Preface

In recent years, computational materials science has clearly emerged as an important field of condensed matter physics. In particular, the development of new computing facilities has made it possible to study physical phenomena at the *atomic* scale by means of *ab initio* electronic structure methods. Among various approaches used, the Linear Muffin-Tin Orbitals method (LMTO) proposed in the seventies by O.K. Andersen has played a key role. In its Atomic Sphere Approximation (ASA), the LMTO method has been widely used to tackle various type of problems. In 1984, O.K. Anderson and coworkers introduced a *localized* LMTO basis set. This new approach, called Tight-Binding LMTO (TB-LMTO), has paved the way to an order-N scheme, giving new impetus to the study of numerous physical properties of systems with large number of atoms.

This book is based on selected contributions presented at a workshop, organized in October 1998 in the monastery of Mont Saint Odile (near Strasbourg, France). A large number of scientists involved in the development and the practice of the LMTO method gathered there for three days. The first part of this book is devoted to the formalisms for ground and excited states. It starts with a review, by Andersen and coworkers, of the TB-LMTO method and its generalization. The Schrödinger equation of Nth order in the energy expansion for an overlapping muffin-tin potential is solved using a minimal basis set. The aim of this third generation LMTO method is to take a further step beyond the limitations of the popular atomic-sphere approximation. The present approach uses wave functions which are accurate not only in the muffin-tin spheres but also in the interstitial region. In the conventional implementations of the LMTO-ASA method it is difficult to determine the forces on the atoms. For this reason Full-Potential LMTO approaches have been developed. In this book two different approaches are described. The first one is proposed by Methfessel and coworkers and is based on smooth Hankel functions. The use of these special functions allows the method to provides a good accuracy of the total energy with an almost minimal basis set. The second approach proposed by Wills and coworkers uses a large basis set which can describe multiple principal quantum numbers within a single *fully hybridized* basis set. This large basis set allows this method to determine the excited states to higher energies without the need for cumbersome multiple energy panel calculations like in the minimal basis set methods. However, the drawback and limitation of these FP methods remains the huge computational effort needed, which inhibits calculations of systems with large

numbers of atoms. To overcome these computational hurdles, Kollar and cowor-
kers presented the so called *full-density* method, a method halfway between the
ASA and the FP, which combines the simplicity of the former and the accuracy
of the latter. In the initial description of the Density Functional Theory (DFT),
the eigenvalues are Lagrange multipliers, and thus no physical meaning can be
associated with them. However the success of excited states calculations based
on DFT can be understood due to the fact that the Kohn–Sham equations can
be viewed as an approximation to the quasi-particle equations where the self-
energy is local and time independent. Alouani and Wills give the basics and
some applications to the determination of optical properties and x-ray magnetic
dichroism.

One of the main success of the LMTO schemes in the last few years has
been the description of magnetic systems. A fully relativistic formalism and the
applications to spectroscopy are presented by Ebert. The key question of the
magnetic anisotropy of bulk and thin films is addressed by Eriksson and Wills,
illustrating the high level of precision reached, whereas Temmerman and co-
workers present a unified formalism to describe localized and delocalized states,
pointing out the importance of the self-interaction correction. Another spectacu-
lar use of the TB-LMTO method is given by Kudrnovsky and coworkers on the
Interlayer Exchange Coupling (IEC). Ab initio formulations of the IEC between
non-collinearly aligned magnetic slabs lead to results in good agreement with
experiment.

One advantage of the TB-LMTO is its use to describe disordered systems such
as alloys with the precision of ab initio methods. A short review of the TB-LMTO
within the Coherent Potential Approximation (CPA) applied to disordered alloys
and surfaces is given by Turek and coworkers, whereas Abrikosov and coworkers
present a locally self-consistent Green's function method. This latter order-N
method is particularly interesting for systems with a large number of inequivalent
atoms.

Mathematical and numerical problems are the building blocks of ab initio
methods, and numerical algorithms for solving various parts of the formalism are
of great interest. In particular, the diagonalisation of sparse matrices, which is at
the heart of the TB-LMTO method, by efficient algorithms is highly desirable. In
this respect, Scott has given an introduction to direct methods for the solution
of large-scale linear systems, emphasizing the progress made in the development
of routines which are now available in numerical libraries. The book ends with
two contributions on the determination of the electronic structure in real space:
a real-space derivation of the TB-LMTO method by Spisak and Hafner, and the
venerable semi-empirical tight-binding method by Cornea and Stoeffler.

I would like to thank each of the sixty-seven scientists from seventeen different
countries who make this book possible, especially those who came from far away
countries, like Argentina, Brasil, India, and Japan. The meeting was held over
three days in a lively atmosphere where the most recent progress in the ab initio
methods was presented and where discussions continued well after the talks.

Besides the fourteen invited talks which form the basis of this book, nineteen shorter presentations offered the opportunity to focus on more precise points.

The "Ab-initio Calculations of Magnetic Properties of Surfaces, Interfaces, and Multilayers" TMR European network provided the first impulse for this meeting. The support of the European Science Foundation (ESF) through the program Ψ_k allowed the participation of a large number of scientists. Finally, the local support of the IPCMS (Institut de Physique et Chimie de Strasbourg) was greatly appreciated. I would also like to thank M. Alouani for constant interest and I. Galanakis, who struggled and succeeded in finalizing the electronic version of the book.

Strasbourg, August 1999   *Hugues Dreyssé*