Theory of Crystal Fields and Magnetism of $f$-electron Systems

BY

MASSIMILIANO COLARIETI TOSTI

ACTA UNIVERSITATIS UPSALIENSIS
UPPSALA 2004
Dissertation presented at Uppsala University to be publicly examined in Polhemssalen, Ångström Laboratory, Uppsala, Wednesday, May 19, 2004 at 10:15 for the degree of Doctor of Philosophy. The examination will be conducted in English.

Abstract

A parameter free approach for the calculation of the crystal field splitting of the lowest Russell-Saunders J-multiplet in f-electron systems has been developed and applied to selected compounds. The developed theory is applicable to general symmetries and is based on symmetry constrained density functional theory calculations in the local density or in the generalised gradient approximation.

The magnetocrystalline anisotropy of Gd has been analysed. It has been shown that the peculiar orientation of the easy axis of magnetisation is consistent with an S-ground state. Further, the temperature dependence of the easy axis of magnetisation has been investigated and it has been shown that the temperature driven reduction of the effective magnetisation is the principal mechanism responsible for it.

A new method has been developed that allows for theoretical studies of the electronic structure and total energy of elements and compounds in an intermediate valence regime. The method combines model and first-principles band structure calculations, therefore being accurate and computationally efficient. It has been applied to Yb metal under pressure obtaining a remarkable agreement with experimental observations for the equation of state and the x-ray absorption spectroscopy.

Keywords: Crystal Field, Magnetism, Electronic Structure

Massimiliano Colarieti Tosti, Department of Physics, Box 530, Uppsala University, SE-75121 Uppsala, Sweden

© Massimiliano Colarieti Tosti 2004

ISSN 1104-232X
ISBN 91-554-5963-3
urn:nbn:se:uu:diva-4257 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-4257)
a
nanni,
mamma,
kia
e min
lilla
blomma
List of papers

This thesis is based on the collection of papers given below. Each article will be referred to by its Roman numeral.

I First-principles theory of intermediate valence $f$-electron systems
M. Colarieti-Tosti, M.I. Katsnelson, M. Mattesini, S. I. Simak, R. Ahuja, B. Johansson, C. Dallera and O. Eriksson

II Electronic Structure of UC$_x$ Films Prepared by Sputter Co-Deposition
M. Eckle, R. Eloirdi, T. Gouder, M. Colarieti-Tosti, F. Wastin, J. Rebizant
J. Nucl. Mater. (accepted).

III Crystal Field Excitations as Quasi-Particles

IV Approximate Molecular and Crystal Field Excitation Energies derived from Density Functional Theory
M. Colarieti-Tosti, M.S.S. Brooks and O. Eriksson
In manuscript.

V Crystal Field Levels in Lanthanide Systems
M. Colarieti-Tosti, O. Eriksson, L. Nordström, M.S.S. Brooks and J.M. Wills
VI Crystal Field Levels and Magnetic Susceptibility in PuO$_2$
M. Colarieti-Tosti, O. Eriksson, L. Nordström, M.S.S. Brooks and J.M. Wills

VII On the Structural Polymorphism of CePt$_2$Sn$_2$; Experiment and Theory
Hui-Ping Liu, M. Colarieti-Tosti, A. Broddefalk, Y. Andersson E. Lidström and O. Eriksson

VIII Origin of Magnetic Anisotropy of Gd Metal
M. Colarieti-Tosti, S.I. Simak, R. Ahuja, L. Nordström, O. Eriksson, D. Åberg, S. Edvardsson and M.S.S. Brooks

IX Theory of the Temperature Dependence of the Easy Axis of Magnetization in Gd Metal
M. Colarieti-Tosti, O. Eriksson, L. Nordström and M.S.S. Brooks
Submitted to Phys. Rev. B.

Reprints were made with permission from the publishers.

The following papers are co-authored by me but are not included in the Thesis

- **Theory of the Magnetic Anisotropy of Gd Metal**
  M. Colarieti-Tosti, S.I. Simak, R. Ahuja, L. Nordström, O. Eriksson and M.S.S. Brooks

- **Magnetic Anisotropy from Electronic Structure Calculations**
  L. Nordström, T. Burkert, M. Colarieti-Tosti and O. Eriksson

- **Magnetic x-ray scattering at relativistic energies**
  M. Colarieti-Tosti and F. Sacchetti

Comments on my contribution
In the papers where I am the first author I am responsible for the main part of the work, from ideas to the finished papers. Concerning the other papers I have contributed in different ways, such as ideas, various parts of the calculations and participation in the analysis.
Contents

List of papers i

Introduction 3

1 Density functional theory 5
   1.1 Introduction ........................... 5
   1.2 Local density approximation and the Kohn-Sham equations 5
   1.3 The success of DFT in local approximations ........ 7

2 Solving the DFT equations: the MTO method 9
   2.1 Introduction ........................... 9
   2.2 LMTO in the atomic sphere approximation .......... 10
   2.3 Full-potential LMTO ........................ 14

3 Crystalline electric field 19
   3.1 Introduction ........................... 19
   3.2 Crystalline electric field, the standard theory .... 19
      3.2.1 CEF parameters evaluation from first principles 24
   3.3 Total energy calculations of CEF splitting .......... 26
      3.3.1 Obtaining the CEF charge density ............ 27
      3.3.2 Total energy of a CEF level: symmetry constrained LDA calculations ................. 31
      3.3.3 Generalisation to the magnetic case .......... 33
      3.3.4 Applications ................................ 35

4 Valence stability of $f$-electron systems 39
   4.1 Introduction ........................... 39
   4.2 Comparing volumes ........................ 40
   4.3 The Born-Haber cycle ........................ 41
   4.4 Adding correlation effects ........................ 42
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4.1 Application to Yb metal under pressure</td>
<td>43</td>
</tr>
<tr>
<td>5 Magnetocrystalline anisotropy in Gd metal</td>
<td>47</td>
</tr>
<tr>
<td>5.1 Introduction</td>
<td>47</td>
</tr>
<tr>
<td>5.2 The force theorem</td>
<td>48</td>
</tr>
<tr>
<td>5.3 The anomaly of Gd</td>
<td>49</td>
</tr>
<tr>
<td>Summary and Outlook</td>
<td>53</td>
</tr>
</tbody>
</table>
Introduktion

Under de senaste åren har den kondenserade materiens teori blommat upp, speciellt inom området beräkningsfysik. Fysiker kan nu förstå, med hjälp av datorsimulationer, förutse egenskaper av extremt komplexa system i minutios detalj. Denna kapacitet, att simulera komplexa system, har tyvärr inte alltid följts av en djupare förståelse av dessa system. Datorsimulationer kan ses som virtuella experiment som därför behöver en förklaring, eller en modell. Vi begriper fysikaliska fenomen genom att bygga modeller utifrån våra experimentella undersökningar. I vissa fall är vi tvungna att välja alltför förenklade modeller för att kunna lösa dom men oftast använder vi oss av numeriskt approximerade lösningar av analytiskt olösbara modeller.

I denna avhandling sambandet mellan modeller och datorsimulationer är en återkommande ingrediens. Modeller användes för att generera en input för datorsimulationer i våra studier av elektriska kristallfält som presenteras i kapitel 3. I detta fall har en modell hjälpt oss att utvidga ramen av elektronstruktureräknningar. I vår studie av blandade valens system har vi däremot använt elektronstruktureräknningar för att utvinna inputparametrar till en modell som kan hjälpa oss att förstå fenomenet. Även i studiet av den magnetokristallina anisotropin av Gd har vi försökt att förstå det underliggande skälet bakom det märkliga beteendet av den lätta magnetiseringsaxeln med hjälp av en enkel modell.

Vi vill avsluta denna introduktion med de ord som A. M. N. Niklasson skrev i sin Doktors avhandling:

"Det verkligt mystiska är sambandet mellan verklighet och modell. Det ena vet vi ingenting om och den andra har vi hittat på själv."
Introduction

In recent years the field of computational condensed matter physics has experienced a blossom. Physicists can nowadays, with computer simulations, predict minute properties of extremely complex systems. This improved capability of simulating complex systems is unfortunately not always correlated to a better understanding of those systems. Computer simulations can be seen as virtual experiments and therefore need an explanation, or a model. We understand physical phenomena by constructing models out of our experimental investigations. Sometimes we are forced to choose oversimplified models in order to be able to solve them but more and more often we resort to numerical approximate methods in order to solve the analytically unsolvable equations of a model.

In this Thesis the interplay between models and computer simulations is an underlying feature. Models are used to generate an input to computer simulations in our crystalline electric field studies presented in chapter 3. In this case a model helped us in widening the range of applicability of electronic structure calculations. In our study of intermediate valence systems, instead, we used electronic band structure calculations in order to obtain input parameters for a model that can give us a better insight in the phenomenon. Also, in the study of the magnetocrystalline anisotropy of Gd, we tried to understand, with the help of a simple model, the reason for the peculiar behaviour of the easy axis of magnetisation.

We would like to conclude this introduction with the words that A. M. N. Niklasson wrote in his PhD thesis

"What is really mysterious is the relation between reality and models. We know nothing about the former and we made up the latter."
Chapter 1

Density functional theory

1.1 Introduction

It is remarkably simple to show that for an interacting electron gas in an external potential \( v(\mathbf{r}) \)

"there exists a universal functional of the density, \( F[n(\mathbf{r})] \), independent of \( v(\mathbf{r}) \), such that the expression \( E \equiv \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})] \) has as its minimum value the correct ground state energy associated with \( v(\mathbf{r}) \)."

The quote is taken from the abstract of the article in Ref. 1 by P. Hohenberg and W. Kohn that, despite the simplicity, was one of the main reasons behind the awarding of the Nobel prize in Chemistry to W. Kohn in 1998. The demonstration (see Ref. 1) is done in two steps: First the fact that the total energy is a unique functional of the density is proved and then it is shown that this functional has its minimum for the correct ground-state density. The work of Hohenberg and Kohn laid the basis for a transition from a quantum theory of solids based on wave-functions to one based on the density with an impressive drop of the number of variables\(^a\). In the following we will show how, based on this theorem, a new way of treating many body systems could be devised.

1.2 Local density approximation and the Kohn-Sham equations

The functional \( F \) introduced in the previous section contains the kinetic energy,

\[
T \equiv \frac{1}{2} \int \nabla \Psi^*(\mathbf{r}) \nabla \Psi(\mathbf{r}) d\mathbf{r},
\]

\(^a\)This at the cost of restricting ourselves to the ground state.
Chapter 1. Density functional theory

and the interaction between the electrons

\[
U \equiv \frac{1}{2} \int \frac{\Psi^*(r)\Psi^*(r')\Psi(r')\Psi(r)}{|r - r'|} dr dr',
\]

where \( \Psi(r) \) is the (unknown) wave function of the entire system and atomic units are used. A more convenient expression for the ground-state energy of an interacting inhomogeneous electron gas in a static potential \( v(r) \) is

\[
E \equiv \int v(r)n(r)dr + \frac{1}{2} \int \frac{n(r)n'(r)}{|r - r'|} dr dr' + G[n], \tag{1.1}
\]

where the long range Coulomb potential is separated out from the functional \( F[n(r)] \). Since the functional \( G[n] \) is not yet specified there is no problem in having the self-interaction term not explicitly excluded in the electron-electron Coulomb interaction. Namely one could have a cancellation of the double counting term present in the Coulomb contribution by a corresponding term in \( G[n] \) as it happens in Hartree-Fock theory.\(^2\)

Now the question to address is how to find the unknown universal functional \( G[n] \). W. Kohn and L. J. Sham in Ref. 3 made the first proposal for an approximate functional leading to a set of self-consistent equations for the determination of \( E \) and \( n(r) \). They divided \( G \) in two parts

\[
G[n] = T_s[n] + E_{xc}[n], \tag{1.2}
\]

where \( T_s[n] \) is the kinetic energy of the non interacting electron gas and \( E_{xc}[n] \) is the exchange-correlation energy, of which Eq. (1.2) is the definition. Therefore \( E_{xc}[n] \) will also contain the difference between the real kinetic energy and \( T_s \), that is, \( T_{xc} \equiv T - T_s \). Supposing now a slowly varying density, one can write\(^3\)

\[
E_{xc}[n] \simeq \int n(r)\epsilon_{xc}[n(r)]dr. \tag{1.3}
\]

Then, once an expression for \( \epsilon_{xc}[n(r)] \) is given, it is possible to find the energy and the density by solving the constrained variational problem

\[
\begin{align*}
\frac{\delta E[n(r)]}{\delta n(r)} &= 0 \\
\int n(r)dr &= N
\end{align*}
\]

where \( N \) is the total number of electrons. One then finds that \( E \) and \( n(r) \) are obtained solving self consistently

\[
\begin{align*}
(-\nabla^2 + V[n(r)])\psi_i &= \epsilon_i\psi_i \\
n(r) &= \sum_i |\psi_i|^2
\end{align*} \tag{1.4}
\]

6
1.3 The success of DFT in local approximations

with $V$ being the sum of the external potential $v(r)$, the electron Coulomb potential and the exchange-correlation potential, $\mu_{xc}[n]$. The latter is defined as

$$
\mu_{xc}[n(r)] = \frac{\delta E_{xc}[n(r)]}{\delta n(r)} = \epsilon_{xc}[n(r)] + n(r) \frac{\delta \epsilon_{xc}[n(r)]}{\delta n(r)}.
$$

Then, the total energy functional can be written in the form,

$$
E = \sum_i \epsilon_i - \frac{1}{2} \int \frac{n(r)n'(r')}{|r-r'|} \, dr \, dr' + \int \{\epsilon_{xc}[n(r)] - \mu_{xc}[n(r)]\} \, dr,
$$

by observing that the kinetic energy for the non interacting electrons can be obtained for the KS equations (1.4) as

$$
T_s[n(r)] = \sum_i \epsilon_i - \int n(r)V[n(r)] \, dr.
$$

1.3 The success of DFT in local approximations

In Ref. 1 it is shown that in the limit of constant density one recovers the Thomas-Fermi theory and therefore, basically, $\epsilon_{xc}[n(r)] \sim n^{1/3}(r)$. In the past 50 years there have been tremendous efforts to find the exact, or at least the best possible, functional for the exchange-correlation term. The approximation in Eqns. (1.2) and (1.3) is called local density approximation (LDA) and, together with the generalisation to magnetic systems, the local spin density approximation (LSDA), it is the most commonly used approximation to DFT. Modern calculations commonly use a $\epsilon_{xc}[n(r)]$ that is parametrised with the help of quantum Monte Carlo simulations on the homogeneous electron gas.

The approximation of a slowly varying density can be improved by taking into account gradient corrections. This is what has led to the generalised gradient approximation (GGA). Another correction to any local approximation to the exchange-correlation has originated from the observation that, with a local exchange, the term with $r'=r$ in the Coulomb contribution is not exactly cancelled by an analogous term of opposite sign in the exchange term as it happens in the Hartree-Fock theory. For this reason the self interaction correction (SIC) has been devised. However, a part of the self interaction (SI) present in the Hartree contribution is actually cancelled by a local approximation to the exact exchange. This poses a problem for the SIC of Ref. 13 that removes correctly the SI of the Hartree part of the potential but fails in completely removing the SI part of the LDA or GGA exchange.

Surprisingly, improvements on the LDA approximation have not always resulted in a better predictive capability and up to date there is still no known

\[^b\text{GGA is also to be considered a local approximation.}\]
way to systematically improve on the exchange-correlation functional in order to obtain theoretical results that have the requested accuracy. This is, probably, the biggest deficit of DFT. In very recent times J. Perdew and coauthors have made an effort in trying to provide such a systematic scheme of approximations (see Ref. 15 and references therein).

Jones and Gunnarsson in Ref. 16 attributed the success of LDA to the fact that LDA reproduces the integral properties of the LDA exchange-correlation functional. In particular they demonstrated that the integral of the ‘exchange-correlation hole’ depends only on its spherical component, that is the one component that LDA describes well. The GGA was therefore designed to obey the sum rule of exchange-correlation hole. Nevertheless, the number of systems, properties and phenomena that LDA has been able to explain has always been a puzzle to physicists. Especially puzzling is the relationship between KS orbitals, i.e. the $\psi_i$ of Eq. (1.4) and the eigenstates of real systems. In principle there is no relation between them but experience shows that absorption and emission spectra often compare well with calculated density of states (DOS). Examples of such an agreement are given in paper I and in paper II.
Solving the DFT equations: the MTO method

2.1 Introduction

In this chapter we will present the basic concepts underlying a common way of solving the KS equations in a solid. We will focus on linear methods and, in particular, the linearised muffin tin orbital method (LMTO) ideated by O. K. Andersen. Our description is going to be far from complete and is intended only as an introduction. In choosing which algebra to show and which to omit we have tried to give preference to equations that have an underlying new concept or that are particularly significant. We refer the reader, for example, to Refs. 19, 20 and references cited therein, for a comprehensive review.

The basic idea behind the development of the Muffin Tin Orbital (MTO) method for solving the DFT problem is that in solids the potential seen by electrons can be divided in two parts: An atomic-like, almost spherical, deep negative potential in the region close to the atomic lattice sites and a free-electron like, almost flat, potential in the region between lattice sites. If the interstitial potential is approximated by a flat potential and the potential inside the atomic spheres approximated by a spherical potential, the total potential becomes a muffin tin (MT) potential. In this case solutions to the wave equation may be obtained to arbitrarily high accuracy by expanding the wave function inside the atomic spheres in terms of partial waves,

\[
\Psi_j(\vec{r}) = \sum_{RL} \phi_{RL}(E_j, \vec{r}) c_{jRL} + \Psi_i(E_j, \vec{r}) \tag{2.1}
\]

where \(\Psi^i\) is the wave function in the interstitial, \(R\) labels the lattice site, \(L\) is a short notation for \(l, m\) and the coefficients \(c^l\) are chosen such that the partial waves from different spheres join continuously and differentiably. The result is
Chapter 2. Solving the DFT equations: the MTO method

the set of homogeneous, linear equations

\[ M(E)c^j = 0. \]  

(2.2)

The secular matrix \( M \) depends upon energy in a complicated, non-linear, manner. Therefore Eq. (2.2) is solved by finding the roots of the determinant of \( M \). Eq. (2.1) is an example of a single-centre expansion.

An alternative methodology is to use fixed basis functions (as in the LCAO method) as trial functions for the solid and to use the variational principle, leading to the Rayleigh-Ritz equation

\[ (\mathcal{H} - E_j \mathbf{O})c^j = 0, \]  

(2.3)

where \( \mathcal{H} \) and \( \mathbf{O} \) are the Hamiltonian and overlap matrices and the wave function has been expanded in the multi-centre expansion

\[ \Psi_j(\mathbf{r}) = \sum_{RnL} \chi_{RnL}(\mathbf{r}_R) \chi_{RnL}^{j} c_{RnL}^j. \]  

(2.4)

The solutions to the algebraic eigenvalue problem, Eq. (2.3), are easier to obtain than the root searching involved in solving Eq. (2.2). Another advantage of the fixed basis set method is that it may be used for potentials of general shape whereas its disadvantage is that the basis set required to obtain high accuracy may be very large.

Linear methods combine some of the better properties of partial waves and fixed basis set expansions by using envelope functions and augmentation. A set of envelope functions, which is reasonably complete in the interstitial region, is chosen and then augmented inside the atomic spheres by functions related to partial waves inside the atomic spheres. The result is an algebraic eigenvalue problem, Eq. (2.3), with a far smaller basis set than atomic orbitals since the basis set is better adapted to the solid state as it is derived from partial waves. The type of method depends upon the chosen envelope functions. For example, envelope functions that are plane waves give rise to the linear augmented plane wave method (LAPW) whereas envelope functions that are Hankel functions give rise to the linear muffin tin orbital method (LMTO).21

Andersen and his collaborators, developed the method we will briefly describe in this chapter that goes by the name linearised muffin tin orbital (LMTO)18 or LMTO in the atomic sphere approximation (LMTO-ASA).

2.2 LMTO in the atomic sphere approximation

The simplest approximation to the real potential is to take, overlapping, space filling spheres inside which the potential is taken to be spherically symmetric.
2.2. LMTO in the atomic sphere approximation

Outside these atomic spheres instead, the potential is approximated with a constant value (sometimes set to zero). This is the atomic sphere approximation. The flatness of the potential in the interstitial region allows one to approximate the basis functions with the solutions to the radial Helmholtz equation:

\[
\left( \frac{d}{dr} r^2 \frac{d}{dr} + r^2 k^2 - l(l+1) \right) R = 0. \tag{2.5}
\]

The solutions to this are

\[
\begin{align*}
    j_l &= \frac{(kr)^l}{(2l+1)!!}, \\
    n_l &= (2l-1)!! \left( \frac{1}{kr} \right)^{l+1}. \tag{2.6}
\end{align*}
\]

Note that \( j_l \) is regular at the origin while \( n_l \) is irregular. It is convenient to scale those functions as follows

\[
\begin{align*}
    J_l &\equiv j_l(2l-1)!! = \frac{1}{2(2l+1)} \left( \frac{r}{s} \right)^l, \\
    K_l &\equiv n_l(2l-1)!! = \left( \frac{s}{r} \right)^{l+1}. \tag{2.7}
\end{align*}
\]

Here \( s \) is a scaling length usually taken to be the average Wigner-Seitz radius.

Inside the atomic spheres (AT), the basis function is the solution, \( \phi \), of the stationary Schrödinger equation

\[
(-\nabla^2 + V - E) \phi = 0. \tag{2.8}
\]

For reason of foresight let us write here also the energy derivative of (2.8)

\[
(-\nabla^2 + V - E) \dot{\phi} = \phi. \tag{2.9}
\]

We will have to match, continuously and differentiably the function \( \phi \) with a linear combination of the regular and irregular solutions to Eq. (2.5). In general, matching a function, \( \phi \), continuously and differentiably to a linear combination of two others, \( J \) and \( K \), at some point, \( s \), is done by solving for the constants \( a \) and \( b \), the coupled equations

\[
\begin{align*}
    \phi(s) &= aJ(s) + bK(s), \\
    \phi'(s) &= aJ'(s) + bK'(s). \tag{2.10}
\end{align*}
\]

The prime here indicates a derivative with respect to \( r \). The resulting matched function is then

\[
\phi(s) = \frac{W\{\phi, K\} J(s) - W\{\phi, J\} K(s)}{W\{J, K\}}, \tag{2.11}
\]

11
Chapter 2. Solving the DFT equations: the MTO method

where the Wronskian, $W$, is defined as

$$ W\{J, K\} \equiv s^2(JK' - KJ'), \quad (2.12) $$

and $J, K, J', K'$ are evaluated at $s$. The Wronskian between the functions defined in (2.7), $W\{K(r), J(r)\}|_{r=s} = s/2$ is readily evaluated since the one between the spherical Bessel and Neumann functions, $W\{n(kr), j(kr)\} = 1$ (here the derivative is with respect to $x = kr$).

The solutions inside the AT are energy dependent. Andersen\textsuperscript{21} observed that it is possible to approximate to first order $\phi(E)$ with a linear combination of $\phi(E)$ and $\dot{\phi}(E)$, where $E$ is a linearisation energy chosen according to the window of energies $E$ of interest. The other Wronskian that is needed is, therefore, the one between the solution to the wave-equation and its energy derivative, $W\{\dot{\phi}, \phi\}$. This can be calculated observing that from Eqns. (2.8) and (2.9) one can write

$$ \int_0^1 \dot{\phi}(-\nabla^2 + V - E)\phi d\vec{r} - \int \phi(-\nabla^2 + V - E)\dot{\phi} d\vec{r} = -1, \quad (2.13) $$

and using Green’s second identity for integrating the above expression, one obtains

$$ W\{\dot{\phi}, \phi\} = 1. \quad (2.14) $$

Next, one introduces a way to write a function on a crystal that explicitly distinguishes between contributions inside any given AT sphere and the ones in the interstitial. Also this notation is due to Andersen and co-authors and uses the vectorial bra-ket notation

$$ |f_R \rangle >^\infty = |f_R \rangle >_{sphere\ at\ R} + |f_R \rangle >^i - \sum_{R', L'} |f_{R'} \rangle >_{sphere\ at\ R'} T_{R'; R}, \quad (2.15) $$

where the superscript $\infty$ indicates that the function, $f$, extends over the entire crystal, the superscript $i$ means that the function is defined only in the interstitial region and no superscript means that the function is truncated outside the AT region corresponding to the site indicated as a subscript. The matrix $T_{R'; R}$ represents a generalised structure constant matrix that is unknown until the envelope function (see below) is specified. Eq. (2.15) highlights the fact that a function belonging to site $R$ can be written as an expansion around a site $R'$ inside the AT centred on $R'$.

One can write the envelope function of the MTO’s in this notation

$$ |K_{RL}^0 \rangle >^\infty = |K_{RL}^0 \rangle >_{sphere\ at\ R} + |K_{RL}^0 \rangle >^i - \sum_{R', L'} |J_{R' L'}^0 \rangle >_{sphere\ at\ R'} S_{R' L'; R; L}. \quad (2.16) $$
2.2. LMTO in the atomic sphere approximation

In this case the coefficients $S_{R'\mathbf{U},R}^{\mathbf{R},L}$ are well known and are referred to as the energy independent structure constants (as they are determined only by the crystal structure). Schematically this is simply written

$$|\mathbf{K} >^\infty = |\mathbf{K} > - |\mathbf{J} > S. \tag{2.17}$$

We have here dropped the part of the wave-function that explicitly corresponds to the interstitial region. This was done because LMTO-ASA uses overlapping, space filling, atomic spheres.

The solutions inside each sphere are then matched to an envelope function of the form of the one in Eq. (2.17), remembering that, because of linearisation, this solution will be a linear combination of $\phi$ and $\dot{\phi}$

$$|\chi >^\infty = |\phi > - |\dot{\phi} > h, \tag{2.18}$$

where $\dot{\phi} = \dot{\phi} + o\phi$ and $o = <\phi|\dot{\phi}>$. The matrix $h$ is related to the Hamiltonian by

$$<\chi|\mathcal{H} - E_\nu|\chi> = h(1 + oh) \tag{2.19}$$

and the overlap matrix is

$$<\chi|\chi> = (1 + hoh) + hph \tag{2.20}$$

with $p =<\phi|\dot{\phi}>$. At the AT sphere boundary $|\mathbf{K} >^\infty$ is matched to $|\chi >^\infty$,

$$|\mathbf{K} >^\infty \rightarrow -|\phi > W\{\mathbf{K},\dot{\phi}\} - |\dot{\phi} > W\{\mathbf{K},\phi\} + W\{\mathbf{J},\phi\} S. \tag{2.21}$$

Since $o = -W\{\dot{\phi},\mathbf{J}\}/W\{\phi,\mathbf{J}\}$, then

$$W\{\mathbf{K},\dot{\phi}\} W\{\mathbf{J},\phi\} = W\{\mathbf{K},\dot{\phi}\} W\{\mathbf{J},\phi\} + o W\{\mathbf{K},\phi\} W\{\mathbf{J},\phi\}$$

$$= \frac{S}{2} \tag{2.22}$$

and

$$|\mathbf{K} >^\infty \rightarrow - W\{\mathbf{K},\dot{\phi}\}\left\{|\phi > + |\dot{\phi} > \left\{- \frac{W\{\mathbf{K},\phi\}}{W\{\mathbf{K},\dot{\phi}\}} + \frac{W\{\mathbf{J},\phi\} S}{W\{\mathbf{K},\phi\}}\right\}\right\}$$

$$|\mathbf{K} >^\infty \rightarrow - W\{\mathbf{K},\dot{\phi}\}\times \left\{|\phi > + |\dot{\phi} > \left\{- \frac{W\{\mathbf{K},\phi\}}{W\{\mathbf{K},\dot{\phi}\}} + \frac{2}{S} W\{\mathbf{J},\phi\} S W\{\mathbf{J},\phi\}\right\}\right\}. \tag{2.22}$$
Chapter 2. Solving the DFT equations: the MTO method

Since \((-W\{K,\dot{\phi}\})^{-1}\) is the normalisation factor arising from the augmentation performed to obtain linearisation, a comparison to (2.18) yields

\[
h = \frac{W\{K,\phi\}}{W\{K,\dot{\phi}\}} - \frac{2}{S}W\{J,\phi\}SW\{J,\phi\}
\]  

(2.23)

for the Hamiltonian.

In Ref. 22 Andersen and co-authors proposed an interesting idea: Since the envelope function can be chosen according to one’s needs, one can choose it in a way that resembles the grounding of spheres with an electrostatic potential in order to get short range or screened wave-functions. 22 Let us consider, as an example, the case in which one wants to minimise the overlap \(o\) instead. Let us take a modified function \(J_\alpha^\alpha(r) = J_\alpha^0(r) - \alpha K_\alpha(r)\) to which \(-\alpha\) of the irregular solution has been added to the regular solution. Observe, then, that

\[
|J\rangle = |J_\alpha^\alpha\rangle + \alpha |K\rangle
\]

\[
|K\rangle = |K\rangle - |J_\alpha^\alpha\rangle + \alpha |K\rangle S
\]

\[
|K\rangle = |K\rangle [1 - \alpha S] - |J_\alpha^\alpha\rangle S
\]

\[
|K_\alpha^\alpha\rangle = |K\rangle - |J_\alpha^\alpha\rangle S
\]  

(2.24)

where

\[
|K_\alpha^\alpha\rangle = |K\rangle > |1 - \alpha S|^{-1}
\]

\[
S_\alpha = S[1 - \alpha S]^{-1}.
\]  

(2.25)

The functions \(\dot{\phi}^\alpha = \dot{\phi} + o\phi\) and \(J_\alpha^\alpha\) have the same logarithmic derivative at the atomic sphere boundary therefore \(W\{\dot{\phi}^\alpha, J_\alpha^\alpha\} = 0\). One has then that

\[
o = -\frac{W\{\dot{\phi}, J_\alpha^\alpha\}}{W\{\dot{\phi}, J_\alpha^\alpha\}} = 0
\]  

(2.26)

for the orthogonal representation characterised by

\[
\alpha = \frac{\{\dot{\phi}, J\}}{\{\dot{\phi}, J\}}.
\]  

(2.27)

2.3 Full-potential LMTO

The LMTO method can be efficiently used also to solve the DFT equations without making any assumption on the shape of the potential and of the charge
density in both the interstitial and the MT region. In this case the calculation scheme is, quite unimaginative, called full potential (FP). The last generation LMTO-ASA implementations\textsuperscript{20} are already accurate but FP-LMTO removes, at the cost of computational time, also the small influence of the spherically assumed potential inside each ASA sphere. In the FP method the division into MT and interstitial regions carries no approximation as in the LMTO-ASA case. It is then important to understand the role of MT radii choice in FP methods. MT radii do not necessarily reflect any physical property of the potential. The division in MT and interstitial region is only a matter of computational convenience. Of course, the physical properties of the system at hand can help also in making an efficient choice for the MT radii but it is important to keep in mind that this convenient geometrical division of the crystal does not influence the shape of the calculated potential or charge density. A good choice of the MT radii can result in a speed-up of the calculations. Nevertheless, if the series expansion representing the solution inside the MT region and in the interstitial are taken to convergence the total energy is virtually insensitive to the choice of the MT radii. In this case, the MT radii can be regarded as variational parameters. In fact, their influence on the total energy is just through the difference in the functional dependence of the basis function inside and outside the MT region. The minimisation of the total energy with respect to the MT choice gives the optimal FP-LMTO solution to DFT equations.

Another important thing that should be mentioned is the fact that in some cases the Hamiltonian is not the same inside and outside the MT region. This is, for example, the case for relativistic calculations where spin-orbit coupling is commonly considered only inside MT spheres. Then the choice of the MT radii requires some care and physical insight.\textsuperscript{23}

The FP-LMTO implementation that is used throughly in this Thesis is the one of Ref 24. We will therefore follow the notation of that reference, which is reported in the following for convenience. The spherical harmonics related functions are

\begin{align}
Y_{lm}(\hat{r}) &= i^l Y_{lm}(\hat{r}) \\
C_{lm}(\hat{r}) &= \sqrt{\frac{4\pi}{2l + 1}} Y_{lm}(\hat{r}) \\
\tilde{c}_{lm}(\hat{r}) &= i^l C_{lm}(\hat{r})
\end{align}

(2.28)
(2.29)
(2.30)
Also the following functions will be used

\[ \mathcal{K}_l(k, r) = -k^{l+1} \begin{cases} n_l(kr) - i j_l(kr) & k^2 < 0 \\ n_l(kr) & k^2 > 0 \end{cases} \] (2.31)

\[ \mathcal{K}_L(k, \vec{r}) = \mathcal{K}_l(k, r) Y_L(\hat{r}) \] (2.32)

\[ \beta_l(k, r) = j_l(kr)/k^l \] (2.33)

\[ \beta_L(k, \vec{r}) = \beta_l(k, r) Y_L(\hat{r}) \] (2.34)

where \( L \) is a short notation for \( lm \) and \( n_l \) and \( j_l \) are the spherical Neumann and Bessel functions, respectively.

Inside a MT of radius, \( s_\tau \), at site \( \vec{\tau} \), it is convenient to define a local coordinate system referred to the centre of the MT, \( \vec{\tau}_r \equiv D_\tau(\vec{r} - \vec{\tau}) \). The latter defines the rotation \( D_\tau \) that brings global crystal coordinates, \( \vec{r} \), to the site-local ones, \( \vec{\tau} \). Schematically, inside a MT sphere, the basis functions, the charge density, \( n \), and the potential, \( V \), are

\[ \psi_{\tau}(k, \vec{r}) \bigg|_{r < s_\tau} = \sum_{lm} \chi_{lm}(k, \vec{r}_\tau) Y_{lm}(\hat{r}_\tau) \] (2.35)

\[ n_{\tau}(\vec{r}) \bigg|_{r < s_\tau} = \sum_h n_{\tau}(h, \vec{r}_\tau) D_h(\hat{r}_\tau) \] (2.36)

\[ V_{\tau}(\vec{r}) \bigg|_{r < s_\tau} = \sum_h V_{\tau}(h, \vec{r}_\tau) D_h(\hat{r}_\tau) \] (2.37)

where

\[ D_h(\hat{r}_\tau) = D_h(D(\hat{r})) = \sum_{m_h} \alpha(h, m_h) \ell_l h, m_h. \] (2.38)

The last functions, called spherical harmonics invariants, make clear the reason why a rotation to site-local coordinates is made. If the latter are chosen so that there exists a transformation \( T \) such that \( D_{\tau'} = D\tau T^{-1} \) if \( T\tau = \tau' \), then the spherical harmonics invariant will depend only on the global symmetry and are site independent. In addition, by this choice, the number of terms in the expansions (2.36) and (2.37) is minimised.

In the interstitial region the basis functions, the charge density and the potential are instead expressed as Fourier series. Schematically, that is written

\[ \psi(k, \vec{r}) \bigg|_{r > s_\tau} = \sum_{\vec{g}} e^{-i(\vec{k} + \vec{g}) \cdot \vec{r}} \psi(\vec{k} + \vec{g}) \] (2.39)

\[ n(\vec{r}) \bigg|_{r > s_\tau} = \sum_\mathbb{Z} n(\mathbb{Z}) \sum_{\vec{g} \in \mathbb{Z}} e^{i\vec{g} \cdot \vec{r}} \] (2.40)

\[ V(\vec{r}) \bigg|_{r > s_\tau} = \sum_\mathbb{Z} V(\mathbb{Z}) \sum_{\vec{g} \in \mathbb{Z}} e^{i\vec{g} \cdot \vec{r}} \] (2.41)
2.3. Full-potential LMTO

where $Z$ indicates the symmetry stars of the reciprocal lattice. To be more precise, the basis functions in the interstitial will be Bloch sums of spherical Hankel or Neumann functions

$$\psi_i(\vec{k}, \vec{r}) \bigg|_{r>s} = \sum_R e^{i\vec{k} \cdot \vec{R}} \mathcal{K}_i(k_i, |\vec{r} - \vec{\tau}_i - \vec{R}|) \mathcal{Y}_{l_i m_i}(\mathcal{D}_{\tau_i}(\vec{r} - \vec{\tau}_i - \vec{R})).$$  \hfill (2.42)

The index $i$ here identifies the lattice site. At the MT spheres the envelope function can be written as (for site $\vec{R} = 0$)

$$\psi_i(\vec{k}, \vec{r}) \bigg|_{r=s} = \sum_R e^{i\vec{k} \cdot \vec{R}} \sum_L Y_L(\mathcal{D}_s \hat{r}_\tau) (\mathcal{K}_i(k_i, s_\tau) \delta(R, 0) \delta(\tau, \tau_i) \delta(L, L_i)$$

$$+ \partial_L(k s_\tau) B_{L, L_i}(k_i, \vec{r} - \vec{\tau}_i - \vec{R}) \bigg)$$

$$= \sum_L Y_L(\mathcal{D}_s \hat{r}_\tau) (\mathcal{K}_i(k_i, s_\tau) \delta(\tau, \tau_i) \delta(L, L_i)$$

$$+ \partial_L(k s_\tau) B_{L, L_i}(k_i, \vec{r} - \vec{\tau}_i - \vec{k}) \bigg),$$  \hfill (2.43)

where $\hat{r}_\tau = \vec{r} - \vec{\tau}$ and $B$ are equivalent to the KKR structure constant. 25, 26

Defining the two-component vectors

$$K_i(k, r) \equiv (\mathcal{K}_i(k, r), \partial_i(k, r)) \hfill (2.44)$$

$$S_{L, L'}(k, \vec{r} - \vec{\tau}_i - \vec{k}) \equiv \begin{pmatrix} \delta(\tau, \tau') \delta(L, L') & \\
B_{L, L_i}(k, \vec{r} - \vec{\tau}_i - \vec{k}) \end{pmatrix}$$  \hfill (2.45)

the value of a basis function at a MT boundary can be compactly written

$$\psi_i(\vec{k}, \vec{r}) \bigg|_{r=s} = \sum_L Y_L(\mathcal{D}_s \hat{r}_\tau) K_i(k_i, s_\tau) S_{L, L'}(k_i, \vec{r} - \vec{\tau}_i - \vec{k})$$  \hfill (2.46)

now the index $i$ includes $\tau, l, m, k$.

The radial part of a basis function inside the MT is a linear combination of atomic-like functions $\phi$ augmented with their energy derivative $\dot{\phi}$. This will be continuosly and differentiably matched at the MT boundary to the radial function $K$ of Eq. (2.46). Let

$$U(E, r) \equiv (\phi(E, r), \dot{\phi}(E, r)) \hfill (2.47)$$

then, the matching conditions can be schematically written

$$U(E, s) \Omega(E, k) = K(k, s)$$  \hfill (2.48)

$$U'(E, s) \Omega(E, k) = K'(k, s)$$  \hfill (2.49)
Chapter 2. Solving the DFT equations: the MTO method

with $\Omega$ being the $2 \times 2$ coefficient matrix. A basis function inside a MT sphere is then

$$\psi_i(\vec{k}, \vec{r})\bigg|_{r<s_r} = \sum_{L} U_{tL}(E_i, \vec{D}_{L_L} \vec{r}_r)\Omega_{tl}(E_i, k_i)S_{L,L_s}(k_i, \vec{r} - \vec{r}_l, \vec{k})$$

(2.50)

with

$$U_{tL}(E_i, \vec{r}) \equiv y_L(\vec{r})U_{tL}(E_i, r).$$

(2.51)

Something has to be said here about the energy parameters $E_i$. In general a basis set must be able to describe accurately energy levels corresponding to the same quantum number $l$ but differing by the principal quantum number $n$. This is particularly important in actinide (An) systems where, for example, $6p$ and $7p$ states give raise to the infamous problem of the so called ghost bands. It is customary, in fact, whenever there is the need of considering semi-core states (like the $6p$’s in An) to have two different energy panels for valence and semi-core states. Whenever those energy panels overlap non physical ghost bands appear in the calculated electronic structure. The FP-LMTO method\textsuperscript{24} that we have used in this Thesis, is different on that regard. The radial dependence of a basis inside a MT is calculated with a single, fully hybridising, basis set, where one uses atomic-like functions, $\phi$ and $\dot{\phi}$ calculated with energies $\{E_{nl}\}$ with different principal quantum number, $n$. Thus, $E_i$ in Eq. (2.50) indicates the energy parameter $E_{nl}$ corresponding to the principal quantum number assigned to the basis $i$.

Another important parameter in the expression (2.50) is the angular momentum cut-off, $l_{\text{max}}$. This has to be determined from time to time depending on the system at hand. Typical values for which most systems are converged are $l_{\text{max}} = 6-8$. Now, using Eqns. (2.43) –or (2.46)–, (2.42) and (2.50) one can evaluate the potential, the overlap matrix and the charge density matrix elements in the entire crystal.
Chapter 3

Crystalline electric field

3.1 Introduction

In a free atom the quantum number, $J$, corresponding to the total angular momentum, is what is called a good quantum number. This reflects the fact that a free atom has a complete rotational symmetry and its ground state is degenerate with degeneracy equal to $2J + 1$. If one imagines to put a free atom in a crystal this situation will no longer be true. The ions surrounding (called ligands) our "formerly free atom" (called central atom) produce an electric field to which the charge of the central atom adjusts and the $2J + 1$ degeneracy will be removed. We refer to this field as the crystalline electric field (CEF) or simply the crystal field. The new eigenstates are eigenstates of the CEF (linear combinations of the original $2J + 1$ eigenstates) and their corresponding densities are non spherical (see Fig. 3.1). The evaluation of the effects of the CEF in $f$-electron systems is the object of the present chapter.

3.2 Crystalline electric field, the standard theory

The potential due to a charge distribution is

$$V(\vec{r}) = \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \quad (3.1)$$

After expanding the denominator in the integrand of the above equation in spherical harmonics function, $Y_{lm}$, one can write\textsuperscript{27}

$$V(\vec{r}) = \sum_{lm} \frac{4\pi}{2l + 1} Y_{lm}(\hat{r}) \int_{r_+}^{r_-} \rho(\vec{r}') Y_{lm}^*(\vec{r}') d\vec{r}', \quad (3.2)$$
Figure 3.1: Charge densities for an $f$ shell with 2 electrons in cubic symmetry. The top figure corresponds to a $\Gamma_1$ symmetry CEF state while the bottom one is a $\Gamma_4$ state.
3.2. Crystalline electric field, the standard theory

or, separating the \( r_\text{<} \) and the \( r_\text{> \) integrals

\[
V(\vec{r}) = \sum_{lm} r^n Y_{lm}(\vec{r}) \frac{4\pi}{2l+1} \int_0^\infty \rho(\vec{r}') \left( \frac{1}{r'} \right)^{l+1} Y_{lm}(\vec{r}') d\vec{r}' \\
+ \sum_{lm} \left( \frac{1}{r} \right)^{l+1} r Y_{lm}(\vec{r}) \frac{4\pi}{2l+1} \int_0^r (r')^l \rho(\vec{r}') Y_{lm}^*(\vec{r}') d\vec{r}'.
\]

(3.3)

In a MT geometry, one has a natural separation between the contribution originating from the ions surrounding the central atom \( r \geq S_{MT} \) and the on-site contribution \( r \leq S_{MT} \). In conventional crystal field theory the latter is usually neglected as it is assumed that the crystal field at an ion site arises from the ions around that site. In this case one can simply consider \( r = S_{MT} \) and the crystal field potential can be written

\[
V(\vec{r}) = \sum_{lm} A_{lm} r^l Y_{lm}(\vec{r}) = \sum_{lm} B_{lm}(r) C_m(\hat{\vec{r}})
\]

(3.4)

where, the crystal field parameters \( A_{lm} \) are

\[
A_{lm} = \frac{4\pi}{2l+1} \int_S \rho(\vec{r}') \left( \frac{1}{r'} \right)^{l+1} Y_{lm}(\vec{r}'),
\]

(3.5)

and \( \int_S^\infty \) indicates integration outside the given site. Eq. (3.4) also defines the parameters

\[
B_{lm}(r) = \left( \frac{2l + 1}{4\pi} \right)^{1/2} r^l A_{lm}
\]

(3.6)

and

\[
C_m(\hat{\vec{r}}) \equiv \tilde{Y}_{lm}(\hat{\vec{r}}) \equiv \left( \frac{4\pi}{2l+1} \right)^{1/2} Y_{lm}(\hat{\vec{r}})
\]

(3.7)

is a tensor operator.

In general, however, the on-site contribution need not be negligible. If the charge distribution in the solid is known both integrals in Eq. (3.3) may be calculated. Then one should replace Eq. (3.4) with

\[
V(\vec{r}) = \sum_{lm} \left[ A_{lm} r^l Y_{lm}(\vec{r}) + A'_{lm} r^{-(l+1)} Y_{lm}(\vec{r}) \right] = \sum_{lm} B_{lm}(r) C_m(\hat{\vec{r}})
\]

(3.8)

where

\[
A'_{lm} = \frac{4\pi}{2l+1} \int_0^r d\vec{r}' \rho(\vec{r}') (r')^l \tilde{Y}_{lm}(\vec{r}')
\]

(3.9)

and

\[
B_{lm}(r) = \left( \frac{2l + 1}{4\pi} \right)^{1/2} \left[ r^l A_{lm} + r^{-l-1} A'_{lm} \right].
\]

(3.10)
Chapter 3. Crystalline electric field

The crystal field potential is now expressed as a linear combination of products of spherical harmonics and crystal field parameters. The ground state density of the system at hand can therefore be used to calculate the $A_{lm}$ and the radial integrals $\langle f| r^l | f \rangle$ and $\langle f| (1/r)^{l+1} | f \rangle$.

Localised states are most naturally expressed as $|JM>$ manifolds and are characterised by the total orbital momentum, $L$, the total spin momentum, $S$, and the total angular momentum, $J$. In order to evaluate the CEF matrix elements for such localised states the latter have to be re-expressed in terms of the operator equivalents of spherical harmonics. This is done via the Wigner-Eckart theorem that factors the angular dependence of the matrix elements of a spherical tensor operator, $X^k_q$, as follows

$$<\alpha j m | X^k_q | \alpha j' m' > = (-1)^j-m <\alpha j || X^{(k)} || \alpha j' > \begin{pmatrix} j & k & j' \\ m & q & m' \end{pmatrix}$$

(3.11)

where $<\alpha j || X^{(k)} || \alpha j' >$ is the reduced matrix element. What we need is a recipe to decompose the N-electron state $|JM>$ in a single electron basis $|l^i R_l Y_{lm} \chi_\sigma > = |lm\sigma, r >$, where $R_l$ is a radial function and $\chi_\sigma$ a spinor, or, equivalently, a definition for the electron creation operator $a_i^\dagger$. Once that is known, one can write

$$|JM> = a_1^\dagger \ldots a_N^\dagger |0> .$$

(3.12)

Then, the matrix elements of the CEF potential can be written as

$$<m'\sigma | B_q^k(r) C_q^k(\hat{r}) | m\sigma > =$$

$$\int Y^*_{lm'}(\hat{r}) C_q^k(\hat{r}) Y_{lm}(\hat{r}) d(\hat{r}) \int r^2 R_l^2(r) B_q^k(r) dr$$

$$\equiv <B_q^k | m' | C_q^k | m> ,$$

(3.13)

where the approximation that the radial wave function, $R_l$, is the same for all localised electrons of given $l$, has been made. It remains to calculate

$$A_q^k = \sum_{m'm'\sigma} a_{m'm'\sigma}^\dagger <m'\sigma | C_q^k | m\sigma > a_{m\sigma}$$

(3.14)

in the basis

$$|JM> = (2J+1)^{1/2} \sum_{MLMS} |LM_LS_M> \times (-1)^{L-S+M} \begin{pmatrix} L & S & J \\ M_L & M_S & -M \end{pmatrix}$$
3.2. Crystalline electric field, the standard theory

The first step is made by observing that

\[ <J M' A^k_q | J M> = \]

\[ (2J + 1) \sum_{M'_L M'_S} \sum_{M_L M_S} (-1)^{M+M'} \left( \begin{array}{ccc}
L & S & J \\
M_L & M_S & -M
\end{array} \right) \]

\[ \times \left( \begin{array}{ccc}
L & S & J \\
M'_L & M'_S & -M'
\end{array} \right) <LM'_L S'M'_S | A^k_q | LM_L S M_S> . \] (3.15)

The problem is now reduced to the evaluation of the matrix elements of \( A^k_q \) in the \( LS \) basis. Since \( A^k_q \) is a tensor operator and is spin independent

\[ <LM'_L S'M'_S | A^k_q | LM_L S M_S> = \] (3.16)

\[ (-1)^{L-M_L} \delta_{MS,MS'} <L || A^{(k)} || L> \left( \begin{array}{ccc}
L & k & L \\
-M_L & q & M_L'
\end{array} \right) . \]

The reduced element, \( <L || A^{(k)} || L> \), may be evaluated by observing firstly that the state \( |LLSS> \) is a single Slater determinant

\[ |LLSS> = a^\dagger_{l+1-N} \cdots a^\dagger_1 |0> \] (3.17)

(this is the recipe we needed). Therefore

\[ <LLSS | A^k_q | LLSS> = \]

\[ \sum_{mm'\sigma} <lm'||C^k_q || lm\sigma> <LLSS |a^\dagger_{m'\sigma} a_{m\sigma}|LLSS> \]

\[ = \sum_{m=l}^{l+1-N} <lm\sigma||C^k_q||lm\sigma> \] (3.18)

\[ = \sum_{m=l}^{l+1-N} \delta_{q,0} (-1)^{l-m} <l||C^{(k)}||l> \left( \begin{array}{ccc}
l & k & l \\
-m & 0 & m
\end{array} \right) . \]

where the reduced matrix element \( <l||C^{(k)}||l> \) is

\[ <l||C^{(k)}||l> = (-1)^l (2l + 1) \left( \begin{array}{ccc}
l & k & l \\
0 & 0 & 0
\end{array} \right) . \] (3.19)

Since \( <LLSS | A^k_q | LLSS> \) may also be written in terms of the reduced matrix element, \( <L || A^{(k)} || L> \)

\[ <LLSS | A^k_q | LLSS> = <L || A^{(k)} || L> \left( \begin{array}{ccc}
L & k & L \\
-L & 0 & L
\end{array} \right) \delta_{q,0} \] (3.20)
Chapter 3. Crystalline electric field

one can write

\[ < L|A^{(k)}|L> = (2l + 1) \left( \begin{array}{ccc} l & k & l \\ 0 & 0 & 0 \\ L & k & L \\ -L & 0 & L \end{array} \right) \times \sum_{m=l}^{l+1-N} (-1)^m \left( \begin{array}{ccc} l & k & l \\ -m & 0 & m \end{array} \right). \] (3.21)

Now the matrix elements of the crystal field are easily evaluated

\[ < J M'|A^k_q|J M > = (-1)^{L+S-M'+k}(2J + 1) \times < L|A^{(k)}|L> \] (3.22)

It is customary to replace the matrix elements of the CEF with operator equivalents. The matrix elements of the Racah operator equivalent, \( \tilde{O}^k_q(J) \), for the manifold \( |JM> \) are, from the Wigner-Eckart theorem

\[ < J M'|\tilde{O}^k_q(J)|J M > = (-1)^{L-M'} \left( \begin{array}{ccc} J & k & J \\ L & L & S \\ -M' & q & M \end{array} \right) < J||\tilde{O}^k_q(J)||J > \] (3.23)

where the reduced matrix element of \( \tilde{O}^k_q(J) \) is given by

\[ < J||\tilde{O}^k_q(J)||J > = \frac{1}{2^J} \left[ \frac{(2J + k + 1)!}{(2J - k)!} \right]^{1/2}, \] (3.24)

consequently, the ratios,

\[ f^k_N = \frac{< LSJM'|A^k_q|LSJM >}{< J M'|\tilde{O}^k_q(J)|J M >} = \] (3.25)

\[ (-1)^{L+S+J+k}(2J + 1) \left( \begin{array}{ccc} J & J & K \\ L & L & S \end{array} \right) \frac{< L|A^{(k)}|L >}{< J||\tilde{O}^k||J >}, \]

are the Stevens factors used to replace the crystal field matrix elements by operator equivalents.

3.2.1 CEF parameters evaluation from first principles

Starting from the work of Schmitt and continuing with the work of Refs. 30–37 and references cited therein, there have been a number of calculations of
CEF parameters in rare-earth elements and compounds, using first-principles theory. The basic procedure in those works is as follows: The ground state charge density of the system at hand is calculated by first principles and then the integrals in Eqns. (3.5) and (3.9) are evaluated. In the more recent calculations both the Coulomb, $V_C = V_N + V_H$ and the exchange correlation potential, $\mu_{ex}$, are contributing to the CEF potential, while in earlier works only the Coulomb potential was considered. The expression for the CEF parameters derived in the previous section is easily generalised, the potential $V = V_C + \mu_{ex}$ is expanded in spherical harmonics instead of $V_C$ alone. Then the procedure is absolutely analogous.

For the calculation of the total charge density the $f$ charge density is constrained to be spherical. This is a natural choice when the on-site contribution to the CEF is neglected. When this is not the case this choice is not fully justifiable since any given symmetry of the $f$ charge density will result in a different valence density. However, the screening effect due to the polarisation of the conduction electrons by the non spherical part of the central atom charge density (see Ref. 38 and paper III) is outside the framework of the standard CEF model that we have just described. In fact, calculating CEF parameters starting from different constrained symmetries of the $f$ charge density may, in principle, give different values of those parameters. The model is then valid and useful only if these changes are negligible.

Fähnle and Co-authors\textsuperscript{39, 40} tried a different, elegant approach to the problem of evaluating CEF parameters, considering the energy change due to the rotation, via an applied magnetic field, of the charge density of the $f$ shell in the frozen potential calculated self consistently with the unrotated $f$ shell. In presence of a molecular field the $f$ shell will be a mixture of various densities corresponding to different CEF states. It is therefore possible, by calculating the energy change in chosen rotations, to obtain the CEF parameters. In Ref. 39 it is observed that, to first order in perturbation theory, there is a cancellation of the kinetic and potential contributions if a given mixture of CEF charge densities is rigidly rotated in a frozen (apart from the rotating charge) potential. This is because the total energy of the unperturbed system is at a variational minimum. The rotation can be seen as a change $\delta \Pi = \delta \Pi(\theta, \phi)$ (with $\int d\Omega \delta \Pi(\theta, \phi) = 0$) in the density $\Pi(\vec{r})$, which corresponds to a change of $O(\delta n^2)$ in the energy. If one divides the energy of the system in the sum of the energy originating from the unperturbed density $\Pi(\vec{r})$, $E(\Pi(\vec{r}))$, and the one originated from $\delta \Pi(\theta, \phi)$, $E(\delta \Pi)$, to first order one can write

$$\delta E(\Pi(\vec{r})) = 0.$$ (3.26)

Then, if the change in the kinetic energy of the $f$ electrons is disregarded,
when the charge density is rotated, one obtains that

$$\delta E[n(\mathbf{r})] = \delta E[\delta n(\theta, \phi)] = \int V(\mathbf{r}(\mathbf{r})) \delta n(\theta, \phi) d\mathbf{r}. \quad (3.27)$$

Since the new rotated charge density will correspond to a linear combination of CEF charge densities (the CEF eigenstates span the entire subspace of the given symmetry), one can use Eq. (3.27) to estimate the CEF parameters. However, in Ref. 40 it is claimed that calculating CEF parameters with this procedure, starting from self consistent solutions corresponding to different molecular field mixtures of CEF charge densities, gives substantially different values for the calculated CEF parameters. This fact could throw some doubts on the validity of the CEF model, leading one to believe that the screening contribution that is left out by the model is not negligible. In Ref. 40 it is also observed that CEF parameters obtained with the above described rotation method in a frozen potential that has been calculated with a spherically constrained $f$ charge density are in agreement with CEF parameters calculated independently. The apparent dependence of the CEF parameters on the state chosen for evaluating the self-consistent potential is explained by noting that Eq. (3.27) is only valid to first order in $\delta n$. Contributions of order $\delta n^2$ can be substantially different for different CEF states. By choosing the frozen potential corresponding to the spherically constrained $f$-charge density one obtains a less biased treatment of the contributions of second order in $\delta n$. The effect of choosing a transition state on second order corrections is analysed in more details in paper IV.

The problem of taking into account the effect on the CEF splitting by the screening from the conduction band remains an open question. In the next section we present an approach$^{41}$ that can solve this problem.

3.3 Total energy calculations of CEF splitting

The ideal experiment of taking a free atom and plugging it into a lattice with a hole is in strong analogy to what is done in most of the implementations of LDA-DFT and certainly in the LMTO method that is used throughout this Thesis. At each single site, focusing only on electrons (nuclei provide a background, external potential since the Born-Oppenheir approximation is usually adopted), one divides the electrons of the atom occupying the site in core and valence or band electrons. Core electrons are not allowed to hybridise with other states in the system and are considered to have a spherical symmetry. Those electrons are regarded to occupy atomic-like states. Band electrons are instead let free to interact with the rest of the crystal and their hybridisation is self consistently evaluated. Any adjustment of the charge density of the
core electrons to the crystal potential is disregarded. The total angular momentum $J$ is still considered to be a good quantum number for them and their full rotational symmetry is maintained. This is a very good approximation in most cases and is especially good for filled shells because they will have a total angular moment that is equal to zero and will not be influenced by the crystalline electric field. For band electrons the interaction with the crystal potential is taken into account in a natural way since those electrons are described by Bloch states and no assumption is made on the shape of their density.

The situation is somewhat more complex for $f$ electrons. Experience has shown that in some case they are well described by treating them as band electrons while in many cases they are better described if treated as core electrons. In the latter eventuality one has a problem with the CEF: Apart for the case in which the $f$ shell is filled or half filled, the above described standard approach will not properly account for the $f$-electron charge density interaction with the electric field generated by the surrounding crystal lattice. The evaluation of this, usually neglected contribution, is the object of this section.

Under the hypothesis that the $f$ states have a negligible hybridisation with any of the other electronic states of the system at study and that the CEF constitutes a small perturbation to the Russel-Saunders coupling scheme, i.e.

\[ \text{exchange coupling} \gg \text{spin-orbit coupling (SOC)} \gg \text{CEF}, \]

a parameter-free scheme for calculating CEF splitting of the lowest $J$ multiplet has been devised.\(^{38}\) Whenever the above is true one can start by considering $J$ as a good quantum number and the CEF as a perturbation. The situation is the one schematically depicted in Fig. 3.2. It is crucial to the method that we will describe in the following that the CEF does not mix levels belonging to different $J$-multiplets.

### 3.3.1 Obtaining the CEF charge density

Let us, from now on, focus on the lowest-energy or ground-state (GS) $J$-multiplet. In the following, the $2J+1$ CEF levels in which the GS $J$-multiplet is split by the CEF will be referred to as the CEF levels. Let $G \leq 2J+1$ be the number of non degenerate CEF levels. Since we restrict ourselves to the GS $J$-multiplet and since the CEF does not mix states belonging to different $J$’s, the eigenvectors $|J_{GS}M_{JGS} \rangle$ with $M_{JGS} = -J_{GS}, -J_{GS} + 1, \ldots, J_{GS}$ can be used as a basis set in which the CEF levels of interest can be expanded (since they span the entire subspace of the lowest $J$-multiplet)

\[ \Psi_i^{CEF} = \sum_{M_J} C_{M_J} |JM_J \rangle. \quad (3.28) \]

Note that the suffix $GS$ has been dropped for the sake of a lighter notation.
Figure 3.2: Schematic representation of the limit in which the method of section 3.3 for CEF calculations is valid. The left hand side levels are the Russel-Saunders $J$ multiplet when the CEF splitting is disregarded. The levels on the right hand side are the CEF levels in which the former are split by the CEF.
3.3. Total energy calculations of CEF splitting

We will in the following show how to write the charge density corresponding to the CEF level of Eq. (3.28) in the form

\[ n^\sigma_f(\vec{r}) = R_f(r) \sum_h \alpha_h^\sigma D_h(\vec{r}), \]  

(3.29)

where \( R_f(r) \) is a radial function common to all the \( 2J + 1 \) levels belonging to the GS \( J \)-multiplet, \( D_h(\vec{r}) \) are the spherical harmonic invariants defined in Eq. (2.38) and \( \alpha_h^\sigma \) are expansion coefficients. The procedure involves tedious tensorial algebra in which the powerful Wigner-Eckart theorem plays the main role and is analogous to what we have shown in section 3.2. We start by writing the density matrix

\[ n^\sigma(r, r') = R_l(r) R_{l'}(r') \sum_{m, m'} \tilde{Y}_{lm'}(r') \chi^\sigma \tilde{Y}_{lm}(r) \chi^{\sigma'} \langle \hat{a}^\dagger_{m\sigma} \hat{a}_{m'\sigma'} \rangle. \]  

(3.30)

Our task is to evaluate the expectation value \( \langle \hat{a}^\dagger_{m\sigma} \hat{a}_{m'\sigma'} \rangle \) in the \( |JM_J> \) basis in which the CEF states are easily expressed. In order to do that, let us define the operator

\[ T(m\sigma, m'\sigma') = \hat{a}^\dagger_{m\sigma} \hat{b}_{m'\sigma'} \]  

(3.31)

where \( \hat{b}_{m\sigma} = (-1)^{l+m+1/2+\sigma} \hat{a}_{-m-\sigma} \) is the hole creation operator. It is easy to show that

\[ \langle \hat{a}^\dagger_{m\sigma} \hat{a}_{m'\sigma'} \rangle = (-1)^{l+m+3/2+\sigma} \langle T(m\sigma, -m' - \sigma') \rangle. \]  

(3.32)

Since we want to obtain an expression for the density in terms of the spherical harmonic invariants, instead of spherical harmonics, we want to rewrite the tensor operator, \( T \), in the \( D_h(\vec{r}) \) basis, denoted in the following with a subscript \( h \). This is done with the standard Clebsch-Gordan coefficient technique

\[ T(l_h m_h, s_h \sigma_h) = \sum_{mm'\sigma\sigma'} T(m\sigma, m'\sigma')(lmlm'|lll_h m_h)(1/2)^{\sigma+\sigma'}(1/2)^{s_h \sigma_h}. \]  

(3.33)

Inverting Eq. (3.33) one obtains

\[ \langle \hat{a}^\dagger_{m\sigma} \hat{a}_{m'\sigma'} \rangle = (-1)^{l-m+1/2-\sigma} \sum_{l_h} \sqrt{2l_h + 1} \binom{l}{m \ -m' \ m - m'} \binom{l_h}{l \ m \ -m'} \langle T(l_h m - m', s_h \sigma - \sigma') \rangle. \]  

(3.34)
We now invoke the Wigner-Eckart theorem in order to step down to an $LS$ basis

$$\langle LSJM|\hat{a}^\dagger_{m_\alpha}\hat{a}_{m_\alpha'}|LSJM'\rangle = \begin{array}{c}
(-1)^{M+M'}(2J+1) \sum_{M_S,M'_S,M_L,M'_L} \left( \begin{array}{cc}
L & S \\
M_L & M_S \\
J & -M
\end{array} \right) \\
\times \langle LM_LSM_S|\hat{a}^\dagger_{m_\alpha}\hat{a}_{m_\alpha'}|LM'_LM'_S\rangle \left( \begin{array}{cc}
L & S \\
M'_L & M'_S \\
J & -M'
\end{array} \right).
\end{array} \tag{3.35}$$

Now the problem is transformed via Eq. (3.34) to the evaluation of

$$\langle LM_LSM_S|T(l_hm_h,s_h\sigma_h)|LM'_LM'_S\rangle = \begin{array}{c}
(-1)^{L-M_L} \left( \begin{array}{cc}
L & l_h \\
M_L & m_h \\
L & -M'_L
\end{array} \right) \langle LM_LSM_S||T(l_h,s_h\sigma_h)||LM'_LM'_S\rangle \\
\times \langle LS||T(l_h,s_h)||LS \rangle.
\end{array} \tag{3.36}$$

The reduced matrix element $\langle LS||T(l_h,s_h)||LS \rangle$ can be calculated observing that, for less than half filling, Eq. (3.36) can be written for the particular case

$$\langle LLSS|T(l_h0,s_h0)||LLSS \rangle = \sum_{m'm'\sigma'\sigma} \langle LLSS||LLSS\rangle\hat{a}^\dagger_{m_\alpha}\hat{b}_{m_\alpha'}(lmml'|llll)(\frac{1}{2} \sigma \frac{1}{2} \sigma'\frac{1}{2} \frac{1}{2} s_h 0) \begin{array}{c}
(-1)^{l+m-1-N} \\
\sum_{m=l}^{l+1-N} (-1)^{l-m}(lm - m|lll_h0)(\frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} s_h 0)
\end{array} \tag{3.37}$$

and therefore

$$\langle LS||T(l_h,s_h)||LS \rangle = \sqrt{(2l_h+1)(2s_h+1)} \begin{array}{c}
(\frac{1}{2} \frac{1}{2} \frac{1}{2} 0) \\
\sum_{m=l}^{l+1-N} (-1)^{l-m}(l l_h 0)
\end{array} \tag{3.38}$$

and therefore

$$\langle LS||T(l_h,s_h)||LS \rangle = \sqrt{(2l_h+1)(2s_h+1)} \left( \begin{array}{cc}
S & S \\
S & 0 \\
S & S
\end{array} \right)^{-1} \left( \begin{array}{cc}
L & l_h \\
L & 0 \\
L & L
\end{array} \right)^{-1} \left( \begin{array}{cc}
\frac{1}{2} & \frac{1}{2} \\
\frac{1}{2} & 0
\end{array} \right) \sum_{m=l}^{l+1-N} (-1)^{l-m}(l l_h 0).$$
3.3. Total energy calculations of CEF splitting

For more than half filling all needed matrix elements are obtained just interchanging the electron and the hole creation operator.

Combining Eqns. (3.32) to (3.38), we are finally able to associate to any given CEF level a one-electron like charge density in the desired form given in Eq. (3.29) and therefore we are able to calculate its total energy, $E_i^{CEF}$, by means of DFT. This is so since any CEF level in which the lowest $J$ multiplet is split will be the GS of a given symmetry. Then, by constraining the $f$-charge density to be the one of the $i^{th}$ CEF levels as calculated above, we can evaluate its total energy, $E_i^{CEF}$. We can do this for all the CEF levels belonging to the GS multiplet and calculate in this way the CEF splitting of the lowest $J$-multiplet.

In passing let us note that, when taking total energy differences, we will be able to exploit a convenient cancellation of errors that will make our results more reliable. In fact, the error generated by the use of the approximated LDA exchange-correlation potential will be very closely the same in all the CEF levels, hence their differences will be closer to the exact values.

3.3.2 Total energy of a CEF level: symmetry constrained LDA calculations

Constraining the symmetry of the $f$ shell to a CEF charge density calculated as in the previous section requires some care. The LDA calculated total energy of a free atom with its $f$-charge density constrained to the one corresponding to the CEF level $\Gamma_i$ will differ from that of the level $\Gamma_j$. This is not a true physical phenomenon, of course. In absence of a CEF the two configurations must have the same energy since the lowest $J$-multiplet has fully rotational symmetry and is $2J + 1$ degenerate. The energy difference comes from the fact that LDA is an approximation to the true exchange-correlation functional. A way to recover the full degeneracy of the GS-CEF levels in the absence of a CEF is to correct the LDA total energy functional by removing the interaction of the non-spherical part of the $f$-charge density with itself. To do this, let us divide the $f$-charge density, $n_f(\vec{r})$ as follows:

$$n_f(\vec{r}) = \bar{n}_f(\vec{r}) + n_{fs}^i(\vec{r}),$$

where $n_{fs}^i(\vec{r})$ is the non-spherical part. The total density can be divided consequently, $n(\vec{r}) = \bar{n}(\vec{r}) + n_{fs}^i(\vec{r})$. Then the Hartree energy should be

$$E_H[n] = \frac{1}{2} \int \frac{\bar{n}(\vec{r})\bar{n}(\vec{r}')}d\vec{r}d\vec{r}' + \int \frac{\bar{n}(\vec{r})n_{fs}^i(\vec{r}')d\vec{r}d\vec{r}'}{|\vec{r} - \vec{r}'|},$$

(3.39)
where a third term containing $n^{ns}_f(\vec{r})n^{ns}_f(\vec{r}')$ has been excluded. The exchange-correlation part of the total energy functional,

$$E_{xc}[n] = \int n(\vec{r})\epsilon_{xc}(n)d\vec{r} = \int \left\{ \bar{n}(\vec{r}) + n^{ns}_f(\vec{r}) \right\} \epsilon_{xc}[\bar{n} + n^{ns}_f]d\vec{r}, \quad (3.40)$$

also contains $O(n^{ns2}_f(\vec{r}))$ interactions which have to be dropped. Since the non spherical part of the $f$-charge density is relatively small one can expand the $E_{xc}[n]$ as follows

$$E_{xc}[n] = \int \left\{ \bar{n}(\vec{r}) + n^{ns}_f(\vec{r}) \right\} \left\{ \epsilon_{xc}[\bar{n}] + n^{ns}_f(\vec{r}) \frac{\delta\epsilon_{xc}[n]}{\delta n}[n=\bar{n}] \right\} d\vec{r}. \quad (3.41)$$

Eliminating contributions of second order in the non spherical $f$ density, one obtains

$$E_{xc}[n] = \int \bar{n}(\vec{r})\epsilon_{xc}[\bar{n}]d\vec{r} + \int n^{ns}_f(\vec{r}) \left\{ \epsilon_{xc}[\bar{n}] + \bar{n}(\vec{r}) \frac{\delta\epsilon_{xc}[n]}{\delta n}[n=\bar{n}] \right\} d\vec{r} \quad (3.42)$$

or, alternatively

$$E_{xc}[n] = \int \bar{n}(\vec{r})\epsilon_{xc}[\bar{n}]d\vec{r} + \int n^{ns}_f(\vec{r})\mu_{xc}[\bar{n}]d\vec{r}. \quad (3.43)$$

Also, the wave equation

$$\left(-\frac{1}{2}\nabla^2 + V_N + V_H + \mu_{xc}\right)\psi_i = \epsilon_i\psi_i \quad (3.44)$$

should be modified, with the first two terms remaining unchanged, whereas

$$V_H = \int \frac{\left\{ \bar{n}(\vec{r}) + n^{ns}_f(\vec{r}) \right\} d\vec{r}}{|\vec{r} - \vec{r}'|} \quad (3.45)$$

for non $f$ states, and

$$V^f_H = \int \frac{\bar{n}(\vec{r})d\vec{r}}{|\vec{r} - \vec{r}'|} \quad (3.46)$$

for $f$ states. Finally the exchange correlation potential should be modified

$$\mu_{xc}[n] = \mu_{xc}[\bar{n}] + n^{ns}_f(\vec{r}) \frac{\delta\mu_{xc}[\bar{n}]}{\delta \bar{n}} \quad (3.47)$$

for non $f$ states, and

$$\mu^f_{xc}[n] = \mu_{xc}[\bar{n}] \quad (3.48)$$
3.3. Total energy calculations of CEF splitting

for $f$ states. Then the kinetic energy, $T_s$, becomes

$$
T_s[n] = \sum_i n_i \epsilon_i - \int V_N(\vec{r}) n(\vec{r}) d\vec{r}
- \int V_H(\vec{r}) \bar{n}(\vec{r}) d\vec{r}
- \int \left\{ \mu_{xc}[\bar{n}] + n_J^{ns}(\vec{r}) \frac{\delta \mu_{xc}[\bar{n}]}{\delta \bar{n}} \right\} \bar{n}(\vec{r}) d\vec{r}
- \int \mu_{xc}[\bar{n}] n_J^{ns}(\vec{r}) d\vec{r} - \int \mu_{xc}[\bar{n}] n_J^{ns}(\vec{r}) d\vec{r}.
$$

(3.49)

The sum of Eqs. (3.39), (3.43) and (3.49) yields the expression we use for calculating the total energy of CEF levels

$$
E = \sum_i n_i \epsilon_i - \frac{1}{2} \int \frac{\bar{n}(\vec{r}) \bar{n}(\vec{r}')} d\vec{r} d\vec{r}'
- \int \frac{\bar{n}(\vec{r}) n_J^{ns}(\vec{r}) d\vec{r}}{d\vec{r} - d\vec{r}'}
+ \int \{ \epsilon_{xc}[\bar{n}] - \mu_{xc}[\bar{n}] \} \bar{n}(\vec{r}) d\vec{r}
- \int n_J^{ns}(\vec{r}) \frac{\delta \mu_{xc}[\bar{n}]}{\delta \bar{n}} \bar{n}(\vec{r}) d\vec{r}.
$$

(3.50)

3.3.3 Generalisation to the magnetic case

If the system one wants to study is magnetic the functional of the density derived in the previous section needs to be changed. To the CEF Hamiltonian one has to add a term corresponding to a magnetic potential generated by an eventual external field, $H_{ext}$, and by the strong, internal exchange field, $B$. The latter is non local and depends, in general, on the magnetisation density of all CEF levels. We chose to approximate this complex behaviour with a simple mean field approximation. The internal field will be the Weiss field generated by the magnetic moment of the GS CEF level.

One can decompose this mean field magnetic contribution in orbital ($L$) and spin ($S$) parts as follows:

$$
E_{magn} = L \cdot H_{ext} + 2S \cdot H_{ext} + 2S \cdot B.
$$

(3.51)

Let us now write the magnetic contribution, $E_{magn}$, in (3.51) on the same footing as the crystal field part using the properties of angular momenta and the Russel-Saunders scheme:

$$
E_{magn} = \sum_{\mu} H_{ext-\mu} \left\{ \sum_{M_L,M'_L} \left\langle L M_L S M_S \frac{1}{2} L_{\mu} | L M_L' S M'_S \right\rangle 
+ \sum_{M_S,M'_S} \left\langle L M_L S M_S | S_\mu | L M_L' S M'_S \right\rangle \right\}
+ \frac{k_B T_c}{\mu_B} \sum_{\mu} \hat{e}_{-\mu} \sum_{M_S,M'_S} \frac{M_S + 1}{M_S} \left\langle L M_L S M_S | S_\mu | L M_L' S M'_S \right\rangle
$$

(3.52)
where the Weiss field has been expressed in the form:

$$B = \frac{k_B T_c (S + 1)}{\mu_B S} \hat{S}$$

with $T_c$ indicating the Curie temperature, $\mu_B$ the Bohr magneton and $k_B$ the Boltzmann constant.

The tensor $\hat{e}_\mu$ stands for

$$\hat{e}_\mu = \begin{cases} \hat{x} - i \hat{y}, & \mu = -1 \\ \sqrt{2} \hat{z}, & \mu = 0 \\ \hat{x} + i \hat{y}, & \mu = 1 \end{cases}$$

$L_{\mu}$, $S_{\mu}$ and $H_{ext,\mu}$ are defined analogously.

The matrix elements in Eq. (3.52) can be evaluated using once again the Wigner-Eckhart theorem

$$\langle L \mu LS | L_0 | LLSS \rangle = \left( \frac{L}{||L_\mu||} \right) \left( \begin{array}{ccc} L & 1 & \mu \\ -M_L & -\mu & M'_L \end{array} \right) \delta_{M_S,M'_S}.$$ 

The reduced matrix elements is evaluated observing that

$$\langle LLLS | L_0 | LLSS \rangle = \left( \frac{L}{||L_\mu||} \right) \left( \begin{array}{ccc} L & 1 & \mu \\ -L & 0 & L \end{array} \right)$$

therefore

$$\left( \frac{L}{||L_\mu||} \right) = \begin{pmatrix} L \\ \frac{L}{L} \\ 0 \end{pmatrix}.$$ 

The procedure is completely analogous for $S_{\mu}$ and the expressions for the spin angular momentum can be obtained from the ones for the orbital angular momentum just interchanging $L \leftrightarrow S$, $M_L \leftrightarrow M_S$ and $M'_L \leftrightarrow M'_S$.

So, substituting the last two expressions in the expression for $E_{magn}$, one obtains:

$$E_{\text{magn}} = \sum_{\mu} H_{\text{ext},\mu} \left( \frac{1}{2} \sum_{M_L,M'_L} (-1)^{(L-M_L)} L \left( \begin{array}{ccc} L & 1 & \mu \\ -M_L & -\mu & M'_L \end{array} \right) \delta_{M_S,M'_S} \right)$$

$$+ \sum_{M_S,M'_S} (-1)^{(S-M_S)} \left( \frac{S}{S} \right) \left( \begin{array}{ccc} S_{\mu} & 1 & S_{\mu} \\ -S_{\mu} & -\mu & S_{\mu} \\ 0 & 0 & 0 \end{array} \right) \delta_{M_L,M'_L}$$

$$+ \frac{k_B T_c}{\mu_B} \sum_{\mu,M_S,M'_S} \hat{e}_{\mu} \frac{M_S + 1}{M_S} (-1)^{(S-M_S)} \left( \frac{S_{\mu} & 1 & S_{\mu} \\ -S_{\mu} & -\mu & S_{\mu} \\ 0 & 0 & 0 \end{array} \right) \delta_{M_L,M'_L}.$$
3.3. Total energy calculations of CEF splitting

If $|\Psi_{i}^{CEF}\rangle$ is one of the eigenstates that diagonalise the CEF Hamiltonian with the above magnetic contribution, the charge and the magnetisation density corresponding to that particular CEF level will be

\[
n_{i}^{CEF} = < \Psi_{i}^{CEF} | 1 | \Psi_{i}^{CEF} >
\]

\[
\vec{m}_{i}^{CEF} = < \Psi_{i}^{CEF} | \vec{\sigma} | \Psi_{i}^{CEF} >,
\]

where $\vec{\sigma}$ represents the vector of the Pauli matrices. The change in the expression for the total energy is slightly more complicated than in the non magnetic case. The derivation follows the same line as the non magnetic case and we report here only the final result.

\[
E = \sum_{\sigma} n_{i}^{\sigma} \epsilon_{i}^{\sigma} - \frac{1}{2} \int \frac{\nabla r^{\sigma} \nabla r^{\sigma}}{|\vec{r} - \vec{r}'|} - \int \frac{\nabla r^{\sigma} c_{n}^{\sigma}(\vec{r}') d\vec{r} d\vec{r}'}{|\vec{r} - \vec{r}'|}
\]

\[
+ \sum_{\sigma} \left\{ \int \left[ \epsilon_{xc} \left[ \nabla \mid ^{\perp}(\vec{r}), \nabla \mid ^{\perp}(\vec{r}) \right] - \mu_{xc}^{\sigma} \left[ \nabla \mid ^{\perp}(\vec{r}), \nabla \mid ^{\perp}(\vec{r}) \right] \right] \nabla \mid ^{\perp}(\vec{r}) d\vec{r} \right\} \right(3.56\right)
\]

\[- \int n_{f}^{n_{n}^{\sigma}}(\vec{r}) \frac{\delta \mu_{xc}^{\sigma} \left[ \nabla \mid ^{\perp}(\vec{r}), \nabla \mid ^{\perp}(\vec{r}) \right]}{\delta n_{f}^{\sigma}} \nabla \mid ^{\perp}(\vec{r}) d\vec{r} \right\}.
\]

Also the exchange correlation potential has to be modified for non $f$ electrons,

\[
\mu_{xc}^{\sigma}[\nabla \mid ^{\perp}(\vec{r}), \nabla \mid ^{\perp}(\vec{r})] = \mu_{xc}^{n_{n}^{\sigma}}[\nabla \mid ^{\perp}(\vec{r}), \nabla \mid ^{\perp}(\vec{r})] \right(3.57\right)
\]

\[
+ \sum_{\sigma'} n_{f}^{n_{n}^{\sigma'}} \frac{\delta^{2}}{\delta n^{\sigma} \delta n^{\sigma'}} \left( \nabla \mid (\vec{r}) \epsilon_{xc} \left[ n^{\perp}(\vec{r}), n^{\perp}(\vec{r}) \right] \right)_{n^{\perp} = n^{\perp} = n^{\perp}}
\]

where

\[
\mu_{xc}^{n_{n}^{\sigma}} = \frac{\delta}{\delta n^{\sigma}} \left[ \nabla \mid (\vec{r}) \epsilon_{xc} \left[ \nabla \mid ^{\perp}(\vec{r}), \nabla \mid ^{\perp}(\vec{r}) \right] \right] \right(3.58\right)
\]

is the potential seen by $f$ electrons.

3.3.4 Applications

We have applied the total energy method here described to a number of systems with some success. In particular in paper V we have investigated the stability of the method with respect to parameters from which the standard CEF model is extremely dependent as the MT radii and the boundary conditions imposed for the radial part of the charge density of the $f$ electrons. We found that our calculated CEF splitting in PrSb does not change significantly when changing any of these two parameters. The reason is, in our opinion, twofold. We are evaluating total energy differences between CEF levels. Each level is
characterised by the change of the angular dependence (or symmetry) of the $f$ electron density. The boundary conditions for the radial part are the same in all CEF levels, therefore eventual changes cancel out when taking total energy differences. Moreover, our method does not recur to a division in on-site and lattice contribution that will naturally lead to a coupling between the CEF size and the chosen geometry. In fact, the integrals for evaluating CEF parameters are evaluated only inside the MT spheres in the standard first-principles CEF method. It is therefore very likely, in that case, that CEF parameters will strongly depend on the MT radii.

Another factor we investigated in paper V is the nature of the screening from valence electrons. In particular we wanted to see whether the re-adjustment of the valence charge density to the particular CEF state in which the $f$ charge density was constrained, were a local effect or not. If the CEF state on site $R_i$ can influence the valence charge density surrounding site $R_j$, CEF splittings will not only depend on the symmetry of the lattice but also on the distribution of CEF charge densities on that lattice. In order to check this we performed supercell calculations in which we compared the splitting obtained in PrSb when all rare earth ions in the supercell were constrained to be in the same CEF state to the splitting obtained when the $f$ charge density at one site of the super cell was constrained to the one corresponding to the CEF level of which the energy was to be evaluated, while the $f$ electron charge density at the remaining sites was put in another CEF state. No significant difference was obtained.

We also applied our total energy method to selected An systems in which the $5f$’s are believed to be localised. The fact that the $5f$ radial density is more extended than the $4f$ one and the overall less atomic-like character of the $5f$ electrons compared to the $4f$’s puts An systems on the border of validity of the CEF model. Therefore we regarded our calculations on An systems as exploratory, the legitimacy of which had to be proven $a$ $posteriori$. The usefulness of being able to calculate CEF splittings from first principles is demonstrated in paper VI. There, we were able to solve an apparent inconsistency between experimental values for the CEF splitting of PuO$_2$ obtained with different techniques. The only transition that is allowed to inelastic neutron scattering is the $\Gamma_1 \rightarrow \Gamma_4$ and for that Kern and co-authors$^{45}$ measured an excitation energy of 123meV. The flatness of the magnetic susceptibility, $\chi$, as a function of temperature$^{46,47}$ (see Fig. 3.3) tends to indicate that the non-magnetic $\Gamma_1$ state is the GS and a simple two-level analysis of $\chi$ finds the excited state, $\Gamma_4$, about 300meV higher in energy. An $f^2$ configuration in a cubic symmetry, if Russel-Saunders coupling is assumed valid, has the lower $J = 4$ multiplet split in four CEF levels, $\Gamma_1$, $\Gamma_3$, $\Gamma_4$ and $\Gamma_5$. We were able to calculate the energy differences between all of these levels and, considering the presence of an antiferromagnetic exchange in PuO$_2$, in analogy to what is
3.3. Total energy calculations of CEF splitting

**Figure 3.3**: The magnetic susceptibility of PuO$_2$. The measurements are the temperature independent straight dotted line and the calculated bare susceptibility with a sole $\Gamma_1 \rightarrow \Gamma_4$ excitation energy of 284 meV which fits the data at $T = 0$ is the dashed line labelled $\Gamma_{14}(284)$. The corresponding calculated bare susceptibility with a sole $\Gamma_1 \rightarrow \Gamma_4$ excitation energy of 123 meV which fits the neutron scattering data is the dotted line labelled $\Gamma_{14}(123)$. Adding calculated additional crystal field transitions to the 123 meV transition produces the improvement shown by the solid line labelled CEF(123) whereas replacing the measured $\Gamma_1 \rightarrow \Gamma_4$ excitation energy by the calculated 99 meV transition produces the solid line labelled CEF(99). The effect of using the antiferromagnetic molecular field deduced from that of UO$_2$ to enhance the latter two bare susceptibilities results in the full curves labelled CEF+I.
observed in UO$_2$, we were able to show that a CEF splitting of about 100meV (that is our calculated value) for the $\Gamma_1 \rightarrow \Gamma_4$ transition could be consistent with a flat magnetic susceptibility over a range of temperature of about 300K.
Chapter 4

Valence stability of $f$-electron systems

4.1 Introduction

The lanthanide (RE) and actinide (An) series differ from the other series constituted by a row in the Periodic Table: Going along the row one adds one electron not always to the chemically active valence band (as is the case, for example, in the transition metal $3d$ series) but to a shell of which the degree of participation in the bonding is not known. The determination of the valence of RE and An in compounds and even in elemental solids is then an interesting question to address. Even if the lanthanide contraction as well as the Curie-Weiss behaviour of the magnetic susceptibility constitutes an evidence for the picture of a chemically inert $4f$ shell in RE-metals\textsuperscript{48} – Ce excluded –, intermediate valence ($IV$) phases can be induced by pressure (see paper I and references therein). The situation is more complex in An systems where, with increasing atomic number, the light An elements show a volume dependence suggesting that the $5f$ electrons are in the valence band –similar to the $3d$, $4d$ and $5d$ transition metals– while the heavier An elements have volumes that follow a pattern similar to the lanthanide contraction, suggesting a localisation of the $f$’s.\textsuperscript{48} Pu, being on the border between these two situations has a very rich phase diagram (see for example Ref. 49 and references therein). The Wigner-Seitz radius, $R_{WS}$, as a function of atomic number in lanthanide and actinide elements, is shown in Fig. 4.1 where also the $R_{WS}$ of the $5d$ transition metals are reported for comparison.\textsuperscript{a} Fig. 4.1 shows clear similarities between the heavy actinides and the lanthanides, and between the light actinides and the transition metals.

\textsuperscript{a}The Wigner-Seitz radius, $R_{WS}$, is defined as the radius of the sphere that has the same volume as the volume per atom in a solid.
Chapter 4. Valence stability of f-electron systems

In this chapter we will present different theoretical methods that we have used to evaluate the valence of RE and An systems. In section 4.2 we will describe the simplest possible approach to try to predict whether or not the f electrons are participating in the bonding, that is comparing LSDA calculated volumes to experimental volumes. A second, more refined method for evaluating the valence of an f-element, first proposed by Johansson in Ref. 50, 51 is described in section 4.3. Finally, in section 4.4, we will present a new approach, designed for intermediate valence (IV) systems, that we have applied to Yb metal under pressure.

4.2 Comparing volumes

If the experimental volume of the compound of interest is known experimentally, then the simplest approach to the valence determination consists in comparing the theoretical volumes obtained in a straightforward LSDA calculation, when the f electrons are considered as valence or core, to the experimental one. Some care is needed in this procedure and an example is given in paper VII where the character of the 4f electron of Ce in CePt$_2$Sn$_2$ was investigated. A direct comparison to the experimental volume would suggest a delocalised scenario for the f-electron of Ce. Comparing, though, the difference between theoretical and experimental volumes in other Ce and RE systems we concluded that the f electron of Ce in CePt$_2$Sn$_2$ is essentially localised. The limitations of such an approach are evident. One needs experimental volumes
4.3 The Born-Haber cycle

Johansson\textsuperscript{50,51,62} observed that the difference in energy in a solid with An or RE as constituents, when the number of the localised $f$ electrons changes from $n$ to $n + 1$ can be evaluated using the Born-Haber cycle depicted in Fig. 4.2. The cycle involves the sublimation energy from the bulk to free atoms in the $f^n$ configuration and a solidification energy by atoms in the $f^{n+1}$ configuration to a solid with ions in the same state. The other quantity involved is the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.2.png}
\caption{Born-Haber cycle for the evaluation of the energetically favourable configuration of $f$-electron ions in a solid compound.}
\end{figure}

\begin{itemize}
\item and, most of all, \textit{standard deviations} between theory and experiment have to be considered in a less well defined way.
\item Another limitation, that is of general character for band structure calculations, is the legitimacy of opposing a fully itinerant to a fully localised scenario for $f$ shells. In nature electrons will most probably oscillate between these two behaviours and one can just say that on the average a certain number, $z$, of the $f$ electrons will occupy atomic-like states while the remaining part, $v$, will have a delocalised character. In standard DFT-LDA there is no possibility of treating part of a shell as localised and part as delocalised. This problem has been addressed with success\textsuperscript{52–60} by the self interaction corrected local spin approximation (SIC-LSDA).\textsuperscript{61}
\end{itemize}
atomic promotion energy that is the link between the two different configuration one wants to compare. The sublimation and solidification energies in Fig. 4.2 are calculated in two steps: LSDA is capable of giving accurate values for cohesive energies when the $f$ electrons are in the grand barycentre of the $f$ multiplet, that is the average over the levels constituting the multiplet. This generalised cohesive energy (approximated by the difference in energy between an atom and the bulk both in a paramagnetic state) must be corrected in order to evaluate the energy gain when atoms in the lowest level of the $f^n$ multiplet solidify, remaining in the very same $f$ configuration. The fact that the configuration of the $f$ multiplet does not change is one key factor for using the cycle of Fig. 4.2: Since we are going to take energy differences we do not need to estimate $f$-intra-shell contributions. Those are simply eliminated in the difference between the energy of free atoms and bulk. The coupling between the $f$ shell and the conduction band (mainly the $d$-band) is instead different in an atom and in the crystal for the very reason that band states are different from atomic states. This difference can be precisely evaluated combining atomic calculations and spectroscopic experimental data. This has been done for the RE elements in Refs. 50, 51. There are no such precise estimations for the An series, the reasons being that elemental An have an itinerant character for half of the series and the lack of experimental data. However, we note that it is possible to approximately reproduce the values obtained for RE elements in Refs. 50, 51 using a simple Stoner-Exchange model for the $f$-$d$ coupling. Exchange integrals, $I_{l,l'}$, for the RE and for the An series have been calculated by Brooks and co-authors. It is then possible to calculate the $f$-$d$ coupling for actinides as well. In the same way it is possible to evaluate spin and orbital polarisation energies.

Within the framework of LDA(GGA) we are not able, unfortunately, to calculate the atomic promotion energy with the required accuracy. This parameter is therefore taken from experiments. It is important here to stress that the very same parameter, for example the promotion energy from $f^2s^2pd$ to $fs^2pd^2$ in a certain RE can be used to analyse the valence of all compounds in which that particular RE assumes those two configurations.

### 4.4 Adding correlation effects

There are two features of the method described in the previous section that we have tried to improve on in paper I. The first one is the possibility to treat $\gamma\gamma$ states in a computationally efficient though accurate way. The second one is to include the effect of the $f$-$d$ hybridisation and of the Coulomb attraction between the hole left behind in the $f$ shell and the electron promoted to the valence band. This we have done by considering the Kimball-Falicov model theory of $\gamma\gamma$ phenomena developed in Refs. 69–71 in combination with the
4.4. Adding correlation effects

approach described in the previous section. The difference in energy between two valence configurations as calculated with the cycle of Fig. 4.2 is the zeroth order solution, $\Delta_0$, to the coupled equations

$$
\begin{cases}
    x = \frac{E_F + |\Delta(x)|}{E_F} \int_{E_F}^{E_F + |\Delta(x)|} dE N(E) \\
    \Delta(x) = \Delta_0 + Gx
\end{cases}
$$

(4.1)

where $x$ is the valence change, $\Delta(x)$ is the renormalised energy difference and $N(E)$ is the density of states per energy, $E$. The parameter $G$ measures the Coulomb attraction between the $f$ hole and the promoted (fraction of an) electron. $G$ can be simply evaluated as the derivative of the position of the centre of mass of the valence band as a function of the $f$-shell filling. The basic idea underlying this model is simple. The first observation is to note that the energy $\Delta_0$ obtained from a Born-Haber cycle is not always sufficient for a complete promotion of an $f$ electron to the conduction band. The effective amount of charge transferred from the $f$-shell to the conduction band is therefore calculated as the integral $\frac{E_F + |\Delta_0|}{E_F} \int_{E_F}^{E_F + |\Delta_0|} dE N(E)$. When this amount of charge is promoted, a corresponding hole is left in the $f$-shell. Now there will be a Coulomb attraction between this hole and the promoted charge. The simplest way to model this attraction is to renormalise the energy difference $\Delta_0$ via the parameter $G$ as in (4.1) (for further details see paper I).

A further refinement of the valence can be obtained by considering the effects of the electron promotion on the $f - band$ hybridisation parameter

$$
v_{eff} \left[ 1 - G \int dE N(E) \sqrt{(E - Y)^2 + 4v_{eff}^2} \right] = v,
$$

(4.2)

where $Y = E_F + |\Delta(x)|$ is the renormalised Fermi energy and $v$ is the bare hybridisation parameter calculated from first principles as suggested in Ref. 72. While $v_{eff}$ is the renormalised one. Then one has to solve Eqs. (4.1) and (4.2) self-consistently.

4.4.1 Application to Yb metal under pressure

Recently the x-ray absorption spectrum of Yb under pressure has been measured in Partial Fluorescence Yield (PFY-XAS). The experiments probed the L-edge by detecting the Partial Fluorescence from the $3d-2p$ decay. This means that the unoccupied $5d$-density of states (DOS) was mapped with a reduced lifetime broadening of the $3d$ core-hole with respect to traditional L-edge XAS. The experimental spectrum, taken at a pressure of 20GPa, is
Figure 4.3: Measured (full line) and calculated x-ray absorption spectrum of elemental bcc Yb at a pressure of 20 GPa. The dotted line shows the calculated spectrum of the $3f^4$ state, whereas the broken line shows the spectrum obtained for a divalent configuration. The first peak is aligned and the zero of the photon energy scale is arbitrarily chosen.
4.4. Adding correlation effects

shown in Fig. 4.3. If a comparison to a 5d-projected DOS of the divalent state (lower curve of Fig. 4.3) is made, a rather large disagreement with experimental data is observed. Although the two peaks at lower energies are reproduced with some accuracy by this calculation, there is a substantial part of the experimental spectrum, at 10eV and above, that is not present at all in the calculated DOS of the purely divalent configuration. A comparison of the DOS of a purely trivalent configuration with the PFY-XAS data in Fig. 4.3 gives an equally poor agreement (data not shown in the figure). The other calculated spectrum shown in Fig. 4.3 (middle curve) is a superposition of contributions to the spectrum both from divalent Yb atoms and from trivalent Yb atoms as calculated from an intermediate valence state, obtained in the coherent potential approximation (CPA). The concentration of divalent and trivalent atoms in the CPA alloy is chosen accordingly to the calculated valence at 20GPa, which is 2.57. This value for the valence was obtained with the model described in section 4.4. In the theoretical IV spectrum in Fig. 4.3 there is an applied shift of 5.7 eV in order to account for the chemical shift of the core states between the two atom types. The IV spectrum reproduces much better the features of the experimental spectrum both in terms of the three peak positions as well as regarding their relative intensities. We regard this as an indication that our calculated valence is accurate. In paper I, we have also evaluated the equation of state of Yb obtaining a good agreement with experimental observations also for this properties, which is another indication that the devised model is sound.
Chapter 4. Valence stability of $f$-electron systems
5.1 Introduction

In a ferromagnet, below the Curie temperature, the energy is found to be dependent on the orientation of the magnetisation. Three physical mechanisms are responsible for such a phenomenon that goes by the name of magnetocrystalline anisotropy. One is of classical origin and relies in the multipole (mainly dipole) interaction between the moments localised at lattice points.\textsuperscript{27,75,76} The second one is related to the interactions between the charge-density multipoles of a given shell and the CEF. This term is of electrostatic origin and is therefore often separated out and treated as a CEF effect for localised shells (for example, the 4\textit{f} electrons in RE metals) where it can be the dominant contribution. It is, instead, smaller for band-like electrons and therefore often disregarded in band structure calculations. The last one is instead related to the orientation of the spin axis and is of pure relativistic character appearing only when the spin-orbit interaction is taken into account.\textsuperscript{77} The SO coupling provides the mechanism that couples the spin moment to the crystal generating thereby a dependence of the energy from the spin axis.

The magnetocrystalline anisotropy energy (MAE) is defined as the difference in energy:

\[ MAE \equiv E(\text{hard axis}) - E(\text{easy axis}). \]

Sometimes, since the hard and easy axes are not known in advance, with MAE one refers to the difference between two crystallographic axes. This pragmatic definition of the MAE is the one we used in papers VIII and IX, where, in a \textit{hcp} crystal, we considered

\[ MAE \equiv E(\text{a axis}) - E(\text{c axis}). \]
Further, one can define an anisotropy energy, or the energy dependence from the magnetisation orientation, \( E_A(\theta) \) as
\[
E_A(\theta) \equiv E(\theta) - E(\text{ref. axis}),
\]
where \( \text{ref. axis} \) indicates the axis chosen as reference (typically the easy axis or a symmetry axis of the crystal) and \( \theta \) is the angle measured from it. The anisotropy energy can also be expanded as
\[
E_A(\theta) = K_1 \sin^2 \theta + K_2 \sin^4 \theta + (K_3 + K_4 \cos \phi) \sin^6 \theta + \ldots \tag{5.1}
\]
where \( K_i \) are the anisotropy constants. Even though this is the expansion most commonly used, a more physically transparent one is
\[
E_A(\theta) = A(\cos 2\theta - 1) + B(\cos 4\theta - 1) + \ldots \tag{5.2}
\]
where the constants \( A, B, C \ldots \) are increasingly small.

### 5.2 The force theorem

The fact that the SO interaction can be introduced as a perturbation to scalar relativistic systems can be exploited in order to speed up the evaluation of the MAE. The way to do so is given by the force theorem for band structure calculations.\(^7\) Consider an unperturbed system \(^a\) with its total energy given by
\[
E = E_{NN} + T_S[n(\vec{r})] + \int V_N(\vec{r})n(\vec{r})d\vec{r} + \frac{1}{2} \int \frac{n(\vec{r})n(\vec{r}')}d\vec{r}d\vec{r}' + E_{xc}[n(\vec{r})]. \tag{5.3}
\]
By switching on a perturbation, one introduces a change in the total energy, to the first order in the charge density change, \( \delta n \), equal to
\[
\delta E = \delta T_S[n(\vec{r})] + \int V_N(\vec{r})\delta n(\vec{r})d\vec{r} + \frac{1}{2} \int \frac{n(\vec{r})\delta n(\vec{r}')d\vec{r}d\vec{r}'}{|\vec{r} - \vec{r}'|} + \int \mu_{xc}[n(\vec{r})]\delta n(\vec{r})d\vec{r} + O(\delta n^2) \tag{5.4}
\]
\(^a\)The perturbation will be, for our purposes the SO interaction, but, the theorem is of more general nature.
5.3 The anomaly of Gd

where the change in the nuclei has been disregarded and the identities

\[ E_{xc} \equiv \int \epsilon_{xc}[n(\vec{r})]n(\vec{r})d\vec{r} \]

\[ n(\vec{r}) \frac{\delta \epsilon_{xc}[n(\vec{r})]}{\delta n(\vec{r})} = \mu_{xc}[n(\vec{r})] - \epsilon_{xc}[n(\vec{r})] \]

\[ V \equiv V_N + V_H + \mu_{xc} \]

have been used. The kinetic energy can be written in the form

\[ T_S[n(\vec{r})] = \sum_i n_i \epsilon_i - \int V(\vec{r})n(\vec{r})d\vec{r}, \quad (5.5) \]

therefore, its change is (also to the first order in the charge density change)

\[ \delta T_S[n(\vec{r})] = \delta \sum_i n_i \epsilon_i - \int \delta V(\vec{r})n(\vec{r})d\vec{r} - \int V(\vec{r})\delta n(\vec{r})d\vec{r} + O(\delta n^2). \quad (5.6) \]

Thus, if the potential is kept frozen, a substitution of Eq. (5.6) in (5.4), yields

\[ \delta E = \delta \sum_i n_i \epsilon_i, \quad (5.7) \]

which is the force theorem we wanted to derive and is valid to order \( O(\delta n) \).

The reason why we wanted to show here the derivation of Eq. (5.7) is that it is interesting to see that some changes in the single contributions to the total energy are not zero but they partially cancel each other to first order.

Since the change in total energy in a frozen potential is equal to just the change in the eigenvalue sum, one can calculate this latter, less computationally demanding quantity, in order to obtain the former. A large number of evaluations of MAE via the force theorem in various elements and compounds have been carried out in the past 20 years (see, for example, Refs. 79–82 and references therein), showing that contributions of order \( O(\delta n^2) \) are most of the time negligible and that the change in the eigenvalue sum is very close to the total energy change.

5.3 The anomaly of Gd

Gd metal is in the middle of the RE series and its \( f \)-shell is half filled. This means that, in a Russel-Saunders (RS) scheme, no orbital moment is to be expected from the \( f \)-electron shell. As a consequence of that, one expects no CEF contribution to the anisotropy and indeed the MAE of Gd (~30\( \mu \)eV/atom) is two orders of magnitude smaller than the MAE of the other RE metals (~meV/atom). Given the sphericity of the 4\( f \) shell one may ask where does
the observed MAE of Gd originate from? In paper VIII we addressed this question and we found that an interplay between the dipole interaction of the large, localised, 4\textit{f} spin moments and the, SO driven, MAE of the conduction band (mainly 5\textit{d}) can well explain the observed anisotropy energy, \( E_A(\theta) \). In particular an easy axis of magnetisation at 20° off the \( c \) axis is predicted in excellent agreement with experiments.\textsuperscript{83} Let us note that the fact that the 5\textit{d} band anisotropy plus the dipole anisotropy from the localised 4\textit{f} moment reproduces the observed MAE is also an indirect demonstration of the localisation of the 4\textit{f}’s in Gd. When the 4\textit{f} electrons are considered as part of the band we obtain a value for the MAE that is about twenty times larger than the observed one since the SO is in this case affecting also the \( f \)’s.

In Fig. 5.3 we report the calculated band anisotropy of Gd for different \( k \)-points in the \( k_x-k_y \) plane (\( k_z=0 \)). It is clear that the MAE is strongly influenced by the states closer to the Fermi surface. This is consistent with the observation made by Franse and Gersdorf\textsuperscript{83} that 21 parameters are required in the expansion of the torque curve in sinusoidal functions in order to obtain a satisfactory fit but that this number could be reduced to only four if one took into account Fermi surface effects with a simple model as proposed in the same paper. It is also consistent with the very large number of \( k \)-points needed to converge our calculations and with the fact that using the Gaussian smearing Brillouin zone integration scheme of Ref. 84 gives different results compared to using the quadratic interpolation of the band structure of Ref. 85.

We continued our investigations on the MAE of Gd in paper IX where we studied also the peculiar temperature dependence of the easy axis of magnetisation. This we attributed mainly to the reduction of the effective magnetisation with increasing temperature. We analysed this effect by means of band structure calculations in which we constrained the 4\textit{f} moment to chosen reduced values. A qualitative agreement between our calculated temperature dependence of the easy axis and the observed one was obtained. In paper IX also the dependence of the anisotropy from the \( c/a \) ratio was investigated, showing that the size of the MAE and the orientation of the easy axis can be tuned via this parameter. As shown in Fig. 5.2, the ratio between the band electron MAE and the dipolar contribution to the magnetic anisotropy can be changed by changing \( c/a \). While the dipole anisotropy favours the \( c \) axis for a \( c/a \) ratio less than the ideal (\( \sqrt{8}/3 \)) and the in-plane orientation for larger \( c/a \) ratios, the band electron MAE has the more complex behaviour reported in Fig. 5.2. The temperature driven \( c/a \) ratio change is of about 0.3% in the temperature range going from zero to the Curie temperature of Gd,\textsuperscript{86} therefore we believe that its role in the temperature dependence of the easy axis is negligible.

Let us note in passing that just the sphericity of the 4\textit{f} shell of Gd makes this metal a perfect playground for testing the accuracy of band structure calculations of the MAE. In fact, the CEF contribution that is not easily accounted
5.3. The anomaly of Gd

Figure 5.1: Calculated $E_A^{\text{band}}$ of Gd metal for different k-points in the $k_x$-$k_y$ plane ($k_z=0$) (top left). The central figure reports contributions from all states with energy $c$: $E_F - 1.714eV \leq \epsilon \leq E_F$ while the top-right figure refers to contributions from states with energy $-\infty \leq \epsilon \leq E_F - 1.714eV$. $E_F$ indicates the Fermi energy. The colour scale (blue, green, brown, yellow) represents an increasing MAE going from $\leq -5000\mu eV/\text{atom}$ (blue) to $\geq +5000\mu eV/\text{atom}$ (yellow). The transition from negative to positive contributions occurs between green and brown colouration.

for in standard electronic structure calculations for localised open shells, is absent in Gd and only weakly correlated conduction electrons have to be properly treated. The other prospective candidate for a similar investigation is therefore Cm, the actinide analogous of Gd.

Finally, let us comment on the anisotropy constant expansion for Gd. It is in most cases sufficient to consider just the first two terms in the expansion (5.2) and this we have done in papers VIII and IX in order to obtain, from a limited number of spin axis orientations, the entire $E_A(\theta)$ curve. However, we must add that it is possible to show\(^8\) that the magnetic anisotropy constants of order $n$ are proportional to the ratio between the SO splitting parameter, $\xi$, over the band width, $W$, roughly in the form $\xi^n/W^n-1$. Therefore, the expansion (5.2) converges rapidly for transition metals where $W$ is considerably larger than the $\xi$ but has a slower convergence for Gd where these two quantities are of comparable size. This observation is also consistent with the, observed and calculated, non-monotonic behaviour of $E_A(\theta)$.

\(^b\)Cm crystallises in the more complex dhcp structure and it is likely that the more extended 5f shell is not in a pure S-state. Hence the analogy has to be taken with some care.
Figure 5.2: Calculated dipolar anisotropy (open squares) and $E_{A}^{\text{band}}(90^\circ) - E_{A}^{\text{band}}(0^\circ)$ (open circles) of Gd metal for different values of the $c/a$ ratio. Lines are guides for the eye.
Summary and Outlook

In chapter 3 we presented a DFT-LDA total energy method for the evaluation of the CEF splitting of the lowest Russell-Saunders $J$-multiplet. A direct evaluation of the splitting has the advantage of taking into account in a natural way the screening from the valence electrons that adjust to the $f$ charge density. With the standing increase in computational power a systematic study of CEF splittings with a total energy approach has become possible. A comparison with the results obtained with a standard CEF model approach would be most valuable. A question that could be answered by such a study is whether or not the screening from the valence electrons can be viewed as a correction to the standard CEF model, i.e. whether it is possible to model CEF effects or one is doomed to electronic structure calculations. A model of the CEF, apart from giving us a better physical insight, could be used to derive, in a simple and physically transparent way, the CEF splittings or parameters of a compound by the knowledge of a similar one (and will define the meaning of similar in the context). Our present impression is that this can be possible but a new parameter must be added to the CEF model in order to represent the degree of mobility of the conduction electrons. Devising such a screened CEF model could be an interesting project for the future. On a more modest level there are a number of systems where the labelling of CEF levels, or even the size of the CEF splitting, is not easily determined experimentally and where such informations could be valuable. As an example, the four phase transitions that UPd$_3$ exhibits below 8K have been recently explained assuming a certain CEF splitting. A first-principles calculation of the CEF splitting at the quasi-cubic U site would be able to confirm the assumptions of Ref. 88.

The MAE of Gd has been investigated in details. The number of k-points needed to converge our calculations has proven to be huge, nevertheless we believe that in the near future it will be possible to calculate the anisotropy energy of Gd including SO effects in a self consistent manner and without having to resort to the force theorem. The interplay between dipolar interactions and conduction band anisotropy giving raise to the peculiar MAE of Gd could also
be present in Cm. A study of the MAE of this actinide metal would be an interesting theoretical challenge. It would also be interesting to see whether or not our predictions on the \( c/a \) ratio dependence of the MAE of Gd have an experimental confirmation. Gd can be grown with \( c/a \) ratios different from its natural one (which is 1.6 at low temperature) in a multilayer structure by using ad hoc chosen substrates. In order to describe this geometry, our dipolar calculations should be slightly changed.

The proposed approach to \( JV \) system of chapter 4.4 has been applied to Yb but is of completely general character. A number of systems could be attacked in the same way and we are looking forward to doing so. In addition, it would be valuable to make the method totally first-principles based by being able to calculate the zeroth order energy difference \( \Delta_0 \) of the model. This could be done, possibly, by means of accurate configuration interaction calculations for the atomic promotion energy and for the atomic polarisation energies.
Acknowledgements

This is going to be long. I am indebted for an enormous number of things to Olle ‘det blir bra’ Eriksson. For an equally large number of things (totally different ones, though) I have to thank Mike ‘det blir nog aldrig bra’ Brooks. Lars Nordström has spent a lot of time in teaching me many things and in pulling my legs. Börje Johansson is, in every single thesis produced in this group, acknowledged for providing a pleasant working atmosphere. It is true and this thesis will be no exception to the rule. I only hope that the last performances of Leksand will not change his good mood. I have learned a lot from Misha Katnelson in the past two years. And from Igor Abrikosov during my first year as a student in Uppsala. I want to thank Gerry Lander for letting me spend a lot of time in Uppsala. Something that I owe also to Jean-Pierre Michel, Roland Schenkel, Maurice Leroy and Jean Rebizant. The administrative amount of work for a student in Karlsruhe has been less overwhelming thanks to the help of Sabine Yael and Frank Wastin who never said no when I needed help. Here in Uppsala there is no administrative work for students because there is Elisabeth Bill. To John Wills I want to say thank you for the three visits to Los Alamos National Laboratory, for spending time with my crystal field problems and for letting me (mis)use your code. Manuel Richter has always found an encouraging or a stimulating word about my work and is also acknowledged for inviting me for two weeks in Dresden. I am grateful to Ingrid Brooks for many meals, a lot of nice chats and for coping with me being around her home during some weekends. Till Burkert deserves all thanking for the work he is doing in keeping John’s FP-LMTO code working at its best on our machines and for always providing a slightly better script for just about everything. I want to give my thanks to Kay Dewhurst for letting me use his EOS code and Jorge Osorio-Guillén for advices about EOS fitting. Rajeek Ahuja and Sergei Simak are acknowledged for being able of co-authoring more than one paper with me without being forced. Weine Olovsson, Lars Bergvist, Per Andersson, Urban Lundin, Anders Ekström, Björn Skubic, Thomas Dziekan, Carlos Ortiz and Erik Holström are acknowledged for keeping our computers going.
I also want to thank Lars Fast, Anders Niklasson Peter James and Anna Delin for introducing me to the group and to Swedish. Elisabeth Sjöstedt and Jonas Fransson have been insisting in the tremendous task of talking with me on a daily basis and they well deserve my gratitude for that. I want to thank Velimir Meded for never discussing anything serious with me. Adrian Taga for helping me with a Linux installation on my lap-top and Leonid Pourovsksii for some late-night chess games. Erik Holmström for helping me in getting an apartment and in getting rid of it and for helping me with the LaTeX packages for this thesis. Alexei Grechnev for always being able to turn a boring conversation into something funny. I am grateful to Pavel Korzhavi for letting me use his office in Stockholm from time to time. Maurizio Matesimi and Olivier Bengone are acknowledged for keeping my Italian from disappearing from my mind while I want to thank Biplab Sanyal for his inspiring storytelling about cricket and how Pakistan is the best team in the world. I am grateful to Cristina Schippa for many vital things and for the fact that she helped me in translating the introduction to this thesis in Swedish in order to fulfill a brilliant new rule of this department. All the other people in Fysik4 are acknowledged for something, for making me laugh, for teaching me something, for an interesting discussion or for a silly one. I have surely forgotten someone in this late night before the deadline falls. Please forgive me for not putting all your names in this final note.

Uppsala, April 2004

Massimiliano Colarieti Tosti
References

REFERENCES


REFERENCES


A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series *Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology*. (Prior to October, 1993, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science”.)