

R. A. Evarestov

Quantum Chemistry of Solids

The LCAO
First Principles
Treatment
of Crystals

固体量子化学

Robert A. Evarestov

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The LCAO First Principles Treatment of Crystals

With 78 Figures and 126 Tables



Springer

图书在版编目(CIP)数据

固体量子化学:晶体的原子轨道线性组合第一性原理计算方法 = Quantum Chemistry of Solids: The LCAO First Princip; 英文/(俄罗斯)叶瓦列斯托夫著. —影印本.
—北京:世界图书出版公司北京公司, 2012. 1
ISBN 978 - 7 - 5100 - 4284 - 3

I. ①固… II. ①叶… III. ①固体—量子化学—研究 IV. ①O641. 12

中国版本图书馆 CIP 数据核字(2011)第 267579 号

书 名: Quantum Chemistry of Solids; The LCAO First Principles Treatment of Crystals
作 者: R. A. Evarestov
中 译 名: 固体量子化学
责任编辑: 高蓉 刘慧

出 版 者: 世界图书出版公司北京公司
印 刷 者: 三河市国英印务有限公司
发 行 者: 世界图书出版公司北京公司(北京朝内大街 137 号 100010)
联系电话: 010 - 64021602, 010 - 64015659
电子信箱: kjb@wpchj.com.cn

开 本: 24 开
印 张: 24
版 次: 2012 年 03 月
版权登记: 图字:01 - 2011 - 2562

书 号: 978 - 7 - 5100 - 4284 - 3/O · 924 定 价: 65.00 元

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Library of Congress Control Number: 2006936622

ISBN 978-3-540-48746-3 Springer Berlin Heidelberg New York

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This book is dedicated to my teacher and friend
Professor Marija I. Petrashen

Preface

Nobel Prize Winner Prof. Roald Hoffmann forewarding a recently published book by Dronskowski [1] on computational chemistry of solid-state materials wrote that one is unlikely to understand new materials with novel properties if one is wearing purely chemical or physical blinkers. He prefers a coupled approach – a chemical understanding of bonding merged with a deep physical description. The quantum chemistry of solids can be considered as a realization of such a coupled approach.

It is traditional for quantum theory of molecular systems (molecular quantum chemistry) to describe the properties of a many-atom system on the grounds of interatomic interactions applying the linear combination of atomic orbitals (LCAO) approximation in the electronic-structure calculations. The basis of the theory of the electronic structure of solids is the periodicity of the crystalline potential and Bloch-type one-electron states, in the majority of cases approximated by a linear combination of plane waves (LCPW). In a quantum chemistry of solids the LCAO approach is extended to periodic systems and modified in such a way that the periodicity of the potential is correctly taken into account, but the language traditional for chemistry is used when the interatomic interaction is analyzed to explain the properties of the crystalline solids. At first, the quantum chemistry of solids was considered simply as the energy-band theory [2] or the theory of the chemical bond in tetrahedral semiconductors [3]. From the beginning of the 1970s the use of powerful computer codes has become a common practice in molecular quantum chemistry to predict many properties of molecules in the first-principles LCAO calculations. In the condensed-matter studies the accurate description of the system at an atomic scale was much less advanced [4].

During the last 10 years this gap between molecular quantum chemistry and the theory of the crystalline electronic structure has become smaller. The concepts of standard solid-state theory are now compatible with an atomic-scale description of crystals. There are now a number of general-purpose computer codes allowing prediction from the first-principles LCAO calculations of the properties of crystals. These codes are listed in Appendix C. Nowadays, the quantum chemistry of solids can be considered as the original field of solid-state theory that uses the methods of molecular quantum chemistry and molecular models to describe the different properties of solid materials including surface and point-defect modeling.

In this book we have made an attempt to describe the basic theory and practical methods of modern quantum chemistry of solids.

This book would not have appeared without the help of Prof. M. Cardona who supported the idea of its writing and gave me useful advice.

I am grateful to Prof. C. Pisani and members of the Torino group of Theoretical Chemistry, Prof. R. Dovesi, Prof. C. Roetti, for many years of fruitful cooperation. Being a physicist-theoretician by education, I would never have correctly estimated of the role of quantum chemistry approaches to the solids without this cooperation. I am grateful to all my colleagues who took part in our common research (Prof. V. Smirnov, Prof. K. Jug, Prof. T. Bredow, Prof. J. Maier, Prof. E. Kotomin, Prof. Ju. Zhukovskii, Prof. J. Choisnet, Prof. G. Borstel, Prof. F. Illas, Dr. A. Dobrotvorsky, Dr. V. Lovchikov, Dr. V. Veryazov, Dr. I. Tupitsyn, Dr. A. Panin, Dr. A. Bandura, Dr. D. Usvyat, Dr. D. Gryaznov, V. Alexandrov) or sent me the recent results of their research (Prof. C. Pisani, Prof. R. Dovesi, Prof. C. Roetti, Prof. P. Deak, Prof. P. Fulde, Prof. G. Stoll, Prof. M. Schütz, Prof. A. Schluger, Prof. L. Kantorovich, Prof. C. Minot, Prof. G. Scuseria, Prof. R. Dronskowski, Prof. A. Titov). I am grateful to Prof. I. Abarenkov, head of the Prof. M.I. Petrashen named seminar for helpful discussions and friendly support. I would like to express my thanks to the members of the Quantum Chemistry Department of St. Petersburg State University, Dr. A. Panin and Dr. A. Bandura, for help in preparing the manuscript – without their help this book would not be here.

I am especially indebted to Dr. C. Ascheron, Mrs. A. Lahee and Dr. P. Capper of Springer-Verlag for encouragement and cooperation.

St. Petersburg,

Robert Evarestov
August, 2006

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Part I

Theory

