Electronic structure of strongly correlated low-dimensional spin 1/2 systems: cuprates and vanadates

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<tr>
<td>AL</td>
<td>atomic limit</td>
</tr>
<tr>
<td>AM</td>
<td>antiferromagnetic</td>
</tr>
<tr>
<td>BZ</td>
<td>Brillouin zone</td>
</tr>
<tr>
<td>CI</td>
<td>configurational interaction</td>
</tr>
<tr>
<td>CF</td>
<td>crystal field</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DMFT</td>
<td>dynamical mean field theory</td>
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<tr>
<td>DOS</td>
<td>density of states</td>
</tr>
<tr>
<td>FM</td>
<td>ferromagnetic</td>
</tr>
<tr>
<td>FPLO</td>
<td>full-potential local-orbital</td>
</tr>
<tr>
<td>GF</td>
<td>Green function</td>
</tr>
<tr>
<td>GGA</td>
<td>generalized gradient approximation</td>
</tr>
<tr>
<td>GKA</td>
<td>Goodenough-Kanamori-Anderson</td>
</tr>
<tr>
<td>GMFA</td>
<td>generalized mean field approximation</td>
</tr>
<tr>
<td>HFA</td>
<td>Hartree-Fock approximation</td>
</tr>
<tr>
<td>HTSC</td>
<td>high-temperature superconductivity</td>
</tr>
<tr>
<td>KS</td>
<td>Kohn-Sham</td>
</tr>
<tr>
<td>LCAO</td>
<td>linear combination of atomic orbitals</td>
</tr>
<tr>
<td>L(S)DA</td>
<td>local (spin) density approximation</td>
</tr>
<tr>
<td>MF</td>
<td>mean field</td>
</tr>
<tr>
<td>RVB</td>
<td>resonant valence bond</td>
</tr>
<tr>
<td>SIC</td>
<td>self-interaction correction</td>
</tr>
<tr>
<td>SO</td>
<td>spin-orbit</td>
</tr>
<tr>
<td>TB</td>
<td>tight-binding</td>
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<tr>
<td>TM</td>
<td>transition metal</td>
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<td>exchange and correlation</td>
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LIST OF ABBREVIATIONS
Introduction

Transition metal (TM) compounds represent one of the most fascinating classes of inorganic solids, exhibiting a wide variety of structures and properties. The origin of those properties is the unique nature of the inner partially filled $d$-electron shell. The involved physics is quite complicated as the shell is well localized and subject to an interplay of crystal field and spin-orbit coupling. The most prominent feature of many TM compounds is magnetism, which is one of a few exceptions demonstrating both quantum and relativistic phenomena in the everyday life. Though magnetism was known to mankind from the antiquity and magnetite $\text{Fe}_3\text{O}_4$ had been used as compass for millennia, it was only the XXth-century physics which shed light on the nature of the magnetic ordering in solids. However the problem is still far from being utterly solved and is at the edge of the modern researches in solid-state physics. Another fascinating phenomenon is high temperature superconductivity (HTSC) which seems also to stem from the partially occupied $3d$-shell of copper. The high temperature superconductors belong to a wide family of intensively investigated compounds (metalates) having an anionic transition metal oxide complex as a basic structural element. In this thesis we will focus on the electronic and magnetic properties of metalates containing oxides of two extremes of the first transition metal series – vanadium and copper. Though vanadium is not the leftmost representative of the $3d$-series its valence state $V^{4+}$ in many oxides leaves exactly one electron in the $d$-shell to be compared with one hole in the case of $\text{Cu}^{2+}$ and the magnetic structure of both classes of compounds can be thought as a system of interacting spin-$1/2$ moments. The properties of vanadates and cuprates have been the subject of numerous theoretical and experimental investigations which were extremely intensified after the discovery of HTSC in 1986. The low-dimensional low-spin systems reveal a number of other unusual properties apart from superconductivity, such as spin-charge separation or spin-Peierls transition. It makes the systems ideal models for checking and improving novel theoretical techniques.

The behavior of a solid at ambient temperature is due to an interplay of
INTRODUCTION

Various excitations. Model Hamiltonians are frequently used to define the excitations with respect to the quantum-mechanical ground state and require a description of the state for computing the model parameters. The application of quantum mechanics for computing the ground state of a solid is not at all a simple task because of the huge number ($\sim 10^{23}$) of interacting particles in a macroscopic sample. The problem can be drastically simplified by assuming perfect translational symmetry of a crystal. That though hardly accounts for reality but serves the only possible and practically good approximation. But even after reducing the computation to the elementary cell the problem remains intractable without some further simplifications as the modern computational techniques are unable to solve the exact many-body problem. One possibility is to guess an ansatz for the many-body wavefunction and to find the best solution with respect to the parameters of the ansatz model. The most simple way to assert the antisymmetry of the exact many-body wavefunction is the Hartree-Fock approximation (HFA), which assumes that the function is a single determinant of one-electron states. This approximation accounts for the exchange interaction and noteworthy involves no self-interaction contrary to the Hartree approximation which treats the electrons as completely independent. However the deviation of the exact solution from the single determinant of fictitious one-electron states leads to false predictions for the electronic structure of many solids. Such compounds are called strongly correlated systems and actually many solids containing ions with partially filled localized shells fall into this category. There were attempts to correct HFA by including the configuration interaction (CI) but the numerical difficulty of treating the additional determinantal states prevents the method from being applied to anything else but atoms and molecules. Reduced CI schemes with coupled clusters as the local ansatz were applied to solids in a few simple cases.

A brilliant alternative to HFA is the density functional theory (DFT) born in works of Hohenberg and Kohn [1] and Kohn and Sham [2], that was appreciated by awarding the Nobel Prize to Kohn in 1998. This theory can be viewed as consisting of two parts. The exact part states that the ground state energy of a many-electron system in a given external potential can be obtained by minimizing a general density functional, and the second one tries to approximate the functional – with no hope to find its exact form. The original and up to now the mostly used approximation is the local (spin) density approximation (LSDA) which adjusts the density functional with parameters that stem from the solvable problem of the homogenous electron

\footnote{That is by solving a three-dimensional variational problem instead of the $3N$-dimensional one for the wave function.}
liquid. Though the approximation does not treat the exchange explicitly and generally contains self-interaction, it includes many essential features of the correlations, so that in many cases (especially for metals and intermetallic compounds) the results of the theory are in very good agreement with experiment. However the method often fails for strongly correlated systems where the electron density of the relevant electrons having the lowest binding energy deviates too much from the uniform distribution. Then, the theory may wrongly predict metallic and sometimes paramagnetic behavior for substances which are known as magnetic insulators, as in the case of the late transition metal monoxides. This failure is traced back to a bad treatment of the correlation effects. The importance of these effects was realized long time ago. It was the discovery of the insulating behavior of the TM monoxides which had stimulated Mott and later Hubbard to develop a theory based on more exact treatment of the correlation effects for explanation of unusual phenomena in partially filled narrow bands originating from the well-localized atomic orbitals.

Many schemes were proposed in the last decades with the object of improving the XC (exchange and correlation) potential of DFT to account for the Mott-Hubbard behavior. It suffices to mention GGA (generalized gradient approximation), SIC-LSDA (self-interaction correction), LSDA+$U$ and LSDA+DMFT (dynamical mean field). An alternative way to treat correlation effects is the construction of a model Hamiltonian.

The LSDA+$U$ method is now widely used both because of its simplicity and rather good agreement with the experiment at the price of at least one adjustable parameter. It is also important that the results of an LSDA+$U$ calculation can be directly interpreted in terms of Hubbard-like models. It is especially simple to implement in the framework of the LCAO (linear combination of the atomic-like orbitals) scheme. The current version of the code developed in Dresden under the guidance of Prof. H. Eschrig – FPLO – includes the exact treatment of the crystal potential. The code belongs to the calculation schemes defining standards of modern DFT calculations.

The thesis is organized as follows. In the Chapters 1 and 2 we sketch the basis of the DFT and the band-calculation scheme, respectively. Also, the rotationally invariant LSDA+$U$ density functional is formulated in the framework of DFT and an explicit LSDA+$U$ correction is derived for the LCAO scheme. In Chapter 3 we test the applicability of LSDA+$U$ to the transition metal monoxides. In Chapter 4 we present a model calculation of the changes in the electronic structure caused by a single Cu→Zn impurity substitution in the CuO$_2$ plane. In Chapter 5 we present DFT results for some novel vanadates, which reveal low-dimensional magnetic phenomena. Finally a short summary and an outlook is given in Chapter 6.
Chapter 1

Density functional theory

The usual approximation in computing the ground state of a crystal is treating the solid as a result of electrostatic pairwise interaction between nuclei and electrons. The complete quantum description of the system would require a calculation of the many-body wavefunction for the involved particles. However it seems for the foreseeable future to be impossible to solve a differential equation involving about $10^{23}$ variables and one should explore the experimentally observed translational symmetry of crystals in a hope to effectively reduce the calculation to the elementary cell. It would be done if nuclei were fixed in the space at translationally invariant positions. It is what one actually does in any solid state calculation and is justified by the fact, that nuclei are much heavier than electrons and on the scale of electron velocities the two systems are decoupled (adiabatic approximation) [3]. Perturbation theory can be applied in succession to account for a coupling known as electron-phonon interaction.

The Hamiltonian of $N$ pairwise interacting electrons in a static external potential $v(\mathbf{r})$ reads

$$
\hat{H}(v, N) = \hat{T}_N + \hat{V}_N + \hat{W}_N = -\frac{1}{2} \sum_{i}^{N} \nabla^2_i + \sum_{i}^{N} v(x_i) + \frac{1}{2} \sum_{i,j}^{N} w(x_i, x_j),
$$

(1.1)

where $w(x_i, x_j) = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$ is the electrostatic repulsion potential. Self-interaction is supposed to be excluded: $w(x_i, x_i) \equiv 0$.

After reducing the original problem to that of electrons moving in a perfect translationally symmetric external potential created by fixed nuclei it

\footnote{Unless otherwise stated the atomic units $|e| = \hbar = m_e = 1$ are used. The argument $x$ accumulates both space coordinate and spin of a particle $\mathbf{r}s$, the integration over $dx$ meaning $\sum_{s, \mathbf{r}} \int d\mathbf{r}$.}
remains still unsolvable as there is no simple ansatz parameterizing the many-electron wavefunction. The real breakthrough came in the mid-sixties when Hohenberg and Kohn [1] and Kohn and Sham [2] established the basis of the density functional theory and provided a recipe for its implementation to real systems. The main idea of the approach is to replace the overcomplicated many-electron wave function as a variational quantity by the charge density, the latter depending only on three space coordinates. Though this idea was explored already in the twenties by Thomas [4] and Fermi [5], it was the Hohenberg-Kohn theorem which put the method on rigorous grounds.

In the rest of the Chapter the basics of the DFT and the computation scheme based on it are sketched. For a thorough discussion the reader is referred to [6, 7].

1.1 Hohenberg-Kohn variational principle

The essence of DFT is based on the convexity properties of the ground state energy considered as a functional of the external potential \( v \) and the number of electrons \( N \). It follows from (1.1) that the functional dependence of \( \hat{H} \) on \( v \) is affine-linear:

\[
\hat{H}[\alpha_1 v_1 + \alpha_2 v_2, N] = \alpha_1 \hat{H}[v_1, N] + \alpha_2 \hat{H}[v_2, N] \quad \alpha_1 + \alpha_2 = 1
\]

and has the following gauge property:

\[
\hat{H}[v + \text{const}, N] = \hat{H}[v] + \text{const} \cdot N. \tag{1.3}
\]

The ground state energy is defined as the lowest expectation value of the Hamiltonian:

\[
E[v, N] = \inf_{\Psi} \left\{ \langle \Psi | \hat{H}[v, N] | \Psi \rangle \mid \Psi \in \mathcal{A}_N \right\} \tag{1.4}
\]

\[
\mathcal{A}_N = \left\{ \Psi \mid \hat{N} \Psi = N \Psi, \hat{P} \Psi = (-1)^{|P|} \Psi, \langle \Psi | \Psi \rangle = 1, \sum_{i=1}^{N} \langle \nabla_i \Psi | \nabla_i \Psi \rangle < \infty \right\}. \tag{1.5}
\]

where \( \Psi(x_1, \ldots, x_N) \) is a normalized \( N \)-particle antisymmetric wavefunction with finite kinetic energy. The argument of the function \( x_i \) accumulates both the spin and the space coordinate of the \( i \)th particle. \( \hat{N} \) and \( \hat{P} \) are the number of particles and permutation of particles operators, respectively. The infimum exists as any reasonable Hamiltonian in nonrelativistic quantum mechanics is bounded from below.\(^2\)

\(^2\)In the relativistic analogue, where both electrons and positrons are solutions to the Hamiltonian, the infimum exists if \( \mathcal{A}_N \) is restricted to electron-like states.
1.1. HOHENBERG-KOHN VARIATIONAL PRINCIPLE

As seen from the definition of the Hamiltonian (1.1), the ground state energy functional (1.4) is defined only for integer numbers of particles \( N \). It is however advantageous to extend the domain of its definition to real numbers. One can achieve this goal by admitting instead of \( N\) -particle pure states \( |\Psi\rangle \) the most general density operator (mixed state):

\[
\hat{\Gamma} = \sum_{K} |\Psi_{K}\rangle p_{K} \langle \Psi_{K}|, \quad \Psi_{K} \in \mathcal{A}_{N_{K}}; \{p_{K}\} \in \mathcal{P}
\]

where \( |\Psi_{K}\rangle \) are the normalized pure states with \( N_{K} \) electrons and \( p_{K} \) is the probability to find the system in such a pure state.

The extension of the definition of the ground state energy functional now reads:

\[
E[v, N] \overset{\text{def}}{=} \inf_{\hat{\Gamma}} \left\{ \text{tr} \left( \hat{H} \hat{\Gamma} \right) \mid \text{tr} \left( \hat{N} \hat{\Gamma} \right) = N \right\}
\]

\[
= \inf_{\{p_{K}, \Psi_{K}\}} \left\{ \sum_{K} p_{K} \langle \Psi_{K}|\hat{H}|v, N_{K}||\Psi_{K}\rangle \mid \{p_{K}, \Psi_{K}\} \in \mathcal{P}_{N} \right\},
\]

where

\[
\mathcal{P}_{N} = \left\{ \{p_{K}, \Psi_{K}\} \mid \Psi_{K} \in \mathcal{A}_{N_{K}}, \{p_{K}\} \in \mathcal{P}, \sum_{K} p_{K} N_{K} = N \right\}.
\]

The definition is reduced to (1.4), if all involved pure states have the same number of particles \( N \). The direct gain of this definition consists in the evident convexity of the functional with respect to the real number \( N \) under fixed external potential \( v \). Let \( \{p_{K}, \Psi_{K}\} \) and \( \{p'_{K}, \Psi'_{K}\} \) be the minimizing sets for \( E[v, N] \) and \( E[v, N'] \) respectively and form the state

\[
\hat{\Gamma}'' = c \hat{\Gamma} + c' \hat{\Gamma}' = \sum_{K} |\Psi_{K}\rangle c p_{K} \langle \Psi_{K}| + \sum_{K'} |\Psi'_{K'}\rangle c' p'_{K'} \langle \Psi'_{K'}|,
\]

where \( 0 \leq c, c' \); \( c + c' = 1 \). Obviously the state \( \hat{\Gamma}'' \) is a mixed state in the sense of (1.6), as \( 0 \leq c p_{K} \), \( 0 \leq c' p'_{K} \) and \( \sum_{K} c p_{K} + \sum_{K'} c' p'_{K'} = 1 \). The number of particles and the energy corresponding to the mixed state are \( \tilde{N}'' = cN + c' N' \) and \( \tilde{E}'' = c E[v, N] + c' E[v, N'] \), respectively. As the set \( \{c p_{K}, \Psi_{K}\} \cup \{c' p'_{K}, \Psi'_{K}\} \) is an admissible subset for minimizing \( E[v, \tilde{N}''] \)

\[
E[v, cN + c' N'] \leq c E[v, N] + c' E[v, N']; \quad 0 \leq c, c' \; ; \; c + c' = 1.
\]
CHAPTER 1. DENSITY FUNCTIONAL THEORY

This proves that the ground state energy is a convex functional with respect to the number of particles.

Using (1.2) and the fact, that the infimum of a sum is not lower than the sum of the corresponding item’s infinima one readily finds that under fixed number of particles \( N \) the ground state energy functional is concave with respect to the external potential \( v \):

\[
E[cv + c'v', N] = \inf_{\{p_K, \Psi_K\}} \left\{ \sum_K p_K \langle \Psi_K | \hat{H}[cv + c'v', N] | \Psi_K \rangle \mid \{p_K, \Psi_K\} \in \mathcal{P}_N \right\}
\]

\[
= \inf_{\{p_K, \Psi_K\}} \left\{ \sum_K p_K \left( \langle \Psi_K | c \hat{H}[v, N] + c' \hat{H}[v', N] | \Psi_K \rangle \right) \mid \{p_K, \Psi_K\} \in \mathcal{P}_N \right\}
\]

\[
\geq c \inf_{\{p_K, \Psi_K\}} \left\{ \sum_K p_K \langle \Psi_K | \hat{H}[v, N] | \Psi_K \rangle \mid \{p_K, \Psi_K\} \in \mathcal{P}_N \right\}
\]

\[
+ c' \inf_{\{p_K, \Psi_K\}} \left\{ \sum_K p_K \langle \Psi_K | \hat{H}[v', N] | \Psi_K \rangle \mid \{p_K, \Psi_K\} \in \mathcal{P}_N \right\}
\]

\[
= cE[v, N] + c'E[v', N]; \quad 0 \leq c, c'; \quad c + c' = 1. \quad (1.12)
\]

Using the convexity of the ground state energy functional with respect to the particle number \( N \) one defines a Legendre transform of the functional by introducing a variable \( \mu \) dual to \( N \):

\[
G[v - \mu] \overset{\text{def}}{=} \sup_N \left\{ \mu N - E[v, N] \right\} = \sup_N \left\{ -E[v, \mu, N] \right\}, \quad (1.13)
\]

where the gauge property (1.3) has been used. The functional \( G[v] \) is just as \(-E[v, N]\) convex in \( v \) and can be Legendre transformed with respect to the variable \( v \) by introducing the dual variable \(-n\):

\[
H[n] \overset{\text{def}}{=} \sup_v \left\{ (-n|v) - G[v] \right\}, \quad (1.14)
\]

where \((f|g)\) means the scalar product \( \int f^*(x)g(x)dx \).

Now one is ready to express the ground state energy functional in terms
of dual (and having the same dimension!) variables \( v \) and \(-n\):

\[
E[v, N] = \sup_{\mu} \left\{ N\mu - G[v - \mu] \right\}
\]

\[
= \sup_{\mu} \left\{ N\mu - \sup_{n} \left\{ (v - \mu|-n) - H[n] \right\} \right\}
\]

\[
= \sup_{\mu} \left\{ N\mu + \inf_{n} \left\{ (v - \mu|n) + H[n] \right\} \right\}
\]

\[
= \sup_{\mu} \inf_{n} \left\{ \mu \left[ N - (1|n) \right] + (v|n) + H[n] \right\}
\]

(1.15)

The expression in the curved braces can be regarded as a functional of \( \mu \)
and \( n \). As the functional is explicitly linear in \( \mu \) and convex in \( n \) the infimum
and supremum in the last line can be interchanged.

\[
E[v, N] = \inf_{n} \sup_{\mu} \left\{ \mu \left[ N - (1|n) \right] + (v|n) + H[n] \right\}
\]

\[
= \inf_{n} \left\{ (v|n) + H[n] \left| (1|n) = N \right. \right\}.
\]

(1.16)

In the chain of expressions (1.11 – 1.16) no physics was involved except
for linearity of the Hamiltonian, and one seems to be left with two unknown
quantities: a function \( n \) and a functional \( H[n] \). The bridge to physics can be
built if one compares (1.16) with the first line of (1.8). One sees immediately
that it is advantageous to treat \( n \) as the electron spin-charge density:

\[
n(x) = \sum_{K} p_{K} N_{K} \int dx_{2} \ldots dx_{N_{K}} \Psi_{K}(xx_{2} \ldots x_{N_{K}})\Psi_{K}(xx_{2} \ldots x_{N_{K}}),
\]

(1.17)

the functional \( H[n] \) corresponding to the density being

\[
H[n] = \sum_{K} p_{K} \langle \Psi_{K}|\hat{T}_{N_{K}} + \hat{W}_{N_{K}}|\Psi_{K} \rangle.
\]

(1.18)

After identifying \( n \) and \( H[n] \) the expression (1.16) is recognized as the
Hohenberg-Kohn variational principle. One should yet determine the domain
of variation of \( n \). Requiring that the kinetic energy and density of the system
be finite one comes to the conclusion \( n \in L^{3} \cap L^{1} \). \(^{3}\) The quantity dual
to the density, the external potential \( v \in L^{3/2} + L^{\infty} \), comprises the Coulomb
potential of point sources.

\(^{3}\) \( f \in L^{p} \) means \( \int |f|^{p} < \infty \).
1.2 Kohn-Sham equation

The theory outlined in the previous section is exact but gives no profit until the functional $H[n]$ is defined. There is however little hope that it can be ever found, with the only exception of the non-interacting electron gas. In this case the functional (1.18) becomes just the kinetic energy of the gas. This fact encouraged Kohn and Sham [2] to split the functional in the general case into three components:

$$H[n] = T[n] + E_{\text{H}}[n] + E_{\text{XC}}[n],$$  \hfill (1.19)

where $T[n]$ is the kinetic energy of the non-interacting electron gas,

$$E_{\text{H}}[n] = \frac{1}{2} \int d\mathbf{r}d\mathbf{r'} \frac{n(\mathbf{r}) n(\mathbf{r'})}{|\mathbf{r'} - \mathbf{r}|}$$  \hfill (1.20)

is the Hartree energy, and the rest is the so-called exchange-correlation energy, which is actually defined by (1.19). The Hartree term contains self-interaction. Otherwise it could not be expressed as a functional of density.

We again admit the solutions to the Hamiltonian in the form of a mixed state (1.6) and expand the pure states $|\Psi_K\rangle$ into orthonormal determinantal states

$$|\Psi_K\rangle = \sum_{I_K} c_{I_K} |\Phi_{I_K}\rangle$$  \hfill (1.21)

where $|\Phi_{I_K}\rangle$ are the $N_K$-particle determinantal states (Slater determinants)

$$\Phi_{I_K}(x_1, \ldots, x_{N_K}) = \frac{1}{\sqrt{N_K!}} \left| \begin{array}{cccc} \phi_{i_1}(x_1) & \phi_{i_1}(x_2) & \cdots & \phi_{i_N}(x_{N_K}) \\ \phi_{i_2}(x_1) & \phi_{i_2}(x_2) & \cdots & \phi_{i_N}(x_{N_K}) \\ \cdots & \cdots & \cdots & \cdots \\ \phi_{i_{N_K}}(x_1) & \phi_{i_{N_K}}(x_2) & \cdots & \phi_{i_N}(x_{N_K}) \end{array} \right|,$$  \hfill (1.22)

$$\langle \phi_i | \phi_j \rangle = \delta_{ij}; \quad I_K = \{ i_1 i_2 \cdots i_{N_K} \mid i_1 < i_2 < \cdots < i_{N_K} \},$$

which are orthonormal and span the antisymmetric sector of the $N_K$-particle states. $\{ \phi(x) \}$ is a complete orthonormal set of one-electron wavefunctions (orbitals).

One readily obtains the expression for the spin-charge density (1.17) in terms of the orbitals

$$n(x) = \sum_{ij} \phi_i(x) \bar{n}_{ij} \phi_j^*(x)$$  \hfill (1.23)
1.2. Kohn-Sham Equation

where

\[ \tilde{n}_{ij} = \sum_{K} p_{K} \sum_{I_K \ni i; J_K \ni j} c_{I_K} (-1)^{||i||_{K} - ||i||_{K}^{*}} c_{J_K}^{*} \]  \quad (1.24)

with ||i||_{I} being the index of orbital \( i \) in the Slater determinant \( \Phi_{I} \).

Apparently the matrix \( \tilde{n}_{ij} \) is hermitian \( \tilde{n}_{ij} = \tilde{n}_{ji}^{*} \) and therefore can be diagonalized by a unitary transformation

\[ U^\dagger \tilde{n}_{ij} U = n_{d} \delta_{ij} \]  \quad (1.25)

leading one to rewrite the expression (1.23) as

\[ n(x) = \sum_{i} n_{i} \psi_{i}(x) \psi_{i}^{*}(x) \]  \quad (1.26)

where the orthonormal one-particle wavefunctions

\[ \psi_{i}(x) = \sum_{j} U_{ij} \phi_{j}(x) \]  \quad (1.27)

are known as Lödwin natural orbitals. The occupation numbers \( n_{i} \) are restricted by the condition [8]

\[ 0 \leq n_{i} \leq 1, \quad \sum_{i} n_{i} = N. \]  \quad (1.28)

In terms of the natural orbitals the expression for the Hohenberg-Kohn functional reads

\[ H[n] = \min_{n_{i} \psi_{i}, \psi_{i}} \left\{ \sum_{i} n_{i} \langle \psi_{i} | \hat{\epsilon} | \psi_{i} \rangle + E_{H}[n] + E_{XC}[n] \right\} \]

\[ \left| \langle \psi_{i} | \psi_{j} \rangle = \delta_{ij}, \quad 0 \leq n_{i} \leq 1, \quad \sum_{i} n_{i} = N, \quad \sum_{i} n_{i} |\psi_{i}|^{2} = n \right\}, \]  \quad (1.29)

where \( \hat{\epsilon} = -\nabla^{2} \).

Substituting the expression in (1.16) and noting that variation over \( n(x) \) means omitting the restriction \( \sum_{i} n_{i} |\psi_{i}|^{2} = n \) one obtains for the ground state energy the expression

\[ E[v, N] = \min_{n_{i} \psi_{i}, \psi_{i}} \left\{ \sum_{i} n_{i} \langle \psi_{i} | \hat{\epsilon} + v | \psi_{i} \rangle + E_{H}[n] + E_{XC}[n] \right\} \]

\[ \left| \langle \psi_{i} | \psi_{j} \rangle = \delta_{ij}, \quad 0 \leq n_{i} \leq 1, \quad \sum_{i} n_{i} = N \right\}. \]  \quad (1.30)
CHAPTER 1. DENSITY FUNCTIONAL THEORY

Under fixed occupation numbers one minimizes the expression by varying it with respect to \( \psi_i^* \), resulting in a system of one-particle equations

\[
(i + v_{\text{eff}})\psi_i = \epsilon_i \psi_i
\]

(1.31)

where \( \epsilon_i \) is Lagrange multiplier for the side condition \( \langle \psi_i|\psi_i \rangle = 1 \) and \( v_{\text{eff}} = v + v_H + v_{\text{XC}} \) with

\[
v_H = \frac{\delta E_H}{\delta n} = \int dr' \frac{n(r')}{|r - r'|}, \quad v_{\text{XC}} \overset{\text{def}}{=} \frac{\delta E_{\text{XC}}}{\delta n}.
\]

(1.32)

A simple analysis shows that the formally introduced Lagrange multipliers \( \epsilon_i \) have the meaning of one particle energies. Varying the expression (1.30) with respect to the occupation numbers one obtains Janak’s theorem [9]

\[
\frac{\partial E}{\partial n_i} = \langle \psi_i|i + v_{\text{eff}}|\psi_i \rangle = \epsilon_i.
\]

(1.33)

Further, the condition \( 0 \leq n_i \leq 1 \), \( \sum_i n_i = N \) yields an aufbau principle, saying that the states with energy below some level are completely occupied and the states above the level are empty. The occupation of the highest occupied level can be a fractional number if this level is degenerate. Thus, the ground state in the Kohn-Sham formalism is a single determinant (1.22) of the orbitals or – in case of degeneracy of the highest occupied level – a linear combination of such determinants. One should underline again that though the state is evidently wrong its energy is correct, provided the “exact” functional \( E_{\text{XC}}[n] \).

As the density of the electron system depends on the solution of (1.31), the system of equations should be solved self-consistently.

Substituting the explicit form of the total energy (1.30) into Janak’s theorem (1.33) one readily obtains its connection to the “band structure energy” \( \sum_i n_i \epsilon_i \):

\[
E = \sum_i n_i \epsilon_i - E_H[n] - \int dx \ n_{\text{XC}} + E_{\text{XC}}[n].
\]

(1.34)

1.3 LSDA and LSDA+U.

As was already mentioned the exchange-correlation functional \( E_{\text{XC}}[n] \) is not known and one needs approximations. The first and so far most used one is the local density approximation [1]

\[
E_{\text{XC}}^{\text{LDA}}[n] = \int dr \ v_{\text{XC}}^{\text{homo}}(n(r))n(r).
\]

(1.35)
1.3. LSDA AND LSDA+U.

where \( \varepsilon^{\text{homo}}_{\text{XC}}(n) \) is the XC-energy of the homogeneous electron liquid with charge density \( n \). This approximation can however be applied only to situations where magnetism is not of interest.

To deal with spin-polarization explicitly one splits the coordinate and spin dependence of the spin-density \( n(x) \) presenting it as \( 2 \times 2 \) hermitian spin-density matrix:

\[
n(x) \rightarrow n_{ss'}(\mathbf{r}) = \begin{pmatrix} n_{++}(\mathbf{r}) & n_{+-}(\mathbf{r}) \\ n_{-+}(\mathbf{r}) & n_{--}(\mathbf{r}) \end{pmatrix},
\]

(1.36)

the components being defined by

\[
n_{ss'}(\mathbf{r}) = N \int \Psi(s \mathbf{r}, x_2, \ldots, x_N) \Psi^*(s' \mathbf{r}, x_2, \ldots, x_N) \, dx_2 \cdots dx_N.
\]

(1.37)

The charge density and the components of the magnetization density can be computed via

\[
n = \text{tr}(\hat{n}) = n_{++} + n_{--}
\]

(1.38)

and

\[
\mathbf{m} = \mu_B \text{tr}(\mathbf{\hat{n}}\mathbf{\hat{\sigma}}) = \mu_B \begin{pmatrix} n_{++} + n_{--} \\ n_{+-} - n_{-+} \\ n_{++} - n_{--} \end{pmatrix},
\]

(1.39)

where \( \mathbf{\hat{\sigma}} = (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z) \) is a tree-dimensional vector composed of the Pauli matrices, the Bohr magneton \( \mu_B = \frac{e^2}{2m} = -\frac{1}{2} \).

A frequently applied approximation, also used in the calculations described below, assumes that quantization axis is fixed throughout the space, so that off-diagonal elements of the spin-density matrix vanish in an appropriately chosen coordinate system. Thus, only collinear magnetic arrangements can be treated.

The local approximation to the XC-energy now reads

\[
E_{\text{XC}}^\text{LSDA} [n] = \int d\mathbf{r} \, \varepsilon^{\text{homo}}_{\text{XC}}(n_+(\mathbf{r}), n_-(\mathbf{r})) n(\mathbf{r}).
\]

(1.40)

The dependence of the XC-energy of the homogeneous electron liquid on the spin-density is well investigated and parameterized. In the calculations described below the parameterization given by Perdew and Zunger [10] is used.

LSDA proves to be a good approximation for compounds with broad bands, as simple metals. It fails however for substances like transition metal
oxides where the chemically active orbitals are well localized. For example FeO and CoO are predicted to be conductors though they are quite good insulators. Even if LSDA predicts correct insulator state as for MnO and NiO the insulating gap appears to be too small. Though the band gap is not a ground state property it is a common belief that Kohn-Sham bands have a physical relevance in the vicinity of the Fermi level and should be reproduced in “exact” calculations. There were numerous attempts to construct other XC-functionals to describe the behavior of the TM compounds. None however has proven to be universal though the complication of the related calculations is sometimes enormous. One of the simplest corrections to LSDA is the so-called LSDA+$U$ which aims at improving the description of the on-site electron correlations, thus accounting for the quasi-localized nature of the d-electrons.

The LSDA+$U$ functional is defined \cite{11, 12} as

$$E^{\text{LSDA}+U}[n] = E^{\text{LSDA}}[n] + E^U[n], \quad (1.41)$$

with

$$E^U[n] = \frac{1}{2} \sum_a \sum_{m \mu \sigma} \sum_{m' \mu' \sigma'} \tilde{n}_{mnm'}^{\alpha \sigma}[n] \tilde{n}_{mnm'}^{\alpha' \sigma'}[n] \left\{ \langle m' \mu' | \tilde{w}_a | m \mu \rangle - \delta_{\sigma' \sigma} \langle m' \mu' | \tilde{w}_a | m \mu \rangle \right\}, \quad (1.42)$$

where $a$ denotes the atomic shell$^4$ corrected for the on-site interaction, $m, \mu$ are the magnetic quantum numbers of the chosen orbitals of the shell, $\tilde{n}_{mnm'}^{\alpha \sigma} = n_{mnm'}^{\alpha \sigma} - n_0^{\alpha \sigma} \delta_{mnm'}$, with the occupation matrix $n_{mnm'}^{\alpha \sigma}$ and its averaged trace $n_0^{\alpha \sigma}$ being defined by Kohn-Sham orbitals $\psi_i$ and its occupation $n_i$ via

$$n_{mnm'}^{\alpha \sigma} = \sum_i \langle a \alpha \sigma | \psi_i \rangle n_i \langle \psi_i | a m \sigma \rangle, \quad n_0^{\alpha \sigma} = \frac{1}{2l_a + 1} \sum_{m=-l_a}^{l_a} n_{mnm}^{\alpha \sigma}, \quad (1.43)$$

so that the resulting matrix $\tilde{n}_{mnm'}^{\alpha \sigma}$ is traceless.

The on-site interaction is treated in Hartree-Fock manner. The form of the correction is evidently rotational invariant \cite{12} and thus does not depend on the particular choice of the angular part of the orbitals. The correction for double counting represented by subtraction of the averaged trace ensures that in the case of completely occupied or completely empty shell the functional reduces to LSDA \cite{11}. Actually the correction for double counting is the weakest point of LSDA+$U$, as nothing is known about the extent in

$^4$The shell $a$ is specified by the position of the nucleus $R_a$ and principal $n_a$ and orbital $l_a$ quantum numbers.
1.3. **LSDA AND LSDA+U.**

which the on-site correlation is already included in the LSDA. The way we used to introduce LSDA+U is somewhat different from the original approach of Anisimov et al. [15]. Instead of artificially introducing the Coulomb on-site correlation, we derive it in the framework of DFT from a variational principle, as – given the local orbitals $|a m \sigma\rangle$ and interaction matrix elements $\langle m' \mu'| \tilde{w}_a | m \mu\rangle$ – the expression (1.42) is evidently a functional of density. One should note that $\tilde{w}$ is not the pure Coulomb interaction. The interaction is screened by the rest of the electrons and depends in general on their distribution. In the implemented version this screening is taken into account by using empirical values for the involved interaction parameters (Slater integrals).
Chapter 2

FPLO band calculation scheme and LSDA+$U$

The scheme used in our calculations is based on density-functional theory within the framework of the Kohn-Sham algorithm described in the preceding chapter. In what follows the solution of the Kohn-Sham equation is only sketched to introduce the calculation of the $U$-correction to the Hamiltonian. Details concerning the calculation of the density and the potential can be found in [13]. The FPLO\(^1\) band calculation scheme is based on expanding the Kohn-Sham states into a set of local nonorthogonal atomic-like orbitals. Projection onto local orbitals is needed for many purposes, for instance to extract model parameters from band-structure calculations or to interpret the results in terms of chemical bonds. It is also the main ingredient of the L(S)DA+$U$. The projection is never free from ambiguity in the choice of the orbitals. Our approach has the advantage of finding the best finite local orbitals set with respect to variation of the total energy.

2.1 The atomic-like basis set

We consider the nonrelativistic Kohn-Sham problem on a perfect lattice. The coordinates of an atom in the lattice are given by $\mathbf{S} = \mathbf{R} + \mathbf{s}$, where $\mathbf{R}$ is a Bravais vector and $\mathbf{s}$ is a basis vector of the unit cell. To solve the KS equation the extended crystal states are expanded into nonorthogonal localized atomic-like orbitals:

$$\langle \mathbf{r} | \mathbf{S} \rangle = \phi_{n \mathbf{m}}(\mathbf{r}) = R_{n \mathbf{m}}(\mathbf{r} \mathbf{s}) \mathcal{Y}_{\mathbf{m}}(\hat{\mathbf{r}} \mathbf{s}),$$

(2.1)

\(^1\)FPLO= Full-Potential Local-Orbital
where \( r_S \) and \( \mathbf{r}_S \) are the absolute value and the unit direction vector of the position vector \( r_S \equiv r - S \), respectively. \( L = \text{nilmo} \) absorbs principal, orbital and magnetic quantum numbers and the spin projection. \( \mathcal{Y}_{lm} \) are spherical harmonics. One should note that instead of standard spherical harmonics one can use any other set derived from the standard one by means of a unitary transformation, so that the functions remain orthonormal. In practice one usually uses the real spherical harmonics (see e.g. [14]). This choice has the advantage that the orbitals and their real linear combinations give the irreducible representations of many symmetry point groups. The drawback is that the harmonics are not anymore eigenfunctions of the orbital moment operator \( \hat{l}_z \) and index \( m \) should not be misunderstood as an eigenvalue of this operator. The radial part of the orbitals does not depend on the magnetic quantum number as the orbitals are solutions of a Schrödinger equation with spherically averaged crystal spin-potential \( v_S^a \) centered at the respective nucleus position \( S \):

\[
v_S^a(r_S) = \frac{1}{S} \int v(r')dS + v_{\text{conf}}(r_S),
\]

where the surface integral is taken over the sphere \( S : |r'| = r_S \) of radius \( r_S \), \( S = \int_S dS \) is the area of the sphere, and \( v_{\text{conf}} \) is a confining spin-independent potential

\[
v_{\text{conf}}(r_S) = \left( \frac{r_S}{r_s} \right)^4
\]

needed to localize the orbitals. The compressed orbitals have higher energy levels and are more suitable for the construction of extended states. [14]. The confining potential is applied to valence orbitals, which are defined as orbitals extending to the neighboring sites in contrast to the core orbitals which do not overlap with the core orbitals centered on the other sites. One should note that due to the confinement potential the valence orbitals are solutions of different Schrödinger equations and thus may be not orthogonal to each other and to the core orbitals.

The extended state is labeled by crystal momentum \( \mathbf{k} \) and band index \( \nu \), the latter accumulating also the spin projection. The state is constructed as a linear combination of the local orbitals:

\[
|\mathbf{k}\nu\rangle = \frac{1}{\sqrt{N}} \sum_{R\epsilon L} |R\nu L\rangle \epsilon_{R\epsilon L}^{k\nu} e^{i(R+e)}
\]

Inserting the ansatz into the Kohn-Sham equation

\[
\hat{H}|\mathbf{k}\nu\rangle = \epsilon_{\mathbf{k}\nu}|\mathbf{k}\nu\rangle
\]
2.2. THE U CORRECTION TO THE LSDA HAMILTONIAN

and projecting the equation onto the basis \(|0s' L\rangle e^{iks}\) yields

\[
\sum_{R_s L} c_{s L}^{k} e^{-iks'} \left[ \langle 0s' L' \mid \hat{H} \mid Rs L \rangle - \epsilon_{k R} \langle 0s' L' \mid Rs L \rangle \right] e^{ik(R+s)} = 0. \tag{2.6}
\]

After summation over Bravais vectors one is left with the finite dimension eigenfunction problem

\[
\sum_{sL} \left[ H_{s' L'; s L}^{k} - \epsilon_{k R} S_{s' L'; s L}^{k} \right] c_{s L}^{k} = 0. \tag{2.7}
\]

where

\[
H_{s' L'; s L}^{k} = \sum_{R} e^{-iks'} \langle 0s' L' \mid \hat{H} \mid Rs L \rangle e^{ik(R+s)}, \tag{2.8}
\]

\[
S_{s' L'; s L}^{k} = \sum_{R} e^{-iks'} \langle 0s' L' \mid Rs L \rangle e^{ik(R+s)} \tag{2.9}
\]

are respectively the effective Hamiltonian and overlap matrices. Due to the condition

\[
\langle R' s' c' \mid Rs c \rangle = \delta_{R'R} \delta_{s's} \delta_{c'c} \tag{2.10}
\]

imposed on the core orbitals \(c\) the eigenvalue problem can be further reduced to the size of the valence basis only \([13]\).

2.2 The U correction to the LSDA Hamiltonian

To simplify the expressions below we assume, that there is only one localized shell per unit cell. In this case the shell can be labeled by the Bravais vector \(R_0\) only. The generalization to the larger number of localized shells is achieved by the additional summation over these shells inside the unit cell. We have however retained the basis vector \(s_0\) for labeling a localized orbital to clarify the indexing of the overlap matrices. The principal \(n\) and the orbital \(l\) quantum numbers are dropped.

To compute the occupation matrix we use the ansatz (2.4) for the Bloch
state and obtain

\[ n_{\sigma}^{\mathbf{R}_0} = \frac{1}{N} \sum_{\mathbf{k}\nu} \sum_{\mathbf{R}_s \mathbf{L}} e^{-i \mathbf{k} \cdot \mathbf{R}_0 + s_0} \langle \mathbf{R}_0 s_0 m \sigma | c_{sL}^{k\nu} \mathbf{R}_s \mathbf{L} \rangle e^{i \mathbf{k} \cdot \mathbf{R} + s} \]

\[ \times \sum_{\mathbf{R}' s' L'} \langle \mathbf{R}' s' L' | \mathbf{R}_0 s_0 m' \sigma \rangle e^{i \mathbf{k} \cdot \mathbf{R}_0 + s_0} \]

\[ = \frac{1}{N} \sum_{\mathbf{k}\nu} \left( \sum_{sL} c_{sL}^{k\nu} S_{s0m\sigma; sL}^{k} \right) \left( \sum_{s'L'} c_{s'L'}^{k\nu} S_{s0m'\sigma; s'L'}^{k} \right)^* , \]  

(2.11)

with the overlap matrix \( S \) defined by (2.9) and \( c_{sL}^{k\nu} \) being solutions of (2.7).

In practice the summation over the occupied states in \( \mathbf{k} \)-space is replaced as usual by the integration over the first Brillouin zone (BZ).

Varying (1.41) one obtains a Kohn-Sham equation

\[ \frac{1}{n_i} \frac{\delta E^{\text{LSDA}+U}}{\delta \langle \psi_i \rangle} = (\hat{H}^{\text{LSDA}} + \hat{H}^U)|\psi_i\rangle = |\psi_i\rangle \epsilon_i \]  

(2.12)

with

\[ \hat{H}^U|\psi_i\rangle = \frac{1}{n_i} \frac{\delta E^U}{\delta \langle \psi_i \rangle} = \frac{1}{n_i} \sum_{\mathbf{R}_0 \sigma \mathbf{m}' \mathbf{m}} \frac{\delta n_{\mathbf{R}_0 \sigma}^{\mathbf{m}' \mathbf{m}}}{\delta \langle \psi_i \rangle} \frac{\partial E^U}{\partial n_{\mathbf{R}_0 \sigma}^{\mathbf{m}' \mathbf{m}}} \]

\[ = \sum_{\mathbf{R}_0 \sigma \mathbf{m}' \mathbf{m}} |\mathbf{R}_0 s_0 m' \sigma \rangle \nu_{m' \mathbf{m}}^{\sigma} \langle \mathbf{R}_0 s_0 m \sigma | \psi_i \rangle, \]  

(2.13)

where the hermitian potential matrix \( \nu_{m' \mathbf{m}}^{\sigma} \) is defined by

\[ \nu_{m' \mathbf{m}}^{\sigma} = \frac{\partial E^U}{\partial n_{\mathbf{R}_0 \sigma}^{\mathbf{m}' \mathbf{m}}} = \sum_{\mu \mu' \sigma'} \tilde{n}_{\mu \mu'}^{\sigma'} \left\{ \langle \mu | \tilde{\omega} | m' \mu' \rangle - \delta_{\sigma \sigma'} \langle \mu m | \tilde{\omega} | m' \mu' \rangle \right\} , \]

\[ \tilde{\nu}_{m'}^{\sigma} = \frac{1}{2l + 1} \sum_{m=-l}^{l} \tilde{n}_{mm}^{\sigma} = 0, \]  

(2.14)

where we omit the superscript \( \mathbf{R}_0 \) as due to the Bloch theorem the occupation matrix calculated from (1.43) does not depend on it. The trace of the potential matrix vanishes, if the interaction between electrons satisfies some reasonable restrictions (see section 2.3). Using the expression (2.14) the functional (1.42) can be rewritten as

\[ E^U = \frac{1}{2} \sum_{\mathbf{R}_0 \mathbf{m}' \mathbf{m}} \tilde{n}_{\mathbf{m}' \mathbf{m}}^{\sigma} \tilde{\nu}_{\mathbf{m}' \mathbf{m}}^{\sigma} \]  

(2.15)
2.3. **Calculation of the Matrix Element**

Using the ansatz (2.4), projecting the equation onto the basis $|og L\rangle e^{ik s}$ and summing over Bravais vectors one obtains the following expression for the $U$ correction to the total Hamiltonian

$$
\hat{H}_s^{U} = \sum_{R} e^{-ik s'} \langle 0 s' L' | \hat{H}_s^{U} | R s L \rangle e^{ik (R + s)} = \sum_{mm'} v_{mm'}^{\sigma} \times \sum_{s_0} e^{-ik (R_0 + s_0)} \langle R_0 s_0 m' \sigma | R s L \rangle e^{ik (R + s)}
$$

One notes that a matrix element between any two states having an overlap with the orbitals corrected for the on-site Coulomb interaction is in general changed. If those are the core states it would damage the reduction of the eigenvalue problem to that of the valence states, mentioned in Section 2.1. To avoid the problem we apply the expression (2.16) only to the valence-valence block of the Hamilton matrix. It can be justified by the fact, that the corrected orbitals are quite well localized and neglecting their overlap with the core states of the neighboring sites does not spoil the results. To be consistent we restrict the computation of the occupation matrix (2.11) to the overlap with the valence orbitals as well.

### 2.3 Calculation of the matrix element

We consider the transitions inside a $nl$-shell of an atom. The atomic potential is assumed to be spherically symmetric, though possibly spin-dependent. The expression for the eigenstates of the atomic-like Hamiltonian (local orbitals) in the nonrelativistic limit reads:

$$
\phi_{n'l'm}(r) = R_{n'l'}^m(r) Y_{l'm}(\theta, \varphi),
$$

where the complete orthonormal set of the $nl$-shell orbitals distinguished by the magnetic quantum number $m$, i.e. by the angular dependence $Y_{l'm}(\theta, \varphi)$, can be obtained from the standard spherical harmonics by means of a unitary transformation $U$:

$$
Y_{l'm} = \sum_{m} U_{m'n}^{(l)} Y_{l'm},
$$

or in the tensor notation, omitting the indices $nl\sigma$:

$$
\phi_{m'} = T^{m'}_{m} \phi_{m}, \quad \phi_{\mu} = T^{\mu}_{\mu} \phi^{\mu},
$$
where $\phi_i$ and $\phi^i$ are the covariant and contravariant (in fact complex conjugated to the covariant one) wavefunctions, respectively. The tensor $T$ is connected to the matrix $U$ via the relations: $T_m^i = U_{mi}, T^m_i = U^*_{mi} = U_m^i$. Thus, $T_m^i T_m'^i = \delta_m^m$.

As $w(\mathbf{r}_1, \mathbf{r}_2)$ is a linear operator, the matrix element $\langle \mu_1, \mu_2 | \tilde{w} | \nu_1, \nu_2 \rangle \equiv w_{\mu_1 \mu_2}^{\nu_1 \nu_2}$ transforms as:

$$w_{\mu_1 \mu_2}^{\nu_1 \nu_2} = T_{n_1}^\nu T_{n_2}^{\nu_2} w_{m_1 m_2}^{n_1 n_2} T_{\mu_1}^{m_1} T_{\mu_2}^{m_2}. \quad (2.20)$$

To proceed further we should make some assumptions about the interaction between electrons localized in the $nl$-shell. We assume that the interaction does not change under applying to the coordinates of the both particles a symmetry operation of the spherical group (i.e., the operation which conserves $|\mathbf{r}_1|, |\mathbf{r}_2|$ and $|\mathbf{r}_2 - \mathbf{r}_1|$) about the nucleus of the atom. In such a case it is possible to decompose the interaction into a sum over the products of spherical harmonics:

$$w(\mathbf{r}_1, \mathbf{r}_2) = \sum_{k=0}^{\infty} \frac{4\pi}{2k + 1} W^k(r_1, r_2) \sum_{m=-k}^{k} Y_{km}(\theta_1, \varphi_1) Y_{*km}^*(\theta_2, \varphi_2). \quad (2.21)$$

Thus, in the basis consisting of the standard spherical harmonics the matrix element is computed as:

$$w_{m_1 m_2}^{m_1' m_2'} = \sum_{k=0}^{\infty} \frac{4\pi}{2k + 1} F^k \sum_{m=-k}^{k} \int d\Omega_1 Y_{km}^{*} Y_{km'} \int d\Omega_2 Y_{km} Y_{km'} \int d\Omega_1 Y_{km} Y_{km'} \int d\Omega_2 Y_{km} Y_{km'}$$

$$= \sum_{k=0}^{\infty} F^k a_{m_1 m_2}^{m_1' m_2'}(k) \quad (2.22)$$

where $F^k = \int d\rho_1 d\rho_2 W^k(r_1, r_2) \tilde{R}_{nl}^2(r_1) \tilde{R}_{nl}^2(r_2)$ with $\tilde{R}_{nl}(r) = r R_{nl}(r)$ and

$$a_{m_1 m_2}^{m_1' m_2'}(k) = \frac{4\pi}{2k + 1} \sum_{m=-k}^{k} \int d\Omega_1 Y_{km}^{*} Y_{km'} \int d\Omega_2 Y_{km} Y_{km'}$$

$$= (2l + 1) \sum_{m=-k}^{k} A_{m_1 m_2}^{km} (A_{m_1 m_2}^{km})^* \quad (2.23)$$

The restriction is always satisfied if the interaction depends only on the distance between the electrons, as in the case of the Coulomb interaction $w(\mathbf{r}_1, \mathbf{r}_2) = |\mathbf{r}_1 - \mathbf{r}_2|^{-1}$, for which the radial term of (2.21) reads:

$$W^k = r_2^k / r_{>, <}^{k+1},$$

where $r_>$ and $r_<$ designate the larger and smaller of $r_1$ and $r_2$, respectively.
2.3. **CALCULATION OF THE MATRIX ELEMENT**

with

\[
A_{\alpha \beta}^{kM} = \frac{1}{2l + 1} \left( \frac{4\pi}{2k + 1} \right)^{1/2} \int d\Omega \ Y_{\alpha \beta}^* Y_{kM} Y_{\alpha \beta}
\]

\[
= (-1)^{m' - M} \langle l \ k \ l \ 0 \ 0 \ 0 \ l \ k \ l \ -m \ M \ m' \rangle . \tag{2.24}
\]

Substituting (2.24) in the equation (2.22) one obtains:

\[
w_{m_1}^{m_1'} m_2^{m_2'} = \sum_{k=0}^{\infty} (-1)^{m_1 + m_2'} (2l + 1)^2 \left( \begin{array}{ccc} l & k & l \\ 0 & 0 & 0 \end{array} \right)^2 F^k
\]

\[
\times \sum_{m=-k}^{k} \left( \begin{array}{ccc} l & k & l \\ -m_1 & m & m_1' \end{array} \right) \left( \begin{array}{ccc} l & k & l \\ -m_2 & m_2 & m_2' \end{array} \right) = (-1)^{m_1 + m_2'} \sum_{k=0}^{l} \delta_{m_1 + m_2, m_1' + m_2'}, \tag{2.25}
\]

where \( \delta_{m_1 + m_2, m_1' + m_2'} = (2l + 1)^2 \left( \begin{array}{ccc} l & 2k & l \\ 0 & 0 & 0 \end{array} \right)^2 F^k \).

Taking into account the identities

\[
\sum_{i=-l}^{l} (-1)^{i+j} \left( \begin{array}{ccc} l & 2k & l \\ -i & 0 & i \end{array} \right) \left( \begin{array}{ccc} l & 2k & l \\ -j & 0 & j \end{array} \right) = \delta_{k0} \quad \text{and} \quad \sum_{i=-l}^{l} \left( \begin{array}{ccc} l & 2k & l \\ -j & j & i \end{array} \right)^2 = \frac{1}{2l + 1} \tag{2.26}
\]

one finds the following contraction properties of the matrix element:

\[
w_{m_1}^{m_1'} m_2^{m_2'} = \delta_{m_2}^{m_2'} C_C, \quad C_C \overset{\text{def}}{=} (2l + 1) F^{(0)}; \tag{2.27}
\]

\[
w_{m_1}^{m_1'} m_2^{m_2'} = \delta_{m_2}^{m_2'} C_X, \quad C_X \overset{\text{def}}{=} (2l + 1) \sum_{k=0}^{l} \left( \begin{array}{ccc} l & 2k & l \\ 0 & 0 & 0 \end{array} \right)^2 F^{(2k)}. \tag{2.28}
\]

From the transformation rule (2.20) it immediately follows that the expressions (2.27, 2.28) are valid for an arbitrary complete orthonormal set of the \(l\)-orbitals.

Therefore the trace of the potential matrix (2.14) vanishes:

\[
\sum_{m} v_{mm} = \sum_{m} \sum_{\mu \mu'} \left\{ \langle m | \hat{m} | m' \rangle \hat{n}_{\mu \mu'} + \left[ \langle m | \hat{m} | m' \rangle - \langle m | \hat{m} | m' \rangle \right] \hat{n}_{\mu \mu'} \right\}
\]

\[
= \sum_{\mu \mu'} \left\{ \delta_{\mu \mu'} C_C \hat{n}_{\mu \mu'} + \delta_{\mu \mu'} [C_C - C_X] \hat{n}_{\mu \mu'} \right\}
\]

\[
= C_C \sum_{\mu} \hat{n}_{\mu \mu} + [C_C - C_X] \sum_{\mu} \hat{n}_{\mu \mu} = 0. \tag{2.29}
\]
2.4 The double-counting term

The usual form of introducing LSDA+$U$ is splitting of the $U$-functional in two parts:

$$E^U = E^{ee} - E^{dc}$$

(2.30)

where $E^{ee}$ is the Hartree-Fock-like electron-electron interaction term

$$E^{ee} = \frac{1}{2} \sum_{m \mu \sigma} \sum_{m' \mu' \sigma'} n_{mm'}^\sigma n_{\mu \mu'}^{\sigma'} \left\{ \langle m \mu | \bar{\psi} | m' \mu' \rangle - \delta_{\sigma \sigma'} \langle \mu m | \bar{\psi} | m' \mu' \rangle \right\},$$

(2.31)

and $E^{dc}$ is the so-called double-counting term, which is meant to account for the part of the on-site exchange-correlation energy already present in the LSDA expression.

It is of interest to write down the explicit form of the double-counting term, used in the definition (1.42). The computing of the term is convenient to carry out in the local basis where the density matrix is diagonal: $n_{mm'} \rightarrow n_\mu \delta_{\mu \mu'}$. In such a basis the functional (1.42) reads:

$$E^U = \frac{1}{2} \sum_{R \sigma \mu} \left\{ \tilde{w}_{m \mu}^{\sigma \mu} (n_\mu^{\sigma} - n_0^{\sigma}) (n_\mu^{\sigma} - n_0^{\sigma}) + [\tilde{w}_{m \mu}^{m \mu} - \tilde{w}_{m \mu}^{m \mu}] (n_\mu^{\sigma} - n_0^{\sigma}) (n_\mu^{\sigma} - n_0^{\sigma}) \right\},$$

(2.32)

From the contraction properties of the matrix element it follows that sums of products containing $n_\mu^{\sigma} (n_\mu^{\sigma} - n_0^{\sigma})$ and $n_0^{\sigma} (n_\mu^{\sigma} - n_0^{\sigma})$ vanish and one is left with:

$$E^U = \frac{1}{2} \sum_{R \sigma \mu} \left\{ \tilde{w}_{m \mu}^{m \mu} n_\mu^{\sigma} (n_\mu^{\sigma} - n_0^{\sigma}) + (\tilde{w}_{m \mu}^{m \mu} - \tilde{w}_{m \mu}^{m \mu}) n_\mu^{\sigma} (n_\mu^{\sigma} - n_0^{\sigma}) \right\}$$

$$= \frac{1}{2} \sum_{R \sigma \mu} \left\{ \tilde{w}_{m \mu}^{m \mu} n_\mu^{\sigma} (n_\mu^{\sigma} + n_0^{\sigma}) + (\tilde{w}_{m \mu}^{m \mu} - \tilde{w}_{m \mu}^{m \mu}) n_\mu^{\sigma} n_\mu^{\sigma} \right\}$$

$$- \frac{1}{2} \sum_{R \sigma} \left\{ \sum_{\mu} \tilde{w}_{m \mu}^{m \mu} (n_\mu^{\sigma} + n_0^{\sigma}) - \sum_{\mu} \tilde{w}_{m \mu}^{m \mu} n_\mu^{\sigma} \right\} \sum_{m} n_\mu^{\sigma},$$

(2.33)

In terms of the Hubbard parameters

$$\tilde{w}_{m \mu}^{m \mu} = U, \quad \tilde{w}_{m \mu}^{m \mu} = \begin{cases} U & m = \mu \\ J & m \neq \mu \end{cases}$$

(2.34)

---

3In this section the symbol $\tilde{w}_{m \mu}^{m \mu}$ is the shortening for $(m \mu | \bar{\psi} | m \mu)$. It does not mean the contraction over the repeated indices.
2.4. **THE DOUBLE-COUNTING TERM**

the last term of (2.33) can be rewritten as

\[
E^{\text{dc}} = \frac{1}{2} \sum_{R\sigma} \left\{ U(2l + 1)(n_{\sigma}^0 + n_{\sigma}^0) - (U + 2lJ)n_{\sigma}^0 \right\} N^\sigma
\]

\[
= \frac{1}{2} \sum_{R\sigma} U N^\sigma (N - n_{\sigma}^0) - JN^\sigma (N^\sigma - n_{\sigma}^0),
\]

(2.35)

where

\[
N^\sigma = \text{tr} n_{mn'}^{\sigma} = \sum_m n_{mm}^{\sigma}; \quad N = N^\sigma + N^\sigma.
\]

(2.36)

Comparing (2.34) with (2.27,2.28) one obtains

\[
U = F^0; \quad J = \frac{2l + 1}{2l} \sum_{k=1}^{l} \begin{pmatrix} 1 2k \end{pmatrix}^2 F^{(2k)}.
\]

(2.37)

One notes that the double-counting term (2.35) is different from the so-called atomic limit [17, 11] used in many LDA+U calculations:

\[
E^{\text{dc}} = \frac{1}{2} \sum_{R\sigma} U N^\sigma (N - 1) - JN^\sigma (N^\sigma - 1).
\]

(2.38)

Though we have implemented such a double-counting term for test purposes it can hardly be justified as the local orbital basis of FPLO is not orthogonal and therefore the value \(n_{mn}^{\sigma}\) is not the occupation of the \(|m\sigma\) orbital in an exact sense. The meaning of \(N^\sigma\) and \(N\) is consequently also obscure. In what follows we refer to calculations using the double-counting term (2.38) as LSDA+\(U^\text{AL}\) (Atomic Limit) and that of (2.35) as LSDA+\(U^\text{MF}\) (Mean Field).

Taking into account the dependence of the occupation matrix \(n_{mn'}\) on the occupation of the Kohn-Sham orbitals one notes that the term \(E^{\text{ex}}\) being quadratic in the KS occupation numbers enters the expression for the total energy in the same manner as the Hartree term,\(^4\) so that the expression (1.34) reads

\[
E = \sum_i n_i \varepsilon_i - E_H - \int dx \, n_i^{\text{LSDA}} + E_{\text{XC}}^{\text{LSDA}} - E^U + \left( \sum_i n_i \frac{\partial E^{\text{dc}}}{\partial n_i} - 2E^{\text{dc}} \right),
\]

(2.39)

the expression in parentheses being equal to zero for the double-counting term (2.35) and \(\frac{U-2}{2} N\) for that of (2.38), respectively [18].

\[\sum_i n_i \frac{\partial E^{\text{ex}}}{\partial n_i} = 2E^{\text{ex}}\]
Chapter 3

Transition metal monoxides

To test LSDA+$U$ we have chosen the series of 3$d$-transition metal (TM) monoxides, all forming in the simple rock-salt crystal structure, which greatly simplifies the required orbital analysis. The first two compounds of the series, TiO and VO, are paramagnetic metals with perfect face-centered cubic structure. They are quite well described by LDA calculations and are not considered below. The four other compounds are antiferromagnetic insulators. Below the Néel temperature an antiferromagnetic structure is formed with ferromagnetic planes alternating in the direction [111] as shown in Fig. 3.1. This structure was first determined by Shull et al. [19] and refined in a later investigation by Roth [20]. The magnetic ordering is accompanied by lattice distortion – either rhombohedral (MnO and NiO) or monoclinic (FeO and CoO). Actually if spin-orbit coupling is taken into account the rhombohedral structure of the former two compounds is not consistent with the magnetic order, as the magnetic moments of the TM ions lie in the plane orthogonal to the rhombohedral axis [20]. However neither the exact direction of the moments nor the corresponding additional distortion of the crystal structure were so far reported. The rhombohedral distortion is of magnetic exchange origin and can be viewed as a contraction of the distance between neighboring ferromagnetic (111) TM planes with antiparallel magnetic moments (cf. Fig. 3.1). Distinct from the situation in MnO and NiO, the ions Fe$^{2+}$ and Co$^{2+}$ should have a considerable orbital moment [21]. The experimentally observed magnetic moments of these ions deviate from the (111) plane but, opposed to what was erroneously claimed for FeO earlier, are not directed along [111] direction, which would be consistent with the rhombohedral symmetry. The monoclinic structure of the antiferromagnetic phase of CoO and FeO can be viewed as a composition of a nearly rhombohedral distortion and an additional tetragonal distortion applied to the fcc structure of the paramagnetic phase. As shown below, the tetragonal distortion can be explained
Figure 3.1: Bravais cell and $d$-level scheme of the transition metal monoxides. The large dark and light circles designate transition metal ions with opposite spin, the oxygen ions are shown as small circles. The tinier solid lines outline the paramagnetic fcc Bravais cell and the thicker lines the antiferromagnetic rhombohedral cell. The ions outlined by thick circles belong to the rhombohedral cell. Also the $p$-orbitals of the central oxygen ion connecting two TM cations of opposite spin are shown. The dotted lines depict the (111) TM ferromagnetic planes. In the level scheme, $\Delta_X$ is the exchange splitting, $\Delta_C$ and $\Delta_R$ are the cubic and rhombohedral crystal field splittings respectively.

by the specific orbital ordering, that arises in the LSDA+$U$ calculation.

In simple spin-unpolarized LDA calculations all six compounds are found to be metals. Allowing spin polarization in the LSDA results in a nonmagnetic metallic state for TiO and VO, metallic antiferromagnetic state for FeO and CoO, and insulating antiferromagnetic state for MnO and NiO. For the latter two compounds the insulating state can be found only under the experimentally observed antiferromagnetic order, characterized by the antiparallel moments on the next-nearest neighboring TM ions, so that oxygen $p$-orbitals connect the ions with opposite spin (Fig. 3.1).

There are only two collinear magnetic structures providing such a next-nearest neighbor order, designated $A$ and $B$ by Li [22]. The rhombohedral structure $A$ is shown in Fig. 3.1, the structure $B$ is cubic ($Fd\overline{3}m$) and has
Figure 3.2: The nearest neighbor arrangement in the antiferromagnetic collinear structures A, B and C. The black and white circles show the two spin sorts of TM ion. The dotted lines depict the (111) planes.

four times more chemical units per primitive unit cell than the structure A. Six of the twelve nearest neighbors of a TM ion have in both structures the same spin as the ion and six – the opposite, but the arrangements of the neighbors are different (see Fig. 3.2).

In the LSDA calculations the density of states (DOS) appears to be almost identical for both structures of each of the four TM monoxides, the structure A being slightly lower in energy than the structure B (from 3.7 meV per formula unit for FeO to 7.5 meV for MnO). For other antiferromagnetic arrangements (with parallel order of the next-nearest TM ions as structure C shown in Fig. 3.2) as well as for ferromagnetic order LSDA calculation gives metallic states as was first pointed out by Terakura et al [23]. The energy of the states is much higher than that of structures A/B with the exception of FeO, where the energy of the ferromagnetic solution lies between those of structures A and B. For NiO a magnetic state can be obtained only in structures A/B. Some details of the LSDA calculations are summarized in Table 3.

Though the correct antiferromagnetic order gives rise to an insulating state in MnO and NiO one can argue that it should not be the only or even main reason for opening the gap, as the insulating state persists above the Néel temperature as well. Moreover, the experimental value of the gap is an order of magnitude larger than the LSDA gap, and antiferromagnetic FeO and CoO even remain metals in the LSDA calculation.

The understanding of the electronic properties of 3d TM compounds has represented a challenge for solid state physicists since the discovery of the insulating behavior of NiO [24]. This example led Mott [25] to the idea of a correlation driven metal-insulator transition, later developed further into
Table 3.1: The total energy $E$ (in eV) and magnetic moment $M$ (in $\mu_B$) of the TM monoxides in LSDA. Both values are given per formula unit. The energy is given with respect to the calculated nonmagnetic metallic state of each compound. The experimental lattice parameters of paramagnetic cubic cells were used. The antiferromagnetic structures $A/B$ explained in text have antiparallel next-nearest neighbor magnetic order. In the antiferromagnetic structure $C$ with alternating (001) ferromagnetic planes (shown in Fig. 3.2) as well as in the ferromagnetic structure $F$ the order is parallel. The underlined numbers refer to an insulating state.

<table>
<thead>
<tr>
<th></th>
<th>MnO</th>
<th>FeO</th>
<th>CoO</th>
<th>NiO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E$</td>
<td>$M$</td>
<td>$E$</td>
<td>$M$</td>
</tr>
<tr>
<td>$A$</td>
<td>$-1.841$</td>
<td>$4.552$</td>
<td>$-1.195$</td>
<td>$3.517$</td>
</tr>
<tr>
<td>$B$</td>
<td>$-1.833$</td>
<td>$4.552$</td>
<td>$-1.191$</td>
<td>$3.518$</td>
</tr>
<tr>
<td>$C$</td>
<td>$-1.767$</td>
<td>$4.598$</td>
<td>$-0.964$</td>
<td>$3.700$</td>
</tr>
<tr>
<td>$F$</td>
<td>$-1.726$</td>
<td>$4.584$</td>
<td>$-1.193$</td>
<td>$4.000$</td>
</tr>
</tbody>
</table>

the Hubbard model [26]. It is now a well-accepted persuasion, that the on-site correlation is indeed the main reason for TM compounds to be magnetic and insulating. The failure of LSDA to predict the correct insulating state is connected with an insufficient description of the on-site correlation effects and the success of the Hubbard model encourages one to apply the LSDA+U Hamiltonian to treat such compounds.

In a magnetic state the 10-fold degenerate one-electron states of a free ion split due to exchange interaction into two 5-fold spin-up and spin-down levels. In the octahedral crystal field\(^1\) each of these levels splits further into two-fold degenerate $e_g$ and three-fold degenerate $t_{2g}$ states. Disregarding spin-orbit coupling, the direction of spin is not related to the real space and the resulting doubled antiferromagnetic primitive cell has rhombohedral symmetry. This allows a further splitting of the $t_{2g}$ manifold into two-fold degenerate $e_g$ and non-degenerate $a_{1g}$ states. For 3$d$-metal oxides the exchange splitting is usually larger than the crystal field splitting resulting in the so-called high-spin state of the ion, which corresponds to Hund’s first rule for free ions.

The real crystal structure in the antiferromagnetic state is still more complicated. However, one may expect that the small lattice distortion modifies the electronic structure insignificantly, provided that the symmetry of the structure is not changed. In the calculations presented below we have used

\(^1\)Here and later the term “crystal field” is used for describing the total effect of the crystal field in the true sense and the ligand field.
the described above rhombohedral structure resulting from the paramagnetic cubic one by introducing two spin sorts of the TM ion. No additional optimization of the rhombohedral distortion was performed.

In the calculations below a basis valence orbital set TM:3s3p3d4s4p, O:2s2p3d was chosen. For the LSDA+U calculations we have used the values of parameters given in Table 3.2. The relation \( F^4/F^2 \) being almost constant for all 3d ions [16] was fixed to 0.625, as was done in Ref. [17].

<table>
<thead>
<tr>
<th></th>
<th>MnO</th>
<th>FeO</th>
<th>CoO</th>
<th>NiO</th>
</tr>
</thead>
<tbody>
<tr>
<td>( U ), eV</td>
<td>6.9</td>
<td>6.8</td>
<td>7.8</td>
<td>8.0</td>
</tr>
<tr>
<td>( J ), eV</td>
<td>0.86</td>
<td>0.89</td>
<td>0.92</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Table 3.2: The Coulomb \( U \) and the exchange \( J \) parameters used in the calculations. The parameters were obtained in Ref. [15] by means of supercell calculation.

### 3.1 Orbital moment

Before discussing the magnetic properties of the transition metal oxides it is necessary to pay attention to the orbital magnetic moment of the TM ion, which is missed in our nonrelativistic calculations. The value of the moment is determined by an interplay between the crystal field and the spin-orbit coupling. The effects of the former and the latter are opposite. Crystal field splitting tends to quench the orbital moment while spin-orbit interaction partially restores it. To illustrate this interplay consider a simplified example of a 3d transition metal ion in the perfect octahedral field. Neglecting the spin-flip process we consider only one partially filled spin subshell. The octahedral field splits the 5-fold degenerate subshell in three-fold degenerate \( t_{2g} \) and two-fold degenerate \( e_g \) states, which can be represented by real \( d \)-functions \([|yz\rangle, |zx\rangle, |xy\rangle\) and \( (|x^2 - y^2\rangle, |3z^2 - r^2\rangle)\) respectively, with

\[
|xy\rangle = \frac{|+2\rangle + |-2\rangle}{\sqrt{2}}
\]

\[
|y^2 - r^2\rangle = \frac{|+2\rangle + |-2\rangle}{\sqrt{2}}
\]

\[
|yz\rangle = \frac{|+1\rangle + |-1\rangle}{\sqrt{2}}
\]

\[
|3z^2 - r^2\rangle = |0\rangle
\]

(3.1)

where \(|m\rangle\) on r.h.s. means the 3d-orbital with magnetic number \( m \).

Let the crystal field splitting between the levels be \( E_c - E_t = \Delta \). As the expectation value of the orbital moment is 0 for each eigenfunction (3.1)
of the crystal Hamiltonian, the moment is completely quenched. The spin-
orbit interaction $\zeta \sum \hat{l}_i \cdot \hat{s}_i$, where $\zeta$ is a positive spin-orbit coupling constant, partially restores the orbital moment. Assuming the quantization axes for spin and orbital moment be the same and the majority spin projection to be positive the Hamilton matrix of the sum of spin-orbit and crystal field interactions in the subspace of the functions (3.1) reads

$$
\begin{align*}
|yz\rangle : & \begin{pmatrix} 0 & -i\zeta/2 & 0 & 0 & 0 \\ |zx\rangle : & i\zeta/2 & 0 & 0 & 0 & 0 \\ |xy\rangle : & 0 & 0 & 0 & -i\zeta & 0 \\ |x^2 - y^2\rangle : & 0 & 0 & i\zeta & 0 & 0 \\ |3z^2 - r^2\rangle : & 0 & 0 & 0 & 0 & \Delta \\
\end{pmatrix},
\end{align*}
$$

(3.2)

Diagonalizing the matrix one notes that spin-orbit interaction lifts the degeneracy of the orbitals and mixes the states in such a way that the expectation value of the orbital moment in the ground state of the ion becomes different from 0. Under the condition $\zeta \ll \Delta$, the eigenstates have energies $-\zeta/2$, $-\zeta^2/\Delta$, $\zeta/2$, $\Delta$ and $\Delta + \zeta^2/\Delta$ with the respective expectation value of the orbital moment projection 1, 4$\zeta/\Delta$, -1, 0 and -$4\zeta/\Delta$. Assuming a typical value $\zeta/\Delta = 0.05$ for 3d transition metal oxides the orbital moments $\langle \hat{l}_z \rangle$ in the ground state are 1, 1.2 and 0.2 $\mu_B$ for Fe$^{2+}$, Co$^{2+}$ and Ni$^{2+}$, respectively. Though the values are smaller than those for free ions (2, 3 and 3 $\mu_B$), the orbital moment is only partially quenched and should be taken into account in interpretation of the calculation results.

The derivation above extends that of Jo and Shishidou [27]. The results are in surprisingly good (taking into account the oversimplified one-electron picture) agreement with measured orbital moments of CoO and NiO [28]. One should especially appreciate the existence of the orbital moment in NiO where it was for long time believed to be quenched. In our model the reason for unquenching the moment is a weak mixing of $|xy\rangle$ and $|x^2 - y^2\rangle$ states, which are separated by finite energy gap $\Delta$.

The derivation implies that the quantization axis is directed in [001] crystallographic direction. At first glance this assumption might seem of no influence, however if one allows arbitrary direction for the axis, it appears that though for CoO the ground state actually corresponds to direction [001] of the magnetic moment, for FeO and NiO it is [111] direction. In this case the orbital moments of Fe$^{2+}$ and Ni$^{2+}$ are drastically reduced by 37% and 42%, respectively. (See Appendix for the details.)

The results of the calculations are presented in the next to last column of Table 3.3 and are in a rather good agreement with experimental data on FeO (at least what concerns the direction of the moment) and CoO, though in the latter case there is an appreciable deviation about 20° of the observed
3.2. Calculation results

Manganese oxide represents the simplest trial system, as the ground state of the Mn$^{2+}$ ion has according to Hund’s rules a $^6S_{5/2}$ configuration with completely occupied majority and empty minority spin $d$-subshells. It thus has no orbital moment, so that the spin-orbit coupling has little relevance. Below the Néel temperature the unit cell of MnO undergoes a rhombohedral distortion with a 1.8% contraction along [111] axis at low temperatures. The spins are aligned in ferromagnetic (111) planes, so that the magnetic crystal symmetry becomes monoclinic $C_{2v}$.

The spin-polarized calculation under the assumption of the experimentally observed antiferromagnetic structure results in an insulating state (Fig. 3.3) with good agreement of the calculated Mn$^{2+}$ magnetic moment 4.57 $\mu_B$ with the experimental value 4.58 $\mu_B$. The gap width of 0.9 eV is in worse agreement with experiment and cannot be much improved by LSDA+$U^{MF}$ as the potential (2.14) is zero if there is no partially filled spin subshell. This can be seen in Fig. 3.3: the DOS is almost unperturbed. In the case of LSDA+$U^{AL}$ calculation the gap becomes much larger (3.7 eV for $d$-$d$ transition) and is in the experimentally observed range. The calculated

<table>
<thead>
<tr>
<th></th>
<th>$\zeta$, meV [29]</th>
<th>$\Delta$, eV [30]</th>
<th>$\zeta/\Delta$</th>
<th>$L_{SO}$, $\mu_B$</th>
<th>$L_{exp.}$, $\mu_B$ [28]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO</td>
<td>40</td>
<td>1.2</td>
<td>0.033</td>
<td>0.61 [111]</td>
<td>(0.40)</td>
</tr>
<tr>
<td>CoO</td>
<td>56</td>
<td>1.1</td>
<td>0.051</td>
<td>1.20 [001]</td>
<td>1.28</td>
</tr>
<tr>
<td>NiO</td>
<td>61</td>
<td>1.1</td>
<td>0.055</td>
<td>0.13 [111]</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Table 3.3: Spin-orbit constants, crystal field splitting and orbital magnetic moments of TM monoxides. The next to last column represents the computed value and direction of the orbital magnetic moment $L$ in the ground-state of the TM$^{2+}$ ion in perfect octahedral field (see text). The “experimental” value for FeO was estimated from the interpolation of the spin component of magnetic moment of other three compounds (Fig. 3.7).

magnetic moment from [001] direction [31]. The result for NiO is in evident contradiction with experimental data, as the observed magnetic moment lies in the plane orthogonal to [111] direction. However the dependence of the energy on the quantization axis direction in the case of NiO is so small (see Appendix), that obviously other effects besides spin-orbit coupling for one single ion have to be taken into consideration. This is supported by the fact that MnO, for which the spin-orbit interaction is irrelevant, has the same magnetic structure as NiO.
and experimental values are given in Table 3.4.

Nickel oxide has in the antiferromagnetic phase the same crystal structure as MnO with a smaller 0.3% rhombohedral contraction along the main diagonal of the paramagnetic cubic cell. It appears also to be an insulator in LSDA calculations but the origin of the gap is different from that of MnO. In the latter case the gap of about 0.9 eV is caused mainly by the exchange splitting (cf. Fig. 3.1) and is larger than the 0.44 eV gap in NiO caused by the crystal field splitting between occupied $t_{2g}$ and empty $e_g$ states. Both versions of the LSDA+$U$ potential considerably improve the width of the gap. The value of the magnetic moment is increased (Table 3.4) by the $U$-correction, but the wide range of reported experimental values does not allow to state that an improvement with respect to LSDA has been achieved. The same is true for FeO and CoO and, following Mazin and Anisimov [32], one can state that at least for the 3$d$ transition metal monoxides the LSDA failure is well-documented only for the spectroscopic properties and mainly connected with the overestimated width of the $d$-bands.

The crystal structure of iron and cobalt oxides is much more complicated.
3.2. CALCULATION RESULTS

Different from the other monoxides, CoO was thought to form in the antiferromagnetic phase a tetragonal structure [33]. Such a structure is evidently inconsistent with the antiferromagnetic arrangement presented in Fig. 3.1 and it was a subject of speculations for decades starting with Roth’s suggestion of a multispin structure [34]. The controversy about the magnetic structure was finally resolved by Herrmann-Ronzaud et al. [35] in the neutron diffraction experiment on a CoO monocrystal under uniaxial stress. The experiment found the collinear magnetic structure in consistency with earlier X-ray measurements of Saito et al. [36] determining the monoclinic $C/2m$ symmetry of antiferromagnetic crystal structure of CoO. The structure has been confirmed and refined in the most resent measurement [31] using synchrotron radiation.

From the electron-hole symmetry one would expect a similar distortion in FeO, as the $t_{2g}$ shell of Fe$^{2+}$ is filled with one electron instead of one hole in the case of Co$^{2+}$. The determination of the crystal structure of FeO was however for a long time obscured as the compound does not exist in stoichiometric form. There is usually a deficiency of at least 2% of iron in the
Figure 3.5: Density of states of FeO in LSDA and LSDA+U calculations.

substance. The structure of the defects is quite complicated [37] and therefore prevents to interpret some of the physical properties unambiguously. Till recently only a rhombohedral distortion was reported [33]. This distortion is similar to that of NiO and MnO, but in the opposite direction: the [111] axis is elongated by about 0.8%. In 2002 the crystal and magnetic structure of nearly stoichiometric FeO was reinvestigated [38] and the fine measurements revealed that below the Néel temperature the compound actually has monoclinic $C2/m$ crystal symmetry, the same as that of CoO [31].

The results of DOS calculation for FeO and CoO are presented in Fig. 3.5 and 3.6, respectively. In the LSDA calculation both compounds are found to be metals as the rhombohedral splitting $\Delta_R$ (Fig. 3.1) is too small to open an insulating gap between the $t_{2g}$ states. The on-site interaction opens the gap in both implemented versions of LSDA+$U$.

In contrast to the LSDA+$U$ results for MnO with a completely filled majority spin band and for NiO with a completely filled $t_{2g}$ band, the LSDA+$U$ calculations for FeO and CoO with a partially filled $t_{2g}$ band show a tendency towards orbital order. The trigonal symmetry is broken, so that the cubic $t_{2g}$
3.2. Calculation Results

![Density of states of CoO in LSDA and LSDA+U calculations.](image)

Figure 3.6: Density of states of CoO in LSDA and LSDA+U calculations.

orbitals ($|xy\rangle$, $|yz\rangle$, $|zx\rangle$) are no more equivalent. One of them has a different occupation compared to the other two indicating a tendency to tetragonal order. The technical reason for such a behavior is the full Brillouin zone integration implemented in the current version of LSDA+U. Such an integration does not guarantee an equal occupation of the orbitals and if – due to numerical noise – the occupations appear to be different the Coulomb interaction drives the less occupied orbital (orbitals) further upwards. A similar behavior was reported earlier [15, 39] and was connected by the authors of Ref. [39] with a considerable tetragonal distortion (a contraction of about 1.2% of the c-axis) of the CoO unit cell. The first measurement on FeO revealing a deviation of the distortion from the simple rhombohedral one was reported only in 2002. Decomposing the measured monoclinic distortion, a “tetragonal elongation” of the c-axis of about 0.5% can be found (see Appendix).

The opposite sign of the tetragonal distortions in CoO and FeO supports the suggestion that it is the orbital ordering which causes the distortion, and not the magnetostriction as was proposed by Kanamori [21] for CoO. Indeed the energy order of doublet ($|yz\rangle$ and $|zx\rangle$) and the singlet ($|xy\rangle$), resulting
Figure 3.7: The lattice constants (left) and the magnetic moments (right) of the TM monoxides. The broken line is a linear interpolation of the observed spin component of the total magnetic moment of the TM ions. The most reliable values of the experimental magnetic moment were chosen.

from the cubic $t_{2g}$ triplet, is inverted upon elongation and contraction of the c-axis, respectively.

The calculated and experimental values of the optical gap, the magnetic moments and the lattice constants are given in Table 3.4 and Figure 3.7. The comparison of the magnetic moments is obscure because of various mutually excluding experimental data. One notes that the observed values of the magnetic moment for all compounds but FeO are in qualitative agreement with the considerations given in Section 3.1. For FeO the orbital moment seems to be quenched much stronger. The considerations given in Section 3.A1 account for the larger part of the quenching. Unfortunately there are no available data about the spin component of the magnetic moment in this compound. However one can note the trend that the observed spin moment is about 0.4 $\mu_B$ less than the “pure” spin value $2S$. Most probably it is connected with the covalency effects.

The left panel of Figure 3.7 shows that, while LSDA underestimates the
lattice constant, LSDA+$U^{AL}$ overestimates it, both following the trend given by the experimental values. The LSDA+$U^{MF}$ results are less systematic and good agreement with the experimental value for FeO seems to be occasional.

<table>
<thead>
<tr>
<th>TO</th>
<th>Exp.</th>
<th>LSDA</th>
<th>LSDA+$U^{MF}$</th>
<th>LSDA+$U^{AL}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO</td>
<td>3.6–3.8&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.90</td>
<td>0.97/1.30</td>
<td>2.06/3.70</td>
</tr>
<tr>
<td>FeO</td>
<td>2.4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0</td>
<td>1.15/1.20</td>
<td>2.50/2.70</td>
</tr>
<tr>
<td>CoO</td>
<td>2.4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0</td>
<td>2.52</td>
<td>3.25/3.38</td>
</tr>
<tr>
<td>NiO</td>
<td>4.0–4.3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.44</td>
<td>3.16/3.25</td>
<td>2.73</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$\mu_\text{B}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO</td>
<td>4.79&lt;sup&gt;a&lt;/sup&gt;, 4.58&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>FeO</td>
<td>3.32&lt;sup&gt;b&lt;/sup&gt;, 4.20&lt;sup&gt;b&lt;/sup&gt;, 4.02&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>CoO</td>
<td>3.35&lt;sup&gt;a&lt;/sup&gt;, 3.80&lt;sup&gt;b&lt;/sup&gt;, 3.98&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>NiO</td>
<td>1.77&lt;sup&gt;a&lt;/sup&gt;, 1.64&lt;sup&gt;a&lt;/sup&gt;, 1.90&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> [15] and references herein, <sup>b</sup> [40], <sup>c</sup> [38], <sup>d</sup> [31].

Table 3.4: The optical gap and the magnetic moment of the transition metal monoxides. The experimental value of the total magnetic moment is given. Calculation results represent the spin component of the moment. For LSDA+$U$ results, the second value of the gap (if given) is the onset of the TM:3d unoccupied states. The states below the onset are mainly of TM:4s character.

3.A Appendix

3.A1 Variation of the quantization axis

To obtain the Hamilton matrix of the model system described in Section 3.1 under arbitrary direction of the quantization axis one needs to transform spherical harmonics between two Cartesian coordinate systems, $xyz$ and $x'y'z'$. This is achieved by using the Wigner rotation matrices<sup>2</sup>

$$Y_{jm} = \sum_{m'} D_{m'm}^{(j)}(\alpha, \beta, \gamma) Y_{jm'}^{'},$$

(3.A1)

where $\alpha, \beta, \gamma$ are the Euler angles of the primed coordinate system in the unprimed one. For the transformation between standard spherical harmonics

<sup>2</sup>We use definitions from Ref. [41].
\( \mathcal{Y} \) the elements of the rotation matrix \( D \), designated for this special case as \( \mathcal{D} \), are defined by the expression

\[
\mathcal{D}^{j}_{m'm}(\alpha, \beta, \gamma) = e^{im'\gamma} \mathcal{D}^{j}_{m}(\beta) e^{im\alpha}.
\]  \hspace{1cm} (3.82)

The general algebraic expression for the real functions \( \mathcal{D}^{j}_{m'm}(\beta) \) defined for integer and half-integer \( jmm' \) reads \[42\]

\[
d^{j}_{m'm}(\beta) = (-1)^{j-m} [(j+m)! (j - m')! (j + m')! (j - m' - m)!]^{\frac{1}{2}} \\
\times \sum_{k} (-1)^{k} \frac{(\cos \frac{\beta}{2})^{m+m'}+2k (\sin \frac{\beta}{2})^{2j-m-m'-2k}}{k! (j - m - k)! (j - m' - k)! (m + m' + k)!}.
\] \hspace{1cm} (3.83)

For arbitrary basis of spherical harmonics

\[
Y_{jm} = \sum_{m'} T^{(j)}_{m'm} Y_{jm'},
\] \hspace{1cm} (3.84)

connected with the standard ones by a unitary transformation \( \hat{T} \), the rotation matrix is

\[
\hat{T}^{(j)}(\alpha, \beta, \gamma) = \hat{T}^{(j)*} \hat{T}^{(j)}(\alpha, \beta, \gamma) \hat{T}^{(j)}.
\] \hspace{1cm} (3.85)

In our case the calculation can be better visualized in the basis of real spherical harmonics, which represent the eigenstates of the octahedral crystal Hamiltonian. The real harmonics\(^3\) are defined by the expression

\[
Y_{jm} = \begin{cases} 
\frac{i}{\sqrt{2}} (Y_{jm} - (-1)^{m} Y_{jm'}), & m < 0 \\
Y_{m0}, & m = 0 \\
\frac{i}{\sqrt{2}} (Y_{jm} + (-1)^{m} Y_{jm'}), & m > 0
\end{cases}
\] \hspace{1cm} (3.86)

Here and below we use the notation convention \( \tilde{m} \equiv -m \).

The matrix form (3.84) of the equation (3.86) for the case \( j = 2 \) reads

\[
Y_{2m} = \sum_{m'} T^{(2)}_{m'm} Y_{2m'},
\]

\[
\hat{T}^{(2)} = \begin{pmatrix}
\frac{\sqrt{2}}{2} & 1 & 0 & 1 & 2 \\
\frac{1}{\sqrt{2}} & 0 & 0 & 0 & \frac{1}{\sqrt{2}} \\
-\frac{1}{\sqrt{2}} & 0 & 0 & \frac{1}{\sqrt{2}} & 0 \\
0 & \frac{\sqrt{2}}{2} & 0 & 0 & 0 \\
0 & \frac{\sqrt{2}}{2} & 0 & 0 & 0
\end{pmatrix}.
\] \hspace{1cm} (3.87)

\(^3\)In fact the harmonics may have a common phase factor depending on the definition of \( \mathcal{Y} \).
the labels at the side and on the top of the matrix designating the running indices, which are also the eigenvalues of the orbital moment projection operator in the case of standard spherical harmonics.

The crystal Hamiltonian and that of spin-orbit interaction are given for the same order of indices by

\[ \hat{H}_{\text{CF}} = \Delta \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \quad \text{and} \quad \hat{H}_{\text{SO}}' = \frac{i\zeta}{2} \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 2 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \] (3.8)

respectively.\(^4\) In the rest of this section we set the energy unit to \(\Delta\).

\(\hat{H}_{\text{CF}}\) and \(\hat{H}_{\text{SO}}'\) are given in different coordinate systems \(xyz\) and \(x'y'z'\), respectively, \(z'\) being the quantization axis for the orbital moment. Transforming the matrix into unprimed system, one obtains the Hamiltonian

\[ \hat{H}(\alpha, \beta, \gamma) = \hat{H}_{\text{CF}} + \hat{D}(\alpha, \beta, \gamma)\hat{H}_{\text{SO}}\hat{D}(\alpha, \beta, \gamma) \] (3.9)

with matrix \(\hat{D}\) given by (3.5).

As the actual directions of \(x'\) and \(y'\) axes are irrelevant the Hamiltonian essentially depends only on two Euler angles \(\alpha\) and \(\beta\) and reads in the explicit form as

\[ \hat{H}(\alpha, \beta) = \hat{H}_{\text{CF}} + \frac{i\zeta}{2} \begin{pmatrix} 0 & -\sin \alpha \sin \beta & 0 & \cos \alpha \sin \beta & -2 \cos \beta \\ \sin \alpha \sin \beta & 0 & \sqrt{3} \cos \alpha \sin \beta & -\cos \beta & \cos \alpha \sin \beta \\ 0 & -\sqrt{3} \cos \alpha \sin \beta & 0 & \sqrt{3} \sin \alpha \sin \beta & 0 \\ -\cos \alpha \sin \beta & \cos \beta & -\sqrt{3} \sin \alpha \sin \beta & 0 & \sin \alpha \sin \beta \\ 2 \cos \beta & -\cos \alpha \sin \beta & 0 & -\sin \alpha \sin \beta & 0 \end{pmatrix}. \] (3.10)

The eigenvalue problem for the matrix (3.10)

\[ 4\lambda^5 - 8\lambda^4 + (4 - 5\zeta^2)\lambda^3 + 6\zeta^2\lambda^2 - \zeta^2(1 - \zeta^2)\lambda - \zeta^4 A(\alpha, \beta) = 0 \] (3.11)

with

\[ A(\alpha, \beta) = \left( \frac{3 \cos^2 \beta - 1}{2} \right)^2 + \frac{3}{4} \cos^2 2\alpha \sin^4 \beta \] (3.12)

\(^4\)Cf. Eq. 3.2. Note that in the equation other order and phase factors (\(1\overline{1}20\) and \(\overline{1}111\), respectively) of the basis functions (3.16) were used.
cannot in general be solved analytically. Under fixed $\zeta$ the solution depends only on the value of $A$, which varies from 0 ($\alpha = \pi/4$, $\beta = \arccos \frac{1}{\sqrt{3}}$ – direction [111]) to 1 ($\beta = 0$ – direction [001]). If $\alpha$ is fixed to $\pi/4$, the complete range of the parameter $A$ can be scanned by varying only the angle $\beta$, which corresponds to the rotation of the quantization axis in the (110) plane.
In Fig. 3.8 we present the results of numerical solution of (3.A11) for \( \zeta = 0.05 \). One sees that for one \((\text{Fe}^{2+})\) and three \((\text{Ni}^{2+})\) electrons in the minority spin-subshell the ground state corresponds to the orbital moment directing in \([111]\) direction, whereas for two \((\text{Co}^{2+})\) and four electrons — in \([001]\) direction. In the case of nickel, where the variation of the energy is of order of some microelectronvolts (assuming that the crystal field splitting is about 1 eV), certainly other physical processes like spin-spin interaction and lattice distortion have to be considered.

The lower panel in Fig. 3.8 shows that the magnetic moments scale linearly with spin-orbit coupling constant in a wide range of its value.

### 3.A2 Decomposition of the monoclinic structure

![Diagram of the monoclinic unit cell of the antiferromagnetic FeO and CoO related to their paramagnetic structure. The magnetic moments lie in the \(ac\) plane. The magnetic cell is doubled in \(c\) direction.]

Due to exchange and magnetostriction (and, as shown in previous section, due to orbital ordering in case of FeO and CoO) the magnetic ordering of TM monoxides below the Néel temperature should be accompanied by a monoclinic distortion, as was first pointed out by Kanamori [21]. The relation between the antiferromagnetic monoclinic unit cell and the paramagnetic cubic one is shown in Fig. 3.9. To preserve the monoclinic symmetry the magnetic moments have to lie in the \((\bar{1}10)\) plane.\(^5\) The most appropriate

---

\(^5\)For better graphical appearance the dependence on \(\sqrt{A}\) is shown.

\(^6\)The Miller indices are given in the undistorted paramagnetic cubic structure. If the magnetic moments point in \([111]\) direction, the symmetry of the magnetic structure be-
description of the monoclinic distortion can be presented by a deformation
of the cubic angles ($\alpha_{xy} \equiv \alpha_1, \alpha_{yz} = \alpha_{zx} \equiv \alpha_2$) and an elongation $\lambda$ of the $z$
cubic axis. One should note that the latter distortion alone also affects the
parameters of the monoclinic structure. This point was missed for example
by the authors of Ref. [31] where the distortion additional to the “tetragonal”
was measured by the monoclinic angle $\beta$ and a conclusion about the scaling
of both distortions was made. However the “scaling” is of pure geometric
origin and does not involve any physics.

After straightforward calculation one obtains the connection between the
parameters of the distortion and those of the monoclinic structure:

$$\cos \alpha_1 = \frac{c^2 - b^2}{b^2 + c^2}, \quad (3.13)$$

$$\cos \alpha_2 = \frac{c(c + a \cos \beta)}{\sqrt{(b^2 + c^2)(a^2 + 2ac \cos \beta + c^2)}}, \quad (3.14)$$

$$\lambda = \sqrt{\frac{a^2 + 2ac \cos \beta + c^2}{b^2 + c^2}}. \quad (3.15)$$

In Table 3.5 we present the distortion parameters calculated from the
experimental monoclinic (or rhombohedral) structure parameters. One sees
that the description of the monoclinic cell of CoO as a composition of tetragonal
and rhombohedral distortions ($\alpha_1 = \alpha_2$) used by many authors is not
exactly satisfied.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ref.</th>
<th>$\cos \alpha_1$</th>
<th>$\cos \alpha_2$</th>
<th>$\lambda - 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO</td>
<td>[43]</td>
<td>-0.0108</td>
<td>-0.0108</td>
<td>0.0000</td>
</tr>
<tr>
<td>FeO</td>
<td>[38]</td>
<td>0.0088</td>
<td>0.0113</td>
<td>0.0047</td>
</tr>
<tr>
<td>CoO</td>
<td>[31]</td>
<td>0.0003</td>
<td>0.0006</td>
<td>-0.0126</td>
</tr>
<tr>
<td>NiO</td>
<td>[43]</td>
<td>-0.0014</td>
<td>-0.0014</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

Table 3.5: The monoclinic distortion parameters of the TM monoxide unit
cells.
Chapter 4

Single zinc impurity in CuO$_2$ plane

A number of experimental and theoretical works was dedicated to the investigation of impurity problems in superconducting cuprates (see, e.g. [44, 45]). Their main goals were to draw some definite conclusions concerning the electronic structure and the superconducting order parameter symmetry. The special focus was on the study of the Zn/Cu substitutions in the CuO$_2$ plane as an example of an inherent nonmagnetic dopant in a strongly correlated electronic system. In order to conceive some of the unexpected consequences caused by Zn, many theoretical models have been investigated, although without proper consideration of the corresponding electronic states.

In a number of papers, the Zn impurity in the CuO$_2$ plane was considered as a local nonmagnetic impurity level at high energy in the Hubbard model [46, 47] or the t-J model [48, 49]. Using the $T$-matrix description, bound impurity states within the Hubbard gap were obtained. Due to strong Coulomb correlations in the model, the bare local impurity potential becomes a dynamic one which results in the resonant scattering and bound state formation of different ($p$, $d$-wave) symmetries in the gap. Formation of local magnetic moments induced by a spin vacancy in underdoped cuprates was considered in [50, 51, 52] within the resonant valence bond (RVB) theory for the two-dimensional spin liquid. Influence of the impurity local moments on magnetic and transport properties in the RVB state were studied within the slave-boson and slave-fermion mean-field theories [53, 54]. The importance of the $4s$ orbital of the Zn$^{2+}$ impurity for charge transfer excitations between copper $3d$ and this orbital was pointed out [55]. To investigate the influence of nonmagnetic impurities on the $d$-wave superconductivity, several phenomenological models of Fermi liquid type were also considered (see, e.g., [56, 57, 58, 59, 60]). In the framework of the many-band $p$-$d$ model,
a general qualitative analysis of the density of state (DOS) modifications caused by Zn and Ni impurities in electron and hole doped cuprates were performed in [61].

It was shown in Ref. [45] that in the low-energy electronic spectrum the contribution of the Zn $3d^{10}$ orbitals can be neglected in comparison with the Cu $3d$ and O $2p$ contributions. This observation permits to consider Zn impurities as vacancies for the $d$-states on Cu sites with the oxygen $p$-states being unaffected within the $p$-$d$ model with strong correlations. Below we investigate the model in order to find the perturbation in the DOS caused by a single Zn-impurity.

4.1 Model and Green function equations

We consider an effective $t$-$J$ model for the CuO$_2$ plane with one Zn impurity. As was shown in [45] the Zn impurity can be treated as a vacancy in the $t$-$J$ model. Such a treatment is justified by the following observations:

- the replacement of a Cu$^{2+}$ ion by Zn$^{2+}$ delivers no additional charge to the [CuO$_2$]$^{2-}$ plane;
- hybridized Zn:3d/O:2p states lie deep below the Fermi energy and can be neglected.

Thus in our model the Zn impurity is treated as a single missing site in the infinite net of Cu:3d states and the Hamiltonian reads:

$$H = H_0 + V_{\text{vac}},$$

where the host lattice without impurity is described by the $t$-$J$ model

$$H_0 = H_{t-J} = \epsilon \sum_{i\sigma} X_i^{\sigma\sigma} + t \sum_{i\neq j, \sigma} X_i^{\sigma0} X_j^{0\sigma} + \frac{1}{4} J \sum_{i\neq j, \sigma} (X_i^{\sigma\sigma} X_j^{\sigma\sigma} - X_i^{\sigma0} X_j^{0\sigma}),$$

written in terms of the Hubbard operators.\(^1\) The vacancy contribution is given by

$$V_{\text{vac}} = -\epsilon \sum_{\sigma} X_0^{0\sigma} - t \sum_{\Delta\sigma} (X_0^{\sigma0} X_0^{\sigma\Delta}) + \text{H.c.} + \frac{1}{4} J \sum_{\Delta\sigma} (X_0^{\sigma\sigma} X_0^{\sigma\sigma} - X_0^{\sigma0} X_0^{0\sigma}) + \text{H.c.},$$

\(^1\) $X_i^{\sigma\sigma} = c_{i\sigma}^\dagger (1 - n_{i\sigma}), X_i^{\sigma0} = (1 - n_{i\sigma}) c_{i\sigma}, X_i^{\sigma\sigma} = n_{i\sigma} (1 - n_{i\sigma}), X_i^{\sigma\sigma} = c_{i\sigma}^\dagger c_{i\bar{\sigma}} (\bar{\sigma} \equiv -\sigma).$
where the summations are performed over the nearest neighbor (n.n.) Cu-sites of the host square lattice, and the Zn-impurity is at the \( i = 0 \) site with \( \Delta = 1, 2, 3, 4 \) denoting its n.n. sites as shown in Fig. 4.1. The Hamiltonian (4.1–4.3) is applicable both for electron \((0 < n < 1)\) and hole \((1 < n < 2)\) doping. In the former case \( \epsilon \) and \( t \) are the on-site energy and the hopping integral for the lowest one-hole state \( |D\rangle \) of the CuO\(_4\) plaquette, whereas in the latter one they are those of the Zhang-Rice singlet state \( |\psi\rangle \), as outlined in [45]. For the sake of simplicity we consider in the following analysis only the electron doping, since the transformation to the hole doping is quite straightforward.

![Figure 4.1: Schematic picture of the impurity influenced cluster](image)

In order to calculate the DOS for one-electron excitations in the system, we consider the equation of motion for the GF in terms of Hubbard operators:

\[
G_{ij\sigma}(t, t') = \langle \{X_i^{0\sigma}(t), X_j^{0\sigma}(t')\} \rangle = -i\theta(t - t')\langle \{X_i^{0\sigma}(t), X_j^{0\sigma}(t')\} \rangle,
\]

where the Zubarev notation [64] is used. By employing the projection technique [65] for the GF we write down the corresponding Dyson equation. Neglecting the self-energy contribution in the generalized mean-field approximation (GMFA) we obtain

\[
\omega G_{ij\sigma}(\omega) = \delta_{ij} + \sum_l E_l G_{lj\sigma}(\omega) + \sum_l V_{il} G_{lj\sigma}(\omega),
\]

where we introduced the normalized GF:

\[
G_{ij\sigma}(\omega) = Q_i^{-1} G_{ij\sigma}(\omega), \quad \int_{-\infty}^{\infty} d\omega \left\{ \frac{1}{\pi} \text{Im} \ G_{ij\sigma}(\omega^-) \right\} = \delta_{ij}
\]
with the correlation function $Q_i = \langle X_i^{00} + X_i^0 \rangle = 1 - n_i/2$. In the paramagnetic state it depends only on the average number of holes

$$n_i = \sum_{\sigma} \langle X_i^{\sigma\sigma} \rangle = Q_i \int_{-\infty}^{\infty} \frac{2 \, d\omega}{e^{(\omega - \mu)/T} + 1} \text{Im} \, G^{\sigma\sigma}(\omega^-); \quad (4.7)$$

where $n_i \approx n$ for $i \neq 0, \Delta$. In (4.6,4.7) and later on we use the notation $\omega^- = \omega - i0$. The equation for the frequency matrix $E_{ij}$ of the host lattice reads

$$E_{ij} = \langle\{X_i^{0\sigma}, H_0\}, X_{j}^{\sigma} \rangle \, Q^{-1}, \quad (4.8)$$

and the perturbation matrix is given by

$$V_{ij} = \langle\{X_i^{0\sigma}, V_{\text{vac}}, X_{j}^{\sigma} \rangle \, Q^{-1} = \delta_{i0} \delta_{j0} V_{00} + \delta_{i0} \sum_{\Delta} \delta_{i\Delta} V_{01} + \delta_{i0} \sum_{\Delta} \delta_{i\Delta} V_{10} + V_{11} \sum_{\Delta} \delta_{i\Delta} \delta_{j\Delta}. \quad (4.9)$$

Equation (4.5) can be written in the form of the Dyson equation (in the matrix notation)

$$\hat{G} = \hat{G}^0 + \hat{G}^0 \hat{V} \hat{G} = \hat{G}^0 + \hat{G}^0 \hat{M} \hat{G}^0, \quad (4.10)$$

where the scattering matrix is

$$\hat{M} = \hat{V} \frac{1}{1 - \hat{G}^0 \hat{V}}. \quad (4.11)$$

and the zero-order GF for the host lattice is given by:

$$\hat{G}^0(\omega) = [\omega - \hat{E}]^{-1}. \quad (4.12)$$

Introducing the $\mathbf{q}$-representation for the ideal host lattice the zero-order GF can be written in the form

$$G_{ij}^{00}(\omega) = \frac{1}{N} \sum_{\mathbf{q}} e^{i \mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)} \frac{1}{\omega - E(\mathbf{q})}, \quad (4.13)$$

where

$$E(\mathbf{q}) = \tilde{\epsilon} + 2\tilde{t}(\cos q_x + \cos q_y). \quad (4.14)$$

In the GMFA, according to (4.8), the hopping energy $\tilde{\epsilon}$ and the on-site energy $\tilde{\epsilon} = \epsilon + \delta \epsilon$ are renormalized due to the kinematic and exchange interactions [65]:

$$\tilde{\epsilon} = \frac{t}{Q}[\langle(1 - n_0/2)(1 - n_\Delta/2)\rangle + \langle S_0 S_\Delta \rangle] - \frac{2J}{Q} \langle X_0^{0\sigma} X_\Delta^{0\sigma} \rangle; \quad (4.15)$$
\[ \delta \varepsilon = \frac{2J}{Q} \left[ \langle (1 - n_0/2)(1 - n_\Delta/2) \rangle + \langle \mathbf{S}_0 \mathbf{S}_\Delta \rangle - Q \right] - \frac{4t}{Q} \langle X_{\sigma 0} | X_{\sigma \sigma} \rangle, \quad (4.16) \]

where \( Q \) is the correlation function for \( n_i = n \). In the same approximation we obtain for the perturbation potential

\[ V_{00} = -\varepsilon, \quad V_{01} = V_{10} = -\tilde{t}, \quad V_{11} = -\delta \varepsilon/4, \quad (4.17) \]

if the correlation functions for the number \( n_i \) and spin \( \mathbf{S}_i \) operators in (4.9) are calculated for the host ideal lattice. Later on we measure the energy \( \omega \) in units of the half-bandwidth \( w = 4t \) (it means \( V_{01} = V_{10} = -1/4 \) from the renormalized on-site energy \( V_{00} = -\varepsilon = 0 \)).

### 4.2 Symmetry analysis

The perturbation matrix has the following form:

\[
\hat{V} = \begin{pmatrix}
V_{00} & V_{01} & V_{01} & V_{01} \\
V_{10} & V_{11} & 0 & 0 & 0 \\
V_{10} & 0 & V_{11} & 0 & 0 \\
V_{10} & 0 & 0 & V_{11} & 0 \\
V_{10} & 0 & 0 & 0 & V_{11}
\end{pmatrix}, \quad (4.18)
\]

the matrix elements being given by (4.17). One can diagonalize the perturbation matrix (4.18) by the unitary transformation

\[
\hat{U} = \begin{pmatrix}
0 & 0 & 0 & 1 & 0 \\
1/2 & 1/\sqrt{2} & 0 & 0 & 1/2 \\
-1/2 & 0 & 1/\sqrt{2} & 0 & 1/2 \\
1/2 & -1/\sqrt{2} & 0 & 0 & 1/2 \\
-1/2 & 0 & -1/\sqrt{2} & 0 & 1/2
\end{pmatrix}, \quad (4.19)
\]

obtaining

\[
\hat{U}^{\dagger} \hat{V} \hat{U} = \begin{pmatrix}
V_s & 0 & 0 \\
0 & V_p & 0 \\
0 & 0 & V_d
\end{pmatrix}, \quad (4.20)
\]

where the \( s, p, \) and \( d \)-symmetry matrices are

\[
V_s = V_{11}, \quad \hat{V}_p = \begin{pmatrix} V_{11} & 0 \\ 0 & V_{11} \end{pmatrix}, \quad \hat{V}_d = \begin{pmatrix} V_{00} & 2V_{01} \\ 2V_{10} & V_{11} \end{pmatrix}. \quad (4.21)
\]
The corresponding $s$-, $p$- and $d$-symmetry wave functions for the impurity cluster shown in Fig. 4.1 are defined by

\[
|s \rangle = \sum_{l=0}^{4} U(l, 0) |l \rangle = \frac{1}{2} \left\{ |1 \rangle - |2 \rangle + |3 \rangle - |4 \rangle \right\};
\]

\[
|p_x \rangle = \sum_{l} U(l, 1) |l \rangle = \frac{1}{\sqrt{2}} \left\{ |1 \rangle - |3 \rangle \right\};
\]

\[
|p_y \rangle = \sum_{l} U(l, 2) |l \rangle = \frac{1}{\sqrt{2}} \left\{ |2 \rangle - |4 \rangle \right\};
\]

\[
|d_1 \rangle = \sum_{l} U(l, 3) |l \rangle = |0 \rangle;
\]

\[
|d_2 \rangle = \sum_{l} U(l, 4) |l \rangle = \frac{1}{2} \left\{ |1 \rangle + |2 \rangle + |3 \rangle + |4 \rangle \right\}.
\]

Using the rectangular $\hat{T}$-matrices [63] which are the columns of the unitary matrix (4.19)

\[
\hat{T}_s = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ -1 & 1 \\ 1 & -1 \end{pmatrix}; \quad \hat{T}_p = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 \\ 1 & 0 \\ -1 & 0 \end{pmatrix}; \quad \hat{T}_d = \begin{pmatrix} 1 & 0 \ 0 & 1/2 \ 0 & 1/2 \end{pmatrix},
\]

we can write the Dyson equation (4.10) for the GF in the form \(^2\)

\[
\tilde{G} = \tilde{G}^0 + \sum_{\mu=s,p,d} \tilde{G}^0 \hat{T}_\mu \hat{M}_\mu \hat{T}_\mu \tilde{G}^0,
\]

where

\[
\hat{M}_\mu = \hat{T}_\mu \hat{V} \frac{1}{1 - \tilde{G}^0 \hat{V}} \hat{T}_\mu = \hat{V}_\mu \left[ 1 - \tilde{G}^0 \hat{V}_\mu \right]^{-1}.
\]

The matrices $\hat{V}_\mu \equiv \hat{T}_\mu \hat{V} \hat{T}_\mu$ are given by (4.21). The matrices $\hat{G}^0_\mu(\omega) \equiv \hat{T}_\mu \tilde{G}^0(\omega) \hat{T}_\mu$, $\hat{I}_\mu(\omega) = 1 - \hat{G}^0_\mu(\omega) \hat{V}_\mu$ and the determinants $D_\mu(\omega) = \text{det} \hat{I}_\mu(\omega)$ are obtained as follows:

\[
\hat{G}^0_s(\omega) = G_{11}^0(\omega) - 2G_{12}^0(\omega) + G_{13}^0(\omega) \equiv \gamma_s(\omega),
\]

\[
\hat{G}^0_p(\omega) = \begin{pmatrix} \gamma_p & 0 \\ 0 & \gamma_p \end{pmatrix}; \quad \gamma_p(\omega) \equiv G_{11}^0(\omega) - G_{13}^0(\omega),
\]

\[
\hat{G}^0_d(\omega) = \begin{pmatrix} G_{00}^0 & 2G_{01}^0 \\ 2G_{01}^0 & \sum_{\Delta} G_{01}^0 \end{pmatrix} \equiv \begin{pmatrix} d_{00} & d_{01} \\ d_{10} & d_{11} \end{pmatrix},
\]

\(^2\)Everywhere the argument of a function is omitted it is assumed to be $\omega$. 

4.3. GREEN FUNCTIONS AND DOS

\[ I_s = D_s = 1 - V_{11} \gamma_s , \quad (4.28) \]
\[ \hat{I}_p = \begin{pmatrix} 1 - V_{11} \gamma_p & 0 \\ 0 & 1 - V_{11} \gamma_p \end{pmatrix} ; \quad D_p = (1 - V_{11} \gamma_p)^2 , \quad (4.29) \]
\[ \hat{I}_d = \begin{pmatrix} 1 - V_{00}d_{00} - 2V_{10}d_{01} & -2V_{01}d_{00} - V_{11}d_{01} \\ -V_{00}d_{10} - 2V_{10}d_{11} & 1 - 2V_{01}d_{10} - V_{11}d_{11} \end{pmatrix} ; \]
\[ D_d = 1 - V_{00}d_{00} - V_{11}d_{11} - 2V_{01}d_{01} - 2V_{10}d_{10} \]
\[ + (V_{00}V_{11} - 4V_{01}V_{10})(d_{00}d_{11} - d_{01}d_{10}) \]
\[ = (\omega - V_{00})(G_{00}^0 - 4V_{11}G_{01}^0) - (1 + 4V_{10})(1 + 4V_{01})G_{01}^0 , \quad (4.30) \]

where, to obtain the last line, we used the relations
\[ d_{11} = 4\omega G_{01}^0 , \quad G_{01}^0 = \omega G_{00}^0 - 1. \]

In (4.25 - 4.27) we have used the symmetry of the zero-order GF \( G_{ij}^0(\omega) \) given by (4.13) for the impurity cluster.

Substituting in (4.30) the perturbation potential given by (4.17) we obtain
\[ D_d(\omega) = \omega[G_{00}^0(\omega) - 4V_{11}G_{01}^0(\omega)]. \quad (4.31) \]

Finally, for the partial scattering matrices \( \hat{M}_\mu = \hat{V}_\mu \hat{I}^{-1}_\mu \) we derive:
\[ M_s(\omega) = \frac{V_{11}}{1 - V_{11} \gamma_s} , \quad (4.32) \]
\[ M_p(\omega) = \frac{V_{11}}{1 - V_{11} \gamma_p} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} , \quad (4.33) \]
\[ M_d(\omega) = \frac{1}{D_d} \begin{pmatrix} V_{00} - |V|d_{11} & 2V_{01} + |V|d_{01} \\ 2V_{10} + |V|d_{10} & V_{11} - |V|d_{00} \end{pmatrix} , \quad (4.34) \]

where \( |V| = V_{00}V_{11} - 4V_{01}V_{10} \) is the determinant of \( \hat{V}_d \) and we used the identity
\[ |1 - AB| (1 - AB)^{-1} = 1 - |A| |B| B^{-1} A^{-1} \]
valid for \( 2 \times 2 \) matrices \( A \) and \( B \).

4.3 Green functions and DOS

We can write the GF (4.23) in the form
\[ G_{ij}(\omega) = G_{ij}^0(\omega) + \sum_{\mu=s,p,d} \Delta G_{ij}^{(\mu)}(\omega). \quad (4.35) \]
To calculate the perturbation parts, we need the following products $\hat{T}_{\mu}^\dagger \hat{G}^0$:

\[
\begin{pmatrix}
0 & 1/2 & -1/2 & 1/2 & -1/2 & 0 & \ldots
\end{pmatrix}_N \hat{G}^0(\omega)
= \left( \ldots \sum (\hat{T}_{\mu}^\dagger)_i G^0_{ij} \ldots \right)_N = \frac{1}{2} \left( \ldots \sum_\Delta (-1)^{1+\Delta} G^0_{\Delta j} \ldots \right)_N, \tag{4.36}
\]

\[
\begin{pmatrix}
0 & 1/\sqrt{2} & 0 & -1/\sqrt{2} & 0 & 0 & \ldots
\end{pmatrix}_N \hat{G}^0(\omega)
= \left( \ldots \sum (\hat{T}_{\mu}^\dagger)_i G^0_{ij} \ldots \right)_N = \frac{1}{\sqrt{2}} \left( \ldots G^0_{ij} - G^0_{(3 j)} \ldots \right)_N, \tag{4.37}
\]

\[
\begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & \ldots
\end{pmatrix}_N \hat{G}^0(\omega)
= \left( \ldots \sum (\hat{T}_{d}^\dagger)_i G^0_{ij} \ldots \right)_N = \left( \ldots \frac{1}{2} \sum_\Delta G^0_{\Delta j} \ldots \right)_N. \tag{4.38}
\]

The corresponding elements $\sum G^0_{\alpha} (\hat{T}_{\mu})_{\alpha \beta}$ can be obtained by transposition of the matrix given in (4.36 - 4.38). Therefore, for the GF in (4.35) we have

\[
\Delta G^{(s)}_{ij} = \frac{V_{11}}{1 - V_{11} \gamma_s} \frac{1}{4} \sum_{\Delta'} (-1)^{\Delta' + \Delta} G^0_{\Delta' \Delta} G^0_{\Delta j}, \tag{4.39}
\]

\[
\Delta G^{(p)}_{ij} = \frac{V_{11}}{1 - V_{11} \gamma_p} \frac{1}{2} \left\{ (G^0_{\xi_1} - G^0_{\xi_3}) (G^0_{\xi_1} - G^0_{\xi_3}) + (G^0_{\xi_0} - G^0_{\xi_4}) (G^0_{\xi_2} - G^0_{\xi_4}) \right\}, \tag{4.40}
\]

\[
\Delta G^{(d)}_{ij} = M_{00}^d G^0_{\xi_0} G^0_{\xi_j} + M_{01}^d \frac{1}{2} \sum_\Delta G^0_{\xi_0} G^0_{\Delta j}
+ M_{10}^d \frac{1}{2} \sum_\Delta G^0_{\Delta \xi} G^0_{\xi_0} + M_{11}^d \frac{1}{4} \sum_\Delta G^0_{\Delta \xi} G^0_{\Delta j}, \tag{4.41}
\]

where $M_{ij}^d$ are given by (4.34). The expression (4.41) can be simplified further using the relation $\sum_\Delta G^0_{\Delta j} = 4 (\omega G^0_{\xi_0} - \delta_{ij})$. For the perturbation potential (4.17) we obtain:

\[
\Delta G^{(d)}_{ij} = \frac{1}{D_d} \left[ \omega (4 V_{11} \omega - 1) G^0_{\xi_0} G^0_{\xi_j}
- 4 V_{11} \omega (G^0_{\xi_0} \xi_{0j} + \delta_{ij} G^0_{\xi_0}) + (4 V_{11} + G^0_{\xi_0}) \delta_{ij} \delta_{0j} \right]. \tag{4.42}
\]
4.4. NUMERICAL RESULTS

The general representation for the DOS is [62, 63]

\[ g(\omega) = g_0(\omega) + \frac{1}{N} \Delta g(\omega); \Delta g(\omega) = \frac{1}{\pi} \text{Im} \frac{D'(\omega^-)}{D(\omega^-)} \] (4.43)

with

\[ D = \det(1 - \hat{G}^0 \hat{V}) = D_s D_{\mu} D_d, \] (4.44)

where \( g_0(\omega) \) is the corresponding DOS for the host lattice and \( D_{\mu}(\omega) \) are given by Eqs. (4.28, 4.29, 4.31).

4.4 Numerical results

![Graph showing \( \Delta g(\omega) \) for different scattering potential \( V_{11} < V_s^c \). The inset shows the position \( \omega_0 \) and the inverse height \( \Gamma \) of the peak.](image)

The additional DOS according to (4.43, 4.44) is given by:

\[ \Delta g(\omega) = \frac{1}{\pi} \text{Im} \frac{d}{d\omega} \ln D(\omega^-) = \frac{1}{\pi} \frac{d}{d\omega} \arg D(\omega^-) = \sum_{\mu} \frac{1}{\pi} \frac{d}{d\omega} \arg D_{\mu}(\omega^-) = \sum_{\mu} \Delta g_{\mu}(\omega). \] (4.45)
Figure 4.3: $\Delta g_p(\omega)$ for different scattering potential $V_{11} < V_p^c$. The inset shows the position $\omega_0$ and the inverse height $\Gamma$ of the peak.

The zero-order GF involved in the expressions for $D_{\mu}(\omega)$ can be reduced to elliptic integrals (see Appendix) which is used in the numerics. The additional DOS $\Delta g_s$ and $\Delta g_p$ are shown in Fig. 4.2 and Fig. 4.3 for $V_{11} < V_p^c$ with

$$V_s^c = \frac{\pi}{4(4 - \pi)}, \quad V_p^c = \frac{\pi}{4(\pi - 2)},$$

respectively, when there are resonant states in the band of the host lattice. For $V_{11}$ larger than the critical values, $V_{11} > V_{11}^c$, $\Delta g_d(\omega)$ has a $\delta$-peak outside the band. The additional $p$-states are doubly degenerated. The additional $d$-states have two modes. However the mode situated at the $i = 0$ site with $\Delta g_d(\omega) \propto \delta(\omega)$ should be excluded from the consideration since there is no state at the vacancy site and the mode has no physical meaning [63]. The other mode has no resonant states but logarithmic divergences at the center and boundaries of the band. At $V_{11} > V_d^c = 0.25$ it has a $\delta$-peak outside the band. The energy dependences of the $s$-, $p$- and $d$- local modes on the interaction $V_{11}$ are shown in Fig. 4.4.

Let us estimate the value of the dimensionless perturbation potential $V_{11}$. For small doping one can neglect the last terms in (4.15) and (4.16) which are proportional to the correlation function $\langle X_0^{\delta 0} | X_0^{\delta 0} \rangle \propto (1 - n) = \delta$. In this
4.4. NUMERICAL RESULTS

Figure 4.4: The position of the local state $\Delta g_\mu = \delta(\omega - \omega_0^\mu)$ outside the band for $V_{11} > V_{11}^c (\mu = s, p, d)$.

approximation we obtain:

$$V_{11} = \frac{J}{8} \left( \frac{1}{t} - \frac{1}{t} \right) \approx 0.45$$

Here we took into account that the bandwidth in the $t$-$J$ model due to spin-fluctuations is strongly renormalized and as many calculations show it becomes of the order of the exchange interaction, $w = 4\tilde{t} \approx J = 0.4t$ (see, e.g., [65]). For a larger doping the last term in (4.16) gives a positive contribution to the perturbation potential $V_{11}$ of the order $t\delta/2t(1 + \delta)$. However, with doping the bandwidth increases that suppresses the first term in (4.16) and as a crude estimation one can use the value $V_{11} \leq 0.5$.

One notes that in the present calculation $V_{11}$ exceeds the critical value for $d$-states whereas the two other local modes are still well above. In contrast to this result the exact diagonalization study for a $20 \times 20$ cluster [48] found that there are bound states for all three modes for $J/t = 0.4$. It cannot be excluded that an improved treatment for the one-particle GF beyond the present Hubbard I approximation yields all three levels localized.
4.A Appendix

4.A1 Zero-order Green functions

Consider the complex function of a real argument

\[ J_{mn}(\omega) = \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \frac{e^{i(mx+ny)}}{\omega - 10 - \epsilon(x,y)} \, dx \, dy, \quad (4.41) \]

where \( \epsilon(x,y) = (\cos x + \cos y)/2 \). Performing in (4.41) the substitution \( \omega \to -\omega, \, x \to \pi - x, \, y \to \pi - y \) one obtains

\[ J_{mn}(-\omega) = (-1)^{m+n+1} J_{mn}^*(\omega). \quad (4.42) \]

Thus, the imaginary component of \( J_{mn} \) has the same parity as \( m+n \), and the real component has the opposite parity. Due to the fact, computation only in the domain of non-negative \( \omega \) is needed.

To compute \( J_{mn}(\omega) \) we integrate at first the expression \( \frac{2e^{iny}}{c(\omega,x) - \cos y} \) with \( c(\omega,x) = 2\omega - \cos x \) over \( y \):

\[ I_n(c) = \int_{-\pi}^{\pi} \frac{4e^{iny}}{2c - (e^y + e^{-y})} \, dy = \frac{4}{i} \int_{|z|=1} \frac{z^n}{c^2 - 1 - (z - c)^2} \, dz, \]

where we have substituted \( z = e^y \). Due to the infinitesimal imaginary component of \( c \) one pole is always inside the integration contour and the other one is outside. Supposing the square root to be analytically continued from the real semiaxis \( |1, +\infty| \) the inner pole is \( c - \sqrt{c^2 - 1} \). To make the branch one-valued the segment \([-1,1]\) of the real axis is cut from the complex plane, so that \( c (|c| < 1) \) is at the lower bank of the cut. The residue at the inner pole can be easily computed giving the result

\[ I_n(c) = 4\pi \frac{(c - \sqrt{c^2 - 1})^n}{\sqrt{c^2 - 1}} = 4\pi \frac{e^{-n\xi}}{\sinh \xi}, \quad (4.43) \]

where \( \xi(\omega,x) = \text{arccosh} \, c(\omega,x) \), the hyperbolic arccosine being a complex function of a real argument. Thus the expression for \( J_{mn}(\omega) \) reads:

\[ J_{mn}(\omega) = \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} I_n(c) e^{ix} \, dx = \frac{1}{\pi} \int_{-\pi}^{\pi} \frac{e^{-n\xi + imx}}{\sinh \xi} \, dx = \frac{2}{\pi} \int_{0}^{\pi} \frac{e^{-n\xi \cos mx}}{\sinh \xi} \, dx. \quad (4.44) \]
4.A. APPENDIX

Substituting in (4.44) \( t = \omega - \cos x \) and neglecting the imaginary component of \( \omega \) one obtains:

\[
J_{mn}(\omega) = \frac{2}{\pi} \int_{-1}^{1} \frac{\left( \omega + t - \sqrt{(\omega + t)^2 - 1} \right)^n \cos m \arccos(\omega - t)}{\sqrt{(\omega + t)^2 - 1} \sqrt{1 - (\omega - t)^2}} \, dt. \tag{4.45}
\]

As \( \cos m \arccos x \) is a polynomial of power \( m \) in \( x \), the expression (4.45) can be reduced to a composition of polynomials and complete elliptic integrals of the first and second kind. The easiest way to find the expressions for \( J_{mn} \) with small \( m, n \) is direct integration of (4.45), which is straightforward, especially for \( \omega > 1 \):

\[
\begin{align*}
J_{00}(\omega) &= \bar{\omega} \tilde{K}(\omega); \\
J_{01}(\omega) &= \tilde{K}(\omega) - 1; \\
J_{02}(\omega) &= \frac{4}{\bar{\omega}} \left[ \frac{\bar{\omega}^2}{4} \tilde{K}(\omega) + \tilde{E}(\omega) - 1 \right]; \\
J_{11}(\omega) &= \frac{2}{\bar{\omega}} \left[ \left( 1 - \frac{\bar{\omega}^2}{2} \right) \tilde{K}(\omega) - \tilde{E}(\omega) \right],
\end{align*}
\tag{4.46-4.49}
\]

where \( \tilde{K}(k), \tilde{E}(k) \) are the complete elliptic integrals of the first and second kind, respectively and \( \bar{\omega} = \omega^{-1} \). To simplify the expressions we have normalized the standard elliptic integrals by a factor of \( 2/\pi \), so that \( \tilde{E}(0) = \tilde{K}(0) = 1 \).

To obtain the explicit expression for \( J_{mn}(\omega) \) with \( \omega < 1 \) one uses the following expansion for the elliptic integrals of the real argument \( 1/k > 1 \):

\[
\begin{align*}
\tilde{K} \left( \frac{1}{k} \right) &= k \left[ \tilde{K}(k) + i \tilde{K}'(k) \right] \\
\tilde{E} \left( \frac{1}{k} \right) &= \frac{1}{k} \left[ \left\{ \tilde{E}(k) - k^2 \tilde{K}(k) \right\} - i \left\{ \tilde{E}'(k) - k^2 \tilde{K}'(k) \right\} \right],
\end{align*}
\tag{4.50}
\]

where \( \tilde{K}'(k) = \tilde{K}(k'), \tilde{E}'(k) = \tilde{E}(k') \) \( (k' = \sqrt{1 - k^2}) \) are the complementary elliptic integrals.

The GF \( G_{ij}^0 \) and the integrals \( J_{mn} \) are related as follows:

\[
G_{00}^0 = J_{00}, \quad G_{01}^0 = J_{01}, \quad G_{13}^0 = J_{02}, \quad G_{12}^0 = J_{11}. \tag{4.51}
\]

4.A2 The critical values of the model parameters

The change in the density of states is determined as

\[
\Delta g_\mu(\omega) = \frac{1}{\pi \omega} \arg D_\mu(\omega^-), \tag{4.52}
\]
\[ D_s(\omega) = 1 - V \gamma_s(\omega); \quad D_p(\omega) = \left[1 - V \gamma_p(\omega)\right]^2, \]

where \( V \) stands for \( V_{11} \) and

\[
\gamma_s(\omega) = J_{00} - 2J_{11} + J_{02} = 4\omega \left[2\tilde{E}(\omega) - (1 - \omega^2)\tilde{K}(\omega) - 1\right]; \tag{4.13}\]

\[
\gamma_p(\omega) = J_{00} - J_{02} = 4\omega \left[1 - \tilde{E}(\omega)\right]. \tag{4.14}\]

One notes that \( \gamma_s \) and \( \gamma_p \) are continuous at \( \omega = 1 \), in particular it means \( \text{Im} \ \gamma_{s(p)}(1^-) = \text{Im} \ \gamma_{s(p)}(1^+) = 0 \).

The critical value \( V_{s(p)c}^* \) above which the density has a \( \delta \)-peak outside the band \( (\omega > 1) \) is easy to compute noting that it is the inverse value of the real component of the function \( \gamma_{s(p)}(\omega) \) at \( \omega = 1 \). The expressions (4.13,4.14) at \( \omega = 1 \) can be easily evaluated:

\[
\frac{1}{V_s^*} = 4 \left(\frac{4}{\pi} - 1\right) \approx \frac{1}{0.915}, \quad \frac{1}{V_p^*} = 4 \left(1 - \frac{2}{\pi}\right) \approx \frac{1}{0.688} \tag{4.15}\]

It is also of some interest to calculate the density of states at the upper band boundary for \( p \) states (especially in the undercritical regime). From (4.12) follows that

\[
\pi \Delta g_p(\omega) = \text{Im} \ \frac{D'_p(\omega^-)}{D_p(\omega^-)} = \text{Im} \ \frac{2\gamma'_p(\omega)}{\gamma_p(\omega) - 1/V},
\]

and \( \gamma'_p(\omega) \) is easily computed:

\[
\frac{d\gamma_p(\omega)}{d\omega} = 4[1 - \tilde{K}(\omega)] = 4[1 - \omega \tilde{K}(\omega) - i\omega \tilde{K}'(\omega)], \tag{4.16}\]

where we have applied the well-known relation

\[
\frac{d\tilde{E}(k)}{dk} = \frac{1}{k} \left[\tilde{E}(k) - \tilde{K}(k)\right]
\]

to find \( \gamma'_p(\omega) \) and then (4.10) to present its components at \( \omega < 1 \).

As \( \gamma_p(1) = 1/V^*_p \), \( \text{Im} \ \gamma'_p(1^-) = -4\tilde{K}'(1) = -4 \), one finally obtains:

\[
\Delta g_p(1^-) = \frac{8/\pi}{1/V - 1/V^*_p}. \tag{4.17}\]
Chapter 5

Electronic and magnetic structure of vanadates

During the last decades a number of theoretical and experimental works have been devoted to the study of low-dimensional magnetic materials. Particular attention has been paid to one-dimensional antiferromagnets. In that respect vanadium oxides are currently intensively investigated as they often form $S = 1/2$ or $S = 1$ systems with reduced dimensionality.

Spin chains and ladders are of fundamental interest for solid state physics due to their peculiar properties [66]. In the last years many spin-chain compounds were found, mostly cuprates [66, 67, 68] and vanadates [70]. One can distinguish between the corner-sharing compounds with a $180^\circ$ (T)ransition metal–(L)igand–T bond ($\text{Sr}_2\text{CuO}_3$ [67, 71]) and the edge-sharing compounds with a $90^\circ$ T–L–T bond ($\text{Li}_2\text{CuO}_2$, $\text{CuGeO}_3$, [68] $\text{MgVO}_3$ [70]). In cuprates the relevant $d$ orbitals are directed towards the ligand ions, which results in a strong antiferromagnetic superexchange interaction for a $180^\circ$ T–L–T bond and a weaker ferromagnetic coupling for a $90^\circ$ T–L–T bond according to the Goodenough-Kanamori-Anderson (GKA) rules [72]. Deviations from the GKA rules are known for $\text{CuGeO}_3$ due to the presence of side groups [73].

Below we present calculations for some novel vanadates.

5.1 MgVO$_3$

Recently, the compound MgVO$_3$ was proposed as a new candidate for a model spin-chain system and magnetic susceptibility as well as ESR measurements were presented [69, 70]. The observed high-temperature Curie-Weiss behavior with $\theta \approx -100$ K suggest short-range antiferromagnetic spin correlations. The data were analyzed within a one-dimensional frustrated spin-$1/2$ Heisen-
berg model with nearest neighbor $J_1$ and next nearest neighbor $J_2$ exchange couplings and a frustration $\alpha = J_2/J_1$ close to the critical value [74] $\alpha_c = 0.24$ was found. Here we present bandstructure calculations for this compound and a corresponding orbital and tight-binding (TB) analysis.

The base-centered orthorhombic crystal structure of MgVO$_3$ was determined by Bouloux et al. [75] to have $Cmc2_1$ symmetry. Recently the compound was reinvestigated [69, 76] and the much more symmetric $Cmcm$ structure shown in Fig. 5.1 was found. The structure can be viewed as consisting of edge-sharing VO$_2$ chains running along the $c$-direction and coupled in $a$-direction by V–O–O–V bonds.

The LSDA calculations were scalar-relativistic, the exchange and correlation potential from Ref. [10] was used. The set of valence orbitals was chosen

<table>
<thead>
<tr>
<th>$Cmcm$</th>
<th>$a = 5.2870$ Å</th>
<th>$b = 10.030$ Å</th>
<th>$c = 5.2390$ Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x$</td>
<td>$y$</td>
<td>$z$</td>
</tr>
<tr>
<td>Mg</td>
<td>0</td>
<td>0.4272</td>
<td>1/4</td>
</tr>
<tr>
<td>V</td>
<td>0</td>
<td>0.0687</td>
<td>1/4</td>
</tr>
<tr>
<td>O1</td>
<td>0.2390</td>
<td>0</td>
<td>1/2</td>
</tr>
<tr>
<td>O2</td>
<td>0</td>
<td>0.2314</td>
<td>1/4</td>
</tr>
</tbody>
</table>

Table 5.1: Crystal structure parameters of MgVO$_3$ [76].
5.1. MgVO₃

Figure 5.2: The five investigated spin patterns. Only vanadium ions are schematically shown (chain zigzag structure is neglected). On the left the computed exchange paths are shown.

to be Mg: 3s3p3d, V: 3s3p3d4s4p and O: 2s2p3d. The inclusion of the vanadium 3s3p states turned out to be unavoidable since the V–O1 distance of about 1.63 Å is small enough to yield a slight overlap of these states with oxygen p-orbitals. The oxygen and magnesium 3d orbitals were taken to increase the basis completeness; though being not occupied they contribute to the overlap density.

We have performed both non-spin-polarized and spin-polarized LDA calculations. In the latter case we have computed five different spin polarization patterns consistent with a primitive unit cell containing up to four chemical formulae, twice as many as in the paramagnetic case. The structures are shown in Fig. 5.2. For each of the patterns we performed two kinds of computation: with parallel and antiparallel spin polarization at the inequivalent vanadium ions. The former calculation was used to check possible numerical inaccuracy of the calculated energy caused by difference of the corresponding Brillouin zones. However no noticeable difference was found. The magnetic moment from the LSDA calculation are to be understood as nominal moments. Their closeness to unity confirms the local spin 1/2 situation. The observed moments should be smaller due to spin fluctuations. The results of the calculations are presented in Table 5.2.

In all spin-polarized calculations we have found magnetic solutions with the total energy being much lower than that of the spin-unpolarized solution. For the ferromagnetic solution the energy gain is about 138.1 meV per formula unit. The deviation of the total energy of the antiferromagnetic solutions from that of the ferromagnetic one is an order of magnitude less and depends on the spin pattern (Table 5.2). The lowest antiferromagnetic solution, AM3, with spins alternating both in a and c directions is about 18.8 meV below the ferromagnetic one. Mapping the results of the calcu-
lated magnetic solutions onto the Heisenberg model

\[ \dot{H} = \frac{1}{2} \sum_{ij} J_{ij} s_i s_j \]  

(5.1)

one finds the following values (all in K) \( J' = 91.2, \ J_a = 19.3, \ J'_a = 3.26, \ J_{ab} = -1.31, \ J'_{ab} = -0.07. \) Thus, as expected, the largest exchange integral connects the neighboring in-chain vanadium atoms, the computed value being in good agreement with experimental value of 100 K [69, 70]. The value of the largest out-of-plane effective ferromagnetic exchange \( 2J_{ab} = -2.6 \) K seems to be too small in comparison with the reported Néel temperature \( T_N = 5.2 \) K [69]. Moreover, for the structure AM3, lowest in the computed total energy, the exchange coupling \( J_{ab} \) is irrelevant, as every vanadium ion has two pairs of diagonal \((ab)\) neighbors with opposite spin, and thus this exchange cancels. In this case the coupling in out-of-plane direction is determined by much weaker exchange integral \( J_b. \) An independent experimental confirmation of the existence of three-dimensional antiferromagnetic phase and its exact structure is desirable.

One should note the qualitative agreement of the relative values of the computed exchange integrals with the results of the TB fit presented below. The reason for the quantitative discrepancy can be an inadequacy of the one-band tight-binding fit or the computation of \( J \) in the framework of the Heisenberg model, as in the latter case the magnetic moment of the vanadium ion differs for different spin-patterns, being about 4–5\% larger than 1 \( \mu_B \) for the ferromagnetic in-chain order and 7.5\% less for the antiferromagnetic one. The magnetic moments of the other ions are much smaller, the only appreciable one occurs at apex oxygen \((01)\) having a value of about 0.05 \( \mu_B \) and being directed opposite to the moment of the neighboring vanadium ion.

The results of the bandstructure calculations are presented in Fig. 5.3. The nonmagnetic solution has metallic character with a half-filled conduction band at the Fermi level, whereas the band splits in the magnetic solutions and an insulator gap opens, being about 0.7 eV and 0.9 eV in ferro- and the

<table>
<thead>
<tr>
<th></th>
<th>AM1</th>
<th>AM2</th>
<th>AM3</th>
<th>AM4</th>
<th>AM5</th>
<th>FM</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E, ) meV</td>
<td>-16.8</td>
<td>-16.4</td>
<td>-18.8</td>
<td>0.5</td>
<td>-4.2</td>
<td>0.0</td>
</tr>
<tr>
<td>( \Delta, ) eV</td>
<td>0.84</td>
<td>0.84</td>
<td>0.91</td>
<td>0.51</td>
<td>0.63</td>
<td>0.68</td>
</tr>
<tr>
<td>( M, ) ( \mu_B )</td>
<td>0.925</td>
<td>0.923</td>
<td>0.926</td>
<td>1.048</td>
<td>1.041</td>
<td>1.049</td>
</tr>
</tbody>
</table>

Table 5.2: The total energy \( E, \) insulating gap \( \Delta, \) and magnetic moment \( M \) of the calculated spin-patterns. The total energy per formula unit is given with respect to that of the ferromagnetic state.
lowest antiferromagnetic cases, respectively. However, it can be expected that the real gap is caused mainly by the electron correlation and is considerably larger than that produced by the magnetic ordering, which is confirmed by the results of the LSDA+\(U\) calculation. The correlation gap should persist in the paramagnetic case as well.

For a deeper understanding of the electronic structure we have performed an orbital analysis for the nonmagnetic solution. For a convenient presentation of the orbital analysis the coordinate system was rotated 90° about the \(a\)-axis so that the quantization axis \(z\) coincides with crystal \(b\)-axis (the \(C_2\)-axis of the VO\(_5\) pyramids). The weight \(w_{sL}^{k}\) of the orbital \(|sL\rangle\) in the Bloch state \(|k\rangle\) (2.4) was taken as

\[
w_{sL}^{k} = |c_{sL}^{k}|^2 / \sum_{sL} |c_{sL}^{k}|^2. \tag{5.2}
\]

According to the analysis, the valence bands consist of a lower oxygen 2\(p\)-orbital complex which is separated by 3 eV from upper vanadium 3\(d\)-orbitals (Fig. 5.3). The 3\(d\)-orbitals are split according to the standard crystal field rules. At \(\Gamma\)-point their energy rises in the order: \(d_{x^2-y^2}, d_{yz}/zx, d_{3z^2-r^2}, d_{xy}\). Only the lowest 3\(d_{x^2-y^2}\)-orbital is partially occupied, being half-filled with two electrons per two vanadium atoms in the primitive unit cell. The corresponding band (Fig. 5.4) is very narrow having a width of only 0.8 eV. The weight of the V: 3\(d_{x^2-y^2}\) orbital in the band is larger than 70 percent, but there are considerable contributions up to 20 percent from the O2: 2\(p_x\) and the V: 3\(d_y\) orbitals, as well as smaller contributions from some other orbitals.

Comparing the situation with that in cuprates having the edge-sharing CuO\(_2\) chains (Li\(_2\)CuO\(_2\) or CuGeO\(_3\)) one observes an important distinction: in the cuprates the relevant Cu:3\(d\)-orbital is directed towards the oxygen ions, whereas in the present case it is directed towards the neighboring vanadium ions. It implies an indirect superexchange mechanism via the intermediate ligand in the cuprates but probably a dominant direct exchange process between neighboring vanadium ions and a much smaller superexchange hopping to the second in-chain neighbor in MgVO\(_3\).

Let us note that the different coordination of the relevant 3\(d\)-orbital in vanadates and cuprates with similar crystal structure has to be a common feature, because in vanadates the half-filled 3\(d\)-orbital is the energetically lowest in contrast to the cuprates, where it is the energetically highest one.

The coupling between the neighboring chains occurs mainly in the \(xy\)-plane via the intermediate O2: 2\(p_x\) orbitals. This is manifested by the strong dispersion along the \((k_\alpha, 0, 0)\) direction (Fig. 5.4) of the lower part of the band,
Figure 5.3: Band structure and density of states of MgVO$_3$ for the nonmagnetic (a) and antiferromagnetic (b) solutions. The symmetry point coordinates of the $C$-base centered orthorhombic Brillouin zone are given in units $\pi(2/a, 2/b, 1/c)$.
which has a remarkable contribution from the orbital, whereas the upper part
having a contribution only from the O2: \(2p_y\) orbital is almost dispersionless.
Fig. 5.5 showing the relevant orbitals at the \(\Gamma\)-point illustrates the interchain
coupling via \(\sigma\)-bonds of neighboring O2: \(2p_x\) orbitals.

To quantify the result a TB analysis has been performed for the relevant
band of the nonmagnetic solution. Hopping processes to the neighbors in
the nearest chains and up to the third in-chain vanadium ion were taken into
account (the lower index of \(t\) designates the chain and the prime signs – the
in-chain order):

\[
E_0 - E_k = 2t' \cos k_c \frac{c}{2} + 2t'' \cos k_c c + 2 \cos k_a a \left( t_a + 2t'_a \cos k_c \frac{c}{2} + 2t''_a \cos k_c c \right) \\
+ 4 \cos k_a a \cos k_b b \left( t_{ab} + 2t'_{ab} \cos k_c \frac{c}{2} + 2t''_{ab} \cos k_c c \right), \quad (5.3)
\]

yielding the following parameters (in meV):
Figure 5.5: Relevant V: 3d_{x^2-y^2} and O2: 2p_{x,y} orbitals coupling the spins in chain y-direction and in the orthogonal x-direction and the chosen in-plane transfer paths. The orbital phases correspond to the Γ-point.

<table>
<thead>
<tr>
<th>$t'$</th>
<th>$t''$</th>
<th>$t_a$</th>
<th>$t_a'$</th>
<th>$t_a''$</th>
<th>$t_{ab}$</th>
<th>$t_{ab}'$</th>
<th>$t_{ab}''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>160.3</td>
<td>19.9</td>
<td>39.6</td>
<td>19.8</td>
<td>7.5</td>
<td>-2.4</td>
<td>4.0</td>
<td>0.4</td>
</tr>
</tbody>
</table>

The data confirm that the ratio $t''/t'$, a measure for the frustration in the chain direction, is much smaller than the corresponding value for CuGeO$_3$ and Li$_2$CuO$_2$ [77, 78]. It should be noted that the parameter $t'$ is much larger than the corresponding inter-ladder hopping in NaV$_2$O$_5$ given in Ref. [79], probably due to a mutual compensation of different transfer paths in the latter compound.

An estimate of the corresponding exchange integrals of the effective Heisenberg Hamiltonian (5.1) can be performed in the one-band Hubbard description, which gives an antiferromagnetic exchange of roughly $J_j = 4t_a^2/U$ with a value of $U$ still to be determined. Using the computed value of $J_j = 7.86$ meV one gets $U = 13$ eV which seems to be heavily overestimated. Most probably, additional ferromagnetic processes (possibly via the 3d$_{yz}$ orbital or indirect processes via oxygen) have to be included to improve the estimate. Our TB analysis suggests a rather large value for $J_a$. It gives two-dimensional antiferromagnetic order with the frustration terms $J''$ and $J_a'$ (Fig. 5.5). Though $t''$ and $t_a'$ are of nearly the same value, due to the larger coordination number, $J_a'$ dominates. In a simple mean field approach one can define an effective
frustration exchange $J'_n = 2J'_a + J''$ yielding an effective frustration $J'_{\text{eff}}/J'$ of roughly 0.05. The discrepancy with the value of 0.24 given in Ref. [70] may result from an overestimate of $J'$ in the one-band Hubbard model or from an inadequacy of the one-dimensional analysis of the experimental results performed in Ref. [70].

Thus, we have found that the VO$_2$ chains of MgVO$_3$ have indeed a spin-1/2 structure with the relevant 3d orbitals of the neighboring in-chain vanadium ions directed towards each other. It suggests a direct antiferromagnetic exchange process between the neighboring in-chain spins. A similar process was proposed for the inter-ladder exchange coupling in MgV$_2$O$_5$. [80] The importance of the direct vanadium $d$-$d$ transfer was also anticipated in Ref. [81] for CaV$_4$O$_9$, a compound with V-V distance slightly larger (3.00 Å) than in MgVO$_3$ (2.96 Å), where a value of 80 meV for the transfer was reported. Besides the direct exchange we have found some additional superexchange terms which give rise to the coupling between the chains in the $y$-direction and to the frustration. The dominant frustration occurs between the neighboring chains in contrast to the naive picture of the frustration due to the next-nearest in-chain neighbor superexchange. It suggests that the experimental data require an analysis in the framework of a two- rather than a one-dimensional Heisenberg model.

5.2 Sb$_2$O$_2$VO$_3$

A recent investigation [82] has proposed the compound Sb$_2$O$_2$VO$_3$ as a new inorganic material exhibiting the spin-Pierls transition. Though the study of such a transition in spin-1/2 one-dimensional antiferromagnetic chains has started a long time ago [83, 84], it was not until 1993 that the first inorganic example CuGeO$_3$ was found [85]. At variance with the copper germanate Sb$_2$O$_2$VO$_3$ has revealed a pseudo-gap which should be a general feature of one-dimensional systems [86]. The reason for the absence of the pseudo-gap in CuGeO$_3$ is not completely clear since one could observe pretransitional lattice fluctuations above the transition temperature [87]. Possibly, these fluctuations are too fast to lead to a pseudo-gap, i.e. CuGeO$_3$ is in the nonadiabatic limit [88]. Three-dimensional phonons also can lead to a significant suppression of the pseudo-gap [89, 90].

The crystal structure of Sb$_2$O$_2$VO$_3$ was defined by Darriet et al. [91]. The structure is base-centered monoclinic $C2/c$. The parameters of the unit cell are $a = 18.03$ Å, $b = 4.800$ Å, $c = 5.497$ Å, $\beta = 94.58^\circ$. The crystal structure can be viewed as consisting of planes of VO$_3$ chains separated in $a$ direction by doubled SbO layers. The structure is shown in Fig. 5.6 (from Ref. [82]).
Figure 5.6: Polyhedral representation of the Sb$_2$O$_2$VO$_3$ crystal structure illustrating the chains of VO$_5$ pyramids. The black circles depict the oxygen ions, the white – the antimony ones. The vanadium ions are inside the pyramids and not shown.

<table>
<thead>
<tr>
<th></th>
<th>VO$_5$ pyramid</th>
<th>Chain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V–O$_A$</td>
<td>V–O$_B$</td>
</tr>
<tr>
<td>MgVO$_3$</td>
<td>1.63</td>
<td>1.95</td>
</tr>
<tr>
<td>Sb$_2$VO$_5$</td>
<td>1.59</td>
<td>1.91/2.04</td>
</tr>
<tr>
<td>Interchain</td>
<td>d$_b$</td>
<td>d$_{ab}$</td>
</tr>
<tr>
<td>MgVO$_3$</td>
<td>5.29</td>
<td>5.67</td>
</tr>
<tr>
<td>Sb$_2$VO$_5$</td>
<td>4.80</td>
<td>9.33</td>
</tr>
</tbody>
</table>

Table 5.3: Parameters characterizing the VO$_5$ chain structure. Distances are given in Å. O$_A$ and O$_B$ designate apex and base oxygen ion, respectively. The “Next chain” section represents the distances between close ions in the different neighboring chains.

The structure of the VO$_5$ chains is very similar to that of MgVO$_3$ as illustrated in Fig. 5.7 with one substantial distinction. While in the latter compound the VO$_5$ pyramids in the nearest chains direct to each other by oxygen ions belonging to the base of the pyramids, in Sb$_2$O$_2$VO$_3$ it is the apex oxygen atom which is directed to the base of a pyramid in the neighboring chain. As the apex oxygen ion is strongly bounded with vanadium ion, the
coupling between the nearest chains in \( \text{Sb}_2\text{O}_2\text{VO}_3 \) should be weaker than in \( \text{MgVO}_3 \) despite the distance between the chains is somewhat shorter. As the distances to the other chains are much larger in \( \text{Sb}_2\text{O}_2\text{VO}_3 \), one can expect that it has much more profound one-dimensional character than \( \text{MgVO}_3 \).

The comparison of some lattice parameters of the two compounds is given in Table 5.3. One sees that though the structure of the \( \text{VO}_3 \) chain in both compounds is almost identical, the interchain arrangement is quite different.

We have carried out scalar-relativistic LSDA calculations for nonmagnetic, ferromagnetic and antiferromagnetic structures of \( \text{Sb}_2\text{O}_2\text{VO}_3 \). Only one antiferromagnetic arrangement with spins alternating along the chain was computed. The basis set was chosen to be \( \text{Sb}:4s4p4d5s5p, \text{V}:3s3p3d4s4p, \text{O}:2s2p3d \). Similar to \( \text{MgVO}_3 \) the spin-polarized calculations give rise to insulating magnetic solutions with the magnetic moment of vanadium ion and the insulating gap being of about 1.024 \( \mu_B/0.52 \) eV and 0.947 \( \mu_B/0.76 \) eV for ferro- and antiferromagnetic solutions respectively, following the trend given by \( \text{MgVO}_3 \). The total energy of the antiferromagnetic solution is 14.2 meV per formula unit lower than that of the ferromagnetic one. In the framework of Heisenberg model (5.1) it corresponds to \( J = 82.4 \) K, three times less than the experimental value reported in Ref. [82].

As in \( \text{MgVO}_3 \) the very narrow band just below the Fermi level is of mostly \( d_{x^2-y^2} \) character\(^1\) and is separated from the rest of the electronic

\(^1\)For the analysis we again change the coordinate system, so that \( z \) quantization axis points in \( b \) direction, and \( y \) axis — in \( c \) direction.
system. However the separation from the above lying states is smaller than for MgVO₃ and one would expect larger hybridization effects. The analysis of hopping processes is more complicated than in the case of MgVO₃ as a part of O2:2p-orbitals there is a considerable admixture of Sb:4p states to the band. The antimony p states mix also strongly with higher lying vanadium dₓz/ᵧz orbitals.

In the nonmagnetic metallic solution a band with a width of about 0.7 eV crosses the Fermi level. The band is shown in Fig. 5.8 together with the band resulting from the tight-binding fit. One sees that the band actually has much smaller dispersion in the direction connecting the nearest chains (TY) especially for the lower part of the band, revealing more profound one-dimensional character than MgVO₃.

For the TB fit of the band we have used the same expression (5.3) as for MgVO₃ with the only distinction that, in accordance with the changed geometry (Fig. 5.7), the coupling in direction b instead of a was included. The calculated parameters are the following (all in meV):

<table>
<thead>
<tr>
<th>t'</th>
<th>t''</th>
<th>tₖb</th>
<th>t'ₖb</th>
<th>tₕb</th>
<th>tₜb</th>
<th>t'ₜb</th>
<th>t''ₜb</th>
</tr>
</thead>
<tbody>
<tr>
<td>154.0</td>
<td>25.7</td>
<td>1.0</td>
<td>0.7</td>
<td>6.3</td>
<td>-7.1</td>
<td>-5.2</td>
<td>3.6</td>
</tr>
</tbody>
</table>

In Table 5.4 we compare the TB parameters, obtained by similar fit for some one-dimensional compounds with spin-Peierls (Sb₂O₂VO₃, CuGeO₃) or antiferromagnetic ground-state (MgVO₃, Sr₂CuO₃, Ca₂CuO₃). One sees that tₜ/t' is 5 times smaller in Sb₂O₂VO₃ than in CuGeO₃ suggesting a 25 times smaller interchain exchange coupling, whereas t' is roughly the same.²

²Also the experimental values for the in-chain exchange couplings are similar with J' ≈ 21 meV and 14 meV for Sb₂O₂VO₃ [82] and CuGeO₃ [92], respectively.
5.3. VOMoO$_4$

<table>
<thead>
<tr>
<th></th>
<th>Sb$_2$O$_2$VO$_3$</th>
<th>CuGeO$_3$ [94]</th>
<th>MgVO$_3$</th>
<th>Sr$_2$CuO$_3$ [71]</th>
<th>Ca$_2$CuO$_3$ [71]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t'$</td>
<td>154</td>
<td>175</td>
<td>160</td>
<td>550</td>
<td>520</td>
</tr>
<tr>
<td>$t''$</td>
<td>26</td>
<td>51</td>
<td>20</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>$t_\perp$</td>
<td>7</td>
<td>34</td>
<td>40</td>
<td>30</td>
<td>65</td>
</tr>
</tbody>
</table>

Table 5.4: The tight-binding parameters for some one-dimensional compounds. $t'$ and $t''$ are the in-chain hopping parameters to the nearest and next-nearest neighbor, respectively. $t_\perp$ is the largest out-of-chain hopping parameter.

In contrast, MgVO$_3$ shows such a large interchain coupling, that it is better regarded as an anisotropic two-dimensional system. Furthermore, $t''/t'$ is two times smaller in Sb$_2$O$_2$VO$_3$ than in CuGeO$_3$ which indicates a four times smaller frustration. It is known that magnetic frustration can lead to a spin gap [93], and can therefore be regarded as the second driving force towards the spin-Peierls transition besides the electron-lattice interaction. It should be even the dominating effect in CuGeO$_3$ due to the remarkable interchain coupling in combination with the large frustration since interchain couplings usually tend to destabilize the spin-Peierls state in the direction of antiferromagnetic order. On the other hand, Sb$_2$O$_2$VO$_3$ can be expected to be a much better model-spin Peierls system in the classical sense. The ratios of $t_\perp/t'$ and $t''/t'$ in Sb$_2$O$_2$VO$_3$ are of the same order than in the edge-sharing cuprate chain Sr$_2$CuO$_3$ being presently the best model compound for 1D spin 1/2 antiferromagnetism [71]. But the absolute values of $t'$ are very different leading to a one-order of magnitude difference for $J'$. That might be the reason for the different ground states in both compounds since the energy gain due to dimerization can be expected to be similar whereas the magnetic order is much more favored in Sr$_2$CuO$_3$.

5.3 VOMoO$_4$

We conclude this chapter with a remark on the electronic structure of VOMoO$_4$. The crystal structure of VOMoO$_4$ was determined by Eick and Kihlborg [95]. It has tetragonal $P4/n$ symmetry and consists of VO$_5$ pyramids connected by MoO$_4$ tetrahedra, each pyramid and tetrahedron sharing one oxygen ion. The structure is shown in Fig. 5.9. Some insignificant deviation from the perfect tetragonal structure was also reported [99].

The compound is interesting to be investigated as its structure is very similar to that of Li$_2$VOSiO$_4$ intensively studied in the last years both experimentally [96, 97] and theoretically [98] as an example of two-dimensional
Figure 5.9: The crystal structure of VOMoO$_4$. The left panel shows the constructing blocks of the structure: VO$_5$ pyramids and MoO$_4$ tetrahedra. The right panel shows the top view. The $x$ and $y$ axes of the pyramidal and tetrahedral local coordinate systems used in the orbital analysis are shown. The dotted line depicts the paramagnetic unit cell and the solid line – the unit cell, used for presentation of spin patterns.

Figure 5.10: The five investigated spin-patterns. The first three structures have tetragonal symmetry, the last two – monoclinic one.

spin-1/2 Heisenberg system. The structural units of the latter compound are the same upon replacing Mo$^{6+}$ ion with Si$^{4+}$ and adding in the interstitial sites Li$^{1+}$ ions needed for the electronic balance. This substitution results in more symmetric $Pnmm$ tetragonal structure, as it removes twisting of the VO$_5$ pyramids and MoO$_4$ tetrahedra present in VOMoO$_4$ (Fig. 5.9). Despite these changes one can expect from the similarity of their crystal structure that VOMoO$_4$ also should have a two-dimensional electronic structure, contrary to the conclusion of Shiozaki [99] that the compound represents an one-dimensional system with electronic transfer between the pyramids stacked in $c$-direction. However, as seen on the example of Sb$_2$O$_5$VO$_3$, such a transfer is hardly possible.
5.3. \( \text{VOMoO}_4 \)

<table>
<thead>
<tr>
<th>( E ), meV</th>
<th>AM1</th>
<th>AM2</th>
<th>AM3</th>
<th>AM4</th>
<th>AM5</th>
<th>FM</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta ), eV</td>
<td>0.32</td>
<td>0.32</td>
<td>0.65</td>
<td>0.18</td>
<td>0.19</td>
<td>-</td>
</tr>
<tr>
<td>( M, \mu_B )</td>
<td>0.795</td>
<td>0.798</td>
<td>0.824</td>
<td>0.857</td>
<td>0.856</td>
<td>0.825</td>
</tr>
</tbody>
</table>

Table 5.5: The total energy \( E \), insulating gap \( \Delta \), and magnetic moment \( M \) of the calculated spin-patterns. The total energy per formula unit is given with respect to that of the corresponding ferromagnetic state.

To resolve the situation we have carried out scalar-relativistic LSDA calculation for the compound. For the magnetic quantum number resolved orbital analysis we used different coordinate systems for vanadium centered pyramids \((x/y)_p\) and molybdenum centered tetrahedra \((x/y)_t\) as shown in Fig. 5.9. The valence orbital set \( V:3s3p3d4s4p, \text{Mo:4s4p4d5s5p, O:2s2p3d} \) was chosen.

We have computed five spin patterns shown schematically in Fig. 5.10. The spin-polarized solutions give stable ferro and antiferromagnetic states with magnetic moment on vanadium ion being about 0.8 \( \mu_B \). The lowest antiferromagnetic state is about 52 meV lower than the ferromagnetic one and gives rise to an insulating state with gap of about 0.32 eV. The ferromagnetic solution as well as the nonmagnetic one are metallic. The details are presented in Table 5.5.

One should mention that distinct from case of \( \text{MgVO}_3 \) the computations reveal a systematic error resulting in a considerable shift of the ferromagnetic state energy of structures AM2/AM3 (~ 40 meV) and AM4/AM5 (~ 10 meV) with respect to structures FM/AM1, whereas within the pairs the energy discrepancy is practically negligible. Though the reason for the systematic error, obviously depending on the shape of the Brillouin zone, is not completely clear, we are deeply convinced that the shift is equally applied to both solutions with parallel and antiparallel spin polarization. Therefore we set the energy zero for each of the structures to the energy of its ferromagnetic solution.

Mapping the results of total energy calculations onto the Heisenberg Hamiltonian \((5.1)\) one obtains the following exchange constants (all in K): \( J_1 = 151.6, J_2 = -10.5, J^z = 2.5, J^z_1 = -0.1, J^z_2 = -0.3 \). The lower indices 1 and 2 designate the nearest and next-nearest in-plane neighbor, respectively. The upper index \( z \) denotes the corresponding parameter in \( c \)-direction. The exchange with the vanadium ions situated above and below the nearest in-plain neighbor are represented in our model by the single parameter \( J^z \). Though the hoppings are in fact inequivalent, it appears to be unimportant as the value of \( J^z \) (as well as that of \( J^z_2 \)) is smaller than the pre-
cision of the current calculation. As regards the other calculated parameters one should especially note that the exchange with the next-nearest neighbor $J_2$ is ferromagnetic. Thus, no two-dimensional frustration is expected.

The computed value of the exchange parameter $J_1$ is in good agreement with the experimental value of 156 K calculated from the magnetic susceptibility\(^3\) [99]. One should however keep in mind that the curve was fitted by the one-dimensional Bonner-Fisher expression [100] for isotropic Heisenberg spin 1/2 chain. It is a well-known result, that for a similar two-dimensional system the ratio $T_{\text{max}}/J$, where $T_{\text{max}}$ is the temperature at which the temperature dependence of the magnetic susceptibility has the maximum, is approximately 1.5 times larger than in one-dimensional case [101]. This would yield a $J_1$ value of about 100 K for VOMoO$_4$. However in the framework of anisotropic Ising-Heisenberg model the ratio $T_{\text{max}}/J$ may drastically reduce [101]. The measured temperature dependencies of longitudinal and transversal magnetic susceptibilities [102] give strong argument in favor of the anisotropic model.\(^4\)

As in previous examples of MgVO$_3$ and Sb$_2$O$_2$VO$_3$ the bandstructure calculation reveal a very narrow (about 1.1 eV) band mostly of V:3$d_{x^2-y^2}$ character crossing in the nonmagnetic solution the Fermi level. The dispersion of the band shows that actually the two-dimensional scenario is realized as in Li$_3$VOSiO$_4$ [98]. However distinct from the latter compound (as well as from the situation in MgVO$_3$ and Sb$_2$O$_2$VO$_3$) the band is not well separated from the rest of the electronic system and in fact is strongly hybridized especially in the vicinity of $M$-point with bands lying above, mostly of V:3$d_{yz/zx}$ character with some admixture of Mo:4$d_{3z^2-r^2}$ and oxygen $2p$ orbitals. Besides, the Mo:4$d_{x^2-y^2}$ orbital is hybridizing with the lower part of the vanadium band over all $k$-space (Fig. 5.11).

From the orbital projected DOS one observes that at most seven orbitals can be important for the electron transfer. However the role of the pyramidal apex oxygen ion (O1) is passive. Its $p$-orbitals do not take part in the electron transfer but rather hybridize with vanadium orbitals. As the energy of V:3$d_{3z^2-r^2}$ orbital is far away from Fermi level, only O1:2$p_{x/y}$ orbitals hybridizing with V:3$d_{zx/yz}$ are important as the electron distribution in the hybridized orbitals changes along the tetragonal axis $c$. However in the plane orthogonal to the axis, the symmetry of the orbital is preserved. The role

\(^3\)The value differs by a factor of 2 from the value reported in Ref. [99] due to another definition of the Heisenberg Hamiltonian.

\(^4\)When this part of the thesis was completed the author learnt of Ref. [103], where the magnetic susceptibility was reinvestigated and the Curie-Weiss high-temperature behavior with $\Theta = 155 \pm 20$ K was reported. As in the two-dimensional spin-1/2 case the Curie-Weiss temperature $\Theta$ is equal to $J_1$ (or more precisely to the value $\frac{1}{2} \sum_{\mathbf{R}} J(\mathbf{R})$), the measured value is in excellent agreement with the result of our calculation.
5.3. VOMoO$_4$

![Graph showing band structure and orbital projected DOS of nonmagnetic state of VOMoO$_4$.](image)

Figure 5.11: Band structure and orbital projected DOS of nonmagnetic state of VOMoO$_4$. The lower panels show the band structure in narrower window around Fermi level. For the magnetic quantum number resolved DOS the coordinate systems centered at vanadium and molybdenum ions shown in Fig. 5.9 were used.

...of the pyramidal base (or tetrahedral) oxygen ions (O2) is more complicated and more important as obviously the electron transfer between vanadium ions is mediated by MoO$_4$ tetrahedra. To understand the role better it is advantageous to abstract for a moment from the twisting of the pyramids and tetrahedra and consider an idealized structure similar to that of Li$_2$VOSiO$_4$.

At first there can be a direct transfer between neighboring oxygen ions. As seen from the partial DOS this process is dominating in the upper part of the band. The transfer is mediated most probably via the oxygen $p_z$ orbitals directed towards each other along the “horizontal” edges of the tetrahedron. As however the orbitals are orthogonal to the corresponding vanadium $d_{x^2-y^2}$-orbitals the Hund’s exchange between the on-site oxygen $p_x$ and $p_y$ orbitals should be involved. From these considerations it follows that the transfer is a) much larger for the hopping to the next-nearest vanadium ion than to the
nearest one and b) the value of transfer is quite small. Both statements are true for Li\textsubscript{2}VOSiO\textsubscript{4} where Si orbitals are unimportant [98].

The second kind of transfer involves Mo:4d-orbitals. In the idealized geometry the chemical bonds are decoupled into two types. The first type involves O2:2p\textsubscript{z} orbitals which connect V:3d\textsubscript{xz/yz} and Mo:4d\textsubscript{3z²-r²} orbitals and the second one – the O2:2p\textsubscript{x/y} (depending on the site) connecting vanadium and molybdenum d\textsubscript{x²-y²} orbitals. The twisting of the pyramids and tetrahedra couples both transfer paths but, even though this twisting is in VOMoO\textsubscript{4} quite appreciable, one is still able to discriminate these two idealized bands in the magnetic quantum number resolved DOS (Fig. 5.11). In the antiferromagnetic state the lower part of the band splits from the rest of the system which is shifted far above the Fermi level. Thus only the transfer via π-bonds V:3d\textsubscript{x²-y²}–O:2p\textsubscript{x/y}–Mo:3d\textsubscript{x²-y²}–O:2p\textsubscript{x/y}–V:3d\textsubscript{x²-y²} should be considered in model calculations. In the idealized structure such kind of transfer should give a factor of 2 for the relation between nearest and next-nearest neighbor transfer in qualitative agreement with the tight-binding fit results presented below.

As was mentioned the relevant band is strongly hybridized with the bands lying above. Such a hybridization impedes the tight-binding analysis. Therefore for the fit we have chosen the part of the band Π–Z–R–A–Z on the top of the Brillouin zone, where the band is less subjected to the hybridization. As it has been done in Ref. [98] we use three TB parameters: \( t_1 \) for the nearest neighbor hopping, \( t_2 \) for the next-nearest one and \( t_z \) for that connecting neighboring planes and fit the band by the expression\(^6\)

\[
E_0 - E_k = 4t_1 \cos k_x a \frac{a}{2} \cos k_y a \frac{a}{2} + 2t_2 [\cos k_x a + \cos k_y a] + 2t_z \cos k_z a.
\]

The results are presented in Table 5.6.

<table>
<thead>
<tr>
<th></th>
<th>( t_1 )</th>
<th>( t_2 )</th>
<th>( t_z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOMoO\textsubscript{4}</td>
<td>136.4</td>
<td>55.5</td>
<td>9.4</td>
</tr>
<tr>
<td>Li\textsubscript{2}VOSiO\textsubscript{4}</td>
<td>8.5</td>
<td>-29.1</td>
<td>4.8</td>
</tr>
</tbody>
</table>

Table 5.6: The tight-binding parameters for VOMoO\textsubscript{4} and Li\textsubscript{2}VOSiO\textsubscript{4}.

One notes, that the nearest neighbor hopping is much larger than the next-nearest one contrary to Li\textsubscript{2}VOSiO\textsubscript{4}, where the situation is just opposite. Further, the drastic change concerns only \( t_1 \) whereas the absolute value of the other parameters increases “only” two times. The results are easy to

\(^6\)In fact the one-band TB fit is not quite appropriate for VOMoO\textsubscript{4} what is evidenced by the lifted degeneracy in \( X-M \) (\( R-A \)) direction.
understand by the role of the Mo$4d_{x^2-y^2}$ orbital in the electron transfer explained above. If one assumes that the direct oxygen-oxygen transfer has the same character as in Li$_2$VOSiO$_4$ the agreement with the estimate $t_1/t_2 = 2$ given above may even improve. One should pay a special attention to the changed sign of $t_2$ which in case of Li$_2$VOSiO$_4$ gives rise to the hole character of the band, so that the authors of Ref. [98] even gave the TB parameters in the framework of the hole picture. The reason for the hole-like transfer in Li$_2$VOSiO$_4$ is not yet understood.

Assuming the same value of the on-vanadium repulsion $U$ in both compounds the effective exchange constant in VOMoO$_4$ should be about 25 times larger. This agrees rather well with the position of the maximum of measured magnetic susceptibility in both substances [96, 99]. Combining the values of the computed $t_1$ and $J_1$ one obtains for $U$ the value of 9.5 eV, which seems, just as in the case of MgVO$_3$, to be overestimated.
Chapter 6

Summary

In this thesis we have considered some aspects of low-dimensional spin-1/2 systems focusing on the properties of cuprates and vanadates. One of the most widely used tools for the investigation of real systems in modern solid state physics is Density Functional Theory. Being exact the theory requires some approximations like L(S)DA for the real calculations. However the latter approximation gives often a wrong ground state for strongly correlated materials.

A simple way to account partly for the on-site correlations is the semiempirical L(S)D+U approximation. In this thesis we derived the effective one-particle Kohn-Sham LSDA+U Hamiltonian introducing an additional term to the Hohenberg-Kohn functional, and thus have incorporated the U correction on the general basis of the Density Functional Theory. The implemented rotational invariant version of LSDA+U based on three (d-shell) or four (f-shell) phenomenological parameters was tested on the series of the late 3d transition metal monoxides. The spectroscopic properties (gap) of the ground state were much improved in comparison with LSDA calculations. The improvement of the magnetic moment is not so evident, as LSDA already gives values close to the experimental ones (if it converges to the magnetic solution). Moreover, the wide scattering of the experimental data impedes the direct comparison of the results. No improvement of lattice constant was achieved. This is most probably connected with an uncertainty in the choice of the double-counting term.

Comparing the experimental values of the magnetic moment with spin-only values of nonrelativistic calculations one needs a tool for estimation of the orbital component of the total magnetic moment, as it is not completely quenched even for 3d transition metals (especially in cases of high local symmetry). We have developed a simple model giving a rather good agreement with experiment for the 3d transition metal monoxides. The model can be
very useful for visualization of the effect of unquenching the orbital moment by spin-orbit interaction.

In the last years many investigations aimed at a description of impurity influence on the electronic structure of cuprates. One of the most intriguing subjects is the replacement Zn/Cu impurity, as already 2\% impurity concentration breaks the superconducting properties of the CuO$_2$ plane. We presented a simple microscopical model, describing the Zn impurity ion as a vacancy for $d$-states on Cu sites. Applying the projection technique for the Green functions in terms of the Hubbard operators we obtained the Dyson equation, that was solved by applying the standard $T$-matrix technique. We took an advantage of full treatment of the $d$-symmetry of the wave functions at Cu-sites of the host lattice that resulted in special forms for the $s$-, $p$- and $d$-symmetry of the wave functions, partial scattering matrices, and Green functions. In particular, the $s$- and $p$-symmetry scattering matrices appear only due to the perturbation potential induced by the vacancy at the nearest neighbor sites. The additional states induced by the perturbation, considered here as a free parameter, are either resonant peaks within the $d$-band of the host lattice or localized states outside the band depending on the strength of the perturbation.

The vanadates attract a growing attention in physical community as like cuprates they readily form low-dimensional systems. We have studied three novel compounds. The main structural element of their structures is VO$_5$ pyramids. The formal valence +4 of the vanadium ion gives rise to spin 1/2 low-dimensional systems. We have applied the LSDA approach to compute the exchange and other related parameters of these compounds. The precision of our calculations proves to be appropriate to extract the exchange parameters from a series of computations with different spin arrangements. The results are complementary to the usual tight-binding approach giving the relation of the antiferromagnetic exchange constants based on the Hubbard model in the limit of large $U$. For two compounds, MgVO$_3$ and VOMoO$_4$, the computed values of the nearest neighbor exchange are in excellent agreement with experiment. For the other compound, VO$_2$Sb$_2$O$_5$, there is a discrepancy of a factor 3 between the computed and measured values. The reason for the discrepancy is not yet clear. Our band-structure calculation reveal that MgVO$_3$ and VO$_2$Sb$_2$O$_5$, are actually one-dimensional compounds, though the former is better to treat as a strongly anisotropic two-dimensional compound. The third compound, VOMoO$_4$, appears to be, contrary to earlier assertion, a pure two-dimensional system. The main distinction from the almost isostructural Li$_2$VOSiO$_4$ is the important role of the Mo:4$d$ orbitals in the exchange between vanadium atoms, which makes the nearest neighbor exchange dominant.
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Dresden, den 22. November 2002

Igor Tchaplyguine