\mathbf{r} - \mathbf{r}_{i}).$$

Using the expectation value of the density operator in the state  $|\psi\rangle$  and the electron density in real space,

$$n(\mathbf{r}) = \langle \psi | \hat{n}(\mathbf{r}) | \psi \rangle = N \int \mathrm{d}\mathbf{r}_2 \dots \mathrm{d}\mathbf{r}_N | \psi (\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) |^2,$$

one can now write, e.g., the external potential by using the definition of the density operator in the following form

$$\hat{V}_{\text{ext}} = \int d\mathbf{r} \ \hat{n}(\mathbf{r}) v(\mathbf{r}) = \int d\mathbf{r} \ \sum_{i}^{N} \delta(\mathbf{r} - \mathbf{r}_{i}) v(\mathbf{r}) = \sum_{i}^{N} v(\mathbf{r}_{i}).$$

The expectation value of same operator in the state  $|\psi\rangle$  can also be expressed via the expectation value of the density operator

$$\langle \psi | \hat{V}_{\text{ext}} | \psi \rangle = \int \mathrm{d}\mathbf{r} \; n(\mathbf{r}) v(\mathbf{r}).$$

The first Hohenberg-Kohn theorem now establishes the ground state density  $n_0(\mathbf{r})$  as the basic variable. It reads

The external potential  $v(\mathbf{r})$  is determined, within a trivial additive constant, by the electron density  $n_0(\mathbf{r})$  of the ground state.

The proof can be found in the original paper [159] or in the cited (and most other) books on DFT. Its disarming simplicity and elegance makes it worth examining though. The proof proceeds by *reductio ad absurdum*. Assume that two different external potentials  $\hat{V}_{\text{ext}}^{(1)} \neq \hat{V}_{\text{ext}}^{(2)}$  exist that still lead to the same ground state density  $n_0(\mathbf{r})$ . If these potentials differ by more than a constant they produce two different Hamiltonians  $\hat{H}^{(1)} \neq \hat{H}^{(2)}$  with two different associated ground state wave functions  $\psi^{(1)} \neq \psi^{(2)}$ , which have the same ground state density  $n_0(\mathbf{r})$  by construction.

Using the variational principle, which states that the minimal expectation value of the Hamiltonian is obtained for its ground state wave function we can state

$$E^{(1)} = \langle \psi^{(1)} | \hat{H}^{(1)} | \psi^{(1)} \rangle < \langle \psi^{(2)} | \hat{H}^{(1)} | \psi^{(2)} \rangle.$$

Above equation can be rewritten as follows

$$E^{(1)} < \langle \psi^{(2)} | \hat{H}^{(1)} | \psi^{(2)} \rangle = \langle \psi^{(2)} | \hat{H}^{(2)} | \psi^{(2)} \rangle - \langle \psi^{(2)} | \hat{H}^{(2)} - \hat{H}^{(1)} | \psi^{(2)} \rangle$$
  
=  $E^{(2)} - \int d\mathbf{r} \, n_0(\mathbf{r}) \left( \hat{V}_{\text{ext}}^{(2)} - \hat{V}_{\text{ext}}^{(1)} \right).$ 

Same can be repeated exchanging the indices (1) and (2) leading to the system of equations

$$E^{(1)} < E^{(2)} - \int d\mathbf{r} \ n_0(\mathbf{r}) \left( \hat{V}_{\text{ext}}^{(2)} - \hat{V}_{\text{ext}}^{(1)} \right)$$
$$E^{(2)} < E^{(1)} - \int d\mathbf{r} \ n_0(\mathbf{r}) \left( \hat{V}_{\text{ext}}^{(1)} - \hat{V}_{\text{ext}}^{(2)} \right),$$

which can be combined giving the desired contradictory result

$$E^{(1)} + E^{(2)} < E^{(1)} + E^{(2)}.$$

An important consequence of the theorem is that the ground state density uniquely determines all properties of the system, since it fixes the number of particles N and the external potential and thereby also the Hamiltonian and the many-body wave functions for all states.

Given the first Hohenberg-Kohn theorem we can now write the ground state energy of the

system as a unique functional of the density

$$E[n(\mathbf{r})] = T[n(\mathbf{r})] + V_{\text{ext}}[n(\mathbf{r})] + V_{\text{ee}}[n(\mathbf{r})]$$

$$= F_{\text{HK}}[n(\mathbf{r})] + \int d\mathbf{r} \ n(\mathbf{r})v(\mathbf{r}).$$
(1.2.3)

Here we have introduced the Hohenberg-Kohn functional  $F_{\text{HK}}[n(\mathbf{r})]$  that contains the universal parts of the energy functional

$$F_{\rm HK}[n(\mathbf{r})] := T[n(\mathbf{r})] + V_{\rm ee}[n(\mathbf{r})].$$

$$(1.2.4)$$

The second Hohenberg-Kohn theorem provides the variational principle to formally solve equation (1.2.3). It can be stated in the following form [324]

For any trial density  $\tilde{n}(\mathbf{r})$ , such that  $\tilde{n}(\mathbf{r}) \ge 0$  and  $\int d\mathbf{r} \ \tilde{n}(\mathbf{r}) = N$  the ground state density  $n_0(\mathbf{r})$  always yields the global minimum of the energy functional

$$E[n_0(\mathbf{r})] \leq E[\tilde{n}(\mathbf{r})].$$

It is implied here that the trial density  $\tilde{n}(\mathbf{r})$  determines its own potential  $\tilde{v}(\mathbf{r})$  (and consequently Hamiltonian and wave function) which coincide with the ground state only for the case  $\tilde{n}(\mathbf{r}) \equiv n_0(\mathbf{r})$ . Thus, a variational treatment of the total energy functional will yield the ground state density

$$\delta \left\{ E[n(\mathbf{r})] - \mu \left( \int \mathrm{d}\mathbf{r} \; n(\mathbf{r}) - N \right) \right\} \stackrel{!}{=} 0.$$

The Lagrange multiplier  $\mu$  is related with the constant electron number N and is identified with the chemical potential [324].

The associated Euler-Lagrange equation reads

$$\mu = \frac{\delta E[n(\mathbf{r})]}{\delta n(\mathbf{r})} = v(\mathbf{r}) + \frac{\delta F_{\rm HK}[n(\mathbf{r})]}{\delta n(\mathbf{r})}.$$
(1.2.5)

A few remarks are in order at this point. First, we mention that both theorems of Hohenberg and Kohn can be easily generalized to spin-dependent densities and degenerate ground states, see, e.g., [233]. A limitation of the original proof of the Hohenberg-Kohn theorems is that they only apply to densities that are *v*-representable (see, e.g., the discussion in [324]). This means that the density is associated with a Hamiltonian of the form of Eq. (1.2.1) containing some external potential  $v(\mathbf{r})$ . The proof can be generalized to *N*-representable densities using the constrained search approach by Levy [251]. A density is said to be *N*-representable if it can be obtained from a properly symmetrized *N*-particle wave function.

The theorems as they stand are exact and their application would in principle yield an exact solution of the many-body Hamiltonian. One problem is, however, that the theorems are mere proofs of the existence of an exact many-body theory based on the density. They give no hint at how a solution of the variational equations is to be worked out. These problems will be addressed in the next section, where the formalism that actually puts the Hohenberg-Kohn theorems to work will be introduced.

### 1.2.1 Kohn-Sham Formalism

The Hohenberg-Kohn theorems presented above are mere proofs of existence of an exact density functional theory. Their application to problems of physical interest has become possible only after Kohn and Sham developed an ingenious ansatz for the solution of the resulting equations [216]. In this approach an auxiliary system S with the following (single particle) Hamiltonian is introduced

$$\hat{H}_{\mathrm{S}} = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \Delta_i + \sum_{i=1}^{N} v_{\mathrm{S}}(\mathbf{r}_i).$$

This Hamiltonian describes a system of N non-interacting particles in an external potential  $v_{\rm S}(\mathbf{r})$ . Since the particles do not interact the corresponding Schrödinger equation can be solved by an antisymmetrized product of single particle orbitals  $\phi_i(\mathbf{r})$ , i.e., a Slater determinant [392]. The basic assumption in the Kohn-Sham formalism is that the density of the auxiliary system  $n_{\rm S}(\mathbf{r})$  equals the density of the original interacting system  $n(\mathbf{r})$  if the potential  $v_{\rm S}(\mathbf{r})$  is chosen properly

$$n_{\rm S}(\mathbf{r}) = \sum_{i}^{N} |\phi_i(\mathbf{r})|^2 \stackrel{!}{=} n(\mathbf{r}).$$
(1.2.6)

The sum in above equation runs over all states i until the correct total number of electrons N is reached. The task that is left is the determination of the correct  $v_{\rm S}(\mathbf{r})$  that will connect the auxiliary problem with the original one. To be able to do this, reconsider the total energy functional

$$E[n(\mathbf{r})] = F_{\mathrm{HK}}[n(\mathbf{r})] + \int \mathrm{d}\mathbf{r} \ n(\mathbf{r})v(\mathbf{r}).$$

The Hohenberg-Kohn functional can be rewritten using the auxiliary system in the fol-

lowing form

$$F_{\rm HK}[n(\mathbf{r})] = T_{\rm S}[n(\mathbf{r})] + (T[n(\mathbf{r})] - T_{\rm S}[n(\mathbf{r})]) + E_{\rm H}[n(\mathbf{r})] + (V_{\rm ee}[n(\mathbf{r})] - E_{\rm H}[n(\mathbf{r})])$$
  
$$= T_{\rm S}[n(\mathbf{r})] + E_{\rm H}[n(\mathbf{r})] + E_{\rm XC}[n(\mathbf{r})]. \qquad (1.2.7)$$

We extracted the classical Coulomb interaction (Hartree-energy)

$$E_{\rm H}[n(\mathbf{r})] = \frac{1}{2} \int d\mathbf{r} \, d\mathbf{r}' \, \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

from the electron-electron interaction term  $V_{ee}[n(\mathbf{r})]$  and introduced the kinetic energy of the auxiliary system

$$T_{\rm S}[n(\mathbf{r})] = \frac{-\hbar^2}{2m} \sum_{i}^{N} \langle \phi_i | \Delta | \phi_i \rangle.$$

The quantities that cannot be computed exactly were absorbed into the functional  $E_{\rm XC}[n(\mathbf{r})]$  that has to be treated approximately. One of the main advantages of this Kohn-Sham separation of the total energy is that the largest contributions to the energy are treated exactly and only the very small contributions from exchange and correlation need to be approximated [188]. This is a huge advantage over Thomas-Fermi theory where the large kinetic energy is also approximated. The universal exchange-correlation functional  $E_{\rm XC}[n(\mathbf{r})]$  contains all the many-body effects of exchange and correlation on the one particle level. If it were known exactly the exact ground state energy and density of the original many-body problem could be computed.<sup>3</sup> Unfortunately, this is not the case and approximations for this functional have to be introduced. A widely known approximation that was already introduced in the original work by Kohn and Sham [216] is the local density approximation (LDA). It uses the homogeneous electron gas as a reference and will be discussed, among other more sophisticated approaches, in the next section.

Using the Kohn-Sham separation of the total energy the Euler-Lagrange equation, Eq. (1.2.5), is rewritten as follows

$$\frac{\delta E[n(\mathbf{r})]}{\delta n(\mathbf{r})} = v(\mathbf{r}) + \frac{\delta F_{\rm HK}[n(\mathbf{r})]}{\delta n(\mathbf{r})} = v(\mathbf{r}) + \frac{\delta T_{\rm S}[n(\mathbf{r})]}{\delta n(\mathbf{r})} + \frac{\delta E_{\rm H}[n(\mathbf{r})]}{\delta n(\mathbf{r})} + \frac{\delta E_{\rm XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})} = \mu.$$
(1.2.8)

<sup>3</sup>This does *not* apply to spectral properties, because of the introduction of a single particle picture, see discussion at the end of the section.

The corresponding Euler-Lagrange equation for the auxiliary system S reads

$$\frac{\delta E_{\rm S}[n(\mathbf{r})]}{\delta n(\mathbf{r})} = \frac{\delta T_{\rm S}[n(\mathbf{r})]}{\delta n(\mathbf{r})} + v_{\rm S}(\mathbf{r}) = \mu.$$
(1.2.9)

It is plain to see from equations (1.2.8) and (1.2.9) that the following relation has to hold for the auxiliary potential

$$v_{\rm S}(\mathbf{r}) = \frac{\delta E_{\rm H}[n(\mathbf{r})]}{\delta n(\mathbf{r})} + v(\mathbf{r}) + \frac{\delta E_{\rm XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})} = v_{\rm H}(\mathbf{r}) + v(\mathbf{r}) + v_{\rm XC}(\mathbf{r}) =: v_{\rm KS}(\mathbf{r}).$$
(1.2.10)

Thus, the so-called Kohn-Sham potential that allows for a mapping of the interacting many-body problem onto a non-interacting one-particle problem has been found. It is composed of the Hartree potential  $v_{\rm H}(\mathbf{r})$ , the external potential  $v(\mathbf{r})$  and the exchange-correlation potential defined formally as

$$v_{\rm XC}(\mathbf{r}) = \frac{\delta E_{\rm XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})}.$$

Using the formal definitions of the Hartree and exchange-correlation potentials  $v_{\rm H}(\mathbf{r})$  and  $v_{\rm XC}(\mathbf{r})$  equation (1.2.8) can be rewritten as

$$\frac{\delta T_{\rm S}[n(\mathbf{r})]}{\delta \phi_i^*(\mathbf{r})} + \left(v_{\rm H}(\mathbf{r}) + v(\mathbf{r}) + v_{\rm XC}(\mathbf{r})\right) \frac{\delta n(\mathbf{r})}{\delta \phi_i^*(\mathbf{r})} = 0.$$

with i = 1, ..., N and requiring orthonormality

$$\int \mathrm{d}\mathbf{r} \,\phi_i^*(\mathbf{r})\phi_j(\mathbf{r}) = \delta_{ij}.$$

Since

$$\frac{\delta T_{\rm S}[n(\mathbf{r})]}{\delta \phi_i^*(\mathbf{r})} = -\frac{\hbar^2}{2m} \Delta \phi_i(\mathbf{r})$$

the correspondence between the non interacting model system and the original system is complete. Now, to obtain the solution of the original interacting problem only the non-interacting problem has to be solved. In order to minimize the energy the Kohn-Sham orbitals  $\phi_i(\mathbf{r})$  have to obey the Schrödinger-like equations

$$\hat{H}_{\rm KS}\phi_i(\mathbf{r}) = \left(-\frac{\hbar^2}{2m}\Delta + v_{\rm KS}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}).$$
(1.2.11)

These equations have to be solved self-consistently since the potential  $v_{\rm KS}(\mathbf{r})$  already depends on the density, see Eq. (1.2.10). They are formally equivalent to the single particle



**Figure 1.2.1:** Illustration of the generic Kohn-Sham DFT self-consistency loop: An initial guess for the electronic density starts the self-consistent loop. The Kohn-Sham potential and the corresponding Kohn-Sham equations are solved, yielding a new density and total energy. The three steps surrounded by the circular arrow are iterated until convergence.

equations in the Hartree approximation. In contrast to the Hartree-Fock approximation the effective potential  $v_{\rm KS}(\mathbf{r})$  is local. The numerical solution does not present a major problem if, additionally, a local approximation for the exchange-correlation functional  $E_{\rm XC}$  is used. The self-consistent solution yields the ground state electronic density via Eq. (1.2.6) and consequently the total energy and other properties derivable from them. The set of equations (1.2.10), (1.2.11) together with the requirement on the density, Eq. (1.2.6), constitute the essence of the Kohn-Sham construction.

The formalism described above can be generalized to systems involving spin [430], more complicated external potentials and magnetic fields, see the book by Kübler [233] for a detailed description. A generic DFT calculation proceeds along the steps shown in Fig. 1.2.1: To start the self-consistency an initial guess for the electronic density is required, which can be taken as the sum of the densities of the individual atoms comprising the system or just as an array of random numbers. Then the Kohn-Sham potential and the corresponding Kohn-Sham equations are solved, yielding a new density and total energy.

These three steeps are then iterated until convergence and the converged quantities, like the ground state density and total energy are output.

Density functional theory is at its heart a method for the calculation of ground state charge densities and total energies and not designed to produce excitation spectra. There is a method by Sham and Kohn, however, to compute excitation energies [384], see also Refs. [357, 356], that makes a connection between the exchange correlation potential and the self-energy of quasiparticles. Anyhow, the ground state Kohn-Sham DFT is formulated using model non-interacting particles and nowhere makes a connection to real electrons. Indeed, only the highest eigenvalue of a metal has a true physical meaning as the negative ionization energy or work function -I [181], see also the discussion of the eigenvalues in Ref. [336]. For insulators the center of the gap is predicted correctly by the *exact* Kohn-Sham-DFT [334], while its size is known to be underestimated even in the exact case (see also [385]). All other eigenvalues have in general no connection to electronic excitations. However, for various s and p electron systems Kohn-Sham-DFT gives excitation spectra remarkably close to the ones found in nature [188, 141]. On the other hand the method fails to reproduce the band gaps of semiconductors and spectra of so-called correlated electron systems with partially filled d or f shells. This is because the method is based on a one-particle approach and cannot capture the many-body physics often involved in these systems. Furthermore, the method can be shown to contains only a static electronic selfenergy, incapable of producing complex many-body phenomena [334, 385]. Even if the exact exchange-correlation functional was known, Kohn-Sham-DFT would still "only" produce the correct electronic density and total energy, whereas the spectra would still be in terms of one-particle excitations, and thus incorrect for correlated systems.

#### **1.2.2 Exchange and Correlation**

Since the exact form of the exchange correlation functional introduced in Eq. (1.2.7) is unknown, approximations have to be devised. The quality of the calculation will depend on the quality of the approximation, that is why we want to spend some time discussing certain exactly known properties of this functional along with some popular approximations.

The method of coupling constant integration allows one to study the connection between the real system and the non-interacting Kohn-Sham auxiliary system in detail [141, 188]. The coupling constant  $\lambda$  is introduced such that  $\lambda = 0$  corresponds to the non-interacting system, while at  $\lambda = 1$  the fully interacting physical system is recovered. The Coulomb interaction is written using the coupling constant as  $\frac{\lambda}{|\mathbf{r}-\mathbf{r}'|}$ . For the electron density  $n(\mathbf{r})$ of the system to remain unchanged during the change of  $\lambda$  from zero to one an additional potential has to be introduced [188]. The exchange correlation energy can then be exactly written as an integral over the coupling constant

$$E_{\rm XC}[n(\mathbf{r})] = \frac{1}{2} \int d\mathbf{r} \, d\mathbf{r}' \, \frac{n(\mathbf{r})n_{\rm XC}(\mathbf{r}, \mathbf{r}' - \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}, \qquad (1.2.12)$$

where  $n_{\rm XC}(\mathbf{r}, \mathbf{r}' - \mathbf{r})$  is the so called exchange-correlation hole

$$n_{\rm XC}(\mathbf{r}, \mathbf{r}' - \mathbf{r}) := n(\mathbf{r}') \int_0^1 \mathrm{d}\lambda \ (g(\mathbf{r}, \mathbf{r}', \lambda) - 1).$$

The hole is defined in terms of the pair-correlation function  $g(\mathbf{r}, \mathbf{r}', \lambda)$ , which is the conditional probability density of finding an electron at  $\mathbf{r}'$  when there is already an electron present at  $\mathbf{r}$ . The exchange-correlation hole thus describes the effect of repulsion between electrons, reducing the probability of an electron being at position  $\mathbf{r}'$  when there is already one at  $\mathbf{r}$ . It can be shown that  $g(\mathbf{r}, \mathbf{r}')$  goes to one in the limit of infinitely large separations of the particles  $|\mathbf{r} - \mathbf{r}'| \rightarrow \infty$ , which makes sense intuitively, since a particle infinitely far away should not inhibit the presence of a particle anywhere else. The exchange-correlation energy may then be interpreted as the interaction of the electron with a positively charged *hole* surrounding it.

An important property of  $E_{\rm XC}$  can be derived stemming from the fact that the Coulomb interaction depends only on the radial distance  $|\mathbf{r} - \mathbf{r}'|$ . Equation (1.2.12) can be thus divided into radial and angular parts

$$E_{\rm XC}[n(\mathbf{r})] = \frac{1}{2} \int d\mathbf{r} \ n(\mathbf{r}) \int_0^\infty dR \ R^2 \ \frac{1}{R} \int d\Omega \ n_{\rm XC}(\mathbf{r}, \mathbf{R}), \qquad (1.2.13)$$

with  $\mathbf{R} = \mathbf{r} - \mathbf{r}'$  and  $R = |\mathbf{R}|$ . This shows that the exchange-correlation energy depends only on the spherical average of the hole density. This does not imply that the hole itself is spherical.

Secondly, the properties of the pair-correlation function require that the hole contains exactly one positive charge

$$\int d\mathbf{r}' \, n_{\rm XC}(\mathbf{r}, \mathbf{r} - \mathbf{r}') = +e. \qquad (1.2.14)$$

Since the hole contains both effects of exchange and correlation further insights can be gained if one considers *only* the effects of exchange. Neglecting all correlations beyond the Pauli exclusion principle one arrives at the Hartree-Fock approximation, where the degree of correlation is controlled only by the exchange and the total energy can be written using the spin orbitals  $\phi_i^{\sigma}(\mathbf{r})$  as

$$\begin{split} E_{\rm HF} &= \sum_{i,\sigma} \int d\mathbf{r} \; (\phi_i^{\sigma}(\mathbf{r}))^* \left[ -\frac{\hbar^2}{2m} \Delta + \hat{V}_{\rm ext} \right] \phi_i^{\sigma}(\mathbf{r}) \\ &+ \frac{1}{2} \sum_{i,j,\sigma_i,\sigma_j} \int d\mathbf{r} \; d\mathbf{r}' \; (\phi_i^{\sigma_i}(\mathbf{r}))^* (\phi_j^{\sigma_j}(\mathbf{r}'))^* \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \phi_i^{\sigma_i}(\mathbf{r}) \phi_j^{\sigma_j}(\mathbf{r}') \\ &- \frac{1}{2} \sum_{i,j,\sigma} \int d\mathbf{r} \; d\mathbf{r}' \; (\phi_i^{\sigma}(\mathbf{r}))^* (\phi_j^{\sigma}(\mathbf{r}'))^* \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \phi_j^{\sigma}(\mathbf{r}) \phi_i^{\sigma}(\mathbf{r}'). \end{split}$$

The last two terms are the direct and exchange interactions. The exchange term represents the Pauli exclusion principle and additionally cancels the spurious self interaction term of the direct interaction. This term, again, may be interpreted as the interaction of the electron with a positively charged *exchange hole* surrounding it. The exchange hole density in Hartree-Fock can be written exactly using the spin orbitals as

$$n_{\mathbf{X}}(\mathbf{r},\mathbf{r}') = -\delta_{\sigma\sigma'} \left| \sum_{i} \left( \phi_{i}^{\sigma}(\mathbf{r}) \right)^{*} \phi_{i}^{\sigma}(\mathbf{r}') \right|^{2}.$$

The quantity at the end is nothing else as the spin diagonal density matrix. This hole density already integrates to exactly one positive charge +e, thus fulfilling the sum rule for the total exchange-correlation hole in Eq. (1.2.14).

Since the Hartree-Fock approximation does not include correlations beyond exchange, the correlation part of the hole  $n_{\rm C}(\mathbf{r}, \mathbf{r}')$  is not accounted for. In fact the separation of the effects of the interaction into exchange and correlation parts is defined via Hartree-Fock, since the latter treats only exchange and anything beyond is defined as correlation [277]. The total exchange-correlation hole can then formally be written as a combination of both exchange and correlation effects beyond exchange

$$n_{\mathrm{XC}}(\mathbf{r}, \mathbf{r}') = n_{\mathrm{X}}(\mathbf{r}, \mathbf{r}') + n_{\mathrm{C}}(\mathbf{r}, \mathbf{r}').$$

Since the total exchange-correlation hole still has to integrate to +e the correlation part of the hole density can only redistribute the charge density of the hole. These considerations show some crucial properties of the *exact* exchange-correlation hole that provide some guidance for approximations and can be used for their evaluation.

The most widely used approximation was already proposed in the original work of Kohn and Sham [216]. It is called the local density approximation (LDA) a term which is often used as a synonym for density functional theory as a whole. The approximation follows in principle the track of Thomas-Fermi theory in using the uniform electron gas as a reference system, but with an important difference. In Thomas-Fermi theory the density *itself* is approximated by the density of a locally uniform electron gas. In LDA, however, *only* the exchange-correlation part of the total energy functional is assumed in every point **r** to be equal to an integral over the exchange-correlation energy density of a locally uniform electron gas  $\varepsilon_{\text{XC}}^u$ 

$$E_{\rm XC}^{\rm LDA}[n(\mathbf{r})] = \int d\mathbf{r} \ n(\mathbf{r}) \varepsilon_{\rm XC}^u(n(\mathbf{r})) = \int d\mathbf{r} \ n(\mathbf{r}) \Big[ \varepsilon_{\rm X}^u(n(\mathbf{r})) + \varepsilon_{\rm C}^u(n(\mathbf{r})) \Big]$$

This approximation can be motivated if one considers a solid, especially a metal as a system which is close to a uniform electron gas. The exchange-correlation energy can then be written as an integral over all space with the exchange-correlation energy density  $\varepsilon_{\rm XC}(n(\mathbf{r}))$ . This exchange-correlation density is now assumed to be at each point identical to the exchange-correlation density of a uniform electron gas with the same electron density  $n(\mathbf{r})$ .

The exchange-correlation density consists of an exchange part  $\varepsilon_{\rm X}(n(\mathbf{r}))$  and a correlation part  $\varepsilon_{\rm C}(n(\mathbf{r}))$ . The former is known exactly for the uniform electron gas

$$\varepsilon_{\rm X}(n) = -\frac{3}{4}e^2 \left(\frac{3n}{\pi}\right)^{\frac{1}{3}},$$

see, e.g., chapter 5 in the book by Mahan [274]. The latter cannot be computed analytically, but is known to great accuracy from quantum Monte Carlo (QMC) calculations [73] for the spin-paired homogenous electron gas for different parametrisations [431]. The correlation part of the functional is thus fit to match the QMC data.

The local density approximation proves to be very successful in practical applications. Above discussion of the exact properties of the exchange-correlation hole already gives some hint why approximations to the exchange-correlation hole can be successful. First of all the sum rule for the charge of the hole along with the dependence of the energy only on the spherically averaged hole, Eq. (1.2.13), imply a possible error cancellation [141]. The LDA involves a spherical hole and fulfills the sum rule on the charge of the hole, which already makes it a viable approximation. The hole itself might not be well described within LDA, but the spherical average of the hole, the quantity important for the energy, is remarkably good, as shown in Ref. [336]. Also the hole in LDA is localized and the nonlocal part of  $E_{\rm XC}$  is very small, when the density  $n(\mathbf{r})$  does not vary rapidly [277]. These combined considerations in part explain the success of the LDA even for some systems with strongly varying densities, like atoms and molecules, where the approximation of a locally uniform electron gas seems inappropriate. Especially the failure of the LDA in quantum chemical applications (such as atomization energies of molecules) called for improved functionals. Extensions can be constructed by viewing the LDA approximation as the first order term of a power series of the density and its derivatives, reminiscent of a Taylor series. The natural extension would thus be to include higher order terms of this series. Such an approach is called gradient expansion approximation (GEA) [277].

Surprisingly, the naïve versions of the GEA often produced results inferior to the LDA. Furthermore, they violate certain relevant conditions on the exact exchange-correlation hole, like sum rules etc. [336, 337, 140]. An improved version of the GEA was devised by explicitly enforcing sum rules and other conditions known from analytic arguments. In this generalized gradient approximation (GGA) [241, 338, 32] the exchange-correlation functional assumes the general form

$$E_{\mathrm{XC}}^{\mathrm{GGA}}[n] = \int \mathrm{d}\mathbf{r} \ f(n(\mathbf{r}), \nabla n(\mathbf{r})).$$

The choice of the form of the function f is nontrivial and yields some freedom in the design of functionals for specific applications. If done properly GGA can be a substantial improvement over LDA, especially for chemistry of molecules, as shown, e.g., in [332]. In solid state physics the GGA functional by Perdew, Burke and Ernzerhof (PBE) [332] is a flavor of GGA often used, which is as the title states a "Generalized Gradient Approximation Made Simple".

There exists a multitude of functionals beyond the LDA/GGA. We will briefly mention here the so-called hybrid functionals [33, 34] with special focus on the B3LYP functional, since it was used in this work in chapter 5. In a hybrid functional the exchange energy is in part replaced by the exact Hartree-Fock exchange

$$E_{\mathbf{X}}^{\mathrm{HF}} = \frac{1}{2} \sum_{i,j,\sigma} \int \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}' \, (\phi_i^{\sigma}(\mathbf{r}))^* (\phi_j^{\sigma}(\mathbf{r}'))^* \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \phi_j^{\sigma}(\mathbf{r}) \phi_i^{\sigma}(\mathbf{r}').$$

The idea behind the hybrid functionals can again be understood using coupling constant integration. In the non-interacting limit  $\lambda = 0$  the exchange-correlation is exactly described by the Hartree-Fock exchange. In the interacting limit the LDA or GGA is considered as correct. A general hybrid functional interpolates between the two cases

$$E_{\mathrm{XC}}^{\mathrm{HYB}} \sim E_{\mathrm{XC}}^{\mathrm{LDA/GGA}} + c \left( E_{\mathrm{X}}^{\mathrm{HF}} - E_{\mathrm{X}}^{\mathrm{LDA/GGA}} \right)$$

in some way controlled by the constant c, typically  $c = \frac{1}{2}$  or smaller. We will focus here on the popular B3LYP (Becke, three-parameter, Lee-Yang-Parr) functional

$$E_{\rm XC}^{\rm B3LYP} = E_{\rm XC}^{\rm LDA} + a_0 (E_{\rm X}^{\rm HF} - E_{\rm X}^{\rm LDA}) + a_x (E_{\rm X}^{\rm GGA} - E_{\rm X}^{\rm LDA}) + a_c (E_{\rm C}^{\rm GGA} - E_{\rm C}^{\rm LDA})$$

with the parameters  $a_0 = 0.2$ ,  $a_x = 0.72$  and  $a_c = 0.81$ . The terms include the Becke 88 exchange functional [32] in  $E_X^{GGA}$  and the correlation functional of Lee, Yang and Parr [245] (LYP) in  $E_C^{GGA}$  and the Vosko-Wilk-Nusair parametrization of the local-density approximation  $E_C^{LDA}$  [431]. The B3LYP functional was not fit to experimental data, instead

the three parameters defining B3LYP have been taken without modification from Becke's original fitting of the analogous B3PW91 functional, the difference being the usage of the LYP correlation part instead of the PW91 [34]. The B3LYP functional considerably improves on total energies, structures and other ground state properties of molecules [34]. It has, however, one substantial problem, which makes it unfeasible for applications to many bulk systems: it fails for metals and small gap semiconductors [319]. The reason behind this failure is that the B3LYP functional does not correctly account for free electron like states, the uniform electron gas limit not being correctly recovered. We have used B3LYP in chapter 5 solely for the purpose of obtaining geometries for single molecules, as well as molecules embedded in a nano contact geometry. Since these were molecular systems far away from a simple free electron like metal the criterion of applicability of the functional was met.

### **1.3 Implementations of DFT**

The Kohn-Sham equations introduced in section 1.2.1 are a set of independent particle Schrödinger equations. This still designates a nontrivial problem that can be attacked from different sides. One line of attack is the all-electron approach, which is mostly used in chemistry, since one is often faced with molecules containing a rather small number of electrons. In an all electron approach all electronic shells of all atoms present in the system are calculated within Hartree-Fock or DFT, see, e.g., [406]. This includes coreshells that often have strongly oscillating wave functions, due to their relative proximity to the nucleus. The problem can be somewhat simplified for a solid: in the region between ions (bonding region) the wave functions are rather smooth, whereas they oscillate rapidly close to the nuclei, due to the large potential. In an idealized picture space can be divided into a spherical region around the nucleus where the potential is spherically symmetric and an interstitial region with a constant potential. The wave function is now represented differently in either region. The wave functions themselves and their first derivative have to remain continuous at the boundary which can become computationally demanding especially for larger unit cells. This is the basic idea behind the all-electron band structure methods like the augmented plane-wave method (APW) [394], muffin-tin orbital (MTO) methods or their respective linear versions (LMTO, LAPW) [13]. Formally, both methods are augmented wave methods differing in principle only in the choice of the envelope function: the LAPW uses plane-waves, while the LMTO employs Hankel functions [13]. A conceptually different approach is taken by pseudopotential theory (see [331] and references therein). Instead of attempting to reproduce the behavior of the wave function close to the nucleus one attempts to replace the original nuclear potential by another, simpler and computationally more convenient, potential in a certain core region. This new pseudopotential reproduces the scattering properties of the original potential over a wide range of energies and additionally is computationally more feasible. There is, however, a cost to pay for the simplified calculation: the core electrons are frozen together with the nucleus and represented by the pseudopotential. Only valence electrons are taken into account in the calculation, hence most of the information on the electronic density in the core region is lost.

Another fundamental problem is common to all numerical electronic structure calculations. In order to solve the Kohn-Sham equations a basis set for the underlying one particle Hilbert space has to be chosen for the expansion of the wave function. Since the basis of a Hilbert space is infinite, the basis has to be truncated in numerical calculations. Expressing the Kohn-Sham equations in a localized basis is particularly popular in chemistry, since it is best suited to small, non periodic systems like molecules. In such a case the wave function can be expressed directly using functions resembling atomic or molecular orbitals. These are most commonly Slater or Gaussian Type Orbitals (STOs, GTOs), that ensure the correct behavior for the core and valence shells. These basis sets often have the useful property of being analytical functions, making in turn all N-electron integrals in the calculation analytically solvable [406]. For solids the periodicity of the crystal makes plane-waves a viable basis set. In this section we will describe two different implementations of Density Functional theory that have been used for all simulations presented later. First, we will describe the local combination of atomic orbitals method with Gaussian Basis Sets, as used in the GAUSSIAN [115] and CRYSTAL [94] code packages. These codes use an expansion of the wave function in localized atomic orbitals, that are in turn expanded using Gaussian functions. Second, we will describe the projector augmented wave method that belongs to the so-called augmented wave methods and uses a plane-wave basis set. It is implemented in the code package VASP [229, 230] that we used extensively as well.

#### **1.3.1** Gaussian Basis Sets

Localized Atomic orbitals or functions resembling orbitals provide a physically motivated basis set for electronic structure calculations within density functional or Hartree-Fock theory [406]. Their appeal is that one only has to deal with a relatively small number of analytically defined functions in real space. However, these functions have to be explicitly defined prior to any calculation and different choices will in general produce different results [406]. This of course gives one more freedom, but also one is more responsible for the outcome of the calculation, unlike using plane waves where convergence with respect to the basis is in principle controlled by a single parameter: the plane wave cutoff.

Using a local combination of atomic orbitals-type ansatz (LCAO) each orbital  $\psi_i(\mathbf{r}, \mathbf{k})$  is

a combination of Bloch functions  $\phi_{\alpha}(\mathbf{r}, \mathbf{k})$ 

$$\psi_i(\mathbf{r}, \mathbf{k}) = \sum_{\alpha} a_{\alpha,i}(\mathbf{k}) \phi_{\alpha}(\mathbf{r}, \mathbf{k}),$$

with coefficients  $a_{\alpha,i}(\mathbf{k})$ . The Bloch functions are in turn defined in terms of local radial atomic orbital functions  $\zeta_{\alpha}(\mathbf{r})$  and spherical harmonics  $Y_{lm}(\mathbf{r})$ 

$$\phi_{\alpha}(\mathbf{r}, \mathbf{k}) = \sum_{\mathcal{R}} \zeta_{\alpha}(\mathbf{r} - \mathbf{R}_{\alpha} - \mathcal{R}) Y_{lm}(\mathbf{r} - \mathbf{R}_{\alpha}) \exp\left(i\mathbf{k} \cdot \mathcal{R}\right),$$

where the sum is over all lattice vectors  $\mathcal{R}$  and  $\mathbf{R}_{\alpha}$  is the coordinate of the nucleus where  $\zeta_{\alpha}$  is centered. If we are concerned with a non-periodic system, the dependence on the k vector is dropped since Blochs theorem does not apply.

The radial atomic orbitals  $\zeta$  now have to be expanded in a suitable basis set. These could be Slater Type Orbitals (STOs) introduced by Slater in 1930 [393] or Gaussian functions first proposed by Boys in his work with the interesting title "A general method of calculation for the stationary states of any molecular system" [59].

Extra radial functions can be added to improve the span of the basis; basis sets are denoted single-zeta, double-zeta and so on, depending on the number of such radial functions per valence state. As Boys noted

... the only obstacle to the evaluation of wave functions of any required degree of accuracy is the labour of computation.

Using Gaussian functions the local orbital can be expanded in a certain number  $n_G$  of contracted Gaussian type functions (GTF) centered on the same coordinate  $\mathbf{R}_{\alpha}$ 

$$\zeta_{\alpha}(\mathbf{r} - \mathbf{R}_{\alpha} - \mathcal{R}) = \sum_{j}^{n_{G}} d_{j} G(\alpha_{j}, \mathbf{r} - \mathbf{R}_{\alpha} - \mathcal{R}),$$

with so-called contraction coefficients  $d_j$  and exponents  $\alpha_j$ . The Gaussian primitives  $G(\alpha, \mathbf{r})$  are just radial Gaussians

$$G(\alpha, \mathbf{r}) = \mathcal{N}r^l \exp\left(-\alpha r^2\right),$$

with the normalization  $\mathcal{N}$ .

In this thesis we have used the 6-31G basis set in chapter 5, which is a so-called splitvalence double zeta basis set. The basis consists of inner shell functions, inner valence and outer valence functions. These are contractions of 6, 3 and 1 primitive Gaussians, respectively. Additionally, since the basis sets are obtained from atomic calculations, there are additional scaling factors for the valence states [406]. The 6-31G basis provides a good trade-off between computational speed and accuracy [406]. By increasing the number of basis functions the accuracy of the calculations can be improved, unfortunately there is no systematic way of doing this and very many different basis sets exist, see e.g. the Basis Set Exchange online database [382].

The primary reason for using Gaussians as a basis is their property that the product of two Gaussians is another Gaussian. This leads to the tremendous advantage that all *N*-center integrals can be computed *analytically* in the Gaussian basis [406]. The integrals, namely the exchange and Coulomb integrals, that have to be computed numerous times in a calculation can be computed analytically in a Gaussian basis set. This makes them a computationally most efficient choice. This also applies to the contracted Gaussian functions, which have the advantage of being constructed in such a way as to resemble atomic orbitals, while primitive Gaussians do not have that property.

#### **1.3.2** Plane-Wave basis set

One might say that the converse approach to a basis localized in real space is taken by using a plane wave basis, since plane waves are maximally delocalized in real space while localized in the space of crystal momentum k. For periodic systems a delocalized plane wave basis set can be used, since Bloch's theorem holds [48]. It ensures that at each point in the Brillouin zone any solution of the Kohn-Sham equations  $\psi(\mathbf{r})$  can be expanded in plane waves

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G}} \exp\left(i\left(\mathbf{k}+\mathbf{G}\right)\mathbf{r}\right), \qquad (1.3.1)$$

where G is a Bravais lattice vector of the reciprocal space (i.e.  $\mathbf{G} \cdot \mathbf{R} = 2\pi z$  with  $z \in \mathbb{Z}$  and any lattice vector  $\mathbf{R}$ ).

In numerical applications one is limited to a finite number of plane waves and since for large reciprocal lattice vectors the kinetic energy dominates one introduces a kinetic energy cutoff. Only plane waves with a kinetic energy lower than some cutoff energy  $E_{\rm cut}$ 

$$\frac{\hbar^2 (|\mathbf{k}| + |\mathbf{G}_{\text{cut}}|)^2}{2m} < E_{\text{cut}}$$

are taken into account. The advantage of using plane waves in contrast to explicit atomic orbitals is the independence of the solution on the specific form of the basis and its systematic behavior with respect to the cutoff. Convergence can be systematically checked by increasing the cutoff at the same time keeping in mind that convergence depends also on different parameters of the calculation, such as the mesh used to sample the Brillouin zone or the size of grids used in Fourier transformations, etc. The main drawback is that large numbers of plane waves are needed to achieve convergence. Additionally, one is restricted to periodic boundary conditions and has to use large supercells for finite systems to avoid interactions between the periodic images of the system. It is thus often more fea-
sible to use a localized basis set when calculating molecules. The usage of plane waves does not prohibit access to local quantities in the calculations though. By projection of the converged wave function onto functions resembling orbitals inside atomic spheres one can obtain local quantities like the projection of the band structure onto certain orbitals.

## **1.3.3** The Projector Augmented-Wave Method

The projector augmented wave (PAW) method developed by Blöchl [50] is based on the idea of expressing the electronic valence wave function  $|\psi\rangle$  in terms of a smooth pseudowave function  $|\tilde{\psi}\rangle$  that does not oscillate rapidly near the nucleus. The method is conceptually and even formally connected to the ultra-soft pseudo potential method as was realized by Kresse and Joubert [230], while also sharing certain ideas with the augmented wave methods mentioned earlier.

It is assumed that the physical and pseudo wave functions are interconnected by a linear transformation  $\hat{\mathcal{T}}$ 

$$|\psi\rangle = \hat{\mathcal{T}}|\tilde{\psi}\rangle = \left(1 + \sum_{R} \hat{\tau}_{R}\right)|\tilde{\psi}\rangle.$$

In a second step a particular transformation was chosen. The real and pseudo wave functions are assumed to coincide outside of a so-called augmentation sphere  $\Omega_R$  enclosing the atom. The part of the transformation that differs from unity acts only in the augmentation sphere  $\Omega_R$ . In each sphere R an expansion in partial waves  $|\phi_i\rangle$  is performed. For each true partial wave a pseudo partial wave  $|\tilde{\phi}_i\rangle$  is chosen that matches to  $|\phi_i\rangle$  at the boundary of the augmentation sphere. The index *i* is a shorthand and denotes the atomic position R, the angular momentum l, m and an additional index *a* to label different partial waves for the same site. The partial waves are solutions of the Kohn-Sham equation for the isolated atom and are possibly unbound.

Now, trivially one can write

$$|\phi_i\rangle = |\tilde{\phi}_i\rangle + |\phi_i\rangle - |\tilde{\phi}_i\rangle$$
 and thus define  $\hat{\tau}_i |\tilde{\phi}_i\rangle = |\phi_i\rangle - |\tilde{\phi}_i\rangle$ .

The above definition of course implies

$$|\phi_i\rangle = \hat{\mathcal{T}} |\phi_i\rangle.$$

The partial wave basis is assumed to be complete in the augmentation region, hence one can write

$$|\tilde{\psi}\rangle = \sum_{i} |\tilde{\phi}_{i}\rangle c_{i}.$$

Applying the transformation  $\hat{\mathcal{T}}$  one finally obtains

$$\left(1+\sum_{i}\hat{\tau}_{i}\right)|\tilde{\psi}\rangle = |\tilde{\psi}\rangle + \sum_{i}\hat{\tau}_{i}|\tilde{\phi}_{i}\rangle c_{i} = |\tilde{\psi}\rangle + \sum_{i}\left(|\phi_{i}\rangle - |\tilde{\phi}_{i}\rangle\right)c_{i}.$$

Since the transformation is linear the coefficients  $c_i$  must be linear functionals of the pseudo wave functions, which can be written as scalar products of  $|\tilde{\psi}\rangle$  with functions  $\langle \tilde{p}_i |$  that are called projector functions

$$c_i = \langle \tilde{p}_i | \psi \rangle.$$

The projector functions are dual to the partial waves and fulfill the completeness condition

$$\sum_{i} \left| \tilde{\phi}_{i} \right\rangle \left\langle \tilde{p}_{i} \right| = 1 \quad , \quad \left\langle \tilde{p}_{i} \right| \tilde{\phi}_{j} \right\rangle = \delta_{ij}.$$

Summarizing, the linear transformation

$$\hat{\mathcal{T}} = 1 + \sum_{i} \left( |\phi_i\rangle - |\tilde{\phi}_i\rangle \right) \langle \tilde{p}_i|$$

allows for the computation of the physical wave function  $|\psi\rangle$  from the pseudo wave function  $|\tilde{\psi}\rangle$  via

$$|\psi\rangle = |\tilde{\psi}\rangle + \sum_{i} \left( |\phi_i\rangle - |\tilde{\phi}_i\rangle \right) \langle \tilde{p}_i |\tilde{\psi}\rangle = |\tilde{\psi}\rangle + \sum_{R} \left( |\psi_R^1\rangle - |\tilde{\psi}_R^1\rangle \right).$$
(1.3.2)

In the last step we have defined the so-called one-center expansions of the wave function centered on site  ${\cal R}$ 

$$\begin{split} |\psi_R^1\rangle &=& \sum_{i\in R} |\phi_i\rangle\,\langle \tilde{p}_i|\tilde{\psi}\rangle \\ |\tilde{\psi}_R^1\rangle &=& \sum_{i\in R} |\tilde{\phi}_i\rangle\,\langle \tilde{p}_i|\tilde{\psi}\rangle\,, \end{split}$$

with the sums now running only over partial waves centered on site R. An example of the true and auxiliary wave functions, along with their respective partial wave expansions is given in Fig. 1.3.2 for the Cl<sub>2</sub> molecule.

The projector functions are defined, similarly to the partial waves  $|\phi_i\rangle$ , as a real function times a spherical harmonic. The partial waves are obtained as solutions of the scalar relativistic Schrödinger equation for the atom at hand [50]. The pseudo partial waves are in turn solutions of the scalar relativistic Schrödinger equation for the scalar relativistic Schrödinger equation for the scalar relativistic Schrödinger equation for the scalar scheme equation for the scalar relativistic Schrödinger equation for the scalar relativistic Schrödinger equation for the scalar scheme equation for the scheme equation for the scheme equation for the scheme equation equation equation for the scheme equation eq



**Figure 1.3.2:** a) Bonding  $p - \sigma$  orbital of the chlorine Cl<sub>2</sub> molecule. b) Decomposition of this orbital into auxiliary wavefunction and the two one-center expansions. Top-left: True wave function  $|\psi\rangle$  (black curve) and the auxiliary wave function  $|\tilde{\psi}\rangle$  (blue); top-right: auxiliary wavefunction  $|\tilde{\psi}\rangle$  (blue) and its partial wave expansion in pseudo partial waves  $|\tilde{\phi}_i\rangle$  (green); bottom-left: comparison of the true partial wave  $|\phi_i\rangle$  (red) and the pseudo partial wave expansion in  $|\psi\rangle$  (black) and its partial wave expansion in  $|\phi_i\rangle$  (red). Adapted from [49].

using a smooth pseudo potential [50]. The pseudo partial waves  $|\tilde{\phi}_i\rangle$  are constructed to coincide with the true partial waves  $|\phi_i\rangle$  outside the augmentation sphere and are a smooth continuation inside. The projector functions are in practice chosen such that the PAW transformation is exact (despite the truncation) for the isolated atom.

Now, that the transformation connecting the pseudo to the true wave function has been formally established it can be used to compute expectation values of operators. Consider an operator  $\hat{A}$ . Its expectation value can be obtained using the pseudo wave function

$$\langle \hat{A} \rangle = \sum_{n} f_{n} \langle \psi_{n} | \hat{A} | \psi_{n} \rangle = \sum_{n} f_{n} \langle \tilde{\psi}_{n} | \mathcal{T}^{\dagger} \hat{A} \mathcal{T} | \tilde{\psi}_{n} \rangle = \sum_{n} f_{n} \langle \tilde{\psi}_{n} | \tilde{A} | \tilde{\psi}_{n} \rangle, \quad (1.3.3)$$

where n is a band index and  $f_n$  denotes the occupation of the state. The *pseudo* operator  $\tilde{A}$  has the form

$$\tilde{A} = \hat{\mathcal{T}}^{\dagger} \hat{A} \hat{\mathcal{T}} = \hat{A} + \sum_{i,j} |\tilde{p}_i\rangle \left( \langle \phi_i | \hat{A} | \phi_j \rangle - \langle \tilde{\phi}_i | \hat{A} | \tilde{\phi}_j \rangle \right) \langle \tilde{p}_j | A \rangle$$

Using this decomposition, equation (1.3.3) can be rewritten using the one center density matrix

$$D_{ij} = \sum_{n} f_n \left\langle \tilde{\psi}_n | \tilde{p}_j \right\rangle \left\langle \tilde{p}_i | \tilde{\psi}_n \right\rangle, \quad i, j \in \mathbb{R}$$

as

$$\langle \hat{A} \rangle = \sum_{n} f_n \langle \tilde{\psi}_n | \hat{A} | \tilde{\psi}_n \rangle + \sum_{i,j} D_{ij} \left( \langle \phi_j | \hat{A} | \phi_i \rangle - \langle \tilde{\phi}_j | \hat{A} | \tilde{\phi}_i \rangle \right).$$

Here, we neglected contributions from the core states, that would appear as an additional term of the form  $\sum_{n=1}^{N_c} \langle \phi_n^c | \hat{A} | \phi_n^c \rangle$ , with the sum running over all core states.

The Kohn-Sham equations transform correspondingly into a generalized eigenvalue problem, since the transformation operator does not depend on the electron density

$$\hat{\mathcal{T}}^{\dagger}\hat{H}_{\mathrm{KS}}\hat{\mathcal{T}}\ket{\tilde{\psi}_n} = \varepsilon_n \hat{\mathcal{T}}^{\dagger}\hat{\mathcal{T}}\ket{\tilde{\psi}_n}.$$

Here,  $\hat{H}_{\text{KS}}$  is the one particle Hamiltonian from equation (1.2.11). Thus, the Kohn-Sham equations in the PAW representation are Schrödinger type equations with the additional overlap operator  $\mathcal{T}^{\dagger}\mathcal{T}$  on the right hand side.

Since the two central quantities of density functional theory are the charge density and the total energy we want to briefly show how they are expressed within the PAW formalism. The electronic density can be shown to decompose into three parts, which stem of course from the transformation, Eq. (1.3.3),

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + \sum_{R} \left( n_{R}^{1}(\mathbf{r}) - \tilde{n}_{R}^{1}(\mathbf{r}) \right),$$

where as usual the *one center* parts (indicated by a 1 in the exponent) exist only inside the augmentation sphere. The three parts are

$$\begin{split} \tilde{n}(\mathbf{r}) &= \sum_{n} f_{n} \langle \tilde{\psi}_{n} | \tilde{\psi}_{n} \rangle + \tilde{n}_{c}(\mathbf{r}) \\ n_{R}^{1}(\mathbf{r}) &= \sum_{i,j \in R} D_{ij} \langle \phi_{j} | \phi_{i} \rangle + n_{c,R}(\mathbf{r}) \\ \tilde{n}_{R}^{1}(\mathbf{r}) &= \sum_{i,j \in R} D_{ij} \langle \tilde{\phi}_{j} | \tilde{\phi}_{i} \rangle + \tilde{n}_{c,R}(\mathbf{r}), \end{split}$$

where we have explicitly included core contributions. Here  $\tilde{n}_c(\mathbf{r})$  denotes the total core density obtained via auxilliary core states  $|\tilde{\phi}_n^c\rangle$ . These are identical to the true core states outside the augmentation region and a smooth continuation inside.  $\tilde{n}_{c,R}(\mathbf{r})$  is identical to  $n_{c,R}(\mathbf{r})$  outside the atomic sphere and smooth inside.

The total energy takes a formally identical form under the PAW transformation

$$E = \tilde{E} + \sum_{R} \left( E_R^1 - \tilde{E}_R^1 \right),$$

where the three parts are

$$\begin{split} \tilde{E} &= -\frac{\hbar^2}{2m} \sum_n \langle \tilde{\psi}_n | \Delta | \tilde{\psi}_n \rangle + E_{\rm H}[\tilde{n}(\mathbf{r}) + \tilde{Z}(\mathbf{r})] + \int \tilde{n}(\mathbf{r}) \bar{v}(\mathbf{r}) \, \mathrm{d}\mathbf{r} + E_{\rm XC}(\tilde{n}) \\ E_R^1 &= -\frac{\hbar^2}{2m} \sum_{i,j \in R} D_{ij} \langle \phi_j | \Delta | \phi_i \rangle + -\frac{\hbar^2}{2m} \sum_{n \in R}^{N_{c,R}} \langle \phi_n^c | \Delta | \phi_n^c \rangle + \\ &+ E_{\rm H}[n_R^1(\mathbf{r}) + Z_R(\mathbf{r})] + E_{\rm XC}(n_R^1) \\ \tilde{E}_R^1 &= -\frac{\hbar^2}{2m} \sum_{i,j \in R} D_{ij} \langle \tilde{\phi}_j | \Delta | \tilde{\phi}_i \rangle + E_{\rm H}[\tilde{n}_R^1(\mathbf{r}) + \tilde{Z}_R(\mathbf{r})] + \int \tilde{n}_R^1(\mathbf{r}) \bar{v}(\mathbf{r}) \, \mathrm{d}\mathbf{r} + E_{\rm XC}(\tilde{n}_R^1) \end{split}$$

The first term contains only smooth functions and is solved by expanding the pseudo wave functions in plane-waves

$$\tilde{\psi}_k(\mathbf{r}) = \langle \mathbf{r} | \tilde{\psi} \rangle = \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G}} \exp\left(i\left(\mathbf{k}+\mathbf{G}\right)\mathbf{r}\right).$$

The other parts, existing only inside atomic spheres are evaluated in a spherical harmonics expansion. The Hartree term  $E_{\rm H}[\tilde{n}(\mathbf{r}) + \tilde{Z}(\mathbf{r})]$  contains the so-called compensation charge density  $\tilde{Z}(\mathbf{r}) = \sum_R \tilde{Z}_R(\mathbf{r})$ , which is constructed such that  $n_R^1(\mathbf{r}) + Z_R(\mathbf{r}) - \tilde{n}_R^1(\mathbf{r}) - \tilde{Z}_R(\mathbf{r})$  has vanishing electrostatic multipole moments for each atomic site. This leads to vanishing electrostatic potentials of the augmentation densities outside the augmentation spheres. The compensation charges are needed to cancel spurious cross terms between different augmentation spheres appearing in the Hartree term.

The potential  $\bar{v} = \sum_R \bar{v}_R$  appearing in above expression is a so-called intelligent zero, because the two terms containing it vanish exactly due to the identity between the pseudo wave function and its own one center expansion within an augmentation sphere

$$\sum_{n} f_n \left( \langle \tilde{\psi}_n | \, \bar{v}_R \, | \tilde{\psi}_n \rangle - \langle \tilde{\psi}_n^1 | \, \bar{v}_R \, | \tilde{\psi}_n^1 \rangle \right) = 0.$$

The potential is introduced to cancel the singularity of the Coulomb potential in  $\tilde{E}$  and apart from that can be used to improve the plane-wave convergence. Now, applying the variational principle to the total energy expression one can obtain the potential and the auxiliary Hamiltonian. Since the expressions are lengthy we refer the interested reader to Blöchls work [50]. The key point of the PAW method becomes apparent now. The physical wave function is never explicitly constructed by adding its different contributions as in Eq. (1.3.2). All relevant quantities involving the wave function  $|\psi\rangle$  can be calculated implicitly using the one center density matrices, pseudo operators and projectors.

# **1.4 Model Hamiltonians and Dynamical mean-field** theory

In the previous sections we were focusing on the density functional theory (DFT) which is extensively used in theoretical physics and chemistry. DFT however fails in describing the properties of strongly correlated materials, namely those with narrow bands and strong electron-electron interactions. This does not come as a surprise, because at its heart DFT in the version of Kohn and Sham is a one particle theory and intrinsically unable to capture many-body effects, that are dominant in correlated materials. For such materials one typically employs a fundamentally different approach. In this context *model Hamiltonians* can provide a description of the physics of a correlated system. A model Hamiltonian has to capture the fundamental physical properties of the system. On the other hand it has to be of a rather simple mathematical form to allow for a numerical, or in some cases and limits even analytical solution.

Prominent examples of model Hamiltonians are the Hubbard model, which describes the physics of correlated electrons on lattices or the Anderson model for magnetic impurities. Both models play an important role in the framework of dynamical mean-field theory that actually connects both models and will be outlined at the end of this section. We begin by introducing some general elements of many-body theory, focussing on Green functions before proceeding to the Hubbard and Anderson models.

# **1.4.1** Green functions and Coherent State Path Integrals

In this part we briefly introduce certain elements of many-body theory and the formalism of coherent state path integrals that will be used in parts of this chapter. The formalism of coherent state path integrals is an elegant way of dealing with many-body theory, especially derivations concerning model Hamiltonians, dynamical mean-field theory and certain impurity solvers will be presented in this formalism. On the other hand the finite temperature Matsubara Green function formalism is the practically more accessible. Both approaches will be briefly sketched here, reviewing only the elements of the formalism needed in later chapters. We follow closely the Books by Negele and Orland [305] and Altland and Simons [8] when discussing coherent states and path integrals, while for the Matsubara Green function formalism we follow Fetter and Walecka [106] and the classic by Abrikosov, Gorkov and Dzyaloshinski [5].

Fermion coherent states are the eigenstates of the Fermion annihilation operator  $\hat{c}$ 

$$\hat{c}_{\alpha} \left| c \right\rangle = c_{\alpha} \left| c \right\rangle.$$

The eigenvalues  $c_{\alpha}$  have to fulfill the anticommutation rules obeyed by the Fermion operators, they are thus anticommuting Grassmann numbers, see, e.g., the Book by Berezin for details [39]. The coherent states are written with reference to the Fock space vacuum  $|0\rangle$  as

$$|c\rangle = e^{-\sum_{\alpha} c_{\alpha} \hat{c}_{\alpha}^{\dagger}} |0\rangle.$$

This definition arises as an analogy to the physical bosonic coherent states, where the power series for the exponential arises from the repeated application of creation operators to the vacuum. The fermionic coherent states are *not* physical states and are used more for notational convenience. The states are not normalized to unity, instead, the overlap of two states is

$$\langle c|c\rangle = e^{-\sum_{\alpha} c_{\alpha}^* c_{\alpha}}$$

The asterisk here does not denote a conjugation operation as for complex numbers, instead the two numbers  $c_{\alpha}^*$ ,  $c_{\alpha}$  are two independent variables, see the discussion in Ref. [8]. The coherent states are thus overcomplete with the closure relation

$$\int \mathrm{d}c^* \,\mathrm{d}c \; e^{-\sum_{\alpha} c_{\alpha}^* c_{\alpha}} \left| c \right\rangle \left\langle c \right| = \mathbb{1},$$

where we used a shorthand for the integration measure  $dc = \prod_{\alpha} dc_{\alpha}$ . Using the closure relation one finds a useful identity for the trace of an operator over a complete set of states  $|n\rangle$ 

$$\operatorname{Tr} \hat{A} = \sum_{n} \langle n | \hat{A} | n \rangle = \int \mathrm{d}c^* \, \mathrm{d}c \, e^{-\sum_{\alpha} c_{\alpha}^* c_{\alpha}} \langle -c | \hat{A} | c \rangle \,. \tag{1.4.1}$$

Another result of utmost importance is the identity for the Gaussian integral over coherent states. It allows explicit evaluation of certain terms in path integrals, while others will have to be treated approximately or perturbatively. It reads

$$\int \mathrm{d}c \; e^{-\sum_{\alpha\beta} c^*_{\alpha} A_{\alpha\beta} c_{\beta} + \sum_{\alpha} (\eta^*_{\alpha} c_{\alpha} + \eta_{\alpha} c^*_{\alpha})} = \det \underline{\underline{A}} \; e^{\sum_{\alpha\beta} \eta^*_{\alpha} A_{\alpha\beta}^{-1} \eta_{\beta}}, \tag{1.4.2}$$

with a matrix  $\underline{A}$  and some Grassmann field  $\eta$ .

Despite being non-physical entities coherent states can be used to conveniently expand any physical state. Using the identity for the trace from Eq. (1.4.1) the partition function can be written in terms of coherent states as

$$\mathcal{Z} = \operatorname{Tr} e^{-\beta(\hat{H}-\mu\hat{N})} = \int \mathrm{d}c^* \, \mathrm{d}c \, e^{-\sum_{\alpha} c_{\alpha}^* c_{\alpha}} \left\langle -c | e^{-\beta(\hat{H}-\mu\hat{N})} | c \right\rangle.$$
(1.4.3)

Now, the partition function may be viewed as the trace over the imaginary-time evolution operator  $\mathcal{U} = e^{-\beta(\hat{H}-\mu\hat{N})}$ , which is connected to its real time part via a Wick rotation of time to imaginary time  $it \to \tau$ . The path integral then represents the sum over all trajectories in imaginary time of length  $\beta$ . Its construction follows the usual steps taken in the Feynman path integral approach [107], namely a formal discretization of the interval followed by subsequent insertion of the closure relation at every discrete step. Using the discrete version of the evolution operator  $\mathcal{U}_M = \left(e^{-\varepsilon(\hat{H}-\mu\hat{N})}\right)^M$  divided into M steps  $(M \to \infty)$  of size  $\varepsilon = \beta/M$  the partition function becomes

$$\mathcal{Z} = \lim_{M \to \infty} \int \prod_{m=0}^{M} \mathrm{d}c_{m}^{*} \,\mathrm{d}c_{m} \,e^{-\sum_{\alpha} c_{\alpha}^{*} c_{\alpha}} \left\langle -c \right| \left( e^{-\varepsilon(\hat{H} - \mu \hat{N})} \right)^{M} \left| c \right\rangle.$$

Insertion of M - 1 closure relations yields the rather lengthy expression

$$\mathcal{Z} = \lim_{M \to \infty} \int \prod_{m=0}^{M} \mathrm{d}c_{m}^{*} \, \mathrm{d}c_{m} \, e^{-\sum_{\alpha} c_{\alpha,M}^{*} c_{\alpha,0}} e^{-\sum_{m} \sum_{\alpha} c_{\alpha,m}^{*} c_{\alpha,m}} \times \\ \times \langle -c_{M} | \left( e^{-\varepsilon(\hat{H}-\mu\hat{N})} \right) | c_{M-1} \rangle \cdots \langle -c_{1} | \left( e^{-\varepsilon(\hat{H}-\mu\hat{N})} \right) | c_{0} \rangle.$$
(1.4.4)

Above expression contains many expectation values of operators between coherent states. These can be evaluated very simply by replacing the original operators  $\hat{A}(\hat{c}^{\dagger}_{\alpha},\hat{c}_{\alpha})$  with their normal ordered versions :  $\hat{A}(\hat{c}^{\dagger}_{\alpha},\hat{c}_{\alpha})$  :, where all creation operators stand to the left of all annihilation operators. For the infinitesimal evolution operators we are dealing with, this is possible up to errors of the order of  $\varepsilon^2$ 

$$e^{-\varepsilon(\hat{H}-\mu\hat{N})} =: e^{-\varepsilon(\hat{H}-\mu\hat{N})} : +\mathcal{O}(\varepsilon^2).$$

Now one uses the simple procedure for evaluation of expectation values for normal ordered operators

$$\langle c|: \hat{A}(\hat{c}^{\dagger}_{\alpha}, \hat{c}_{\alpha}): |c'\rangle = A(c^{*}_{\alpha}, c'_{\alpha})e^{\sum_{\alpha}c^{*}_{\alpha}c'_{\alpha}}$$

for every expectation value in Eq. (1.4.4)

$$\langle c_m|:e^{-\varepsilon(\hat{H}-\mu\hat{N})}:|c_{m-1}'\rangle=e^{\sum_\alpha c_{\alpha,m}^*c_{\alpha,m-1}'+\varepsilon\mu c_{\alpha,m}^*c_{\alpha,m-1}'-\varepsilon(H(c_{\alpha,m}^*,c_{\alpha,m-1}'))}.$$

Observing the antiperiodic boundary conditions imposed by the trace (remember Eq. (1.4.3))  $c_{\text{initial}} = -c_{\text{final}}$ ,  $c_M^* = c_{\text{final}}$  and  $c_0 = c_{\text{initial}}$  and collecting all exponentials one finds

$$\mathcal{Z} = \lim_{M \to \infty} \int \prod_{m=0}^{M} \mathrm{d}c_m^* \, \mathrm{d}c_m \, e^{-\varepsilon \sum_m^M \left( \sum_\alpha c_{\alpha,m}^* \left\{ \frac{c_{\alpha,m} - c_{\alpha,m-1}}{\varepsilon} - \mu c_{\alpha,m-1} \right\} + H(c_{\alpha,m}^*, c_{\alpha,m-1}) \right)},$$

where the quantity in the exponential is the discretized action  $S(c^*, c)$ 

$$S(c^*, c) = \varepsilon \sum_{m}^{M} \left( \sum_{\alpha} c^*_{\alpha, m} \left\{ \frac{c_{\alpha, m} - c_{\alpha, m-1}}{\varepsilon} - \mu c_{\alpha, m-1} \right\} + H(c^*_{\alpha, m}, c_{\alpha, m-1}) \right).$$

Finally, one introduces continuum notation for the discrete expressions for the *derivative* in the first term and the path integrals to obtain the familiar expression for the partition function

$$\begin{aligned} \mathcal{Z} &= \int_{c_{\alpha}(\beta)=-c_{\alpha}(0)} \mathcal{D}(c_{\alpha}^{*}(\tau),c_{\alpha}(\tau))e^{-S(c^{*},c)} \\ &= \int_{c_{\alpha}(\beta)=-c_{\alpha}(0)} \mathcal{D}(c_{\alpha}^{*}(\tau),c_{\alpha}(\tau))e^{-\int_{0}^{\beta} \mathrm{d}\tau \left\{\sum_{\alpha} c_{\alpha}^{*}(\tau)(\partial_{\tau}-\mu)c_{\alpha}(\tau)+H(c_{\alpha}^{*}(\tau),c_{\alpha}(\tau))\right\}}. \end{aligned}$$

For a Hamiltonian including a one body term and a two-body interaction that we will frequently encounter

$$\hat{H}(\hat{c}^{\dagger},\hat{c}) = \sum_{ij} t_{ij} \hat{c}_i^{\dagger} \hat{c}_j + \frac{1}{2} \sum_{ijkl} U_{ijkl} \hat{c}_i^{\dagger} \hat{c}_j^{\dagger} \hat{c}_l \hat{c}_k$$

the coherent state action is

$$S(c^*, c) = \int_{0}^{\beta} \mathrm{d}\tau \,\left\{ \sum_{ij} c_i^*(\tau) \left[ (\partial_{\tau} - \mu) \delta_{ij} + t_{ij} \right] c_j(\tau) + \frac{1}{2} \sum_{ijkl} U_{ijkl} c_i^*(\tau) c_j^*(\tau) c_l(\tau) c_k(\tau) \right\}.$$

From this point one may start and develop approximations or a perturbation theory. We will use this notation only when formal developments are discussed, such as dynamical mean-field theory. Since general thermal averages of operators use the partition function

$$\langle \hat{A}(\hat{c}^{\dagger},\hat{c})\rangle = \frac{1}{\mathcal{Z}} \int \mathcal{D}(c^*_{\alpha}(\tau), c_{\alpha}(\tau)) \ A(c^*, c) \ e^{-S(c^*, c)}$$

we can also write the (two-point) Green function in this way

$$G(\alpha_1 \tau_1, \alpha_2 \tau_2) = -\frac{1}{\mathcal{Z}} \int \mathcal{D}(c_{\alpha}^*(\tau), c_{\alpha}(\tau)) c_{\alpha_1}(\tau_1) c_{\alpha_2}^*(\tau_2) e^{-S(c^*, c)}.$$
 (1.4.5)

If the Hamiltonian we are facing is diagonal, i.e.,

$$\hat{H}^{(0)} = \sum_{\alpha} \varepsilon_{\alpha} \hat{c}^{\dagger}_{\alpha} \hat{c}_{\alpha},$$

the partition function involved in the calculation of the Green function can be evaluated via Eq. (1.4.2) to be the determinant of a simple matrix. The Green function of above Hamiltonian can also be evaluated<sup>4</sup>

$$G^{(0)}(\alpha_{1}\tau_{1},\alpha_{2}\tau_{2}) = -\frac{\int \mathcal{D}(c_{\alpha}^{*}(\tau),c_{\alpha}(\tau)) c_{\alpha_{1}}(\tau_{1})c_{\alpha_{2}}^{*}(\tau_{2}) e^{-\int d\tau} \left\{ \sum_{\alpha} c_{\alpha}^{*}(\tau)[(\partial_{\tau}+\varepsilon_{\alpha}-\mu)]c_{\alpha}(\tau) \right\}}{\int \mathcal{D}(c_{\alpha}^{*}(\tau),c_{\alpha}(\tau)) e^{-\int d\tau} \left\{ \sum_{\alpha} c_{\alpha}^{*}(\tau)[(\partial_{\tau}+\varepsilon_{\alpha}-\mu)]c_{\alpha}(\tau) \right\}}$$
$$= -\left(\partial_{\tau}+\varepsilon_{\alpha}-\mu\right)_{\alpha_{1}\tau_{1},\alpha_{2}\tau_{2}}^{-1}.$$
(1.4.6)

In other words

$$-\left(\partial_{\tau}+\varepsilon_{\alpha}-\mu\right)_{\alpha_{1}\tau_{1},\alpha_{2}\tau_{2}} G^{(0)}(\alpha_{1}\tau_{1},\alpha_{2}\tau_{2})=\delta_{\alpha_{1},\alpha_{2}} \delta(\tau_{1}-\tau_{2}).$$

That means, that the exponential of the non-interacting action contains the inverse of the Green function. This important result will be used in later methodological developments, especially in the parts on the Anderson model and DMFT.

For practical applications it is more suitable to work in the Matsubara operator formalism. A quantity that we will make extensive use throughout this work is the Green function. The Green function, also called propagator, is a quantity that contains all the information about the state of a system. This applies to equilibrium as well as to non-equilibrium properties, see, e.g., the Book by Rammer [354].

In the context of quantum mechanics a propagator describes the propagation of a disturbance created by injection of a particle into a state at one time and its removal from another state at another time. We use here the finite-temperature Matsubara formalism [106, 305]. The quantity of interest for us is the fermionic single particle Green function

$$G_{\alpha\beta}(\mathbf{r}-\mathbf{r}',\tau-\tau')=-\langle \hat{T}\hat{c}_{\alpha}(\mathbf{r},\tau)\hat{c}_{\beta}^{\dagger}(\mathbf{r}',\tau')\rangle_{S}.$$

<sup>4</sup>We use continuum notation for brevity, for the actual derivation of the discrete expressions, see Section 2.2 and 2.3 in Ref. [305].

Here  $\tau$  is imaginary time, **r** a position,  $\hat{T}$  is the imaginary time ordering operator,  $\hat{c}_{\alpha}(\mathbf{r},\tau), \hat{c}_{\alpha}^{\dagger}(\mathbf{r},\tau)$  are creation and annihilation operators in the imaginary time Heisenberg picture and the thermal average  $\langle \cdot \rangle_S$  is taken with respect to the action S. The function is antiperiodic in imaginary time. By application of the Fourier transform one obtains the Green function on fermionic Matsubara frequencies  $\omega_n = \frac{\pi}{\beta}(2n+1)$  and momenta **k** 

$$G_{\alpha\beta}(\mathbf{k}, i\omega_n) = \int_0^\beta \mathrm{d}\tau \int \mathrm{d}\mathbf{r} \ G_{\alpha\beta}(\mathbf{r}, \tau) e^{i\omega_n \tau} e^{-i\mathbf{k}\mathbf{r}},$$

where the imaginary time integral extends from zero to the inverse temperature  $\beta = 1/k_{\rm B}T$ . Since we will be mostly concerned with local quantities, i.e. quantites not depending on k, we drop the position/momentum dependence in what follows. The matsubara Green function also possesses a spectral representation connecting it to the spectral function  $A_{\alpha\beta}$  in Källén-Lehmann representation [204, 248]

$$G_{\alpha\beta}(i\omega_n) = \int_{-\infty}^{\infty} \mathrm{d}\omega \frac{A_{\alpha\beta}(\omega)}{i\omega_n - \omega} = \frac{1}{\mathcal{Z}} \sum_{n,m} \frac{\langle n|\hat{c}_{\beta}|m\rangle \langle m|\hat{c}_{\alpha}^{\dagger}|n\rangle}{i\omega_n + E_n - E_m} (e^{-\beta E_n} + e^{-\beta E_m}) \quad (1.4.7)$$

This particular representation is only useful in practice when the full many-body spectrum, i.e. all eigenvalues  $E_n$  and eigenstates  $|n\rangle$  are known. Since this can only be the case for a small system, this direct connection between Green function and spectral function can be used only in exact diagonalization of small clusters.

A more generally useful connection between the spectral function and the Green function can be made by performing an analytical continuation to the real energy axis by setting  $i\omega \rightarrow \omega + i\delta$ , with a small offset  $\delta$ . The retarded Green function  $G^r(\omega)$  thus obtained is directly connected to the spectral function

$$A_{\alpha\beta}(\omega) = -\frac{1}{\pi} \mathrm{Im} G^r_{\alpha\beta}(\omega).$$

For the example of non-interacting particles the spectrum is composed of a series of delta peaks at the eigenenergies  $\varepsilon_i$  of the one-particle states

$$A^{0}(\omega) = \sum_{i} A_{i}^{0}(\omega) = \sum_{i} \delta(\omega - (\varepsilon_{i} - \mu)).$$

Using the analytical continuation and the spectral representation one readily obtains the Green function for state  $\alpha$ 

$$G^{0}_{\alpha}(\omega) = \int_{-\infty}^{\infty} \mathrm{d}\omega' \frac{A^{0}_{\alpha}(\omega')}{\omega - \omega' + i\delta} = \int_{-\infty}^{\infty} \mathrm{d}\omega' \frac{\delta(\omega' - (\varepsilon_{\alpha} - \mu))}{\omega - \omega' + i\delta} = \frac{1}{\omega - \varepsilon_{\alpha} + \mu + i\delta},$$

where the shorhand  $G_{\alpha\alpha} = G_{\alpha}$  was used.

For the general interacting case another quantity, the so-called self-energy  $\Sigma_{\alpha\beta}(\omega)$  comes into play

$$G_{\alpha\beta}(\omega) = \frac{1}{\omega - \varepsilon_{\alpha\beta} + \mu - \Sigma_{\alpha\beta}(\omega)}.$$

It is defined as the difference between the inverse non-interacting and interacting Green functions

$$\Sigma_{\alpha\beta}(\omega) = [G^{-1}(\omega)]_{\alpha\beta} - [G_0^{-1}(\omega)]_{\alpha\beta}$$

or using matrices  $\underline{\underline{G}}$  and  $\underline{\underline{\Sigma}}$ 

$$\underline{\underline{\Sigma}} = \underline{\underline{G}}^{-1} - [\underline{\underline{G}}^0]^{-1}.$$

This can be rearranged to yield the Dyson equation

$$\underline{\underline{G}} = \underline{\underline{G}}^0 + \underline{\underline{G}}^0 \underline{\underline{\Sigma}} \, \underline{\underline{G}}.$$

The self-energy contains all many-body effects and modifies the spectral function considerably

$$A_{\alpha}(\omega) = \frac{1}{\pi} \frac{\mathrm{Im}\Sigma_{\alpha}(\omega)}{(\omega - \varepsilon_{\alpha} + \mu - \mathrm{Re}\Sigma_{\alpha}(\omega))^{2} + (\mathrm{Im}\Sigma_{\alpha}(\omega))^{2}}$$

The real part acts as a shift of the approximate energy levels, while the imaginary part introduces a broadening of the energy levels. For not too large imaginary parts this spectrum can be understood in the quasiparticle picture. The maxima of the spectral function are then located approximately at the zeros of

$$\omega + \mu - \varepsilon_{\alpha} - \operatorname{Re}\Sigma_{\alpha}(\omega) = 0,$$

differing from the non-interacting case by the shift introduced by the real part of the selfenergy and a small broadening via the imaginary part.

In this picture the quantities

$$Z_{\alpha}(\omega) = \frac{1}{1 - \operatorname{Re}\Sigma'_{\alpha}(\omega)}$$
 and  $\tau_{\alpha}(\omega) = \frac{1}{-Z_{\alpha}(\omega)\operatorname{Im}\Sigma(\omega)}$ 

are the quasi particle weight and lifetime and can be used to approximate the Green function in the vicinity of the maxima  $\omega = E_{\alpha}$  of  $A_{\alpha}(\omega)$ 

$$G_{\alpha}(\omega) = \frac{Z_{\alpha}(E_{\alpha})}{\omega - E_{\alpha} + [i\tau_{\alpha}(E_{\alpha})]^{-1}}.$$

Above  $\Sigma' = \partial \Sigma / \partial \omega$  is the derivative of the self-energy. Such a situation is realized for example in the Landau Fermi liquid picture [5], which describes the behaviour of a low

temperature Fermi liquid for energies close to the Fermi level. In this regime the selfenergy behaves for small frequencies and temperatures as

$$\Sigma(T,\omega) \sim \Sigma(T,0) - \alpha_R \omega - i\alpha_I (\omega^2 + T^2),$$

with proportionality constants  $\alpha_{R,I}$  for the real and imaginary parts respectively. Thus, the real part of the self-energy is linear in  $\omega$ , while the imaginary part is quadratic in both  $\omega$  and the temperature T. To lowest order in  $\omega$  the quasi particle weight will be determined by the prefactor  $\alpha_R$ , which is nothing else as the derivative of the real part of the self-energy  $\alpha_R = \text{Re}\Sigma'(T, 0)$  at zero frequency

$$Z_{\alpha}(0) = \frac{1}{1 - \operatorname{Re}\Sigma'(0)}.$$

On Matsubara frequencies the criterion for Fermi liquid behaviour can be inferred by analytical continuation to Matsubara frequencies, where

$$\Sigma(T, i\omega_n) \sim \operatorname{Im}\Sigma(T, 0) - \operatorname{Im}\Sigma'(T, 0)\omega_n,$$

with  $\text{Im}\Sigma(T,0) \propto T^2$ . This means that the imaginary part of the self-energy is linear in  $\omega_n$  for small Matsubara frequencies and quadratic in T. The quasiparticle weight on Matsubara frequencies is also readily obtained by analytical continuation of the real energy formula to yield

$$Z_{\alpha}(0) = \frac{1}{1 - \frac{\partial \operatorname{Im}\Sigma(i\omega_n)}{\partial \omega_n}}\Big|_{\omega_n = 0}.$$

#### 1.4.2 Hubbard Model



Figure 1.4.3: Schematic illustration of the one band Hubbard model on a two dimensional square lattice. Lattice sites (red circles) can be occupied by fermions (blue arrows), which can hop from one site to another with an amplitude t. If two fermions occupy the same site, their energy increases by the Coulomb interaction U.

After the brief introduction of many-body theory in the context of condensed matter, we introduce the paradigm example of a quantum lattice model. An example of a *classical* lattice model would be the Ising model, where classical spins occupy lattice sites and interact with their nearest neighbors via a classical exchange interaction. The model proposed by Gutzwiller [142], Hubbard [165] and Kanamori [191] in 1963, commonly referred to as the Hubbard model, is one of the most widely studied quantum lattice models in theoretical physics [173, 409]. It can be stated in second quantized form as follows

$$\hat{H} = t \sum_{\langle ij \rangle \sigma} \hat{c}^{\dagger}_{i\sigma} \ \hat{c}_{j\sigma} + U \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}.$$

The operator  $\hat{c}_{i\sigma}^{\dagger}$  ( $\hat{c}_{i\sigma}$ ) creates (annihilates) an electron of spin  $\sigma$  on lattice site  $\mathbf{R}_i$ . The operator  $\hat{n}_{i\sigma} = \hat{c}_{i\sigma}^{\dagger} \hat{c}_{i\sigma}$  is the number operator. The first term describes the motion of the electrons from site to site. It is customary to set the chemical potential to zero, which amounts to a trivial shift of the energy scale. If a neighboring site is empty or occupied by an electron of opposite spin, the electron can hop to it with the amplitude t, paying a penalty in energy of the magnitude U in the latter case which is given by the third term. This situation is illustrated in Fig. 1.4.3 for a two dimensional square lattice. This very simple model already captures interesting physical phenomena, like superconductivity, magnetism, metal-insulator transitions, etc. and can show a rich phase diagram, see Refs.

[86, 180, 67, 275, 420, 376] for reviews. Indeed, many parts of the phase diagrams for Hubbard models with different interactions (repulsive/attractive) and on different lattices (cubic/honeycomb/triangular etc.) are a matter of controversy. Recently, in the light of advances in experimental physics of cold atoms, the bosonic Hubbard model [126], also called Bose-Hubbard model, received renewed attention in the theory, because in optical lattices one can realize an unprecedented control over certain parameters of the model facilitating a direct comparison between theory and experiment.

The model was proposed as such, but it can also be heuristically derived starting from the electronic structure Hamiltonian, Eq. (1.2.1), in second quantized form, which already can be written in the form of a general lattice model

$$\hat{H} = \sum_{ij\sigma} t_{ij} \hat{c}^{\dagger}_{i\sigma} \hat{c}_{j\sigma} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} \langle ij|V_{ee}|kl\rangle \, \hat{c}^{\dagger}_{i\sigma} \hat{c}^{\dagger}_{j\sigma'} \hat{c}_{l\sigma'} \hat{c}_{k\sigma}.$$
(1.4.8)

The electron occupies a localized Wannier orbital  $\phi(\mathbf{r} - \mathbf{R}_i)$  centered at site  $\mathbf{R}_i$ . (cf. Eq. (2.1.1) in section 2.1.) Using Bloch functions as a basis is also possible, the Wannier basis is albeit more convenient for calculations and also more intuitive for a lattice model, where one assumes a tight-binding picture with electrons localized at the lattice sites and an inter-site hopping. The hopping for the one band case is in general a matrix of the following form

$$t_{ij} = \int \mathrm{d}\mathbf{r} \,\phi^*(\mathbf{r} - \mathbf{R}_i) \left(-\frac{\hbar^2}{2m}\Delta + V_{\mathrm{ext}}(\mathbf{r})\right) \phi(\mathbf{r} - \mathbf{R}_j).$$

The matrix elements of the Coulomb interaction read

$$U_{ijkl} = \langle ij|V_{ee}|kl\rangle = \int d\mathbf{r} d\mathbf{r}' \phi^*(\mathbf{r} - \mathbf{R}_i)\phi^*(\mathbf{r}' - \mathbf{R}_j) \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \phi(\mathbf{r} - \mathbf{R}_k)\phi(\mathbf{r}' - \mathbf{R}_l),$$

see section 1.5.2 for a detailed survey of this quantity. The coherent state action is for such a case

$$S(c^*, c) = \int_{0}^{\beta} \mathrm{d}\tau \left\{ \sum_{ij} c_i^*(\tau) \left[ (\partial_{\tau} - \mu) \delta_{ij} + t_{ij} \right] c_j(\tau) + \frac{1}{2} \sum_{ijkl} U_{ijkl} c_i^*(\tau) c_j^*(\tau) c_l(\tau) c_k(\tau) \right\}.$$
(1.4.9)

We limit ourselves to the one orbital case here, the extension to the multi-orbital case is straightforward: the hopping will allow for transfer of electrons between different orbitals  $\alpha, \beta$  and different sites i, j and will thus become  $t_{ij}^{\alpha\beta}$ , the Coulomb interaction will also couple different sites as well as orbitals and will attain additional orbital indices  $U_{ijkl}^{\alpha\beta\gamma\delta}$ :

$$t_{ij}^{\alpha\beta} = \int d\mathbf{r} \,\phi_{\alpha}^{*}(\mathbf{r} - \mathbf{R}_{i}) \left( -\frac{\hbar^{2}}{2m} \Delta + V_{ext}(\mathbf{r}) \right) \phi_{\beta}(\mathbf{r} - \mathbf{R}_{j}),$$
$$U_{ijkl}^{\alpha\beta\gamma\delta} = \int d\mathbf{r} \,d\mathbf{r}' \,\phi_{\alpha}^{*}(\mathbf{r} - \mathbf{R}_{i}) \phi_{\beta}^{*}(\mathbf{r}' - \mathbf{R}_{j}) \,\frac{e^{2}}{|\mathbf{r} - \mathbf{r}'|} \,\phi_{\gamma}(\mathbf{r} - \mathbf{R}_{k}) \phi_{\delta}(\mathbf{r}' - \mathbf{R}_{l}).$$

The Hubbard model is a simplified version of the general lattice model from Eq. (1.4.8). Under the assumption of very well localized orbitals hoppings beyond the nearest neighbor sites can be neglected. The hopping matrix thus reduces to a single parameter tAdditionally, the intraatomic Coulomb matrix elements with i = j = k = l will strongly dominate. For brevity one defines  $U_{iiii} := U$  and thus obtains the Hubbard model

$$\hat{H} = t \sum_{\langle ij \rangle \sigma} \hat{c}_{i\sigma}^{\dagger} \hat{c}_{j\sigma} + U \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}.$$

Despite the simple mathematical form of the model an analytical solution is only possible for the one band case in one dimension. The dimensionality of the lattice plays an important role for the model as do the temperature and the filling  $N_e/2N_s$  ( $N_e$  is the number of electrons and  $N_s$  the number of sites in the lattice). For the one dimensional case Lieb and Wu [257] were able to show that no metal-insulator transition takes place for nonzero Uat half filling using the Bethe ansatz. The system is an insulator at finite values of U. The Hubbard model is of course very simplistic, but it already captures *real world* physical phenomena like the Mott transition, its orbitally selective version was studied controversially [212, 213, 205, 260, 258, 261], or superconductivity in cuprates [270]. Numerical solutions are often limited either by the exponentially growing Hilbert space of the problem or by issues like the fermionic sign problem in the quantum Monte Carlo method [265]. Therefore, it is inevitable even in the one band case to apply approximations like the dynamical mean-field approximation that will be discussed in section 1.4.4.

## **1.4.3** Anderson Impurity Model



**Figure 1.4.4:** Schematic illustration of the Anderson impurity model (left) showing an abstract electronic bath and one impurity atom embedded into same. Additionally a level diagram for an impurity with one orbital is shown (right).

The Anderson model for magnetic impurities, often called Anderson impurity model (AIM) or just Anderson model was devised by P. W. Anderson (who shared a Nobel prize with N.F. Mott and J.H. van Vleck in 1977) for the problem of localized magnetic impurities embedded in metals [15]. Impurities in metals lead under certain conditions to intricate many-body effects, the most prominent being the Kondo effect [156], see also the discussion in chapter 5. The model is very different from the Hubbard model as it does only take into account local electronic correlations on the impurity site and not on the host metal sites. An illustration of the model is shown in Fig. 1.4.4. The model has gained additional significance in the context of dynamical mean-field theory, which requires the repeated solution of Anderson impurity models in its self-consistent mapping of a lattice model to an impurity model. The situation of a single impurity atom hybridized with a bath of conduction electrons is described by the Hamiltonian of the AIM, which reads for the general multi orbital case

$$\hat{H}_{AIM} = \sum_{\nu} \varepsilon_{\nu} \hat{c}_{\nu}^{\dagger} \hat{c}_{\nu} - \mu \sum_{i} \hat{d}_{i}^{\dagger} \hat{d}_{i} + \sum_{\nu i} \left( V_{\nu i} \hat{c}_{\nu}^{\dagger} \hat{d}_{i} + V_{\nu i}^{*} \hat{d}_{i}^{\dagger} \hat{c}_{\nu} \right)$$

$$+ \sum_{ij} t_{ij} \hat{d}_{i}^{\dagger} \hat{d}_{j} + \frac{1}{2} \sum_{ijkl} U_{ijkl} \hat{d}_{i}^{\dagger} \hat{d}_{j}^{\dagger} \hat{d}_{l} \hat{d}_{k}, \qquad (1.4.10)$$

$$\underbrace{H_{hor}}_{\hat{H}_{hor}}$$

where  $\hat{c}_{\nu}$  and  $\hat{d}_i$  are the bath and impurity degrees of freedom respectively. We have also included an intra-orbital hopping  $t_{ij}$  and the full local Coulomb interaction in the last two terms. The latin indices in the Hamiltonian now refer to the different orbitals of the magnetic impurity and *not* to lattice sites as in the preceding section. The interaction term is discussed in more detail in section 1.5.2. The energy levels of the bath are given by  $\varepsilon_{\nu}$ and the hybridization parameters  $V_{\nu i}$  give the amplitude for transitions of particles from the bath onto the impurity and vice versa. They comprise what is called the dynamical, i.e., energy dependent, hybridization, whereas the impurity levels or crystal field constitute the static part. The second line of above equation constitutes the local part of the Hamiltonian  $\hat{H}_{loc}$  that acts only on the impurity. If the bath consists of infinitely many sites the hybridization becomes an energy dependent continuous function of the form

$$\Delta_{ij}(\omega) = \sum_{\nu} \frac{V_{\nu i} V_{\nu j}^*}{\omega - \varepsilon_{\nu}}.$$

The model was designed and is best suited for the description of d or f shell impurities in simple metal hosts.

Let us examine it a little closer and discuss some limiting cases. In absence of dynamical hybridization ( $V \equiv 0$ ) the interacting model (U > 0) reduces to an atom with the atomic levels  $\varepsilon_i$ , in other words to an atom in a crystal field. In the one band case with  $\varepsilon$  as the impurity level the model then has the four states illustrated in figure 1.4.4 on the right hand side. The spectrum in this case shows two delta peaks at energies  $\varepsilon$  and  $\varepsilon + U$ , reflecting the atomic character of the system. For a multi-orbital case the spectrum will show many more levels and atomic multiplets; it can still be solved exactly using exact diagonalization with arbitrary interactions  $U_{ijkl}$ .

The converse limit is the one where the interaction vanishes and the hybridization is finite:  $U \equiv 0$  and  $V \neq 0$ . Upon hybridization with the conduction electrons, the impurity level  $\varepsilon$ broaden due to the hybridization. This reflects the fact that the lifetime of quasi particles in the system is now finite, due to the hybridization. The impurity spectrum  $A(\omega)$  of the system is then modified by the hybridization function

$$A(\omega) = -\frac{1}{\pi} \operatorname{Im} G(\omega) = -\frac{1}{\pi} \operatorname{Im} \left( \frac{1}{\omega + i\delta - \varepsilon - \Delta(\omega)} \right).$$

It will thus consist of a peak centered at  $\varepsilon$  broadened and augmented by the hybridization. These two limits are relatively simple to understand and not particularly interesting. The interesting physics arises when both interaction and hybridization are present and compete with each other. The quantity  $U/\Delta$  is the natural indicator of this competition. If it is large the single broadened level will split into two with energy separation U, giving rise to a mean-field local moment  $m = n_{\uparrow} - n_{\downarrow}$ . This occurs when  $U/\Delta = \pi$  in mean-field theory [156]. Beyond the mean-field description lies the realm of Kondo Physics, that is one of the major fields of the application of the Anderson model. Indeed using the formalism of the Schrieffer-Wolff transformation the Anderson model can be mapped onto the spinonly s-d or Kondo model [381], see also chapter 5. In the general case  $U \neq 0$  and  $V_k \neq 0$  the impurity spectrum will contain both the hybridization and the electronic self-energy stemming from the local Coulomb interaction term

$$A(\omega) = -\frac{1}{\pi} \operatorname{Im} G(\omega) = -\frac{1}{\pi} \operatorname{Im} \left( \frac{1}{\omega + i\delta - \varepsilon - \Delta(\omega) - \Sigma(\omega)} \right).$$

One has to remember, that the Anderson model defined in Eq. (1.4.10), despite its simple form and certain exactly tractable limits, still in general constitutes a quantum mechanical many-body problem. This means, that an exact solution for the general case is not possible and one has to resort to approximations for certain parts. This is rooted in the exponential growth of the Hilbert space of the problem. We will discuss numerical solvers for the Anderson model in the context of DMFT in section 1.6 and discuss their merits, drawbacks and the involved approximations. Bluntly, they can be summarized as either treating the interaction or the hybridization approximately, sometimes also both.

The Anderson model can be recast by integrating out the bath degrees of freedom. This can be done since they are non-interacting and the resulting contribution to the path integral will have a Gaussian form. Then the identity from Eq. (1.4.2) can be used to simplify the integral. As shown above the partition function can be written as

$$\mathcal{Z} = \int \mathcal{D}(c^*, c, d^*, d) \ e^{-S_{\text{AIM}}(c^*, c, d^*, d)}$$

The full coherent state action of the AIM can be written as

$$S_{\text{AIM}}(c^*, c, d^*, d) = \int_0^\beta d\tau \left\{ \sum_{\nu, \nu'} c_{\nu}^*(\tau) \left[ \partial_{\tau} + \varepsilon_{\nu} \right] c_{\nu'}(\tau) + \sum_{ij} d_i^*(\tau) \left[ \partial_{\tau} - \mu \right] d_j(\tau) + \sum_{\nu, i} \left[ c_{\nu}^*(\tau) V_{\nu i}^* d_i(\tau) + d_i^*(\tau) V_{\nu i} c_{\nu}(\tau) \right] + H_{\text{loc}}(d^*, d) \right\}.$$

The quantities  $\propto [\partial_{\tau} + \varepsilon_{\nu}]$  constitute the inverse of Green functions  $G^{-1}$ , as was shown in Eq. (1.4.6). The parts containing the bath degrees of freedom fulfill a (slightly more complicated) version of the Gaussian identity introduced in Eq. (1.4.2)

$$\int \mathcal{D}(c^*,c) e^{-c_i^* G_{ij}^{-1} c_j + d_j^* V_{ij} c_j + c_i^* V_{ij}^* d_j} = (\det \underline{\underline{G}}^{-1}) e^{d_i^* \left[ \underline{\underline{V}} \underline{\underline{G}} \underline{\underline{V}}^* \right]_{ij} d_j},$$

where we have named the general matrices appearing in this identity  $\underline{G}^{-1}$  and  $\underline{V}$ . Combining this result with the rest of the action, we see that the *effective* action depends only

parametrically on the bath degrees of freedom via a quantity that we call the bath Green function

$$S_{\text{eff}}(d^*, d) = -\int_0^\beta \mathrm{d}\tau \int_0^\beta \mathrm{d}\tau' \sum_{ij} d_i^*(\tau) \mathcal{G}_{ij}^{-1}(\tau - \tau') d_j(\tau') + \int_0^\beta \mathrm{d}\tau \ H_{\text{loc}}(d^*, d).$$
(1.4.11)

This form will recur in the next section on the dynamical mean-field theory that will use exactly this form of the action to self-consistently connect the Anderson impurity model and Hubbard like lattice models. The Green function of the effective medium now comprises all one particle processes between impurity and bath, i.e. hopping on and off the impurity. It can be written in Matsubara frequency space for practical applications as

$$\mathcal{G}_{ij}(i\omega) = \frac{1}{(i\omega - \mu)\delta_{ij} - \Delta_{ij}(i\omega)}.$$
(1.4.12)

This bath Green function, or equivalently the hybridization function, along with the local Hamiltonian completely specify the Anderson impurity model. This is a convenient reformulation, since quantities like the Green function or the hybridization function are accessible form first principles density functional theory calculations, as we will discuss in chapter 2 and can be used to construct Anderson type models ab initio.

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### 1.4.4 Dynamical Mean-Field Theory

**Figure 1.4.5:** Illustration of the dynamical mean-field theory mapping. The lattice problem on the left is mapped onto the problem of an impurity atom embedded into a bath of electrons. The dynamics of electrons are captured in the approximation as indicated by the time arrow. Electrons can hop onto the impurity atom and back into the bath over time. The hybridization gives the amplitude for such processes.

Now that the Hubbard and Anderson models have been introduced we can describe the theory that connects the two: the dynamical mean-field theory (DMFT). The important part of the story begins with the now seminal paper by Metzner and Vollhardt [286], who investigated fermion lattice models in infinite dimensions. Possibly, the most important result of this investigation was the fact, that in infinite dimensions, or equivalently in the limit of infinite lattice coordination number z, the irreducible self-energy becomes a purely local quantity <sup>5</sup>. This is the foundation of the dynamical mean-field theory (DMFT) developed by Georges and Kotliar [125] few years later, who found the connection between the Hubbard model in  $d \rightarrow \infty$  dimensions and the Anderson impurity model. Although being only formally exact in infinite dimensions this approach proved to be a useful approximation in fewer dimensions, sparkling a very important body of scientific work since its discovery over 20 years ago.

Metzner and Vollhardt found that a specific scaling of the hopping amplitude t is necessary to obtain a nontrivial model in the limit  $d \to \infty$ . For the classical Ising model the limit of infinite lattice coordination number z leads to an exact mean-field theory (the Weiss mean-field theory) [415]. For this theory to yield sensible results the coupling between the Ising spins J must be scaled as  $J = J^*/z$  in order for the entropy and energy to remain finite. For the Hubbard model, the same scaling could be employed as well for

<sup>&</sup>lt;sup>5</sup>This result was actually obtained first by Müller-Hartmann [296].

the hopping  $t = t^*/z$ , however, in this case the kinetic energy would vanish in the limit  $z \to \infty$  leading to a rather uninteresting model.

The scaling of the hopping for the Hubbard model that leads to a kinetic energy that is of the same magnitude as the Coulomb interaction is found to be  $t = t^*/\sqrt{2d}$ , which can be justified by inspection of the density of states for the non-interacting case (U = 0) for the hypercubic lattice [286]

$$D_{\infty}(E) = \lim_{d \to \infty} \frac{1}{2t\sqrt{\pi d}} \exp\left[-\left(\frac{E}{2t\sqrt{d}}\right)^2\right].$$
 (1.4.13)

The nontrivial limit of this equation with the scaling of t given above leads to the Gaussian form required by the central-limit-theorem

$$D_{\infty}(E) = \frac{1}{t\sqrt{2\pi}} \exp\left(-\frac{E^2}{2t^2}\right)$$

This scaling allows for the kinetic and potential energies to compete, leading to interesting many-body physics. Surprisingly, the density of states for the hypercubic lattice in d = 3 dimensions is already very close to a Gaussian, the average deviation that stems mostly from the square-root van Hove singularities is only about 10% [296, 124]. This is illustrated in Fig. 1.4.6. For a face-centered cubic lattice in d = 3 the coordination number is already z = 12, which shows why the DMFT is working so well in solids. More importantly it could be shown that each electron propagator  $G_{ij}$  in the diagrammatic series for the lattice self-energy scales as

$$G_{ii} \sim t^{||\mathbf{R}_i - \mathbf{R}_j||} \sim d^{-||\mathbf{R}_i - \mathbf{R}_j||/2}$$

where  $||\mathbf{R}_i - \mathbf{R}_j||$  is the distance between sites *i* and *j* in the so-called taxi-cab or Manhattan metric, see e.g. [183]. As a consequence of the above, the off-diagonal, i.e. inter-site contributions to the self-energy  $\sum_{i \neq j}$  vanish as the limit  $d \to \infty$  is evaluated, leaving the self-energy a purely local quantity. Together with the translational invariance of the lattice the self-energy becomes

$$\Sigma_{ij}(i\omega_n) = \delta_{ij}\Sigma(i\omega_n).$$

This is of course a tremendous simplification, since this implies that the momentum conservation requirement at the vertices of the diagrammatic expansion can be disregarded [296]. Still the system under study remains a nontrivial many-body problem. These findings led to advances like the exact solution of the Falicov-Kimball model in infinite dimensions [60] which gave an important conceptual insight for the development of dynamical mean-field theory. One of the results of this body of work was that the lattice problem in infinite dimensions can be exactly mapped onto the solvable problem of a single site in a time-dependent external field. This is possible, because spatial fluctuations



**Figure 1.4.6:** Density of state for tight-binding electrons with nearest neighbor hopping on a hypercubic lattice of various dimensionalities. Reproduced after Ref. [124].

are completely suppressed in the infinite dimension limit. It can then be shown using different approaches (e.g. the cavity construction, see Ref. [124]) that the action of a Hubbard-like lattice model, see Eq. (1.4.9), becomes formally identical to the Anderson model action with integrated out bath degrees of freedom (see Eq. (1.4.11)):

$$S_{\rm eff}(d^*,d) = -\int_0^\beta \mathrm{d}\tau \int_0^\beta \mathrm{d}\tau' \sum_{ij} d_i^*(\tau) \mathcal{G}_{ij}^{-1}(\tau-\tau') d_j(\tau') + \int_0^\beta \mathrm{d}\tau \ H_{\rm loc}(d^*,d) \quad (1.4.14)$$

The bath Green function  $\mathcal{G}_{ij}$  of the Anderson model can be shown to act as a dynamical mean-field, since it is a time dependent field that takes into account local quantum fluctuations. The correspondence between the lattice and impurity models is only achieved when the dynamical mean-field is computed self-consistently as we will see below. In the case of DMFT the mean-field can be shown to be the bath Green function of the Anderson

impurity model, cf. Eq. (1.4.12),

$$(\mathcal{G}(i\omega_n))^{-1} = i\omega_n + \mu - \Delta(i\omega_n),$$

where  $\Delta(i\omega_n)$  is the hybridization function familiar from section 1.4.3. This dynamical mean-field theory for the Hubbard model was formulated by Georges and Kotliar [125]. Independently, Jarrell [183] formulated essentially the same ideas and provided a numerically exact solution via a self-consistent quantum Monte Carlo (QMC) scheme.

The ultimate objective of the DMFT is to obtain a solution of a quantum lattice model. In the many-body theory all quantities of interest can be computed via the Green function and the self-energy of the system. The goal of the DMFT is to find a set of equations that allow the determination of the self-energy  $\Sigma$  of the lattice model. The self-energy is defined from the interacting lattice Green function as

$$G(\mathbf{k}, i\omega_n) = (i\omega_n + \mu - \varepsilon(\mathbf{k}) - \Sigma(\mathbf{k}, i\omega_n))^{-1}.$$
 (1.4.15)

Here,  $\mu$  is the chemical potential and  $\varepsilon(\mathbf{k})$  is the non-interacting single particle energy of the original lattice model, i.e. the band structure

$$\varepsilon(\mathbf{k}) = \frac{1}{\sqrt{V_{\rm BZ}}} \sum_{ij} t_{ij} e^{i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)}$$

The normalization factor contains the volume of the Brillouin zone  $V_{BZ}$ . Since we are in infinite dimensions the self-energy has the properties described above: It is local and thus does not depend on the k vector in Fourier space

$$\Sigma(\mathbf{k}, i\omega_n) = \Sigma(i\omega_n).$$

The interacting Green function of the impurity problem can be calculated using the effective action from Eq. (1.4.14)

$$G_{\rm imp}(\tau,\tau') = -\langle \hat{T}\hat{c}(\tau)\hat{c}^{\dagger}(\tau')\rangle_{S_{\rm eff}}$$

and after Fourier transformation also the self-energy becomes available via

$$G_{\rm imp}(i\omega_n) = \left(\mathcal{G}^{-1}(i\omega_n) - \Sigma_{\rm imp}(i\omega_n)\right)^{-1}$$

For the mean-field theory to work we have to assume some sort of correspondence with the real lattice problem. In the limit of infinite dimensions the interacting Green function of the impurity model coincides with the local Green function of the original Hubbard model

$$G_{\rm imp}(i\omega_n) = \sum_{\mathbf{k}} G(\mathbf{k}, i\omega_n) = G_{\rm loc}(i\omega_n), \qquad (1.4.16)$$



Figure 1.4.7: Illustration of the DMFT self-consistency loop with the self-energy  $\Sigma(i\omega)$  as the adjustable quantity. Fourier transforms are understood where needed. The loop is started normally by constructing an initial Green function by setting  $\Sigma(i\omega) = 0$ .

which implies the same for the self-energies  $\Sigma_{imp}(i\omega) = \Sigma(i\omega)$ . The local lattice Green function is then given by

$$G_{\rm loc}(i\omega_n) = \frac{1}{V_{\rm BZ}} \sum_{\mathbf{k}} \frac{1}{i\omega_n + \mu - \varepsilon(\mathbf{k}) - \Sigma(i\omega_n)},$$
(1.4.17)

which is known as the k-integrated Dyson equation. Above equations can be combined to yield the DMFT self-consistency condition [124]

$$G_{\rm loc}(i\omega_n) = \frac{1}{V_{\rm BZ}} \sum_{\mathbf{k}} \left[ i\omega_n + \mu - \varepsilon(\mathbf{k}) - \Sigma_{\rm imp}(i\omega_n) \right]^{-1} = G_{\rm imp}(i\omega_n).$$
(1.4.18)

This in principle establishes  $G_{imp}(i\omega_n)$  as a functional of the bath Green function  $\mathcal{G}(i\omega_n)$ , since  $G_{imp}(i\omega_n)$  can be computed via the action, Eq. (1.4.14). The self-energy can be obtained from

$$\Sigma(i\omega_n) = \mathcal{G}^{-1}(i\omega_n) - G_{\rm imp}^{-1}(i\omega_n).$$
(1.4.19)

Now, that the connection between the Anderson model and the Hubbard model in infinite dimensions has been established a way for solving the DMFT equations is needed. Given that  $G_{imp}$  is computed from the action, which in turn is determined by the bath Green function  $\mathcal{G}$ , we have a coupled problem, which has to be solved self-consistently. The self-consistency loop for the DMFT is shown schematically in Fig. 1.4.7. In the first iteration a starting guess for  $\mathcal{G}$  is needed, usually  $G_{loc}^0$  is used, then by solution of the impurity problem  $G_{imp}$  and in the next step  $\Sigma$  are generated. These are input into the self-consistency condition to yield a new  $\mathcal{G}$  and so on until self-consistency is reached. The bottleneck in this algorithm is the repeated solution of the impurity problem. Since

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impurity models have been studied for decades before the invention of DMFT different approaches to the impurity problem exist: Hubbard I [165], Iterated Perturbation Theory (IPT) [125], Numerical Renormalization Group (NRG) [456, 66], Fluctuation Exchange (FLEX) [42], Density Matrix Renormalization Group (DMRG) [453, 380], Exact Diagonalization (ED), the Non-Crossing and One-Crossing Approximations (NCA/OCA) [198, 134, 237, 349, 144, 146] and Quantum Monte Carlo (QMC)[158, 367, 448], to name the most prominent ones, see also Refs. [124, 153, 225] for reviews in the context of DMFT. Since we have used different impurity solvers in the work presented in this thesis we have devoted section 1.6 to a brief description of them.

The main advantage of the DMFT is that it can describe both band-like behavior (quasi particles) and atomic-like behavior (multiplets). It captures the physics in the intermediate range of the U, t parameter space that are unaccessible by perturbative approaches. The competition between delocalization and localization is a very important element of the physics of strongly correlated systems. This competition is captured by the DMFT, which makes it such a valuable tool. We have described the DMFT here in the limit of infinite dimensions d or lattice coordination z, where it originated from and where it is *exact*. The theory can be also very successfully applied to systems with fewer dimensions, like d = 2,3 that are the physically most important ones. We have seen from Fig. 1.4.6 that the key assumption behind the DMFT is approximately fulfilled already for lower dimensions and coordination numbers. For such cases the momentum independence of the self-energy is not fulfilled. The DMFT then amounts to the *approximation* 

$$\Sigma(\mathbf{k}, i\omega) \approx \Sigma_{\rm imp}(i\omega),$$

where the momentum dependence of the lattice self-energy is ignored. This approximation is justified, when the physics of the system under consideration is sufficiently local. Various efforts exist to overcome the limitation to purely local phenomena imposed by the DMFT. There are cluster extensions of the DMFT in real space, the cluster or cellular DMFT [226], cluster extensions in reciprocal space, the dynamical cluster approach (DCA) [155], and other methods that include non-local correlations beyond DMFT, like the Dual-Fermion approach [366], the dynamical vertex approximation (D $\Gamma$ A) [419] or the recently proposed one-particle irreducible functional approach (1PI) [360].

# **1.5 DFT++ Framework**

We have so far discussed DFT as a powerful method for electronic structure calculations, a method best suited to systems with s or p valence electrons, where correlations play a minor role. It provides accurate band structures employing a single particle formalism. However, DFT fails to correctly describe correlated systems containing localized elec-

trons in partially filled d or f shells. In such systems genuine many-body effects, like the Mott metal-insulator transition or Kondo physics can occur [295, 156]. Such many-body effects were studied using simplified models like the Falicov-Kimball, Hubbard, Anderson or Kondo models, to name only a few. The dynamical mean-field theory provides a framework for the solution of lattice models via the self-consistent solution of an impurity model. Despite the information about the fundamental physics of model systems the model Hamiltonian approach is quite limited when it comes to quantitative predictions for real materials. Material specific quantities on the other hand are well accounted for in the DFT, therefore, it would be desirable to combine both methods. Such approaches are summarized under the name LDA++ [255], or more generally DFT++.

# 1.5.1 General idea of DFT++

The first step of any DFT++ procedure is to properly identify the correlated subset of orbitals that can account for the low-energy electronic properties of the system. The uncorrelated part is assumed to be correctly treated by DFT. The set of correlated orbitals has to be chosen accordingly for the system one wants to study. Typical examples of correlated materials are the 3d of 4f transition metals, where the correlated subspace is identified with the partially filled d or f orbitals. The Kohn-Sham Hamiltonian is now downfolded into a smaller effective Hamiltonian, see chapter 2, to make calculations feasible and supplemented with a local multiband Hubbard-like part that acts only on the correlated orbitals on the same site

$$\hat{H}_{\rm DFT++} = \hat{H}_{\rm KS} - \hat{H}_{\rm DC} + \underbrace{\frac{1}{2} \sum_{i} \sum_{m,m',m'',m'''} \sum_{\sigma\sigma'} U_{mm'm''m'''} \hat{d}^{\dagger}_{im\sigma} \hat{d}^{\dagger}_{im'\sigma'} \hat{d}_{im''\sigma'} \hat{d}_{im''\sigma'}}_{\hat{H}_{\rm loc}} \cdot (1.5.1)$$

The notation here becomes a little cumbersome: *i* labels the lattice site, *m* labels different orbitals and finally  $\sigma$  labels the spin. The downfolded Kohn-Sham Hamiltonian is labeled  $\hat{H}_{\text{KS}}$ . Since this is a multi orbital model the Coulomb interaction *U* is a tensor

$$U_{mm'm''m'''} = \langle mm' | V_{\rm ee} | m''m''' \rangle$$

that includes the interaction between the correlated orbitals. Despite being formally quite simple this quantity has its intricacies, that we deal with in the next section. The Hamiltonian, Eq. (1.5.1), constitutes a general lattice model in the fashion of the Hubbard model, where the non-interacting part is taken from DFT. We may thus identify the Kohn-Sham Hamiltonian in a localized basis with the hopping part of the general lattice model already

shown in section 1.4

$$\hat{H}_{\rm KS} \propto t_{ij}^{\alpha\beta} = \int d\mathbf{r} \,\phi_{\alpha}^*(\mathbf{r} - \mathbf{R}_i) \left(-\frac{\hbar^2}{2m}\nabla^2 + V_{\rm KS}(\mathbf{r})\right) \phi_{\beta}(\mathbf{r} - \mathbf{R}_j).$$
(1.5.2)

This identification of the Kohn-Sham spectrum with the non-interacting part of a lattice model leads to an intrinsic issue of DFT++ approaches. While density functional theory does not include all the interactions between strongly correlated d or f electrons, it captures some portion of them through the Hartree and exchange-correlation terms. The model Hamiltonian part now tries to account for as much of the interactions as possible thorough the Coulomb interaction tensor of the impurity model  $U_{mm'm''m'''}$ . This ultimately leads to the problem that some contributions to the interaction are included twice, we are doubly counting interactions. This has to be explicitly compensated by adding a shift in the chemical potential of the correlated orbitals to the Hamiltonian. The DFT++ Hamiltonian, Eq. (1.5.1), contains the double counting correction

$$\hat{H}_{\rm DC} = \mu_{\rm DC} \sum_{m,\sigma} \hat{n}_{m,\sigma}.$$

The double counting potential  $\mu_{DC}$  acts as an additional impurity chemical potential. It can be absorbed into the chemical potential of the full problem when we are considering *only* correlated orbitals. As soon as one tries to include uncorrelated states in the DFT++ treatment the choice for the double counting potential  $\mu_{DC}$  becomes important, since it controls the filling of the correlated subspace. We will explore the consequences of different choices for the double counting in such a situation in chapter 3.

Additionally, one has to decide on a method of treatment for the interaction part of the Hamiltonian. As often in theoretical physics one has the choice between approximation or brute force numerics, we will discuss a few methods in section 1.6. One of the first attempts at such a unified theory is the LDA+U (or more general DFT+U) method developed in the early 1990s, that will be discussed in section 1.5.3. Many physical phenomena in strongly correlated systems like the insulating gap of antiferromagnetic Mott insulators, unaccessible within DFT alone, can already be reproduced by DFT+U. In the region of intermediate correlation strength, however, the DFT+U method is not applicable, because of its static nature. It neglects dynamical correlations and is thus too simple to account, e.g. for Kondo physics or the Mott metal-insulator transition. A more sophisticated methodology is applied within the DFT+DMFT approach, which employs the dynamical mean-field theory for the solution of the many-body Hamiltonian.

# **1.5.2** The Coulomb interaction tensor

In this section we will note some important properties of the Coulomb interaction tensor, often called the U-matrix, appearing in DFT++ approaches. For practical applications it is very important to understand the properties of the tensor in general and the differences between different parametrizations of the tensor that exist. The general screened Coulomb interaction Hamiltonian can, as we have seen above, be written as

$$\hat{H}_{ee} = \frac{1}{2} \sum_{m,m',m'',m'''} \sum_{\sigma\sigma'} U_{mm'm''m'''} \hat{d}^{\dagger}_{m\sigma} \hat{d}^{\dagger}_{m'\sigma'} \hat{d}_{m''\sigma'} \hat{d}_{m''\sigma}.$$
(1.5.3)

The matrix elements of the local Coulomb interaction are

$$U_{mm'm''m'''} = \langle mm' | V_{ee} | m''m''' \rangle = \int d\mathbf{r} \, d\mathbf{r}' \, \phi_m^*(\mathbf{r}) \phi_{m'}^*(\mathbf{r}') \, \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \, \phi_{m''}(\mathbf{r}) \phi_{m'''}(\mathbf{r}').$$
(1.5.4)

The tensor of the screened Coulomb interaction that appears here is the atomic Coulomb interaction known from atomic physics, see e.g. Ref [396], augmented with the screening due to the electronic environment. In atoms the dominant values of the tensor are of the order of tens of electron volts, see, e.g., Refs. [439, 440], while in solids the interaction is screened by itinerant electrons and thus reduced considerably, to values on the order of one electron volt, see, e.g., Refs. [426, 84]. Since it has the same form as its bare atomic version it is instructive to inspect the bare Coulomb interaction tensor. We consider atomic orbitals of the Hydrogen type

$$\phi(\mathbf{r}) = \psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta, \phi),$$

with the radial functions  $R_{nl}(r)$ 

$$R_{nl}(r) = \sqrt{\frac{(n-l-1)!Z}{n^2[(n+l)!]^3}} \exp\left(\frac{-x}{2}\right) x^{l+1} L_{n-l-1}^{2l+1}(x),$$

containing the Laguerre polynomials  $L_{n-l-1}^{2l+1}(x)$ , the shorthand  $x = \frac{2Zr}{n}$ , and the complex spherical harmonics

$$Y_{lm}(\theta,\phi) = (-1)^m \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_{lm}(\cos\theta) \exp(im\phi),$$

containing the associated Legendre functions  $P_{lm}(\cos \theta)$ , see, e.g., Refs. [285, 396]. The Coulomb interaction for such orbitals can be expressed using spherical coordinates in the



Figure 1.5.8: The angular parts of the five 3d orbitals represented by the real spherical harmonics with  $m = -2, \ldots, 2$ . Color indicates the sign of the lobe: red (+), blue (-). Source: Public domain image.

following form

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{k=0}^{\infty} \frac{r_{<}^{k}}{r_{>}^{k+1}} \frac{4\pi}{2k+1} \sum_{q=-k}^{k} Y_{qk}(\theta', \phi') Y_{qk}^{*}(\theta, \phi),$$
(1.5.5)

where as usual  $r_{<}(r_{>})$  is the smaller (larger) of r and r'. In what follows we limit the general consideration of the matrix elements of the Coulomb interaction, found, e.g., in Refs. [392, 396], to the case of one electronic shell, i.e. one specific n and l with the only remaining variable m. An example is the 3d shell (n = 3; l = 2; m = -2, -1, 0, 1, 2), so important for the properties of the transition metals of the iron series. Inserting the expansion from Eq. (1.5.5) into Eq. (1.5.4), we write the expectation value in bra-ket notation for brevity, one obtains the angular integrals

$$\frac{4\pi}{2k+1}\sum_{q=-k}^{k} \langle m|Y_{qk}(\theta',\phi')|m'\rangle \langle m''|Y_{qk}^{*}(\theta,\phi)|m'''\rangle =: a_{k}(mm';m''m'''),$$

that we call, following Slater,  $a_k(mm'; m''m''')$  [392, 396]. These contain integrals over products of three spherical harmonics, that can be expressed via Wigner 3 - j symbols [427]. The radial integrals [392, 396] also simplify for the case of fixed n and l to

$$F^{k} := F^{k}(nl;nl) = \int \mathrm{d}r \; r^{2} \int \mathrm{d}r'(r')^{2} R_{nl}^{2}(r) \frac{r_{<}^{k}}{r_{>}^{k+1}} R_{nl}^{2}(r').$$

Thus, combining the angular and radial parts, the Coulomb interaction matrix for the case of a spherically symmetric atom can be written in short as

$$U_{mm'm''m'''} = \sum_{k=0}^{2l} a_k(mm', m''m''')F^k.$$

In practice one usually parametrizes the Coulomb interaction by using only two parame-

ters U and J. These constitute the orbital averages of the full tensor

$$U = F^{0} = \frac{1}{(2l+1)^{2}} \sum_{mm'} U_{mm'mm'}$$

$$U - J = \frac{1}{2l(2l+1)} \sum_{mm'} (U_{mm'mm'} - U_{mm'm'm}).$$
(1.5.6)

From that, one explicitly obtains  $J = \frac{1}{14}(F^2 + F^4)$ . Additionally, it was shown in Hartree-Fock calculations for 3d ions [439, 440, 89], as well as for spherical harmonics [408] that the ratio between  $F^2$  and  $F^4$  (or equivalently the ratio between the Racah parameters C and B in Ref. [408]) is almost a constant. Hartree-Fock calculations gave a slight variation of the ratio depending on the filling of the shell and an average of about  $F^4 = 0.625F^2$ , while for Slater type orbitals the ratio is independent of filling and  $F^4 \approx 0.651F^2$  [89]. Newer Hartree-Fock calculations for 3d series crystals employing an ab initio Wannier basis show a ratio of  $F^4 \approx 0.615F^2$  [379]. In f electron systems the  $F^6$  integral contributes as well, leading to  $J = (286F^2 + 195F^4 + 250F^6)/6435$ . It is thus possible to parametrize the full rotationally invariant Coulomb tensor in a spherically symmetric situation by using only few parameters. A different, but equivalent, set are the Racah parameters, that are for a d system related to the Slater integrals by  $A = F^0 - \frac{49}{441}F^4$ ,  $B = \frac{1}{49}F^2 - \frac{5}{441}F^4$ ,  $C = \frac{35}{441}F^4$  [351].

The dominant parts of the tensor are the direct and exchange density-density matrices  $U_{mm'}$  and  $J_{mm'}$ , that can be written as

$$U_{mm'} = \sum_{k=0}^{2l} a_k(mm; m'm')F^k$$
$$J_{mm'} = \sum_{k=0}^{2l} a_k(mm'; m'm)F^k.$$

In some methods, especially in some flavors of QMC, one has to resort to an approximation, where the interaction contains only density-density terms  $\propto \hat{n}_{m\sigma} = \hat{d}^{\dagger}_{m\sigma} \hat{d}_{m\sigma}$ . In this approximation the Hamiltonian can be written as

$$\hat{H}_{\rm ee}^{\rm dens-dens} = \frac{1}{2} \sum_{m,m',\sigma} U_{mm'} \hat{n}_{m,\sigma} \hat{n}_{m',-\sigma} + \frac{1}{2} \sum_{m \neq m',\sigma} (U_{mm'} - J_{mm'}) \hat{n}_{m,\sigma} \hat{n}_{m',\sigma}$$

The interaction matrices  $U_{mm'}$  and  $J_{mm'}$  can be analytically expressed for a five band

system as follows: We introduce the shorthands [328]

$$U_{0} = F^{0} + \frac{8}{7} \frac{F^{2} + F^{4}}{14}$$

$$J_{1} = \frac{3}{49}F^{2} + \frac{20}{9} \frac{1}{49}F^{4}$$

$$J_{2} = -2\frac{5}{7} \frac{F^{2} + F^{4}}{14} + 3J_{1}$$

$$J_{3} = 6\frac{5}{7} \frac{F^{2} + F^{4}}{14} - 5J_{1}$$

$$J_{4} = 4\frac{5}{7} \frac{F^{2} + F^{4}}{14} - 3J_{1}.$$

Furthermore, we utilize the basis of cubic harmonics  $K_{lm}$  defined in terms of the complex spherical harmonics  $Y_{lm}$  (for m > 0) by [427]

$$K_{l,+m} = \frac{1}{\sqrt{2}} \Big[ (-1)^m Y_{lm} + Y_{l,-m} \Big]$$
  

$$K_{l0} = Y_{l0}$$
  

$$K_{l,-m} = \frac{1}{i\sqrt{2}} \Big[ (-1)^m Y_{lm} - Y_{l,-m} \Big].$$

The orbitals for the 3d shell are shown in Fig. 1.5.8 with the orbitals ordered corresponding to their respective value of m as  $(d_{xy}, d_{yz}, d_{3z^2-r^2}, d_{xz}, d_{x^2-y^2})$ . The interaction in this basis can be written as

$$U_{mm'} = \begin{pmatrix} U_0 & U_0 - 2J_1 & U_0 - 2J_2 & U_0 - 2J_1 & U_0 - 2J_3 \\ U_0 - 2J_1 & U_0 & U_0 - 2J_4 & U_0 - 2J_1 & U_0 - 2J_1 \\ U_0 - 2J_2 & U_0 - 2J_4 & U_0 & U_0 - 2J_4 & U_0 - 2J_2 \\ U_0 - 2J_1 & U_0 - 2J_1 & U_0 - 2J_4 & U_0 & U_0 - 2J_1 \\ U_0 - 2J_3 & U_0 - 2J_1 & U_0 - 2J_2 & U_0 - 2J_1 & U_0 \end{pmatrix}$$
(1.5.7)

and

$$J_{mm'} = \begin{pmatrix} U_0 & J_1 & J_2 & J_1 & J_3 \\ J_1 & U_0 & J_4 & J_1 & J_1 \\ J_2 & J_4 & U_0 & J_4 & J_2 \\ J_1 & J_1 & J_4 & U_0 & J_1 \\ J_3 & J_1 & J_2 & J_1 & U_0 \end{pmatrix}.$$
 (1.5.8)

This is exactly the density-density part of the full rotationally invariant Coulomb interaction written above in Eq. (1.5.3), transformed into cubic harmonics. We want to point out, that the diagonal elements of the  $J_{mm'}$  matrix, albeit formally correct, are never used in calculations, because they violate the Pauli principle.  $J_{mm'}$  will only be evaluated for  $m \neq m'$ . In the density-density case even including the diagonal in  $J_{mm'}$  poses no fundamental problem, because the diagonals of  $U_{mm'}$  and  $J_{mm'}$  exactly cancel and only  $U_{mm'} - J_{mm'}$  is really used. For compactness the density-density interaction matrices can be combined into one spin dependent super matrix

$$U_{mm'}^{\sigma\sigma'} = \begin{pmatrix} U_{mm'} - J_{mm'} & U_{mm'} \\ & &$$

where the blocks are the spin diagonal and off diagonal parts.

For the two or three band case the interaction can be exactly parametrized using fewer parameters. The full rotationally invariant interaction is then

$$\hat{H}_{ee}^{2,3band} = \frac{1}{2} \sum_{m,m',\sigma} U_{mm'} \hat{n}_{m,\sigma} \hat{n}_{m',-\sigma} + \frac{1}{2} \sum_{m \neq m',\sigma} (U_{mm'} - J_{mm'}) \hat{n}_{m,\sigma} \hat{n}_{m',\sigma} \quad (1.5.10)$$
$$+ \frac{1}{2} \sum_{m \neq m',\sigma} J_{mm'} \left( \hat{d}_{m,\sigma}^{\dagger} \hat{d}_{m',-\sigma}^{\dagger} \hat{d}_{m,-\sigma} \hat{d}_{m',\sigma} + \hat{d}_{m,\sigma}^{\dagger} \hat{d}_{m,-\sigma}^{\dagger} \hat{d}_{m',-\sigma} \hat{d}_{m',-\sigma} \right).$$

The matrix is parametrized using the following three parameters U, U' and J [191, 113]

$$U = \langle mm | V_{ee} | mm \rangle, \quad U' = \langle mm' | V_{ee} | mm' \rangle, \quad J = \langle mm' | V_{ee} | m'm \rangle$$

The first term describes the interaction of particles (electrons or holes) belonging to the same orbitals, the second describes the interaction of particles belonging to different orbitals that remain in their respective orbital after scattering. The third term is the so-called exchange term, where the particles are exchanged between two different orbitals. From symmetry considerations which arise from the symmetry preserved between the Coulomb matrix elements for free d orbitals in a central field additionally U' = U - 2J is required. For the example of a three band model the matrices  $U_{mm'}$  and  $J_{mm'}$  then read

$$U_{mm'} = \begin{pmatrix} U & U - 2J & U - 2J \\ U - 2J & U & U - 2J \\ U - 2J & U - 2J & U \end{pmatrix} , \quad J_{mm'} = \begin{pmatrix} U & J & J \\ J & U & J \\ J & J & U \end{pmatrix}.$$

The parameters U and J are a necessary input for the Hamiltonian. This simple parametrization already incorporates Hund's (first) rule, since the inter orbital interaction for two particles with parallel spins U - 3J is lower than for antiparallel spins U - 2J and of course lower than for antiparallel spins on the same site U. The caveat concerning the diagonal of  $J_{mm'}$  applies here also, of course. Another parametrization proposed by Kanamori [191] uses four parameters derived from the interaction integrals

$$U_{mmmm} = \langle mm | V_{ee} | mm \rangle = \int d\mathbf{r} d\mathbf{r}' \phi_m^*(\mathbf{r}) \phi_m^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \phi_m(\mathbf{r}) \phi_m(\mathbf{r}') =: U_{\mathrm{K}}$$

$$U_{mm'mm'} = \langle mm' | V_{ee} | mm' \rangle = \int d\mathbf{r} d\mathbf{r}' \phi_m^*(\mathbf{r}) \phi_{m'}^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \phi_m(\mathbf{r}) \phi_{m'}(\mathbf{r}') =: U_{\mathrm{K}}'$$

$$U_{mm'm'm} = \langle mm' | V_{ee} | m'm \rangle = \int d\mathbf{r} d\mathbf{r}' \phi_m^*(\mathbf{r}) \phi_{m'}^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \phi_{m'}(\mathbf{r}) \phi_m(\mathbf{r}') =: J_{\mathrm{K}}$$

$$U_{mmm'm'} = \langle mm | V_{ee} | m'm' \rangle = \int d\mathbf{r} d\mathbf{r}' \phi_m^*(\mathbf{r}) \phi_m^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \phi_{m'}(\mathbf{r}) \phi_{m'}(\mathbf{r}) =: J_{\mathrm{K}}$$

These parameters are assumed to be constant irrespective of m and m'. The spin flip  $J_{\rm K}$  and the pair hopping  $J'_{K}$  coupling parameters are different in general. For a real basis (cubic harmonics) the defining integrals for  $J_{\rm K}$  and  $J'_{K}$  become identical and thus  $J_{\rm K} = J'_{K}$ . In general the relation

$$J_{\rm K} = \frac{1}{2l(2l+1)} \sum_{m \neq m'} J_{mm'} = \frac{5}{7} J$$

holds between the interaction parameters J and  $J_{\rm K}$  which is the actual average of the corresponding matrix. The SU(2) symmetrical Kanamori interaction Hamiltonian can then be written as

$$\hat{H}_{ee}^{\text{Kanamori}} = U_{\text{K}} \sum_{m} \hat{n}_{m,\uparrow} \hat{n}_{m,\downarrow} + \sum_{m > m',\sigma} \left[ U'_{K} \hat{n}_{m,\sigma} \hat{n}_{m',-\sigma} + (U'_{K} - J_{\text{K}}) \hat{n}_{m,\sigma} \hat{n}_{m',\sigma} \right] \\ + \frac{1}{2} J_{\text{K}} \sum_{m \neq m'} \left( \hat{d}^{\dagger}_{m,\sigma} \hat{d}^{\dagger}_{m',-\sigma} \hat{d}_{m,-\sigma} \hat{d}_{m',\sigma} + \hat{d}^{\dagger}_{m,\sigma} \hat{d}^{\dagger}_{m,-\sigma} \hat{d}_{m',\sigma} \hat{d}_{m',-\sigma} \right)$$

It is assumed in the Kanamori scheme that the inter-orbital Coulomb repulsion is equal to  $U'_{\rm K}$  between all different orbitals, which is in general not true of course, as we have seen for the five band case above. Nevertheless, the Kanamori type interaction contains spin-flip and pair-hopping terms lacking in the density-density only description. For the case of two and three band models the full interaction can be written in this way exactly, as we have shown above, for the five band case, however, this form misses certain terms that are only included in the full interaction matrix  $U_{ijkl}$ . Thus, apart from the cases where it is exact, the Kanamori Hamiltonian constitutes an intermediate case between the density-density and the full interaction containing all interaction terms.

The parametrizations described above are very useful in practical calculations, but nevertheless only parametrizations that are approximate in general. The only exact parametrization, for the case of a spherically symmetric single atom is the one based on the Slater integrals  $F^k$ , or equivalently the Racah parameters, but also this parametrization does only apply to a single atom. Thus if one wants to calculate a solid or nanostructure from first principles using any of the described parametrizations of the interaction is an approximation. The interaction tensor can be calculated in an ab initio manner using different methods like constrained DFT (cDFT) [282, 167, 139, 138, 18] or the more recent constrained random phase approximation (cRPA) [401]. Latter method yields the full tensor that can be used in DFT++ calculations. These calculations do not rely on approximations concerning the symmetry of the system etc., but they are performed in a symmetry adapted basis set reflecting the true underlying symmetry of the system<sup>6</sup>. Furthermore, the reduction of the bare Coulomb interaction due to screening is computed in cRPA from first principles and also the frequency dependence of the interaction, which arises as a consequence of downfolding and has been shown to be rather large, can be explored [27].

We want to note that if a transformation of the basis of the Hamiltonian is performed it is imperative to also transform the Coulomb interaction matrix  $U_{ijkl}$  in the subsequent many-body treatment. The matrix is usually computed in the basis of complex spherical harmonics and subsequently transformed to the cubic harmonic basis. If one chooses to rotate the orbital basis or to use linear combinations of the cubic harmonics, like the symmetry adapted crystal field basis, the Coulomb interaction matrix has to be transformed accordingly using a transformation matrix <u>T</u>. Schematically, we write

$$U_{ijkl}' = \underline{\underline{T}} U_{ijkl} \, \underline{\underline{T}}^{\dagger}$$

If one wishes to use only the density-density interaction matrix  $U_{ij}^{\sigma\sigma'}$  the transformed density-density part  $(U_{ij})'$  can be computed *only* after the full tensor  $U_{ijkl}$  has been transformed. The entries of the density-density matrix  $U_{ij}^{\sigma\sigma'}$  are linear combinations of elements of the full tensor  $U_{ijkl}$  that each will transform differently in general.

# 1.5.3 DFT+U

One of the first succesful combinations of DFT with a many-body Hamiltonian was the LDA+U method [23, 21, 262, 399], for a review see [22]. The LDA+U or more generally DFT+U uses the machinery of the Kohn-Sham self-consistency cycle, but adds an orbital dependent potential to the Kohn-Sham Hamiltonian. This potential arises from inclusion of the Coulomb interaction in the atomic subshells that are not treated satisfactorily in

<sup>&</sup>lt;sup>6</sup>In some cases of high symmetry, e.g., cubic the Coulomb interaction can still be parametrized using Slater integrals, but the number of parameters is significantly higher than for the spherical case [254].

DFT alone. In this way the DFT+U tries ro remedy the shortcomings of DFT as compared to the unknown exact density functional. However, the interaction is included only on a static mean-field level, similarly to the Hartree-Fock approach. Unlike in pure DFT the system is now divided into a *correlated* and an *uncorrelated* subspace. The latter is assumed to be described correctly in DFT, while the former is not. The correlated subspace is usually a partially filled d or f shell, since in these shells electronic correlations are known to play an important role, while s and p shells are usually satisfactorily described within DFT. For the DFT+U method to work one has to have a formal notion of what *the d-shell* is, i.e., a local basis set that describes this shell. Since the DFT+U is usually implemented on top of a working DFT code it uses the codes internal scheme for the projection of the wave function on certain electronic shells. Usually this works by projecting the wave function inside an atomic sphere on atomic orbitals of a certain character. For the implementation within PAW we refer to Refs. [359, 38].

The total energy in DFT+U now contains two additional terms as compared to DFT

$$E_{\text{DFT+U}}[n] = E_{\text{DFT}}[n] + E_{\text{U}}[n_{mm'}^{\sigma}] - E_{\text{DC}}.$$

The first one is the orbital dependent Coulomb energy, that depends on the density matrix of the correlated subspace  $\langle \hat{n}_{mm'}^{\sigma} \rangle = \langle \hat{c}_{m\sigma}^{\dagger} \hat{c}_{m'\sigma} \rangle$ , while the second term is a so-called double counting correction. The double counting term is needed to ensure that certain parts of the Coulomb interaction that have been already included on the DFT level are not counted twice. Explicitly writing the term  $E_{\rm U}$  as a static mean-field version of the general Coulomb interaction the total energy within DFT+U becomes (for every site *i*)

$$E_{\rm DFT+U}[n] = E_{\rm DFT}[n] + \frac{1}{2} \sum_{i\sigma} \sum_{mm'm''m'''} U_{mm''m'm''} \langle \hat{n}_{imm'}^{\sigma} \rangle \langle \hat{n}_{im''m'''}^{\sigma} \rangle \\ + \frac{1}{2} \sum_{i\sigma} \sum_{mm'm''m'''} (U_{mm''m'm''} - U_{mm''m'''n'}) \langle \hat{n}_{imm'}^{\sigma} \rangle \langle \hat{n}_{im''m'''}^{\sigma} \rangle \\ - E_{\rm DC}.$$

For the functional to be completely defined one needs to specify a double counting term  $E_{\rm DC}$ . This is an inherent problem of the DFT+U and of all DFT++ approaches. Since the system is separated into two parts that are treated on a different, formally incompatible, footing there is no way of identifying the doubly counted terms exactly. So, approximations have to be devised to at least partially overcome this problem.

Two common choices in DFT+U are the around-mean-field (AMF) and the fully localized limit (FLL) [85, 399, 23], that we will introduce here. We will visit them again in chapter 3 on the double counting in DFT+DMFT. The AMF starts from the assumption that the LDA is in principle a mean-field theory without explicit orbital-dependence and thus all
orbitals belonging to a shell should have the same average occupancy<sup>7</sup>

$$\bar{n}^{\sigma} = \frac{1}{2l+1} \sum_{m} \langle \hat{n}_{mm}^{\sigma} \rangle$$

Starting from this insight a functional is constructed, that for identical occupancies of all m subshells of a given l-shell gives the same energy as LDA alone

$$E_{\rm DFT+U}^{\rm AMF}[n] = E_{\rm DFT}[n] + \frac{1}{2} \sum_{i\sigma} \sum_{mm'm''m'''} U_{mm''m'm''} \left( \langle \hat{n}_{imm'}^{\sigma} \rangle - \bar{n}_{i}^{\sigma} \right) \left( \langle \hat{n}_{im''m'''}^{-\sigma} \rangle - \bar{n}_{i}^{\sigma} \right) \\ + \frac{1}{2} \sum_{i\sigma} \sum_{mm'm''m''} \left( U_{mm''m'm''} - U_{mm''m''m'} \right) \left( \langle \hat{n}_{imm'}^{\sigma} \rangle - \bar{n}_{i}^{\sigma} \right) \times \\ \times \left( \langle \hat{n}_{im''m''}^{-\sigma} \rangle - \bar{n}_{i}^{\sigma} \right).$$

Since the AMF functional has deficiencies in the description of strongly correlated systems and is better suited to metals as to, e.g., Mott insulators another functional is commonly used: the so-called fully localized limit (FLL) functional [85]. The construction starts from the opposite situation as the AMF. It is known that the LDA usually gives quite good total energies for atoms, while the orbital energies, identified with the derivative of the total energy by the orbital occupancy  $\varepsilon_i = \partial E / \partial n_i$  [181], are often wrong. The prototypical example is the hydrogen atom, where LDA gives a total energy of -0.8913 Ry (LSDA: -0.9573 Ry), fairly close to the exact -1.0 Ry, but completely fails for the orbital energy, which is -0.4669 Ry (LSDA: -0.538 Ry) instead of -1.0 Ry [336, 227]. Another important point is that the LDA (also GGA) potential is a continuous function of the electron number, whereas it has been shown that the exact density functional must jump discontinuously as the number of electrons passes an integer [141, 335].

These considerations motivate the identification of an atomic energy of the correlated shell (per site) as the double counting term

$$E_{\rm DC}^{i} = \frac{1}{2}U\sum_{m} \langle \hat{n}_{mm} \rangle (\langle \hat{n}_{mm} \rangle - 1) - \frac{1}{2}J\sum_{m,\sigma} \langle \hat{n}_{mm}^{\sigma} \rangle (\langle \hat{n}_{mm}^{\sigma} \rangle - 1)$$
$$= \frac{1}{2}UN_{c}(N_{c} - 1) - \frac{1}{2}J\sum_{\sigma} N_{c}^{\sigma}(N_{c}^{\sigma} - 1),$$

where U and J are the average interaction parameters from Eq. (1.5.6) and  $N_c$  the number of electrons in the correlated shell. This approach leads to the total energy functional

<sup>7</sup>This is of course not true exactly, because of the crystal field, that explicitly can split a shell.

$$E_{\rm DFT+U}^{\rm FLL}[n] = E_{\rm DFT}[n] + \frac{1}{2} \sum_{i\sigma} \sum_{mm'm''m'''} U_{mm''m'm''} \langle \hat{n}_{imm'}^{\sigma} \rangle \langle \hat{n}_{im''m'''}^{-\sigma} \rangle \\ + \frac{1}{2} \sum_{i\sigma} \sum_{mm'm''m'''} (U_{mm''m'm''} - U_{mm''m'''n''}) \langle \hat{n}_{imm'}^{\sigma} \rangle \langle \hat{n}_{im''m'''}^{-\sigma} \rangle \\ - \frac{1}{2} U \sum_{i,m} \langle \hat{n}_{imm} \rangle (\langle \hat{n}_{imm} \rangle - 1) + \frac{1}{2} J \sum_{i,m,\sigma} \langle \hat{n}_{imm}^{\sigma} \rangle (\langle \hat{n}_{imm}^{\sigma} - 1).$$

This approach produces a discontinuity in the total energy, since completely filled orbitals are reduced in energy by  $\frac{1}{2}(U-J)$ , while completely empty orbitals are increased in energy by the same amount. The maximal potential shift appearing for integer fillings leads to an increasing localization in FLL as compared to the AMF functional. Another approach combining the two functionals was proposed by Pethukov et al. [339] and interpolates both the AMF and FLL contributions such that the DFT total energy remains unchanged.

The DFT+U describes the magnetically ordered Mott insulating state and the associated spectral gap successfully. Only ordered states with a high degree of localization can be described by DFT+U. Apart from that true correlation effects are absent in DFT+U, because it relies on the formalism of Kohn-Sham DFT, which is a one particle theory regardless of the potential used. The DFT+U self-energy is a crude approximation, being static, i.e. not energy dependent, and having no imaginary part, i.e. producing quasiparticles with an infinite lifetime. It is thus capable of describing e.g. the magnetically ordered insulator NiO, but the metal insulator *transition* that occurs well above the critical temperature for magnetism will elude the method. Same is true for generic many-body effects like the Kondo effect or spectral weight transfer via Hubbard bands.

### **1.5.4 DFT+DMFT**

The key improvement in DFT+DMFT, over DFT+U, is that it uses the more sophisticated DMFT for the solution of the model Hamiltonian part. This allows for an energy dependent (dynamical) self-energy including real and imaginary parts and consequently for the description of finite lifetime excitations, Kondo physics etc. Formally, the methods are constructed analogously. Again, the DFT Hamiltonian is supplied with a multi band Hubbard-like model:

$$\hat{H}_{\rm DFT++} = \hat{H}_{\rm KS} - \hat{H}_{\rm DC} + \underbrace{\frac{1}{2} \sum_{i} \sum_{m,m',m''} \sum_{\sigma\sigma'} U_{mm'm''m'''} \hat{d}^{\dagger}_{im\sigma} \hat{d}^{\dagger}_{im'\sigma'} \hat{d}_{im''\sigma'} \hat{d}_{im''\sigma'}}_{H_{\rm loc}} \hat{H}_{\rm loc} + \underbrace{\frac{1}{2} \sum_{i} \sum_{m,m',m'',m'''} \sum_{\sigma\sigma'} U_{mm'm''m'''} \hat{d}^{\dagger}_{im\sigma} \hat{d}^{\dagger}_{im'\sigma'} \hat{d}_{im'''\sigma'} \hat{d}_{im''\sigma'} \hat{d}_{im''\sigma'}}_{H_{\rm loc}} \hat{H}_{\rm loc}} \hat{H}_{\rm loc} \hat{H}_{\rm loc}} \hat{H}_{\rm loc$$

To avoid a double counting in the energy again a term  $\hat{H}_{DC} = \mu_{DC} \sum_{m,\sigma} \hat{n}_{m,\sigma}$ , with the double counting potential  $\mu_{DC}$ , has to be subtracted.

The many-body part of the Hamiltonian will be treated in the same way as in the *model* DMFT formulation, with the difference that now the Kohn-Sham Hamiltonian defines the non-interacting part, cf. Eq. (1.5.2). The Hubbard-like model can be treated within the DMFT approximation as an Anderson type impurity coupled to a bath. The action, Eq. (1.4.11), will in this case be a multi orbital quantity as we have seen in section 1.4.3:

$$S_{\rm imp}(d^*,d) = -\int_0^\beta \mathrm{d}\tau \int_0^\beta \mathrm{d}\tau' \sum_{ij} d_i^*(\tau) \mathcal{G}_{ij}^{-1}(\tau-\tau') d_j(\tau') + \int_0^\beta \mathrm{d}\tau \ H_{\rm loc}(d^*,d).$$
(1.5.11)

The quantities of interest like the Green functions and the self-energy are now matrices in orbital space. As pointed out above the impurity solver computes the impurity Green function

$$G_{mm'}^{\rm imp}(\tau,\tau') = -\left\langle \hat{T}_{\tau} \hat{d}_m(\tau) \hat{d}_{m'}^{\dagger}(\tau') \right\rangle_{S_{\rm imp}}$$

from the action, Eq. (1.5.11). The self-energy is then obtained after Fourier transformation by

$$\Sigma_{mm'}^{\rm imp}(i\omega_n) = \mathcal{G}_{mm'}^{-1}(i\omega_n) - (G^{\rm imp})_{mm'}^{-1}(i\omega_n).$$

Now, a connection between the DFT and the impurity part has to be established. The key point of the DFT+DMFT formalism is the generalization of the self-consistency condition (k-integrated Dyson equation), Eq. (1.4.17), to contain the Kohn-Sham Hamiltonian and thus all material specific information from it [20, 255].

We follow the work by Lechermann et al. [244] and Amadon et al. [12] and describe the LDA+DMFT procedure using projectors.<sup>8</sup> As in DFT+U the first step is the identification of the correlated subspace of orbitals (say d or f orbitals). Thus, a set of localized single-particle orbitals  $\{|\chi_m^{\mathbf{R}}\rangle\}$  is chosen (**R** labels the correlated atom inside the unit cell and m is the orbital degree of freedom). These orbitals form the *correlated subspace C* of the Hilbert space. A projection onto this subspace is done with the projection operator

$$\hat{P}_{\mathbf{R}}^{\mathcal{C}} = \sum_{m \in \mathcal{C}} \left| \chi_m^{\mathbf{R}} \right\rangle \left\langle \chi_m^{\mathbf{R}} \right|$$

Another important set is the basis  $\{|B_{\alpha}^{\mathbf{k}}\rangle\}$  in which the full electronic structure problem is formulated. Here  $\alpha$  labels the basis functions for each  $\mathbf{k}$  in the Brillouin zone. To be clear about this point, the full basis set  $\{|B_{\alpha}^{\mathbf{k}}\rangle\}$  can be LMTOs, plane waves or any other basis set, whereas the set  $\{|\chi_m^{\mathbf{R}}\rangle\}$  are a set of localized orbitals, like Wannier functions

<sup>&</sup>lt;sup>8</sup>A similar presentation was given by Anisimov et al. [19].

or atomic orbitals. In this notation the self-consistency condition that relates the impurity Green function with the Green function of the solid for atom  $\mathbf{R}$  can be written in the following form

$$G_{mm'}^{\mathbf{R},\mathrm{imp}}(i\omega_n) = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} \sum_{\alpha\alpha'} \langle \chi_{\mathbf{k}m}^{\mathbf{R}} | B_{\alpha}^{\mathbf{k}} \rangle \left\{ \left[ i\omega_n + \mu - H_{\mathrm{KS}}(\mathbf{k}) - \Sigma^B(\mathbf{k}, i\omega_n) \right]^{-1} \right\}_{\alpha\alpha'} \langle B_{\alpha'}^{\mathbf{k}} | \chi_{\mathbf{k}m'}^{\mathbf{R}} \rangle \right\}$$
(1.5.12)

Here,

$$|\chi_{\mathbf{k}m}^{\mathbf{R}}\rangle = \sum_{\mathbf{T}} e^{i\mathbf{k}(\mathbf{T}+\mathbf{R})} |\chi_{\mathbf{T}m}^{\mathbf{R}}\rangle$$

is the Bloch transform of the local orbitals, **T** is the Bravais lattice vector and  $1/N_{\mathbf{k}}$  is the normalization factor for the k summation. The quantity in curly brackets is the full Green function of the solid  $G_{\alpha\alpha'}(\mathbf{k}, i\omega_n)$  in the basis  $\{|B_{\alpha}^{\mathbf{k}}\rangle\}$ :

$$G^{B}_{\alpha\alpha'}(\mathbf{k}, i\omega_n) = \left[ \left( i\omega_n + \mu \right) \delta_{\alpha\alpha'} - H_{\rm KS}(\mathbf{k}) - \Sigma^{B}_{\alpha\alpha'}(\mathbf{k}, i\omega_n) \right]^{-1}$$
(1.5.13)

or if the basis  $\{|B^{\mathbf{k}}_{\alpha}\rangle\}$  diagonalizes the Kohn-Sham Hamiltonian

$$G^{B}_{\alpha\alpha'}(\mathbf{k}, i\omega_n) = \left[ \left( i\omega_n + \mu - \varepsilon^{\mathrm{KS}}_{\alpha}(\mathbf{k}) \right) \delta_{\alpha\alpha'} - \Sigma^{B}_{\alpha\alpha'}(\mathbf{k}, i\omega_n) \right]^{-1}.$$
 (1.5.14)

Thus, the right hand side of equation (1.5.12) can be understood as the projection of the full Green function of the solid onto the correlated subspace.

The quantity  $\Sigma^B(\mathbf{k}, i\omega_n)$  in Eqs. (1.5.12) and (1.5.14) is the self-energy for the solid that already contains the double counting correction. It is obtained by *promoting (upfolding)* the impurity self-energy to the lattice:

$$\Sigma_{\alpha\alpha'}^{B}(\mathbf{k}, i\omega_{n}) = \sum_{\mathbf{R}} \sum_{mm'} \langle B_{\alpha}^{\mathbf{k}} | \chi_{\mathbf{k}m}^{\mathbf{R}} \rangle \left( \Sigma_{mm'}^{\mathbf{R}, imp}(i\omega_{n}) + \Sigma_{\mathrm{DC}} \right) \langle \chi_{\mathbf{k}m'}^{\mathbf{R}} | B_{\alpha'}^{\mathbf{k}} \rangle .$$
(1.5.15)

An approximation that is employed here is that the self-energy only has non-zero elements inside the correlated subspace C, thus only on-site components in the chosen orbital set appear. Also we have defined the double counting correction to the self-energy as  $\Sigma_{\rm DC} = -\mu_{\rm DC}$ .

Figure 1.5.9 shows that the DFT+DMFT calculation commences with the solution of the Kohn-Sham equations by the DFT. In a second step the projection onto the correlated subset  $\{|\chi_{\mathbf{R}m}\rangle\}$  is computed. The Kohn-Sham Green function is then computed and used as an initial guess for the mean-field  $\mathcal{G}$  of the DMFT cycle, which consists of the usual steps detailed before. In usual applications the DFT+DMFT loop will stop after DMFT self-consistency is obtained. It has, however, recently become possible to continue the cycle supplying the DFT code with an altered charge density that includes correlation effects. In such a unified approach changes in the charge density induced by correlations can be studied [244, 135, 136]. It allows furthermore for the accurate calculation of total



Figure 1.5.9: Illustration of the DFT+DMFT procedure. As a first step, the Kohn-Sham (KS) equations, determining the Kohn-Sham potential and thus the Hamiltonian, are solved. Secondly, the KS Green function and from it the starting value for the bath Green function  $\mathcal{G}$  is constructed and passed on to the DMFT loop, which consists of the usual steps described before. A potential self-consistency over the charge density  $n(\mathbf{r})$  is also indicated.

energies, that allow the determination of crystal structures and other coupled electronic and structural effects. We will briefly sketch here the most important elements of the charge self-consistent implementation of DFT+DMFT following Refs. [244, 135]. In chapter 2 we will return to this topic and show how this methodology works in the PAW basis.

Let us begin by defining a Kohn-Sham Green function as follows

$$G_{\alpha\alpha'}^{\rm KS}(\mathbf{k}, i\omega_n) = \left[ \left( i\omega_n + \mu^{\rm KS} - \varepsilon_\alpha^{\rm KS}(\mathbf{k}) \right) \delta_{\alpha\alpha'} \right]^{-1}, \qquad (1.5.16)$$

which contains the result of an ordinary Kohn-Sham DFT calculation. The chemical potential in this case has to be adjusted such that the particle number remains unchanged, when going to finite temperature. In our case the  $\mu^{\rm KS}$  is defined with respect to the DFT chemical potential, which we set to zero in the subsequent many-body treatment.

The trace over this Green function is just the charge density

$$n^{\rm KS}(\mathbf{r}) = \frac{1}{\beta} \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}, n, \alpha, \alpha'} \langle \mathbf{r} | B_{\alpha}^{\mathbf{k}} \rangle G_{\alpha \alpha'}^{\rm KS}(\mathbf{k}, i\omega_n) \langle B_{\alpha'}^{\mathbf{k}} | \mathbf{r} \rangle.$$
(1.5.17)

Utilizing the upfolded Green function obtained from a DFT+DMFT calculation one can

write the charge density from DFT+DMFT in the same way

$$n(\mathbf{r}) = \frac{1}{\beta} \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k},n,\alpha,\alpha'} \langle \mathbf{r} | B_{\alpha}^{\mathbf{k}} \rangle G_{\alpha\alpha'}^{B}(\mathbf{k}, i\omega_{n}) \langle B_{\alpha'}^{\mathbf{k}} | \mathbf{r} \rangle .$$
(1.5.18)

The difference between the two is

$$\Delta n(\mathbf{r}) = \frac{1}{\beta} \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k},n,\alpha,\alpha'} \langle \mathbf{r} | B_{\alpha}^{\mathbf{k}} \rangle \left\{ \underline{\underline{G}}^{\mathrm{KS}}(\mathbf{k}, i\omega_{n}) \left[ (\underline{\underline{G}}^{\mathrm{KS}}(\mathbf{k}, i\omega_{n}))^{-1} - (\underline{\underline{G}}^{B}(\mathbf{k}, i\omega_{n}))^{-1} \right] \right.$$
$$\underline{\underline{G}}^{B}(\mathbf{k}, i\omega_{n}) \left. \frac{\underline{\underline{G}}^{B}(\mathbf{k}, i\omega_{n})}{\beta_{\alpha\alpha'}} \left\langle B_{\alpha'}^{\mathbf{k}} | \mathbf{r} \right\rangle \right]$$
$$= \frac{1}{\beta} \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k},n,\alpha,\alpha'} \langle \mathbf{r} | B_{\alpha}^{\mathbf{k}} \rangle \Delta N_{\alpha\alpha'}(\mathbf{k}) \left\langle B_{\alpha'}^{\mathbf{k}} | \mathbf{r} \right\rangle.$$

The quantity  $\Delta N_{\alpha\alpha'}(\mathbf{k})$  can be rewritten using the upfolded self-energy, Eq. (1.5.15), as

$$\Delta N_{\alpha\alpha'}(\mathbf{k}) = \frac{1}{\beta} \sum_{n} \left\{ \underline{\underline{G}}^{\mathrm{KS}}(\mathbf{k}, i\omega_n) \left( \underline{\underline{\Sigma}}^B(\mathbf{k}, i\omega_n) - (\mu - \mu^{\mathrm{KS}}) \delta_{\alpha\alpha'} \right) \underline{\underline{G}}^B(\mathbf{k}, i\omega_n) \right\}_{\alpha\alpha'}$$

The total charge including effects beyond DFT can then be written as

$$n(\mathbf{r}) = \frac{1}{\beta} \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}, n, \alpha, \alpha'} \left\langle \mathbf{r} | B_{\alpha}^{\mathbf{k}} \right\rangle \left( f(\varepsilon_{\alpha}(\mathbf{k}) - \mu^{\mathrm{KS}}) \delta_{\alpha \alpha'} + \Delta N_{\alpha \alpha'}(\mathbf{k}) \right) \left\langle B_{\alpha'}^{\mathbf{k}} | \mathbf{r} \right\rangle,$$

with the Fermi function  $f(\varepsilon_{\alpha}(\mathbf{k}) - \mu^{\text{KS}})$  corrected by the Kohn-Sham chemical potential. This charge density can be input into a density functional code and a new Kohn-Sham potential is obtained from it along with an updated set of Kohn-Sham wave functions. After one iteration of the Kohn-Sham cycle one again makes a projection onto the correlated subspace to enter the DMFT loop again. This procedure is then repeated until convergence on the self-energy and the charge is obtained. Note that, as before, correlation effects are explicitly included only on a correlated subspace of bands.

An important advantage of the implementation of such a method is the possibility to compute the total energy of the system, including changes in the charge density brought about by correlation effects. This allows, e.g., for the accurate determination of structural parameters of crystals. Such an approach with two self-consistency loops, over the charge *and* the self-energy (or equivalently hybridization function) was pioneered by Savrasov et al. [374] for the determination of the electronic and crystal structure of  $\delta$ -Plutonium. Savrasov and Kotliar have subsequently elaborated on the subject and have found an elegant way of unifying DFT and other methods on the level of the Luttinger-Ward functional [373]. Following Refs. [11, 344] the total energy in a DFT+DMFT calculation is in analogy to DFT+U

$$E_{\rm DFT+DMFT} = E_{\rm DFT}[n] - \sum_{\mathbf{k},\alpha} \varepsilon_{\alpha}^{\rm KS}(\mathbf{k}) \Delta N_{\alpha\alpha}(\mathbf{k}) + \langle \hat{H}_{\rm U} \rangle - E_{\rm DC},$$

where  $\langle \hat{H}_{\rm U} \rangle$  is the energy contribution from the correlated DMFT part and  $E_{\rm DC}$  a double counting correction. The energy from the two particle Hamiltonian  $\hat{H}_{\rm U}$  can be evaluated using different approaches. If one has access to accurate data for Green functions and self-energies on the Matsubara axis with correct asymptotical behavior etc. as provided by Hubbard I or exact diagonalization impurity solvers one may use the Galitskii-Migdal energy formula [117]

$$\langle \hat{H}_{\mathrm{U}} \rangle = \frac{1}{2} \mathrm{Tr} \left[ \Sigma G \right] = \frac{1}{2\beta} \sum_{n} \Sigma(i\omega_{n}) G(i\omega_{n}),$$

where the Matsubara sum has to be evaluated carefully. With some modifications this formula can be used with noisy QMC data [344], but in general this is not possible, because of the intrinsic statistical noise in QMC. There is another approach based on the double occupancy (used in e.g. [152, 249])

$$\langle \hat{H}_{\rm U} \rangle = \frac{1}{2} \sum U_{mm'} \langle \hat{n}_m \hat{n}_{m'} \rangle,$$

where above equation is just the expectation value of the interaction Hamiltonian. The double counting for the latter formula can be identified with

$$E_{\rm DC} = \frac{1}{2} \sum U_{mm'} \langle \hat{n}_m \rangle \langle \hat{n}_{m'} \rangle,$$

but as Leonov et al. have shown in their investigation of the  $\alpha - \gamma$  transition in Iron [249], also the standard fully localized limit expression, known from DFT+U, can be used with qualitatively the same result.

## **1.5.5** DFT+ $\Sigma$ for equilibrium and coherent transport

Before we move on, we want to mention that not always self-consistent methods like DFT+U or DFT+DMFT are necessary to describe correlations in certain systems. Sometimes the system under study is a single atom or molecule embedded in a host or adsorbed on a surface and in itself constitutes a case of the Anderson impurity model (AIM). In such a case one does not need the self-consistent mapping onto an impurity model and can directly set up an AIM, solve it and supply the DFT calculation with a local self-energy. We will call such an approach DFT+ $\Sigma$  and will use it later in chapters 5 and 6. One might say, that in such a case the DFT+DMFT loop stops after the impurity problem has been solved

the first time, it may be thus called *single-shot DMFT*, although the name is somewhat misleading, since no DMFT self-consistency is involved.

The procedure begins with a standard DFT calculation. As usual a correlated subset of orbitals is selected to play the role of the impurity in the Anderson model, usually the d or f shell of the appropriate material. As a next step the hybridization function for the impurity is calculated from the DFT Green function

$$\Delta_{\rm imp}(\omega) = \omega + \mu - \varepsilon_{\rm imp}^0 - \left[G_{\rm imp}^0(\omega)\right]^{-1},$$

where  $\varepsilon_{imp}^0$  are the impurity levels and  $G_{imp}^0(\omega)$  is the Kohn-Sham Green function projected onto the correlated subspace. Now all ingredients for setting up a general Anderson model are at hand and can be used along with the Coulomb interaction to calculate the electronic self-energy  $\Sigma_{imp}$ . The resulting correlated impurity Green function is then

$$G_{\rm imp}(\omega) = \left(\omega + \mu - \varepsilon_{\rm imp}^0 - \Delta_{\rm imp}(\omega) - \Sigma_{\rm imp} + \Sigma_{\rm DC}\right)^{-1}$$

which can be used to compute the spectral function. A double counting correction  $\Sigma_{\rm DC}$  is assumed as before. This procedure is in contrast to self-consistent approaches, like DMFT only carried out once. For cases, like adatoms on surfaces, that intrinsically already resemble impurity problems, no self-consistency over a lattice Green function is necessary, because there *is* no lattice in the first place.

This methodology can also be used, with some modifications, on top of a DFT coherent transport calculation to include local correlation effects. In principle, DFT++ works in the same way as shown above for coherent transport methodologies based on DFT. The formulation of an ab initio coherent transport theory based on DFT has its very own intricacies, see, e.g., Refs. [175, 176, 177, 179], that do not concern us here. We will limit ourselves to the methodological details that are necessary to understand how the DFT++ works in this case.

For a DFT transport calculation one usually assumes a scattering geometry as shown in Fig. 1.5.10 (a). The system is divided into two leads and a central scattering region, the so-called device region, where the studied *device* resides. The red central atom symbolizes a correlated site. The calculation is carried out using a periodic supercell. It is important to note that the device supercell needs to be large enough and to contain a sufficient amount of lead. Then the lead geometry can be assumed to have relaxed at the border to, or very close to, the one of an infinite lead. The Hamiltonian of the device region  $H_D$  can then be safely obtained from a calculation using periodic supercells. Separately one calculates infinite versions of the attached leads with right and left hand unit cells, shown in Figs. 1.5.10 (b) and (c). From these calculations of the leads one obtains the local Hamiltonian  $H_{L,R}^0$  and the hopping matrices to adjacent unit cells  $V_{L,R}$ .

These are then used to attach semi-infinite leads to the device region from both sides, as shown in Fig. 1.5.10 d. Then using the so called lead self-energies  $\Sigma_{L,R}$  (not to be



Figure 1.5.10: Schematic illustration of the supercell approach for DFT based transport calculations: (a) Periodic supercell used for the calculation of the device region. (b), (c) Infinite wires calculated with left and right unit cells. (d) Device region with semiinfinite wires attached from both sides, via the hopping matrices computed in (b) and (c). From Ref. [176].

confused with the electronic self-energies!) one can compute the central quantity of the method: the device Green function

$$G_{\rm D}^0(\omega) = (\omega + \mu - H_{\rm D} - \Sigma_{\rm L} - \Sigma_{\rm R})^{-1}$$

Here the lead self-energies describe the coupling of the device region to the semi-infinite leads attached from both sides. These can be obtained from the Hamiltonians and hopping matrices of the leads by use of a Dyson equation

$$\Sigma_{\mathrm{L,R}} = V_{\mathrm{L,R}} \left( \omega + \mu - H_{\mathrm{L,R}}^{0} - \Sigma_{\mathrm{L,R}} \right)^{-1} V_{\mathrm{L,R}}^{\dagger}.$$

The device Green function contains of course the impurity Green function for the correlated site in the center. That can be used to set up an Anderson impurity model by using the hybridization function. As before the proper correlated impurity subspace of the problem has to be selected. Then from the Green function of the impurity we can compute the hybridization function

$$\Delta_{\rm imp}(\omega) = \omega + \mu - \varepsilon_{\rm imp}^0 - \left[G_{\rm imp}^0(\omega)\right]^{-1},$$

where  $\varepsilon_{imp}^0$  are the Kohn-Sham energy levels of the correlated orbitals and  $G_{imp}^0(\omega)$  is the Kohn-Sham Green function projected onto the correlated subspace. This quantity can then can be used by an impurity solver, resulting in a local electronic self-energy  $\Sigma_{imp}$ . Applying this self-energy to the device Green function and using the machinery of the partitioning approach one obtains a correlated version of the Green function including local correlation effects on the impurity

$$G_{\rm D}(\omega) = \left(\omega + \mu - H_{\rm D} - \Sigma_{\rm L} - \Sigma_{\rm R} - \Sigma_{\rm imp} + \Sigma_{\rm DC}\right)^{-1}$$

Here we have included, as usual, a double counting correction term  $\Sigma_{DC}$ . Now that the Green function has been obtained we can proceed to calculate the spectral function and in this case also the coherent transport properties of our system. In an exact approach the formula derived by Meir and Wingreen would yield the current [283]. Unfortunately this formula would require the knowledge of the true non-equilibrium lesser Green function  $G^{<}$ , which in turn requires more advanced methodologies, like the Keldysh technique, see e.g. [354]. It has been shown, however, that for low temperatures and small bias voltages the Meir-Wingreen formula in the steady state is well approximated by the Landauer formula for the current

$$I(V) = \frac{2e}{\hbar} \int_0^{eV} T(\omega) \,\mathrm{d}\omega,$$

where  $T(\omega)$  is the Landauer transmission function. The transmission function can be calculated from the device Green function using the expression by Caroli et al. [72]

$$T(\omega) = \operatorname{Tr}\left[\Gamma_{\mathrm{L}}(\omega)G_{\mathrm{D}}^{\dagger}(\omega)\Gamma_{\mathrm{R}}(\omega)G_{\mathrm{D}}(\omega)\right],\,$$

with  $\Gamma_{L,R} = i(\Sigma_{L,R} - \Sigma_{L,R}^{\dagger})$ . In this way one can use DFT++ for the calculation of coherent transport properties of nanosystems with strong electronic correlations. We will use this methodology in chapter 5 to study the coherent transport through single molecules in presence of electronic correlations.

# **1.6 Impurity Solvers**

The connection between the Hubbard model in infinite dimensions and the Anderson impurity model is a very fortunate one because the latter is a model studied already for decades making techniques available for its solution. The task of the impurity solver in the DMFT procedure is to repeatedly compute the Green function

$$G(\tau,\tau') = -\langle \hat{T}_{\tau} \hat{c}_{\sigma}(\tau) \hat{c}_{\sigma}^{\dagger}(\tau') \rangle_{S}$$

from the action S. There exist a multitude of methods to achieve this goal, stemming from the investigations of impurity models preceding the invention of DMFT. We will focus here on the solvers we used in the cited results of this thesis, these are quantum Monte Carlo, the non-crossing/one-crossing approximations and exact diagonalization.

## 1.6.1 Hirsch-Fye Quantum Monte Carlo Method

The work of Hirsch and Fye (HF) [158] is based on the determinant QMC method introduced by Blankenbecler, Scalapino and Sugar for the study of coupled boson-fermion systems [46]. The algorithm proves to be free of numerical instabilities and extensions to multi-orbital models are available. Recent developments in so-called continuous-time QMC methods [367, 448] probably will render the HF-QMC method obsolete in the future. These methods explicitly discard the discretization of the imaginary time and are capable of producing numerically exact results in a much wider parameter range than the conventional HF-QMC. Additionally, more general interaction terms can be included without greater problems. The HF-QMC works in discretized imaginary time and produces imaginary time Green functions  $G(\tau, \tau')$ . To extract real space quantities like the spectral function one is forced to analytically continue the data to the real axis by means of, e.g., the maximum entropy method [184] that we will briefly discuss in section 1.7. The algorithm is limited, however, to relatively high temperatures T since CPU time scales as  $1/T^3$ . We will give an outline of the algorithm following Refs. [151, 124] and the original work Refs. [46, 158].

We begin our discussion by revisiting the definition of the Green function in the coherent state path integral representation, cf. Eq. (1.4.5),

$$G(\alpha_1\tau_1, \alpha_2\tau_2) = -\frac{1}{\mathcal{Z}}\int \mathcal{D}(c^*_{\alpha}(\tau), c_{\alpha}(\tau)) c_{\alpha_1}(\tau_1)c^*_{\alpha_2}(\tau_2) e^{-S(c^*, c)},$$

with the action

$$S(c^*, c) = \int_0^\beta d\tau \left\{ \sum_{ij\sigma} c^*_{i\sigma}(\tau) \left[ (\partial_\tau - \mu) \delta_{ij} + t_{ij} \right] c_{j\sigma}(\tau) + \frac{1}{2} \sum_{ij\sigma\sigma'} U^{\sigma\sigma'}_{ij} c^*_{i\sigma}(\tau) c^*_{j\sigma'}(\tau) c_{j\sigma'}(\tau) c_{i\sigma}(\tau) \right\}.$$

We have reduced the general interaction  $U_{ijkl}$  to only density-density terms, since this is the original domain of the HF-QMC. The methodology works best in such a case, extensions will be discussed at the end of the section. If only quadratic terms in the operators or Grassmann numbers would be present, as is the case of, e.g., the noninteracting limit U = 0, the Green function can be evaluated using Wicks theorem, which is equivalent to the identity for Grassmann Gaussian integrals, Eq. (1.4.2). This is not possible in general, due to the presence of the quartic interaction term. One may, however, attempt to approximately bring the integral into Gaussian form. To this end the continuous imaginary time integral appearing in the action is discretized into L time slices with length  $\Delta \tau = \beta/L$ . The discretized action then is

$$S_{\text{disc}}(c^*,c) = -(\Delta\tau)^2 \sum_{\sigma mn} \sum_{l,l'=0}^{L-1} c^*_{\sigma ml} \mathcal{G}_{\sigma mn}^{-1} (l\Delta\tau, l'\Delta\tau) c_{\sigma nl'} + \frac{1}{2} \Delta\tau \sum_{\sigma\sigma',mm'} U_{mm'}^{\sigma\sigma'} \sum_{l,l'=0}^{L-1} c^*_{\sigma ml} c^*_{\sigma'm'l} c_{\sigma'm'l} c_{\sigma ml}.$$

Here we have written the Coulomb interaction as a supermatrix in spin indices with the components  $U_{mm'}^{\sigma=\sigma'} = U_{mm'} - J_{mm'}$  and  $U_{mm'}^{\sigma\neq\sigma'} = U_{mm'}$  as shown in Eq. (1.5.9). Secondly, the Trotter-Suzuki formula [422, 404]

$$e^{-\Delta\tau(\hat{H}_0+\hat{H}_1)} = e^{-\Delta\tau\hat{H}_0}e^{-\Delta\tau\hat{H}_1} + \mathcal{O}(\Delta\tau^2)$$

is introduced at every time slice. The error of order  $\Delta \tau^2$  stems from neglecting the commutator  $[\hat{H}_0, \hat{H}_1]$ , which becomes exact in the limit  $\Delta \tau \rightarrow 0$ . The exponential of the action can thus be decoupled

$$\exp\left(-S_{\text{disc}}(c^*,c)\right) = \prod_{l=0}^{L-1} \left\{ \exp\left((\Delta\tau)^2 \sum_{\sigma mn} \sum_{l,l'=0}^{L-1} c^*_{\sigma ml} \mathcal{G}_{\sigma mn}^{-1} (l\Delta\tau, l'\Delta\tau) c_{\sigma nl'}\right) \times \left(-\frac{1}{2} \Delta\tau \sum_{\sigma \sigma', mm'} U^{\sigma \sigma'}_{mm'} \sum_{l,l'=0}^{L-1} c^*_{\sigma ml} c^*_{\sigma'm'l} c_{\sigma'm'l} c_{\sigma ml}\right) \right\} + \mathcal{O}(\Delta\tau^2).$$

Now, shifting the chemical potential to its half-filling value (M labels the number of orbitals)

$$\mu = \mu_0 - \left( U \left( M - \frac{1}{2} \right) - J \left( \frac{M}{2} - \frac{1}{2} \right) \right),$$
(1.6.1)

which reduces to the familiar shift of  $\frac{U}{2}$  for the one orbital case<sup>9</sup>, the remaining quartic

<sup>9</sup>Equation (1.6.1) applies in the general case of the density-density part of the full rotationally

term can be rewritten using the following identity

$$\hat{n}_{\uparrow}\hat{n}_{\downarrow} = -\frac{1}{2}\left(\hat{n}_{\uparrow} - \hat{n}_{\downarrow}\right)^2 + \frac{1}{2}(\hat{n}_{\uparrow} + \hat{n}_{\downarrow}).$$
(1.6.2)

This is valid because  $n_{\sigma}^2 = n_{\sigma}$  for Fermions. The interaction terms can now be recast via a special discrete Hubbard-Stratonovich (HS) transformation due to Hirsch [157]. In general the HS transformation allows for the mapping of an interacting fermion problem onto a non-interacting system with a fluctuating auxiliary field. It is based on the identity

$$\exp\left(\frac{1}{2}\hat{A}^{2}\right) = \sqrt{2\pi}\int \mathrm{d}x \exp\left(-\frac{1}{2}x^{2} - x\hat{A}\right),$$

 $\hat{A}$  being a quantum mechanical operator. The transformation of Eq. (1.6.2) was needed to introduce the square of an operator into the interaction term and to allow for a HS decoupling. Hirsch was able to show that, since fermion occupation numbers can only take the values 0 or 1, an auxiliary field that takes only two discrete values suffices. The auxiliary variables thus have the properties of an Ising field. The interaction part in the action is rewritten using the Ising variable  $s_{lmm'}^{\sigma\sigma'}$ 

$$\exp\left(-\frac{1}{2}\Delta\tau U_{mm'}^{\sigma\sigma'}\left(c_{\sigma ml}^{*}c_{\sigma ml}-c_{\sigma'm'l}^{*}c_{\sigma'm'l}\right)^{2}\right)$$
$$=\frac{1}{2}\sum_{\substack{s_{lmm'}^{\sigma\sigma'}=\pm 1}}\exp\left(\Lambda_{lmm'}^{\sigma\sigma'}s_{lmm'}^{\sigma\sigma'}\left(c_{\sigma ml}^{*}c_{\sigma ml}-c_{\sigma'm'l}^{*}c_{\sigma'm'l}\right)\right)$$

with  $\cosh\left(\Lambda_{lmm'}^{\sigma\sigma'}\right) = \exp\left(\frac{1}{2}\Delta\tau U_{mm'}^{\sigma\sigma'}\right)$ . The electronic interaction has now been replaced by an interaction with an auxiliary Ising spin field  $s_{lmm'}^{\sigma\sigma'} = \pm 1$ . This allows to write the Green function, cf. Eq. (1.4.5), as a sum over the configurations of the Ising fields  $\{s\}$ 

$$G_{\sigma mm'l_1l_2} = -\frac{1}{\mathcal{Z}} \sum_{\{s\}} \int \mathcal{D}(c^*, c_{-}) c_{\sigma ml_1} c^*_{\sigma m'l_2} \exp\left(-\sum_{\sigma, l, l', m, m'} c^*_{\sigma ml} \mathcal{M}^{\{s\}}_{\sigma ll' mm'} c_{\sigma m'l'}\right),$$

with

$$\mathcal{M}^{s}_{\sigma l l' m m'} = -\left(\Delta\tau\right)^{2} \mathcal{G}^{-1}_{\sigma m n}(l\Delta\tau, l'\Delta\tau) + \delta_{l l'} \sum_{m'\sigma'} \Lambda^{\sigma\sigma'}_{lmm'} \sigma^{\sigma\sigma'}_{mm'} s^{\sigma\sigma'}_{lmm'}$$

Here  $\sigma_{mm'}^{\sigma\sigma'} = 2\Theta \left(\sigma - \sigma' + \delta_{\sigma\sigma'}[m - m'] - 1\right)$  is the multi orbital generalization of the

invariant Coulomb interaction as shown in Eqs. (1.5.7,1.5.8). For a Kanamori type interaction or a simplified 2 or 3 band case the particle hole symmetry is obtained for a shift of  $U\left(M-\frac{1}{2}\right) - 5J\left(\frac{M}{2}-\frac{1}{2}\right)$ .

anti periodic delta function and changes sign if  $(m\sigma)$  and  $(m'\sigma')$  are exchanged. Since the action is now quadratic the solution for the partition function and Green function can be obtained via Eq. (1.4.2) or Wicks theorem to yield

$$\mathcal{Z} = \sum_{\{s\}} \det \underline{\mathcal{M}}_{\uparrow}^{\{s\}} \det \underline{\mathcal{M}}_{\downarrow}^{\{s\}}$$

and

$$G_{\sigma mm'l_1l_2} = \frac{1}{\mathcal{Z}} \sum_{\{s\}} \left(\underline{\mathcal{M}}_{\sigma}^{\{s\}}\right)_{l_1,l_2}^{-1} \det \underline{\mathcal{M}}_{\uparrow}^{\{s\}} \det \underline{\mathcal{M}}_{\downarrow}^{\{s\}}$$

In above equation we have introduced for brevity the matrix  $\underline{\mathcal{M}}^{\{s\}}$  that contains elements  $\mathcal{M}^s_{\sigma ll'mm'}$ . For the calculation of the partition function and Green function the phase space of the configurations of the Ising fields has to be explored. This can, of course, be attempted by summing all configurations in a brute-force way. This is unfeasible in general, because the number of configurations grows exponentially. A more efficient approach is the scanning of the phase space by a Markov process: Configurations  $(s_1, \ldots, s_L)$  are generated via single spin flips, which means that one Ising spin is flipped while all other are kept fixed. This is also referred to as a local move or local update. Other types of updates may be used to improve convergence, such as cluster or global updates, where a cluster containing more than one Ising spin or the whole configuration (all spins) is updated respectively. The implementation of the algorithm has its subtleties, especially in the context of DMFT, where Fourier transformations between imaginary time and Matsubara frequency space are required. Comprehensive presentations, including the discussion of Fourier transformations can be found in Refs. [53, 124]. The algorithm is still in use despite certain limitations. The most evident is the error of order  $\mathcal{O}(\Delta \tau^2)$  due to the time discretization, that also enters the Green function [225]. Since the time discretization is performed normally on a regular grid steep parts of the Green functions are resolved worse than relatively flat parts. This becomes a problem at low temperatures and strong interactions or far away from half filling. A recently proposed multigrid version of the Hirsch-Fye algorithm can in principle overcome this limitation. Simulations with different discretizations are performed in a single run and an extrapolation  $\Delta \tau \rightarrow 0$  is performed, which yields results to any desired accuracy [51, 52, 53]. Additionally, in practice, when the HF-QMC method is used, one is limited to density-density interactions. This is rooted in the specific discrete Hubbard-Stratonovich transformation introduced earlier, which is only applicable to density-density terms. A Hubbard-Stratonovich decoupling of the spin-flip and pair-hopping terms is possible in principle, but a severe sign problem is encountered [154]. Some progress in this direction can be made if different decoupling schemes are used [370]. Recently, Belozerov et al. [37] presented an implementation of the Hirsch-Fye algorithm with restored SU(2) symmetry of the interaction

term.

## **1.6.2** Continuous-Time Quantum Monte Carlo

The realization that the imaginary time discretization used in QMC methods for the simulation of discrete systems can be overcome by applying a different calculation paradigm appears first in the pioneering works of Prokof'ev et al. [347, 346] and Beard and Wiese [31]. This new paradigm is the diagrammatic quantum Monte Carlo method, that allows the stochastic sampling of a diagrammatic expansion (of, e.g., the partition function), instead of obtaining it by sampling a complete configuration space. The systematic and numerical errors stemming from the Trotter-Suzuki decomposition and of the explicit discretization of imaginary time can be completely eliminated, leaving as the only source of error the stochastic errors of the Monte Carlo method (that can be made arbitrarily small, if enough computational time is available)<sup>10</sup>. The original continuous-time QMC methods were developed for bosons, that do not suffer from a sign problem. The method was nevertheless quickly adapted to fermionic systems [361]. Unfortunately the fermionic sign problem in the lattice models studied by Rombouts and co-workers [361] proved to be very severe in the relevant ranges of parameters. It took a few more years before it was realized that impurity models, like the Anderson impurity model introduced in section 1.4.3, have a much smaller sign problem and in certain cases even no sign problem at all. Based on this realization the first diagrammatic impurity solver for fermions was proposed by Rubtsov and Lichtenstein [368, 367]. It is often called weak coupling expansion, because it expands the partition function in powers of the interaction, see below. A complementary solver based on an expansion in powers of the hybridization was soon after proposed by Werner et al. [448, 449]. The historical genesis and all other recent developments in the field of CT-QMC methods can be followed in the recent review on the subject [137]. We will here briefly present the basic ideas behind the CT-QMC focussing on the hybridization expansion following Refs. [137, 447].

The procedure begins by separating the Hamiltonian of the Anderson impurity model, Eq. (1.4.10), into two parts  $\hat{H} = \hat{H}_a + \hat{H}_b$  and introducing the interaction picture operators with respect to  $\hat{H}_a$  as  $\hat{O}(\tau) = e^{\tau \hat{H}_a} \hat{O} e^{-\tau \hat{H}_a}$ . The partition function can be expressed trivially as  $\mathcal{Z} = \text{Tr}[e^{-\beta \hat{H}_a} e^{\beta \hat{H}_a} e^{-\beta \hat{H}}]$ . Now using the identity

$$\frac{\mathrm{d}(e^{\beta\hat{H}_a}e^{-\beta\hat{H}})}{\mathrm{d}\beta} = e^{\beta\hat{H}_a}(\hat{H}_a - \hat{H})e^{-\beta\hat{H}} = -\hat{H}_b(\beta)e^{\beta\hat{H}_a}e^{-\beta\hat{H}_a}$$

one can write  $e^{\beta \hat{H}_a} e^{-\beta \hat{H}} = \hat{T}_{\tau} \exp\left[-\int_0^\beta \mathrm{d}\tau \hat{H}_b(\tau)\right]$ , where  $\hat{T}_{\tau}$  denotes the imaginary time

<sup>10</sup>This is the often cited *numerical exactness* of CT-QMC, although it becomes *numerically exact* (i.e. no statistical error at all) only in the limit of infinite computational time.

ordering operator. Secondly, one can expand the exponential in the partition function into a power series

$$\mathcal{Z} = \operatorname{Tr} \hat{T}_{\tau} e^{-\beta \hat{H}_{a}} \exp\left[-\int_{0}^{\beta} \mathrm{d}\tau \ \hat{H}_{b}(\tau)\right]$$
$$= \sum_{n} (-1)^{n} \int_{0}^{\beta} \mathrm{d}\tau_{1} \cdots \int_{\tau_{n-1}}^{\beta} \mathrm{d}\tau_{n} \operatorname{Tr}\left[e^{-\beta \hat{H}_{a}} \hat{H}_{b}(\tau_{k}) \hat{H}_{b}(\tau_{n-1}) \cdots \hat{H}_{b}(\tau_{1})\right].$$

The two complementary CT-QMC approaches differ by the choice of what  $\hat{H}_a$  and  $\hat{H}_b$  are. In the weak coupling approach  $\hat{H}_a$  consists of the quadratic parts of the Hamiltonian and the partition function is expanded in powers of the quartic interaction part, i.e.

$$\hat{H}_b = \frac{1}{2} \sum_{ijkl} U_{ijkl} \hat{d}_i^{\dagger} \hat{d}_j^{\dagger} \hat{d}_l \hat{d}_k.$$

The converse approach, the hybridization expansion, uses the local part of the Hamiltonian as  $\hat{H}_a$ , while the expansion is performed in powers of the impurity-bath hybridization

$$\hat{H}_b = \sum_{\mathbf{k}\nu i} \left( V_{\mathbf{k}\nu i} \hat{c}^{\dagger}_{\mathbf{k}\nu} \hat{d}_i + V^*_{\mathbf{k}\nu i} \hat{d}^{\dagger}_i \hat{c}_{\mathbf{k}\nu} \right) = \hat{H}_{\text{hyb}} + \hat{H}^{\dagger}_{\text{hyb}}.$$
(1.6.3)

We will focus here on the hybridization expansion, that is most often called CT-HYB. The expansion of the partition function is in this approach

$$\begin{aligned} \mathcal{Z} &= \sum_{n=0}^{\infty} \int_{0}^{\beta} \mathrm{d}\tau_{1} \dots \int_{\tau_{n-1}}^{\beta} \mathrm{d}\tau_{n} \int_{0}^{\beta} \mathrm{d}\tau'_{1} \dots \int_{\tau_{n'-1}}^{\beta} \mathrm{d}\tau'_{n} \times \\ &\times \mathrm{Tr} \left[ \hat{T}_{\tau} e^{-\beta \hat{H}_{a}} \hat{H}_{\mathrm{hyb}}(\tau_{n}) \hat{H}_{\mathrm{hyb}}^{\dagger}(\tau'_{n}) \cdots \hat{H}_{\mathrm{hyb}}(\tau_{1}) \hat{H}_{\mathrm{hyb}}^{\dagger}(\tau'_{1}) \right] \end{aligned}$$

or explicitly

$$\begin{aligned} \mathcal{Z} &= \sum_{n=0}^{\infty} \int_{0}^{\beta} \mathrm{d}\tau_{1} \cdots \int_{\tau_{n-1}}^{\beta} \mathrm{d}\tau_{n} \int_{0}^{\beta} \mathrm{d}\tau_{1}' \cdots \int_{\tau_{n-1}'}^{\beta} \mathrm{d}\tau_{n}' \sum_{i_{1}, \cdots, i_{n}} \sum_{i_{1}', \cdots, i_{n}'} \sum_{\substack{\mathbf{k}_{1}, \cdots, \mathbf{k}_{n} \\ \nu_{1}, \cdots, \nu_{n}}} \sum_{\substack{\mathbf{k}_{1}', \cdots, \mathbf{k}_{n}' \\ \nu_{1}', \cdots, \nu_{n}'}} V_{\mathbf{k}_{1}\nu_{1}i_{1}} V_{\mathbf{k}_{1}'\nu_{1}'i_{1}'}^{*} \cdots \\ \cdots V_{\mathbf{k}_{n}\nu_{n}i_{n}} V_{\mathbf{k}_{n}'\nu_{n}'i_{n}'}^{*} \mathrm{Tr} \Big[ \hat{T}_{\tau} e^{-\beta \hat{H}_{a}} \hat{d}_{i_{n}}(\tau_{n}) \hat{c}_{\mathbf{k}_{n}\nu_{n}}^{\dagger}(\tau_{n}) \hat{c}_{\mathbf{k}_{n}'\nu_{n}'}(\tau_{n}') \hat{d}_{i_{n}'}^{\dagger}(\tau_{n}') \hat{d}_{i_{n}''}^{\dagger}(\tau_{n}') \hat{d}_{i_{n}''}^{\dagger}(\tau_{n}') \hat{d}_{i_{n}''}^{\dagger}$$

The bath and impurity degrees of freedom can be separated, each with their own time

evolution given by  $\hat{H}_{loc}$ , the second line from from Eq. (1.4.10), for the impurity and by  $\hat{H}_{bath} = \hat{H}_{AIM} - \hat{H}_{loc} - \hat{H}_b$ , with  $\hat{H}_b$  from Eq. (1.6.3). The partition function then becomes

$$\begin{aligned} \mathcal{Z} = & \sum_{n=0}^{\infty} \int_{0}^{\beta} \mathrm{d}\tau_{1} \cdots \int_{\tau_{n-1}}^{\beta} \mathrm{d}\tau_{n} \int_{0}^{\beta} \mathrm{d}\tau_{1}' \cdots \int_{\tau_{n-1}'}^{\beta} \mathrm{d}\tau_{n}' \sum_{i_{1}, \cdots, i_{n}} \sum_{i_{1}', \cdots, i_{n}'} \sum_{\substack{\mathbf{k}_{1}, \cdots, \mathbf{k}_{n} \\ \nu_{1}, \cdots, \nu_{n}'}} \sum_{\mathbf{k}_{1}', \cdots, \mathbf{k}_{n}'} V_{\mathbf{k}_{1}\nu_{1}i_{1}} V_{\mathbf{k}_{1}'\nu_{1}'i_{1}'}^{*} \cdots V_{\mathbf{k}_{n}\nu_{n}i_{n}} V_{\mathbf{k}_{n}'\nu_{n}'i_{n}'}^{*} \mathrm{Tr} \Big[ \hat{T}_{\tau} e^{-\beta \hat{H}_{\mathrm{loc}}} \hat{d}_{i_{n}}(\tau_{n}) \hat{d}_{i_{n}'}^{\dagger}(\tau_{n}') \cdots \hat{d}_{i_{1}}(\tau_{1}) \hat{d}_{i_{1}'}^{\dagger}(\tau_{1}') \Big] \times \\ & \times \mathrm{Tr} \Big[ \hat{T}_{\tau} e^{-\beta \hat{H}_{\mathrm{bath}}} \hat{c}_{\mathbf{k}_{n}\nu_{n}}^{\dagger}(\tau_{n}) \hat{c}_{\mathbf{k}_{n}'\nu_{n}'}(\tau_{n}') \cdots \hat{c}_{\mathbf{k}_{1}'\nu_{1}}(\tau_{1}) \hat{c}_{\mathbf{k}_{1}'\nu_{1}'}(\tau_{1}') \Big]. \end{aligned}$$

Since the bath and impurity degrees of freedom are no longer mixed it is possible to integrate out the bath. First one observes that the bath is noninteracting and thus its partition function is just  $Z_{\text{bath}} = \text{Tr}e^{-\beta\hat{H}_{\text{bath}}} = \prod_{\mathbf{k}\nu} (1 + e^{-\beta\varepsilon_{\mathbf{k}\nu}})$ . The bath part of the full partition function can also be obtained via Wicks theorem or equivalently the identity from Eq. (1.4.2) as the determinant of a matrix  $\underline{F}$ 

$$\det \underline{\mathcal{F}} = \frac{1}{\mathcal{Z}_{\text{bath}}} \operatorname{Tr} \Big[ \hat{T}_{\tau} e^{-\beta \hat{H}_{\text{bath}}} \sum_{\substack{\mathbf{k}_{1}, \cdots, \mathbf{k}_{n} \\ \nu_{1}, \cdots, \nu_{n}}} \sum_{\substack{\mathbf{k}_{1}', \cdots, \mathbf{k}_{n}' \\ \nu_{1}', \cdots, \nu_{n}'}} V_{\mathbf{k}_{1}' \nu_{1}' i_{1}} V_{\mathbf{k}_{1}' \nu_{1}' i_{1}'}^{*} \cdots V_{\mathbf{k}_{n} \nu_{n} i_{n}} V_{\mathbf{k}_{n}' \nu_{n}' i_{n}'}^{*} \times \hat{c}_{\mathbf{k}_{n}' \nu_{n}}^{\dagger} (\tau_{n}) \hat{c}_{\mathbf{k}_{n}' \nu_{n}'}^{\dagger} (\tau_{n}') \cdots \hat{c}_{\mathbf{k}_{1}' \nu_{1}}^{\dagger} (\tau_{1}) \hat{c}_{\mathbf{k}_{1}' \nu_{1}'}^{\dagger} (\tau_{1}') \Big].$$

By inspecting the first order contribution (n = 1) one finds for the element  $\mathcal{F}^1$ 

$$\begin{aligned} \mathcal{F}^{1} &= \sum_{\mathbf{k}_{1},\mathbf{k}_{1}',\nu_{1},\nu_{1}'} \frac{1}{\mathcal{Z}_{\text{bath}}} V_{\mathbf{k}_{1}\nu_{1}i_{1}} V_{\mathbf{k}_{1}'\nu_{1}'i_{1}'}^{*} \text{Tr} \Big[ \hat{T}_{\tau} e^{-\beta \hat{H}_{\text{bath}}} \hat{c}_{\mathbf{k}_{1}\nu_{1}}^{\dagger}(\tau_{1}) \hat{c}_{\mathbf{k}_{1}'\nu_{1}'}(\tau_{1}') \Big] \\ &= \sum_{\mathbf{k}_{1},\nu_{1}} \frac{V_{\mathbf{k}_{1}\nu_{1}i_{1}} V_{\mathbf{k}_{1}'\nu_{1}'i_{1}}^{*}}{1 + e^{-\beta\varepsilon_{\mathbf{k}_{1}\nu_{1}}}} \begin{cases} -e^{-\varepsilon_{\mathbf{k}_{1}\nu_{1}}(\beta-(\tau_{1}-\tau_{1}'))}, & \tau_{1} > \tau_{1}' \\ e^{-\varepsilon_{\mathbf{k}_{1}\nu_{1}}(\tau_{1}'-\tau_{1})}, & \tau_{1} < \tau_{1}' \end{cases} . \end{aligned}$$

In general the elements of  $\underline{\mathcal{F}}$  are the  $\beta$ -antiperiodic hybridizations

$$\mathcal{F}_{lm}(\tau) = \sum_{\mathbf{k}\,\nu} \frac{V_{\mathbf{k}\,\nu\,l} V_{\mathbf{k}'\nu'm}^*}{1 + e^{-\beta\varepsilon_{\mathbf{k}\nu}}} \begin{cases} -e^{-\varepsilon_{\mathbf{k}\nu}(\beta-\tau)}, & \tau > 0\\ e^{-\varepsilon_{\mathbf{k}\nu}(-\tau)}, & \tau < 0 \end{cases}$$

that are connected to the hybridization on Matubara axis via a Fourier transform

$$\Delta(-i\omega_n) = \int \mathrm{d}\tau \; e^{-i\omega_n\tau} \mathcal{F}(\tau).$$

These are the hybridization functions for the *holes* generated in the bath, when an electron hops out of it onto the impurity. We want to note that orbital off-diagonal elements in the hybridization can lead to a sign problem, this can be remedied by a rotation of the basis into the crystal field or another basis [111]. With these ingredients the expansion for the partition function can be finally written as

$$\mathcal{Z} = \mathcal{Z}_{\text{bath}} \sum_{n=0}^{\infty} \int_{0}^{\beta} \mathrm{d}\tau_{1} \cdots \int_{\tau_{n-1}}^{\beta} \mathrm{d}\tau_{n} \int_{0}^{\beta} \mathrm{d}\tau_{1}' \cdots \int_{\tau_{n-1}'}^{\beta} \mathrm{d}\tau_{n}' \sum_{i_{1}, \cdots, i_{n}} \sum_{i_{1}', \cdots, i_{n}'} \mathrm{Tr} \Big[ \hat{T}_{\tau} e^{-\beta \hat{H}_{\text{loc}}} \hat{d}_{i_{n}}(\tau_{n}) \hat{d}_{i_{n}'}^{\dagger}(\tau_{n}') \cdots \\ \cdots \hat{d}_{i_{1}}(\tau_{1}) \hat{d}_{i_{1}'}^{\dagger}(\tau_{1}') \Big] \mathrm{det} \, \underline{\mathcal{F}}.$$

The Green function in the hybridization expansion is

$$G_{lm}(\tau_l, \tau_m) = -\mathcal{Z}_{\text{bath}} \sum_{n=0}^{\infty} \int_0^\beta \mathrm{d}\tau_1 \cdots \int_{\tau_{n-1}}^\beta \mathrm{d}\tau_n \int_0^\beta \mathrm{d}\tau_1' \cdots \int_{\tau_{n-1}'}^\beta \mathrm{d}\tau_n' \sum_{i_1, \cdots, i_n} \sum_{i_1', \cdots, i_n'} \times \operatorname{Tr} \Big[ \hat{T}_\tau e^{-\beta \hat{H}_{\text{loc}}} \hat{\mathbf{d}}_l(\tau_l) \hat{\mathbf{d}}_m^\dagger(\tau_m) \hat{d}_{i_n}(\tau_n) \hat{d}_{i_n'}^\dagger(\tau_n') \cdots \hat{d}_{i_1}(\tau_1) \hat{d}_{i_1'}^\dagger(\tau_1') \Big] \det \underline{\mathcal{F}},$$

which shows that the configurations entering the Green function are partition function configurations with two additional operators present in the trace that we have highlighted in boldface in above equation. The weights

$$w_{n} = \operatorname{Tr} \left[ \hat{T}_{\tau} e^{-\beta \hat{H}_{\text{loc}}} \hat{d}_{i_{n}}(\tau_{n}) \hat{d}_{i_{n}'}^{\dagger}(\tau_{n}') \cdots \hat{d}_{i_{1}}(\tau_{1}) \hat{d}_{i_{1}'}^{\dagger}(\tau_{1}') \right]$$

are now sampled using a Monte Carlo procedure. Different ways to evaluate the operator traces involved in the calculation have been proposed, see discussion in Ref. [137]. One particularly efficient formulation is the so-called segment picture, applicable for density-density type interactions. In this picture the imaginary time evolution is depicted as a series of *segments*, where each segment represents a time interval in which an electron of a certain flavor (spin, orbital) resides on the impurity. An example of a segment configuration for a one band model is shown in Fig. 1.6.11. Such a formulation is possible, since the local Hamiltonian  $\hat{H}_{loc}$  commutes with the occupation number operator for each flavor. At each time the weight for an N orbital model can be computed as



**Figure 1.6.11:** Pictorial depiction of a term in the segment version of CT-HYB for the single band Anderson model. The upper (lower) line corresponds to the spin up (down) band. Bold lines indicate an occupied band, light lines an empty one. The total lenght of the bold lines determines the contribution to the chemical potential in the first term of the weight in Eq. (1.6.4). The orange shaded areas indicate an overlap of both segments, which corresponds to double occupancy and enters as the second term in Eq. (1.6.4). From Ref. [137].

$$w_n = s \, \exp\left(\mu \sum_{j=1}^{N} l_j - \sum_{i (1.6.4)$$

where  $l_j$  is the total lenght of the segments for flavor j,  $O_{ij}$  is the total overlap between segments of flavors i and j,  $U_{ij}$  is the Coulomb interaction,  $\mu$  is the chemical potential and s is a permutation sign factor.

## 1.6.3 Non-Crossing / One-Crossing Approximation

The non-crossing approximation (NCA) [198, 134, 237] impurity solver and all its subsequent improvements, like the one-crossing approximation (OCA) [349, 144, 146, 225] and others are based on a self-consistent perturbation expansion of the impurity problem around the atomic limit in the hybridization function, see Ref. [41] for a review. We base our brief account of the method on the description given in Refs. [144, 146]. The method is an impurity solver, thus we begin with the general Anderson impurity model from Eq. (1.4.10). The procedure begins by an exact diagonalization of the correlated subspace of the impurity

$$\hat{H}_{\rm imp} = \sum_{i} \varepsilon_i \hat{d}_i^{\dagger} \hat{d}_i + \frac{1}{2} \sum_{ijkl} U_{ijkl} \hat{d}_i^{\dagger} \hat{d}_j^{\dagger} \hat{d}_l \hat{d}_k$$

This yields the full many-body spectrum  $E_m$  and eigenstates  $|m\rangle$  of the atom. Now each atomic state is represented with a so-called pseudo particle, introduced in this context by Coleman [77], such that

$$|m\rangle =: \hat{a}_m^{\dagger} |0\rangle_{\rm PP},$$

where  $|0\rangle_{\rm PP}$  denotes the pseudo particle vacuum. The completeness of the atomic eigenstates  $\sum_{m} |m\rangle \langle m| = 1$  imposes a constraint on the pseudo particles

$$\sum_m \hat{a}_m^\dagger \hat{a}_m =: Q = 1.$$

The physical electron creation and annihilation operators can then be expressed utilizing the pseudo particle operators and the matrix elements of the electronic operators

$$\begin{aligned} \hat{d}_i^{\dagger} &= \sum_{nm} \langle n | \hat{d}_i^{\dagger} | m \rangle \, \hat{a}_n^{\dagger} \hat{a}_m =: \sum_{nm} (F^{i\dagger})_{nm} \hat{a}_n^{\dagger} \hat{a}_m \\ \hat{d}_i &= \sum_{nm} \langle n | \hat{d}_i | m \rangle \, \hat{a}_n \hat{a}_m^{\dagger} =: \sum_{nm} (F^i)_{nm} \hat{a}_n \hat{a}_m^{\dagger}. \end{aligned}$$

This allows for the Hamiltonian of the Anderson model to be rewritten using the pseudo particle representation as follows

$$\hat{H}_{\text{AIM}}^{\text{PP}} = \sum_{m} E_{m} \hat{a}_{m}^{\dagger} \hat{a}_{m} + \sum_{\mathbf{k}\nu} \varepsilon_{\mathbf{k}\nu} \hat{c}_{\mathbf{k}\nu}^{\dagger} \hat{c}_{\mathbf{k}\nu} + \lambda(Q-1) + \sum_{mn\mathbf{k}\nu i} \left( V_{\mathbf{k}\nu i} \hat{c}_{\mathbf{k}\nu}^{\dagger} \hat{a}_{m}^{\dagger} \hat{a}_{n}(F^{i})_{nm} + V_{\mathbf{k}\nu i}^{*} \hat{c}_{\mathbf{k}\nu} \hat{a}_{m} \hat{a}_{n}^{\dagger}(F^{\dagger i})_{nm} \right),$$

where the constraint on the pseudo particles enters as a Lagrange multiplier. By comparison with the original Anderson Hamiltonian one realizes that the hybridization term now takes the role of the interaction in the pseudo particle picture. Indeed, inspecting the imaginary time action it becomes apparent

$$S_{\text{AIM}}^{\text{PP}} = \sum_{m} \int d\tau \ a_{m}^{*} \left(\partial_{\tau} + E_{m} + \lambda\right) a_{m} \\ + \sum_{nn'mm'} (F^{i\dagger})_{mn} (F^{j})_{n'm'} \int d\tau \ d\tau' \ a_{m}^{*}(\tau) a_{n}(\tau) \Delta_{ij}(\tau - \tau') a_{n'}^{*}(\tau') a_{m'}(\tau'),$$

since the quartic term now involves the Hybridization function  $\Delta_{ij}$ . The anticommutation rules for the underlying electronic ladder operators require that the pseudo particles have either bosonic or fermionic character depending on the particle number contained in them. The bosonic and fermionic (anti-)commutation rules allow for a diagrammatic perturbation expansion of the hybridization term.

The NCA and OCA equations constitute the diagrammatic expansion for the pseudo particle self-energy shown in Fig. 1.6.12. In NCA the only allowed processes connect the Hilbert spaces for N and N + 1 electrons, this means that the diagrams describe processes where a single particle (electron or hole) hops from the bath to the impurity. Since N and



**Figure 1.6.12:** Top: NCA diagrams representing the Eq. (1.6.6) and Eq. (1.6.5) respectively. Bottom: Additionally to the NCA diagrams the OCA contains 6 additional diagrams of the type shown.

N + 1 are either even or odd there will be a contribution from fermionic and bosonic pseudo particles respectively; i.e. the first and second term in the NCA self-energy in Fig. 1.6.12. Analytically, the diagrams correspond to the expressions

$$\Sigma_{b_2b_1}(\omega) = \sum_{f_1f_2ij} -(F^j)_{b_2f_1}(F^{i\dagger})_{f_2b_1} \int \frac{\mathrm{d}y}{\pi} f(y) \mathrm{Im}\Delta_{ij}(y) G_{f_1f_2}(\omega+y) \quad (1.6.5)$$

$$\Sigma_{f_2 f_1}(\omega) = \sum_{b_1 b_2 ij} -(F^j)_{b_2 f_1} (F^{i\dagger})_{f_2 b_1} \int \frac{\mathrm{d}y}{\pi} f(-y) \mathrm{Im} \Delta_{ij}(y) G_{b_1 b_2}(\omega - y).$$
(1.6.6)

The connection to the diagrams in Fig. 1.6.12 is clear: one F is added for each vertex, one G for each propagator and one interaction line for  $\Delta$ . The indices b and f run over the states with N - 1 and N particles respectively. The pseudo particle Green functions are connected to the self-energies via a Dyson equation and thus

$$G_m(\omega) = \frac{1}{\omega - \lambda - E_m - \Sigma_m(\omega)},$$

where  $\lambda$  acts as a chemical potential and the pseudo particle self-energy describes the interaction between the pseudo particles. The physical spectral function of the impurity is in the NCA given by

$$A_{ji}^{\rm imp}(\epsilon) = \frac{1}{e^{\beta\lambda} \langle Q \rangle f(-\epsilon)} \sum_{b_1 b_2 f_1 f_2} \int dy \ e^{-\beta y} (F^j)_{b_2 f_1} (F^{i\dagger})_{f_2 b_1} {\rm Im} G_{b_1 b_2}(y) {\rm Im} G_{f_1 f_2}(y+\epsilon).$$

The NCA impurity solver is very fast and works directly on the real axis (an implemen-

tation in the Matsubara axis is problematic, due to divergencies, see discussion in Ref. [146]), which gives direct access to spectra as well as self-energies. It is not without problems though, see Refs. [238, 231, 79, 146]:

- the Kondo temperature is correct in NCA only when one type of charge fluctuation of the type N → N ± 1 is dominant. At half filling, this would be N → N − 1, which corresponds to the limit U = ∞. When more fluctuations, like N → N + 1 and N → N − 1 have to be considered the Kondo temperature is underestimated
- the asymmetry of the Abrikosov-Suhl (Kondo) resonance and its height are overestimated
- at temperatures below the Kondo temperature  $T \ll T_{\rm K}$  an additional spurious peak at zero energy can appear due to missing vertex corrections.

The problems can be cured or at least remedied, by including the next order of diagrams, which is then called one-crossing approximation (OCA). The diagrams contain one crossing interaction line, hence the name. The corresponding equations for OCA connect the N-1, N and N+1 Hilbert spaces at the same time. The second line in Fig. 1.6.12 shows a prototype OCA diagram for the self-energy. The explicit equations are quite lengthy and are given, e.g., in Ref. [146].

The spectral function is in OCA

$$\begin{split} A_{lk}^{imp}(\epsilon) &= -\sum_{\substack{ijf_{1}f_{2}f_{3}f_{4}\\b_{1}b_{2}a_{1}a_{2}}} \left[ (F^{l})_{b_{2}f_{3}}(F^{j})_{f_{4}a_{1}}(F^{k\dagger})_{a_{2}f_{1}}(F^{i\dagger})_{f_{2}b_{1}} + \\ &+ (F^{j})_{b_{2}f_{1}}(F^{l})_{f_{2}a_{1}}(F^{i\dagger})_{a_{2}f_{3}}(F^{k\dagger})_{f_{4}b_{1}} \right] \times \\ &\times \frac{1}{e^{i\lambda} \langle Q \rangle f(-\epsilon)} \int dy \; e^{-iy} \int \frac{dx}{\pi} f(x) \mathrm{Im} \Delta_{ij}(x) \times \\ &\times \mathrm{Im} \left[ G_{b_{1}b_{2}}(y) G_{f_{1}f_{2}}(x+y) \right] \mathrm{Im} \left[ G_{f_{3}f_{4}}(\epsilon+y) G_{a_{1}a_{2}}(\epsilon+x+y) \right]. \end{split}$$

The indices b, f and a this time run over the states with N - 1, N and N + 1 particles respectively and the i in  $e^{-iy}$  is the index, not the imaginary unit. In the implementation of the NCA/OCA impurity solver by K. Haule that we used, the matrix elements needed for the computation of self-energies and spectra

$$C^{ij}_{b_1b_2f_1f_2} = \sum_{f_1f_2b_1b_2ij}' (F^j)_{b_2f_1} (F^{i\dagger})_{f_2b_1}$$

in NCA and

$$D_{f_1f_2f_3f_4b_1b_2a_1a_2}^{ijkl} = \sum_{f_1f_2b_1b_2i_j}' (F^l)_{b_2f_3}(F^j)_{f_4a_1}(F^{k\dagger})_{a_2f_1}(F^{i\dagger})_{f_2b_1}$$

in OCA are precomputed before the actual calculation. The sums here run only over degenerate states f, b, a and over components i, j, k, l that are degenerate in the crystal field, which is indicated by the prime on top of the summation symbol. This procedure allows for an efficient evaluation of above quantities, since the precomputed matrix elements identify degeneracies in the system and thus not all possible combinations of the indices have to be evaluated explicitly. Furthermore, the solver allows for an analysis of the contributions of the atomic states to the ground state, similar in spirit to the sector analysis used in CT-QMC [450].

#### **1.6.4** Exact Diagonalization and Lanczos method

In contrast to QMC the exact diagonalization (ED) method is limited to small clusters. On the other hand it provides direct access to data on the real axis and is not hampered by the problem of analytical continuation. Additionally, it is not a problem to use the full Coulomb interaction in the solver. Within the ED solver the hybridization function  $\Delta$  is approximated by the hybridization function  $\Delta_{CL}$  of an Anderson impurity model for a finite cluster. This cluster contains the impurity levels  $\varepsilon_m$  plus additional discrete bath sites  $\varepsilon_k$  hybridized with it via parameters  $V_{mk}$ . The total size of the cluster is  $n_S$  and is limited to below 10 with full exact diagonalization, but can be extended to 15 or even higher when the Lanczos algorithm is used [70].

Thus, the approximation to the bath hybridization function is explicitly written as

$$\Delta(i\omega_n) \approx \Delta_{\rm cl}(i\omega_n) = \sum_{k}^{n_S} \frac{|V_{mk}|^2}{i\omega_n - \varepsilon_k}.$$

The optimal set of bath parameters  $\varepsilon_k$  and  $V_{mk}$  is found by fitting the full lattice hybridization function  $\Delta(i\omega_n)$  via same parameters. Since the original hybridization function is only recovered in the limit of infinitely many bath sites, the quality of the approximation critically depends on the number of bath sites included in the calculation. Since there is no unambiguous way to approximate the continuous hybridization function with a small number of sites a strategy has to be chosen to do so and in general the results will depend on this choice. The simplest and naïve strategy is to perform a least squares fit of the full hybridization or the bath Green function to the cluster version. This is achieved by minimization of a properly chosen distance function, like

$$d_{\Delta} = \frac{1}{N_{\max}} \sum_{n}^{N_{\max}} \sum_{ij} F \left| \Delta_{ij}(i\omega_n) - \Delta_{ij}^{cl}(i\omega_n) \right|^2,$$

with a cutoff  $N_{\text{max}}$ . Even at zero temperature, the fit is performed on the Matsubara frequencies associated with a *fictitious* temperature, which serves as a low-energy cutoff. However, such a fitting procedure does not guarantee that the most important physical characteristics of the system are reproduced. Thus, one can introduce a guiding procedure to the fit to increase the weight of the low energy part of the hybridization or the high energy tail, depending on the part one assumes relevant. Therefore we have included a *fudge factor*  $F = |i\omega_n|^{-x}$ , where the factor x can be used to introduce a bias to the fit. The fitting procedure is not trivial, can lead to problems [219] and different methods have been proposed to deal with it [365, 124, 211]. Especially in the metallic phase it is important to explicitly place one bath site at the Fermi level [365]. In principle one can say that the fitting procedure is arbitrary, since a continuous function is approximated using very few parameters. In the extreme case only one Lorentzian is used to approximate the whole hybridization function for a certain orbital, which can be problematic.

In the context of the Anderson model, or DMFT the bath Green function will be approximated by the discrete expression for the finite cluster

$$\mathcal{G}^{-1}(i\omega_n) \approx \mathcal{G}_{\rm cl}^{-1}(i\omega_n) = i\omega_n + \mu - \varepsilon_m - \sum_k^{n_S} \frac{|V_{mk}|^2}{i\omega_n - \varepsilon_k}.$$

It can also be fitted directly with the distance function

$$d_{\mathcal{G}} = \frac{1}{N_{\max}} \sum_{n}^{N_{\max}} \sum_{ij} F \left| \mathcal{G}_{ij}^{-1}(i\omega_n) - \left( \mathcal{G}_{ij}^{cl}(i\omega_n) \right)^{-1} \right|^2,$$

with the same F as above.

After setting up the cluster the full Hamiltonian for the system consisting of impurity and bath is evaluated in a suitable basis and diagonalized exactly. In the occupation number representation the Hilbert space for the cluster is spanned by the basis

$$|n_1,\ldots,n_{N_i},n_1,\ldots,n_{N_b}\rangle^{\uparrow}|n_1,\ldots,n_{N_i},n_1,\ldots,n_{N_b}\rangle^{\downarrow}$$

with  $N_i$  impurity states and  $N_b$  bath sites. Since the occupancies are only 0 or 1 for Fermions the state vectors are conveniently stored as a bitmap

$$|\dots, 1, 0, 1, 1, 1, 1, 0, 1, \dots\rangle^{\uparrow} |\dots, 0, 1, 0, 0, 0, 0, 1, 0, \dots\rangle^{\downarrow}$$

The Hamiltonian can then be expressed in this basis and subsequently diagonalized. The Green function can then be evaluated using the Lehmann representation from equation (1.4.7), since the full energy spectrum  $E_i$  and the eigenstates  $|i\rangle$  are known

$$G(i\omega_n) = \frac{1}{\mathcal{Z}} \sum_{ij} \frac{\langle i|\hat{d}|j\rangle \langle j|\hat{d}^{\dagger}|i\rangle}{i\omega_n + E_i - E_j} \left(e^{-\beta E_i} + e^{-\beta E_j}\right).$$

The partition function is also readily evaluated, when the full spectrum is known

$$\mathcal{Z} = \sum_{i} e^{-\beta E_i}$$

When using ED within DMFT one has to remember that self-consistency will never be actually achieved, because of the approximation of the electronic bath by a discrete cluster. Additionally, the basis grows exponentially with the number of sites like  $2^{2M}$ , where M is the total number of bath sites and impurity orbitals. In the common situation of a 5 band impurity (e.g. 3d transition metals) when using only one bath site per orbital the basis already contains  $\sim 10^6$  states. Thus calculations for realistic systems where the hybridization function may require more than one bath site become unfeasible very quickly. Symmetries of the system can be exploited to optimize the diagonalization procedure. For example, if the total number of particles and total spin are conserved the corresponding operators will commute with the Hamiltonian, which means that the Hamiltonian does not mix states with different particle number and different values of the total spin. These quantum numbers define a symmetry sector of the Hamiltonian. The Hamiltonian matrix takes a blockdiagonal structure so that it is possible to diagonalize it in each of the subspaces separately, see e.g. [264]. The block diagonal structure of the Hamiltonian also facilitates the evaluation of the Green function, since the creation and annihilation operators  $\hat{d}^{\dagger}$ ,  $\hat{d}$  will only couple states that are allowed by symmetry. The matrices  $\langle j | \hat{d}^{\dagger} | i \rangle$ , will thus also become rather sparse block matrices.

#### Lanczos Method

In the exact diagonalization of course the most time consuming and frequent operation is the diagonalization of a matrix. The Lanczos methos, named after Cornelius Lanczos<sup>11</sup> is an iterative algorithm to do exactly that. It uses the concept of the invariant subspace of a matrix to facilitate its (approximate) diagonalization. In our brief outline of the method we follow Refs. [264, 210].

A subspace of an  $n \times n$  matrix  $\underline{\underline{H}}$  is the set of all n vectors that can be written as linear combinations of a set  $S = {\mathbf{s}_1, \dots, \mathbf{s}_m}$  of n vectors. The subspace is said to be invariant under  $\underline{\underline{H}}$  if for any vector  $\mathbf{s}$  in the subspace the vector  $\underline{\underline{H}}\mathbf{s}$  is also contained in the subspace. How is this useful? It can be shown that the eigenvalues and eigenvectors of a matrix  $\underline{\underline{H}}$ can be found from those of a (much) smaller matrix under certain conditions. Let S be the basis of an invariant subspace of the  $n \times n$  matrix  $\underline{\underline{H}}$ . One can then write the vectors

<sup>&</sup>lt;sup>11</sup>The Hungarian name Lanczos is very often falsely pronounced "the Polish way", IPA: [lantʃɔs]. Correctly the 'cz' in Hungarian pronounces as a 'c', while the 's' at the end is actually a 'sh' sound, IPA: [lantsɔʃ].

 $\mathbf{s}_i$  as the columns of a matrix  $\underline{S}$  of dimension  $n \times m$ . We may then write

$$\underline{H} \underline{S} = \underline{S} \underline{T}, \tag{1.6.7}$$

with an  $m \times m$  matrix  $\underline{T}$ . The product  $\underline{S}$  will produce an  $n \times m$  matrix that contains linear combinations of the vectors  $\mathbf{s}_i$ . Because S is an invariant subspace each vector  $\underline{H}\mathbf{s}_i$ is contained in the subspace and the linear combinations may be expressed as the product  $\underline{S} \underline{T}$ . Assuming orthonormality of the basis S one can write

$$\underline{S}^T \underline{H} \underline{S} = \underline{T}$$

Now, if E and v are eigenvalue and eigenvector of  $\underline{T}$ ,

$$\underline{T}\mathbf{v} = E\mathbf{v}$$

then by multiplication of above equation with  $\underline{S}$  from the left and using Eq. (1.6.7) one obtains

$$\left(\underline{\underline{S}} \underline{\underline{T}}\right) \mathbf{v} = E\left(\underline{\underline{S}} \mathbf{v}\right) \implies \underline{\underline{H}}\left(\underline{\underline{S}} \mathbf{v}\right) = E\left(\underline{\underline{S}} \mathbf{v}\right),$$

which is the desired result. The eigenvalues and eigenstates of  $\underline{H}$  can thus be obtained from the diagonalization of the smaller matrix  $\underline{T}$  and a matrix-vector product  $\underline{S}\mathbf{v}$ .

In the Lanczos method the invariant subspace used is the the L + 1 dimensional Krylov subspace of  $\underline{\underline{H}}$ 

$$\mathcal{K}^{L}(\ket{v_{0}}) = \operatorname{span}(\ket{v_{0}}, H \ket{v_{0}}, H^{2} \ket{v_{0}}, \dots, H^{N} \ket{v_{0}})$$

generated by repeated application of <u>H</u>. This particular choice for the subspace will render the matrix  $\underline{T} \equiv \underline{H}^{\mathcal{K}}$  tridiagonal. After *L* steps the Hamiltonian matrix of the *L* + 1 dimensional Krylov space looks as follows

$$\underline{\underline{H}}^{\mathcal{K}} = \begin{pmatrix} a_0 & b_1 & 0 & 0 & \cdots & 0 & 0 \\ b_1 & a_1 & b_2 & 0 & \cdots & 0 & 0 \\ 0 & b_2 & a_2 & b_3 & \cdots & 0 & 0 \\ 0 & 0 & b_3 & a_3 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & a_{L-1} & b_L \\ 0 & 0 & 0 & 0 & \cdots & b_L & a_L \end{pmatrix}$$

The construction of further basis vectors follows the same scheme

$$b_{n+1} |v_{n+1}\rangle = |\tilde{v}_{n+1}\rangle = \underline{\underline{H}}^{\mathcal{K}} |v_n\rangle - \sum_{i=0}^n |v_i\rangle \langle v_i | \underline{\underline{H}}^{\mathcal{K}} |v_n\rangle = \underline{\underline{H}}^{\mathcal{K}} |v_n\rangle - a_n |v_n\rangle - b_n |v_{n-1}\rangle.$$

Rearranging shows that  $\underline{\underline{H}}^{\mathcal{K}}$  is indeed tridiagonal

$$\underline{\underline{H}}^{\mathcal{K}} \left| v_n \right\rangle = b_n \left| v_{n-1} \right\rangle + a_n \left| v_n \right\rangle + b_{n+1} \left| v_{n+1} \right\rangle,$$

which implies that  $\underline{\underline{H}}^{\mathcal{K}} |v_i\rangle$  is orthogonal to all basis states, except  $|v_i\rangle$  and  $|v_{i\pm 1}\rangle$ . The coefficients are found as  $a_j = \langle v_j | H v_j \rangle$  and  $b_j = \langle v_j | H v_{j-1} \rangle = \langle v_{j-1} | H v_j \rangle$ . This tridiagonalization of H is the essence of the Lanczos algorithm. The convergence of the method is very rapid, typically only  $\sim 30 - 100$  Lanczos iterations are needed for a  $10^7 \times 10^7$  matrix [264]. Diagonalization of  $\underline{\underline{H}}^{\mathcal{K}}$  after the Lanczos procedure yields, as the lowest eigenvalue a very good approximation of the ground state energy of  $\underline{\underline{H}}$  in the full Hilbert space.

# **1.7** Analytic Continuation

Impurity solvers that allow for the solution of impurity models at finite temperature, especially those based on quantum Monte Carlo, intrinsically work on imaginary time  $\tau$  and Matsubara frequencies  $i\omega_n$ . However, the physics is for many phenomena best visible on the real frequency axis; we are interested in spectral functions, that can be computed from the Green function, and in some cases also the self-energies on real frequencies. These can then easier be related to measurable phenomena. For a solver like exact diagonalization, the analytical continuation does not pose a problem and can be performed by the standard prescription  $i\omega_n \rightarrow \omega + i\delta$ , where  $\delta$  is a small offset, see e.g. [106]. This is possible, because the data provided by the solver are exact (within the approximation used) and are not subject to any noise. This is very different in QMC solvers. The data provided there are subject to statistical noise and cannot be continued to the real axis in a simple manner, since small features in the imaginary axis data can have a large effect on the real axis. QMC simulations are usually done in imaginary time, see the discussion on Hirsch-Fye and Continuous Time QMC in sections 1.6.1 and 1.6.2. This means, that the solver calculates the quantity

$$G(\tau) = -\langle \hat{T}_{\tau} \hat{c}_{\sigma}(\tau) \hat{c}_{\sigma}^{\dagger}(0) \rangle_{S},$$

where we have exploited that the Green function can be shown to depend only on the imaginary time distance  $\tau = \tau_1 - \tau_2$ , so only one time argument is needed. We focus here

on fermions only. This function is related to the Matsubara frequency Green function via the Fourier transform

$$G(\tau) = \frac{1}{\beta} \sum_{n} e^{-i\omega_n \tau} G(i\omega_n).$$

The Matsubara Green function is in turn related to the sought quantity, the spectral function  $A(\omega)$ 

$$G(i\omega_n) = \int_{-\infty}^{\infty} \mathrm{d}\omega \; \frac{A(\omega)}{i\omega_n - \omega}.$$

Combining the two relations it can be shown that the connection between the imaginary time Green function and the spectral function is

$$G(\tau) = \int_{-\infty}^{\infty} d\omega \, \frac{e^{-\tau\omega}}{1 + e^{-\beta\omega}} A(\omega).$$
(1.7.1)

Now, to obtain  $A(\omega)$  from  $G(\tau)$  above equation would have to be inverted, which is basically the problem of inverting the Mellin transform (or double sided Laplace transform), known from mathematics to be ill posed in general. Since Laplace transforms are useful tools in problems involving differential equations, they have been studied extensively in mathematics. Finding the inverse transform, also called Bromwich integral, has proven to be very difficult. For some simple functions the integral can be performed analytically, however, in general it must be integrated numerically. Many numerical methods have been proposed to do this, see, e.g., the review articles [88, 103, 95, 2]. The problems arise, because the integration kernel

$$K(\tau,\omega) = \frac{e^{-\tau\omega}}{1+e^{-\beta\omega}}$$

becomes exponentially small at large frequencies. The problem is even worse in QMC, since the data are known only on a discrete set of points and in addition subject to statistical noise. This, in combination with the exponentially ill-posed character of the transformation, leads to infinitely many possible solutions [184]. In such a case, if some approximate solution of the problem is desired, one has to decide on a formalism for finding the best estimate of the solution. The properties of the spectral function for fermions (it is positive  $A(\omega) \ge 0$  and bounded  $\int A(\omega) d\omega = N$ ) allow its interpretation as a probability distribution. The integral over the spectrum can be always renormalized to unity, since it is finite. For such a case one may use the method of Bayesian inference [184]. One thus works with probabilities and aims to find the most probable spectrum A given the measured data  $\overline{G}$ :  $\Pr[A|\overline{G}]$ . The naïve approach would be to perform a least squares fit

by proposing and varying  $A(\omega)$  such that we obtain the  $G(\tau)$  closest to the QMC result. Since we have numerical data on a discrete mesh the relation between the Green function and the spectrum, Eq. (1.7.1), becomes

$$G_i = \sum_{ij} K_{ij} A_j,$$

where  $K_{ij} = K(\tau_i, \omega_j)$  and  $A_j = A(\omega_j)\Delta\omega_j$  are the discrete versions of the kernel and the spectrum respectively. A least squares fit would now aim at minimizing the distance between fit and data

$$\chi^2 = \sum_{ij}^{L} \left( \overline{G}_i - G_i \right) C_{ij}^{-1} \left( \overline{G}_j - G_j \right),$$

where  $\overline{G}$  is the QMC average

$$\overline{G}_i = \frac{1}{M} \sum_{k=1}^M G_i^k$$

and  $G_i$  are the fitting points and  $C_{ij}$  is the covariance matrix

$$C_{ij} = \frac{1}{M(M-1)} \sum_{k=1}^{M} \left(\overline{G}_i - \overline{G}_i^k\right) \left(\overline{G}_j - \overline{G}_j^k\right).$$

The straightforward application of such a maximum likelihood fitting procedure to QMC data would lead to very noisy and non-unique results, due to overfitting of the data, i.e.  $\chi^2 \sim 0$ . In such a case the fit is rather reproducing the noise instead of the underlying data, a problem known from statistics. The procedure can be improved by regularization using Bayesian inference with a prior probability obtained from the principle of maximum entropy (MaxEnt) [185, 186]. It states that the values of a probability distribution should be assigned by maximizing the (Shannon) informational entropy [386]

$$S = -\int d\omega \ A(\omega) \log(A(\omega)/m(\omega)),$$

where  $m(\omega)$  is the so-called default model. The entropy will be zero if  $A(\omega) = m(\omega)$  and negative otherwise. It is a measure of distance between  $A(\omega)$  and the default model. The discrete version of the above is

$$S = \sum_{i} \left( A_i - m_i - A_i \log(A_i/m_i) \right)$$

with the discrete  $A_i$  and  $m_i$  defined as shown above. The default model can be a flat

function, a Gaussian or another model distribution. If the data are good enough the dependence on the choice of the model should be small [184]. In the maximum entropy procedure the functional

$$Q[A] = \alpha S[A] - L[A] = \alpha S[A] - \frac{1}{2}\chi^2[A]$$

is to be maximized:  $\delta Q[A]/\delta A = 0$ . The second equality holds for independent Gaussian errors [391]. The entropy will be maximized subject to the conditioning provided by the data via the distance functional L[A]. This choice is motivated by the fact that the conditional probability  $\Pr[A|\overline{G}, \alpha, m]$ , that is, the probability of A given the data  $\overline{G}$ , the default model m and a parameter  $\alpha$  is proportional to the exponential of Q

$$\Pr[A|\overline{G}, \alpha, m] \propto \exp(\alpha S[A] - L[A]).$$

The parameter  $\alpha$  controls the competition between the entropy S and the distance function  $\chi^2$ : when  $\alpha$  is small the smoothing effect of the entropy will be small and the problem of oversampling will again dominate, conversely, if  $\alpha$  is large the entropy term will dominate and the procedure will not be able to move far from the default model, the data will be undersampled, i.e., the procedure will not be flexible enough to reproduce the correct trend of the data [391]. The determination of  $\alpha$  is basically the point in which maximum entropy methods in general differ [391, 184]. The first idea (often called historic Max-Ent) was to adjust  $\alpha$  is such a way as to make  $\chi^2$  equal to the number of data points, but this is an ad-hoc choice and not optimal in most cases, in some even not applicable at all [391]. In the method of Skilling and Gull, the now called classic MaxEnt, the conditional probability  $\Pr[\alpha|\overline{G}, m]$  for  $\alpha$  given  $\overline{G}$  and the default model m is maximized. This is applicable when the distribution is sharply peaked around an optimum value  $\hat{\alpha}$ ; the method then produces an optimal solution, otherwise it may not even converge [64]. A more general procedure was proposed by Bryan [64], that does not rely on the specific form of the distribution and can deal with distributions containing many equally probable  $\alpha$ . Instead, the problem of finding  $\alpha$  is addressed by marginalization. The optimal spectra for each  $\alpha$ ,  $\hat{A}_{\alpha}$ , are determined and averaged over  $\alpha$  ( $\alpha$  is marginalized) to give the solution  $\overline{A}$ 

$$\overline{A}(\omega) = \int \mathrm{d}\alpha \; \hat{A}_{\alpha} \; \Pr[\alpha | \overline{G}, m].$$

In practice the integral over  $\alpha$  will be performed numerically in an iterative fashion, starting with a high value of  $\alpha$  ( $\alpha_{max}$ ) for which  $\Pr[\alpha|\overline{G}, m]$  effectively vanishes and from there working towards a lower cutoff  $\alpha_{min}$ . Throughout this work we have used Bryan's algorithm for the reconstruction of spectra from imaginary time Green functions. Another approach based on stochastic optimization, that can in some cases give results superior to MaxEnt was given in Ref. [287]. A different approach is to use data on Matsubara frequencies for the analytical continuation. In that case one can use Padé approximants to fit the Green function or self-energy [428]. Alternatively, for density-density type interactions a MaxEnt reconstruction of the self-energy is possible [437, 146].

# Chapter 2 DFT++ in the PAW framework

M. Karolak, T. O. Wehling, F. Lechermann, and A. I. Lichtenstein, General DFT++ method implemented with projector augmented waves: Electronic structure of SrVO<sub>3</sub> and the Mott Transition in  $Ca_{2-x}Sr_xRuO_4$ , J. Phys.: Condens. Matter **23** (2011), 085601

As we have discussed in the preceding chapter the ab initio treatment of correlated electron systems requires the calculation of Green functions and hybridization functions in terms of local orbitals. An important point at the interface between DFT and many-body methods is a suitable choice for a basis of the one-electron Kohn-Sham states. The local Hubbard-like interaction in the correlated subspace (usually d or f orbitals) is best represented in a set of localized orbitals. This is readily achieved when using a basis set, which is localized in real space, such as linear muffin-tin orbitals or Gaussian type orbitals. Thus, earliest implementations of the DFT+DMFT used the linear muffin-tin orbital (LMTO) basis and represented the correlated subspace with the subset of LMTO's with the specific character. This choice is certainly sensible, however, it might not be optimal and other basis sets have been investigated. A basis set, that has been heavily used in recent years, is the basis of Wannier functions. These have been utilized in different flavors in the context of DFT+DMFT: Anisimov [19], Amadon [12], Haule [146] and Aichhorn [6] used different schemes for projections onto a subset of Bloch functions, Pavarini [329] used Nth order muffin-tin orbitals (NMTOs) and Lechermann [244] used maximally localized Wannier functions (MLWFs) [278]. Many implementations of the density functional theory use a delocalized plane wave basis set. This has the advantages, that the basis set is simple, universal and its convergence is controlled in principle by a single parameter, the energy cutoff. As we already discussed in section 1.3.3 the projector augmented wave method (PAW), being a representative of plane-wave based methods, is a fast and accurate way of implementing DFT [50]. We will elucidate here how an interface between a DFT code using the PAW method and a subsequent many-body method can be formulated. We lay out methodological details concerning the use of projections of Bloch states onto local orbitals, as introduced in Refs. [12, 222] in the framework of the

projector augmented wave method [50]. We will refer to the method in what follows as PLO (projected local orbitals), following Ref. [12]. We present a general DFT++ method in the PAW basis set using the VASP [229, 230] code and explore different methods to construct the underlying Wannier functions.

# 2.1 Wannier Functions

Up to now we have discussed the electronic structure problem employing density functional theory in a Bloch wave basis set. This is convenient for solids, because in the simplest case they form an infinite periodic lattice of atoms filled with an electron gas. Here we want to introduce a new basis. The basis is formed by so-called Wannier functions, introduced by Wannier in the context of insulating crystals [438]. The states of electrons in a periodic potential, such as in a solid, are conveniently expressed using Bloch functions  $\psi_{\mathbf{k}n}(\mathbf{r})$ , where *n* is the band index and **k** is a vector of the reciprocal space confined to the first Brillouin zone. These functions are eigenfunctions of a Hamilton operator

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(\mathbf{r})$$

containing a periodic potential  $V(\mathbf{r})$  and simultaneously of the translation operator  $\hat{T}_{\mathbf{R}}$  (see e.g. [28])

$$\hat{T}_{\mathbf{R}}\psi_{\mathbf{k}n}(\mathbf{r}) = \psi_{\mathbf{k}n}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\mathbf{R}}\psi_{\mathbf{k}n}(\mathbf{r})$$

The Wannier functions are defined as the Fourier transform of Bloch functions from momentum space into real space

$$\phi_n \left( \mathbf{r} - \mathbf{R} \right) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{R}} \psi_{\mathbf{k}n}(\mathbf{r}).$$
(2.1.1)

The sum runs over all k inside the first Brillouin zone. The Bloch states can be obtained from a standard density functional band calculation, since density functional codes for solids use the Bloch basis to expand the wave function. The orthogonality and completeness of the Wannier functions is readily verified by making use of the properties of Bloch functions:

$$\int \phi_n^*(\mathbf{r} - \mathbf{R}) \phi_{n'}(\mathbf{r} - \mathbf{R}') d\mathbf{r} = \frac{1}{N} \sum_{\mathbf{k}, \mathbf{k}'} \int e^{i(\mathbf{k} \cdot \mathbf{R} - \mathbf{k}' \cdot \mathbf{R}')} \psi_{\mathbf{k}n}^*(\mathbf{r}) \psi_{\mathbf{k}'n'}(\mathbf{r}) d\mathbf{r}$$
$$= \frac{1}{N} \sum_{\mathbf{k}} e^{i\mathbf{k}(\mathbf{R} - \mathbf{R}')} \delta_{nn'} = \delta_{\mathbf{R}\mathbf{R}'} \delta_{nn'}$$

and

$$\sum_{n,\mathbf{R}} \phi_n^*(\mathbf{r} - \mathbf{R}) \phi_n(\mathbf{r}' - \mathbf{R}) = \frac{1}{N} \sum_{n,\mathbf{R}} \sum_{\mathbf{k},\mathbf{k}'} e^{i\mathbf{R}(\mathbf{k} - \mathbf{k}')} \psi_{\mathbf{k}n}^*(\mathbf{r}) \psi_{\mathbf{k}'n}(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}').$$

The existence of a localized set of Wannier functions, and their general properties have been discussed long time ago in different contexts by, e.g., Koster [224] or Parzen [327]. There is, however, an ambiguity in the linear transformation from Bloch to Wannier functions, which is partly the reason why quantitative calculations using Wannier functions have appeared only recently.<sup>1</sup> Even in the simplest case – one dimension, one band – the transformation is not unique. There is still the freedom in the choice of the phase factor of the Bloch orbitals. Kohn has shown for this particular case, that in fact infinitely many proper Wannier functions exist, due to the phase factor [214]. Yet, only one real, high-symmetry Wannier function exists that falls of exponentially. Through optimization of the phase factor the localization properties of the Wannier functions can be improved. The situation gets considerably more complicated if more bands are considered. The observation made by Kohn can be generalized and extended for several bands, which has been achieved by Marzari and Vanderbilt [278].

A set of generalized Wannier functions belonging to a set of bands S can be written as

$$W_n\left(\mathbf{r}-\mathbf{T}\right) = \frac{V}{\left(2\pi\right)^3} \int \mathrm{d}\mathbf{k} \; e^{-i\mathbf{k}\mathbf{T}} \sum_{m \in \mathcal{S}} U_{mn}^{(\mathbf{k})} \psi_{\mathbf{k}m},$$

where V denotes the volume of the primitive cell and the integration runs over the Brillouin zone. The freedom in the choice of the phase factor in the one band case transforms to the freedom of performing a unitary transformation  $U_{mn}^{(\mathbf{k})}$  in the multiband case. This freedom can be exploited to construct Wannier functions with special properties. Marzari and Vanderbilt propose the criterion of optimal (or maximal) localization as a desired property. They define a functional

$$\Omega = \sum_{n} \left( \langle r^2 \rangle_n - \langle \mathbf{r} \rangle_n^2 \right)$$

which is nothing else as the sum of the quadratic spreads of the Wannier probability distributions. This functional is then minimized with respect to the transformation  $U_{mn}^{(\mathbf{k})}$ . The maximally localized Wannier functions thus obtained have certain desirable features, e.g. they turn out to be real functions [278]<sup>2</sup>.

<sup>1</sup>Wannier functions can also be obtained directly without knowledge of the Bloch functions by a variational procedure [224, 327].

<sup>2</sup>No general proof of this property exists, but it is strongly supported by empirical observations, see discussion in [278].

As an initial guess before the variational procedure a set of trial orbitals in the form of atomic orbitals is chosen. It has been shown for the case of transition metal oxides that this initial guess is usually so good that the variational procedure can be dropped as shown by Ku et al. [232]. We rely on this approximation and use the projection of the trial orbitals onto a subspace of Bloch function to define the unitary transformation  $U_{mn}^{(k)}$  as will be elaborated below.

# 2.2 Implementation within PAW

At the heart of the PAW method is, as discussed in section 1.3.3, the following theorem, stating that the wave function  $|\psi\rangle$  can be decomposed exactly as follows

$$\begin{aligned} |\psi\rangle &= \hat{\mathcal{T}} |\tilde{\psi}\rangle = \left(1 + \sum_{i} \hat{\tau}_{i}\right) |\tilde{\psi}\rangle \\ &= |\tilde{\psi}\rangle + \sum_{i} \left(|\phi_{i}\rangle - |\tilde{\phi}_{i}\rangle\right) \langle \tilde{p}_{i} |\tilde{\psi}\rangle \,. \end{aligned}$$
(2.2.1)

Here  $\hat{\mathcal{T}}$  is the operator denoting the transformation, which is different from the identity only inside an augmentation region,  $|\tilde{\psi}\rangle$  is the so called *pseudo* wave function and the sum runs over all augmentation channels *i*. As in the construction of pseudopotentials, physical partial waves  $|\phi\rangle$  are solutions of the Schrödinger equation of isolated atoms, while the corresponding auxiliary (pseudo) functions  $|\tilde{\phi}\rangle$  are chosen to match  $|\phi\rangle$  outside the augmentation spheres, being smooth inside and continuously differentiable in all space. The projectors  $|\tilde{p}_i\rangle$  are finally defined by

$$\langle \tilde{p}_i | \phi_j \rangle = \delta_{ij},$$

where the tilde as usually in the PAW formalism discriminates *pseudo* from *physical* quantities. The Kohn-Sham equations in PAW representation are obtained by applying the variational principle to the total energy functional with respect to the auxiliary wave functions: Since the transformation operator T does not depend on the electron density, the Kohn-Sham equations transform according to

$$\hat{\mathcal{T}}^{\dagger}\hat{H}_{\mathrm{KS}}\hat{\mathcal{T}}\left|\tilde{\psi}_{\mathbf{k}}
ight
angle=arepsilon_{\mathbf{k}}\hat{\mathcal{T}}^{\dagger}\hat{\mathcal{T}}\left|\tilde{\psi}_{\mathbf{k}}
ight
angle$$

Here,  $\hat{H}_{\rm KS}$  is the Kohn-Sham Hamiltonian, so that above equation is a Schrödinger type equation, but with the overlap matrix occurring on the right hand side. To solve the

equation the auxiliary wave functions are expanded in terms of plane waves:

$$\tilde{\psi}_{\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r} | \tilde{\psi}_{\mathbf{k}} \rangle = \sum_{\mathbf{G}} c_{\mathbf{k},\mathbf{G}} \exp\left(i(\mathbf{k} + \mathbf{G})\mathbf{r}\right).$$

Following the discussion in section 1.5.4 and Ref. [244], the desired quantity for an implementation of a DFT++ method is a projection  $\underline{\mathcal{P}} = \sum_{L} |L\rangle \langle L|$  of the full Kohn-Sham Green function  $\underline{\mathcal{G}}^{\text{KS}}(\omega)$  on a set of localized orbitals  $\{|L\rangle\}$ :

$$\underline{\underline{G}}_{\{|L\rangle\}}^{\mathrm{KS}}(\omega) = \underline{\underline{\mathcal{P}}} \, \underline{\underline{G}}^{\mathrm{KS}}(\omega) \underline{\underline{\mathcal{P}}}^{\dagger}.$$
(2.2.2)

The subspace span( $\{|L\rangle\}$ ) is usually termed correlated subspace. It is the subspace of orbitals in which many-body correlations play a major role and where corrections to the DFT will be considered. In plane-wave based calculations,  $\underline{G}^{KS}(\omega)$  is available in terms of a (truncated) set of Bloch states  $|K\rangle$  that are eigenstates of the Kohn-Sham Hamiltonian  $\hat{H}_{KS} |K\rangle = \varepsilon_K |K\rangle$ :

$$\underline{\underline{G}}^{\mathrm{KS}}(\omega) = \sum_{K} \frac{|K\rangle \langle K|}{\omega - \varepsilon_{K} + i\delta}.$$
(2.2.3)

Inserting equation (2.2.3) into equation (2.2.2) shows that one needs to evaluate projections of the type  $\langle L|K\rangle$  in order to access the matrix elements  $G_{LL'}^{\text{KS}}(\omega)$  of the local Green function

$$G_{LL'}^{\rm KS}(\omega) = \sum_{K} \frac{\langle L|K\rangle \langle K|L'\rangle}{\omega - \varepsilon_K + i\delta}.$$

In most cases, the correlated orbitals are d or f orbitals, which are to a good approximation localized inside the PAW augmentation spheres. For  $|L\rangle$  within these spheres and given the PAW decomposition of a Bloch state  $|K\rangle$ , Eq. (2.2.1), one obtains

$$\langle L|K\rangle = \langle L|\tilde{K}\rangle + \langle L|\left(\sum_{i} (|\phi_i\rangle - |\tilde{\phi}_i\rangle)\langle \tilde{p}_i|\tilde{K}\rangle\right),$$

which simplifies for a converged partial wave expansion to

$$\langle L|K\rangle = \sum_{i} \langle L|\phi_i\rangle \langle \tilde{p}_i|\tilde{K}\rangle.$$

The index *i* of the augmentation functions  $|\phi_i\rangle$  includes site  $\alpha$ , angular momentum *l* and *m* as well as an index  $\nu$  labeling the radial function:  $i = (\alpha, l, m, \nu)$ . In practice, the localized orbitals can be also chosen to be angular momentum eigenstates at a given site
$\alpha$ , which leads to

$$\langle L|K\rangle = \sum_{\nu} \langle L|\phi_{\nu}\rangle \langle \tilde{p}_{\nu}|\tilde{K}\rangle$$
(2.2.4)

with  $\nu$  abbreviating  $i = (\alpha, l, m, \nu)$  where  $\alpha$ , l, and m are fixed. In the PAW approach, the first augmentation function,  $\nu = 0$ , for each channel is usually taken to be an atomic eigenfunction (c.f. Ref. [50]). Defining the correlated subspace in terms of atomic eigenfunctions leads consequently to  $|L\rangle = |\phi_{\nu=0}\rangle$ , and thus

$$\langle \phi_{\nu=0} | K \rangle = \sum_{\nu} \langle \phi_{\nu=0} | \phi_{\nu} \rangle \langle \tilde{p}_{\nu} | \tilde{K} \rangle .$$
(2.2.5)

As higher augmentation functions,  $\nu > 0$ , are in general not orthogonal to the  $|\phi_{\nu=0}\rangle$  state, evaluation of equation (2.2.5), requires accounting for overlaps of the form  $\langle \phi_{\nu=0} | \phi_{\nu'} \rangle$ . This approach has been implemented to the AB-INIT code [128, 417] by Amadon [12]. In the present work we have used the Vienna Ab Initio Simulation Package (VASP) [229, 230] to implement the same method. It will be referred to as PLO(A) in what follows. The first order approximation to equation (2.2.5) has also been implemented to investigate how accurate it is. In this case one *only* uses the first term of the sum in equation (2.2.5)

$$\langle \phi_{\nu=0} | K \rangle = \langle \phi_{\nu=0} | \phi_{\nu=0} \rangle \langle \tilde{p}_{\nu=0} | \tilde{K} \rangle \tag{2.2.6}$$

while disregarding all other terms. This approximation will be referred to as PLO(0). In addition to the above methods we have implemented another scheme: As in the LDA+U method implemented in VASP [359, 38] we choose

$$|\langle L|K\rangle|^{2} = \sum_{\nu,\nu'} \langle \tilde{K}|\tilde{p}_{\nu}\rangle \langle \phi_{\nu}|\phi_{\nu'}\rangle \langle \tilde{p}_{\nu'}|\tilde{K}\rangle.$$
(2.2.7)

Hence, the absolute value of the projections is in this scheme given by the projection onto a subspace of augmentation channels with given angular momentum (l, m). The phase is determined by

$$\arg\left(\langle L|K\rangle\right) = \arg\left(\sum_{\nu} \langle \tilde{p}_{\nu}|\tilde{K}\rangle\right).$$
(2.2.8)

This particular construction will be referred to as PLO(V) in the following. If higher augmentation channels are negligible,  $|\langle \tilde{p}_{\nu=0} | \tilde{K} \rangle| \gg |\langle \tilde{p}_{\nu>0} | \tilde{K} \rangle|$ , and additionally  $\langle \phi_{\nu} | \phi_{\nu'} \rangle = \delta_{ij}$  (which is not the case in general) equation (2.2.6), equation (2.2.5) as well as equations (2.2.7)-(2.2.8) become formally identical. The approach defined in equations (2.2.7) – (2.2.8) differs from the approach in equation (2.2.4) in one important point. In the former approach a specific radial function  $|\phi_{\nu=0}\rangle$  is used for the projection and only overlaps of the type  $\langle \phi_{\nu=0} | \phi_{\nu} \rangle$  are taken into account, whereas in the latter approach the radial dependence is averaged out by including general overlaps  $\langle \phi_{\nu} | \phi_{\nu'} \rangle$ . As

constructed, the projections in equation (2.2.5) as well as in equations (2.2.7) and (2.2.8) are not properly normalized for two reasons: (1) the Bloch basis is incomplete since only a limited number of Bloch bands is included and (2) the PAW augmentation functions are in general not orthonormal. In our implementation we orthonormalize the projection matrices by the following Wannier type construction: By definition, the localized states  $|L\rangle$  are labeled by site and angular momentum indices:  $L = (\alpha, l, m)$ . We split the site index  $\alpha = \mathbf{R} + \mathbf{T}$  such that  $\mathbf{R}$  labels the position within the unit cell and  $\mathbf{T}$  is the Bravais lattice vector of the unit cell in which  $\alpha$  is located. This allows us to construct the Bloch transform of the localized states,

$$|L_{\mathbf{k}}\rangle = \sum_{T} e^{i\mathbf{kT}} |L_{\mathbf{T}}\rangle, \qquad (2.2.9)$$

where **k** is from the first Brillouin zone and  $|L_{\mathbf{T}}\rangle \equiv |L\rangle = |\alpha, l, m\rangle$  with  $\alpha = \mathbf{R} + \mathbf{T}$ . The sum in equation (2.2.9) runs over the Bravais lattice. Labeling the Bloch states  $|K\rangle = |\mathbf{k}, n\rangle$  by their crystal momentum, **k**, and band index, *n*, we normalize the projection matrices  $\mathcal{P}_{Ln}(\mathbf{k}) = \langle L_{\mathbf{k}} | \mathbf{k}, n \rangle$  using the overlap operator (Löwdin Orthonormalization)

$$O_{LL'}(\mathbf{k}) = \sum_{n} \mathcal{P}_{Ln}(\mathbf{k}) \mathcal{P}_{L'n}^{\dagger}(\mathbf{k}),$$

where

$$\mathcal{P}_{Ln}^{\dagger}(\mathbf{k}) = \langle \mathbf{k}, n | L_{\mathbf{k}} \rangle.$$

The orthonormalized projection matrices are then

$$\overline{\mathcal{P}}_{Ln}(\mathbf{k}) = \sum_{L'} \left[ O(\mathbf{k}) \right]_{LL'}^{-1/2} P_{L'n}(\mathbf{k})$$

These orthonormalized projection matrices are calculated once at the beginning of a calculation, or repeatedly if charge self-consistency is used, see discussion below. The projection matrices can then be used to obtain the local Green function of the correlated orbitals from the full Bloch Green function

$$G_{LL'}(\omega) = \sum_{\mathbf{k},nn'} \overline{\mathcal{P}}_{Ln}(\mathbf{k}) G_{nn'}^{\mathrm{B}}(\mathbf{k},\omega) \overline{\mathcal{P}}_{L'n'}^{\dagger}(\mathbf{k})$$
$$= \sum_{\mathbf{k},nn'} \overline{\mathcal{P}}_{Ln}(\mathbf{k}) \Big[ (\omega + i\delta + \mu - \varepsilon_n(\mathbf{k})) \,\delta_{nn'} \Big]^{-1} \overline{\mathcal{P}}_{L'n'}^{\dagger}(\mathbf{k})$$

Similarly, the hybridization function,  $\Delta(\omega)$ , is available. It is related to the local Green function by

$$G_{LL'}^{-1}(\omega) = (\omega + i\delta)\delta_{LL'} - \varepsilon_{LL'} - \Delta_{LL'}(\omega), \qquad (2.2.10)$$

which can be solved to yield

$$\Delta_{LL'}(\omega) = -\left[G_{LL'}^{-1}(\omega) + \varepsilon_{LL'} - (\omega + i\delta)\,\delta_{LL'}\right],\,$$

where  $\varepsilon_{LL'}$  is the static crystal field. To separate the dynamical, i.e. frequency dependent, hybridization from the static DFT crystal field, we numerically evaluate the limit  $\omega \to \infty$ , where  $\omega - G_{LL'}^{-1}(\omega) \to \varepsilon_{LL'}$ .

In a DFT+DMFT calculation the projection matrices  $\overline{\mathcal{P}}_{Ln}(\mathbf{k})$  are used for up- and downfolding quantities like the Green function and the self-energy in the course of the iterative DMFT procedure in exactly the same way as shown for the local Green function above. For example, the self-energy obtained by an impurity solver for the effective impurity model  $\Sigma_{LL'}(\omega)$  can be upfolded to the Bloch basis as follows:

$$\Sigma_{nn'}^{\rm B}(\mathbf{k},\omega) = \sum_{LL'} \overline{P}_{Ln}^{\dagger}(\mathbf{k}) \left[ \Sigma_{LL'}(\omega) + \Sigma_{\rm DC} \right] \overline{P}_{L'n'}(\mathbf{k}).$$

Here we have included a possible double counting correction to the self-energy  $\Sigma_{\rm DC} = -\mu_{\rm DC}\delta_{LL'}$ . Since the self-energy in DMFT is a purely local quantity, the index k on  $\Sigma_{nn'}^{\rm B}(\mathbf{k},\omega)$  reflects the momentum dependence brought about by the projection matrices. The Green function in Bloch basis is obtained by applying the self-energy to the band structure

$$G_{nn'}^{\rm B}(\mathbf{k},\omega) = \left[ \left(\omega + i\delta + \mu - \varepsilon_n(\mathbf{k})\right) \delta_{nn'} - \Sigma_{nn'}^{\rm B}(\mathbf{k},\omega) \right]^{-1}.$$

With the above quantities, like hybridization function or Green function, available we can proceed to perform DFT++ calculations of different kinds. The local Green function or the hybridization function can be used as an input for impurity calculations, e.g. impurities on surfaces as discussed for the examples of Co on Cu(111) in Ref. [132] as well as Co on graphene in Ref. [444]. The DFT+DMFT implementation based on the projectors from equations (2.2.7)-(2.2.8) has been compared to NMTO [329, 330] and other plane wave Wannier function based implementations [421, 222] for various cases (e.g. for Ca<sub>2</sub>RuO<sub>4</sub>, Sr<sub>2</sub>RuO<sub>4</sub>, LaTiO<sub>3</sub>, YTiO<sub>3</sub>, NiO and others), where the results were in good accordance [192, 131].

We want to note that our construction does not suffer from any entagling problems as faced in the construction of maximally localized Wannier functions (MLWF), as proposed by Marzari and Vanderbilt [278], since our construction is made employing an atomistic picture. Of course our Wannier functions will not be maximally localized, in fact they will correspond to the first guess in the procedure of maximal localization in the MLWF scheme, which is usually already very good for transition metal oxides [232]. In our experience the PLO methodology works very well and we have not met a case where an additional localization or other treatment of the projection was required.

The presented projection scheme allows for the inclusion of both correlated and uncorrelated states in the procedure. Therefore, information about the interplay of correlated orbitals with their uncorrelated ligands can be obtained. It has to be pointed out, however, that the inclusion of more bands into the problem does not present a priori an improvement of the description of the system as one might naïvely assume. The results obtained for a model containing only correlated orbitals can differ even qualitatively from results obtained taking the ligand states into account. A recent controversy over LaNiO<sub>3</sub> heterostructures illustrates this point very nicely. While the Fermi surface in DFT+DMFT calculations using only the Ni d bands agrees with experiments, the one obtained within a d-p model, including ligand states, does not. The reasons for that have been investigated in detail in Ref. [326]. The most important differences between the d only and the d - pmodels stems from the hybridization between d and p bands, which means that there will be some d spectral weight within the p bands and vice versa. This is shown for  $SrVO_3$ in figure 2.3.2. Now, including the p states in the model one automatically modifies the description of the d states. The dominant effects will be a change in the crystal field level position and the splitting of the levels along with a modification, in general an increase, of the filling of the d states. These are important model parameters for the subsequent manybody calculation and will in general have a strong influence on the results of these. If the changes lead to an improvement or a worsening of the results of the DFT+DMFT calculation will depend on the system and seems difficult to assess a priori. There are cases where the inclusion of ligand states leads to an improvement over the d only description, like for SrVO<sub>3</sub> as we will see below and NiO in chapter 3, see also Refs. [234, 235], but also different cases where one has to limit the calculation to the d states only to obtain the correct physics.

What is the source of these problems? One can say in general that the DFT++ or DFT+DMFT methodology is sound when only the correlated subspace is taken into account, that is only the correlated d or f states. In such a case the method is truly ab initio, free of parameters, like the double counting (see discussion in chapter 3), and the only approximation used is the DMFT approximation of a local self-energy. Going beyond this point and including other states in the calculation one introduces a certain approximation that apparently works for some systems, however, in some cases gives an unsatisfactory description of the system. In this approximation one tacitly assumes that, for example, the ligand p states are not correlated at all or speaking formally one neglects the matrix elements of the Coulomb interaction within the p shell  $U_{pp}$ . Additionally, one also neglects the Coulomb interaction between d and p states  $U_{pd}$  and keeps only the matrix elements within the d shell  $U_{dd}$ . Going beyond such an approximation is difficult because the number of orbitals in the system increases making it prohibitively hard to calculate in many cases. In addition, the p states are centered on ligand atoms surrounding the impurity and not on the impurity itself ultimately making a cluster approach necessary.

#### 2.2.1 Wannier Hamiltonian and tight-binding quantities

Using the projection matrices the Hamiltonian in the Wannier basis can be obtained, by application of the projection matrices to the Bloch Hamiltonian  $H_{nn'}^{\rm B}(\mathbf{k}) = \varepsilon_n(\mathbf{k})\delta_{nn'}$  in the following way

$$H_{LL'}^{W}(\mathbf{k}) = \sum_{nn'} \overline{\mathcal{P}}_{Ln}(\mathbf{k}) H_{nn'}^{B}(\mathbf{k}) \overline{\mathcal{P}}_{L'n'}^{\dagger}(\mathbf{k}).$$
(2.2.11)

The Hamiltonian can be used to check the quality of the projected band structure and can also be used as an input for an impurity solver. Fourier transformation of the k-dependent Wannier Hamiltonian  $H_{LL'}^{W}(\mathbf{k})$  yields the on-site energies and hopping integrals

$$t_{LL'}^{\mathbf{RR'}} = \frac{1}{N} \sum_{\mathbf{k}}^{N} \exp(i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R'})) H_{LL'}^{\mathbf{W}}(\mathbf{k}),$$

where  $t_{LL'}^{00} = \varepsilon_{LL'}$ . In above formula L, L' label the orbitals and  $\mathbf{R}, \mathbf{R'}$  are lattice vectors. These provide the basis for a tight-binding description of the system.

### 2.2.2 Comparison between projection formalism and formalism relying explicitly on the Wannier Hamiltonian

As mentioned above the formalism allows for the explicit computation of the Hamiltonian in the basis of localized orbitals via Eq. (2.2.11). Since there exist codes, that contain a DMFT self-consistency loop based explicitly on the Wannier Hamiltonian, we want to briefly compare this approach to our approach based on the Bloch Hamiltonian and projection matrices. We begin with the non-interacting Green function, which in the projection formalism is

$$G_{LL'}(\mathbf{k},\omega) = \sum_{nn'} \overline{\mathcal{P}}_{Ln}(\mathbf{k}) \left[ \left( z - \varepsilon_n(\mathbf{k}) \right) \delta_{nn'} \right]^{-1} \overline{\mathcal{P}}_{L'n'}^{\dagger}(\mathbf{k}).$$

For brevity we have accumulated the energy grid and the chemical potential into the variable  $z = \omega + i\delta + \mu$ . Using the Hamiltonian, constructed as in Eq. (2.2.11), explicitly, the same quantity can be written as

$$G_{LL'}(\mathbf{k},\omega) = \left[z - \sum_{nn'} \overline{\mathcal{P}}_{Ln}(\mathbf{k})\varepsilon_n(\mathbf{k})\delta_{nn'}\overline{\mathcal{P}}_{L'n'}^{\dagger}(\mathbf{k})\right]^{-1} = \left[z - H_{LL'}^{W}(\mathbf{k})\right]^{-1}.$$

Now, formally the question if both approaches lead to the same Green function is down

to the following

$$\sum_{nn'} \overline{\mathcal{P}}_{Ln}(\mathbf{k}) \left[ \left( z - \varepsilon_n(\mathbf{k}) \right) \delta_{nn'} \right]^{-1} \overline{\mathcal{P}}_{L'n'}^{\dagger}(\mathbf{k}) \stackrel{?}{=} \left[ z - \sum_{nn'} \overline{\mathcal{P}}_{Ln}(\mathbf{k}) \varepsilon_n(\mathbf{k}) \delta_{nn'} \overline{\mathcal{P}}_{L'n'}^{\dagger}(\mathbf{k}) \right]^{-1}.$$
(2.2.12)

This equality can be shown to be valid under certain conditions. First, one observes that for three square matrices  $\underline{A} \underline{B} \underline{C}$  (also for any number of square invertible matrices) the inverse is  $(\underline{A} \underline{B} \underline{C})^{-1} = \underline{C}^{-1} \underline{B}^{-1} \underline{A}^{-1}$ . A special case of this general property is that for a square matrix  $\underline{A}$  the inverse  $\underline{A}^{-1}$  can be written using the eigendecomposition  $\underline{A} = \underline{P} \underline{A} \underline{P}^{-1}$ , with the diagonal matrix  $\underline{A}$ 

$$\underline{\underline{A}}^{-1} = \left(\underline{\underline{P}} \underline{\underline{\Lambda}} \underline{\underline{P}}^{-1}\right)^{-1} = \underline{\underline{P}} \underline{\underline{\Lambda}}^{-1} \underline{\underline{P}}^{-1}$$
(2.2.13)

or using the eigendecomposition via Hermitian matrices,  $\underline{\underline{A}} = \underline{\underline{P}} \underline{\underline{\Lambda}} \underline{\underline{P}}^{\dagger}$  with  $\underline{\underline{P}}^{\dagger} \underline{\underline{P}} = \underline{\underline{P}}^{-1} \underline{\underline{P}} = \mathbb{1}$ , as

$$\underline{A}^{-1} = \left(\underline{\underline{P}} \underline{\underline{\Lambda}} \underline{\underline{P}}^{\dagger}\right)^{-1} = \underline{\underline{P}} \underline{\underline{\Lambda}}^{-1} \underline{\underline{P}}^{\dagger}.$$
(2.2.14)

For convenience we introduce the notation  $\underline{\varepsilon} := \text{diag}(\varepsilon_1, \ldots, \varepsilon_n)$ , for a diagonal matrix with  $\varepsilon_1, \ldots, \varepsilon_n$  on the diagonal and zeros otherwise. Now, applying the above to our problem, Eq. (2.2.12), we can show that for each k-point

$$\begin{split} \left[ z\mathbbm{1} - \underline{P} \underline{\varepsilon} \underline{P}^{\dagger} \right]^{-1} &= z^{-1} \left[ \mathbbm{1} - z\underline{P} \underline{\varepsilon} \underline{P}^{\dagger} \right]^{-1} \\ &= z^{-1} \left[ \underline{P} \mathbbm{1} \underline{P}^{\dagger} - z\underline{P} \underline{\varepsilon} \underline{P}^{\dagger} \right]^{-1} \\ &= z^{-1} \left[ \underline{P} \left( \mathbbm{1} - z\underline{\varepsilon} \right) \underline{P}^{\dagger} \right]^{-1} \\ &= z^{-1} \underline{P} \left( \mathbbm{1} - z\underline{\varepsilon} \right)^{-1} \underline{P}^{\dagger} \\ &= \underline{P} \left( z\mathbbm{1} - \underline{\varepsilon} \right)^{-1} \underline{P}^{\dagger}, \end{split}$$

proving, that Eq. (2.2.12) is valid for some square matrices  $\underline{P}$ , that form the eigendecomposition of the Wannier hamiltonian  $H^{W}(\mathbf{k}) = \sum_{n} P_{nn}(\mathbf{k})\varepsilon_{n}(\mathbf{k})P_{nn}^{\dagger}(\mathbf{k})$ . The symbol 1 denotes the  $n \times n$  unit matrix. The square matrices  $\underline{P}$  can be identified with the projection

matrices  $\overline{\mathcal{P}}_{Ln}(\mathbf{k})$  if and only if the latter are square, i.e. L = n, and thus constitute a unitary rotation of the basis only. In general this will not be the case, since often n > L and the projection is then a *real* projection of a larger space onto a smaller space and thus a procedure involving information loss. In addition, this makes the projection matrices rectangular prohibiting simple application of procedures like inversion, which is defined rigorously only for square matrices.

When a self-energy is involved the above procedure still applies, now not relying on the eigendecomposition, but only on the general properties of the inversion of matrix products, since the self-energy is not a priori diagonal. Since  $\underline{\underline{G}} = \left( [\underline{\underline{G}}^0]^{-1} - \underline{\underline{\Sigma}} \right)^{-1}$ , the problem posed in Eq. (2.2.12) complicates by application of the self-energy to

$$\begin{split} &\sum_{nn'} \overline{\mathcal{P}}_{Ln}(\mathbf{k}) \Big[ (z - \varepsilon_n(\mathbf{k})) \,\delta_{nn'} - \Sigma_{nn'}(\mathbf{k}, \omega) \Big]^{-1} \overline{\mathcal{P}}_{L'n'}^{\dagger}(\mathbf{k}) \\ &= \sum_{nn'} \overline{\mathcal{P}}_{Ln}(\mathbf{k}) \Big\{ (z - \varepsilon_n(\mathbf{k})) \,\delta_{nn'} - \sum_{LL'} \overline{\mathcal{P}}_{Ln}^{\dagger}(\mathbf{k}) \Big[ \Sigma_{LL'}(\omega) \Big] \overline{\mathcal{P}}_{L'n'}(\mathbf{k}) \Big\}^{-1} \overline{\mathcal{P}}_{L'n'}^{\dagger}(\mathbf{k}) \\ &\stackrel{?}{=} \Big\{ z - \sum_{nn'} \overline{\mathcal{P}}_{Ln}(\mathbf{k}) \varepsilon_n(\mathbf{k}) \delta_{nn'} \overline{\mathcal{P}}_{L'n'}^{\dagger}(\mathbf{k}) - \sum_{LL'} \overline{\mathcal{P}}_{Ln}^{\dagger}(\mathbf{k}) \Big[ \Sigma_{LL'}(\omega) \Big] \, \overline{\mathcal{P}}_{L'n'}(\mathbf{k}) \Big\}^{-1} \\ &= \Big\{ z - \sum_{nn'} \overline{\mathcal{P}}_{Ln}(\mathbf{k}) \varepsilon_n(\mathbf{k}) \delta_{nn'} \overline{\mathcal{P}}_{L'n'}^{\dagger}(\mathbf{k}) - \Sigma_{nn'}(\mathbf{k}, \omega) \Big\}^{-1}. \end{split}$$

Again, for every k-point we show with an  $L \times L$  matrix  $\underline{\Sigma}$  in real space (and L = n)

$$\begin{split} \left[ z\mathbbm{1} - \underline{P} \underline{\varepsilon} \underline{P}^{\dagger} - \underline{\Sigma} \right]^{-1} &= \left[ z\mathbbm{1} - \underline{P} \underline{\varepsilon} \underline{P}^{\dagger} - \underline{P} \underline{P}^{\dagger} \underline{\Sigma} \underline{P} \underline{P}^{\dagger} \right]^{-1} \\ &= z^{-1} \left[ \mathbbm{1} - z\underline{P} \underline{\varepsilon} \underline{P}^{\dagger} - z\underline{P} \underline{P}^{\dagger} \underline{\Sigma} \underline{P} \underline{P}^{\dagger} \right]^{-1} \\ &= z^{-1} \left[ \underline{P} \mathbbm{1} \underline{P}^{\dagger} - z\underline{P} \underline{\varepsilon} \underline{P}^{\dagger} - z\underline{P} \underline{P}^{\dagger} \underline{\Sigma} \underline{P} \underline{P}^{\dagger} \right]^{-1} \\ &= z^{-1} \left[ \underline{P} \left( \mathbbm{1} - z\underline{\varepsilon} - z\underline{P}^{\dagger} \underline{\Sigma} \underline{P} \right) \underline{P}^{\dagger} \right]^{-1} \\ &= \underline{P} \left( z\mathbbm{1} - \underline{\varepsilon} - \underline{P}^{\dagger} \underline{\Sigma} \underline{P} \right)^{-1} \underline{P}^{\dagger}. \end{split}$$

The matrices  $\underline{P}$  can only be identified with the projection matrices  $\overline{\mathcal{P}}_{Ln}(\mathbf{k})$  if the projec-

tion matrices are square and unitary as above. In the general case  $L \neq n$  self-consistency loops based on either formalism will give different results.

#### 2.2.3 Charge Self-consistency

The central quantity for the charge self-consistent implementation is the difference of charge densities  $\Delta N_{nn'}(\mathbf{k})$ , see section 1.5.4. In the PLO approach it is written using the Bloch space quantities as

$$\Delta N_{nn'}(\mathbf{k}) = \frac{1}{\beta} \sum_{n} \left\{ \underline{\underline{G}}^{\mathrm{KS}}(\mathbf{k}, i\omega_n) \left[ \underline{\underline{\Sigma}}^{\mathrm{B}}(\mathbf{k}, \omega) - (\mu - \mu^{\mathrm{KS}}) \mathbb{1} \right] \underline{\underline{G}}^{\mathrm{B}}(\mathbf{k}, i\omega_n) \right\}_{nn'}$$

After each DFT step the projection matrices have to be recalculated, to account for changes brought about by the feedback of the self-energy into the charge. A charge self-consistent implementation within PAW is possible, in the same way as discussed in section 1.5.4, see Ref. [10, 135, 136]. The only difference in the PAW framework will be the PAW decomposition, Eq. (1.3.3) of the charge density, see section 1.3.3:

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + \sum_{R} \left( n_{R}^{1}(\mathbf{r}) - \tilde{n}_{R}^{1}(\mathbf{r}) \right),$$

where as usual the *one center* parts (indicated by a 1 in the exponent) exist only inside the augmentation sphere. The three parts are

$$\tilde{n}(\mathbf{r}) = \sum_{n} f_{n} \langle \tilde{\psi}_{n} | \tilde{\psi}_{n} \rangle + \tilde{n}_{c}(\mathbf{r})$$

$$n_{R}^{1}(\mathbf{r}) = \sum_{i,j \in R} D_{ij} \langle \phi_{j} | \phi_{i} \rangle + n_{c,R}(\mathbf{r})$$

$$\tilde{n}_{R}^{1}(\mathbf{r}) = \sum_{i,j \in R} D_{ij} \langle \tilde{\phi}_{j} | \tilde{\phi}_{i} \rangle + \tilde{n}_{c,R}(\mathbf{r}).$$

The core charges  $n_c$  will not be modified by the charge self-consistent DFT+DMFT procedure, since they are fixed (frozen core approximation). Thus, the quantity we need for the updated one-center parts is the modified one center density matrix

$$D_{ij} = \sum_{n} \langle \tilde{\psi}_n | \tilde{p}_j \rangle \left( f(\varepsilon_n(\mathbf{k})) \delta_{nn'} + \Delta N_{nn'}(\mathbf{k}) \right) \langle \tilde{p}_i | \tilde{\psi}_n \rangle, \quad i, j \in \mathbb{R},$$

that now contains the difference between DFT and DFT+DMFT charges. In section 2.4 we demonstrate the implementation with charge-self-consistency using an exact diagonalization impurity solver.

#### 2.2.4 Transformations of the basis

The unorthonormalized projection matrices obtained from the DFT code contain an angular part represented by real spherical harmonics  $K_{lm}$  (also called cubic harmonics) corresponding to the angular momentum l, see section 1.5.2, for a definition. They are defined inside the code with respect to a fixed cubic coordinate system. In systems with a cubic symmetry this is the perfect choice and the projection matrices can be used directly. However, in many systems the local symmetry is different from cubic or the local coordinate system differs from the intrinsic coordinate system of the DFT code. In such cases local rotations of the orbitals have to be considered in order to be able to obtain the correct orbitally resolved density of states and correct projectors in the PLO framework. In this context *local* means that the orbitals are rotated on the site of the correlated atom. The transformation properties under rotations of the cubic harmonics  $Y_{lm}$  [362, 100] and were given in, e.g., Ref. [402]. In general, a rotation is carried out using a unitary transformation

$$\underline{\underline{P}}' = \underline{\underline{T}} \, \underline{\underline{P}} \, \underline{\underline{T}}^{\dagger},$$

where  $\underline{P}'$  is the rotated projection matrix and  $\underline{T}$  is the transformation matrix. How the elements of the rotation matrix are calulated for cubic harmonics will be given for completeness below, see also Refs. [402, 192].

Let C and C' be two Cartesian coordinate systems. The two coordinate systems are interconnected by a unitary transformation, that can be expressed using the three Euler angles  $(\alpha, \beta, \gamma)$ . The convention used here for the definition of the Euler angles is the so-called z, y, z convention, that is the transformation consists of successive rotations of  $\gamma$ ,  $\beta$  and  $\alpha$  about the  $e_3$ ,  $e_2$  and  $e_3$  axes of the original *unrotated* coordinate system C. The Euler angles have the domain of definition

$$0 \le \alpha \le 2\pi$$
 ,  $0 \le \beta \le \pi$  and  $0 \le \gamma \le 2\pi$ .

The coordinates transform accordingly with the unitary matrix  ${f R}$ 

$$\hat{\mathbf{R}} = \begin{pmatrix} \cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma & \cos\alpha\sin\gamma + \sin\alpha\cos\beta\cos\gamma & -\sin\beta\cos\gamma \\ -\cos\alpha\cos\beta\sin\gamma - \sin\alpha\cos\gamma & \cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma & \sin\beta\sin\gamma \\ \cos\alpha\sin\beta & \sin\alpha\sin\beta & \cos\beta \end{pmatrix}.$$

Under rotations of the coordinate system the complex spherical harmonics transform according to

$$Y_{lm}(\theta',\phi') = \sum_{m'} D^l_{m'm}(\alpha\beta\gamma)Y_{lm'}(\theta,\phi),$$

where we have introduced the Wigner D-matrices (the convention here differs slightly

from Wigners original work, see footnote on page 52 of [362]). The D matrices can be written as

$$D^{l}_{m'm}(\alpha,\beta,\gamma) = e^{im'\alpha} d^{l}_{m'm}(\beta) e^{im\gamma}, \qquad (2.2.15)$$

where the small d symbol can be written in the following way [362]

$$d_{m'm}^{l}(\beta) = \left[ (l+m)!(l-m)!(l+m')!(l-m')! \right]^{1/2} \times \sum_{\kappa} \frac{(-1)^{\kappa}}{(l-m-\kappa)!(l+m-\kappa)!(\kappa+m'-m)!\kappa!} \times \left(\cos\frac{\beta}{2}\right)^{2l+m-m'-2\kappa} \left(-\sin\frac{\beta}{2}\right)^{m'-m+2\kappa}.$$

The sum in above formula runs over all values of the integer  $\kappa$  for which the factorial arguments are defined. From the knowledge of Eq. (2.2.15) and the definition of the  $K_{lm}$ , see section 1.5.2, one can deduce the transformation properties of the cubic harmonics under rotations [402]. For brevity we omit the argument of the small d function and write  $d_{m'm}^l(\beta) =: d_{m'm}^l$ . Furthermore, we omit the arguments of the cubic harmonics on the right hand side of the following equations, since they are always  $(\theta, \phi)$ . The transformations thus read

$$\begin{split} K_{l,+m}(\theta',\phi') &= (-1)^m d_{0m}^l \cos(m\gamma) \sqrt{2} K_{l0} + \sum_{m'=1}^l \left\{ \left[ (-1)^{m+m'} d_{m'm}^l \cos(m\gamma + m'\alpha) \right. \\ &+ (-1)^m d_{-m'm}^l \cos(m\gamma - m'\alpha) \right] K_{l,+m'} + \left[ (-1)^{m+m'} d_{m'm}^l \sin(m\gamma + m'\alpha) \right. \\ &- (-1)^m d_{-m'm}^l \sin(m\gamma - m'\alpha) \right] K_{l,-m'} \right\} \\ K_{l,-m}(\theta',\phi') &= (-1)^{m+1} d_{0m}^l \sin(m\gamma) \sqrt{2} K_{l0} + \sum_{m'=1}^l \left\{ \left[ (-1)^{m+m'+1} d_{m'm}^l \sin(m\gamma + m'\alpha) \right. \\ &+ (-1)^{m+1} d_{-m'm}^l \sin(m\gamma - m'\alpha) \right] K_{l,+m'} + \left[ (-1)^{m+m'} d_{m'm}^l \cos(m\gamma + m'\alpha) \right. \\ &- (-1)^m d_{-m'm}^l \cos(m\gamma - m'\alpha) \right] K_{l,-m'} \right\} \\ K_{l0}(\theta',\phi') &= d_{00}^l K_{l0} + \frac{1}{\sqrt{2}} \sum_{m'=1}^l \left\{ \left[ (-1)^{m'} d_{m'0}^l + d_{-m'0}^l \right] \cos(m'\alpha) K_{l,+m'} \\ &+ \left[ (-1)^{m'} d_{m'0}^l + d_{-m'0}^l \right] \sin(m'\alpha) K_{l,-m'} \right\}. \end{split}$$

Apart from rotations also linear combinations of basis functions can, and some times have to be used, to capture the local symmetry of the system correctly. Especially when using a QMC based impurity solver one has to take care to keep the hybridization function diagonal to avoid a sign problem, see, e.g., Ref. [111]. This is a nontrivial problem, since the hybridization function is energy dependent and in general one *unique* basis transformation will *not* make it diagonal at all energy points. One useful and often used choice is to choose the basis such that the local crystal field, i.e. the on-site energy matrix

$$\varepsilon_{LL'} = \frac{1}{N} \sum_{\mathbf{k}}^{N} H_{LL'}^{W}(\mathbf{k})$$

is diagonal. This is equivalent to diagonalizing the static tails of the real part of the hybridization function on Matsubara frequencies  $\varepsilon_{LL'} = \text{Re}\Delta_{LL'}(i\omega \to \infty)$ . The quantity  $\varepsilon_{LL'}$  is often called the crystal field. By diagonalizing it we obtain the crystal field basis, which reflects the local symmetry of the system in the static limit. In the language of crystal field theory the basis is modified by the effect of the static electric fields of the ligands [81]. Other choices may be more suitable for situations where the hybridization function is non-diagonal, e.g., a transformation of the basis which minimizes the off diagonal elements on average. In a charge self-consistent calculation for a system with a non cubic local symmetry the basis has to be transformed after every DFT step.

We want to note that if a basis rotation is performed it is imperative to also transform the Coulomb interaction tensor  $U_{ijkl}$  in the subsequent many-body treatment. The tensor is usually computed in the basis of complex spherical harmonics, see section 1.5.2, and subsequently transformed to the cubic harmonic basis. If one chooses to rotate the orbital basis or to use linear combinations of the cubic harmonics, like the crystal field basis, the Coulomb interaction tensor has to be transformed accordingly. Schematically one can write

$$U_{ijkl}' = \underline{\underline{T}} U_{ijkl} \, \underline{\underline{T}}^{\dagger}$$

If one uses only the density-density interaction matrix  $U_{ij}^{\sigma\sigma'}$  the transformed densitydensity part  $(U_{ij}^{\sigma\sigma'})'$  can be computed *only* after the full tensor has been transformed.

#### 2.2.5 DFT++ for inequivalent atoms and layered systems

In the preceding sections we have tacitly assumed that the system we study within DFT++ contains a single correlated site or if more than one atom is contained in the unit cell that these atoms are all equivalent or can be made equivalent by application of symmetry

operations. This is, however, not true in general and we will discuss here how we can deal with inequivalent sites within DFT++ and also how layered systems can be treated. The conceptual step to generalize the DFT++ formalism to systems containing different correlated atoms is rather small. Our formalism based on quantities in Bloch space and projections onto correlated orbitals can deal with such a situation very naturally. Let us assume we have correlated atoms located on sites **R** within the unit cell. For a layered system with equivalent atoms within one layer the index **R** can be understood as the layer index. The subsequent discussion applies in the same way to this case as to the more general case with inequivalent atoms. The necessary starting point, the full Green function of the system in Bloch basis, is calculated without any modification, since it carries only band indices. The projection matrices on the other hand now attain a site index:  $\overline{\mathcal{P}}_{Ln}^{\mathbf{R}}(\mathbf{k})$ . It is understood that local basis transformations, can be performed on every site individually and absorbed into the projection matrices. The local Green function for the atom on site **R** is then just

$$G_{LL'}^{\mathbf{R}}(\omega) = \sum_{\mathbf{k},nn'} \overline{\mathcal{P}}_{Ln}^{\mathbf{R}}(\mathbf{k}) G_{nn'}^{\mathrm{B}}(\mathbf{k},\omega) \overline{\mathcal{P}}_{L'n'}^{\dagger \mathbf{R}}(\mathbf{k}).$$

The calculation can be thus started in the usual way by beginning with the Bloch Green function obtained from DFT. Now, one Anderson model is setup and solved for each correlated site where every site has its own bath Green function  $\mathcal{G}^{\mathbf{R}}$  and Coulomb interaction tensor  $U_{ijkl}^{\mathbf{R}}$ . The total chemical potential  $\mu$  is of course the same for the whole system. A small caveat is in order in the context of the calculation of the self-energy and a possible DMFT self-consistency. Since the local self-energy will be a site dependent quantity  $\Sigma_{LL'}^{\mathbf{R}}(\omega)$ , the upfolding to Bloch space will produce a set of self-energies in Bloch basis containing only the upfolded self-energy contribution of site  $\mathbf{R}$  that have to be summed up to obtain the new full Bloch basis self-energy

$$\Sigma_{nn'}^{\rm B}(\mathbf{k},\omega) = \sum_{\mathbf{R}} \Sigma_{nn'}^{\mathbf{R},{\rm B}}(\mathbf{k},\omega) = \sum_{\mathbf{R},LL'} \overline{P}_{Ln}^{\dagger\mathbf{R}}(\mathbf{k}) \left[ \Sigma_{LL'}^{\mathbf{R}}(\omega) + \Sigma_{\rm DC}^{\mathbf{R}} \right] \overline{P}_{L'n'}^{\phantom{\dagger\mathbf{R}}}(\mathbf{k}).$$

This can be then used as usual to obtain the new Bloch Green function etc. Since the correlated sites can be different atoms with different charges and different Coulomb interaction matrices the double counting potential  $\Sigma_{DC}^{\mathbf{R}}$  will also be site dependent. Within a DMFT self-consistency loop the procedure outlined in section 1.4.4 has not to be modified greatly. The only modification is the introduction of an additional outer loop over the correlated sites that controls the repeated application of the impurity solver to each site. The chemical potential, the double counting potentials, and the respective bath Green functions  $\mathcal{G}^{\mathbf{R}}$  are updated after the self-energies on each site have been obtained and applied in combination.



**Figure 2.2.1:** Schematic illustration of the DFT++ for vacuum states using the example of an atom adsorbed on a surface. The real scanning tunneling microscopy (STM) situation, where a metallic tip probes the impurity is modeled by an empty sphere placed above the impurity for the evaluation of the green function within. The (exponentially decaying) wavefunction in the vacuum region is indicated by the background.

#### 2.2.6 DFT++ for vacuum states

The presented DFT++ method in PAW basis can also be used to obtain the local density of states in the vacuum region above a correlated sample, a quantity related to scanning tunneling microscopy (STM) [413]. We will give here a general outline and present first promising results. The additional ingredient required here is the capability of the code to include so-called empty spheres in its formalism. An empty sphere is just an atomic sphere, where projections on different augmentation channels can be performed as usual, but without an atom inside the sphere. One thus obtains a projection of the wave function of the system in the vacuum on different channels. In the context of DFT alone we have exploited the capability of VASP to perform projections inside empty-spheres in the recent calculation of graphene on top of a Ni(111) surface [96]. In this way we were able to compute the local density of states (LDOS) in the vacuum, and compare calculations directly to scanning tunneling microscope measurements. We want to emphasize that the STM does *not* measure the LDOS on the surface atom itself and direct comparison between the atomic LDOS and STM spectra is dangerous and can lead to misleading interpretations of STM images and the physics behind them, see e.g. Ref. [62].

Since the VASP code treats empty spheres in the same way as atoms projection matrices

 $\underline{\mathcal{P}}^{\nu}$  for the vacuum region can be constructed analogously to the bulk projection matrices  $\underline{\mathcal{P}}$ . The procedure begins as usual with the calculation of the self-energy on the correlated sites via an impurity solver and its subsequent upfolding to the Bloch basis set. As a second step we project the full Bloch Green function onto orbitals inside an empty sphere in the vacuum region

$$G_{ll'}^{\mathcal{V}}(\omega) = \sum_{\mathbf{k},nn'} \overline{\mathcal{P}}_{ln}^{\mathcal{V}}(\mathbf{k}) \left\{ \left[ G_{nn'}^{\mathrm{B}}(\mathbf{k},\omega) \right]^{-1} - \Sigma_{nn'}^{\mathrm{B}}(\mathbf{k},\omega) \right\}^{-1} \overline{\mathcal{P}}_{l'n'}^{\dagger \mathcal{V}}(\mathbf{k}).$$
(2.2.16)

Since we rely on the Tersoff-Hamann approximation in this case, the projection is customarily performed onto an s orbital (l = 0), although also other symmetries of possible tip states can be used. Schematically, the situation is illustrated in Fig. 2.2.1 for a single correlated impurity adsorbed on a surface. The empty sphere *models* the tip used for scanning tunneling or related techniques. Now, that we have the vacuum Green function we can obtain the local densities of states for the vacuum including local electronic correlations on the impurity. This method allows to see the signatures of many-body effects, like the Kondo effect in the vacuum.

## **2.3 Benchmark: Cubic Perovskite SrVO<sub>3</sub>**

The correlated metal SrVO<sub>3</sub> has become a common testing ground for first-principles many-body techniques and has been the subject of multiple theoretical and experimental investigations [170, 116, 276, 171, 383, 259, 307, 329, 464, 433, 398, 306, 101, 6]. It has a perfectly cubic perovskite structure (space group Pm3m) with a lattice constant of 3.84 Å [119]. The vanadium ion is surrounded by oxygen ligands in a perfectly octahedral configuration leading to a splitting of the *d* orbitals into  $t_{2g}$  and  $e_g$  crystal-field states. The density of states (DOS), and band-structure, figure (2.3.2), obtained using the VASP code and LDA reveals three isolated bands at the Fermi level which are formed by the degenerate  $t_{2g}$  states of vanadium. The bandwidth of this block amounts to 2.5 eV. The Van Hove singularity 1eV above the Fermi level in the DOS corresponding to these bands shows their predominantly two dimensional character. The  $e_g$  states of vanadium are mostly located above the  $t_{2g}$  bands as conventional ligand-field theory would suggest [81]. The bands below the V *d* bands, extending from -8 eV to -2 eV are predominantly of oxygen 2*p* character, but also show hybridization between O 2*p* and the V *d* states, figure 2.3.2.

The whole series of transition metal oxides  $SrVO_3$ -Ca $VO_3$ -La $VO_3$ -YVO\_3 ranging from the metal  $SrVO_3$  to the insulator  $YVO_3$  can be classified, following Zaanen, Sawatzy and Allen [466], as Mott-Hubbard systems, since the ligand *p* bands are clearly separated from the transition metal *d* states at the Fermi level. Thus, the low energy physics of the mate-



**Figure 2.3.2:** DFT(LDA) total and orbital projected density of states for SrVO<sub>3</sub>, DFT(LDA) band structure of SrVO<sub>3</sub> with fatbands highlighting the V  $t_{2g}$  (blue) states and the O 2p states (red).

rial is mainly determined by the three V  $t_{2g}$  bands around the Fermi level. This suggests to use only these bands for the construction of the effective low energy Hamiltonian for the DFT+DMFT calculations. Such a construction, however, will not give any information on the behaviour of the O 2p states, yet this might be of crucial importance for the description of the physics of the material. An important example where this is the case is NiO, where the charge-transfer behaviour of the system cannot be described by taking only the Ni 3d states into account [234, 235, 194].

#### 2.3.1 Tight-binding discussion of the three band case

The tight-binding like Hamiltonian created via the PLO method, Eq. (2.2.11), from only the V  $t_{2g}$  states is compared to other schemes for generating Wannier functions, the maximally localized Wannier functions (MLWF) as defined by Marzani and Vanderbilt [278] in the PAW and the full-potential linearized augmented plane-wave (FLAPW) basis sets and the Nth order muffin-tin method (NMTO) [14] in table 2.3.1. The nearest neighbor hopping clearly dominates, which shows the short range of the bonding in SrVO<sub>3</sub>. The three compared methods, although very different in cost and conception, yield virtually identical descriptions of the system. An explicit comparison of the PLO method with MLWFs generated by the WANNIER90 package [294] yields quantitative agreement with the present implementation. This underlines the validity of the our implementation. This is another instance of the known fact, that the first guess in the procedure of maximal localization in the MLWF scheme is usually already a very good one for transition metal oxides [232]. Since our implementation is such a *first guess* procedure without any additional localization procedure the good agreement is not surprising. Additionally, the specifics of the system, like its high symmetry and the well separated block of  $t_{2g}$  bands

xyz	001	100	011	101	111	002	200
PLO(VASP)	-261.5	-28.5	-87.1	6.7	-6.4	7.5	0.1
MLWF(VASP+WANNIER90)	-261.5	-28.5	-87.2	6.7	-6.4	7.5	0.1
MLWF(FLAPW)	-266.8	-29.2	-87.6	6.4	-6.1	8.3	0.1
NMTO(LMTO-ASA)	-264.6	-27.2	-84.4	7.3	-7.6	12.9	3.5

**Table 2.3.1:** Intersite hopping integrals  $t_{yz,yz}^{xyz}$  for SrVO<sub>3</sub> from PLO compared with maximally localized Wannier functions in different basis sets and Nth order muffin-tin orbitals (reference data from Ref. [244]). Energies in meV.

make it a rather elementary case.

#### **2.3.2** Comparison of different PLO methods

Differences in the different PLO methods can become significant if the oxygen 2p bands are included. These states are essential in understanding the physics of many transition metal oxides. Their importance for the physics of the SrVO<sub>3</sub>-CaVO<sub>3</sub>-LaVO<sub>3</sub>-YVO<sub>3</sub> series has been pointed out by Mossanek [293]. The oxygen 2p bands are located below the V  $t_{2g}$  block and hybridize considerably with them as shown in figure 2.3.2. The number of bands to be taken into account in the Wannier construction is now 12. The resulting local densities of states (LDOS) for the effective three band model are shown in figure 2.3.3. While the LDOS created by the PLO(A) and PLO(V) methods are virtually indistinguishable, the approximation PLO(0) creates a different LDOS. The distribution of the spectral weight is different in the PLO(0) method. In fact, the amplitudes of the projectors in PLO(V) and PLO(A) are close to identical, while the PLO(0) projectors can differ significantly from the other two methods, leading to the difference in the resulting LDOS. The difference  $\delta_n(\mathbf{k})$  between the projections PLO(0) ( $\overline{\mathcal{P}}_{Ln}(\mathbf{k})$ )<sub>0</sub> and PLO(A) ( $\overline{\mathcal{P}}_{Ln}(\mathbf{k})$ )<sub>A</sub> is shown pictorially in figure 2.3.3 for every band n. Here the total difference between the amplitudes of the  $t_{2q}$  projectors

$$\delta_n(\mathbf{k}) = \sum_L \left| \left| \overline{\mathcal{P}}_{Ln}(\mathbf{k})_A \right| - \left| \overline{\mathcal{P}}_{Ln}(\mathbf{k})_0 \right| \right|^2$$
(2.3.1)

has been computed. For better visibility 15 eV  $\delta_n(\mathbf{k})$  is shown as the width of the corresponding bands in Fig. 2.3.3. On the same scale the difference between PLO(A) and



**Figure 2.3.3:** Effective impurity local density of states as obtained by PLO(V) (green), PLO(A) (red), and PLO(0) (blue) methods using the V  $t_{2g}$  as well as the O 2p bands in the projection. Difference between the amplitudes of the orthonormalized  $t_{2g}$  projectors in the PLO(0) and PLO(A) methods for V  $t_{2g}$  as well as the O 2p bands in the projection. 15 eV· $\delta_n(\mathbf{k})$  (see equation 2.3.1) is shown as the width of the corresponding bands.

PLO(V) would be by far smaller than the linewidth used for drawing the LDA bands in figure 2.3.3. The values attained in this case are  $\delta_n(\mathbf{k}) < 5.5 \cdot 10^{-5}$ . This figure gives a qualitative picture of where the higher order terms of the expansion equation (2.2.4) give significant contributions. This is the case outside of an energy window extending from -0.5 eV to -2.5 eV where no significant difference between PLO(0) and PLO(A) is observed. The quite large differences outside this window stem from the fact that the first order projector is constructed as the atomic eigenfunction and thus the projected bands from it overweight the lower lying bands leading to an underestimation of the spectral weight at and above the Fermi level. This leads to a higher occupancy of the effective impurity in the PLO(0) approximation as compared to the other methods. The PLO(A)and PLO(V) methods yield impurity occupancies of 0.7 electrons per orbital (including spin degeneracy), while the PLO(0) yields a filling of 0.85. This stems from the fact, that the impurity level is much lower in PLO(0), because the lower lying bands are overweighted. In fact, the impurity level (static crystal field) lies at about -1.1 eV when using the PLO(0) method, whereas it it is centered at approximately -0.6 eV for the other methods. A difference between the PLO(A) and PLO(V) constructions is that in the former a specific radial function  $|\phi_{\nu=0}\rangle$  is chosen for the projection, while in the latter an averaging over radial dependencies takes place by the inclusion of general overlaps  $\langle \phi_{\nu} | \phi_{\nu'} \rangle$ . This did not make any noteworthy difference here or in other systems we have considered, though.



**Figure 2.3.4:** Impurity spectral function obtained by DFT+DMFT(QMC) for U = 4 eV at the inverse temperature  $\beta = 20 \text{ eV}^{-1}$ . Only the three V  $t_{2g}$  bands were used in the projection. Momentum resolved impurity spectral function obtained by DFT+DMFT(QMC) for U = 4 eV, for the same projection. For comparison the DFT(LDA) band structure of the V  $t_{2g}$  Bloch states is shown as white lines.

#### 2.3.3 DFT+DMFT calculations

Let us now turn to the results obtained by DFT+DMFT using the projection scheme explained above. We have performed calculations using the HF-QMC solver for the material. We obtain momentum resolved spectral functions and are thus also able to compare our results with recent ARPES studies [464, 463]. For the calculations including only the  $t_{2g}$  bands we have used the on-site interaction U = 4 eV and for the calculations including ing also the O p bands U = 6 eV was used. In all cases J = 0.65 eV was applied. This set of parameters was chosen to be able to compare with earlier studies of the material that used the same values [244, 12]. Calculations were performed at inverse temperature  $\beta = 20 \ eV^{-1}$  using 200 time slices and  $10^6$  Monte Carlo sweeps. Spectral functions were obtained from the measured Green function via the maximum entropy method [184].

First, we examine results obtained by the minimal three band model obtained only from the three V  $t_{2g}$  bands. As in earlier studies [244, 12, 306, 6] we obtain the local impurity spectral function for the V  $t_{2g}$  states. The typical three-peak structure is apparent in the spectral function in figure 2.3.4, with upper and lower Hubbard bands at  $\sim 3$  eV above and at  $\sim 2$  eV below the Fermi level, respectively. The data agree very well with other studies [244, 12, 306, 6]. We also estimated the mass renormalization

$$Z = \left[1 - \left.\frac{\partial}{\partial \omega} \text{Re}\Sigma(\omega)\right|_{\omega=0}\right]^{-1}$$

from the imaginary part of the self-energy at the first Matsubara frequency to be Z = 0.61, which means, that the mass enhancement is  $m^*/m \sim 1.65$  in accordance with ARPES estimates of  $m^*/m \sim 1.8 \pm 0.2$  [464]. We also computed the momentum-resolved spectral



Figure 2.3.5: Orbitally resolved spectral function obtained by DFT+DMFT(QMC) and PLO(0) (left) and PLO(V) (right) for U = 6 eV. The V  $t_{2g}$  and O 2p states were used in the projection.

function from the QMC data

$$A_i(\mathbf{k},\omega) = -\frac{1}{\pi} \mathrm{Im} \left(\omega + \mu - \varepsilon_i(\mathbf{k}) - \Sigma_i(\omega)\right)^{-1},$$

which is shown in figure 2.3.6 together with the three V  $t_{2g}$  DFT(LDA) bands for comparison. The Hubbard bands are clearly recognizable as non-coherent features around -2eV and in the range of 2 eV to 4 eV above the Fermi level. The agreement with ARPES energy dispersions is generally quite good, especially the bottom of the quasiparticle band is found at -0.6 eV in contrast to the LDA value of -1 eV [464]. The overall width of the quasiparticle bands around the Fermi level is reduced to about 1.5 eV, similarly to earlier reported data [306].

Since the inclusion of the oxygen 2p states into the model is important we also show results for that situation. The aforementioned problems that occur in some systems when including ligand states in the calculation do not appear here, the approximation of  $U_{pp} = U_{pd} = 0$  thus seems a posteriori justified, see discussion at the end of section 2.2. The Wannier functions created in this case will be more localized than in the  $t_{2g}$  only model, because they are now composed of a larger number of Bloch functions. The effective impurity problem is now constructed encompassing also the p bands and thus also the residual d spectral weight contained in them, see figure 2.3.2. The impurity spectral functions will now also have some spectral weight inside the oxygen block. The spectral functions obtained via two different PLO methods while using QMC as impurity solver within DMFT are shown in figure 2.3.5 for PLO(0) and PLO(V), respectively. In this case the parameter values U = 6 eV and J = 0.65 eV were applied. The impurity clearly shows the spectral weight inside the oxygen block which is stronger for the PLO(0) for



**Figure 2.3.6:** Momentum resolved impurity spectral function obtained by DFT+DMFT(QMC) and PLO(V) for U = 6 eV. The V  $t_{2g}$  and the O 2p states were used in the projection (12 bands). Again the LDA band structure of the V  $t_{2g}$  and O 2p Bloch states is shown for comparison using white lines.

reasons outlined above. The quasi-particle renormalization is Z = 0.62 (from PLO(V), from PLO(0) it is slightly higher at Z = 0.66) in this case, which is in agreement with the previous  $t_{2g}$ -only estimate. Along with the impurity spectral function figure 2.3.5 also shows the spectral function decomposed by the respective Bloch bands. These can be obtained by applying the projection matrices and thus upfolding the impurity back to the Bloch basis.

The assignment of a certain band to a certain group, say O p is performed using the dominant character of the band, as in the DFT analysis. The lowest lying nine bands are thus labeled as oxygen bands, the following three bands are labeled V  $t_{2g}$ . The differences between the PLO(0) and PLO(V) methods carry over into the DFT+DMFT description. The effective impurity shows considerably more spectral weight inside the oxygen block around -5 eV for the PLO(0) consistent with the LDA LDOS. While the PLO(A) and PLO(V) yield occupancies of 0.66 per orbital one finds 0.81 with PLO(0). The differently distributed spectral weight also gives rise to different densities of states at the Fermi level. For the PLO(V) case it is  $\sim 0.62 \text{ eV}^{-1}$  while it is reduced to  $\sim 0.56 \text{ eV}^{-1}$  for PLO(0). Furthermore, the quasi-particle peak is considerably reduced in PLO(0) at the expense of the enhanced spectral weight at lower energies. The upper and lower Hubbard bands also appear shifted in the direction of the Fermi level by some 0.5 eV. These effects show, that the PLO(0) approximation does not capture the whole spectral function, calculated using 12 bands in the Hamiltonian, is shown in figure 2.3.6. The  $t_{2g}$  bands around the

Fermi level are in close agreement with the ones obtained in the  $t_{2g}$ -only case, showing a considerable renormalization as compared to the LDA bands, as before in accord with experimental studies. The upper Hubbard band is visible at 3 eV above the Fermi level, while the lower Hubbard band is hidden inside the oxygen bands starting at about 2 eV below the Fermi energy. The oxygen bands appear slightly broadened and shifted with respect to the  $t_{2g}$  bands, but essentially unchanged as compared to the LDA bands.

The inclusion of oxygen states gives rise to the so-called double counting problem of DFT+DMFT, or more generally of any DFT++ method which includes correlated and uncorrelated states. To avoid a double counting in the energy a term  $\hat{H}_{DC} = \mu_{DC} \sum_{m,\sigma} \hat{n}_{m,\sigma}$ , with the double counting potential  $\mu_{DC}$  and orbital index m, has to be subtracted from the Hamiltonian, because the local Coulomb interaction is already contained in DFT in an averaged manner, see section 1.5 and especially chapter 3. In the present case we used a constraint on the electronic charge to define a double counting correction. The occupancies of the correlated subspace computed from the local non-interacting Green function and the interacting impurity Green function are required to be identical, which can be stated in the following form

$$\operatorname{Tr} G_{mm'}^{\operatorname{imp}}(\beta) \stackrel{!}{=} \operatorname{Tr} G_{mm'}^{0,\operatorname{loc}}(\beta).$$
(2.3.2)

The double counting potential  $\mu_{DC}$  is iteratively adjusted to fulfill equation (2.3.2). The most obvious effect of a change in the double counting is a shift of the oxygen states versus the V d states. The effect of the double counting is not so dramatic for the case at hand as shown in Ref. [12], yet it influences quantitative results. This problem could be resolved within DFT+DMFT by calculating the interaction between the d and the p states  $(U_{pd})$  and within the p shell  $(U_{pp})$  and including both in the self-consistent calculation.

## 2.4 Charge Self-consistency: The Volume of paramagnetic bcc Iron

We have implemented the charge self-consistent DFT+DMFT methodology along the lines described in section 2.2.3. Presently, we have interfaced the PAW based VASP code with a CT-QMC(HYB) solver that works in the segment picture and an exact diagonalization (ED) solver using Lanczos' method, cf. section 1.6. The charge self-consistent DFT+DMFT allows for the precise determination of total energies including local electronic correlation effects. It is, however, important to choose the right formula to account for the contribution of electronic correlation to the total energy. As discussed in section 1.5.4 one can use the Galitskii-Migdal formula if the Green functions and self-energies are smooth enough for a correct evaluation of the involved Matsubara sum. Especially in QMC this is usually not the case due to the statistical noise inherent in the method. A



**Figure 2.4.7:** Total energy versus unit cell volume curves of bcc iron for LDA and charge selfconsistent LDA+DMFT(ED) and LDA+DMFT(QMC). The energies are plotted with respect to the minimum.

formula based on the double occupancy can be used in that case, see section 1.5.4.

Here we present as a first application a calculation of the unit cell volume of paramagnetic iron in the body-centered cubic (bcc) crystal structure using both solvers. This structure is referred to as  $\alpha$  iron and is the room temperature structure of ferromagnetic iron, see e.g. [249] for a phase diagram. We use a projection onto the eight lowest bands of s - p - d character. The calculations were performed with interaction parameters U = 2.3eV and J = 0.9eV [256] using the self-consistent fully localized limit double counting [399], see chapter 3, at inverse temperature  $\beta = 40eV^{-1}$ . To guarantee a precise evaluation of charges and energies from Matsubara sums we used 4000 Matsubara frequencies. This reduced the mismatch between the total density calculated within the solvers via a Matsubara sum and the density calculated within the DFT code from the updated charge density to  $\sim 10^{-5}$ . Inside the ED solver we used a ten site cluster to model the 3d shell of iron, i.e. 5 orbitals and 5 bath sites. Apart from the different ways employed for the energy calculation, the two solvers differ also in the local Coulomb interaction: QMC uses the density-density interaction, while ED is capable of using the full rotationally invariant interaction tensor, cf. section 1.5.2.

The calculated energy versus volume curves E(V) for LDA, LDA+DMFT(ED) and LDA+DMFT(QMC) are shown in Fig. 2.4.7.

	LDA	LDA+DMFT(QMC)	LDA+DMFT(ED)	GGA [467]	Exp. [467]
$V_0$	65.8	71.4	$\sim 71.0$	69.9	79.5
$B_0$	301	192	$\sim 190$	288	172
Β'	4.81	4.97	$\sim 5.0$	4.76	5.0

**Table 2.4.2:** The equilibrium cell volume  $V_0((a.u.)^3)$ , bulk modulus at zero pressure  $B_0$  (GPa) and its pressure derivative B' obtained from a fit of the energy versus volume curves to Eq. (2.4.1). The results of LDA+DMFT(ED) were obtained from a fit including only few points close to the equilibrium volume, where the E(V) curve is approximately parabolic. For comparison a paramagnetic GGA calculation and experimental data for ferromagnetic iron is shown. The data have been reported in Ref. [467].

The effect of the relatively moderate local Coulomb interaction is already considerable. The minimum is shifted to higher volumes and a softening towards larger volumes is clearly visible in comparison to the LDA result. We observe that both solvers agree close to the equilibrium volume, while deviations between ED and QMC appear away from it. This can be traced back to factors that are actually all intertwined. First, ED performs a fitting of the hybridization function using a single bath site in our model, which can be inadequate. Second, albeit starting from the same point the two solvers converge to slightly different fillings of the 3d shell away from the equilibrium. This is connected to the double counting, which is a parameter that acts as an impurity chemical potential, see the next chapter. Away from equilibrium ED apparently converges to a different solution due to its different representation of the bath and a different value of the double counting potential.

For a more quantitative analysis we fitted the energy versus volume curves E(V) with the third order Birch-Murnaghan equation of state [297, 298, 45]

$$E(V) = E_0 + \frac{9V_0B_0}{16} \left\{ \left[ \left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1 \right]^3 B' + \left[ \left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1 \right]^2 \left[ 6 - 4 \left(\frac{V_0}{V}\right)^{\frac{2}{3}} \right] \right\}, \quad (2.4.1)$$

where  $V_0$  is the equilibrium volume,  $B_0$  the bulk modulus and B' its pressure derivative. For the form used here and a comparison to other equations of state, like the Vinet equation, see, e.g., Refs. [149, 102]. The results of the fit are shown in table 2.4.2. They show an increased equilibrium volume and a reduction of the zero pressure bulk modulus by over 30%. We compare our data with previous DFT studies and experiments, compilations of data can be found in Refs. [221, 467]. Our LDA data are similar to the ones obtained from a GGA calculation in the paramagnetic phase by Zeng et al. [467], the LDA shows an even stronger overbinding tendency and a larger bulk modulus. A sound comparison to experiment is difficult, since we did not include magnetic order in our calculations. In the LDA+DMFT calculations we find an equilibrium volume close to the GGA result and a much smaller bulk modulus that is quite close to the experimental value. It is known that the inclusion of magnetic order on the level of GGA already gives satisfactory results for lattice constants and bulk moduli of iron and other transition metals, improving considerably over LSDA, see e.g. [221, 467]. Our data show that the inclusion of the Coulomb interaction and with it also Hund's rule and unordered spin and orbital moments gives already a substantial correction to the studied properties, especially the bulk modulus and its derivative. The remaining differences may be well accounted for by magnetic order. Our results agree qualitatively with the charge self-consistent calculations by Grånäs et al. [133] for ferromagnetic  $\alpha$  iron using a spin-polarized T-matrix fluctuation exchange solver (SPTF) [196, 345]. The authors find a good agreement with experiment using U = 1.2 eVand J = 0.8 eV in the ferromagnetic phase. The differences to the data presented in Ref. [133] probably stem from the fact, that we did not take into account magnetic order and focussed on the paramagnetic state or in part might also be rooted in the different impurity solvers employed.

## **2.5** DFT+ $\Sigma$ for vacuum states: Co on Cu(111)

Here we want to briefly present first results obtained by employing the DFT++ method for vacuum states as described above. As the first test system we used a single Co atom adsorbed on the fcc hollow site of the (111) surface of Cu. The geometry of the system was relaxed and subsequently the density of states, shown in Fig. 2.5.8(a) was obtained using DFT and the PW91 GGA functional [333]. The spectrum is generic for an adatom adsorbed on a surface showing a peak close to the Fermi level. We also computed the hybridization function via Eq. 2.2.10 and verified it against the calculations of Surer and co-workers for the same system [403].

In the subsequent DFT+ $\Sigma$  calculations we resorted to a model approach for the computation of the self-energy. We used the self-energy of a half filled single band Anderson model solved within the one-crossing approximation (OCA), see section 1.6. This model was set up with a Gaussian bath Green function constructed such that the hybridization at the Fermi level was identical to the one obtained ab initio. The interaction parameter was chosen as U = 2eV, the resulting model has a Kondo temperature of about  $k_{\rm B}T_{\rm K} = 0.03\text{eV} \sim 350\text{K}$ , which is within the range of temperatures obtained from ab initio calculations for the Co 3d shell at different fillings [403]. The self-energy we ob-



**Figure 2.5.8:** (a) Spectral functions obtained in DFT(GGA) (blue) and DFT+ $\Sigma$  (red) for the 3*d* shell of a single Co atom on a Cu (111) surface. (b) Real and Imaginary parts of the self-energy as obtained for a one band Anderson model with a Gaussian bath within the one-crossing approximation (OCA). Constant shifts of the real part have been remove to better fit the two curves in the figure.

tained is shown in Fig. 2.5.8(b) evaluated at T = 0.005eV (constant shifts of the real part have been remove to better fit the two curves in the figure). It shows the characteristic Fermi-liquid behaviour close to the Fermi level, cf. section 1.4.1.

This self-energy was applied to all five 3d orbitals of Co and thus the GGA+ $\Sigma$  spectrum, shown in Fig. 2.5.8 (a), was obtained. It clearly shows the signature Abrikosov-Suhl resonance of the Kondo effect, cf. chapter 5. Following the prescription from equation (2.2.16) we evaluated the Green function for an *s* orbital located inside an empty sphere above the Co atom, as shown schematically in Fig. 2.2.1. The spectral function obtained from this procedure is shown in Fig. 2.5.9 for a sphere placed 2Å and 4Å above the Co atom.

The spectra are modified in the vicinity of the Fermi level as compared to the non interacting case and clearly show a sharp peak at the Fermi level. This peak stems, for symmetry reasons, predominantly from the Kondo resonance in the Co  $dz^2$  orbital. In STM experiments, there is an electric field between tip and sample, which modifies the shape of the tunneling barrier [316]. The exact shape of the tunneling barrier is unknown but can be approximated by a trapezoidal barrier in the most simple model. Besides any density of states effects, this leads to an energy and tip-height dependence of the dI/dV-signal according to [363]

$$\frac{\mathrm{d}I}{\mathrm{d}V} \sim \exp\left(-\int_{0}^{s} \mathrm{d}z \left[\frac{8m}{\hbar^{2}} \left(\Phi + eV\frac{z}{s} - eV\right)\right]^{-\frac{1}{2}}\right),\,$$



**Figure 2.5.9:** Local density of states obtained from evaluating the Green function projected on an *s* orbital inside a vaccum sphere located (a) 2Å and (b) 4Å above the Co atom.

where  $\Phi$  is the work function of the tip and the sample and s is the distance between the tip and the sample. Expanding the exponent to first order in U we arrive at

$$\frac{\mathrm{d}I}{\mathrm{d}V} \sim c_0 \exp\left(-\frac{eV}{E_0}\right),\,$$

where  $E_0$  is a constant depending on the materials of the tip and the sample as well as on their distance.

To simulate STM spectra, we therefore use the vacuum LDOS from our DFT+ $\Sigma$  calculations (which accounts for the tunneling barrier due to the sample work function) and scale this vacuum LDOS by a factor of  $\exp(-E/E_0)$  to account for electric field induced dependencies of the effective tunneling barrier height on the bias voltage. This procedure was successfully applied in our DFT-only study of the Nickel (111) surface and graphene on Ni(111) [96].  $E_0$  is treated as a free parameter. In Fig. 2.5.9 we used  $E_0 = 2$ eV.

## 2.6 Summary and Conclusions

We have presented a general interface between a projector augmented wave based DFT method and many-body methods based on Wannier functions obtained from a projection on local orbitals. The method is general and can take into account different correlated sites or layers and access also the charge density in the vacuum. Different schemes to obtain projection matrices from PAW calculations have been explored and explicitly compared to other schemes, like Nth order muffin-tin orbitals or maximally localized Wannier functions for the cubic perovskite SrVO<sub>3</sub>. We find that care has to be taken to

correctly represent all the spectral weight of the correlated subspace in the construction of the projected local orbitals. The simplest scheme, taking into account only the first PAW projector can be a bad approximation and leads to an incomplete description of the system. Only constructions taking into account higher PAW projectors are capable of a correct description of correlation physics on the DFT as well as on the DFT++ level. Our momentum resolved spectral functions show dispersive quasiparticle features around the Fermi energy resembling renormalized LDA bands as well as incoherent features that can be identified as Hubbard bands. Mass renormalization factors are consistent with previous experimental [464] as well as theoretical studies [329, 306].

We have also shown the capability of our approach to access the local density of states in the vacuum above a surface or other system. This is crucial for comparison of calculations with STM data, that are assumed to measure just the same quantity. In our first application, a Co atom on the (111) surface of Cu, we were able to show that the signature of the Kondo resonance can be seen also in the local density of states in the vacuum above the Co atom.

Additionally, we have presented results from an interface to perform charge selfconsistent DFT+DMFT calculations. The calculated volume versus energy curves for bcc iron were in qualitative agreement with previous calulations [133]. We find that upon inclusion of local electronic correlations the equilibrium volume increases as compared to LDA. In addition, the bulk modulus, which is strongly overestimated in LDA and GGA is considerably reduced and is within LDA+DMFT close to the experimental observations. Our DFT++ implementation is very flexible and allows for applications ranging from the bulk systems, to magnetic nanostructures or isolated correlated impurities.

# Chapter 3

## **Double Counting in DFT+DMFT**

M. Karolak, G. Ulm, T. Wehling, V. Mazurenko, A. Poteryaev, and A. Lichtenstein, *Double counting in LDA+DMFT - The example of NiO*, Journal of Electron Spectroscopy and Related Phenomena **181** (2010), no. 1, 11 – 15

In this chapter we will explore the influence of the double counting correction in DFT+DMFT approaches using the example of nickel oxide (NiO). To this end we have performed complementary studies using Hirsch-Fye QMC (HF-QMC), Exact diagonalization (ED) and for validation of certain results also Continuous Time QMC in the segment formulation as solvers and have explicitly tested the performance of many common approaches to fix the double counting. We will show that great care has to be taken to fix the double counting in a manner that is consistent with the physics of the material under study and that the issue of the double counting is by no means small. Nickel oxide is a strongly correlated transition metal oxide, that is a prototypic member of the class of charge transfer insulators. We use the example of NiO for two main reasons: First it is an insulator, which introduces the issue of the gap size, additionally in NiO, and charge transfer systems in general, the relative position of the nickel 3d states and the oxygen 2pstates is important to describe the correct physics of the material. In recent years a number of authors applied the DFT+DMFT method in different flavours to this system generating a body of promising results [358, 234, 235, 222]. We will explore in detail below how the double counting influences the DFT+DMFT results and what the consequences are for the DFT+DMFT description of such systems in general. Additionally, we will argue that focussing on the gap size as the only criterion for the assessment of a theoretical calculation for an insulator can lead to an unsatisfactory description of the electronic structure of the system. The presented data will be mostly obtained from HF-QMC, the ED study yielded the same qualitative picture as presented here.



**Figure 3.1.1:** Schematic illustration of the effect of the Coulomb interaction on the energy levels in a Mott-Hubbard (a) and a Charge-Transfer Insulator (b). Figure from [170].

## **3.1** NiO — a charge transfer insulator

According to Zaanen, Sawatzky, and Allen [466] transition metal oxides can exhibit a behavior different from the classic Mott-Hubbard picture. In this picture the interplay of transition metal 3d states and oxygen 2p states plays an important role. In a Mott-Hubbard insulator the charge gap opens through splitting of the d band by the Hubbard U. In the charge-transfer system the gap typically opens between ligand p bands and the upper Hubbard band corresponding to the d band of the transition metal. Thus, it is the so-called charge transfer energy  $\Delta = |\varepsilon_d - \varepsilon_p|$  that determines the size of the gap. Both situations are shown schematically in Fig. 3.1.1. In the scheme by Zaanen, Sawatzky and Allen materials can be classified by their respective values of U and  $\Delta$  [54]. For  $\Delta > U$ the system is a Mott-Hubbard insulator, whereas for  $\Delta < U$  it belongs to the charge transfer class. In general, systems with completely filled  $d(e_a)$  and partially filled  $d(t_{2a})$ shells, like titanates, vanadates and some ruthenates belong to the Mott-Hubbard class. Prominent examples of charge transfer insulators are NiO, MnO, manganites and cuprates [54]. In these systems the  $e_q$  shell is partially filled and the  $t_{2q}$  shell is fully occupied. Such a situation where the relative positions of the correlated and uncorrelated parts of a system are important is particularly challenging to capture within DFT++ approaches like DFT+DMFT. In such a case the double counting, as introduced in section 1.5, also see below, cannot be absorbed into the chemical potential and constitutes an explicit relative shift of the correlated orbitals (e.g. transition metal 3d) with respect to the uncorrelated ones (e.g. oxygen 2p). As we have commented in section 2.2 this is a consequence of the approximation to the Coulomb interaction that includes only non-zero terms on the dshell  $U_{dd} \neq 0$ , while neglecting the interaction on the ligand p states,  $U_{pp} \equiv 0$ , as well as the p - d interaction  $U_{pd} \equiv 0$ .

The density of states and the band structure of NiO as obtained by DFT using the LDA



**Figure 3.1.2:** Density of states (left) and band structure (right) of NiO as obtained by LDA calculations. In the band structure the 5 bands crossing the Fermi level are Ni 3d bands, the 3 bands below correspond to oxygen 2p states.

functional are shown in Fig. 3.1.2. For the density of states and the subsequent construction of the Wannier Hamiltonian using the projection formalism described in the previous chapter 1728 k-points were used within the Brillouin zone. The band structure shows five Ni 3d bands in the energy window -2.5eV to +1.5eV crossing the Fermi energy and three separated O 2p bands below, extending down to -8eV. These bands contain 14 electrons in total, in an atomistic picture 6 occupy the oxygen 2p bands and the remaining 8 the Ni 3d bands. It is clear from the density of states, shown in Fig. 3.1.2 that the oxygen and nickel states hybridize and show considerable spectral weight in the respective other band block. In contrast to the DFT prediction paramagnetic NiO is not a metal, on the contrary, experiments revealed a charge gap of about 4eV [375]. The inclusion of antiferromagnetic order on the level of DFT opens a gap in the system, however only a very small one, on the order of a few tenths of an electron volt [281]. The experimental spectrum, obtained by X-ray-photoemission (PES) and bremsstrahlung-isochromat-spectroscopy (BIS) showing both occupied and unoccupied parts, is depicted in Fig. 3.1.3 (right). The spectrum recorded at 120eV is predominantly of Ni 3d character, while the 66eV spectrum contains a strong contribution of O 2p at about -4eV. Additionally, the detailed decomposition of the spectra showed contributions of both O 2p and Ni 3d at the top of the valence band [375, 98].

NiO exhibits antiferromagnetic order below the Néel temperature of  $T_N = 525$  K. Our computations were carried out in the paramagnetic phase, which is not problematic, since the gap opened by electronic correlations does not depend on whether the system is magnetically ordered. It has been shown in angular resolved photoemission spectroscopy (ARPES), that passing the Néel temperature does not qualitatively alter the valence band spectrum [416]. The experimental valence band spectrum as obtained by ARPES for the  $\Gamma - X$  direction in the Brillouin zone is shown in Fig. 3.1.3 (left). We will compare our



**Figure 3.1.3:** Experimental electronic structure of NiO. Left: Angle resolved photo emission data from Shen et al. [388] along the line  $\Gamma$ -X in the Brillouin zone. Right: Combined results of x-ray-photoemission (PES) and bremsstrahlung-isochromat-spectroscopy (BIS) showing the occupied and unoccupied parts of the spectrum [375].

calculations against these data obtained by Shen et al. [389, 388] below.

## 3.2 Methodology

In DFT+DMFT (see chapter 1.5) the converged Kohn-Sham Hamiltonian is augmented with a local Coulomb interaction  $\hat{H}_{loc}$  in a subsequent many-body calculation

$$\hat{H}(\hat{c}^{\dagger},\hat{c},\hat{d}^{\dagger},\hat{d}) = \hat{H}_{\rm KS}(\hat{c}^{\dagger},\hat{c}) + \hat{H}_{\rm loc}(\hat{d}^{\dagger},\hat{d}) - \hat{H}_{\rm DC}(\hat{d}^{\dagger},\hat{d})$$

that aims to capture all interactions inside the correlated subspace. The operators  $\hat{c}^{\dagger}$ ,  $\hat{c}$  and  $\hat{d}^{\dagger}$ ,  $\hat{d}$  indicate the domain of action of the parts of the Hamiltonian on the uncorrelated and correlated parts respectively. Since the DFT already contains some portion of these interactions a double counting in the energy  $\hat{H}_{\rm DC} = \mu_{\rm DC} \sum_{m,\sigma} \hat{d}^{\dagger}_{m,\sigma} \hat{d}_{m,\sigma}$ , with the double counting potential  $\mu_{\rm DC}$ , has to be subtracted. We have written the double counting as as additional impurity chemical potential, i.e. a static shift of the impurity with respect to the uncorrelated rest of the system. This is possible, since the Kohn-Sham potential inside the DFT is not explicitly orbitally dependent [23]. The effective Wannier Hamiltonian includes the five 3d bands of nickel as the correlated subspace and the three 2p bands of oxygen as the uncorrelated part. The inclusion of the 2p bands is physically motivated since in a charge transfer compound the oxygen bands play an important role



**Figure 3.2.4:** Comparison of the exact diagonalization and Hirsch-Fye quantum Monte Carlo impurity solvers for a double counting of  $\mu_{DC} = 59$ eV. The overall agreement is satisfactory, apart from a possible multiplet splitting of the  $t_{2g}$  states at -3.5eV that the HF-QMC is incapable of capturing.

in the physics of the system. A computation taking into account only the Ni 3d states is capable of reproducing the insulating behavior and the size of the gap as shown by Ren et al. [358]. Additionally, the double counting is reduced to a trivial shift in calculations that contain only the Ni 3d bands, since the full Wannier Hamiltonian belongs to the correlated subspace. The double counting can thus be absorbed into the total chemical potential. However, the physics of the charge transfer insulator cannot be captured without taking into account the oxygen 2p states. Since we have a correlated and an uncorrelated part in our Hamiltonian the self-energy matrix will have block form. It will be only non-zero inside the  $5 \times 5$  block of the correlated subspace, corresponding to the 3dshell of Ni. Either way, a five band model has to be solved in the impurity solver, which makes the calculations rather involved. The impurity solvers, as introduced in section 1.6 rely on very different approximations to the full problem of the Anderson impurity model: In HF-QMC the hybridization function is fully taken into account, while in ED it has to be approximated with a finite number of sites. For the interaction part the situation is reversed, the ED can take into account the full interaction tensor  $U_{ijkl}$ , while HF-QMC is limited to density-density interactions. As we will see these differences between the solvers play a role in the description of the physics of NiO, but are unimportant to the double counting issue. The calculations were performed at inverse temperature  $\beta = 5 \text{eV}^{-1}$ , which corresponds to 2321K, using up to 80 time slices and on the order of  $\sim 10^6$  Monte Carlo sweeps. Within ED we used a ten site cluster to represent the Ni 3d shell, i.e. 5 correlated orbitals and 5 bath sites. This might seem as a very crude approximation, but

surprisingly the two solvers ED and QMC agree very well for the same set of parameters as shown in Fig. 3.2.4. The secondary peak seen at about 3.5eV below the Fermi level in the ED spectrum in Fig. 3.2.4 probably stems from multiplet splitting brought about by the inclusion of the full Coulomb interation as compared to HF-QMC. It shows considerable dependence on the Hunds rule coupling J (data not shown), which corroborates the multiplet assumption. Further studies yet have to be performed to confirm this. The temperature is low enough to give a qualitatively correct description of the physics of the material. Computations at lower temperatures within QMC and including more bath sites in ED pose no fundamental problem, the amount of calculations performed for this study (>100) would have made them too expensive though. We have used a Coulomb interaction matrix generated via the Slater integrals  $F^0$ ,  $F^2$  and  $F^4$ , which corresponds to the parameter values U = 8eV and J = 1eV as obtained from contrained LDA calculations [23].

## **3.3 Double counting approaches**

Since other DFT++ approaches, like the DFT+U method, also include a double counting the issue is not new. We will here discuss different approaches to fix the double counting, their performance for NiO will be reviewed below. In what follows, unless otherwise stated, we use the following definitions of the parameters U and J, see section 1.5.2,

$$U = F^0$$
 and  $J = \frac{F^2 + F^4}{14}$ . (3.3.1)

Over the years different methods to fix  $\mu_{DC}$  have been devised. Two prominent examples are the around mean-field (AMF) approximation and the fully localized or atomic limit (FLL) [23, 399, 85], that we already mentioned in section 1.5.3. Both methods use analytic arguments to devise a double counting correction. The AMF is based on the conjecture that DFT corresponds to a mean-field solution of the many-body problem, as was argued by Anisimov et al. [23]. The resulting double counting potential can be written as

$$\mu_{\rm DC}^{\rm AMF} = U(N_{\rm imp} - \bar{n}) - J(N_{\rm imp}^{\sigma} - \bar{n}), \qquad (3.3.2)$$

where  $N_{\rm imp}$  is the total occupancy of the impurity,  $N_{\rm imp}^{\sigma}$  the occupancy per spin ( $N_{\rm imp}^{\sigma} = N_{\rm imp}/2$  for the paramagnetic case) and  $\bar{n} = \frac{1}{2(2l+1)} \sum_{m,\sigma} n_{m\sigma}$  is the average occupancy. We use the global average and not the spin dependent version proposed in Ref. [85], since we were performing paramagnetic calculations in which both spin components are equally occupied. One thus assumes in this criterion all orbitals belonging to a certain value of the angular momentum l to be equally occupied and subtracts a corresponding mean-field energy. This is, however, incorrect, since DFT contains the crystal field splitting explicit.

itly and will in general not produce equally occupied orbitals even for weakly correlated systems. The AMF functional is known to produce unsatisfactory results for strongly correlated systems, which led to the development of another method, the so called FLL. The FLL functional takes the converse approach to the AMF and begins with the atomic limit. It has been shown, that this new potential can also be written as a correction of the AMF solution, Eq. (3.3.2), [85]

$$\mu_{\rm DC}^{\rm FLL} = U\left(N_{\rm imp} - \frac{1}{2}\right) - J\left(N_{\rm imp}^{\sigma} - \frac{1}{2}\right) = \mu_{\rm DC}^{\rm AMF} + (U - J)\left(\bar{n} - \frac{1}{2}\right).$$

This addition to the AMF potential has the effect of a shift of the centroid of the level depending on its occupation. An empty level is raised in energy by  $\frac{1}{2}(U-J)$  and the converse happens to a fully occupied level. The form of the functional is based on the property of the exact density functional that the one electron potential should jump discontinuously at integer electron number [141, 335, 21], which is not fulfilled in LDA or GGA. Ultimately the FLL leads to a stronger trend towards integer occupancies and localization. The general problem with analytic expressions like the ones presented is that their scope is limited to certain classes of systems that fulfill the assumptions made in the derivation process. This was already realized for the case of DFT+U and Petukhov et al. [339] proposed a scheme that interpolates between the AMF and the FLL via a parameter  $\alpha$ . This parameter is found self-consistently and is a material dependent constant in principle. Values in between the AMF and FLL corrections are thereby generated which constitutes a methodological improvement. As an additional complication, both approaches can be used employing the average orbital occupancies obtained from DFT or in a self-consistent manner allowing the occupancies to be determined within the DFT+DMFT loop. We will see below, that this again will lead to different results.

Other analytical formulae for the double counting correction have been proposed for the case of NiO, see the work by Korotin et al. [222] and Kuneš et al. [234]. In the former work the correction has the form

$$\mu_{\rm DC} = \bar{U} \left( N_{\rm imp} - \frac{1}{2} \right), \qquad (3.3.3)$$

where  $N_{\rm imp}$  is the number of electrons on the impurity and  $\bar{U}$  is the average Coulomb interaction for the case of cubic symmetry

$$\bar{U}_{\rm cub} = \frac{\mathcal{U} + (M-1)(\mathcal{U} - 2\mathcal{J}) + (M-1)(\mathcal{U} - 3\mathcal{J})}{2M - 1}$$
(3.3.4)

Such a correction was deduced before when considering the atomic limit of LDA in the work by Anisimov et al. [23], see also Ref. [399]. We will label it as ANI in what follows. In Eq. (3.3.4) M ist the total number of interacting orbitals, i.e. M = 5 in our case, and the values of the interaction parameters  $\mathcal{U}$  and  $\mathcal{J}$  are determined as follows:

The parameters  $\mathcal{U}$  and  $\mathcal{J}$  correspond respectively to the diagonal of the interaction matrix  $\mathcal{U} = U_{mm} = U_{mmmm} = F^0 + \frac{8}{7} \frac{F^2 + F^4}{14}$  and the average exchange matrix element  $\mathcal{J} = \frac{1}{2l(2l+1)} \sum_{m \neq m'} J_{mm'} = \frac{5}{7} \frac{F^2 + F^4}{14}$ . One should be very careful to avoid confusing different definitions and notations concerning the interaction parameters U and J. We want to note that for the general Coulomb interaction matrix as introduced in Eqs. (1.5.7) and (1.5.8) the definition of the average density-density interaction generalizes to

$$\bar{U}_{\text{full}} = \frac{1}{M(2M-1)} \left( \sum_{mm'} U_{mm'} + \sum_{mm', m \neq m'} (U_{mm'} - J_{mm'}) \right).$$
(3.3.5)

Equation (3.3.4) constitutes an orbitally averaged version of Eq. (3.3.5) in the five band case and will give the same result if applied properly. The form of the ANI constraint is based on the assumption, that the DFT total energy for the Coulomb interaction between d electrons is

$$E_{\rm DFT} = \frac{1}{2} \bar{U} N_{\rm imp} (N_{\rm imp} - 1)$$

and on the fact that the one electron energies in DFT are derivatives of the total energy with respect to the orbital occupation as shown by Janak [181]

$$\varepsilon_i = \frac{\partial E}{\partial n_i}$$

Such a correction works very well for metals (we have, e.g., studied bulk iron and nickel using this approach successfully), but as we will see below not so much for the insulator NiO. The latter work by Kuneš et al. [234] proposes the correction

$$\mu_{\rm DC} = (2M - 1)\bar{U}\bar{n},$$

where  $\bar{n} = \bar{n}_{\rm DFT}$  is the average DFT occupation per orbital, 2M = 10 is the total number of orbitals including spin and  $\bar{U}$  is the average Coulomb repulsion as defined above. In another publication concerning a different system (Hematite) Kuneš et al. [236] use essentially the same formula, but instead of the DFT average occupancy  $\bar{n}_{\rm DFT}$  use the self-consistent DMFT value  $\bar{n}_{\rm SC}$ , that will in general differ from the DFT result. This criterion will be referred to as KUN in what follows. The intrinsic problem with analytic approaches to the double counting still remains, different systems with different physical characteristics have to be treated on different footing. In addition, one has to decide which value of the impurity occupancy to use, the DFT value or the self-consistent DFT+DMFT one.

The obvious problems with analytical formulae make conceptually different approaches worth exploring. It would certainly be an improvement if the double counting could be found self-consistently along with the chemical potential in the DMFT self-consistency loop. One possible ansatz using the impurity self-energy  $\Sigma_{mm'}^{imp}$  is to constraint the high energy tails in the real part of the self-energy to sum up to zero

$$\operatorname{ReTr}(\Sigma_{mm'}^{\operatorname{imp}}(i\omega_N)) \stackrel{!}{=} 0.$$

Here,  $\omega_N$  is the highest Matsubara frequency included in the calculation. Physically this amounts to the requirement that the shift in the centroid of the impurity orbitals contains no static component. Since the self-energy is a quantity computed self-consistently via the quantum Monte Carlo in our case one has to ensure, that a reasonably high number of Matsubara frequencies is included in the calculation and additionally that the Monte Carlo data is well converged. Double counting corrections based on the self-energy have been applied successfully to *metallic* systems, see e.g. [61, 256].

Another possible approach is to constraint the total charge in the impurity, which is based on the Friedel sum rule [156]. The Friedel sum rule gives at zero temperature, a relationship between the extra states induced below the Fermi level by a scattering center (an impurity) and the phase shift at the chemical potential, obtained by the transfer matrix  $\underline{T} \sim V^2 \underline{\underline{G}}^{imp}$ , where V is the scattering potential. For the Anderson model the extra states induced are given by the occupation number of the impurity states, and the scattering potential is the hybridization that affects the conduction electrons. One version of this approach for the double counting requires the charges in the correlated subspace and the impurity to remain unchanged from the noninteracting result within self-consistency

$$\operatorname{Tr} G_{mm'}^{\operatorname{imp}}(\beta) \stackrel{!}{=} \operatorname{Tr} G_{mm'}^{0,\operatorname{loc}}(\beta).$$
(3.3.6)

A different version requires the charges in the self-consistent bath and the impurity to be equal

$$\operatorname{Tr} G_{mm'}^{\operatorname{imp}}(\beta) \stackrel{!}{=} \operatorname{Tr} \mathcal{G}_{mm'}(\beta).$$
(3.3.7)

The value of the imaginary time Green function at  $\tau = \beta$  gives the orbital occupancy, thus the trace over them amounts to the total occupancy of the impurity. Both versions of the method give very similar results and work well in metallic systems, since in a metal the total particle number of the system  $N_{\text{tot}}$  and of the impurity  $N_{\text{imp}}$  are both very sensitive to small variations in  $\mu$  and  $\mu_{\text{DC}}$ . Also the likeness to the Friedel sum rule, that applies to metals, indicates that such a constraint will work for metals only. As NiO has a quite large gap the charge does almost not vary with neither the chemical nor the double counting potential in the gap. Over a region of several electron volts

$$\frac{\delta N_{\rm tot}}{\delta \mu} \approx 0 \quad \text{and} \quad \frac{\delta N_{\rm imp}}{\delta \mu_{\rm DC}} \approx 0.$$
We will see below which consequences for this specific double counting prescription and for double countings in general arise from the presence of the insulating gap.

The presented criteria were tested on NiO and their performance will be discussed next. We are aware that certain criteria have been introduced to deal with specific systems exclusively (metals or insulators), so we did not expect some of them to perform well for an adverse situation. Nevertheless, the *blind* application of double counting criteria to a system whose physical properties are well known is certainly enlightening, as will become clear below.

### 3.4 Results

Now that we have introduced the double counting in the context of DFT+DMFT and discussed ways to fix the underlying parameter we can elucidate on our test case: NiO. The double counting potential has been treated here as an adjustable parameter and has been varied between 55eV and 60eV. The most prominent effects of the double counting on the spectral properties are the shift of the oxygen 2p bands with respect to the nickel 3d bands, as well as the variation in gap size. The  $\mu_{\rm DC}$  controls the filling of the Ni 3d orbitals and since the total number of particles in the system is fixed at  $N_{\rm tot} = 14.0$  the chemical potential  $\mu$  of the full system must be varied together with  $\mu_{\rm DC}$ . The filling of the Ni 3d orbitals can be varied from  $N_{\rm imp} \approx 8.1$  at  $\mu_{\rm DC} = 55 \text{eV}$  to  $N_{\rm imp} \approx 8.3$  at  $\mu_{\rm DC} = 60 \text{eV}$ . The double counting potential  $\mu_{\rm DC}$  has profound impact on the spectrum  $A_m(\omega) = -\frac{1}{\pi}G_m(\omega)$  shown in Fig. 3.4.5 and the k-resolved spectral function

$$A_m(\mathbf{k},\omega) = -\frac{1}{\pi} \mathrm{Im} \left( \omega + \mu - \varepsilon_m(\mathbf{k}) - \Sigma_m^{\mathrm{imp}}(\mathbf{k},\omega) \right)^{-1}$$

shown along the line  $\Gamma - X$  in the Brillouin zone in Fig. 3.4.6. All spectral functions were obtained by the maximum entropy method from imaginary time Green functions. With increasing  $\mu_{DC}$  the system evolves from a large gap Mott insulator at  $\mu_{DC} = 55\text{eV}$ (Fig. 3.4.5 (a)) with a gap of about 4eV opening between the Ni 3d states and almost no oxygen at the valence band edge towards an almost closed gap at  $\mu_{DC} = 60\text{eV}$  (Fig. 3.4.5 (d)). Plainly speaking, the double counting correction allows for a tuning of the spectral properties from a large gap Mott insulator in the region  $\mu_{DC} \leq 55\text{eV}$  to a metal at  $\mu_{DC} > 60\text{eV}$ . The regime of the charge transfer insulator, the expected physical state of NiO, lies somewhere in between at  $\mu_{DC} \sim 59\text{eV}$  (Fig. 3.4.5 (c)). In this state the oxygen states make up about half the spectral weight at the valence band edge, as observed in experiments [375, 98]. The gap, however, is much smaller than 4eV, thus if the only criterion of the quality of the calculation would be the gap the double counting of choice would be around  $\mu_{DC} = 55\text{eV}$ , missing the physics of the system entirely.



Figure 3.4.5: LDA+DMFT(QMC) spectral functions at  $\beta = 5 \text{eV}^{-1}$  for different values of the double counting  $\mu_{\text{DC}}$ , illustrating its impact on the spectrum.

Let us now turn to the k-resolved spectral functions shown in Fig. 3.4.6 and compare them with ARPES data [389, 388]. We have superimposed the ARPES data on top of our calculated spectral functions; the data were aligned at the valence band edge to facilitate comparison.<sup>1</sup> The uppermost band in Figs. 3.4.6 (a) and (b) at 2eV above the Fermi level is a Ni  $e_g$  band, while the other bands can be identified with the ones obtained by ARPES. The two lowest lying bands correspond to oxygen 2p states, the bands above are formed by Ni 3d states. The characteristic features seen in ARPES, like the broadening of the oxygen bands around the midpoint of the  $\Gamma - X$  line, are clearly present. The quantitative features, especially the relative band energies can strongly differ, depending on the double counting chosen. The bands in Fig. 3.4.6 (a) ( $\mu_{\rm DC} = 55eV$ ) show a clear separation between the oxygen and the nickel part at the  $\Gamma$ -point as well as the X-point.

<sup>1</sup>The ARPES data were extracted from the plot, Fig. 3.1.3, using a plot digitizer tool [1].



**Figure 3.4.6:** k-resolved spectral functions  $A(\mathbf{k}, \omega)$  along the line  $\Gamma - X$  in the Brillouin zone for different values of the double counting  $\mu_{DC}$ . On the right the spectra integrated along the shown crystal momentum direction are shown.

At the increased value of the double counting  $\mu_{\rm DC} = 59eV$ , Fig. 3.4.6 (b), the oxygen bands are shifted towards the Fermi level, coming to overlap with the Ni 3d bands at the  $\Gamma$  point as in the ARPES data. A detailed comparison of the calculated band structures with experiments shows that the bands calculated with  $\mu_{\rm DC} = 59eV$  agree very well with the experimental data. These calculations reproduce the flat bands at -4eV and another at about -2eV becomes more prominently visible at  $\mu_{\rm DC} = 59eV$ , while it is very faint at  $\mu_{\rm DC} = 55eV$ . This feature can be identified as the Zhang-Rice state, a bound state between the p hole and the d spin [468], and has along the  $\Gamma - X$  direction exclusively Ni  $e_g$  character, see the discussion in [235]. The dispersive bands in the region -4eV to -8eV also agree very well with experiment. Our calculations at this value of  $\mu_{\rm DC}$  yield very similar results as those obtained by Kuneš et al. [235]. Calculations with other values



**Figure 3.4.7:** Surface created by different combinations of the chemical potential  $\mu$  and the double counting potential  $\mu_{DC}$ . The particle number has been color coded: the green plateau corresponds to a particle number very close to the desired value of 14, values below are encoded in blue, values above in red. In addition the dotted line indicates the location of the N vs  $\mu$  curve for  $\mu_{DC} = 59$ eV that is shown on the right. The line is a guide to the eye only.

of the double counting can strongly differ from the experimental data, as shown by the example of  $\mu_{\rm DC} = 55 eV$ .

The dimension of the problem of the double counting becomes apparent if the parameter space of the overall chemical potential  $\mu$  and the double counting potential  $\mu_{\rm DC}$  versus the total particle number in the system N is examined. The result is shown in Fig. 3.4.7 on the left with the particle number color coded. The picture shows that in principle any combination of  $\mu$  and  $\mu_{\rm DC}$  that yields a point in the green plateau, corresponding to the desired particle number  $N \approx 14$  a priori describes the system equivalently well. The problem that arises here is that conventionally fixing the total chemical potential  $\mu$  in

the middle of the gap, or converging it numerically as far as possible, thereby reducing the two dimensional plateau to a line, still leaves one the freedom of choosing different values for  $\mu_{\rm DC}$  without violating any physical constraints. The plot on the right hand side of Fig. 3.4.7 shows a cut along the line indicated by  $\mu_{\rm DC} = 59$ eV in the two dimensional plot. It shows that the total particle number is insensitive to changes in the chemical potential within the gap. An additional condition is required to completely determine the systems position in the ( $\mu$ ,  $\mu_{\rm DC}$ ) parameter space and thus in the end its spectral properties. As we have argued above this choice is of crucial relevance for the results of the DFT+DMFT simulation and not just an unimportant technicality. The different approaches to fix the double counting that were introduced above each correspond to one particular point in the ( $\mu$ ,  $\mu_{\rm DC}$ ) parameter space. We have collected the results that all the presented approaches yield in table 3.4.1. In the case of analytical formulas containing either the total charge of the correlated subspace or the average charge we have given three values for the corresponding double counting corrections: the first was obtained using the formal charge

Name of prescription (charge used)	Constraint	$\mu_{ m DC}~({ m eV})$
AMF(F)		54.4
AMF(LDA)	$\mu_{\rm DC} = U(N - \bar{n}) - J(N_{\sigma} - \bar{n})$	58.5
AMF(SC)		55.0
FLL(F)		56.5
FLL(LDA)	$\mu_{\rm DC} = U(N - \frac{1}{2}) - J(N_{\sigma} - \frac{1}{2})$	61.0
FLL(SC)		57.7
KUN(F)		54.4
KUN(LDA)	$\mu_{\rm DC} = (2M - 1)\bar{U}\bar{n}$	58.5
KUN(SC)		55.0
ANI(F)		56.7
ANI(LDA)	$\mu_{ m DC} = ar{U}\left(N - rac{1}{2} ight)$	61.2
ANI(SC)		57.9
	Tr Re $(\Sigma_{mm'}^{imp}(i\omega_N)) \stackrel{!}{=} 0$	55.2
	$\operatorname{Tr} G^{\operatorname{imp}}_{mm'}(\beta) \stackrel{!}{=} \operatorname{Tr} G^{0,\operatorname{loc}}_{mm'}(\beta)$	60.5

**Table 3.4.1:** Numerical values of the double counting obtained by different approaches for NiO. In the case of analytical formulas containing charges we have given three values for the corresponding double counting corrections: one obtained using the formal charge of Ni in the compound which is  $N_{3d} = 8$  electrons (F); secondly the values using the LDA charge from  $G_{3d}^0$  indicated by (LDA) and thirdly the charges adjusted self-consistently until convergence, this is indicated by (SC).

of Ni in the compound NiO which is  $N_{3d} = 8$  electrons, these values are indicated by an (F); secondly the values using the LDA charge from the first integration of  $G_{3d}^0$  are given and indicated by (LDA) and thirdly we give the values obtained by allowing the charge and along with it the double counting to be adjusted self-consistently until convergence, this is indicated by (SC). The LDA charge as obtained from  $G_{3d}^0$  in the first iteration was  $N_{3d} = 8.6$  in our case. The collected data in table 3.4.1 show that the different criteria give double counting potentials ranging over 10eV from below 55eV to about 65eV. We have identified a range of optimal values for  $\mu_{\rm DC}$  from 58.5eV to 59.5eV, centered around 59eV, which is in our study the best a posteriori estimate. In this range the system is an insulator showing the characteristics of a charge transfer system.

The approaches that fall into this range are AMF and the approach by Kuneš et al. (KUN) in both cases with LDA charges. Let us first point out some similarities between the analytical approaches that we encountered. The AMF and KUN approaches actually give

identical values, and in fact can be shown to *be* identical in the five band case. The proof is just simple algebraic manipulation. The AMF functional for general interaction matrices can be written as [85]

$$\mu_{\rm DC}^{\rm AMF} = \frac{1}{M} \sum_{mm'} U_{mm'} \bar{n} + \frac{1}{M} \sum_{mm',m' \neq m} (U_{mm'} - J_{mm'}) \bar{n}.$$

Comparison with the definition of the average interaction from Eq. (3.3.5) shows that, since  $\bar{n}$  can be pulled out of the both sums, above equation can be written using  $\bar{U}$ 

$$\mu_{\rm DC}^{\rm AMF} = (2M - 1)\bar{U}\bar{n}, \qquad (3.4.1)$$

which is exactly the formula proposed by Kuneš and co-workers.

The same can be shown assuming a  $\overline{U}_{cub}$ . First, one harmonizes the notation by using  $U = F^0$  and  $J = \frac{F^2 + F^4}{14}$  in the AMF formula and  $\mathcal{U} = F^0 + \frac{8}{7} \frac{F^2 + F^4}{14} = F^0 + \frac{7}{8} J$  and  $\mathcal{J} = \frac{5}{7} \frac{F^2 + F^4}{14} = \frac{5}{7} J$  in the formula for  $\overline{U}_{cub}$  in the KUN criterion. The double counting potentials then become

$$\mu_{\rm DC}^{\rm AMF} = F^0(N_{\rm imp} - \bar{n}) - J\left(\frac{N_{\rm imp}}{2} - \bar{n}\right)$$
(3.4.2)

$$\mu_{\rm DC}^{\rm KUN} = \bar{n} \left( F^0 + 2(M-1)F^0 \right) + \bar{n} \left( \frac{8}{7}J - (M-1)\frac{9}{7}J \right), \qquad (3.4.3)$$

where we have collected the terms proportional to  $F^0$  and J. In above formulas M is the number of orbitals,  $N_{\rm imp}$  the total number of particles and  $\bar{n}$  the average particle number per orbital. Now observing that  $\bar{n} = \frac{N_{\rm imp}}{2M}$  we can rearrange Eq. (3.4.3)

$$\mu_{\rm DC}^{\rm KUN} = F^0 \left( N_{\rm imp} - \frac{N_{\rm imp}}{2M} \right) - J \left( \frac{9}{7} \frac{N_{\rm imp}}{2} - \frac{17}{7} \frac{N_{\rm imp}}{2M} \right), \tag{3.4.4}$$

where the first term, proportional to  $F^0$ , is already identical to the AMF result. Equating the terms proportional to J one readily verifies that both terms are identical if and only if M = 5. This will not apply in general, i.e. for different interaction matrices and impurity sizes.

The criterion based on constraining the tails of the self-energy to sum up to zero

$$\operatorname{ReTr}(\Sigma_{mm'}^{\operatorname{imp}}(i\omega_N)) \stackrel{!}{=} 0,$$

gives a very similar result to the AMF criterion with self-consistently computed charges. In fact, both should give the same value, the difference stems just from the numerics in the calculation. The two constraints are actually just rephrased version of one another. Removing the static shift from the real part of the electronic selfenergy corresponds to removing the Hartree-Fock static mean-field contribution to the self-energy.

Interestingly, one also does not fail to observe a similarity in the results produced by the FLL and ANI criteria. As one can show this is, again, not a coincidence. Both criteria are built around an atomic limit extracted from LDA. First, one harmonizes the notation by using  $U = F^0$  and  $J = \frac{F^2 + F^4}{14}$  in the FLL formula and  $\mathcal{U} = F^0 + \frac{8}{7} \frac{F^2 + F^4}{14} = F^0 + \frac{7}{8} J$  and  $\mathcal{J} = \frac{5}{7} \frac{F^2 + F^4}{14} = \frac{5}{7} J$  inside the  $\overline{U}$  within the ANI criterion. We focus here on the cubic case for convenience and find

$$\mu_{\rm DC}^{\rm FLL} = F^0 \left( N_{\rm imp} - \frac{1}{2} \right) - J \left( \frac{N_{\rm imp}}{2} - \frac{1}{2} \right)$$
$$\mu_{\rm DC}^{\rm ANI} = F^0 \left( N_{\rm imp} - \frac{1}{2} \right) - J \left( \frac{9 \left( N_{\rm imp} - \frac{1}{2} \right) \left( M - 1 \right)}{7(2M - 1)} - \frac{8 \left( N_{\rm imp} - \frac{1}{2} \right)}{7(2M - 1)} \right).$$

The first term, proportional to  $F^0$  in the ANI criterion is identical to the FLL term irrespective of the number of orbitals M. For the second term this is in general not the case. In fact one can show that the terms become identical only for M = 5 and  $N_{imp} = 5$ , i.e. for a half-filled 5 band system<sup>2</sup>. For a five band system with M = 5 one obtains a small correction to the FLL formula

$$\mu_{\rm DC}^{\rm ANI} = \underbrace{F^0\left(N - \frac{1}{2}\right) - J\left(\frac{N}{2} - \frac{1}{2}\right)}_{\mu_{\rm DC}^{\rm FLL}} + J\left(\frac{N}{18} - \frac{5}{18}\right),\tag{3.4.5}$$

which at most, that is for a completely empty  $(N_{\rm imp} = 0)$  or completely full shell  $(N_{\rm imp} = 10)$ , amounts to a difference from FLL of  $\frac{5}{18}J \approx 0.28J$ . A correction of this size can be called negligible in the case we are discussing because the double counting amounts to about 60eV, the correction on the order of J thus amounts to lesser than one percent of the value. When the criterion can be related to the FLL it can also be related to the AMF because the two are likewise related, the result obtained by inserting the definition of  $\bar{U}$  from Eq. (3.3.5) explicitly into the definition of the ANI criterion, Eq. (3.3.3), is then

$$\mu_{\rm DC}^{\rm ANI} = \frac{2M\left(N - \frac{1}{2}\right)}{N_{\rm imp}(2M - 1)} \,\mu_{\rm DC}^{\rm AMF}.$$
(3.4.6)

So, to summarize, we find that the approaches to the double counting based on analytical formulas, AMF, FLL, ANI and KUN will give identical values for a half filled five band model.

<sup>2</sup>Other solutions making the terms identical exist, yet they violate certain criteria, like the positivity of  $N_{imp}$  and M.

As shown in table 3.4.1 the criterion based on the traces of the non-interacting and interacting Green functions does not work well in this case. This is a consequence of the assumptions made in the construction of the criterion and the insulating gap of the system that invalidates these assumptions. Within the gap the constraint of fixed particle number can be fulfilled to a very good approximation in the whole gap region, the criteria Eqs. (3.3.6,3.3.7) essentially break down, because the charge on the impurity is independent of the double counting potential and chemical potential within the gap. That means that any criterion based on the charge of the impurity has to fail for an insulator. Nevertheless, this method has proven to be very reliable in metallic systems and also in small gap insulators, where the plateau region is small. Since the gap in NiO is large this method fails and produces in the end a metallic system at double counting  $\mu_{\rm DC} = 60.5$  eV. For metallic systems we have the most experience with the criterion from Eq. (3.3.6). It works very well for metals, giving results similar to the criterion derived by Anisimov Eq. (3.3.3). We have applied the criterion with satisfactory outcome to, inter alia,  $SrVO_3$ ,  $Sr_2RuO_4$ , bulk Fe and Ni. It works so well for metals and fails so badly for insulators, because it relies on the charge to be sensitive to changes in  $\mu$  and  $\mu_{DC}$ .

### 3.5 Summary and Conclusions

Our study has shown that the double counting correction in the DFT+DMFT formalism, has to be very carefully assessed when performing calculations with a correlated and uncorrelated part in the Hamiltonian. A well defined analytical expression for the double counting potential  $\mu_{DC}$  cannot be formulated in the context of DFT+DMFT. This is rooted in the fact that DFT and DMFT are two conceptually different methods and cannot be exactly linked. There are ways to fix the value of  $\mu_{DC}$  within DFT+DMFT that work successfully for a large number of systems. For metals the criterion from Eq. (3.3.6) works very reliably. It performs badly, however, when the system has an insulating gap. This problem could be resolved within DFT+DMFT by explicitly calculating the interaction between the d and the p states  $(U_{pd})$  and within the p shell  $(U_{pp})$  and including both in the calculation. At the time of writing we became aware of the paper by Nekrasov and co-workers [308] who propose a different way to avoid the double counting issue, that focusses on the DFT part of the calculation. The authors propose to explicitly exclude the exchange-correlation contribution of the DFT functional for the correlated subspace of states via a redefinition of the charge density used for its calculation. This reduces the DFT contribution to the Coulomb energy to the simple Hartree term that is known exactly and can be compensated. The approach looks promising, it is not clear to us at the moment, however, how the removal of the exchange-correlation term for a certain part of the system will influence the description on the DFT level. The general situation can also be improved when using the GW approximation for the one electron part [26] and then performing GW+DMFT simulations [43]. This methodology is conceptually superior to DFT+DMFT and avoids the problem of double counting terms, but on the other hand has its own methodological issues, see, e.g., Ref. [26]. Additionally, GW+DMFT is presently computationally prohibitively heavy for anything else than simple bulk systems.

## Chapter 4

# **Spin State Transition in LaCoO**<sub>3</sub>

When studying transition metal systems one notices that many of the most intriguing effects of electronic correlations can be found in perovskite systems. High temperature superconductivity is probably one of the most publicized, it earned their discoverers the nobel prize in 1987 [36], and at the same time most elusive features exhibited by this class of materials [246]. However, one might say that perovskites have it all when it comes to correlation effects: perovskites can be correlated metals, Mott insulators, exhibit any kind of magnetic order and superconductivity of different kinds. Most interestingly all these different phases can be exhibited by the same material or a class of materials depending on composition, temperature or pressure. The  $Ca_{2-x}Sr_xRuO_4$  compound is one example from the so called (2 1 4) perovskites, that shows unconventional superconducting, magnetic, metallic or Mott insulating behavior depending on the composition [273, 114, 131]. Recently, influenced by the increased interest in topologically protected states since the advent of graphene, also nontrivial topological states have been proposed to occur in certain perovskite heterostructures [459]. Despite being interesting from a theory point of view, perovskites are also key in the quest for finding materials with increased efficiency and reduced waste residuals in the energy production cycle. In this framework, LaCoO<sub>3</sub> (LCO) and related compounds have recently gained a lot of attention due to their potential applications in various optimized, environmental-friendly energy production domains like: catalytic oxidation of volatile organic contaminants (VOCs) [253], hydrocarbons [7], CO and lean NO<sub>x</sub> trapping (LNT) that could lead to new diesel engines [202], oxygen membranes to operate at high temperatures in oxyfuel power plants [65], fuel cells technology [9, 247] and thermoelectric power generation [410]. In many of these applications, the performance of LCO is well above that of other perovskite oxides like manganites [202, 65, 247]. Tailored applications of LCO and related materials rely on a deep comprehension of their physical properties. In the case of LCO, two important modifications of the electronic structure with temperature have been reported: a diamagneticto-paramagnetic spin transition (ST) around 100 K and a broad semiconductor-to-metal transition (SMT) between 350 K and 650 K. Both transitions are evidenced by changes in

magnetic susceptibility, resistivity, atomic structure [150, 47, 284, 189, 300, 352, 40, 353] and phonon spectrum [460, 209]. In spite of the overall wealth of studies performed over the years (see Ref. [172] for a review) a unified understanding of the electronic properties of LCO and, in particular, of the change of magnetic configuration at the spin transition is still lacking.

On the theory side the physics of LCO is a topic for discussion for over 50 years. The two anomalies occurring in the magnetic susceptibility were interpreted as spin state transitions, starting with the work of Goodenough in the late 1950s [130]. Two scenarios subsequently emerged as the prevailing explanation of the spin transitions of LCO: I) a "low spin" - "high spin" (LS-HS) crossover upon thermal excitation with a high spin population of 50% at room temperature and long-range order and the subsequent destruction of the order at higher temperatures by complete transition into the HS state and II) a "low spin" - "intermediate spin" (LS-IS) transition with orbital ordering due to hybridization with the oxygen states and a subsequent transition between ordered and disordered "intermediate spin" states. The methods employed to resolve the spin state puzzle range from model type single ion or configuration-interaction (CI) cluster calculations to ab initio methods like DFT and DFT++ in various flavors.

Scenario I was championed by Goodenoughs analysis [130] essentially based on the ionic Tanabe-Sugano model of multiplet changes in a crystal field [408]. In such a model, one finds for a  $d^6$  configuration that a transition between the high-spin atomic ground state and a low spin state occurs at some critical value of the crystal field [408], see also next section. LCO is now assumed to have a crystal field very close to this critical value, such that the spin state transition can be brought about by small changes in the crystal field with temperature. When the ratio of Co atoms with LS and HS configurations approaches 1:1 an order is formed with alternating LS and HS atoms [130, 129]. Later Raccah and Goodenough [352] expanded on the idea and introduced a detailed model of cobalt-ion configurations over a wide temperature range. On the basis of the anomalous behavior of the Debye Waller factor with temperature, they suggested the possible existence of dynamic short-range LS-HS order with a crossover in the range of  $10^{-8}$  s around 200 K. Combined experimental and theoretical support was lended to the LS-HS transition idea by Abbate et al. [3] who compared X-ray absorption and photoelectronic spectroscopy (XAS and XPS) measurements to configuration-interaction cluster calculations (see Ref. [166]). More recent ionic and cluster calculations can be found for example in the work of Haverkort [147, 148, 341], that corroborates the propositions of the LS-HS transition mechanism.

The relevance of Scenario II, involving the intermediate spin state, in the literature on  $LaCoO_3$  is largely due to the LDA+U study performed by Korotin and co-workers [268], although it was found also in CI cluster models [369] and Hartree-Fock studies [290] as a

possible scenario as well. Another possible route to the intermediate spin state is found in cluster calculations for certain parameter sets for the crystal field and the charge transfer [343, 147]. This is, however, more relevant to the  $d^5$  system SrCoO<sub>3</sub> than for the  $d^6$  configuration in LaCoO<sub>3</sub> [147]. In the LDA+U calculations in Ref. [268] the authors found that energetically the first excited state above the LS ground state is a magnetically ordered intermediate spin state with S = 1. The high spin state (also magnetically ordered <sup>1</sup>) was found *always* to be higher in energy than the IS state. This picture is true, the authors claim, assuming both a homogeneous, i.e. both Co atoms are in the same state, and inhomogeneous orbitally ordered state. The introduction of orbital order stabilizes the IS state even more. The authors paint the picture of the spin transitions in LCO based on their findings in the following way: first, a transition from low spin to orbitally ordered intermediate spin occurs, subsequently the orbital order is destroyed at higher temperature leading ultimately to a homogeneous intermediate spin state. There are a few issues with the approach taken in Ref. [268] though. The authors assume certain magnetically ordered states to be relevant excluding other possibilities, i.e. their high spin state is ferromagnetically ordered, same as the homogeneous intermediate spin state, whereas the orbitally ordered intermediate spin state requires antiferromagnetic (AFM) order. In addition the AFM order is required to make the IS state insulating. It has been shown in a Hartree-Fock study, however, that there are nine possible states for the rhombohedral unit cell of LCO with two formula units [472]. Of these states the intermediate state, ordered or not, is never the ground state, see Fig. 4 in Ref. [472]. The most probable transition was found to be one from the low spin into an ordered LS-HS mixture. The same has been found in more recent DFT+U studies for the bulk [207, 206] as well as for thin films of LCO [163]. Another criticism focussed on the values of interaction parameters used in the study, namely U = 7.8eV and J = 0.92eV, that were obtained using constrained DFT (cDFT), in line with other estimates [397, 164]. Recent constrained DFT points towards U = 6.0eV and J = 0.8eV [201]. Newer DFT+U studies used the rather moderate values of U = 3.5 eV [322] or  $U_{\text{eff}} := U - J = 2.7 \text{eV}$  [207, 206].

There are many papers concerned with the *values* of U and J and their effects within DFT+U: Ma and Cang [269] studied the effects of U and J on the gap of the LS ground state finding that it increased with higher U, while it decreases with increasing J, for both LDA+U and GGA+U; Yang and co-workers [461] find that a gap opens in the LS state at about U = 1.2eV (with J = 0.95eV), reaches a maximum of 0.85eV for U = 4eV and subsequently drops to zero for higher values, which is explained by a subsequent population of the  $e_g$  states. Such an increase in  $e_g$  population also accompanies the LS to HS or LS to IS transition, so possibly for certain values of the U a transition occurs into a different ground state. Unfortunately, no spectra are shown for LCO. In addition, the

<sup>1</sup>Magnetic order can well be an artifact of the LDA+U methodology as the authors of Ref. [268] comment.

trend of the gap size as a function of the Hunds rule coupling J (Fig. 6 in Ref. [461]) is opposite to the one found in Ref. [269] (Fig. 2). A structurally consistent Hubbard U was proposed by Hsu *et al.* [164], i.e. a U that varies (by a few percent) with the unit cell volume. Finally, an experimental estimate of the value of U found it to be U = 3.4eV [74]. Since estimates of the Coulomb interaction from first principles are dependent on a lot of features of the system, like the unit cell volume, and especially (and understandably) the chosen basis set and furthermore the consequences of the application of the interaction depends on the methodology (i.e. approximation) used, discussing *numbers* in the context of U and J is mostly of very limited use.

We do not want to conceal that studies based on DFT alone have claimed to explain the spin transitions or spectra of LCO. Klie and co-workers [203] inferred from EELS (electron energy loss spectroscopy) data and their simulation within DFT (and DFT+U, but only DFT(GGA) is shown in the paper) that the HS spin state does not exist in LCO. Also photoemission spectra have been claimed to be reproduced by LSDA [372]. The agreement between the spectra is not completely unexpected, since the LS ground state of LCO constitutes a pseudo closed shell system, where multiplet effects are expected to play no role [4]. It might be called serendipitous though, because the LSDA gives a semimetallic state and is unable to reproduce satellite structures [4]. Additionally, as known for other charge transfer compounds like NiO, see chapter 3, an analysis of orbital character of the peaks in the spectra reveals differences between experiment and simple DFT theory [4].

The first serious many-body calculations based on DFT+DMFT and variational cluster approximation (VCA, see Ref. [342]) were made by Craco and Müller-Hartmann [83] and Eder [99] respectively. Former authors use a multi-orbital extension of iterated perturbation theory (IPT) to investigate the spectra of LS, IS and HS solutions. They find that a contribution of *all* three states best describes certain experimental findings (XAS), and in addition find a Kondo effect in the homogeneous high spin state. The spin state transition is described as a smooth crossover from the homogeneous LS state into a non homogeneous mixture of all three spin states.

On the other hand the study by Eder finds that only the LS and HS states have appreciable weight in the density matrix over a wide temperature range. In general the study corroborates the scenario involving the LS to HS crossover.

Recently, that is 2012, two papers appeared that attempt to settle the issue of the spin states in LCO by means of the DFT+DMFT approach [201, 469] using the numerically exact CT-QMC as a solver. This methodology allows for the inclusion of local dynamical effects and also temperature, which is not possible within the inherently zero temperature DFT and DFT+U methodologies discussed before. On the technical methodology side both the study by Křápek and co-workers [201] and Zhang et al. [469] employ the full-potential linearized augmented plane-wave (FLAPW) based WIEN2K code in combination with the WANNIER90 package for the construction of the local Hamiltonian in real space. Latter authors employ Wannier functions for the calculation of crystal field splittings, but subsequently use the Nth order muffin tin (NMTO) downfolding scheme within the DMFT. Křápek et al. make a strong case against the IS state. The study involves lattice parameters from experiment for different temperatures as well as temperature effects in the DMFT. The employed CT-QMC impurity solver based on the hybridization expansion allows the authors to explicitly investigate the contributions of LS, IS and HS states to the many-body state of the system via the so-called sector analysis [450]. Although the authors go beyond the  $d^6$  ionic picture including also  $d^7$  and  $d^8$  configurations the IS state is never found to play a role in the system. Based on their data the authors interpret the spin state transitions as an LS (with few HS ions) to LS-HS short range ordered phase with a subsequent melting of the order at higher temperatures.

The more comprehensive study of Zhang et al. concludes the same scenario for the spin transitions in LCO. The authors, however, argue this not only from CT-QMC calculations of the ground state, but also investigate the whole series of Rare earth 113 Cobaltates in the ionic picture including anisotropy of the Coulomb interaction, Jahn-Teller and other distortions and also within an effective model for the superexchange. In addition the approximation to the Coulomb interaction to density-density terms only as in the work of Křápek et al. is not employed, instead the whole Coulomb vertex  $U_{ijkl}$  is treated within the weak-coupling CT-QMC scheme.

So, to sum up, the most sophisticated calculations based on VCA or DFT+DMFT so far corroborate the idea of a low spin to high spin crossover excluding an intermediate spin state.

### **4.1** Spin state Transitions in the ionic Picture

LaCoO<sub>3</sub> is known from both experiment and theory to exhibit different Co<sup>3+</sup>  $3d^6$  electronic states at different temperatures and/or pressures. The two scenarios that have been proposed to explain the transitions involve the low spin (LS), intermediate spin (IS) and high spin (HS) states. These states are shown schematically in Fig. 4.1.1 and are LS:  $t_{2g}^6$ , S = 0, HS:  $t_{2g}^4 e_g^2$ , S = 2 and IS:  $t_{2g}^5 e_g^1$ , S = 1. Transitions between the spin states will in a real system be controlled by an interplay of many effects, among them, the crystal field splitting and the Hunds rule coupling J.

The origin of a possible transition between HS and LS states can be very simply understood in the ionic picture. We thus look at a single  $d^6$  ion in an octahedral crystal field, whose  $t_{2g}$  and  $e_g$  orbitals are split by an energy quantified as 10Dq, see Fig. 4.1.1, where one assigns -4Dq to the  $t_{2g}$  and +6Dq to the  $e_g$  states. We assume at the moment that the octahedron is perfect and no additional splittings of the shells occur. The energies



Figure 4.1.1: Simplified schematic illustration of the three  $d^6$  states relevant in the physics of LCO. For simplicity we have assumed that the splitting within the  $t_{2g}$  and  $e_g$  sets is negligible.

of the LS and HS configurations can be calculated by hand, when one assumes a simplified density-density interaction containing only  $U_{\rm K}$ ,  $U_{\rm K} - 2J_{\rm K}$  and  $U_{\rm K} - 3J_{\rm K}$ , where  $U_{\rm K} = F^0 + \frac{8}{7} \frac{1}{14} (F^2 + F^4)$  and  $J_{\rm K} = \frac{5}{7} \frac{1}{14} (F^2 + F^4)$ , cf. section 1.5.2. We use only the simplified interaction Hamiltonian

$$\hat{H}_{\text{ee}} = \sum_{i} U_{\text{K}} \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow} + \sum_{i>j,\sigma} \left[ U'_{K} \hat{n}_{i,\sigma} \hat{n}_{j,-\sigma} + (U'_{K} - J_{\text{K}}) \hat{n}_{i,\sigma} \hat{n}_{j,\sigma} \right].$$
(4.1.1)

Counting the interaction terms and crystal field contributions one obtains the following energies

$$E_{\rm LS} = 15U_{\rm K} - 30J_{\rm K} - 24Dq = 15F^0 - \frac{30}{98} \left(F^2 + F^4\right) - 24Dq$$
$$E_{\rm IS} = 15U_{\rm K} - 33J_{\rm K} - 14Dq = 15F^0 - \frac{45}{98} \left(F^2 + F^4\right) - 14Dq$$
$$E_{\rm HS} = 15U_{\rm K} - 38J_{\rm K} - 4Dq = 15F^0 - \frac{70}{98} \left(F^2 + F^4\right) - 4Dq,$$

where we have translated into Slater integral language after the second equality. The energy of the Hunds rule ground state for a  $d^n$  configuration can always exactly be written as

$$E_{\rm HR}(n) = \alpha_I(n)I + \alpha_{F^0}(n)F^0 + \alpha_J(n)\frac{1}{14}\left(F^2 + F^4\right) + \alpha_C(n)\frac{1}{14}\left(\frac{9}{7}F^2 - \frac{5}{7}F^4\right),$$

for the full Coulomb interaction, with the  $\alpha$  parameters tabulated for example in Ref. [426]. The formula agrees for  $d^6$  with our result, which is due to the particular nature of



**Figure 4.1.2:** Energy-level diagram of the  $d^6$  multiplet as a function of the crystal field 10Dq. (a) Simplified density-density interaction with Hunds rule coupling  $J = 0.8 \text{eV} = J_K \approx 0.57 \text{eV}$ , see Eq. (4.1.1) (b) Calculation including the full multiplet structure for the parameters  $F^2 = 10 \text{eV}$  and  $F^4 = 6.25 \text{eV}$ , that is J = 1.16 eV and  $J_K \approx 0.80 \text{eV}$ , shown for qualitative comparison only. From Ref. [147].

the  $d^6$  configuration, which does not include contributions from the angular part of the multiplet splitting [426]

$$C = \frac{1}{14} \left( \frac{9}{7} F^2 - \frac{5}{7} F^4 \right).$$

This is not to be confused with the Racah parameter C. A diagram showing the energies as a function of the crystal field splitting is shown in Fig. 4.1.2(a) for  $J_{\rm K} \approx 0.57 \,{\rm eV}$ , corresponding to  $J = \frac{1}{14}(F^2 + F^4) = 0.8 \,{\rm eV}$ . In the figure we have omitted the energy contribution of  $15U_{\rm K}$  common to all states and additionally we have set the energy zero equal to the low spin state without crystal field. As one can make out, the system is in its Hunds rule ground state, i.e. the high spin state, for crystal fields up to  $\sim 2.3 \,{\rm eV}$  and subsequently Hunds rule is invalidated making the LS state energetically most favorable. Within this picture the IS state is *never* the ground state. The HS to LS transition is expected in this approximation for  $10Dq \sim 2.86J$ . In the language of Tanabe and Sugano the transition would occur at 2.48Dq/B for the parameters used, where B is a Racah parameter. The transition at exactly 2Dq/B for the d<sup>6</sup> configuration in Ref. [408] is specific for the parameters used there, especially  $\gamma = C/B$ , and *not* a universal number. The different spin states and the transitions between them have been studied in great detail in the ionic picture, assuming one Co ion in a crystal field, and within cluster calculations

for a Co ion surrounded by six oxygen atoms by Haverkort [147]. Including the full multiplet structure complicated the energy level diagram, as shown in Fig. 4.1.2 (b). The relevant part for the ground state albeit remains similar and the IS state still never is the ground state. In the ionic picture the HS to LS transition occurs close to  $10Dq \sim 1.8J$ . Numerical calculations suggest that for the full Coulomb interaction the transition occurs in the ionic picture at 1.6Dq/B, or equivalently at about  $10Dq \sim 1.84J$ , irrespective of  $F^2$  and  $F^4$ , as long as the ratio  $F^4/F^2 = 0.625$  [325]. A possibility to make an intermediate spin state (there are more than one in full multiplet theory) the ground state is to introduce a tetragonal distortion into the picture. The distortion required for this to occur is albeit quite sizable, see Ref. [147] for details. Another possible route to the intermediate state is found in cluster calculations for certain parameter sets for the crystal field and the charge transfer [343, 147]. This is however more relevant to the  $d^5$  system  $SrCoO_3$  than for the  $d^6$  configuration in LaCoO<sub>3</sub> [147]. As we have already discussed in the introduction the relevance of the IS state in the literature on LaCoO<sub>3</sub> is largely due to the LDA+U study performed in Ref. [268]. In newer studies based on DFT+DMFT the intermediate spin state is not found [201, 469] to play a role.

In the rest of the chapter we attempt to clarify the issue of spin states in LCO by means of DFT+DMFT calculations using exact diagonalization as a solver. Specifically, we want to explore how far an understanding of the spin state transition can be obtained from an investigation based on the Co  $d^6$  multiplets only.

## 4.2 DFT and Projections

LaCoO<sub>3</sub> is a distorted perovskite system showing a tetragonal distortion of the  $CoO_6$  octahedra that varies with temperature. We calculated the system using the crystal structures that were reported in Ref. [353]. These data were obtained by neutron powder diffraction for a wide range of temperatures, 5K to 1000K, spanning the whole phase diagram of the system including the two spin transitions. We selected as appropriate representatives of the sought phases the three structures reported for the temperatures 5K, 300K and 650K. We used a rhombohedral unit cell containing two formula units which is shown in Fig. 4.2.5. Calculations were performed using the PBE-GGA functional [332]. The densities of states and corresponding band structures are shown in Figs. 4.2.3 and 4.2.4 for the 5K and 650K structures respectively. The spectra show very sharp resonances from the (empty) 4f orbitals of La at +3.5 to +4 eV above the Fermi level (we will here denote states below the Fermi level with a minus sign and states above with a plus sign). In addition one recognizes roughly two blocks of predominantly cobalt 3d and oxygen 2pcharacter: one block extends from about -7eV up to -1.8eV and the second block from -1.8eV up to about +3eV. The two blocks are separate to a very good approximation, the only band crossings seem to appear close to the  $\Gamma$  point in both cases, see Fig. 4.2.4.



Figure 4.2.3: Densities of states obtained in DFT(PBE). (a) 5K structure from Ref. [353]. (b) 650K structure from Ref. [353].

One does not fail to notice that the spectra as well as the band structures do not differ very much. The small differences can be entirely explained by small differences in the distortions of the  $O_6$  octahedra surrounding every Co atom. In the band structure a small band narrowing at higher temperature is observed. The stark variance in the physics of the compound over this range of temperatures is clearly not represented in the DFT. This is of course due to the electronic correlations on Co that are not taken into account properly. We have thus performed additional DFT+DMFT calculations.

As we laid out before we used the projection formalism to interface the VASP code with impurity solvers. The projection method, as well as all other methods used for interfacing DFT with many-body methods requires some care. The case of LCO is no different. For the physics of LCO it is imperative to correctly capture the crystal field splitting in the Co 3d shell as well as the correct form and orientation of the d orbitals inside the CoO<sub>6</sub> octahedra. The two problems are of course connected. To tackle them we resorted to using two different projection windows in the self-consistency loop. The first window was chosen to encompass the 3d states of Co and the 2p states of O in the vicinity of the Fermi level, that is the block of bands from -1.8eV up to +3eV. We call this window the *small window* in what follows. The Co 3d states within the small window contain six electrons to a good approximation. We diagonalized the on-site Hamiltonian obtained from the projection, as in Eq. (2.2.11), to obtain the crystal-field symmetry adapted orbitals, that are linear combinations of cubic harmonics. For the 5K structure using the unit cell and cubic axes shown in Fig. 4.2.5 the orbitals read in order of energy from lowest to highest labeled as  $|1\rangle$  to  $|5\rangle$ 



Figure 4.2.4: Band structures obtained in DFT(PBE). Note that the axis showing the k-path in the Brillouin zone is drawn assuming equal lenght segments between the high symmetry points. (a) 5K structure from Ref. [353]. (b) 650K structure from Ref. [353].

$$\begin{aligned} |1\rangle &= -0.57 |xy\rangle - 0.14 |yz\rangle + 0.57 |xz\rangle - 0.57 |x^2 - y^2\rangle \\ |2\rangle &= -0.57 |xy\rangle - 0.57 |yz\rangle - 0.15 |xz\rangle + 0.57 |x^2 - y^2\rangle \\ |3\rangle &= 1.0 |z^2\rangle \\ |4\rangle &= 0.17 |xy\rangle - 0.60 |yz\rangle - 0.54 |xz\rangle - 0.56 |x^2 - y^2\rangle \\ |5\rangle &= -0.56 |xy\rangle + 0.54 |yz\rangle + 0.60 |xz\rangle - 0.17 |x^2 - y^2\rangle .\end{aligned}$$

In above equations we have also written the cubic 3d orbitals in bra-ket notation, that is,  $d_{xy} = |xy\rangle$  etc. The orbitals thus obtained are shown in Fig. 4.2.5. The since the symmetry is lower than cubic the orbitals split into three groups: The  $e_g^{\pi}$  orbitals are  $|1\rangle$ ,  $|2\rangle$  the  $a_{1g}$  is  $|3\rangle$  and finally the  $e_g$  orbitals are  $|4\rangle$ ,  $|5\rangle$ . Since the difference in energy between the  $e_g^{\pi}$  and the  $a_{1g}$  orbitals is small and does not play a role in our investigation we will refer to the orbital blocks for brevity as  $t_{2g}$  and  $e_g$  mostly. A second large projection window including all bands is used in the self-consistency procedure to keep track of changes to the other bands arising from the self-energy on the Co 3d states. For this broad window we used the crystal-field symmetry adapted orbitals obtained above. This procedure allows to include a self-energy on the Co 3d states and keep track of its indirect influence on different states, like the oxygen 2p states. We note that the bands outside of the small window are merely spectators in the self-consistency loop and can only indirectly be influenced by the self-energy on the bands that were included explicitly. Such an approach was necessary here, because taking into account the Co 3d states in the whole window from -8eV to about +3eV reduced the distance between the centers of the  $t_{2g}$  and  $e_g$ 



**Figure 4.2.5:** Rhombohedral unit cell containing two formula units of LaCoO<sub>3</sub> (5K structure from Ref. [353]) along with the crystal field orbitals, and their projection in the *xy* plane, obtained from the small window (see text) for the same structure. On the top are the two  $e_g^{\pi}$  orbitals  $|1\rangle$ ,  $|2\rangle$  in the center the  $a_{1g}$ ,  $|3\rangle$  and on the bottom the  $e_g$ ,  $|4\rangle$ ,  $|5\rangle$  orbitals. The shown cubic axes are (almost) the same in both the unit cell and orbital plots. The structure plot was obtained using the XCrySDen program [217].

orbitals drastically, in contrast to the findings of Ref. [201]. The static crystal field was no longer correctly reproduced and an interpretation in terms of the competition of the crystal field with the Hund's rule coupling was not possible.

The crystal field levels we obtained are shown in Tab. 4.2.1 for the three temperatures we considered. They show a clear splitting, as expected by the symmetry into two  $e_g^{\pi}$  states one  $a_{1g}$  orbital and two  $e_g$  orbitals. The splitting, e.g. between the highest and lowest lying orbitals, increases when the temperature is reduced, differing by about 100meV between 5K and 650K. In absolute terms the total splitting between the centroid of the  $e_g$  states is about 1.6eV at 650K and increases to 1.7eV at 5K. In addition, the increasing distortions of the CoO<sub>6</sub> octahedra introduce additional small splittings between the  $e_g^{\pi}$  and  $e_g$  orbitals that are degenerate at high temperatures. We have analyzed the hopping integrals at the different temperatures that can sometimes give a hint at localization, see, e.g., [330]. For LCO we have calculated the hopping

matrices between the adjacent unit cells in all directions, i.e. in units of the primitive lattice vectors the  $(\pm 1, 0, 0)$ ;  $(0, \pm 1, 0)$ ;  $(0, 0, \pm 1)$  directions. The unit cell shape and the positions of the two Co atoms within dictate that the dominant hopping contribution will always be from Co(1) in one unit cell to Co(2) in the neighboring cell; the hopping in-

	1 angle	$ 2\rangle$	$ 3\rangle$	$ 4\rangle$	$ 5\rangle$	
5K	-0.51	-0.50	-0.47	+1.18	+1.19	
300K	-0.48	-0.48	-0.45	+1.18	+1.18	
650K	-0.47	-0.47	-0.44	+1.11	+1.10	

# **Table 4.2.1:** On site energies in eV versus the Fermi level for the five symmetry adapted basisfunctions for each temperature considered. Temperatures refer to the ones given inRef. [353].

tegrals can then be labeled, e.g.  $t_{2\rightarrow 1}^{100}$ . Since we were interested in trends only and not in a detailed analysis we have averaged the hoppings. To avoid any directional bias we averaged not only over the contributions from all orbitals, but also over all directions. The average hopping we employed is

$$\bar{t} = \frac{1}{N_{\rm t} \cdot N_{\rm dir}} \sum_{ij} 2\Big( \left[ t_{2 \to 1}^{100} \right]_{ij} + \left[ t_{2 \to 1}^{010} \right]_{ij} + \left[ t_{2 \to 1}^{001} \right]_{ij} \Big), \tag{4.2.1}$$

where  $N_t$  is the number of entries in the hopping matrix,  $N_{dir}$  the number of directions and the factor of 2 comes from the equality required by symmetry of the neighboring unit cells and the hoppings, e.g.  $t_{2\rightarrow 1}^{100} = t_{1\rightarrow 2}^{-100}$ . The average hoppings thus obtained are  $\bar{t}_{5K} = 74 \text{meV}$ ,  $\bar{t}_{300K} = 74 \text{meV}$ ,  $\bar{t}_{650K} = 72 \text{meV}$ . They show no clear trend as a function of temperature and thus the physics of the compound is not expected to be governed primarily by a competition between band width, connected to t, and Coulomb interaction. This comes as no surprise since the band width shows virtually no variation with temperature in DFT, the ratio of band width versus the local Coulomb interaction can thus not be responsible for metal-insulator transitions etc. in this case, unlike in the perovskites studied in Refs. [330, 131]. It remains that the interplay of the crystal field and the Hunds exchange interaction is expected to be the key ingredient in the mechanism of the high-spin to low-spin transitions as in the ionic picture.

## 4.3 DFT+DMFT

Since the DFT alone cannot account for the physics of LCO we have performed additional calculations within the framework of DFT+DMFT. To this end we employed an impurity solver based on the Lanczos method for exact diagonalization (ED) at finite temperature.



Figure 4.2.6: The LS to HS spin transition as a function of the Hunds rule coupling J signified by the respective occupancies of the  $t_{2g}$  and  $e_g$  states. An LS state with occupancy  $t_{2g}^6 e_g^0$  is realized for J = 0.55eV, while the HS is obtained for all temperatures at J = 0.8eV. In between the two extremes an interstitial region with mixed LS and HS states exist. The temperatures refer to the lattice setup; calculations have been performed at  $\beta = 100$ eV<sup>-1</sup>,  $\beta = 40$ eV<sup>-1</sup>,  $\beta = 15$ eV<sup>-1</sup> for the 5K, 300K and 650K structures respectively

As required by the method we have approximated the system by a finite cluster, see section 1.6.4. The bulk of the calculations has been performed using a ten site cluster, i.e. a model with five impurity orbitals and five bath sites. For a few parameter sets we also performed calculations with a ten site bath, i.e. a 15 site cluster in total. This did not alter any conclusions though and data will not be shown here. To fit the bath to its discrete counterpart we have applied an unbiased least squares fit on the Matsubara axis. The ED solver is capable of using the whole rotationally invariant Coulomb interaction  $U_{ijkl}$  that was rotated into the crystal field basis.

We are aware that the bath discretization in ED can be an issue, so we have performed also comparative calculations using a hybridization expansion QMC solver, based on the segment picture. The results are similar, showing only small deviations due to the discretized hybridization over the whole range of temperatures and parameters. One has to observe however, that the QMC code uses only the density-density part of the Coulomb interaction, while the ED solver is capable of using the whole rotationally invariant Coulomb tensor. Since the QMC calculations were only performed as checks and add nothing to the story, data will not be shown here.

We have performed calculations for different temperatures using the 5K, 300K and 650K crystal structures. In addition to the crystal field that we obtained ab initio we varied the interaction parameters to get a clear picture of possible spin state transitions in LCO. The self-energy was obtained for one Co atom via ED and was subsequently applied also to the other Co atom in the unit cell via symmetry transformations. This is an approximation, since the two atoms are constrained to be in the same spin state at all times. Calculations treating both atoms independently in DFT+DMFT are possible within our formalism and are being performed at the time of writing. Such calculations have been performed already within DFT+U by Knížek et al. [207, 206].

Since the LDA+U work or Korotin et al. [268] it has been widely believed, the literature reflecting this fact, that LCO is a strongly correlated electron system with an on-site Coulomb interaction of U = 8eV. Recently a work by Křápek et al. [201] showed a cDFT result on the order of U = 6eV. It is a known fact, however, that the values of the static interaction parameters obtained from constrained DFT as well as constrained RPA are basis set dependent (as they should be). This in turn makes discussions based solely on the numerical *values* of the interaction parameters futile, since the numbers have not much meaning without the context in which they have been obtained, as we have commented in the introduction already. As we have seen in the case of SrVO<sub>3</sub> depending on the basis of localized orbitals the values of U can change by a few electron volts. In general the value will be higher the more localized the basis is chosen. It is not surprising that different values of U are around. To find the value appropriate in our case, i.e. for the Co 3d shell only we have relied on measurements of the excitation gap in LCO. The measurements give a value of about 0.9eV from photoemission and absorption spectra [3], while optical measurements gave values between 0.6eV [74] and 0.3eV [25]. We have thus performed a few calculations with different parameters starting from the recent cRPA estimates. We find that a value of U = 3eV is sufficient to produce a charge gap on the order of 1eV, we have consequently used this value. Since the value of the Hunds rule coupling J is, for a fixed U and crystal field splitting  $\Delta$ , the critical parameter for the spin state transition we have calculated spectra at different values of J. To include also some effect of temperature the calculations were performed for different temperatures for the different crystal structures namely at  $\beta = 100 \text{eV}^{-1}$ ,  $\beta = 40 \text{eV}^{-1}$ ,  $\beta = 15 \text{eV}^{-1}$  for the 5K, 300K and 650K structures respectively. We find that for the three crystal structures and their respective crystal fields a spin state transition occurs at about the point where  $\Delta \sim 2J$ . We show the LS to HS transition, indicated by the increasing population of the  $e_q$  states, as a function of J in Fig. 4.2.6. One can see that depending on the crystal field splitting and the temperature the transition occurs at slightly different points. Also, the transition is smoother for higher temperatures, showing a population of the HS state at relatively small values of J. The states we observe are only composed of the low spin and high spin states, i.e. contributions of the  $d^6$ , S = 0 and  $d^6$ , S = 2 with no contribution from any S = 1 states. The same is true within the QMC sector analysis; the absence of the IS



Figure 4.3.7: Orbitally resolved spectral functions of LCO, showing the gradual transition from the low spin to the high spin state, obtained using the 300K structure and different values of J.

state is thus not an artifact of the ED treatment. The transition region is governed by an increased admixture of the HS contribution to the LS ground state. The analysis shown in Fig. 4.2.6 also is a way of estimating the Hunds rule coupling. The Hunds rule coupling in LCO must be such, that the low temperature ground state is the LS state and the high temperature state is the HS state. At about 300K a transition between the two states mimicking an IS state takes place. In our model a choice of about J = 0.7eV reproduces this behaviour as a function of temperature.

Let us now turn to the spectra. In Figs. 4.3.7 (a) to 4.3.7 (c) and Figs. 4.3.8(a) to 4.3.8(c) we show the momentum integrated orbitally resolved and momentum resolved spectral functions for the pure LS (J = 0.6 eV), the mixed state (J = 0.7 eV) and the pure HS (J = 0.8 eV) states of the 300K crystal structure. We choose this crystal structure to discuss the electronic features, since it features all relevant spin states and features of the whole temperature range. The non-magnetic low-spin state in Fig. 4.3.7 (a) is closest to the DFT solution, the strongest modification is the rigid upward shift of the  $e_g$  bands and, as a consequence, the gap opening between  $t_{2g}$  and  $e_g$  states. In accordance with combined DFT and cluster calculations [4] as well as recent QMC [201] we find that the states at the gap edge are predominantly of Co 3d character, while at lower energies O 2p states dominate. The formation of local moments in the higher temperature HS states leads to the appearance of incoherent features in the spectrum. As a result the gap changes its character from  $t_{2g} - e_g$  to  $t_{2g} - t_{2g}$  with incoherent  $t_{2g}$  excitations on both gap edges. The occupied parts of the spectra exhibit a transfer of spectral weight away from the strong  $t_{2q}$  excitation peak towards higher binding energies as the LS to HS crossover commences. The momentum resolved spectra shown in Fig. 4.3.8 (a) show very coherent and dispersive bands in the LS state, while the HS state shows increasingly incoherent and nondispersive features stemming from the Co 3d states, see Fig. 4.3.8 (c). The localized La 4 f bands at about 3-4eV above the Fermi level remain unchanged along the transition. The features of the oxygen 2p spectrum also remain mostly unchanged, apart from the states close to the Fermi level that show some spectral weight being transfered away from the peak at -2.5eV to the gap edges. Clearly, the strongest overall changes are visible for the unoccupied part of the spectra shown in Figs. 4.3.8 (a-c).

Comparing the spectra to the ones obtained by Křápek et al. within CT-QMC we find a good overall agreement. Some additional band splittings are observed in our case, which is due to the inclusion of the full multiplet structure, while Křápek et al. limited themselves to density-density interactions. On the other hand they included more p - d hybridization and treated it exactly while we used only one bath site mostly. The spin state transition becomes better visible if we single out the Co 3d states from the k-resolved spectral functions as we have done in Fig. 4.3.9. Clearly the LS state shows dispersive, almost DFT like bands, while the HS state is spread out over a larger energy range and shows mostly nondispersive features. Including another bath site does not influence the results on a qualitative level. The spectra as well as the spin transition remain stable.



Figure 4.3.8: Momentum resolved spectral functions of LCO, showing the gradual transition from the low spin to the high spin state, obtained using the 300K structure and different values of J.



Figure 4.3.9: Momentum resolved spectral functions for the Co 3d states of the 300K structure (a) LS state (b) HS state, note the reduced scale.

#### 4.4 Summary and Conclusions

We have studied LaCoO<sub>3</sub> within the DFT+DMFT formalism using an ED solver employing the Lanczos method. We find that the spin state transition as a function of the crystal field splitting takes place between the Hund's rule ground state, the high-spin state and the low-spin state. We do not find contributions from the S = 1 intermediate state. Our study thus further corroborates the scenario put forward by Goodenough [130]. Our calculations agree qualitatively with the recent CT-QMC study by Křápek et al. [201] concerning the spectra and their interpretation. This shows that the interpretation of the local physics of LCO is possible using only the  $d^6$  multiplets of Co.

We are aware, of course, of the limitations of our study and possible improvements: First, both Co atoms within the unit cell should be treated independently. This would possibly entail different interaction parameters U and J (cluster analyses of spectra point towards  $U_{\rm HS} - U_{\rm LS} \sim 1.3 {\rm eV}$  [469]), as well as different occupancies. Ultimately, such a treatment also allows for ordered states of the LS-HS type or more complicated types, when more unit cells are included. Second, the whole hybridized block of dp character, extending from +4eV down to  $-8{\rm eV}$  should be taken into account. This, however, complicates the picture and necessitates a departure from the strict  $d^6$  picture for the Co ion. The hybridization will increase the occupancy of the Co d shell making a description including contributions from  $d^7$  and  $d^8$  states necessary. Additionally, the effects of the Coulomb interaction are not so easily understood as in our picture which is closer to the ionic model. A study that remedies some of the limitations of the present approach is under way at the time of writing, however, at the moment we can conclude that the basic ideas of Goodenough from the 1950s and 1960s seem to have stood the test of time.

## Chapter 5

# **Correlation Effects in Transition Metal Benzene Molecules**

M. Karolak, D. Jacob, and A. I. Lichtenstein, *Orbital Kondo Effect in Cobalt-Benzene Sandwich Molecules*, Phys. Rev. Lett. **107** (2011), 146604

As we have seen in the preceding chapters electronic correlations arising from the Coulomb repulsion between the electrons can have a strong impact on the electronic properties of a material. For example, the Mott metal-insulator transition, the Kondo effect, heavy fermion behavior, and high temperature superconductivity are important phenomena that arise from electronic correlations [123, 220, 156, 272]. Moreover, the electronic properties of strongly correlated materials can often be tuned sharply by application of external fields or doping. This opens a route to the design of novel electronic devices based on strongly correlated materials [112]. Up to now we have focussed on bulk materials that can be seen as infinite lattices populated by itinerant or localized electrons. We will in this and the following chapter turn to nanoscale devices, where correlation effects should even be enhanced compared to bulk materials due to the lower coordination of the atoms resulting in a reduced screening of the Coulomb interaction. Furthermore, nanoscale devices such as atomic and molecular conductors offer a further experimental handle to control the electronic and transport properties of these systems by manipulation of the molecular geometry [168, 76]. Particularly interesting systems both from the point of view of applications and fundamental physics are magnetic atoms and molecules deposited either on metal surfaces or contacted by metallic contacts. From the point of view of application such devices built from molecular magnets [122] offer the possibility of ultimately miniaturized magnetic storage devices and for spintronics applications [457, 432, 55, 378]. On the other hand, whenever a magnetic atom or molecule is coupled to a metal substrate or metal electrodes the Kondo effect can arise [220, 156]. We will dwell a bit on this interesting many-body effect in the next section. The importance of dynamical correlations in nanoscopic devices in general is further substantiated by the

recent observation of the Kondo effect in nanocontacts made from the transition metals (TM) Fe, Co and Ni [69].

Here we explore the impact of dynamic correlations on the electronic structure of different transition metal benzene sandwich molecules trapped between the tips of Cu nanowires as examples of molecular magnetic devices. The investigation of these and related sandwich complexes is driven by their relevance in various chemical applications (e.g. catalysis) and more recently also because of their prospective nanotechnological applications for example as molecular magnets [122] or spintronic devices [458, 280, 291].

Molecules with a transition metal center coupled to aromatic groups are also of high interest from a fundamental point of view. The strong electronic correlations in the d shell of the transition metal can modify the ground state and electronic transport properties of such molecules, leading to many-body phenomena like the Kondo effect [156] as recently observed in TM-phthalocyanine molecules [471, 118].

We will show that transition metal benzene sandwich molecules with Cobalt and Vanadium atom centers can exhibit a so-called orbital Kondo effect when the sandwich is slightly compressed as compared to the free molecule. We investigate the effect of replacing the central atom with other 3d transition metals. We also show that the Kondo effect can be controlled by application of a gate voltage which changes the occupancy of the transition metal center, and by the geometry of the molecule.

#### 5.1 The Kondo effect in metals and nanoscopic devices

What we refer to today as the Kondo effects was puzzling physicists for decades in the twentieth century, see e.g. the book by Hewson for a historical review [156]. Experimentally the effect was manifesting itself in an anomalous behavior of the resistivity of metals at low temperatures. The prototypical example is the resistivity of gold as reported in 1934 down to temperatures below 2K [90]. Conventional theory at that time would predict that for a pure metal the resistivity goes to zero or decreases monotonically to a finite value at low temperatures, while it increases via phononic contributions as  $T^5$  for higher temperatures. However, the experiments showed a resistivity minimum and an *in*crease at temperatures below it. The generic behavior of the resistivity is shown in Fig. 5.1.1 on the left hand side for different types of metals. At the time this was unexpected and a challenge for physicists. As could be established in further experiments, e.g. Ref. [371], the behavior of the resistivity could be manipulated via the concentration of magnetic impurities in the host metal. It was not until 1964, however, that in the work of Jun Kondo the theoretical mechanism behind the phenomenon was discovered [220]. Kondo was able to show that assuming the impurities have a local magnetic moment that interacts with the itinerant host metal electrons via an antiferromagnetic exchange interaction J the resistivity minimum can be explained. Kondo's calculation of the resistivity was



**Figure 5.1.1:** Left: Resistance as a function of temperature for a normal metal (blue) superconductor (green) and for metals containing magnetic impurities (red). Right: Conductance as a function of temperature for a quantum dot system containing an even number of electrons (blue) and an odd number of electrons and thus a local moment (red). Figure adapted from Ref. [228].

carried out for the s - d model (often also referred to as the Kondo model) that describes a local magnetic moment (the impurity) coupled to the conduction electrons of the host metal via a Heisenberg exchange interaction with coupling constant  $J_{\alpha\alpha'}$ :

$$\hat{H}_{\rm sd} = \sum_{\alpha,\sigma} \varepsilon_{\alpha} \hat{c}^{\dagger}_{\alpha}{}_{,\sigma} \hat{c}_{\alpha}{}_{,\sigma} + \sum_{\alpha,\alpha'} J_{\alpha\alpha'} \left( \hat{S}^{+} \hat{c}^{\dagger}_{\alpha}{}_{,\downarrow} \hat{c}_{\alpha',\uparrow} + \hat{S}^{-} \hat{c}^{\dagger}_{\alpha}{}_{,\uparrow} \hat{c}_{\alpha',\downarrow} + \hat{S}_{z} \left[ \hat{c}^{\dagger}_{\alpha}{}_{,\uparrow} \hat{c}_{\alpha',\uparrow} - \hat{c}^{\dagger}_{\alpha}{}_{,\downarrow} \hat{c}_{\alpha',\downarrow} \right] \right) + \hat{C}_{\alpha} \hat{c}_{\alpha',\uparrow} \hat{c}_{\alpha',\downarrow} \hat$$

In above equation the operators  $\hat{c}^{\dagger}_{\alpha,\sigma}$  and  $\hat{c}_{\alpha,\sigma}$  are the creation and annihilation operators of the energy eigenstates and  $\hat{S}_z$ ,  $\hat{S}^{\pm}$  are the z component of the spin and spin ladder operators, respectively. Within perturbation theory to the third order in  $J_{\alpha,\alpha'}$  Kondo was able to show that the total resistivity as a function of temperature of a metal in the presence of localized magnetic impurities can be written as

$$R(T) = aT^{5} + cR_{0} - cR_{1}\ln(k_{\rm B}T/D),$$

where D is the conduction electron bandwidth and the rest are constants [156]. Together with the phononic contribution that increases with temperature as  $T^5$  a minimum at a certain temperature, the Kondo temperature  $T_{\rm K}$ , can be produced, thus explaining the experimental findings. Since the  $\ln T$  contribution will diverge for low temperatures Kondo's solution could not be considered complete. Within perturbation theory one already obtains a general characteristic, exponential, dependence of the Kondo temperature on the



Figure 5.1.2: Spectral function of the symmetric one band Anderson model obtained via Numerical Renormalization group at half filling for different values of the interaction U. One can observe the evolution from the non-inteacting spectrum towards the interacting spectrum showing a Kondo resonance as well as lower and upper Hubbard bands. The inset is a detail of the region around the Fermi level for the two largest interactions. From Ref. [156].

exchange coupling [156]

$$k_{\rm B}T_{\rm K} \sim De^{-\frac{1}{2|J|\rho_0}}$$
 (up to order  $J^2$ ) or  $k_{\rm B}T_{\rm K} \sim D|2J\rho_0|^{\frac{1}{2}}e^{-\frac{1}{2|J|\rho_0}}$  (up to order  $J^3$ ),

where D is the conduction electron band width and  $\rho_0$  the constant density of states of the host metal. It was furthermore assumed that  $J_{\alpha,\alpha'} = J$ . The theoretical *Kondo problem* was widely studied and a review is beyond the scope of our brief introduction; a comprehensive review of the theory viewpoint on "all things Kondo" can be found in the Book by Hewson [156] or the extensive review by Cox and Zawadowski for the more *exotic* Kondo effects [80]. Finding solutions that are valid in both high and low temperature regimes was the subject of great theoretical effort and it was not until the machinery of Wilson's numerical renormalization group (NRG) (see e.g. the reviews [456, 66]) was at hand that the Kondo effect was understood theoretically to a satisfactory degree. A further important conceptual step was taken by Nozières who showed that the Kondo regime could be characterized by a low energy Fermi liquid [314]. In the Fermi liquid theory by Landau, the low energy excitations of a system of interacting electrons are interpreted in terms of quasiparticles, see the brief discussion at the end of section 1.4.1. In the Kondo regime the density of states corresponding to these quasiparticles takes the form of a resonance at (or in general close to) the Fermi level with a width proportional to the Kondo temperature, as shown in Fig. 5.1.2 for a one band Anderson model. Taking into account more of the structure of the impurity, e.g., multiple orbitals and charge fluctuations makes the problem even more complex, see, e.g., [315]. In such more complex cases the s - dmodel is too simplistic and more realistic models, like the Anderson impurity model are used, see section 1.4.3. It can be shown that in the limit of frozen charge fluctuations the s - d model can be derived from the Anderson model via a canonical (Schrieffer-Wolff) transformation [381]. The exchange coupling can be shown to be a combination of the parameters of the Anderson model [156]

$$J_{\alpha,\alpha'} = V_{\alpha}^* V_{\alpha'} \left( \frac{1}{U + \varepsilon_d - \varepsilon_{\alpha'}} + \frac{1}{\varepsilon_\alpha - \varepsilon_d} \right),$$

where  $\varepsilon_{\alpha}$  and  $\varepsilon_d$  are the bath and impurity levels and  $V_{\alpha}$  is the hybridization strength. One of the striking features of the Kondo problem is its apparent simplicity and its deeply hidden complexity that requires the application of the most sophisticated theoretical tools. It was not until 2009 that the Kondo effect of iron impurities in gold (one of the original problems that started the Kondo business) was more or less settled [78]. Another is universality. Universality implies that the low energy properties of a class of systems exhibiting a Kondo effect are controlled by only one relevant energy scale, the Kondo temperature  $T_{\rm K}$ , which can be very different over the class of systems. For example, the Kondo temperature in the single band Anderson model can be shown to depend on the interaction U, the position of the impurity level  $\varepsilon$ , and the broadening of the level via hybridization  $\Gamma$  [143]

$$k_{\rm B}T_{\rm K} = \frac{1}{2} \left(\Gamma U\right)^{\frac{1}{2}} \exp\left(\frac{\pi\varepsilon(\varepsilon+U)}{\Gamma U}\right),$$

where  $\Gamma = V^2 \rho_{\text{bath}}(E_{\text{F}})$  is the broadening obtained by integrating out the bath. Now, since this formula depends exponentially on the interaction and the broadening tiny changes in these parameters can have a dramatic effect on the Kondo temperature. Interestingly, physical quantities, like the resistivity, can, in the Kondo regime, be expressed as a universal function of the dimensionless parameter  $T/T_{\text{K}}$ . This means that even if the parameters of these systems differ very much, their behavior in the Kondo regime is universal for all of them and determined *only* by the Kondo temperature.

Interest in the Kondo effect surged again as new experimental devices, such as quantum dots [127] or the scanning tunneling microscope (see Refs. [44, 454] for the classical and a recent review) allowed a microscopic study and manipulation of small systems exhibiting the Kondo effect. Usually, the Kondo effect leads to the screening of the magnetic moment by the conduction electrons of the metal due to the formation of a total spin-singlet



**Figure 5.1.3:** Fano lineshapes with the parameters  $q = 0, \pm 1, +\infty$ . The plotted function is normalized and shifted:  $0.5 + \frac{1}{1+q^2} \frac{(\varepsilon+q)^2}{1+\varepsilon^2}$ .

state, and is signaled by the appearance of a sharp and strongly temperature-dependent resonance in the spectral function at the Fermi level, the so-called Kondo resonance or Abrikosov-Suhl resonance, as shown in Fig. 5.1.2. The Kondo resonance in turn gives rise to a zero-bias anomaly in the conductance characteristics of the nanoscale device. These anomalies can be described by so-called Fano lineshapes [104] in the low bias conductance. The classical Fano formula describes the interference that appears when one discrete state and one continuum state scatter. In such a case characteristic asymmetric peaks were observed in excitation spectra of He, which was the original problem addressed by Fano. For the Kondo problem the scattering occurs in transport between the Kondo resonance within the localized d states and s states on the same impurity. The generalized Fano formula for the low bias conductance C(V) in such a case can be written as

$$C(V) = c + \frac{A}{1+q^2} \frac{(\varepsilon+q)^2}{1+\varepsilon^2},$$

where c is some static offset, A is the amplitude of the Fano resonance, q is the Fano

factor determining the lineshape and  $\varepsilon$  is the reduced energy variable

$$\varepsilon = \frac{eV - \varepsilon_{\rm K}}{\frac{1}{2}\Gamma_{\rm K}}$$

containing the position of the Kondo resonance  $\varepsilon_K$  as well as its width  $\Gamma_K$ . The Fano factor is actually a complicated function associated with transition probabilities that is assumed to be a constant in the relevant (small) energy limit [104]. The two limits  $q \to \infty$ and  $q \rightarrow 0$  correspond to the situation where the conductance through the impurity is solely through the d level or solely through the s level coupled to the Kondo resonance, respectively. For |q| = 1 the conductance is still dominated by the indirect transport through the s channel with the difference, that the s level is now not close to the Fermi level. The Fano lineshapes for these parameters are shown in Fig. 5.1.3. In fact, such zero bias anomalies have been observed in numerous experiments involving magnetic atoms and molecules depositied on surfaces or attached to leads [271, 252, 208, 471, 118, 303]. Hence the Kondo effect can be problematic for applications of molecular magnetic devices in spintronics or for magnetic information storage devices. In quantum dots the underlying physics that the impurity spin is flipped on classically forbidden timescales via virtual states remains the same, the effect on the conductance of such a device is albeit different. For the itinerant electrons in a metal impurities with local magnetic moments act as scattering centers that increase resistance, in a quantum dot the appearance of states at the Fermi level via the Kondo resonance actually facilitates conduction [127, 228]. The Kondo resonance leads to the formation of states at the Fermi level facilitating conduction and overcoming the Coulomb blockade. The Kondo effect thus has the converse effect on the conductance in a quantum dot as in a bulk metal. This is illustrated in Fig. 5.1.1 on the right hand side.

We have assumed the simplest possible picture in our discussion, however, not always does the occurrence of the Kondo effect imply a screening of the entire magnetic moment of the atom or molecule. Therefore, it is important to fully understand under which circumstances and conditions the Kondo effect can occur. From a more fundamental point of view, the Kondo effect is one of the most intriguing many-body phenomena. In real systems there exist the possibility for a variety of flavors of Kondo physics that are related to the interplay between orbital and spin degrees of freedom of the strongly interacting electrons. For example, a so-called underscreened Kondo effect where the magnetic moment is only partially screened can occur when the spin of the magnetic atom or molecule is higher than the total spin of the available screening channels [315]. Such an underscreened Kondo effect has recently been reported for a magnetic molecule trapped in a breakjunction [323]. While the Kondo effect is commonly associated with the screening of a local magnetic moment by the conduction electrons, it is also possible that another internal degree of freedom associated with a degeneracy gives rise to a Kondo effect [80]. One example is the so-called *orbital Kondo effect* where the pseudo-spin arising from an



Figure 5.1.4: (a) Spin S = 1/2 Kondo effect in a quantum dot (b) Orbital Kondo effect in a quantum dot. Figure adapted from Ref. [182].

orbital degeneracy is screened by the conduction electrons [218, 182]. The difference between a spin Kondo effect and an orbital Kondo effect occurring in a quantum dot is illustrated in Fig. 5.1.4 that we have in part reproduced from Ref. [182]. In part a) of the figure the initial and final states leading to a spin Kondo effect are shown, while part b shows the same process involving an orbital flip. In the spin Kondo effect the spin  $|\uparrow\rangle$  or  $|\downarrow\rangle$  is flipped via virtual processes. In the orbital Kondo case the degenerate orbitals are assigned a pseudo spin  $|+\rangle$  and  $|-\rangle$ , which is subsequently flipped. The prerequisites for such an effect to occur are two degenerate orbitals at an appropriate filling. In principle also a combination of both can occur, a so called SU(4) symmetric Kondo effect [56], that has been observed experimentally in carbon nanotubes [182] and also very recently in a double quantum dot device [199].

#### 5.2 Transition Metal Benzene Complexes

The discovery of ferrocene and bisbenzene chromium [197, 110] over half a century ago was the starting point for experimental and theoretical work both in chemistry and physics concerning the intricate properties of organometallic compounds. The characteristic sand-wich structure was first proposed for ferrocene by Wilkinson and co-workers [455] and subsequently verified by the second key player in the "sandwich business" E.O. Fischer, who also began to synthesize sandwich molecules with different centers [109]. Here, we consider single transition metal (TM) benzene (Bz) sandwich molecules in contact with two semi-infinite Cu nanowires as shown schematically in Fig. 5.4.6 (g). The sandwich

is formed by two benzene rings  $(Bz=C_6H_6)$  covering a metal atom. Wilkinson and Fischer shared the Nobel Prize in chemistry in 1973 for

their pioneering work, performed independently, on the chemistry of the organometallic, so called sandwich compounds.

Fischer remained active in the field, first synthesizing bisbenzene complexes, like VBz<sub>2</sub> [108]. The TMBz<sub>2</sub> molecules are the smallest instance of a general class of  $M_nBz_m$  organometallic complexes, where M stands for a metal atom, that have been prepared and investigated starting from the prototype CrBz<sub>2</sub> in 1955, see Refs. [390, 97] for reviews. Vanadium half sandwich VBz complexes were first synthesized and characterized in pentane solution by Andrews and Ozin in the mid 1980s. These discoveries along with extensive experimental and theoretical calculations also for VBz<sub>2</sub> (that we will revisit below) on the level of  $X_{\alpha}$  theory were reported in a series of papers [17, 16].

Starting about a decade late Kaya and colleagues [162, 239, 240, 301] have synthesized and investigated general metal-benzene complexes comprised of n metal atoms and mbenzene rings:  $M_nBz_m$ . They successfully produced a variety of complexes in the gas phase using the whole 3d transition metal series from Sc to Cu. Concerning the structure of the complexes with M=Sc,Ti,V the authors established, experimentally, that the complexes form linear sandwich clusters of the form  $M_nBz_{n+1}$  without exterior metal atoms, whereas the late transition metals form so-called rice ball structures where one or more metal atoms are covered by benzene rings in an almost spherical fashion. Stern-Gerlach experiments for the early transition metal sandwiches revealed a magnetic moment of  $0.4\mu_B$  (0.4 Bohr magnetons) for ScBz<sub>2</sub> and  $0.7\mu_B$  for VBz<sub>2</sub> and no magnetic moment for TiBz<sub>2</sub> [289].

On the theory side these complexes were studied using different methods ranging from simple ligand field calculations over  $X_{\alpha}$  and DFT calculations up to wave function based quantum Monte Carlo by various authors usually focussing on a specific metal center. The generic bonding mechanism for the MBz<sub>2</sub> complexes was established from ligand field theory arguments supported by  $X_{\alpha}$  calculations for CrBz<sub>2</sub> [442, 317] and VBz<sub>2</sub> [16]. The mechanism is similar to the bonding of single transition metal atoms to a single benzene ring [30]. First, ligand field theory for the  $C_{6v}$  symmetry dictates that the 3d orbitals of the metal center will be split into three irreducible representations:  $a_{1q}^{\sigma}(d_{z^2}), e_{1q}^{\pi}(d_{xz}, d_{yz})$ and  $e_{2q}^{\delta}(d_{xy}, d_{x^2-y^2})$ . Notations concerning the symmetry differ in the literature, the representations sometimes being called  $a_1, e_1, e_2$  or just using the symbol for the symmetry group and representation synonymously, capitalizing the symbol  $A_1, E_1, E_2$ . In the results section we will use the latter notation. The z-axis is here the axis going through the center of the benzene rings and constitutes the 6-fold rotation axis. The  $e_{2a}^{\delta}$  orbital has a strongly bonding character through in-phase combinations of the in-plane metal orbitals with the benzene  $\pi$  orbitals, leading to its energetic stabilization, i.e. it is energetically most favorable and occupied preferentially. The  $e_{1q}^{\pi}$  orbitals form out of phase combinations with
the ligand  $\pi$  electron system and are thus antibonding in character, while the  $a_{1a}$  remains nonbonding since it points through the center of the benzene. The primary bonding interactions are brought about by electron transfer from the benzene  $\pi$  to the metal  $e_{1a}^{\pi}$  relieved by backtransfer from the metal  $e_{2q}^{\delta}$  to the  $\pi^*$  orbitals of the ligands. In  $X_{\alpha}$  calculations by Andrews et al. [16] it could be shown that the attachment of benzene rings to a V atom leads to the loss of  $0.5 \ 3d$  electrons per benzene attached, leading to a  $3d^4$  configuration on the metal. At the same time the direct interaction between the benzene rings is small due to their relative large distance. These mechanisms in principle apply to the whole series of TMBz<sub>2</sub> molecules. Following the successful preparation of TMBz<sub>2</sub> complexes in the gas phase the interest in these complexes was renewed. A DFT study for the whole series from Sc to Ni was carried out by Pandey et al. [321] who investigated TMBz and TMBz<sub>2</sub> complexes and their respective cationic and anionic versions. Assuming a hexagonal  $D_{6h}$ symmetry (i.e. the form of the complex shown in Fig. 5.4.6 (b)) they find a nonmonotonic evolution of the size of the TMBz<sub>2</sub> complexes. By size, here, the distance between metal atom and center of the benzene rings is meant. The authors, however, note, that although their calculations agree quite well with experiments for Sc to Cr, the agreement is poor for Co and Ni complexes. They speculate that the assumption that the CoBz<sub>2</sub> and NiBz<sub>2</sub> complexes have a  $D_{6h}$  symmetry might be incorrect, as is actually the case as we will see below. Pandey et al. calculate also the valence configurations and spin multiplicities for all complexes, assuming  $D_{6h}$  symmetry. Weng and co-workers [446, 445] performed GGA and for the first time also GGA+U calulations for the symmetric sandwich structures of Sc, Ti and V centered clusters with  $TM_nBz_{n+1}$  typically for n = 2. The authors focussed on magnetic properties, especially on how they can be manipulated and tuned from FM to AFM order within the cluster. They found that an increasing local Coulomb interaction U leads to a general increase of the magnetic moment in the Vanadium 3dshell in a finite cluster as well as for an infinite chain.

More recent calculations for  $\text{CoBz}_2$  [470] and  $\text{NiBz}_2$  [355] revealed that the ground state of these systems is an asymmetric sandwich arrangement with merely  $C_1$  symmetry (see Fig. 5.4.6 (c)). The lowering of energy by breaking the  $D_{6h}$  symmetry can be understood as an effect of the 18 electron rule [242, 82], that causes the complexes with more than 18 valence electrons (CoBz<sub>2</sub>, NiBz<sub>2</sub> have 21, 22 respectively) to bend due to the symmetry of the HOMO (highest occupied molecular orbital). The HOMO is lowered in energy when the relative orientation of the two benzene rings is tilted. In the asymmetric sandwich structure the magnetic moments were found to be  $1\mu_B$  (one Bohr magneton) for CoBz<sub>2</sub> and vanishing for NiBz<sub>2</sub>. The quenching of the moment of Ni was explained by the strong hybridization between the Ni 3*d* states and the  $\pi$  electrons of benzene [355].

A very recent study of the structural properties of TMBz and TMBz<sub>2</sub> with TM=Sc,...,Zn within Møller-Plesset second order perturbation theory (MP2) calls the established DFT results into question [465]. The authors find that the perfectly symmetric sandwich structure with  $D_{6h}$  symmetry is formed only by VBz<sub>2</sub>. CrBz<sub>2</sub> and MnBz<sub>2</sub> form sandwiches

where the two benzene rings are slightly rotated around the z axis (their respective  $C_6$  axis) with respect to each other. The other complexes show either strongly distorted sandwich structures (Sc, Ti, Fe, Ni) or a completely different arrangement (Cu, Zn). The authors note in passing, that they were not able to obtain a geometry for CoBz<sub>2</sub> due to convergence problems. An ab initio wave function based QMC study could probably settle the matter of the structures, unfortunately it is computationally so demanding that at the moment only studies of TMBz half-sandwiches are possible and have been performed [161]. Since the structures of TMBz show qualitatively the same structure for the whole 3d series the comparison between MP2 and QMC in that case can only give weak hints for TMBz<sub>2</sub>. In addition the methods generally do not agree on the metal-benzene distances, MP2 giving values up to 0.5 smaller than QMC.

Considerable effort from theory was invested in the understanding of multidecker vanadium sandwich complexes [436, 458, 280, 291, 445, 160], since they showed half-metallic behavior possibly allowing for spintronics applications. The  $V_nBz_{n+1}$  complexes or nanowires show a half-metallic ferromagnetic behavior, which means that one spin species shows weight at the Fermi level and is available for transport, while the other spin species is gapped and thus insulating. Such a situation is shown for example in Fig.5.5.9 (b) for the  $a_1^{\sigma}$  channel of VBz<sub>2</sub> in a nanocontact and could be exploited to build a spin filter device. Since we are not aware of any experimental confirmations of this behavior the discussion remains theoretical at this point. Additionally, it is unclear how a possible Kondo effect in such devices would influence the conductance characteristics of a general  $V_nBz_{n+1}$  device. As we show below for VBz<sub>2</sub> the conductance is only influenced mildly by the occurrence of a Kondo effect, however further studies in this direction are required.

### 5.3 Theoretical Setup

The state of the art for calculating the electronic structure and transport properties of nanoscale conductors consists in combining the Kohn-Sham density functional theory (DFT) calculations with the Landauer or non-equilibrium Greens function approach [174, 411]. In this approach the Kohn-Sham DFT effectively yields a (static) mean-field approximation for the complicated many-body problem. Hence the DFT based transport calculations cannot describe the dynamic correlations that give rise to the Kondo effect. Therefore the DFT based transport approach for nanoscopic conductors implemented in the ALACANT software package [320, 179] has recently been extended by the developers [176, 178, 177] in order to capture the effect of dynamical correlations arising from strong local interactions by adapting the DFT++ approach which is the de facto standard in the theory of solids [225] to the case of nanoscopic conductors. As we have discussed in preceding chapters in this approach the incorrect behaviour of the Kohn-Sham DFT for



Figure 5.3.5 & Table 5.3.5: Schematic picture showing the division of the system into device region D and the two leads L and R. The periodic supercell as well as the wire unit cells are used are used in DFT calculations of the system. The device region is the primary scattering region in the subsequent transport calculations. The lead self-energies representing the coupling of the devide region to the semi-infinite leads are indicated by  $\Sigma_L$  and  $\Sigma_R$ , the local Coulomb interaction on the central atom is indicated by U. The values of the interaction parameters U and J used LDA+OCA calculations are indicated in the table on the right.

strongly correlated electrons is remedied by augmenting the DFT with a local Hubbardlike interaction. Here we use the DFT+ $\Sigma$  approach for nanoscopic conductors, cf. section 1.5.5 that combines DFT calculations for the entire system with a many-body impurity solver. In the present case we used the one-crossing approximation (OCA) [144, 225], see section 1.6.3, for solving the generalized Anderson impurity problem for the strongly correlated orbitals. The latter yields the energy-dependent self-energy describing the dynamic correlations arising from the strong electron-electron interactions within correlated orbitals. Similar approaches for describing strong correlations in nanoscopic conductors have recently also been implemented by a few other groups [267, 93, 425, 223].

For the DFT calculations we use the CRYSTAL06 code [94] employing the LDA [216], PW91 [338] and the hybrid functional B3LYP [34], together with the all-electron Gaussian 6-31G basis set, cf. sections 1.2 and 1.3. The geometries of the wires were relaxed beforehand and kept fixed during the calculations. The schematic in Fig. 5.3.5 shows the setup we used for the subsequent calculations. The geometry of the molecule in contact with the wires was relaxed employing the B3LYP functional. In order to perform the DFT electronic structure calculations we use the supercell approach introduced in section 1.5.5. The system is divided into three parts: The two semi-infinite leads L and R and the device region D containing the molecule and parts of the leads. Figure 5.3.5 shows the different regions used here, compare with Fig. 1.5.10 in section 1.5.5. The device region is the central scattering region for the electrons. As described in section 1.5.5 the calculations on the DFT level commence as follows: First, a calculation with the periodic unit

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cell shown in Fig. 5.3.5 is performed. Additionally, the infinite wire is calculated using both left and right unit cells, indicated by the dotted boxes in Fig. 5.3.5. Then the device region is "cut out" and the semi-infinite leads are attached on both sides. The Kohn-Sham Green function of the device region can now be obtained from the DFT electronic structure. Next, the mean-field Kohn-Sham Hamiltonian is augmented by a Hubbard-like interaction term that accounts for the strongly interacting electrons in the 3d shell of the TM center. Here we use a simplified interaction which only takes into account the direct Coulomb repulsion  $U \equiv U_{ijij}$  and the Hund's rule coupling  $J \equiv U_{ijji}$ . We assume that the interaction is somewhat increased as compared to the bulk values since the screening should be weaker than in bulk. Ab initio values for the bulk obtained by the constrained random phase approximation (cRPA) have been reported, e.g., in Ref. [84]. Here we use the values provided in table 5.3.5; but indeed we find that our results are qualitatively stable for a reasonable range of values for U and J (see below). An estimation based on the work by Solovyev et al. [397] performed in Ref. [446] for TiBz and VBz clusters indicates also a value of  $U \sim 3 \text{eV}$  for these molecules. We note that the method presented in Ref. [397] only the  $t_{2q}$  states are assumed to be correlated, while the  $e_q$  states are treated as itinerant and contribute to the screening.

The interacting TM 3d shell coupled to the rest of the system (benzene+leads) constitutes a generalized Anderson impurity model (AIM) [15], cf. section 1.4.3. As already described the AIM is completely defined by the interaction parameters U and J, the energy levels  $\varepsilon_{3d}$  of the 3d orbitals and hybridization function  $\Delta_{3d}(\omega)$ . As usual in DFT++ approaches a double counting correction (DCC) has to be subtracted to compensate for the overcounting of interaction terms. In the calculations involving Co and Ni we employ the so-called fully localized (FLL) or atomic limit correction as introduced in chapter 3

$$\mu_{\rm DC} = U\left(N_{\rm 3d} - \frac{1}{2}\right) - J\left(\frac{N_{\rm 3d}}{2} - \frac{1}{2}\right).$$
(5.3.1)

This approach was successfully applied to single 3d transition metal atoms (Fe, Co, Ni) in nanocontact junctions [176]. We find that this correction works well also for the molecules with the late transition metals Co and Ni as centers. However, we have found that the FLL correction leads to unrealistically high occupancies when applied to molecules centered on the early transition metals Sc, Ti, V. The same would be true on an even larger scale for the AMF correction. As we have shown in chapter 3 and as is known already from DFT+U and related approaches, that the double counting can not be rigorously defined. For the early transition metal sandwiches we have thus adjusted the occupation of the 3dshell to be close to the value obtained from DFT. The DCC can be viewed as an impurity chemical potential as we have discussed in chapter 3 and gives one the freedom to shift the impurity levels around to a certain degree. This can be exploited to mimic the effect of an additional gate electrode on the nanosystem and to push the system into different regimes.



**Figure 5.4.6:** The three structures found in the literature for TMBz<sub>2</sub> molecules: (a) the so-called onion structure, (b) the symmetric sandwich structure and (c) the asymmetric sandwich structure. Relaxed geometries of CoBz<sub>2</sub> between Cu nanowires obtained starting from a distance d = 3.6 Å between Co atom and Cu tip atoms and (d) a linear geometry, (e) a strongly tilted geometry. (f) Geometry obtained with the same starting molecule structure as in (b) but with a smaller electrode separation d = 3.4 Å. (g) The geometry used in the nanocontact calculations along with definitions of the distances d and h. (h) Dependence of the molecule size on the electrode to TM center separation. Equilibrium sizes of the free molecules are indicated by corresponding horizontal lines using the same line style and color.

## 5.4 General Observations

Let us first discuss some general observations applying to the whole class of molecules. As we have mentioned, the molecules of the TMBz<sub>2</sub> series show different structures in nature depending on the central atom. Here we focus on the representatives ScBz<sub>2</sub>, TiBz<sub>2</sub>, VBz<sub>2</sub>, CoBz<sub>2</sub> and NiBz<sub>2</sub>. It has been found that the series with (Sc-Mn) in the center forms in the symmetric sandwich structure shown in Fig. 5.4.6(b), whereas for the (Fe-Ni) series two structures have been proposed, namely the onion and the asymmetric sandwich structure illustrated in Fig. 5.4.6(a) and (c), respectively [240, 470].

We find in agreement with Refs. [470, 355] that the asymmetric sandwich is the energetically most favorable for the Co and Ni centers. Although the difference in total energies is only about 0.048eV for the Co sandwich and 0.062eV for the Ni centered molecule in DFT using the B3LYP functional with the 6-31G basis set. Another structure proposed for the (Fe-Ni) centered molecules is the so-called onion structure shown in Fig. 5.4.6(a). We find that the onion structure is always even higher in energy than the symmetric sand-



Figure 5.4.7: (a) Projected density of states for the 3d shell of Sc for d = 3.2 Å, (b) d = 3.8 Å and (c) d = 4.6 Å. The corresponsing transmission functions are shown in panels (d), (e) and (f) respectively.

wich structure. As already mentioned, according to the 18-electron rule for stable one metal atom compounds, the additional electrons cause the complex to distort to a tilted sandwich structure, see e.g. [242, 82], which leads to different geometries for Co and Ni centered sandwiches than for the early transition metals. For the cationic complex NiB $z_2^+$  the structure is found to tend to be closer to the symmetric sandwich than the neutral complex [355]. When the molecules are brought in contact with electrodes, say in a break-junction or scanning tunneling microscope (STM) experiment, they will interact with the electrodes and their structure will be subject to change. We have used copper electrodes in a hexagonal geometry, as proposed in Ref. [418]. For ScB $z_2$ , TiB $z_2$  and VB $z_2$ , only small changes in geometry occur, the molecule remains in its symmetrical sandwich structure and can, in our idealized picture, only be compressed or elongated by the electrodes.

Conversely, the asymmetric structures as formed by  $\text{CoBz}_2$  and  $\text{NiBz}_2$ , show considerable changes in geometry when in contact with the electrodes. In general though the benzene rings are brought into a more symmetric arrangement as shown in Fig. 5.4.6. Figure 5.4.6(d) shows the relaxed geometry using d = 3.6Å and starting from the linear configuration of the CoBz<sub>2</sub> sandwich aligned with the axis defined by the Cu nanowires. In this case the linear geometry and alignment is preserved. Figure 5.4.6(e) shows the relaxed geometry obtained when starting from a strongly tilted geometry of the sandwich molecule. In this case the linear configuration of the idealized sandwich molecule is approximately recovered. The lifting of the orbital degeneracy in the  $E_2$  channel is on the order of few tens of meV. We additionally show (Fig. 5.4.6(f)) that the effect of the leads



Figure 5.4.8: (a) Projected density of states for the 3d shell of Ti for d = 3.2 Å, (b) d = 3.8 Å and (c) d = 4.6 Å. The corresponsing transmission functions are shown in panels (d), (e) and (f) respectively.

is even stronger at smaller lead-molecule separation. The relaxed geometry obtained for a distance d = 3.4 Å between Co atom and Cu tip atoms shows an even smaller tilting of the Benzene rings, leading to a reduced splitting in the  $E_2$  channel.

Even starting from the strongly asymmetric sandwich structure the presence of the leads favours a parallel arrangement of the Bz rings. Thus in the end the molecules we investigated here are brought into the symmetric sandwich structure, when in contact with the leads. Hence for the study of correlation effects we have assumed the symmetric sandwich structure for all molecules.

We investigate the different molecules at different Cu-tip-TM distances. In the case of Co and Ni we use 3.6 Å, 4.0 Å and 4.3 Å (see Fig. 5.4.6 (g) and (h), whereas for ScBz<sub>2</sub>, TiBz<sub>2</sub> and VBz<sub>2</sub> we used 3.2 Å, 3.4 Å, 3.8 Å, 4.2 Å and 4.6 Å. The Bz-Bz distance *h* varies depending on the distance *d* of the Cu tip to the TM atom in the center of the molecule. Figure 5.4.6(h) shows the general trend of the molecule size versus the electrode distance, the free diameters (obtained for the symmetric sandwich structure using the B3LYP functional) of the molecules are indicated also, showing that the molecules are compressed at small electrode separations. Horizontal lines with the same line style and color indicate the equilibrium geometries of the free molecules. We find in agreement with an earlier DFT study that the center - benzene distance varies non monotonously over the series of transition metal centers, with Cr, Mn and V as the smallest instances [321]. This behavior is very different from the half-sandwiches TMBz where the size decreases from Sc to Ni with a strong jump from Cr to Mn.



Figure 5.5.9: (a) Projected density of states for the 3d shell of V for d = 3.2 Å, (b) d = 3.8 Å and (c) d = 4.6 Å. The corresponsing transmission functions are shown in panels (d), (e) and (f) respectively.

#### **5.5** Electronic structure on the DFT level

We begin by discussing the electronic structure of the molecules in contact with the nanowires on the level of DFT. We have performed calculations using DFT with the L(S)DA and B3LYP functionals. We have collected data concerning occupancies in table 5.9.7 and magnetic moments in table 5.5.6. The LDA will show the smallest moment, while B3LYP contains a 20% admixture of the exact exchange and should thus have a moment higher that LDA at all times.

As we mentioned already the hexagonal symmetry of the sandwich structure leads to a lifting of the degeneracy of the 3d shell. The strong crystal field splits the shell into a singlet  $A_1$  consisting of the  $d_{3z^2-r^2}$  and two doublets  $E_1$  consisting of the  $d_{xz}$  and  $d_{yz}$  orbitals and  $E_2$  consisting of the  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals. We assume an atomistic point of view concerning the 3d shell of the central atom in the light of our subsequent Anderson impurity model treatment. That means that we define the symmetry adapted basis in terms of the orbitals of the metal of the corresponding symmetry. Since the 6-31G basis set provides 10 (or 12 depending on the representation [406]) basis functions for the d shell our five orbitals are formed by diagonalization of the 10 orbital set within the crystal field. The diagonalization yields in all cases five 3d orbitals in the vicinity of the Fermi level and five 3d orbitals very high  $\sim 20 - 50$ eV above the Fermi level. In this manner we obtain the best symmetry adapted atomic-like orbitals for our subsequent OCA calculations. Let us begin with Sc. The projected densities of states (PDOS) obtained from LSDA of

the 3d shell of Sc is shown in Fig. 5.4.7 (a), (b) and (c) for increasing electrode-molecule separation. The two spin projections are plotted as the positive and negative ordinate respectively. Only a very small spectral weight of the 3d states at the Fermi level is observed in all cases. The changes over the whole range of d are continuous and towards larger energy separations the levels become sharper showing the increasing decoupling of the molecule from the leads. The transmission function also follows this general trend. We want to point out that the transmission function reflects the transport through the whole molecule, not only the transition metal center. It is thus clear, that there are other states, like the benzene  $\pi$  system contributing here, as one can see in Fig. 5.4.7(d), where the transport at low bias is certainly not brought about by transition metal 3d states. This effect is strongest at smallest electrode separations, because the benzene rings are forced closer together leading to direct interactions between their respective  $\pi$  electron systems and to stronger interactions with the Cu electrodes' s orbitals. For the smallest electrodetransition metal distance the Sc atom is occupied by two electrons equally distributed in the  $E_1$  and  $E_2$  shells, leaving the  $A_1$  shell empty, see table 5.9.7. Towards larger electrode separations the charge redistributes in favor of the  $E_2$  set. Since the free Sc centered sandwich is the largest, its electronic structure is influenced considerably by the electrodes. One observes, for example, that the  $E_2$  orbitals are energetically stabilized by the increased interaction with the  $\pi$  electron system of the benzene rings if they are pushed closer towards the metal. Also the population of the  $E_1$  set increases by the stronger interaction with the  $\pi$  system. The system shows no magnetic polarization within LSDA, but in B3LYP at d = 4.6 Å and without electrodes a small magnetic moment of about  $0.4\mu_{\rm B}$  arises, in accordance with Stern-Gerlach experiments reported in Ref. [289]. Since the formal spin multiplicity M = 2S + 1 of the free molecule is 2, one unpaired electron is expected, its moment is probably quenched by the stronger interaction with the benzene rings at small electrode separations, similarly to  $NiBz_2$  [355].

The case of Ti is different, as the system already shows a large spectral weight at the Fermi level in LSDA at small electrode molecule separations, see Fig. 5.4.8(a) and (b). This weight is brought about by the  $A_1$  channel, which compared to Sc now holds about one electron. The  $A_1$  channel also dominates the transmission at small biasses as can be seen best in Fig. 5.4.8(e). At the smallest electrode separation states derived from benzene are pushed towards the Fermi level and contribute significantly to the transmission. The spin polarization of about 0.45 $\mu_{\rm B}$  arises in LSDA when the molecule is in close contact with the leads at d = 3.2 Å and d = 3.4 Å. At d = 3.4 Å the system is almost a half metal, one spin channel being conducting the other almost insulating, see Fig. 5.4.8 (b), (e). This behavior makes it similar to the  $V_nBz_{n+1}$  systems, where this behavior has been predicted, see the discussion in section 5.2. At larger distances the magnetic moment continuously reduces and finally vanishes at d = 4.6 Å as shown in Fig. 5.4.8 (c) and table 5.5.6. The occupancies indicate that the  $A_1$  channel gets depopulated at larger distances and thus the magnetic moment vanishes. B3LYP calculations show a similar behavior with a moment



**Figure 5.5.10:** (a) Projected density of states for the 3*d* shell of Co for d = 3.6 Å, (b) d = 4.0 Å and (c) d = 4.3 Å. The corresponsing transmission functions are shown in panels (d), (e) and (f) respectively.

of 1  $\mu_B$  at small separations and a vanishing moment at large separations and for the free molecule. It was shown in Stern-Gerlach experiments in Ref. [289] that the free TiBz<sub>2</sub> molecule does not exhibit a magnetic moment, which is in accordance with our findings and the formally assigned spin multiplicity of 1, i.e. a singlet.

The VBz<sub>2</sub> sandwich shows the converse behavior to the Ti centered sandwich. The magnetization increases for large d and is quenched when the electrodes are brought closer. It remains, however, at all times above  $1\mu_{\rm B}$  in agreement with earlier theoretical [436, 280] and experimental work [288, 289]. Since the benzene rings carry a small negative moment the moment of the molecule as a whole will be reduced below the atomic 3d value by about  $0.1 - 0.3\mu_{\rm B}$  per benzene ring depending on the electrode separation [436, 280]. The system is expected to have a spin multiplicity of 2 and to be in a  $3d^4$  configuration, donating  $0.5e^-$  to each benzene ring [16]. Figures 5.5.10(a) and (d) show the LSDA density of states and the transmission functions for different d. One can see the increasing polarization inside the  $A_1$  channel, also increasing, but still smaller in the other two channels. This is also reflected in the transmission that especially in the vicinity of the Fermi level shows increasing spin polarization, since it stems mostly from the  $A_1$  channel. Depending on the bias voltage the current through the VBz<sub>2</sub> will be of one spin species or the other exclusively, making this system interesting in the field of spintronics [458, 280]. At d = 3.8 Å, for example, the system can be characterized as a half-metallic ferromagnet since the density of states is metallic at the Fermi level for the minority electrons and shows a gap for the majority electrons. Our calculations agree qualitatively with the transport calculations by Maslyuk et al. for V<sub>3</sub>Bz<sub>4</sub> clusters [280].



Figure 5.5.11: (a) Projected density of states for the 3d shell of Ni for d = 3.6 Å, (b) d = 4.0 Å and (c) d = 4.3 Å. The corresponsing transmission functions are shown in panels (d), (e) and (f) respectively.

CoBz<sub>2</sub> follows in the same direction with an increasing magnetic moment at increased electrode separation. The states at and in the vicinity of the Fermi level are now dominated by the  $E_1$  and  $E_2$  channels, the  $A_1$  orbital being full. The magnetic moment in LSDA is quenched at small distances, while in B3LYP it constantly remains at about  $2\mu_{\rm B}$ . Also the total filling increases the more free the molecule becomes from the leads. Figure 5.5.10 shows the LSDA density of states and the transmission function for different d. The  $A_1$  channel is also spin polarized and shows large spectral weight at 1 - 2.5eV below the Fermi energy. Calculations for the free molecule in symmetric or asymmetric sandwich geometry show a magnetic moment of about  $1\mu_{\rm B}$  for the whole molecule and about  $1.4\mu_{\rm B}$  for the 3d orbitals only. This is in agreement with earlier calculations by Zhang et al. for the free asymmetric sandwich structure [470]. So again the enhanced interaction with the benzene rings and the leads considerably changes the magnetic properties of the molecule. The transmission shows some smooth dependence on molecule-lead distance, with increasing sharp molecular resonances at larger d. One can also, as for  $VBz_2$  identify regions where the density of states and transmission is fully spin polarized, e.g. for d = 4.0 Å and d = 4.3 Å at small positive biases, making spintronics applications conceivable. Since the larger clusters of  $Co_n Bz_m$  form closed rice-ball like clusters [240] growing wires as in the case of  $V_n B z_m$  is probably not possible, limiting possible applications in this direction to the single sandwich.

Albeit being very similar in structure to  $CoBz_2$  the Ni centered molecule behaves differently. Its projected density of states shows the logical evolution of the foregoing molecule with one more electron in the 3d shell. Similarly as in Co the states at the Fermi level

	3.2 Å	3.4 Å	3.8 Å	4.2 Å	4.6 Å	Free
Sc(LSDA)	0.0	0.0	0.0	0.0	0.0	
Sc(B3LYP)	0.0	0.0	0.0	0.0	0.25	0.37
Ti(LSDA)	0.45	0.44	0.31	0.15	0.0	
Ti(B3LYP)	1.0	1.0	1.0	0.0	0.0	0.0
V(LSDA)	0.44	0.75	0.9	1.0	1.1	
V(B3LYP)	1.15	1.25	1.25	1.30	1.32	1.45
		3.6 Å	4.0 Å	4.3 Å		Free
Co(LSDA)		1.2	1.15	1.4		
Co(B3LYP)		2.0	2.0	2.0		1.35 (1.44)
Ni(LSDA)		0.0	0.0	0.0		_
Ni(B3LYP)		0.0	0.0	0.0		0.0

**Table 5.5.6:** Magnetic moments in units of the Bohr magneton  $\mu_B$  of the 3*d* shell of the center of sandwich molecules in the Cu nanocontact using LSDA and B3LYP functionals. The second value given for CoBz<sub>2</sub> was obtained for the symmetric structure with  $D_{6h}$  symmetry.

are the  $E_1$  and  $E_2$  states while the  $A_1$  shell is almost full showing spectral weight at energies 2eV below the Fermi level, see Fig. 5.5.11(c). The Ni atom is not magnetic, the asymmetry between spin projections being negligible. This is in line with measurements and calculations of NiBz<sub>2</sub> [355] and also typical for Ni adatoms on gold and silver surfaces [35, 243, 120], see also the next chapter. Accordingly, the NiBz<sub>2</sub> sandwich is never magnetic. The transmission is of course also fully symmetric in both spin channels, prohibiting possible spintronics applications in this case.

## 5.6 Discussion of LDA Hybridization Functions

Here, we discuss some general features of the hybridization functions applying to all molecules in the light of an Anderson model treatment. In general the molecules can be compressed considerably by reducing the molecule-lead distance as shown in Fig. 5.4.6(b). When the leads are sufficiently far away, the molecules relax towards their equilibrium distances which are in agreement with the ones computed in Ref. [321]. The differences in size for different TM centers can be explained by the occupation of bonding or anti-bonding symmetry adapted orbitals [321].



**Figure 5.6.12:** (a) Imaginary part of the hybridization function for the  $A_1$ -channel for different TM centers. For Ni and Co the distance between lead and TM center is d = 3.6 Å and for Sc, Ti and V d = 3.2 Å. (b) Same as (a) but for the  $E_1$ -channel. (c) Same as (c) but for the  $E_2$ -channel. (d) Total imaginary part of hybridization function for Co center (summed for all Co 3*d*-orbitals) in dependence on the distance between lead and Co center.

Figures 5.6.12(a)-(c) show the imaginary parts of the hybridization functions obtained from the LDA electronic structure for different TM centers. Obviously, the general structure of the hybridization function is generic for all molecules: The imaginary part of the hybridization function exhibits a distinct peak close to the Fermi level  $(E_{\rm F})$  in the  $E_2$ channel, whose position, width and height depend significantly on the molecular geometry, specifically on the Bz-TM distance as shown in Fig. 5.6.12 (d) for  $CoBz_2$ . The  $E_1$ channel shows a small hybridization and the  $A_1$  channels hybridization close to  $E_{\rm F}$  is negligible. The hybridization in general, however, increases when the molecule is compressed by the leads. This increase at smaller h can bring about a Kondo effect in the  $E_1$ or the  $E_2$  channel, as will be discussed for VBz<sub>2</sub> and CoBz<sub>2</sub> below. The dominant feature in the hybridization in the  $E_2$  channel stems, similarly as shown for graphene [444, 178] from hybridization with the  $\pi_z$  molecular orbital state of the benzene rings. The feature does not depend qualitatively on the DFT functional used, as we have found the same feature within GGA and also in B3LYP calculations. The  $E_1$  orbitals show some interaction with the  $\pi$  system of the Bz rings, but relatively far away from the Fermi level. Close to the Fermi level the magnitude of the hybridization is quite low compared to the  $E_2$  channel. On the other hand, the  $A_1$  orbitals do not hybridize with the Benzene rings for symmetry reasons as we already mentioned above (again similar to the case of Co on graphene [444, 178]). Hence these orbitals have to couple directly to the conduction electrons in the leads explaining their small to negligible hybridizations. The presence of strong molecular resonances in the hybridization function makes this case different from the case of nanocontacts with magnetic impurities where the hybridization functions are generally much smoother (see Ref. [176] for comparison).

At larger distances between the molecule and the leads, the molecular character of the sandwich becomes more pronounced. This is reflected in the hybridization function as shown in Fig. 5.6.12(d) for the CoBz<sub>2</sub> sandwich molecule: For larger distances the peak in the hybridization function corresponding to the  $E_2$  channel coupling to the  $\pi$ -molecular orbital of the benzene rings becomes sharper and shifts to higher energies. This strong dependence of the hybridization in the  $E_2$  channel on the molecular geometry gives us a handle for controlling the electronic structure and in particular the Kondo effect by compressing or stretching the molecule with the Cu contacts, as we will see later on.

#### 5.7 DFT+ $\Sigma$ results

#### 5.7.1 Orbital Kondo Effect in CoBz<sub>2</sub> and VBz<sub>2</sub>

Let us first discuss the molecules that we have found to exhibit a Kondo effect:  $\text{CoBz}_2$  and  $\text{VBz}_2$ . The strong crystal field combined with the Coulomb interaction modify the electronic structure considerably. We begin with  $\text{CoBz}_2$ , whose LDA+OCA spectral function  $A_{3d}(\omega) \sim \text{Im}G_{3d}$  is shown in Fig. 5.7.13 (b) for the three distances considered here at high temperatures on a large energy scale. The spectra vary considerably as the distance d changes. The only channel showing considerable weight at the Fermi level is the  $E_2$  channel, which retains a filling of about  $2.7e^-$  (2.7 electrons), very close to its LDA value, meaning that it holds 3 electrons and a S = 1/2 predominantly. In the other channels the distribution changes: The  $A_1$  channel gains one electron as compared to LDA and is now half filled, while the  $E_1$  channel gains one electron to be almost full at  $3.75e^-$ . This leaves the system in a (predominantly) S = 1 state, with one spin 1/2 in the  $A_1$  channel and one in the  $E_2$ . Most importantly, for d around 3.6 Å when the molecule is slightly compressed, a sharp temperature-dependent peak appears right at  $E_F$ , as can be seen from Fig. 5.7.13(c). The peak is strongly renormalized (i.e. it only carries a small fraction of the spectral weight) due to the strong electron-electron interactions.

The sharp peak in the spectral function at  $E_{\rm F}$  that starts to develop already at temperatures of  $k_{\rm B}T = 0.01 \text{ eV} \approx 120 \text{ K}$  stems from the  $E_2$  channel which is the only channel with appreciable hybridization near  $E_{\rm F}$ , see Fig. 5.7.13(a), cf. the discussion of the hybridizations in the previous section. Correspondingly, the transmission function (Fig. 5.7.13(d)) shows a Fano-like feature around zero energy. A renormalized, sharp and temperature-dependent resonance in the spectral function at  $E_{\rm F}$  is commonly associated with the Kondo effect,



Figure 5.7.13: (a) LSDA density of states of the Co 3d shell at d = 3.6 Å. (b,c) LDA+OCA Spectral and transmission functions of the molecule at d = 3.6 Å for different temperatures. (e) LDA+OCA Spectral functions of the Co 3d shell for different dat temperature  $T \sim 1200$  K. (f) Orbitally resolved LDA+OCA Spectral functions of the Co 3d shell for d = 3.6 Å at temperature  $T \sim 1200$  K.

as we have discussed in section 5.1. Looking at the orbital occupations, we find that the  $E_2$  channel that gives rise to the resonance for d = 3.6 Å has an occupation of about  $2.8e^-$  while the total occupation of the 3d shell is  $N_{3d} \sim 7.5e^-$  as shown in table 5.9.7. The fractional occupation numbers indicate the presence of valence fluctuations where the charges in the individual impurity levels fluctuate in contrast to the *pure*, s - d model-like, Kondo regime, that we have discussed in the introduction, section 5.1, where these fluctuations are frozen.

Since the OCA solver allows for the analysis of the contributions of atomic states to the many-body wave function, similarly to the sector analysis on CT-QMC we can use this information to get more information about the possible Kondo state and its origin. Analyzing the atomic states of the Co 3d shell contributing to the ground state of the system we find that the principal contribution (~ 45%) is an atomic state with 8 electrons and a total spin of S = 1 ( $d^8, S = 1$ ) as shown in Fig. 5.7.17. The total spin 1 stems from holes in the  $E_2$  and  $A_1$  channels. The charge fluctuations in the  $E_2$  channel are mainly due to the contribution (~ 17%) of an atomic ( $d^7, S = 3/2$ ) state. There are considerably weaker contributions (~ 4%) from atomic ( $d^7, S = 1/2$ ) and ( $d^9, S = 1/2$ ) states. The individual contributions of the remaining atomic states are very small (below 1%) but add up to a total contribution of 34%.

By exclusion of individual atomic states from the calculation of the spectra we can determine which fluctuations are responsible for the different spectral features. We find that the fluctuations between the  $(d^8, S = 1)$  and the  $(d^7, S = 3/2)$  states are primarily re-



Figure 5.7.14: (a) Spectral function around the Fermi energy for d = 3.6 Å. Arrows indicate spectral features arising from the fluctuations between atomic states shown in Fig. 5.7.17. (b) Orbital (red) and spin flip (blue) fluctuations in a doubly degenerate channel filled with 3 electrons that can lead to an orbital Kondo effect and to an underscreened spin Kondo effect, respectively.

sponsible for the three spectral features close to  $E_{\rm F}$  including the sharp Kondo peak right at  $E_{\rm F}$ , as illustrated in Fig. 5.7.14(a). Also the broad peak around 4 eV below  $E_{\rm F}$  originates from these fluctuations while the broad peak about 2.5 eV above  $E_{\rm F}$  arises from fluctuations between the  $(d^9, S = 1/2)$  atomic state and the principal  $d^8$  atomic state. The two peaks in the spectral function nearest to the Kondo resonance arise from the strong energy dependence of the hybridization function whose real part has poles just below and above  $E_{\rm F}$  roughly at the positions of these two spectral features.

Note that the fluctuations from the  $(d^8, S = 1)$  to the  $(d^7, S = 3/2)$  states that give rise to the Kondo peak at  $E_F$  actually cannot lead to a spin Kondo effect since the spin 3/2of the  $d^7$  state is higher than the spin 1 of the principal  $d^8$  state. This means that the spin cannot be flipped via virtual fluctuations involving the  $(d^7, S = 3/2)$  state. Instead the fluctuations between the  $(d^8, S = 1)$  and the  $(d^7, S = 3/2)$  states which give rise to the Kondo resonance at  $E_F$  correspond to an *orbital Kondo effect* in the doubly-degenerate  $E_2$  levels of the Co 3d shell as illustrated in Fig. 5.7.14(b). Here the index labeling the two orbitals with  $E_2$  symmetry takes the role of a pseudo spin. One can assign  $|+\rangle$  to one orbital and  $|-\rangle$  to the other. In the principal  $d^8$  atomic state the  $E_2$  levels are occupied with three electrons and hence have a pseudo spin of 1/2. By excitation to the  $(d^7, S = 3/2)$ state the electron with minority real spin and with some pseudo spin state is annihilated. By relaxation to the principal electronic  $(d^8, S = 1)$  state a minority real spin electron can now be created in one of the two pseudo spin states. Those processes that lead to a flip of the pseudo spin then give rise to the orbital Kondo effect and the formation of the Kondo peak at  $E_F$ .

The absence of a spin Kondo effect where the total spin 1 of the principal  $d^8$  atomic state is screened, is understood on the following grounds: First, in general the Kondo scale decreases exponentially with increasing spin of the magnetic impurity [309]. In



Figure 5.7.15: Variations of the Kondo peak in the  $E_2$  channel with respect to the model parameters. (a) The double counting correction is varied around the FLL value of  $\mu_{\rm DC} = 31$  eV, while U = 5 eV, J = 1 eV. (b) U is varied, while  $\mu_{\rm DC} = 31$  eV, J = 1 eV (c) J is varied, while  $\mu_{\rm DC} = 31$  eV, U = 5 eV.

addition, here the  $A_1$  level does not couple at all to the conduction electrons around  $E_{\rm F}$  (no hybridization). Thus the spin 1/2 associated with it cannot be flipped directly through hopping processes with the conduction electron bath.

On the other hand, an *underscreened* Kondo effect as reported in Ref. [323] where only the spin 1/2 within the  $E_2$  shell is screened is also suppressed compared to the orbital Kondo effect due to Hund's rule coupling: Screening of the spin 1/2 in the  $E_2$  shell can take place by fluctuations to the  $(d^7, S = 1/2)$  state. However, the Hund's rule coupling J favors the high spin  $(d^7, S = 3/2)$  state over the low spin  $(d^7, S = 1/2)$  state as can also be seen from the smaller weight of the latter compared to the former. Hence the Kondo scale is considerably lower for the underscreened Kondo effect than for the orbital Kondo effect found here. At even lower temperatures (not accessible within the OCA) the two Kondo effects may in fact coexist. Hence in principle the setup holds the possibility of an SU(4) Kondo effect [56].

We have checked the dependence of the LDA+OCA spectra on the double counting correction (DCC) as well as on the interaction parameters U and J. The results of this scan of the model parameters is shown in Fig. 5.7.15. The preferred parameter set used in the calculations ( $U = 5 \text{ eV}, J = 1 \text{ eV}, \mu_{\text{DC}} = 31 \text{ eV}$ ) is shown as a solid black line in all panels. We find that the Kondo peak is qualitatively stable for U ranging from 3 to 7 eV (Fig 5.7.15(b)), and for J ranging from 0.5 to 1 eV (Fig 5.7.15(c)). The physics of the system is also qualitatively stable against variations of the DCC around the fully localized limit (FLL) correction as shown in Fig. 5.7.15(a). The contributions of atomic states to the ground state show a continuous trend while the parameters are varied. The largest contribution to the ground states stems from the ( $d^8, S = 1$ ) state. Depending on the choice of parameters the size of the  $d^7$  and  $d^9$  contributions is varying. In particular, changes in the DCC (and consequently the filling of the Co 3d shell) shift the balance between  $d^7$  and  $d^9$  admixtures to the ground state. So in general we find the spectra and also

the Kondo peak to be qualitatively robust against shifts of the impurity levels in energy over a range of several electron volts, and changes of U between 3 and 7 eV, and of Jbetween 0.5 to 1 eV. As expected for the Kondo effect the sharp resonance stays pinned to the Fermi level when shifting the impurity levels in energy, and only height and width somewhat change. The stability of the Kondo effect against variations of J is another hint towards our conjecture that we have found an effect related to orbital degrees of freedom and *not* to spin. For the spin Kondo effect the dependence of the Kondo temperature on Jis exponential, see section 5.1, and thus we would expect a strong influence of a variation in J, which is not the case here.

Stretching the molecule by displacing the tips of the Cu nanowires the Kondo resonance and the concomitant Fano line shape in the transmission disappear for distances  $d \ge 4$  Å. This is accompanied by an increase of the occupation of the Co 3d shell, as can be seen from Tab. 5.9.7. The new regime is characterized by a strong valence mixing between the  $d^8$  and  $d^9$  atomic state of roughly equal contribution indicating that the system is now in the so-called mixed valence regime (see e.g. Ref. [156], Chap. 5). Hence the orbital Kondo effect and the associated spectral features can be controlled by stretching or compressing the molecule via the tip atoms of the Cu nanocontact. This strong sensitivity on the molecular conformation stems from the sharp features in the hybridization function which change considerably when the molecule is stretched or compressed as can be seen from Fig. 5.6.12(d). This peculiar behavior is qualitatively different from the case of the nanocontacts containing magnetic impurities where the hybridization functions are much smoother [176].

Let us now turn to VBz<sub>2</sub>. Figure 5.7.16(a) and (d) show the LSDA density of states at d = 3.2 Å and the transmission function for different d. In contrast to the case of Co the density of states at the Fermi level, as well as the spin, is dominated by the  $A_1$  channel. The spin polarization is still small, the  $E_1$  and  $E_2$  channels showing no spin polarization at all. The d shell is in total filled with about  $4e^-$  in LSDA as well as LDA, see Tab. 5.9.7. In Figure 5.7.16(e) we compare the spectral functions  $A_{3d}(\omega) \sim \text{Im}G_{3d}$  of the V 3d electrons for the five distances considered here at high temperature. The spectra show considerable changes over the wide range of d used in this case. A sharpening of features in the spectrum reflects the increasingly free molecular character of the system at higher distances from the leads. In Figure 5.7.16(f) the orbitally resolved spectral function for d = 3.2 Å is shown. In LDA+OCA the situation changes qualitatively as compared to LDA. The  $A_1$  channel shows a broad peak at the Fermi level.

Since the total charge was fixed close to its LDA value of  $4e^-$ , for reasons discussed above in the methodology section, only a redistribution of charge was possible within the 3d shell. This redistribution is, however, considerable and from Tab. 5.9.7 we can identify two regimes. In the first regime at d = 3.2 Å the  $E_1$  channel, formerly occupied by one electron increases its filling to about  $2.6e^-$  at the expense of the other channels, that are



Figure 5.7.16: (a) LSDA density of states of the V 3d shell at d = 3.6 Å. (b,c) LDA+OCA Spectral and transmission functions of the molecule at d = 3.2 Å for different temperatures. (e) LDA+OCA Spectral functions of the V 3d shell for different d at temperature  $T \sim 1200$  K. (f) Orbitally resolved LDA+OCA Spectral functions of the V 3d shell for d = 3.2 Å at temperature  $T \sim 1200$  K.

now occupied by less than one electron each. This means, similarly to the Co  $E_2$  shell discussed above, the V  $E_1$  shell now predominantly holds 3 electrons and a S = 1/2, while the remaining channels hold about one electron altogether. In the second regime at d > 3.2 Å the charge redistributes such, that the  $A_1$  and  $E_2$  channels hold one electron each, while the  $E_1$  channel is occupied by two electrons.

However, let us for the moment remain at d = 3.2 Å since in this case a sharp temperaturedependent peak appears at  $E_{\rm F}$ , as shown in Fig. 5.7.16(b). Its formation can be observed at temperatures below  $k_{\rm B}T = 0.005 \text{eV} \approx 120 \text{K}$ . The resonance develops only in the  $E_1$  channel and only at d = 3.2 Å in the charge regime discussed above. An analysis of the hybridization function shown in Fig. 5.6.12 indicates that the molecule has been compressed to such extent, that the hybridization in the  $E_1$  channel has risen considerably; higher than for any other molecule we considered.

In this case the 3d shell is filled with  $\sim 4e^-$ , distributed to the different channels as follows:  $A_1 : 0.9e^-$ ,  $E_1 : 2.6e^-$  and  $E_2 : 0.6e^-$ . By exclusion of individual atomic states from the calculation of the spectral functions we can determine which fluctuations are responsible for the different spectral features. In the case of V there is one atomic  $(d^4, S = 1)$  state that contributes with  $\sim 30\%$  to the ground state, see Fig. 5.7.17. Other notable contributions stem from a  $(d^3, S = 3/2)$ , a  $(d^5, S = 3/2)$  and a  $(d^5, S = 1/2)$  state. All these four atomic states have one electron in the  $A_1$  channel and an empty  $E_2$  channel.

Our analysis indicates that an orbital Kondo effect now occurs in the  $E_1$  channel. In this

case the orbital degree of freedom in the doubly degenerate  $E_1$  channel takes the role of a pseudo-spin, which is then screened by the conduction electrons of the leads. Here, we can again exclude that the spin degree of freedom is the most important one. The reasoning here is completely analogous to the Kondo effect in the  $E_2$  channel of CoBz<sub>2</sub>. One possibility for a spin Kondo effect would be a spin 1 Kondo effect screening the total spin in the 3d shell. This is possible, but very improbable since the  $A_1$  channel couples to the bath very weakly, thus a flipping of the spin via exchange of particles with the bath is very unlikely. A second possibility would be an underscreened spin S = 1/2 Kondo effect occurring only in the  $E_1$  shell. This is again possible, but is strongly suppressed due to the Hund's coupling to the  $A_1$  electron. Additionally, the states bringing about the resonance, shown in Fig. 5.7.17, are not the ones needed for a spin Kondo effect. Thus, the only effect that is consistent with our observations is the orbital Kondo effect in the  $E_1$  channel.

Correspondingly, the transmission function shows a small feature at the Fermi level. The size of this feature is much smaller than seen for  $\text{CoBz}_2$ , since the  $E_1$  channel has much smaller hybridization with the rest of the system due to symmetry as discussed above. Therefore the indirect effects of the local correlations on the surroundings like the feature in the transmission are much smaller also.

#### 5.7.2 ScBz<sub>2</sub>, TiBz<sub>2</sub> and NiBz<sub>2</sub>

The sandwich molecules with Sc, Ti and Ni centers show no Kondo effect in the regimes that we have investigated, albeit being very similar in structure to the Co and V sandwiches. We will discuss them briefly in this paragraph pointing out the main differences to the ones discussed in the previous section. We again begin with Sc. When applying a local Coulomb interaction, the total charge of two electron accumulates almost exclusively in the  $E_1$  channel, leaving both the  $A_1$  and  $E_2$  channels empty, leading to a  $d^2, S = 1$ ground state. This is reflected in the LDA+OCA spectral functions in Fig. 5.7.18(a). The half filled  $E_1$  shell shows a pseudogap at the Fermi level, while the other states are empty. The ground state along with principal admixtures is again shown in Fig. 5.7.17. At larger d the spectral function shows a smooth variation towards d = 4.6 Å, where molecular resonances appear most strongly, see Fig. 5.7.18. When applying the local Coulomb interaction to the 3d shell of Ti in TiBz<sub>2</sub> the  $E_1$  channel gains an additional electron making it half filled, as in the case of Sc. Additionally, the  $A_1$  channel increases its population to  $0.85e^-$ , while the  $E_2$  channel is almost empty, see Tab. 5.9.7. The strongest contribution to the ground state is a  $d^3$ , S = 3/2 state, see Fig 5.7.17. The LDA+OCA spectral function in Fig. 5.7.18 (b) thus shows us two half filled shells ( $A_1$  and  $E_1$ ) showing a gap or pseudo gap and the empty  $E_2$  shell. Interestingly, the hybridization is not much smaller here than in  $VBz_2$ , where a Kondo effect is observed. This stems from the different ground state of the TiBz<sub>2</sub>: The spin S = 3/2 state with half filled  $A_1$  and  $E_1$  shells. A spin S = 3/2



**Figure 5.7.17:** Atomic states governing the low energy physics of the TMBz<sub>2</sub> molecules for the smalles distance d used respectively. In all panels the dominant contribution is shown lowest with a black frame. For VBz<sub>2</sub> and CoBz<sub>2</sub> the fluctuations bringing about the orbital Kondo effect are indicated by a red frame and arrows along with another important non-Kondo contribution.

Kondo, albeit possible would require a switching of 3 spins, which significantly reduces its probability. Same applies to an underscreened Kondo effect screening only the  $A_1$ spin. An orbital Kondo effect as in VBz<sub>2</sub> and CoBz<sub>2</sub> also cannot occur, because Hund's rule enforces equal occupation of both degenerate  $E_1$  levels. Finally, Fig. 5.7.18(e) shows the correlated spectral functions  $A_{3d}(\omega) \sim \text{Im}G_{3d}$  of the Ni 3d electrons for the three distances considered here at high temperatures on a large energy scale. The spectra do not vary as much as in the other cases as the distance d changes. In Fig. 5.7.18(c) we show the orbitally resolved spectrum around the Fermi level. The system is characterized by a prominent peak in the density of states around 0.5eV below the Fermi level in the  $E_2$ channel and broad peaks in the  $E_1$  and  $A_1$  channels at -1eV and -1.5eV respectively. The Ni 3d shell is filled with approximately 9 electrons and hence is approximately integer, the most important atomic states are again shown in Fig. 5.7.17. However, the occupa-



**Figure 5.7.18:** (a,b,c) Orbitally resolved spectral functions of the Sc and Ti 3d shell for d = 3.2 Å and Ni for d = 3.6 Å at temperature  $T \sim 1200$  K. (d,e,f) Spectral functions of the Sc,Ti and Ni 3d shell for different d at temperature  $T \sim 1200$  K.

tions of the individual channels are fractional  $(N(E_2) = 3.44e^-, N(E_1) = 3.76e^-, N(A_1) = 1.85e^-)$  indicating that the system is in the mixed valence regime in this case. Since the hybridization as well as the interaction parameters are the same as for CoBz<sub>2</sub> it is the valence that dictates the behaviour of the system.

## 5.8 Spin and magnetism in DFT and DFT++

We want to comment here on the magnetic moments obtained on the level of DFT and their apparent agreement with experiments and the apparent discrepancy with the local moments within LDA+OCA presented later. As was recognized a long time ago LDA has problems in describing electron localization and exchange effects [429, 187]. Attempts to identify and overcome these deficiencies led to inter alia the development of the LDA+U method. We quote the classic paper by Czyżyk and Sawatzky [85] that pinpoint a serious limitation:

The first problem is that the LDA attempts to treat the second-Hund-rule correlation together with spin polarization (Stoner-like). This is obviously incorrect, but it seems to be the only possibility within a formalism based on the electron-gas model. The correlation effects which are behind the second Hund rule are responsible for orbital polarization (ordering) and the formation of local (atomic-like) moments. Stoner-like effects alone are treated rather accurately within the LDA. The simple example of this intrinsic deficiency of the LDA is a transition from a spin-split ferromagnetic to a paramagnetic state. In the so-called nonmagnetic solution within the LDA the magnetic moments vanish. This leads to a huge difference in the energy between the magnetic and the nonmagnetic solution, and the critical temperature is related to the moment formation rather than the order-disorder transition. The inability of developing local moments leads also to a failure in the description of Mott insulators within the LDA, which is a very serious limitation.

Exchange splitting is included in LSDA only on the Stoner level as a function of the magnetization  $m(\mathbf{r})$  ( $n(\mathbf{r})$  are charge densities)

$$\frac{\delta E^{\text{LSDA}}}{\delta n_{\uparrow}(\mathbf{r})} - \frac{\delta E^{\text{LSDA}}}{\delta n_{\downarrow}(\mathbf{r})} \sim m(\mathbf{r})$$
(5.8.1)

obained from the LSDA total energy functional

$$E^{\text{LSDA}} = E^{\text{LDA}}[n(\mathbf{r})] + E_{\text{XC}}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})] - E_{\text{XC}}[n(\mathbf{r})].$$
(5.8.2)

In short, there are no local moments in LSDA without order. Additionally, in the spin polarized version of LDA the error cancellation between exchange and correlation parts of the exchange-correlation energy does not work so well anymore [429]. Apart from this possibly subtle technicality, it is clear that local moments without order *do* exist if Hund's rules are taken into account properly. A simple example is iron, which orders ferromagnetically below  $\sim 1000$ K. It is not that the local magnetic moments on the iron atoms appear at the transition temperature, they are there above it as well in the paramagnetic phase of the material, the transition merely signals their ordering. The LDA (although it works at T = 0 of course) can conceptually not account for this.

It is known for a long time now, that although spin moments in the ordered phase can be well described within LSDA, see e.g. Ref. [221], the orbital moment is strongly underestimated [311, 312, 313, 423, 400]. This fact along with the inherent deficiencies described earlier leads to some well known failures of DFT in the prediction of magnetic properties. For the undoped cuprates LSDA predicts a non magnetic ground state, while the compounds are generally antiferromagnetic insulators, see Ref. [340] for a review. Self interaction corrected (SIC [336]) LDA calculations [405], LDA+U [85], DFT calculations using the hybrid B3LYP functional [407] and also (single-site) LDA+DMFT [441] find the correct insulating ground state.

A converse situation was encountered for the iron pnictide materials  $LaO_{1-x}F_xFeAs$  and  $BaFe_2As_2$  [190]. While DFT (LDA/GGA) strongly overestimates the magnetic moment (and gives a wrong ground state), DFT+DMFT calculations give results much closer to the experiment [145, 462].

Calculations of TMBz<sub>2</sub> sandwiches within GGA+U also showed increased moments on the 3d shells [446, 445]. This is a known property of DFT+U, since it includes the leading

terms of the Coulomb interaction, see section 1.5.3. Still, GGA+U is capable only of describing ordered states.

In our LDA+OCA treatment the Hund's rule coupling is taken into account, which allows for local moments to appear irrespective of order. This leads to discrepancies between the local moments on the TM 3d shell within LDA+OCA and the magnetic moment of the TM 3d shell in LSDA. At the same time the LSDA agrees with experiments measuring the moment of the free molecules centered on Sc Ti and V [289]. This apparent conundrum can be resolved in part considering the comments we made above and also taking into account what is measured/calculated by each method. The Stern-Gerlach experiments used for the determination of the magnetic moment, measure the whole molecule, transition metal center and benzene ligands, at finite temperatures, in a magnetic field, while LSDA calculates a magnetically ordered state of the whole molecule at T = 0, whereas in LDA+OCA we calculate a paramagnetic molecule including Coulomb interaction and Hund's rules only on the 3d shell of the transition metal center. These are in general three entirely different things. For a sound comparison between experiment and theory one should calculate the whole molecule including the full Coulomb interaction on and between all atoms respectively within a cluster approach. This is, however, computationally prohibitively heavy. So, to conclude, the LDA/GGA might agree with experiments sometimes, unfortunately often for reasons that are not simple to understand.

It is of course also possible that the DFT description of the sandwich molecules we studied is correct and our choice of interaction parameters, combined with the strong crystal field unduly favors a high-spin configuration in some cases. As we have seen in chapter 4 for the case of LaCoO<sub>3</sub>, depending on the size of the crystal field and the Hund's rule coupling J transitions between high-spin and low-spin configurations can occur. Generally, the (first) Hund's rule will favor high-spin, due to the reduced Coulomb energy for such configurations  $\sim U - 3J$  as compared to an antiparallel spin alignment with energy contribution  $\sim U - 2J$ . At large enough crystal fields, however, the gain in crystal field energy will offset the gain in Coulomb interaction energy and the low-spin state will become favored. Since the interaction parameters we used are only estimates based on reported interaction parameters for other systems, it is possible, that in some cases our interaction parameters favor the high-spin over the low-spin state. Since we are not aware of ab inito calculations of the Coulomb interaction parameters for these systems probably a detailed analysis of the spin states of each molecule will have to be performed for a whole range of interaction parameters focussing on J. In this way we would be able to discriminate between the different ground states of each molecule and to identify the interaction parameters for which crossovers between high-spin and low-spin occur.

Unfortunately, measurements concerning the ground state are only available for single molecules at present. The interaction with the leads in our setup could also change the spin state qualitatively by inducing changes in the crystal field. Already on the level of DFT, the magnetic moments can strongly differ for the free molecule and for the molecule

in the nanocontact, see table 5.5.6.

### 5.9 Summary and Conclusions

We have investigated the TMBz<sub>2</sub> molecules with Sc,Ti, V, Co and Ni centers coupled to Cu nanowires. Dynamical correlations originating from the strongly interacting 3delectrons give rise to different correlation effects. Depending on the specific regime, the molecule is in while in contact with the electrodes we observe an orbital Kondo effect (V,Co) or a mixed-valence/empty-orbital behaviour (Sc,Ti, Ni). The Kondo effect occurs in the doubly degenerate  $E_1$  or  $E_2$  shells in vanadium and cobalt respectively and follows the same mechanism in both cases.

Our study shows, that the parameters of an Anderson model could be tuned using a realistic nanodevice. In the case of  $\text{TMBz}_2$  molecules in a nanocontact the hybridization strength ( $\Delta$ ) can be controlled by the proximity of the electrodes to the molecule, while the local Coulomb interaction (U) as well as the filling of the 3d shell (N) are controlled by the species of the central atom.

Further studies have to be performed for larger instances of the  $TM_nBz_m$  class of systems. Nanowires made from the sandwich molecules can become important in spintronics applications. It would thus be worthwhile to investigate how the predictions concerning the properties of such wires, obtained mostly from DFT and other single particle methods, hold up when electronic correlations are included.

		3.	2 Å			3.4	Å			3.8	Å			4.2	Å			4.6	Å	
	$A_1$	$E_1$	$E_2$	Tot	$A_1$	$E_1$	$E_2$	Tot	$A_1$	$E_1$	$E_2$	Tot	$A_1$	$E_1$	$E_2$	Tot	$A_1$	$E_1$	$E_2$	Tot
Sc (LDA)	0.11	0.87	1.03	2.00	0.10	0.85	1.04	1.99	0.09	0.80	1.07	1.96	0.09	0.75	1.15	1.99	0.09	0.71	1.27	2.06
Sc (LDA+OCA)	0.01	1.94	0.11	2.06	0.01	1.94	0.12	2.07	0.02	1.94	0.06	2.02	0.02	1.94	0.02	1.98	0.03	1.94	0.02	1.99
Ti (LDA)	0.45	1.02	1.36	2.83	0.36	1.00	1.39	2.74	0.24	0.96	1.45	2.65	0.17	0.92	1.53	2.61	0.12	0.91	1.60	2.63
Ti (LDA+OCA)	0.85	1.96	0.22	3.03	0.84	1.96	0.22	3.02	0.87	1.93	0.28	3.08	0.66	1.93	0.44	3.03	0.59	1.93	0.55	3.07
V (LDA)	1.33	1.04	1.59	3.97	1.34	0.98	1.63	3.95	1.27	0.97	1.68	3.92	1.19	0.93	1.76	3.88	1.06	0.92	1.81	3.79
V (LDA+OCA)	0.89	2.58	0.61	4.08	0.90	1.94	1.22	4.06	0.91	1.94	1.22	4.07	0.91	1.93	1.22	4.06	0.91	1.93	1.16	4.0
					3.6	Å				4.0	Å				4	Å				
				$A_1$	$E_1$	$E_2$	Tot		$A_1$	$E_1$	$E_2$	Tot		$A_1$	$E_1$	$E_2$	Tot			
Co (LDA)				1.78	2.75	2.83	7.36		1.80	3.52	2.80	7.85		1.80	3.54	2.87	8.21			
Co (LDA+OCA)				1.02	3.74	2.74	7.50		0.98	3.78	3.28	8.03		0.96	3.80	3.50	8.26			
Ni (LDA)				1.82	3.66	3.07	8.55		1.80	3.69	3.02	8.51		1.80	3.74	3.04	8.58			
Ni (LDA+OCA)				1.84	3.76	3.34	8.94		1.25	3.77	3.56	8.58		1.44	3.79	3.45	8.68			
		J 2					F C	101	L - 17				1 1 1							
<b>Table 5.9.7:</b>	Fillin	igs of	the ort	oitals c	ompri	sing th	he $3d$ :	shell of	f the T	MBz	2 syste	in on	the LI	<b>DA as</b>	well a	us on th	le LD/	A+OC	A leve	5

## Chapter 6

# **Excitation spectra of transition metal atoms on the Ag (100) surface**

S. Gardonio, M. Karolak, T. O. Wehling, L. Petaccia, S. Lizzit, A. Goldoni, A. I. Lichtenstein, and C. Carbone, *Excitation Spectra* of Transition-Metal Atoms on the Ag (100) Surface Controlled by Hund's Exchange, Phys. Rev. Lett. **110** (2013), 186404

Strongly correlated multi-orbital quantum systems present a classical yet unsolved problem in solid state physics which appears in various systems ranging from periodic solids to isolated atoms on surfaces. In nanoscopic systems, atomic scale control of correlated electrons holds promises for novel modes of information processing [200, 266] and offers possibilities to understand fundamental quantum effects such as itinerant electron magnetism, the competition of local with non-local magnetic interactions [302, 57, 156] or the transition from isolated atoms to extended solids [63, 71, 121]. Here, the multi orbital nature of realistic nanoscale transition metal (TM) structures is generally believed to control physical properties such as magnetic anisotropies [63], magnetic excitations [318] or Kondo temperatures [309].

While there has been huge experimental progress in fabricating nanoscale correlated electron systems, our theoretical understanding of the physical mechanisms determining their electronic and magnetic properties is still at a rather basic qualitative level: Often experiments on transition metal impurity systems are interpreted in terms of Kondo type models where a generalized spin is coupled to a bath of conduction electrons [156, 79, 318] or in terms of single orbital Anderson models [424, 208, 350, 263, 304, 412, 435, 348]. However, links between these models and *realistic* systems are usually ambiguous, difficult to establish [78] and can typically only be made a posteriori [424, 208, 350, 263, 304, 412, 435, 348]. It is often largely unclear which microscopic degrees of freedom are active at a given energy scale and how their contribution in excitation spectra measured with different spectroscopy techniques can be disentangled.

In this chapter, we consider the series of isolated Mn, Fe, Co and Ni adatoms on the Ag

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(100) surface and explain their excitation spectra. We report on valence electron photo emission experiments revealing the complex evolution of the electronic spectra through this series: we find a monotonous decrease in the splitting of higher energy features and a non-monotonous variation of low energy spectral weight. By means of calculations using the DFT++ formalism we explain the photoemission results and show that both observations can be traced back to Hund's exchange. First, the splitting between final state multiplets with different spin decreases monotonously due to a monotonous reduction of effective exchange splittings  $J(n_{\uparrow} - n_{\downarrow})$  with increasing filling of the 3d shell. Second, the effective charging energies [426, 451, 91, 92]  $U_{\text{eff}}(n) = E(n+1) + E(n-1) - 2E(n)$ , with E(n) being the ground state energy of the impurity adatom with n electrons, vary due to Hund's exchange in a strongly non-monotonous way from Mn to Ni. Therefore, the amount of charge fluctuations and the weight of quasiparticle peaks at the Fermi level evolves non-monotonously through this 3d series. We find sizable charge fluctuations and mixed valence behavior for Fe and Ni. In contrast Mn and Co come closer to a multiorbital Kondo limit with a generalized impurity spin being coupled to a bath of conduction electrons and less charge fluctuations.

### 6.1 Experiment

Here we want to briefly outline the experimental data that has been collected for the transition metal atoms on the silver (100) surface by S. Gardonio and colleagues in the group of C. Carbone in Trieste. Details concerning the experiments can be found in the cited paper [120]. In Fig. 6.1.1 (a-d) we show the experimental photoelectron energy distribution curves in the valence band of isolated Mn, Fe, Co and Ni atoms on the Ag(100) surface. The curves are difference spectra between the clean Ag surface and the surface covered with a few adatoms and correspond to the contribution from 3*d* impurity electronic states. We observe a remarkable evolution of the impurity spectra through this series of adatoms: Mn has one structure (labeled 1) at an energy (versus the Fermi energy  $E_F$ ) of -3.3 eV; Fe has two structures, one (1) at -2.3 eV and the other one (2) near the Fermi energy; Co has one (1) broad structure at -2.6 eV, one structure (2) at -0.8 eV, and one structure (3) close to  $E_F$ ; and Ni has one broad structure (1) at -0.3eV.

#### 6.2 Theoretical setup

To explain the experimental spectra we applied the DFT++ formalism in the flavor of DFT+ $\Sigma$ , to the system. First, we performed DFT calculations using the GGA(PBE) [332] functional to obtain the geometries of the transition metals on the Ag(100) surface. In these calculations, single transition metal atoms on Ag(100) have been modeled using



**Figure 6.1.1:** Experimental valence band spectra of (a) Mn, (b) Fe, (c) Co, and (d) Ni adatoms on Ag (100). The spectra are obtained as the difference between the spectra of the clean Ag(100) and spectra recorded after deposition of few adatoms.

 $4 \times 4$  surface supercells with slab thicknesses of five layers. The crystal structures have been relaxed until the forces acting on each atom were smaller than 0.01eV/Å. Top and side views of the supercell we used in the calculations are shown in Fig. 6.2.3(d) and (e) (Ni on Ag(100) is shown as an example). The calculations show that all transition metal adatoms adsorb to high symmetry positions continuing the Ag lattice, i.e. sitting in the center of a square of Ag atoms. The adsorption height above the surface differs only little, from Mn at 1.3 Å to Ni at approximately 1.4 Å.

In Fig. 6.2.2 the GGA densities of states of the 3d transition metal series from Mn to Cu adsorbed on the Ag(100) surface are shown. The series starting from the formally  $3d^5$  atom Mn up to the  $3d^8$  atom Ni shows spectral weight at and close to the Fermi level, while the  $3d^{10}$  atom copper, that we have included for comparison, shows no weight at the Fermi level and is centered about 2 eV below the Fermi level. Since the 3d shell of Cu is full it generally exhibits only weak effects of electronic correlations and will especially



Figure 6.2.2: Densities of states obtained within GGA for the 3d shell of the transition metals from Mn to Cu adsorbed on the Ag(100) surface.

not be susceptible to the effects of the Hund's exchange, since the  $d^{10}$  configuration has no multiplets, analogously to  $d^0$ . Comparing the spectra to the measurement shows that GGA is incapable of describing the evolution of the spectra along the series. The GGA spectra consist mainly of a peak of about 0.5eV width that is shifted gradually below the Fermi level as the 3d shell is filled. Especially, the example of Mn clearly shows the failure of DFT in this case: the experiment shows that the occupied spectral weight of Mn is centered around 3eV below the Fermi level, with negligible weight at the Fermi level, while in DFT the spectral weight is largest at and in close proximity to the Fermi level. Including magnetism on the DFT level into the calculation can only partly remedy the situation due to the incomplete description of local moments within the theory. We have addressed this issue in the preceding chapter 5.

For understanding the evolution of the spectra along the series a superior theory is required. For a DFT++ description the starting point is the hybridization function that establishes the connection between the DFT and an Anderson impurity model that we applied in this case. Again, no self-consistency is required and we are applying the DFT+ $\Sigma$ flavor of DFT++, since no mapping on a lattice model is performed as already explained in chapter 2. The hybridization function is defined as

$$\Delta_{mm'}(\omega) = \left(G_{mm'}^{-1}(\omega) - \varepsilon_{mm'} - (\omega + i\delta)\delta_{mm'}\right).$$

Above,  $m, m' = -2, \ldots, +2$  label the z-component of the angular momentum. In line with the similar adsorption geometries the hybridization functions, Im  $\Delta(\omega)$ , are similar



**Figure 6.2.3:** (a) Hybridization functions of all four adatoms (lines), along with the Ag d and sp density of states of the four nearest neighbor atoms. (b,c) Orbitally resolved real and imaginary parts of the hybridization of Co on Ag(100) (d,e) Top and side views of the supercell used in the DFT part of the calculations (Ni on Ag(100) is shown).

for all atoms as shown in Fig.6.2.3(a) and follow the trend given by the Ag 4d density of states at higher binding energies, while near the Fermi level hybridization with the 5sand 5p states dominates. In Fig. 6.2.3 (b,c) we show the orbitally resolved hybridization function for the example of the Co adatom. The main difference between the adatoms is a monotonous overall decrease of  $|\text{Im }\Delta(\omega)|$  from Mn to Ni which is well in line with an increasing adatom surface distance and the increasing localization of the 3d orbitals from Mn to Ni. For the case of Co on Ag (100) Im $\Delta(\omega)$  is in agreement with Ref. [364]. Most importantly, the hybridization function is rather featureless for all atoms in the energy region between -3 eV and +1 eV. Thus, the complex evolution of the spectra observed experimentally also cannot be a single particle hybridization effect. The second ingredient that makes the mapping onto the Anderson model complete is the Coulomb interaction. We defined the Coulomb interaction matrices via the Slater integrals [396] (cf. section 1.5.2)  $F^0 = U$ ,  $F^2 = \frac{14}{(1 + 0.625)}J$  and  $F^4 = 0.625F^2$  with U = 3 eVfor Mn and Fe, U = 5 eV for Co and Ni as well as Hund's exchange J = 1 eV. In detail this means we used the values  $F^0 = 3 \text{eV}$ ,  $F^2 = 8.615 \text{eV}$ , and  $F^4 = 5.38 \text{eV}$  for Mn and Fe atoms and  $F^0 = 5 \text{eV}$  for Co and Ni (with  $F^2$  and  $F^4$  unchanged). The densitydensity matrices obtained from these parameters have exactly the form shown in Eqs. (1.5.7) and (1.5.8). The interaction parameters we used in this work are in the range of



**Figure 6.2.4:** Valence band spectra of Mn, Fe, Co, and Ni adatoms on Ag (100). (a) Experimental photoemission spectra (b) Theoretical spectra obtained from QMC calculations at  $\beta = 20 \text{eV}^{-1}$  with imaginary time discretization of  $\Delta \tau = 0.125$  via analytical continuation [184]. The 3*d* shell occupancies used in the simulations are n = 5.0 for Mn, n = 6.0 for Fe, n = 7.8 for Co, and n = 8.4 for Ni.

parameters obtained from ab initio calculations within the constrained Random-Phase-Approximation by Şaşıoğlu, et al. for bulk transition metals [84] and also for certain surfaces [169]. The interaction parameters are also not very critical, qualitatively the same spectra can be obtained by using U = 5 eV for all adatoms (see supplementary material of Ref. [120]). The impurity models were solved using the Hirsch-Fye quantum Monte Carlo method (QMC) [158] (keeping the density-density part of the local Coulomb interaction) as well as exact diagonalization (ED), see section 1.6. In this way, we obtain the adatom spectra including electron correlation effects in QMC as well as a detailed insight into the atomic multiplet structure via ED. As the occupancies n of the 3d impurity orbitals are not exactly known, they are kept as (the only) free parameters.

### 6.3 **Results and Discussion**

Since the 3d transition metals are known to exhibit strong effects of electronic correlations, especially the Kondo effect in e.g. Co on Cu [403] one might suspect that the spectra can be qualitatively understood in this general framework. For Mn, the spectral

peak at -3.25 eV and virtually no quasiparticle peak at the Fermi level could be well in line with Mn acting effectively as a spin S = 5/2 Kondo impurity. Indeed, this would be very similar to the situation found for Mn impurities in bulk Ag, which has been derived from photoemission spectroscopy and measurements of the magnetic susceptibility [156]. The virtually absent quasiparticle peak would then be well understandable as the large spin S = 5/2 leads to very low Kondo temperatures [309]. With increasing filling of the 3d shell the impurity spin should be gradually reduced and the spectral weight of the quasiparticle peak near the Fermi level should be growing exponentially. Indeed, Fe, Co, and Ni exhibit spectral weight near the Fermi level but the shape and weight of these low energy spectral features varies very non-monotonically through the series of Fe, Co and Ni. In particular, we do not find a monotonous increase of the quasiparticle spectral weight as would be expected in spin-only Kondo models [309]. The brief foregoing discussion indicates that the evolution of the spectra cannot be explained solely by spin-only Kondo models and that it is imperative to consider the combined effects of spin and charge degrees of freedom. Since our ab initio calculations make no a priori assumptions about the dominant physics of the system, except that it has to be local, we expect to identify the mechanism responsible for the nontrivial spectra.

The spectral functions of Anderson impurity models obtained from QMC are shown in Fig. 6.2.4 in a direct comparison to experiment and in Fig. 6.3.5 compared to ED results. In agreement with the experiments, the Mn spectrum consists mainly of one peak far below the Fermi level for 3d shell fillings  $n \approx 5$ . In fact, already a diagonalization of the atom in the crystal field ( $\Delta_{CF}$ ) of the surface shows the basic structure found in the experiment (Fig. 6.3.5(a)). Thus, a low energy description of Mn on Ag (100) in terms of a spin S = 5/2 Kondo model is well in line with our results. This is indeed similar to the case Mn in bulk Ag [156] and also in agreement with DFT calculations for Mn on Ag(100) [310, 68]. Comparison of the QMC calculations to the experimental spectra reveals good agreement also for the Fe, Co, and Ni adatoms. We thus use the QMC results to understand the physical mechanisms behind the evolution of the spectra in the series of 3d adatoms.

For Fe with n = 6, our calculations show a broad peak around -3 eV and a relatively narrow peak right below the Fermi level, which reproduce the experimental features 1 and 2, respectively. The broad satellite around -3 eV appears in all orbitals and is found also in the ED calculations (Fig. 6.3.5(b)). It can be identified as a  $d^6 \rightarrow d^5$  ionization peak. Analyzing the orbitally resolved spectral function shown in Fig. 6.3.6(b) we see that feature 2 from the experiment stems from the  $d_{x^2-y^2}$  orbital. This orbital contains  $1.6e^-$  in contrast to the other orbitals which are approximately half filled. Therefore, the feature 2 cannot be a quasiparticle peak due to spin-only Kondo physics. Indeed, this peak appears already in an ED description of Fe in the crystal field (Fig. 6.3.5 (b)) of the surface, which shows that it corresponds to a  $d^6 \rightarrow d^5$  transition. Consequently, the spectral features 1 and 2 of Fe stem both from ionization processes of the impurity. Our ED calculations



**Figure 6.3.5:** Spectral functions for (a) Mn, (b) Fe, (c) Co and (d) Ni impurities obtained from QMC calculations at  $\beta = 20 \text{eV}^{-1}$  with imaginary time resolution of  $\Delta \tau = 0.125$  via analytical continuation [184] (thick black lines). The 3*d* shell occupancies used in the simulations are n = 5 for Mn, n = 6 for Fe, n = 7.8 for Co, and n = 8.4 for Ni. Additionally spectra obtained by ED are shown (orbitally resolved in a) and b); total spectra for different filling of the 3*d* shell in c) and d)).

further show that the energy separation of these peaks traces back to different  $d^5$  final state multiplets: S = 5/2, L = 0 for feature 2 near  $E_{\rm F}$  and higher energy multiplets such as S = 3/2,  $L \ge 0$  for feature 1. The splitting between these multiplets can be understood as an effective exchange splitting  $\sim J(n_{\uparrow} - n_{\downarrow})$  due to Hund's exchange.

The experimental Co spectrum consisting of three peaks is well reproduced in our QMC simulations for n = 7.8 (Figs. 6.2.4 and 6.3.5 (c)). Analyzing the orbitally resolved spectral function shown in Fig. 6.3.6 (a,c) and the corresponding occupation matrices we find that the  $d_{xz,yz}$  and  $d_{x^2-y^2}$  orbitals are almost fully occupied and mostly responsible for the peak at -1 eV, which corresponds to the feature 2 in the experimental spectra. Again, the spectral weight further below the Fermi level (feature 1) traces also back to an ionization process, here  $d^8 \rightarrow d^7$ , with higher energy final state multiplets. As in the case of Fe, the splitting between the features 1 and 2 can thus be understood as atomic multiplet effect due to Hund's exchange. For Co, the effective exchange splitting reduces as compared to the case of Fe by an amount on the order of J. This explains why the



Figure 6.3.6: Orbitally resolved spectral functions of Co (n = 7.8 (a) and n = 7.9 (c)) and Fe (n = 6.0 (b) and n = 6.4 (d)) impurities as obtained from QMC.

separation of the peaks 1 and 2 is 0.5 eV smaller for Co than for Fe.

The spectrum of Ni turns out to consist mainly of a broad peak below the Fermi level without clearly resolvable multiplet features. This is qualitatively in line with an even further reduced effective exchange splitting  $\sim J(n_{\uparrow} - n_{\downarrow})$  for Ni. Indeed, in our GGA and GGA+U calculations, the Ni adatoms turn out to be nonmagnetic on this surface which is in agreement with calculations in Ref. [243] and experiments for Ni on Au [35]. It remains to be explained why feature 2 in the Fe spectrum and the whole Ni spectral peak are rather close to  $E_{\rm F}$  and what the nature of the peak 3 near  $E_{\rm F}$  in the Co spectrum is. Therefore, we discuss the issues of valence fluctuations as well as Kondo physics in the following. As we have mentioned above, see section 1.5.2, the general Coulomb interaction Hamiltonian can be written as

$$\hat{H}_{\rm ee} = \frac{1}{2} \sum_{m,m',m'',m'''} \sum_{\sigma\sigma'} U_{mm'm''m'''} \hat{c}^{\dagger}_{m\sigma} \hat{c}^{\dagger}_{m'\sigma'} \hat{c}_{m''\sigma'} \hat{c}_{m''\sigma}.$$
(6.3.1)

In some methods, especially in some flavors of QMC, one has to resort to an approximation, where the interaction contains only density-density terms  $\propto \hat{n}_{m\sigma} = \hat{c}^{\dagger}_{m\sigma} \hat{c}_{m\sigma}$ . In this approximation the Hamiltonian can be written as



Figure 6.3.7: Spectra obtained by exact diagonalization of the atom in the crystal field are shown for fillings from n = 5 (a) to n = 9 (b,c). We used U = 3eV and J = 1eV for all fillings, here. In this way the pronounced occupancy dependence of  $U_{\text{eff}}$  becomes clearly visible.

$$H_{\rm ee}^{\rm dens-dens} = \frac{1}{2} \sum_{m,m',\sigma} U_{mm'} \hat{n}_{m,\sigma} \hat{n}_{m',-\sigma} + \frac{1}{2} \sum_{m \neq m',\sigma} (U_{mm'} - J_{mm'}) \hat{n}_{m,\sigma} \hat{n}_{m',\sigma} \quad (6.3.2)$$

In above approximation the interaction matrices  $U_{mm'}$  and  $J_{mm'}$  can be analytically expressed for a five band system as shown in Eqs. (1.5.7),(1.5.8). Using the rotationally invariant Coulomb interaction and different approximations one obtains different effective interactions, or charging energies for different fillings n [426]

$$U_{\text{eff}}(n) = E(n-1) + E(n+1) - 2E(n).$$
(6.3.3)

As shown in Refs. [147, 91] for Kanamori type interactions, see section 1.5.2 for a definition, only two situations are found: the half-filled ( $U_{\text{eff}} = U_{\text{K}} + 4J_{\text{K}}$ ) and the non-halffilled case ( $U_{\text{eff}} = U_{\text{K}} - J_{\text{K}}$ ). For the Coulomb interaction defined through  $F^0$ ,  $F^2$ , and  $F^4$ more different cases are found. We find that using the density-density part, Eq. (1.5.7), or the full matrix, Eq. (6.3.1) does not make a difference for the charging energies. In the range of fillings n = 5 to n = 9, which is of interest here, one finds a pronounced occupancy dependence of the effective charging energies [426, 147]

$$U_{\text{eff}}(n) = \begin{cases} F^0 + \frac{14}{49}F^2 + \frac{126}{441}F^4 = U + 4J & \text{for } n = 5; \\ F^0 - \frac{8}{49}F^2 - \frac{9}{441}F^4 = U - \frac{138}{91}J \approx U - 1.52J \approx U - (3/2)J & \text{for } n = 6; 9; \\ F^0 + \frac{1}{49}F^2 - \frac{54}{441}F^4 = U - \frac{44}{91}J \approx U - 0.48J \approx U - (1/2)J & \text{for } n = 7; 8. \end{cases}$$

We have assumed  $F^4 = 0.625F^2$  after the second equality, cf. section 1.5.2. The above  $U_{\text{eff}}$  hold exactly a free spherically symmetric atom. Our exact diagonalization calcu-
lations in Fig. 6.3.7 show that this also holds to a very good approximation when the local crystal field ( $\Delta_{CF}$ ) on the Ag(100) surface is included: the crystal field modifies the effective charging energies only very slightly, at most up to 2.5%. This is well understandable, since the crystal field is small as compared to the interaction parameters U and J. For larger crystal fields  $\Delta_{CF} \sim 2J$  the spin state of the atom can undergo substantial modifications, as we have seen in chapter 4, but this is not the case, here.

Mn has n = 5 and thus the highest  $U_{\text{eff}}$ , as shown in Fig. 6.3.7 (a), which further corroborates our conclusion of Mn resembling an atomic spin S = 5/2 with nearly frozen valence and is in line with the discussion of Kanamori type Coulomb interactions in Refs. [451, 91]. In contrast to the Kanamori model, here  $U_{\text{eff}}$  also varies between the non-half filled cases (n = 6, ..., 9). Most importantly, one finds that the  $d^6$  and  $d^9$  atomic configurations yield the smallest  $U_{\text{eff}}$ , see Fig. 6.3.7(b), and are most susceptible to valence fluctuations. This gives a hint towards mixed valence behavior of the Fe and Ni adatoms, which is substantiated by our QMC results.

For the Fe  $d_{z^2}$  orbital, there are no well defined upper Hubbard bands but only spectral peaks above  $E_F$  which extend to or even below  $E_F$  (Fig. 6.3.6 (b) and (d)). We further find that this overall structure of the spectra remains stable also at larger fillings, like n = 6.4 shown in Fig. 6.3.6 (d). In this entire range (6 < n < 6.4) of occupancies the Fe adatoms are in a mixed valence situation. We note that n = 6.4 corresponds to the occupancies naively extracted from spin-polarized GGA as well as GGA+U calculations with with U = 2 eV up to 5 eV, whereas for n = 6 best quantitative agreement of experimental and calculated spectra is achieved.

The experimental spectrum of Ni consists mainly of a broad peak below the Fermi level and we find good agreement between the QMC calculations and the measured 3d spectra of Ni adatoms for occupancies 8.3 > n > 8.7. Towards integer occupancies like  $d^8$  or  $d^9$ a distinct satellite peak forms at -2.5eV resembling the feature present in the ED spectra shown in Fig.6.3.5(d). Since the experimental data show a minimum around this energy the filling of the Ni 3d shell has to be in between n = 8 and n = 9. In this range, the Ni spectra obtained from our QMC simulations and the experiments are qualitatively more similar to the "non-interacting" GGA density of states than to the ED spectra shown in Fig.6.3.5 (d). There are no well defined upper Hubbard bands in any of the Ni orbitals but only broad spectral weight distributions above  $E_{\rm F}$  which extend below  $E_{\rm F}$ . This points towards a mixed valence situation for also for Ni.

In this respect Fe and Ni are very different from Co: For Co, the experiments (feature 3) and calculations show a quasi particle peak at the Fermi level, which is well separated from clearly formed upper and lower Hubbard bands. There are, thus, less charge fluctuations for Co on Ag (100) and so this system comes closer to the (multi-orbital) Kondo limit. Therefore, our results confirm the interpretation of low energy resonances in STM spectroscopy experiments of Co on Ag(100) in terms of a Kondo effect [434]. The QMC results further show that all Co orbitals are involved in the quasiparticle resonance (Fig.

6.3.6 (a,c). Thus, excitations of the orbital degree of freedom must be available at energies on the order of our simulation temperature  $1/\beta = 0.05 \text{ eV}$ . This is similar to the case of Co on Cu (111) [403]. For Co we find best agreement of calculated and measured spectra in the range n = 7.8 - 7.9 (Fig. 6.3.6 (a,c)). Thus, the Co is closer to a  $d^8$  than to a  $d^7$  configuration which supports recent coupled cluster calculations [387]. We note that a prediction of the Co valency based on DFT type approaches can be misleading: GGA+U calculations with 2 eV < U < 5 eV yield an occupancy of the 3d shell between n = 7.0 and 7.2.

The spectral function of Mn (a group VII-element) could be well understood assuming a filling of  $n \approx 5$  for the Mn 3d orbitals. However, noble metals like Cu (group XIelements having 4 electrons per atom more than the corresponding group VII elements) have an almost full d shell (i.e.  $n \approx 10$ ) due to one electron from the 4s orbitals being promoted to the 3d orbitals. If this promotion of one electron from the 4s to the 3d orbitals would occur homogeneously, the 3d occupancy should increase by 1.25 electrons between each two atoms of the 3d series under investigation. Such an increase is in line with our results and the mixed valence behavior for Fe (6 < n < 6.4) and Ni (8.3 > n > 8.7) but not with Co which comes closer to the Kondo limit of nearly frozen  $d^8$  valence.

## 6.4 Summary and Conclusions

Our joint experimental and theoretical study shows that Hund's exchange controls the physics of 3d adatoms on the surfaces of Ag (100). It fosters the formation of multiplets, determines multiplet splittings and modulates effective charging energies. Our results show that any realistic description of magnetic nanosystems should account for these manifestations of Hund's exchange. Particularly the mixed valence behavior of Fe and Ni challenges discussions of transition metal based nanomagnetic structures or impurity systems in terms of spin-only models. The situation is complex and challenging. Further spectroscopy studies, including photoelectron spectroscopy with higher energy resolution and as a function of temperature, will be useful to fully describe the nature of general excitation spectra of magnetic impurities on surfaces.

## **General Summary and Outlook**

The aim of the present thesis was, first, to present a general DFT++ framework for ab initio calculations combining density functional theory and model Hamiltonian approaches and, second, to apply this methodology to transition metal systems ranging from three dimensional bulk materials to zero dimensional single atoms adsorbed on a surface. The methodology behind DFT++ was introduced and expanded in chapters 1 and 2. We have presented a general interface between a projector augmented wave based DFT method and many body methods based on Wannier functions obtained from a projection on local orbitals. The method is general and can take into account different correlated sites or layers and access also the charge density in the vacuum. Different schemes to obtain projection matrices from PAW calculations have been explored and explicitly compared to other schemes. Our implementation is very flexible and can be applied to bulk systems including self-consistency within dynamical mean-field theory or also charge self-consistency, as well as to impurity problems requiring only an Anderson model treatment. As example applications we showed DFT+DMFT calculations for SrVO<sub>3</sub>, the volume of iron in the paramagnetic phase employing a charge self-consistent DFT+DMFT and also first results for vacuum states.

The methodological part also in part encompasses chapter 3 that was devoted to the technical problem of the double counting of interaction terms that is an obstacle to finding a parameter free DFT++. We show, using the example of NiO that DFT++ or DFT+DMFT in that specific case is only a parameter free theory when the whole system is treated on the same footing. If the system is divided into correlated (Coulomb interaction is applied) and uncorrelated (Coulomb interaction is mostly neglected) parts and information is to be obtained on both, the results will depend on the choice of the double counting. By carefully examining different prescriptions for the double counting correction we have found some interesting relationships between them. We find that certain, in general different, formulas used to determine the correction actually become identical in certain limiting cases that are quite common. The problem of the double counting does not have a *solution* in the simple sense of the word. It arises from the approximation that the Coulomb interaction is only appreciable on the *d* or *f* shells of a system and can be neglected on other shells, i. e. *s* or *p* shells. Same applies to the Coulomb interaction *between* different shells. Such an approximation can be justified in some cases, where the dependence of the result on the double counting is small, in other cases it can lead to qualitatively wrong results. Further work has to be performed to be able to tell when such an approximation fails, ultimately, however, the only real *cure* for the problem is the explicit inclusion of all interaction effects on all relevant shells within a cluster treatment of the correlated d, f-shell metal and its s, p-shell ligands.

As the first presented application of DFT++ we have studied LaCoO<sub>3</sub> within the DFT+DMFT formalism. We employed a solver using exact diagonalization using the Lanczos method. Our model was based on an atomistic point of view, focussing on the Co  $3d^6$  multiplet states. We find that the spin state transition as a function of the crystal field splitting takes place between the Hund's rule high-spin ground state and the low-spin state. We do not find contributions from the S = 1 intermediate state. Our study further corroborates the scenario put forward by Goodenough [130]. Our, relatively simple and cheap calculations agree qualitatively with the recent CT-QMC studies concerning the spectra and their interpretation. This shows that the interpretation of the local physics of this compound is possible to some degree using only the  $d^6$  multiplets of Co.

Further studies are being performed at the moment, where the approximation of a homogeneous spin state in the unit cell is lifted and the two Co atoms are treated independently within DFT+DMFT. Preliminary results indicate that the proposed mechanism of HS-LS order might be realized also within DFT+DMFT. Efforts to include charge into the selfconsistency cycle are also under way. This is imperative if genuine orbital order is to be established within the system on the level of DFT++.

We subsequently turned to the transition metal benzene sandwich molecules (TMBz<sub>2</sub>) with Sc, Ti, V, Co and Ni centers coupled to Cu nanowires. Dynamical correlations originating from the strongly interacting 3d electrons give rise to different effects. Depending on the specific regime the molecule is in while in contact with the electrodes we observe an orbital Kondo effect (V, Co) or a mixed-valence/empty-orbital behavior (Sc, Ti, Ni). The Kondo effect occurs in the doubly degenerate  $E_1$  or  $E_2$  shells in vanadium and cobalt respectively and follows the same mechanism in both cases. Our study shows, that the parameters of an Anderson model could be tuned using a real molecule. In the case of TMBz<sub>2</sub> molecules in a nanocontact the hybridization strenght can be controlled by the proximity of the electrodes to the molecule, while the local Coulomb interaction as well as the filling of the 3d shell are controlled by species of the central atom.

We are planning to investigate further into  $V_nBz_{n+1}$  clusters, since studies based on DFT or DFT+U have shown that these systems can have intriguing magnetic properties and can also behave as half-metals. In the light of spintronics this is the system most promising for applications. A study within DFT++ including the effects of the dynamical self-energy and magnetism would certainly be worthwhile.

Finally, we considered the series of isolated Mn, Fe, Co and Ni adatoms on the Ag (100) surface and explained their excitation spectra. Our joint experimental and theoretical

study showed that Hund's exchange controls the physics of 3d adatoms on the surfaces of Ag (100). Our theoretical simulations based on calculations of atomic multiplets and an ab initio study within DFT++ using a QMC solver showed, that it fosters the formation of multiplets, determines multiplet splittings and modulates effective charging energies. Our results show that any realistic description of magnetic nanosystems should account for these manifestations of Hund's exchange. Particularly the mixed valence behavior of Fe and Ni challenges discussions of transition metal based nanomagnetic structures or impurity systems in terms of spin-only models.

We would like to note, as a closing remark, that although considerable progress has been made over, say, the last two to three decades in the understanding of correlated electron systems and their properties, the journey towards a predictive theoretical methodology still continues. A few successes in predicting certain properties of materials using DFT+DMFT or GW+DMFT have been claimed, mostly however the theory works to provide a posteriori explanations, though. Nevertheless, the combination of band structure methods like DFT or GW with model Hamiltonian approaches like DMFT seem to be the most promising way of getting closer to the sought method with *predictive power*. A few obstacles on the way are on the side of the band structure approaches, a few are on the model Hamiltonian side, e.g., momentum dependence of the self-energy in solids, but some issues that seem simpler and more technical, but still defy an exact solution lie on the interface between the two. The construction of a good low-energy Hamiltonian from a band structure calculation is not trivial at all in certain cases. We hope that we could shed some light on the power and at the same time limitations of the DFT++ approach at the present stage of its development and trust that it will evolve and continue to be the state of the art method (or one of them) for the simulation of realistic correlated electron systems.

## **List of Publications**

- S. Gardonio, M. Karolak, T. O. Wehling, L. Petaccia, S. Lizzit, A. Goldoni, A. I. Lichtenstein, and C. Carbone, *Excitation Spectra of Transition-Metal Atoms on the Ag (100) Surface Controlled by Hund's Exchange*, Phys. Rev. Lett. **110** (2013), 186404
- M. Karolak, T. O. Wehling, F. Lechermann, and A. I. Lichtenstein, *General DFT++ method implemented with projector augmented waves: Electronic structure of SrVO*<sub>3</sub> and the Mott *Transition in Ca*<sub>2-x</sub>*Sr*<sub>x</sub>*RuO*<sub>4</sub>, J. Phys.: Condens. Matter **23** (2011), 085601
- L. V. Dzemiantsova, M. Karolak, F. Lofink, A. Kubetzka, B. Sachs, K. von Bergmann, S. Hankemeier, T. O. Wehling, R. Frömter, H. P. Oepen, A. I. Lichtenstein, and R. Wiesendanger, *Multiscale magnetic study of Ni(111) and graphene on Ni(111)*, Phys. Rev. B 84 (2011), 205431
- M. Karolak, D. Jacob, and A. I. Lichtenstein, *Orbital Kondo Effect in Cobalt-Benzene Sandwich Molecules*, Phys. Rev. Lett. **107** (2011), 146604
- S. Gardonio, T. O. Wehling, L. Petaccia, S. Lizzit, P. Vilmercati, A. Goldoni, M. Karolak, A. I. Lichtenstein, and C. Carbone, *Spectral Functions of Isolated Ce Adatoms on Paramagnetic Surfaces*, Phys. Rev. Lett. **107** (2011), 026801
- E. Gorelov, M. Karolak, T. O. Wehling, F. Lechermann, A. I. Lichtenstein, and E. Pavarini, *Nature of the mott transition in Ca*<sub>2</sub>*RuO*<sub>4</sub>, Phys. Rev. Lett. **104** (2010), no. 22, 226401
- M. Karolak, G. Ulm, T. Wehling, V. Mazurenko, A. Poteryaev, and A. Lichtenstein, *Double counting in LDA+DMFT The example of NiO*, Journal of Electron Spectroscopy and Related Phenomena **181** (2010), no. 1, 11 15

Unrelated work

A. Westphalen, A. Schumann, A. Remhof, H. Zabel, M. Karolak, B. Baxevanis, E. Y. Vedmedenko, T. Last, U. Kunze, and T. Eimüller, *Magnetization reversal of microstruc-tured Kagomé lattices*, Phys. Rev. B 77 (2008), 174407

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