

Introductory Information

Abstract In this introductory chapter a short historical note on the history of linear muffin-tin orbital methods is given, together with general background information and units used throughout the book. The main objectives with the book are presented as well as information about web-based information, which easier enables using the full-potential linear muffin-tin orbitals method.

1.1 Objectives and What You Will Learn from Reading This Book

The purpose of this book is to give a full account of an implementation of a method for calculating the electronic structure of materials, using linear muffin-tin orbitals as basis functions. The method is referred to as RSPT (relativistic spin-polarized test), where after some 20 years of use and development the letter “t” is a mystery. The invention of linear muffin-tin orbitals is due to Andersen [11] and the first step toward what now is RSPT was taken by Wills and Cooper [258]. From reading this book you will be familiar with electronic structure theory in general, including density functional theory [116, 140], a theory for which Walter Kohn shared the Nobel Prize in chemistry 1998. You will also be familiar with the use of linear muffin-tin orbitals as basis functions for calculations of electronic structures of solids. This book contains in addition to a technical description of linear muffin-tin orbitals and their implementation in RSPT, several examples of the use of RSPT in the field of phase stability, magnetism, optics, and excited state properties. Simple instructions on how to download the source code from the RSPT web site (<http://www.rspt.net/>), how to compile it and perform test runs of the code, and a manual for input and output are also provided here, with the hope that from reading this book you will be comfortable in setting up the code, run it on a single- or multi-processor computer architecture, assess the quality of the calculations, and to analyze the calculated results. By

the time you have read this book, you will find that a database with calculated electronic structures using the RSPt method is available at the web site <http://gurka.fysik.uu.se/esp/>, where tens of thousands of results from already made electronic structure calculations can be found and extracted.

In order to successfully absorb the information provided in this book, it is recommended that you have studied elementary textbooks in solid state physics, e.g., the book of Kittel [134], Marder [163], or by Ashcroft and Mermin [22]. It is also recommended to study a book on molecular orbital theory, e.g., the book by Atkins [24].

1.2 On Units

Throughout this book we make use of atomic Rydberg units, in which $\hbar = 1$, $e^2 = 2$, and the electron mass $m = 1/2$. The unit of length is the Bohr radius $a_0 = \hbar^2/me^2 = 0.529178 \text{ \AA}$, the unit of energy is the Rydberg, $\text{Ry} = e^2/2a_0 = 13.6058 \text{ eV}$, and the rest energy of the electron $mc^2 = e^2/a_0\alpha^2$ where $\alpha \sim 1/137$ is the fine-structure constant.

1.3 Obtaining RSPt and the RSPt Web Site

The source code, RSPt, can be downloaded from <http://www.rspt.net/>. Here one finds also a manual for the input and the output of the code, information on how to install the source code, as well as a user's forum, where one can obtain answers for most technical questions concerning installing and running RSPt. A full account of the installation and running of RSPt is given in Chap. 9. The RSPt source code is freely available.

1.4 A Short Comment on the History of Linear Muffin-Tin Orbitals and RSPt

The RSPt method is an all-electron, full-potential (FP) implementation of density functional theory using linear muffin-tin orbitals (LMTOs) as basis functions, and the technique is in general often referred to as an FP-LMTO method. By “all-electron” it is meant that all electrons in the solid are considered in the calculation of electron density and total energy (as opposed, for instance, to a pseudo-potential method, where only the valence electrons are considered). The term “full potential” implies that no approximation is made to the shape of the electron density or the electronic potential (as opposed to the popular atomic sphere approximation, ASA [11], where the crystal is considered to be composed of space-filling atomic spheres, with a spherically symmetric potential inside each sphere).

The development of linear muffin-tin orbitals is due to Andersen, as is the use of linear augmented plane waves [11]. The LMTO basis set can be obtained from the older Korringa–Kohn–Rostocker (KKR) method [139, 142], where the main difference is the linearization of the energy-dependent basis functions. We will describe this technical difference between the two methods in Chaps. 5 and 6. The use of linear muffin-tin orbitals is by now well documented, and since the original suggestion of their usefulness some 4,000 applications have to this date been published (according to ISI web of knowledge). By now, several implementations of electronic structure methods which are based on LMTOs can be found, with varying degrees of sophistication. The most efficient and computationally least demanding variant of the method relies on the aforementioned atomic sphere approximation (ASA). An early account of this method, which often is described as LMTO-ASA, is the original reference of Andersen, but also in the book of Skriver [209] and in the works of [38]. Extensions of the original ideas of LMTOs can be found in the tight-binding version of the method [12], as well as the full-charge density implementation of it [248]. The LMTO-ASA method has also been adopted in a Green’s function formalism with the capability of treating disordered alloys in the coherent-potential approximation (CPA) [1, 210, 254]. In addition to the RSPt implementation of a full-potential LMTO method, there exists other independent, separate full-potential implementations using linear muffin-tin orbitals [199]. It should also be mentioned here that a derivative of the LMTO method exists in the form of the exact muffin-tin orbitals method (EMTO) [13, 247].

The main advantage with a full-potential implementation using linear muffin-tin orbitals, as described here, is that the electronic structure problem is solved with very high accuracy, so that total energies and Hellman–Feynman forces can be calculated with high precision, while maintaining a limited basis set, which makes the analysis of the calculated results straightforward. As will be shown in Chap. 11, an accuracy of the total energy (or rather difference in total energy for two different crystallographic geometries) of order μRy is needed to calculate, e.g., the elastic constants of materials. In Chap. 12 it is argued that an accuracy better than $0.1\mu\text{Ry}$ is needed to calculate the difference in total energy for two different magnetic orientations of regular magnetic transition metals like bcc Fe or hcp Co, and that the RSPt method can reach such high accuracy.

This implementation in RSPt is the result of both planning and evolution. One motivation for developing the method that eventually became RSPt was to be able to investigate the properties of *f*-electron elements and compounds, testing the applicability of density functional theory (DFT), in the local or nearly local approximation in describing the often unusual properties of these materials. Thus RSPt was born as a “full-potential” electronic structure method, expressing the shape of the electron density and potential in full generality. There were (and are) several other approximations to overcome, such as the “frozen core” approximation, in which the core electron density

is an external, constant input, and the lack of relativistic effects, particularly the spin-orbit interaction. RSPt treats all electrons on the same footing (“all-electron”) and includes relativistic effects such as the spin-orbit interaction in the one-electron Hamiltonian as well as spin polarization.

Another motivation for developing a new method was to provide a basis, based on first principles, for going beyond DFT, to include many-electron effects (strong correlation). The first use of the method, in fact, was to parametrize a Schrieffer–Wolff Hamiltonian to treat hybridization-mediated magnetic interactions in cerium mononictides [258]. The Schrieffer–Wolff Hamiltonian, like most phenomenological Hamiltonians treating strong correlation in solids, treats on-site correlation explicitly. As this was a motivating factor for the development of a new method, therefore, the natural choice was to use a site-centered basis. Thus RSPt uses linear muffin-tin orbitals (LMTOs), described in this book, as the basis for one-electron wave functions. Chapter 7 illustrates the usefulness of this choice. By choosing LMTO bases, RSPt, like other FP-LMTO methods, builds on a minimal basis set, emphasizing the applicability of the basis functions rather than basis set size, simplicity, or completeness.

The FP-LMTO method, as expressed in RSPt, solves the DFT electronic structure problem using a standard variational procedure based on the Kohn–Sham procedure [140] with a local (e.g., LDA [140]) or nearly local (e.g., GGA [179, 180]) approximation for the exchange and correlation functional as appropriate for that procedure. An input potential, an estimate of the exact potential (RSPt uses the one-electron potential as the variational parameter), is used to construct a one-electron Hamiltonian, and the eigenvalues and eigenvectors of this Hamiltonian are found within the span of a particular basis (the FP-LMTO method uses non-orthogonal linear muffin-tin orbitals). The Fermi energy is found by occupying the eigenstates in order, constrained by the required number of electrons, and the electron density is constructed by summing the occupied one-electron densities and used to construct a new one-electron potential. This potential is combined with the input potential to produce a new estimate of the exact potential, and the process continued until the input and output potentials are identical within a specified tolerance. When this self-consistency is achieved, the total energy calculated from self-consistent potential is the accurate ground state energy for the exchange-correlation functional used.

There have been several “FP-LMTO” implementations [168, 198, 199, 225, 255, 258]. In what follows, we try to distinguish features common to many implementations (labeled as “FPLMTO”) from our particular methodology (labeled “RSPt”).

Full-Potential Electronic Structure Method
Energy and Force Calculations with Density Functional
and Dynamical Mean Field Theory

Wills, J.M.; Alouani, M.; Andersson, P.; Delin, A.;

Eriksson, O.; Grechnev, O.

2010, XII, 200 p., Hardcover

ISBN: 978-3-642-15143-9