R. A. Evarestov **Quantum Chemistry of Solids** The LCAO First Principles Treatment of Crystals



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Robert A. Evarestov

Quantum Chemistry of Solids

The LCAO First Principles Treatment of Crystals

With 78 Figures and 126 Tables



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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 Blochtype 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 condensedmatter 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.

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St. Petersburg,

Robert Evarestov August, 2006

Contents

Part I Theory

1	Intr	roduct	ion	3	
2	Space Groups and Crystalline Structures				
	2.1	Trans	lation and Point Symmetry of Crystals	7	
		2.1.1	Symmetry of Molecules and Crystals: Similarities and	_	
			Differences	7	
		2.1.2	Translation Symmetry of Crystals. Point Symmetry		
		~	of Bravais Lattices. Crystal Class	11	
	2.2	Space	Groups	16	
		2.2.1	Space Groups of Bravais Lattices. Symmorphic		
			and Nonsymmorphic Space Groups	16	
		2.2.2	Three-periodic Space Groups	18	
		2.2.3	Site Symmetry in Crystals. Wyckoff Positions	22	
	2.3	Cryst	alline Structures	26	
		2.3.1	Crystal-structure Types. Structure Information		
		2.3.2	for Computer Codes Cubic Structures: Diamond, Rocksalt, Fluorite, Zincblende,	26	
			Cesium Chloride, Cubic Perovskite	28	
		2.3.3	Tetragonal Structures: Rutile, Anatase and La_2CuO_4	34	
		2.3.4	Orthorhombic Structures: LaMnO ₃ and YBa ₂ Cu ₃ O ₇	37	
		2.3.5	Hexagonal and Trigonal Structures: Graphite, Wurtzite,		
			Corundum and $ScMnO_3$	42	
3	\mathbf{Syn}	ametr	y and Localization of Crystalline Orbitals	47	
	3.1	Trans	lation and Space Symmetry of Crystalline Orbitals.		
		Bloch	Functions	47	
		3.1.1	Symmetry of Molecular and Crystalline Orbitals	47	
		3.1.2	Irreducible Representations of Translation Group.		
			Brillouin Zone	51	
		3.1.3	Stars of Wavevectors. Little Groups. Full Representations		
			of Space Groups	58	

		3.1.4	Small Representations of a Little Group. Projective	
		a. a	Representations of Point Groups	61
	3.2	Site S	ymmetry and Induced Representations of Space Groups	66
		3.2.1	Induced Representations of Point Groups.	
			Localized Molecular Orbitals	66
		3.2.2	Induced Representations of Space Groups in q -basis	71
		3.2.3	Induced Representations of Space Groups in k -basis.	
			Band Representations	73
		3.2.4	Simple and Composite Induced Representations	76
		3.2.5	Simple Induced Representations for Cubic Space Groups	
			O_h^1, O_h^5 and O_h^7	78
		3.2.6	Symmetry of Atomic and Crystalline Orbitals	
			in MgO, Si and SrZrO ₃ Crystals	83
	3.3	Symm	netry of Localized Crystalline Orbitals. Wannier Functions	86
		3.3.1	Symmetry of Localized Orbitals and Band Representations	
			of Space Groups	86
		3.3.2	Localization Criteria in Wannier-function Generation	90
		3.3.3	Localized Orbitals for Valence Bands: LCAO approximation	94
		3.3.4	Variational Method of Localized Wannier-function Generation	
			on the Base of Bloch Functions	96
4	Har	tree–I	Fock LCAO Method for Periodic Systems	105
	4.1	One-	electron Approximation for Crystals	105
		4.1.1	One-electron and One-determinant Approximations	
			for Molecules and Crystals	105
		4.1.2	Symmetry of the One-electron Approximation Hamiltonian	109
		4.1.3	Restricted and Unrestricted Hartree–Fock LCAO Methods	
			for Molecules	111
		4.1.4	Specific Features of the Hartree–Fock Method	
			for a Cyclic Model of a Crystal	116
		4.1.5	Restricted Hartree–Fock LCAO Method for Crystals	119
		4.1.6	Unrestricted and Restricted Open-shell Hartree–Fock Methods	
			for Crystals	122
	4.2	Speci	ial Points of Brillouin Zone	124
		4.2.1	Supercells of Three-dimensional Bravais Lattices	124
		4.2.2	Special Points of Brillouin-zone Generating	125
		4.2.3	Modification of the Monkhorst–Pack Special-points Meshes	128
	4.3	Densi	ty Matrix of Crystals in the Hartree–Fock Method	132
	1.0	4.3.1	Properites of the One-electron Density Matrix of a Crystal	132
		4.3.2	The One-electron Density Matrix of the Crystal	
		1.0.2	in the LCAO Approximation	137
		433	Interpolation Procedure for Constructing an Approximate	101
		1.0.0	Density Matrix for Periodic Systems	140
			2 child, haven for 1 childre 5,500mb	110
5	Elee	ctron (Correlations in Molecules and Crystals	147
	5.1	Electr	on Correlations in Molecules: Post-Hartree–Fock Methods	147
		5.1.1	What is the Electron Correlation ?	147

		5.1.2	Configuration Interaction and Multi-configuration	
			Self-consistent Field Methods	150
		5.1.3	Coupled-cluster Methods	154
		5.1.4	Many-electron Perturbation Theory	155
		5.1.5	Local Electron-correlation Methods	158
	5.2	Incren	nental Scheme for Local Correlation in Periodic Systems	163
		5.2.1	Weak and Strong Electron-correlation	163
		5.2.2	Method of Increments: Ground State	166
		5.2.3	Method of Increments: Valence-band Structure	
			and Bandgap	169
	5.3	Atom	ic Orbital Laplace-transformed MP2 Theory	
		for Pe	riodic Systems	174
		5.3.1	Laplace MP2 for Periodic Systems:	
			Unit-cell Correlation Energy	174
		5.3.2	Laplace MP2 for Periodic Systems:	
			Bandgap	177
	5.4	Local	$\operatorname{MP2}$ Electron-correlation Method for Nonconducting Crystals .	180
		5.4.1	Local MP2 Equations for Periodic Systems	180
		5.4.2	Fitted Wannier Functions for Periodic Local Correlation	
			Methods	184
		5.4.3	Symmetry Exploitation in Local MP2 Method	
			for Periodic Systems	188
6	Sen	iemni	rical LCAO Methods for Molecules and Periodic	
U	Svs	tems	incar Derio Methods for Molecules and Feriodic	193
	6.1	Exten	ded Hückel and Mulliken–Rüdenberg Approximations	193
		6.1.1	Nonself-consistent Extended Hückel–Tight-binding Method	193
		6.1.2	Iterative Mulliken–Rüdenberg Method for Crystals	199
	6.2	Zero-o	differential Overlap Approximations for Molecules and Crystals	203
	0.2	6.2.1	Zero-differential Overlap Approximations for Molecules	203
		6.2.2	Complete and Intermediate Neglect of Differential Overlap	-00
		0.2.2	for Crystals	208
	6.3	Zero-o	differential overlap Approximation in Cyclic-cluster Model	211
	0.0	6.3.1	Symmetry of Cyclic-cluster Model of Perfect Crystal	211
		6.3.2	Semiempirical LCAO Methods in Cyclic-cluster Model	215
		6.3.3	Implementation of the Cyclic-cluster Model in MSINDO	-10
		0.0.0	and Hartree–Fock LCAO Methods	220
-	TZ 1	CI		0.9.1
1	N 01	n-sna	am LCAO Method for Periodic Systems	231
	(.1	Found	ations of the Density-functional Theory	231
		(.1.1	The Basic Formulation of the Density-functional Theory	231
		7.1.2	I ne Konn–Sham Single-particle Equations	234
		1.1.3	Exchange and Correlation Functionals	0.07
			in the Local Density Approximation	237
		F 1 4		0.40
		7.1.4	Beyond the Local Density Approximation	240
		7.1.4 7.1.5	Beyond the Local Density Approximation The Pair Density. Orbital-dependent Exchange-correlation	240

7.2	Density-functional LCAO Methods for Solids		
	7.2.1	Implementation of Kohn–Sham LCAO Method	
		in Crystals Calculations	249
	7.2.2	Linear-scaling DFT LCAO Methods for Solids	253
	7.2.3	Heyd–Scuseria–Ernzerhof Screened Coulomb Hybrid	
		Functional	259
	7.2.4	Are Molecular Exchange-correlation Functionals Transferable	
		to Crystals?	263
	7.2.5	Density-functional Methods for Strongly Correlated Systems:	
		SIC DFT and DFT+U Approaches	270

Part II Applications

8	\mathbf{Bas}	is Sets	s and Pseudopotentials in Periodic LCAO Calculations .	281
	8.1	Basis	Sets in the Electron-structure Calculations of Crystals	281
		8.1.1	Plane Waves and Atomic-like Basis Sets. Slater-type Functions	281
		8.1.2	Molecular Basis Sets of Gaussian-type Functions	285
		8.1.3	Molecular Basis Sets Adaptation for Periodic Systems	291
	8.2	Nonre	lativistic Effective Core Potentials and Valence Basis Sets	298
		8.2.1	Effective Core Potentials: Theoretical Grounds	298
		8.2.2	Gaussian Form of Effective Core Potentials	
			and Valence Basis Sets in Periodic LCAO Calculations	302
		8.2.3	Separable Embedding Potential	304
	8.3	Relati	vistic Effective Core Potentials and Valence Basis Sets	310
		8.3.1	Relativistic Electronic Structure Theory: Dirac–Hartree–Fock	
			and Dirac–Kohn–Sham Methods for Molecules	310
		8.3.2	Relativistic Effective Core Potentials	314
		8.3.3	One-center Restoration of Electronic Structure	
			in the Core Region	316
		8.3.4	Basis Sets for Relativistic Calculations of Molecules	318
		8.3.5	Relativistic LCAO Methods for Periodic Systems	320
9	LC	AO C	alculations of Perfect-crystal Properties	327
	9.1	Theo	retical Analysis of Chemical Bonding in Crystals	328
		9.1.1	Local Properties of Electronic Structure in LCAO HF	
			and DFT Methods for Crystals and Post-HF Methods	
			for Molecules	328
		9.1.2	Chemical Bonding in Cyclic-cluster Model: Local Properties	
			of Composite Crystalline Oxides	333
		9.1.3	Chemical Bonding in Titanium Oxides: Periodic	
			and Molecular-crystalline Approaches	342
		9.1.4	Wannier-type Atomic Functions and Chemical Bonding	
			in Crystals	350
		9.1.5	The Localized Wannier Functions for Valence Bands:	
			Chemical Bonding in Crystalline Oxides	358

		9.1.6	Projection Technique for Population Analysis of Atomic Orbitals. Comparison of Different Methods of the Chemical- bonding Description in Crustels	260
	9.2	Elect	ron Properties of Crystals in LCAO Methods	$309 \\ 375$
		9.2.1	One-electron Properties: Band Structure, Density of States, Electron Momentum Density	375
		9.2.2	Magnetic Structure of Metal Oxides in LCAO Methods:	515
	0.2	Total	Magnetic Phases of LaMnO ₃ and ScMnO ₃ Crystals	383
	9.5	for So	lids	393
		9.3.1	Equilibrium Structure and Cohesive Energy	393
		9.3.2	Bulk Modulus, Elastic Constants and Phase Stability of	
			Solids: LCAO ab-initio Calculations	398
		9.3.3	Lattice Dynamics and LCAO Calculations	40.9
			or vibrational Frequencies	403
10	Moo	deling	and LCAO Calculations of Point Defects in $\ensuremath{Crystals}\ldots$	409
	10.1	Symm	netry and Models of Defective Crystals	409
		10.1.1	Point Defects in Solids and Their Models	409
		10.1.2	Symmetry of Supercell Model of Defective Crystals	413
		10.1.3	supercell and Cyclic-cluster Models of Neutral	417
		10.1.4	Molocular cluster Models of Defective Solids	417
	10.2	Point	Defects in Binary Oxides	426
	10.2	10.2.1	Oxygen Interstitials in Magnesium Oxide:	120
		10.0.0	Supercell LCAO Calculations	426
		10.2.2	Neutral and Charged Oxygen Vacancy in Al_2O_3 Crystal:	490
		10 2 3	Supercell and Cyclic-cluster Calculations	429
	10.3	Point	Defects in Perovskites	438
	10.0	10.3.1	Oxygen Vacancy in SrTiO ₂	438
		10.3.2	Supercell Model of Fe-doped SrTiO ₃	445
		10.3.3	Modeling of Solid Solutions of $La_cSr_{1-c}MnO_3$	452
11	Sur	face N	Modeling in LCAO Calculations of Metal Oxides	459
	11.1	Diperi	odic Space Groups and Slab Models of Surfaces	459
		11.1.1	Diperiodic (Layer) Space Groups	459
		11.1.2	Oxide-surface Types and Stability	466
		11.1.3	Single- and Periodic-slab Models of MgO and TiO_2 Surfaces	470
	11.2	Surfac	e LCAO Calculations on TiO_2 and SnO_2	482
		11.2.1 11.2.2	Cluster Models of (110) TiO_2 Adsorption of Water on the TiO_2 (Rutile) (110) Surface:	482
			Comparison of Periodic LCAO-PW and Embedded-cluster LCAO Calculations	487
		11.2.3	Single-slab LCAO Calculations of Bare and Hydroxylated SnO ₂ Surfaces	495
	11.3	Slab	Models of $SrTiO_3$, $SrZrO_3$ and $LaMnO_3$ Surfaces	507

	11.3.1 Hybrid HF-DFT Comparative Study of $SrZrO_3$	
	and $SrTiO_3$ (001) Surface Properties	507
	11.3.2 F Center on the $SrTiO_3$ (001) Surface	513
	11.3.3 Slab Models of LaMnO ₃ Surfaces	515
A	Matrices of the Symmetrical Supercell Transformations of 14 Three dimensional Brazis Lattices	591
	Three-dimensional Dravais Lattices	921
в	Reciprocal Matrices of the Symmetric Supercell Transformations	
	of the Three Cubic Bravais Lattices	525
\mathbf{C}	Computer Programs for Periodic Calculations in Basis	
	of Localized Orbitals	527
Ref	ferences	531
Ind	lex	553

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 solidstate 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 electronicstructure 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 consequency 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.

Space Groups and Crystalline Structures

2.1 Translation and Point Symmetry of Crystals

2.1.1 Symmetry of Molecules and Crystals: Similarities and Differences

Molecules consist of positively charged nuclei and negatively charged electrons moving around them. If the translations and rotations of a molecule as a whole are excluded, then the motion of the nuclei, except for some special cases, consists of small vibrations about their equilibrium positions. Orthogonal operations (rotations through symmetry axes, reflections in symmetry planes and their combinations) that transform the equilibrium configuration of the nuclei of a molecule into itself are called the symmetry operations of the molecule. They form a group F of molecular symmetry. Molecules represent systems from finite (sometimes very large) numbers of atoms, and their symmetry is described by so-called point groups of symmetry. In a molecule it is always possible to so choose the origin of coordinates that it remains fixed under all operations of symmetry. All the symmetry elements (axes, planes, inversion center) are supposed to intersect in the origin chosen. The point symmetry of a molecule is defined by the symmetry of an arrangement of atoms forming it but the origin of coordinates chosen is not necessarily occupied by an atom.

In modern computer codes for quantum-chemical calculations of molecules the point group of symmetry is found automatically when the atomic coordinates are given. In this case, the point group of symmetry is only used for the classification of electronic states of a molecule, particularly for knowledge of the degeneracy of the one-electron energy levels . To make this classification one needs to use tables of irreducible representations of point groups. The latter are given both in books [13–15] and on an Internet site [16] Calculation of the electronic structure of a crystal (for which a macroscopic sample contains 10^{23} atoms) is practically impossible without the knowledge of at least the translation symmetry group. The latter allows the smallest possible set of atoms included in the so-called primitive unit cell to be considered. However, the classification of the crystalline electron and phonon states requires knowledge of the full symmetry group of a crystal (space group). The structure of the irreducible representations of the space groups is essentially more complicated and use of existing tables [17] or the site [16] requires knowledge of at least the basics of space-group theory.

Discussions of the symmetry of molecules and crystals are often limited to the indication that under operations of symmetry the configuration of the nuclei is transformed to itself. The symmetry group is known when the coordinates of all atoms in a molecule are given. Certainly, the symmetry of a system is defined by a geometrical arrangement of atomic nuclei, but operations of symmetry translate all equivalent points of space to each other. In equivalent points the properties of a molecule or a crystal (electrostatic potential, electronic density, etc.) are all identical. It is necessary to remember that the application of symmetry transformations means splitting all space into systems of equivalent points irrespective of whether there are atoms in these points or not. In both molecules and in crystals the symmetry group is the set of transformations in three dimensional space that transforms any point of the space into an equivalent point. The systems of equivalent points are called orbits of points (This has nothing to do with the orbitals – the one-electron functions in manyelectron systems). In particular, the orbits of equivalent atoms in a molecule can be defined as follows. Atoms in a molecule occupy the positions q with a certain site symmetry described by some subgroups F_q of the full point symmetry group F of a molecule. The central atom (if one exists) has a site-symmetry group $F_q = F$. Any atom on the principal symmetry axis of a molecule with the symmetry groups C_n , C_{nv} , S_n also has the full symmetry of the molecule $(F_q = F)$. Finally, $F_q = F$ for any atom lying in the symmetry plane of a molecule with the symmetry group $F = C_s$. In other cases F_q is a subgroup of F and includes those elements R of point group F that satisfy the condition Rq = q. Let F_1 be a site-symmetry group of a point q_1 in the molecular space. This point may not be occupied by an atom. Let the symmetry group of a molecule be decomposed into left cosets with respect to its site-symmetry subgroup $F_{\boldsymbol{a}}$:

$$F = \sum_{j} R_{j}F_{j}, \quad R_{1} = E, \quad j=1,2,...,t$$
(2.1)

The set of points $q_j = R_j q_1$, j=1,2,...,t, forms an orbit of the point q_1 .

The point q_j of the orbit has a site-symmetry group $F_j = R_j F R_j^{-1}$ isomorphic to F_1 . Thus, an orbit may be characterized by a site group F_1 , (or any other from the set of groups F_j). The number of points in an orbit is equal to the index $t = n_F/n_{F_j}$ of the group F_j in F.

If the elements R_j in (2.1) form a group P then the group F may be factorized in the form $F = PF_j$. The group P is called the permutation symmetry group of an orbit with a site-symmetry group F_j (or orbital group).

In a molecule, all points of an orbit may be either occupied by atoms of the same chemical element or vacant. Only the groups C_n , C_{nv} , C_s may be site-symmetry groups in molecules. A molecule with a symmetry group F may have F as a sitesymmetry group only for one point of the space (for the central atom, for example). For any point-symmetry group a list of possible orbits (and corresponding site groups) can be given. In this list some groups may be repeated more than once. This occurs if in F there are several isomorphic site-symmetry subgroups differing from each other by the principal symmetry axes C_n , two-fold rotation axes U perpendicular to the principal symmetry axis or reflection planes. All the atoms in a molecule may be partitioned into orbits.