

## Part I

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### Theory



## Introduction

Prof. P. Fulde wrote in the preface to the first edition of his book [5]: Monographs are required that emphasize the features common to quantum chemistry and solid-state physics. The book by Fulde presented the problem of electron correlations in molecules and solids in a unified form. The common feature of these fields is also the use of the LCAO (linear combination of atomic orbitals) approximation: being from the very beginning the fundamental principle of molecular quantum chemistry LCAO only recently became the basis of the first-principles calculations for periodic systems. The LCAO methods allow one to use wavefunction-based (Hartree-Fock), density-based (DFT) and hybrid Hamiltonians for electronic- structure calculations of crystals. Compared to the conventional plane-waves (PW) or muffin-tin orbitals (MTO) approximations the LCAO approach has proven to be more flexible. To analyze the local properties of the electronic structure the LCAO treatment may be applied to both periodic- and molecular-cluster (nonperiodic) models of solid. Furthermore, post-Hartree-Fock methods can be extended to periodic systems exhibiting electron correlation. LCAO methods are able to avoid an artificial periodicity typically introduced in PW or MTO for a slab model of crystalline surfaces. The LCAO approach is a natural way to extend to solid-state procedures of the chemical bonding analysis developed for molecules. With recent advances in computing power LCAO first-principles calculations are possible for systems containing many (hundreds) atoms per unit cell. The LCAO results are comparable with the traditional PW or MTO calculations in terms of accuracy and variety of accessible physical properties. More than 30 years ago, it was well understood that the quantum theory of solids based on LCAO enabled solid-state and surface chemists to follow the theoretically based papers that appeared ([2]). As an introduction to the theory of the chemical bond in tetrahedral semiconductors the book [3](translation from the Russian edition of 1973) appeared. Later other books [6] and [7] appeared. These books brought together views on crystalline solids held by physicists and chemists. The important step in the computational realization of the LCAO approach to periodic systems was made by scientists from the Theoretical Chemistry Group of Turin University (C. Pisani, R. Dovesi, C. Roetti) and the Daresbury Computation Science Department in England (N.M. Harrison, V.R. Saunders) with their coworkers from different countries who developed several versions of the CRYSTAL computer code-(88, 92, 95, 98, 03, 06) for the first- principles LCAO calculations of periodic systems. This code is now

used by more than 200 scientific groups all over the world. Many results applying the above code can be found in the book published about ten years ago by Springer: [4]. The publication includes review articles on the Hartree–Fock LCAO approach for application to solids written by scientists actively working in this field. The book by Fulde mentioned earlier takes the next step to bridge the gap between quantum chemistry and solid-state theory by addressing the problem of electron correlations. During the next ten years many new LCAO applications were developed for crystals, including the hybrid Hartree–Fock–DFT method, full usage of the point and translational symmetry of periodic system, new structure optimization procedures, applications to research related to optical and magnetic properties, study of point defects and surface phenomena, generation of the localized orbitals in crystals with application to the correlation effects study. Also, LCAO allowed the development of  $O(N)$  methods that are efficient for large-size many-atom periodic systems. Recently published books including [8–11] may be considered as the high-quality modern text books. The texts provide the necessary background for the existing approaches used in the electronic-structure calculations of solids for students and researchers. Published in the Springer Series in Solid State Sciences (vol. 129) a monograph [12] introduces all the existing theoretical techniques in materials research (which is confirmed by the subtitle of this book: From Ab initio to Monte Carlo Methods). This book is written primarily for materials scientists and offers to materials scientists access to a whole variety of existing approaches. However, to our best knowledge a comprehensive account of the main features and possibilities of LCAO methods for the first-principles calculations of crystals is still lacking. We intend to fill this gap and suggest a book reflecting the state of the art of LCAO methods with applications to the electronic-structure theory of periodic systems. Our book is written not only for the solid-state and surface physicists, but also for solid-state chemists and material scientists. Also, we hope that graduate students (both physicists and chemists) will be able to use it as an introduction to the symmetry of solids and for comparison of LCAO methods for solids and molecules. All readers will find the description of models used for perfect and defective solids (the molecular-cluster, cyclic-cluster and supercell models, models of the single and repeating slabs for surfaces, the local properties of the electronic-structure calculations in the theory of the chemical bonding in crystals). We hope that the given examples of the first-principles LCAO calculations of different solid-state properties will illustrate the efficiency of LCAO methods and will be useful for researchers in their own work. This book consists of two parts: theory and applications. In the first part (theory) we give the basic theory underlying the LCAO methods applied to periodic systems. The translation symmetry of solids and its consequence is discussed in connection with a so-called cyclic (with periodical boundary conditions) model of an infinite crystal. For chemists it allows clarification of why the  $\mathbf{k}$ -space introduction is necessary in the electronic-structure calculations of solids. The site-symmetry approach is considered briefly (it is given in more detail in [13]). The analysis of site symmetry in crystals is important for understanding the connection between one-particle states (electron and phonon) in free atoms and in a periodic solid. To make easier the practical LCAO calculations for specific crystalline structures we explain how to use the data provided on the Internet sites for crystal structures of inorganic crystals and irreducible representations of space groups. In the next chapters of Part I we give the basics of Hartree–Fock and Kohn–Sham methods

for crystals in the LCAO representation of crystalline orbitals. It allows the main differences between the LCAO approach realization for molecules and periodic systems to be seen. The hybrid Hartee–Fock–DFT methods were only recently extended from molecules to solids, and their advantages are demonstrated by the LCAO results on bandgap and atomic structure for crystals.

In the second part (applications) we discuss some recent applications of LCAO methods to calculations of various crystalline properties. We consider, as is traditional for such books the results of some recent band-structure calculations and also the ways of local properties of electronic- structure description with the use of LCAO or Wannier-type orbitals. This approach allows chemical bonds in periodic systems to be analyzed, using the well-known concepts developed for molecules (atomic charge, bond order, atomic covalency and total valency). The analysis of models used in LCAO calculations for crystals with point defects and surfaces and illustrations of their applications for actual systems demonstrate the efficiency of LCAO approach in the solid-state theory. A brief discussion about the existing LCAO computer codes is given in Appendix C.

Quantum Chemistry of Solids

The LCAO First Principles Treatment of Crystals

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