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Full-Potential Electronic Structure Method

Energy and Force Calculations with Density
Functional and Dynamical Mean Field Theory

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Full-Potential Electronic Structure Method

Energy and Force Calculations
with Density Functional
and Dynamical Mean Field Theory

With 59 Figures

 Springer

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We dedicate this book to
Barry, Börje, Hans, Mike, and Ole

Preface

This is a book describing electronic structure theory and application within the framework of a methodology implemented in the computer code RSPt. In 1986, when the code that was to become RSPt was developed enough to be useful, it was one of the first full-potential, all-electron, relativistic implementations of DFT (density functional theory). While RSPt was documented parasitically in many publications describing the results of its application, it was many years before a publication explicitly describing aspects of the method appeared. In the meantime, several excellent all-electron, full-potential methods had been developed, published, and become available. So why a book about RSPt now?

The code that became RSPt was initially developed as a personal research tool, rather than a collaborative effort or as a product. As such it required some knowledge of its inner workings to use, and as it was meant to be maximally flexible, the code required experience to be used effectively. These attributes inhibited, but did not prevent, the spread of RSPt as a research tool. While applicable across the periodic table, the method is particularly useful in describing a wide range of materials, including heavier elements and compounds, and its flexibility provides targeted accuracy and a convenient and accurate framework for implementing and assessing the effect of new models. A fair number of informal developers arose in the course of doctoral, post-doctoral, and professional research, principally at Uppsala University and at many other institutions as well. As a consequence, a number of innovative extensions to the code were developed, many of which were never integrated in the “official” version of RSPt and were consequently lost or shelved, often to be re-invented at a later date.

This situation started to change in 2006 when a group of researchers with a stake in the methodology met to establish a protocol for continuous development of a single RSPt thread. We established a code repository with developing branches merged periodically and a web site to facilitate communication, disseminate stable versions of the code, and provide a forum for user support and discussion. This group meets yearly to evolve the organization and suggest

ongoing and future efforts. The results of this organization have been gratifying. Computationally, data structures and memory allocation have been substantially reworked, eliminating non-standard and annoying remnants of Fortran 77 and enhancing modularity. RSPt is now k-point-, band-, and FFT-parallel. In methodology, physics modules such as DMFT and SIC are now present in the stable version, and forces are finally available without restriction.

No one is explicitly paid to do this development. At best, code and method development support particular research directions. The development continues, however, largely because the developers believe that expanding the capability and efficiency of RSPt will benefit their research, and that making RSPt more accessible will enhance the research of others. This book, encompassing electronic structure theory, technical detail, and representative application, is another step in this process.

Los Alamos
Uppsala
August 2010

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Formalisms

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 monpnictides [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”).

Density Functional Theory and the Kohn–Sham Equation

Abstract The basic formulas of density functional theory (DFT) are derived, together with a discussion about the form and accuracy of different approximations to the energy functional used in DFT. Central concepts in DFT, like exchange and correlation hole, exchange and correlation energy, and the Kohn–Sham equation are presented. A short description about the historical development of density functional theory as also given.

Calculations of material properties using density functional theory (DFT) have become a very active field of research in recent years. The basic idea of DFT is to use the electron charge density $n(\mathbf{r})$ as the basic variable instead of the many-electron wave function used in Hartree–Fock theory. This seemingly small – but in reality very nontrivial – step has provided the framework for fast and efficient calculations on highly complex materials, so it is easy to understand that DFT is popular. Figure 2.1 illustrates how the field

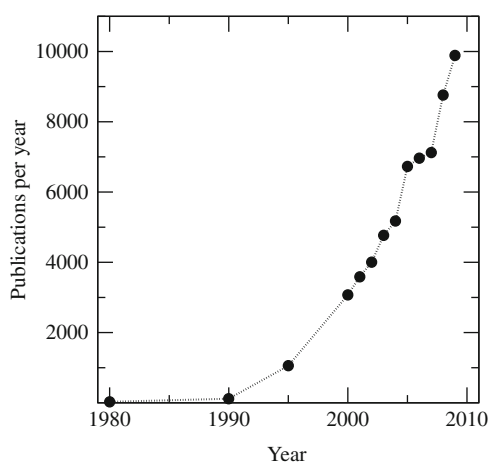


Fig. 2.1. Number of publications per year with topic “density functional” according to Web of Science (www.isiknowledge.com)

has grown in recent years. The number of publications per year in the field appears to have increased nearly exponentially during the last two decades. Nowadays, DFT-based computational methods are must-have tools in materials research and quantum chemistry. In recognition of the enormous success of DFT and computational schemes based on DFT, Walter Kohn and John A. Pople received the 1998 Nobel Prize in chemistry.

Over the years, the original formulation of DFT and the Kohn–Sham approach has been extended to cover a large number of situations, as, for instance, degenerate ground states [138], spin-polarized systems [188, 250], relativistic systems [162, 189], diamagnetic effects [246], finite temperature [166], excited states [102, 182, 234], fractional occupation numbers [158, 183], or multicomponent systems like electron–hole liquids [130, 196] and systems where the Born–Oppenheimer approximation is not valid [44]. In this chapter, we give a brief overview of the basic DFT machinery. More complete treatments can be found, e.g., in [75, 164].

2.1 The Many-Particle Problem

The basic problem in condensed matter theory which DFT attempts to solve is how to deal mathematically with the interactions of a large number of particles. If the system we are interested in is an atom or a small molecule, the number of particles is still rather small, but if we are dealing with larger systems, describing the wave function of the system explicitly becomes infeasible.

Despite these seemingly insurmountable difficulties, let us anyway start by writing the full Hamiltonian, in the non-relativistic case, of the many-body problem for a metal or other material in terms of the individual coordinates of each particle. The solid is a strongly coupled system consisting of two species – electrons and nuclei – with Coulomb interaction both between themselves and each other. The Hamiltonian (in SI units) will therefore consist of the following terms:

$$\begin{aligned} \mathcal{H} = & -\frac{\hbar^2}{2} \sum_I \frac{\nabla_I^2}{M_I} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{4\pi\epsilon_0 |\mathbf{R}_I - \mathbf{R}_J|} - \frac{\hbar^2}{2m} \sum_i \nabla_i^2 \\ & + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i, I} \frac{Z_I e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_I|}, \end{aligned} \quad (2.1)$$

where the indices i, j are used for electrons and I, J are for atomic nuclei, M_I denotes nuclear masses, m is the electron mass, \mathbf{R}_I and \mathbf{r}_i stand for nuclear and electron coordinates, respectively, and Z_I denotes atomic number. All attempts to find the eigenvectors and eigenvalues to this Hamiltonian involve approximations. To begin with, the nuclei are far more massive than the electrons and their velocities are therefore relatively low in comparison. Therefore, one may assume that the time scale for electron relaxation is much

shorter than the time scale of atom movement, so that the electron cloud can be assumed to be completely relaxed at any moment even if the atoms are, e.g., vibrating. This is called the Born–Oppenheimer (BO) approximation, which permits us to separate the time scales of electron and atom motion and thus to treat the terms in (2.1) dealing with the electron states separately from the ones dealing with the atomic nuclei. Further, the BO approximation allows us to recast the term describing the Coulomb interaction between the atomic nuclei and the electron cloud – the last term in (2.1) – as an external potential acting on the electrons. Although the Born–Oppenheimer approximation is very accurate in most cases, it does not always apply. One example is graphene [128].

Thus, our many-particle problem has been reduced to a strongly interacting “gas”¹ or liquid of electrons moving in an external potential, and the Hamiltonian acting on the electrons can now be written as

$$\mathcal{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} = T + W + V_{\text{ext}}. \quad (2.2)$$

The first term, T , is the kinetic energy operator of the electrons. The second, W , is the Coulomb potential from electron–electron interaction, and the third term, V_{ext} , is the external potential, i.e., the Coulomb potential from the interactions between the electrons and the nuclei. The corresponding total energy E is the expectation value of \mathcal{H} in (2.2), i.e.,

$$E = \langle \Psi | \mathcal{H} | \Psi \rangle = T + W + \int d^3r V_{\text{ext}}(\mathbf{r})n(\mathbf{r}), \quad (2.3)$$

with T and W now denoting the expectation values of the kinetic energy and electron–electron interaction operators, respectively. From classical physics we know that the Coulomb energy of a charge density interacting with itself is

$$E_{\text{Hartree}} = \frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (2.4)$$

This term is called the Hartree energy and is an important part of the middle term W in (2.3), but obviously not the full story. To begin with, the Hartree energy contains a spurious self-interaction. Further, since electrons are particles, their motions will be correlated causing a depletion in the charge density around each electron. In addition, the quantum-mechanical nature of electrons causes a special type of correlation – exchange – due to the exclusion principle. These extra terms are usually grouped together in the so-called exchange–correlation energy E_{xc} .

¹ The original meaning of the word gas, *chaos*, may provide a better association.