

Springer Series in SOLID-STATE SCIENCES

Series Editors:

M. Cardona P. Fulde K. von Klitzing R. Merlin H.-J. Queisser H. Störmer

The Springer Series in Solid-State Sciences consists of fundamental scientific books prepared by leading researchers in the field. They strive to communicate, in a systematic and comprehensive way, the basic principles as well as new developments in theoretical and experimental solid-state physics.

- | | | | |
|-----|---|-----|--|
| 138 | Phase Separation
in Soft Matter Physics
Micellar Solutions, Microemulsions,
Critical Phenomena
By P.K. Khabibullaev and A.A. Saidov | 147 | Electron Scattering in Solid Matter
A Theoretical
and Computational Treatise
By J. Zabloudil, R. Hammerling,
L. Szunyogh, and P. Weinberger |
| 139 | Optical Response of Nanostructures
Microscopic Nonlocal Theory
By K. Cho | 148 | Physical Acoustics in the Solid State
By B. Lüthi |
| 140 | Fractal Concepts
in Condensed Matter Physics
By T. Nakayama and K. Yakubo | 149 | Solitary Waves
in Complex Dispersive Media
Theory · Simulation · Applications
By V.Yu. Belashov and S.V. Vladimirov |
| 141 | Excitons in Low-Dimensional
Semiconductors
Theory, Numerical Methods,
Applications By S. Glutsch | 150 | Topology in Condensed Matter
Editor: M.I. Monastyrsky |
| 142 | Two-Dimensional Coulomb Liquids
and Solids
By Y. Monarkha and K. Kono | 151 | Particle Penetration and Radiation
Effects
By P. Sigmund |
| 143 | X-Ray Multiple-Wave Diffraction
Theory and Application
By S.-L. Chang | 152 | Magnetism
From Fundamentals
to Nanoscale Dynamics
By H.C. Siegmann and J. Stöhr |
| 144 | Physics of Transition Metal Oxides
By S. Maekawa, T. Tohyama,
S.E. Barnes, S. Ishihara,
W. Koshibae, and G. Khaliullin | 153 | Quantum Chemistry of Solids
The LCAO First Principles
Treatment of Crystals
By R.A. Evarestov |
| 145 | Point-Contact Spectroscopy
By Y.G. Naidyuk and I.K. Yanson | 154 | Low-Dimensional Molecular Metals
By N. Toyota, M. Lang and J. Müller |
| 146 | Optics of Semiconductors
and Their Nanostructures
Editors: H. Kalt and M. Hetterich | | |

Volumes 91–137 are listed at the end of the book.

Robert A. Evarestov

Quantum Chemistry of Solids

The LCAO First Principles Treatment of Crystals

With 78 Figures and 126 Tables

 Springer

Professor Dr. Robert A. Evarestov

St. Petersburg State University
Chemistry Department
Stary Peterghof University Prospect 26
198504 St. Petersburg, Russia
E-mail: evarest@hm.csa.ru

Series Editors:

Professor Dr., Dres. h. c. Manuel Cardona

Professor Dr., Dres. h. c. Peter Fulde*

Professor Dr., Dres. h. c. Klaus von Klitzing

Professor Dr., Dres. h. c. Hans-Joachim Queisser

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany

* Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Strasse 38
01187 Dresden, Germany

Professor Dr. Roberto Merlin

Department of Physics, 5000 East University, University of Michigan
Ann Arbor, MI 48109-1120, USA

Professor Dr. Horst Störmer

Dept. Phys. and Dept. Appl. Physics, Columbia University, New York, NY 10027 and
Bell Labs., Lucent Technologies, Murray Hill, NJ 07974, USA

Library of Congress Control Number: 2006936622

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

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilm or in any other way, and storage in data banks. Duplication of this publication or parts thereof is permitted only under the provisions of the German Copyright Law of September 9, 1965, in its current version, and permission for use must always be obtained from Springer. Violations are liable to prosecution under the German Copyright Law.

Springer is a part of Springer Science+Business Media
springer.com

© Springer-Verlag Berlin Heidelberg 2007

The use of general descriptive names, registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Typesetting: Digital data supplied by authors

Production: LE- \TeX Jelonek, Schmidt & Vöckler GbR, Leipzig

Cover production: Manfred Bender, WMX Design GmbH, Heidelberg

SPIN 11555100 Printed on acid-free paper 57/3100/YL - 5 4 3 2 1 0

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

Preface

Nobel Prize Winner Prof. Roald Hoffmann forwarding 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

Contents

Part I Theory

1	Introduction	3
2	Space Groups and Crystalline Structures	7
2.1	Translation 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	Crystalline Structures	26
2.3.1	Crystal-structure Types. Structure Information for Computer Codes	26
2.3.2	Cubic Structures: Diamond, Rocksalt, Fluorite, Zincblende, 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 $\text{YBa}_2\text{Cu}_3\text{O}_7$	37
2.3.5	Hexagonal and Trigonal Structures: Graphite, Wurtzite, Corundum and ScMnO_3	42
3	Symmetry and Localization of Crystalline Orbitals	47
3.1	Translation 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 Representations of Point Groups	61
3.2	Site Symmetry 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 \mathbf{q} -basis	71
3.2.3	Induced Representations of Space Groups in \mathbf{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	Symmetry 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	Hartree–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	Special 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	Density Matrix of Crystals in the Hartree–Fock Method	132
4.3.1	Properties of the One-electron Density Matrix of a Crystal ...	132
4.3.2	The One-electron Density Matrix of the Crystal in the LCAO Approximation	137
4.3.3	Interpolation Procedure for Constructing an Approximate Density Matrix for Periodic Systems	140
5	Electron Correlations in Molecules and Crystals	147
5.1	Electron Correlations in Molecules: Post-Hartree–Fock Methods	147
5.1.1	What is the Electron Correlation ?	147

degenerated states corresponds the same one-electron energy it is enough to identify energy levels only for one ray of the wavevector star as it is made in the figures showing the electronic band structure. The degeneracy of levels at the symmetry points of the BZ is defined by the dimensions of wavevector point-group representations (ordinary or projective). To identify the one-electron energies at the symmetry lines the compatibility relations are used. In Sect. 3.2.6 we discuss the band structure of some crystals using the considered information.

When the space group is realized in a crystalline structure the atomic states included in the LCAO basis define the symmetry of crystalline orbitals appearing in the electronic-structure calculations. The symmetry connection of atomic and crystalline orbitals is given by induced representations of space groups considered in the next subsection.

3.2 Site Symmetry and Induced Representations of Space Groups

3.2.1 Induced Representations of Point Groups. Localized Molecular Orbitals

In the previous section we examined the use of space-group irreducible representations for the classification of the delocalized (Bloch-type) crystalline states. In this traditional approach the crystal is considered as a whole system and the symmetry properties of the environment of constituent atoms are ignored. This results in a loss of information about the connection between the atomic and crystalline states. This information is widely used in the quantum chemistry of solids as it allows the crystalline properties to be explained from the knowledge of the chemical nature of the constituent atoms and their interactions. In the plane-waves methods of electronic-structure calculations the Bloch-type delocalized states are not directly connected with the states of the separate atoms. However, in the LCAO methods the Bloch-type delocalized functions are represented as the linear combination of the functions of separate atoms. Therefore, the symmetry connection between the delocalized Bloch and localized atomic states appears to be important. If we use not only the space symmetry of a crystal as a whole but also the site symmetry of different groups of constituent atoms we can considerably extend the possibilities of the group-theory applications. To study this in more detail the reader is referred to our previous book [13] where we examined the theory and the applications of the site-symmetry approach to the electron, phonon, magnetic properties of crystals and in the theory of phase transitions. In this section, we examine only those theoretical aspects of the site-symmetry approach that concern the electron states and allow analysis of the symmetry connection between the delocalized Bloch-type and localized Wannier-type electron states in crystals. We begin from the short description of the site (local) symmetry approach in molecular quantum chemistry.

In the molecular systems with the point symmetry group G the site-symmetry subgroup $H_{\mathbf{q}}$ includes those symmetry operations that keep the point \mathbf{q} fixed: $h\mathbf{q} = \mathbf{q}$. As an example, we consider a tetrahedral molecular ion $[\text{MnO}_4]^-$ (see Fig. 3.8). The Mn atom site-symmetry group coincides with the whole symmetry group T_d . The site-symmetry group of any of the four oxygens is $C_{3v} \subset T_d$.

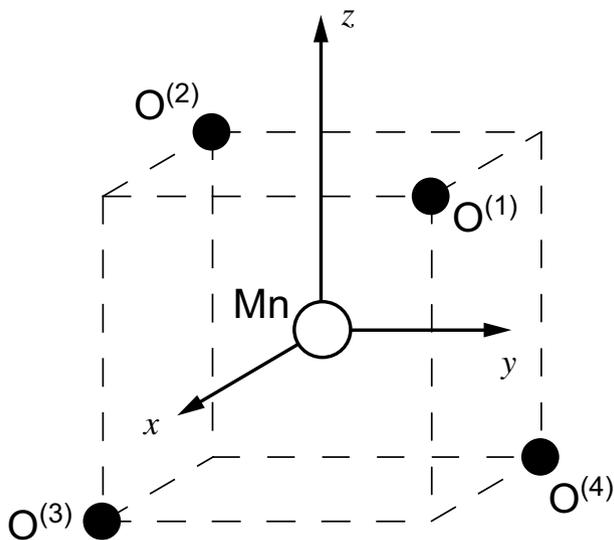


Fig. 3.8. MnO_4^- ion

Let $\hat{D}(g)$ be a rep of a group G ($g \in G$). A set of operators $\hat{D}(h)$ ($h \in H \subset G$) is a rep of H subduced by rep $\hat{D}(g)$ of G . The subduced irrep is denoted as $\hat{D} \downarrow H$. Even if $\hat{D}(g) = \hat{D}^{(\alpha)}(g)$, $g \in G$ is an irrep of G the subduced rep is, in general, reducible and may be decomposed into irreps $d^{(\gamma)}$ of H :

$$D^{(\alpha)} \downarrow H = \sum_{\gamma} r_{\gamma}^{(\alpha)} d^{(\gamma)}(h) \tag{3.42}$$

The multiplicities are equal to

$$r_{\gamma}^{(\alpha)} = n_H^{-1} \sum_h \chi^{(\alpha)}(h) [X^{(\gamma)}(h)]^* \tag{3.43}$$

where $\chi^{(\alpha)}(h)$ and $\chi^{(\gamma)}(h)$ are the characters of irreps $D^{(\alpha)}(h)$ and $d^{(\gamma)}(h)$ of the groups G and $H \subset G$ respectively.

Subducing the irreps of the group G with respect to its subgroup H and decomposing the subduced rep over the irreps of a subgroup one obtains a correlation table. The rows of this table are labeled by irreps of a group G ; the columns denote different subgroups H of this group G . The frequencies of subduction by each irrep of G for the irreps of these subgroups are listed in the body of the table. One also has to take into account the possibility of different orientations of isomorphic subgroups with respect to the group G .

As an example we consider the correlation table for the point group T_d (Table 3.5).

The subduction of the subgroup irreps by the group irrep can be considered as the reciprocal operation to the induction of the group reps by the irreps of the subgroup

Table 3.5. Correlation table for the point group T_d

T_d	C_{2v}	C_{3v}
a_1	a_1	a_1
a_2	a_2	a_2
e	$a_1 a_2$	e
t_1	$a_2 b_1 b_2$	$a_2 e$
t_2	$a_1 b_1 b_2$	$a_1 e$

H. Let group G be decomposed into left cosets with respect to H:

$$G = \sum_{j''}^t g_{j''}H, \quad g_1 = E, \quad t = n_G/n_H \tag{3.44}$$

and L be a basis space of some rep of a group G. It is also a rep of its subgroup H. Let $L^{(1)}$ be a subspace of L with the basis $e_{i1}^{(\gamma)}$, $(i = 1, 2, \dots, n_\gamma)$ transforming according to an irrep $d^\gamma(h)$ of H:

$$D(h)e_{i1}^{(\gamma)} = \sum_{i'} d_{ii'}^{(\gamma)}(h)e_{i'i}^{(\gamma)}, \quad i = 1, 2, \dots, n_\gamma \tag{3.45}$$

To express the invariance of $L^{(1)}$ under $\hat{D}(h)(h \in H)$ independently of a particular choice of basis we write

$$\hat{D}(h)L^{(1)} = L^{(1)} \tag{3.46}$$

The linearly independent basis set

$$e_{ij}^{(\gamma)} = \hat{D}(g_j)e_{i1}^{(\gamma)}, \quad j = 1, \dots, t; \quad i = 1, 2, \dots, n_\gamma \tag{3.47}$$

spans a space $L^{(n)}$ of the dimension $n = t \cdot n_\gamma$. This space is invariant under the operators $\hat{D}(g), g \in G$ and is defined as the space of the group G induced by the irrep $d^{(\gamma)}$ of its subgroup H and is written as $d^{(\gamma)} \uparrow G$. The matrices $D^{[\gamma]}(g)$ of the induced rep $d^{(\gamma)} \uparrow G$ have a block structure. Nonzero blocks are matrices of the irrep $d^{(\gamma)}$ of H. Every row and every column of $D^{[\gamma]}(g)$ has only one nonzero block. In the general case, a rep $d^{(\gamma)} \uparrow G$ is reducible

$$d^{(\gamma)} \uparrow G = \sum_{\alpha} r_{\alpha}^{[\gamma]} D^{(\alpha)}(g) \tag{3.48}$$

The Frobenius reciprocity theorem is proved [13]: the multiplicity of an irrep $D^{(\alpha)}(g)$ of G in a rep $d^{[\gamma]} \uparrow G$ induced by an irrep $d^{(\gamma)}$ of $H \subset G$ is equal to the multiplicity of an irrep $d^{(\gamma)}$ of H in the rep $D^{(\alpha)} \downarrow H$ subduced by $D^{(\alpha)}$ of H.

Using the Frobenius theorem one can also write the reciprocal correlation table in which the irreps of the point group induced by irreps of its different point subgroups are given. Representations of the point group T_d induced by irreps of its point subgroups C_{2v} and C_{3v} are given in Table 3.6. The latter subgroup may be considered as the site-symmetry group of the oxygen atom in the molecular ion $(MnO_4)^-$.

Table 3.6. Induced irreps of the point group T_d

C_{2v}	T_d	C_{3v}	T_d
a_1	$a_1 e t_2$	a_1	$a_1 t_2$
a_2	$a_2 e t_1$	a_1	$a_2 t_1$
b_1	$t_1 t_2$	e	$e t_1 t_2$
b_2	$t_1 t_2$		

The first and third columns in Table 3.6 contain the symbols of the point subgroups C_{2v} and C_{3v} and their irreps. The rest of the columns give the symbols of the induced representations of point group T_d decomposed over the irreps of this group.

The comparison of Tables 3.5 and 3.6 allows the Frobenius theorem to be checked. The tables of induced representations of the point groups are given in [13] and are the reciprocal correlation tables. The latter are given in [14]. In MO LCAO calculations the canonical MO (delocalized over the whole space) are found. Their symmetry is defined by the irreps of the symmetry group of the whole molecule induced by the irreps of the site-symmetry groups of the constituent atoms. Use of the induced representations of point groups allows the canonical MO to be divided into sets, connected with the localized MO (LMO) and find the possible center of localization. In many cases this procedure can be done in several ways. Let us examine MO and LMO in the $(\text{MnO}_4)^-$ molecular ion. The $4s$ -, $4p$ - and $3d$ -functions of the Mn atom span the space of the irreps $a_1, t_2, e + t_2$ of the molecular symmetry group T_d . The site symmetry group of the O atom is C_{3v} . As follows from Table 3.6 the $2s$ and $2p_z$ functions of the oxygen atom contribute to the canonical orbitals of a_1 and t_2 symmetry, and oxygen $2p_x, 2p_y$ functions contribute to functions with the symmetries e, t_1, t_2 . The site group C_{3v} may correspond to localized functions centered on oxygen atoms as well as on the Mn–O bond axis. The site group C_{2v} may be related to a two-centered O–O bond or to a three-centered O–Mn–O bond. The latter may also have C_s symmetry. Table 3.7 lists one-electron energies of the $(\text{MnO}_4)^-$ ion valence orbitals calculated by a) the nonempirical MO LCAO method, b) the SWX $_{\alpha}$ method, c) a semiempirical CNDO method (see Chap. 6). The weights of valence atomic orbitals in molecular orbitals are also given in cases a) and c) (in parentheses).

The valence canonical MO given in Table 3.7 may be distributed over sets according to their symmetry. There are three possible variants of distribution compatible with the symmetry requirements:

- 1) $C_{3v}(a_1) - 5a_1, 4t_2; C_{3v}(a_1) - 6a_1, 6t_2; C_{3v}(e) - 1e, 1t_1, 5t_2$
- 2) $C_{3v}(a_1) - 5a_1, 4t_2; C_{2v}(a_1) - 6a_1, 1e, 5t_2; C_{2v}(b_1) - 1t_1, 6t_2$ (3.49)
- 3) $C_{3v}(a_1) - 5a_1, 4t_2; C_s(a') - 6a_1, 1e, 5t_2, 6t_2, 1t_1$

The first variant is the most preferable as it corresponds to two-centered bonds, whereas the second and the third possibilities contain sets with bonds of more than two centers. The greater the number of centers participating in a bond, the less localized it seems to be. Table 3.7 shows that the sets $C_{3v}(a_1)$ correspond to orbitals localized near the oxygen atoms, the s -type is the lowest in energy and the $2p_z$ -type (directed along the O–Mn line) is higher. The localized functions of symmetry contain

Table 3.7. Electronic structure of $(\text{MnO}_4)^-$

State symmetry	One-electron energies [eV]			Atomic contributions [%]				
	$SW X_\alpha$	CNDO	HF LCAO	$3d$	$4s$	$4p$	$2s$	$2p$
1	-9.28	-7.01	-7.62					100 (100)
$6a_1$	-10.53	-8.95	-8.03		8 (5)		4 (2)	88 (93)
$6t_2$	-10.37	-9.68	-9.06	3 (17)		7 (2)	2 (5)	88 (76)
$1e$	-12.24	-10.15	-11.48	29 (23)				72 (77)
$5t_2$	-12.43	-11.26	-12.82	53 (18)		2 (2)	6 (4)	39 (72)
$4t_2$	-24.30	-32.68	-29.44	7 (2)		4 (17)	87.5 (79)	15 (2)
$5a_1$	-24.65	-36.43	-30.01		7.5 (21)		91.5 (78)	- (1)

a considerable admixture of Mn $3d$ states. So the center of localization is apparently displaced along the bond line towards the Mn atom.

Each of the three sets (3.50) contains states of t_2 symmetry and in two sets there are states of a_1 symmetry. When generating localized orbitals it is possible to take the linear combinations of initial canonical functions of the same symmetry and to vary the coefficients to get the orbitals with the best spatial localization. However, in the case of $(\text{MnO}_4)^-$ the orbitals $5a_1$ and $6a_1$ have considerably different energies. Therefore, the linear combinations must be used only for orbitals of t_2 symmetry (especially $5t_2$ and $6t_2$).

The analysis of the calculated one electron-states is often made only according to the weights of the atomic functions, and symmetry considerations are not taken into account. As a result, the $6t_2, 6a_1, 1t_1$ states can be treated as being in the set corresponding to the localized functions of $2p$ -type centered on oxygen atoms. As follows from Table 3.7, these states do not span the space of the rep induced by some irrep of the site group of the oxygen atom. Therefore, it is impossible to generate any function localized on the oxygen atom. Hence, simply the analysis of the atomic orbital contributions in molecular states with close energies does not permit one to correctly relate the canonical orbitals to the localized ones.

As we can see, induced reps of point groups, in combination with an analysis of the atomic contributions in molecular eigenfunctions, are a good tool to find the regions of localization of electron density on atoms and bonds in a molecule. Of course the energy criterion must also be taken into consideration: a set is chosen so as to unite states with close energies.

Table 3.7 shows that the symmetry of localized orbitals does not depend in practice on the method of calculation of electronic structure. In particular, the method described here is equally applicable to results of SWX_α calculations where the atomic basis is not used at all. The change in energy ordering of the $6a_1$ and $6t_2$ levels from that of the nonempirical method does not change the symmetry found for the localized orbitals.

The localized orbitals generation from the set of canonical MO allowed by symmetry requires additional choice of the localization criteria. The different orbital localization methods are implemented in molecular computer codes [35]. All of them are connected with the search for the coefficients connecting LMO with the canonical MO to satisfy the localization criteria.

The method due to Edmiston and Ruedenberg [36] works by maximizing the sum of the localized orbitals two-electron self-repulsion integrals. The method requires the two-electron integrals, transformed into the MO basis. Because only the orbitals to be localized are needed, the integral transformation is actually not very time consuming. However, the extension of this method to crystals is practically difficult as this requires the transformations of lattice sums of two electron integrals.

The population method due to Pipek and Mezey [37] maximizes a certain sum of gross atomic Mulliken populations. The latter are not realistic when the LCAO basis includes diffuse atomic orbitals as is necessary for crystalline solids.

The most appropriate for the extension to crystal appears to be the Boys method. The Boys method [38] minimizes the sum of spreads of the localized orbitals $\phi_i(\mathbf{r})$

$$\min I = \sum_{i=1}^N [\langle \mathbf{r}^2 \rangle_i - \langle \mathbf{r} \rangle_i^2], \quad \left(\langle \mathbf{r}^m \rangle_i \equiv \int \mathbf{r}^m |\phi_i(\mathbf{r})|^2 d\mathbf{r} \right) \quad (3.50)$$

The summation in (3.50) is made over N occupied canonical MO found in LCAO self-consistent calculations.

$\sum_{i=1}^N \langle \mathbf{r}^2 \rangle_i$ is invariant with respect to any unitary transformation among functions ϕ_i :

$$\phi'_i = \sum_{i'}^N U_{i'i} \phi_{i'} \quad (3.51)$$

The minimum of the functional I corresponds to the maximum of the functionals:

$$\tilde{I} = \sum_{i=1}^N \langle \mathbf{r}^2 \rangle_i, \quad \text{or} \quad \tilde{\tilde{I}} = \sum_{i>j=1}^N [\langle \mathbf{r} \rangle_i - \langle \mathbf{r} \rangle_j]^2 \quad (3.52)$$

Thus, the Boys method can also be considered as maximization of the sum of distances between the orbital centroids $\tilde{\tilde{I}}$. The modifications of the Boys method are necessary to extend it for the localized crystalline orbitals generation. These modifications are considered in Sect. 3.3

3.2.2 Induced Representations of Space Groups in \mathbf{q} -basis

Any subgroup rep can generate some induced rep of a group (see Sect. 3.2.1). In the particular case of a space group G the small irreps of the little group $G_{\mathbf{k}} \subset G$ induce its full irreps.

In this and the next subsections we consider induced reps of space groups generated by the irreps β of the site-symmetry subgroup $G_{\mathbf{q}}$ of point \mathbf{q} in the direct lattice space ($\beta \uparrow G$). This type of induced rep of space groups was considered in [13]. In [39] a more general concept of band reps was introduced. All elements of the space group G can be written in the form $t_{\mathbf{v}_R + \mathbf{a}_n} R$, where \mathbf{v}_R is a fractional lattice translation associated with the F point-group element R and \mathbf{a}_n is a direct lattice translation vector.

The elements of the site-symmetry group $G_{\mathbf{q}} \subseteq G$ of the point \mathbf{q} in the direct lattice space are those elements of G for which $g_{\mathbf{q}}\mathbf{q} = t_{\mathbf{v}_R + \mathbf{a}_n} R_{\mathbf{q}}\mathbf{q} = \mathbf{q}$. The space-group elements $g_{\mathbf{q}}$ are supposed to be given in the coordinate system whose origin is at one of the Wyckoff positions. The site-symmetry group elements for the other Wyckoff positions are mapped by the space-group elements with the point-symmetry operators R . Thus the site-symmetry group $G_{\mathbf{q}} \subseteq G$ is isomorphic with the point group $F_{\mathbf{q}}$ formed by $R_{\mathbf{q}}$. When the coordinate system origin is moved to the other Wyckoff position \mathbf{q}_1 the site-symmetry group elements of this new origin are elements of the point group $F_{\mathbf{q}_1}$ but the site-symmetry group elements $g_{\mathbf{q}}$ of the former origin \mathbf{q} contain translations. As an example we consider the space group O_h^7 for the two origin choices given in the International Tables for Crystallography [19]. The site-symmetry group of Wyckoff position a(000) is mapped to the pure point-symmetry operations of the group for the first origin choice and to the set of operations with the translational part for the second origin choice.

Let the representatives $g_{jn} (j = 1, 2, \dots, n_q = n_G/n_F)$ in the decomposition

$$G = \sum_{j, \mathbf{n}} g_{jn} G_{\mathbf{q}}, \quad g_{j\mathbf{n}} = t_{\mathbf{v}_j + \mathbf{a}_n} R_j \quad (3.53)$$

be chosen so that the points

$$\mathbf{q}_j = t_{\mathbf{v}_j} R_j \mathbf{q} \quad (3.54)$$

occupy the positions within the smallest unit cell (primitive or Wigner–Seitz). The operations $g_{j\mathbf{n}}$ generate from the point \mathbf{q} sublattices $\mathbf{q}_j + \mathbf{a}_n (j = 1, 2, \dots, n_q)$.

Let the local functions $W_{i1}^{(\beta)}(\mathbf{r}) \equiv W_i(\mathbf{r} - \mathbf{q})$, ($i = 1, 2, \dots, n_\beta$) be centered at point \mathbf{q} of the direct lattice and span the space of the irrep β of the site-symmetry group $G_{\mathbf{q}} \subset G$ with matrices $d^{(\beta)}(g_{\mathbf{q}})$ and characters $\chi^{(\beta)}(g_{\mathbf{q}}) (g_{\mathbf{q}} \in G_{\mathbf{q}})$. The nature of these functions depends on the physical problem under consideration. In the electron-band theory of crystals $W_i^{(\beta)}(\mathbf{r} - \mathbf{q}_A)$ are atomic functions of atom A . In phonon spectroscopy applications $W_i^{(\beta)}(\mathbf{r} - \mathbf{q}_A)$ mean the components of atomic displacements of an atom A , in magnetically ordered crystals these functions are the magnetic moments of atoms [13].

Functions $W_{i1}^{(\beta)}(\mathbf{r})$ transform as

$$\begin{aligned} \hat{g}_{\mathbf{q}} W_{i1}^{(\beta)}(\mathbf{r}) &= W_i^{(\beta)}(R_{\mathbf{q}}^{-1}(\mathbf{r} - \mathbf{v}_{\mathbf{q}} - \mathbf{a}_n - R_{\mathbf{q}}\mathbf{q})) \\ &= W_i^{(\beta)}(R_{\mathbf{q}}^{-1}(\mathbf{r} - \mathbf{q})) = \sum_{i'=1}^{n_\beta} d_{i'i}^{(\beta)}(R_{\mathbf{q}}) W_{i'1}^{(\beta)}(\mathbf{r}) \end{aligned} \quad (3.55)$$

since the vector \mathbf{q} remains invariant under the operations of the site group $G_{\mathbf{q}}$. All the functions $W_{i1}^{(\beta)}(\mathbf{r}) (i = 1, 2, \dots, n_\beta)$ are associated with the site \mathbf{q} .

The local functions associated with the smallest unit cell are obtained from local functions $W_{i1}^{(\beta)}(\mathbf{r})$ through

$$W_{ij}^{(\beta)}(\mathbf{r}) = \hat{t}_{\mathbf{v}_j} R_j W_{i1}^{(\beta)}(\mathbf{r}) = \mathbf{W}_i^{(\beta)} \left(\mathbf{R}_j^{-1}(\mathbf{r} - \mathbf{q}) \right), \quad (3.56)$$

$$i = 1, 2, \dots, n_\beta; \quad j = 1, 2, \dots, n_{\mathbf{q}}$$

Functions in other unit cells are obtained through

$$W_{ij}^{(\beta)}(\mathbf{r} - \mathbf{a}_n) = \hat{t}_{\mathbf{a}_n} W_{ij}^{(\beta)}(\mathbf{r}) = W_{ij}^{(\beta)}(R_j^{-1}(\mathbf{r} - \mathbf{q}_j - \mathbf{a}_n)) \quad (3.57)$$

The local functions $W_{ij}^{(\beta)}(\mathbf{r} - \mathbf{a}_n)$ form the basis of an induced rep $\beta \uparrow G$ of space group G . Indeed, let the element $t_{\mathbf{v}_R} R$ transform the j th sublattice into the j' th one and be written in the form

$$t_{\mathbf{v}_R} R = t_{\mathbf{a}_{jj'}} t_{\mathbf{v}_{j'}} R_{j'} t_{\mathbf{v}_q} R_q (t_{\mathbf{v}_j} R_j)^{-1} \quad (3.58)$$

where $R = R_{j'} R_q R_j^{-1}$ ($R_q \in F_q$) and $\mathbf{a}_{jj'}$ is the lattice vector. Equation (3.58) may be checked directly. From (4.2.6) we get for the local functions

$$t_{\mathbf{v}_R} R W_{ij}^{(\beta)}(\mathbf{r} - \mathbf{a}_n) = \sum_{i'} \left(R_{j'}^{-1} R R_j \right) W_{i'j'}^{(\beta)}(\mathbf{r} - R\mathbf{a}_n - \mathbf{a}_{j'j}) \quad (3.59)$$

The dimension of the rep $\beta \uparrow G$ is infinite for the model of an infinite crystal. In a cyclic model, the infinite crystal is replaced by a main region consisting of N smallest unit cells and periodic boundary conditions are introduced. The total number of local functions $W_{ij}^{(\beta)}(\mathbf{r} - \mathbf{a}_n)$ becomes finite and equals $n_\beta n_{\mathbf{q}} N$ ($i = 1, 2, \dots, n_\beta, j = 1, 2, \dots, n_{\mathbf{q}}; n$ takes N values). These functions form an $n_\beta n_{\mathbf{q}} N$ -dimensional space of the rep of the space group G . This rep matrix consists of $n_\beta n_{\mathbf{q}}$ blocks arising from $d^{(\beta)}$.

To specify the induced rep $\beta \uparrow G$ in the basis of local functions $W_{ij}^{(\beta)}(\mathbf{r} - \mathbf{a}_n)$ one has to indicate the symmetry center \mathbf{q} of local functions by its Wyckoff position and the irrep β of the site-symmetry point group $G_{\mathbf{q}}$. Thus, in the \mathbf{q} basis the induced rep $\beta \uparrow G$ is specified by the index (\mathbf{q}, β) .

As an example, we consider oxygen atom $2s$ functions in the perovskite CaTiO_3 structure. The oxygen atoms occupy Wyckoff position c of the space group O_h^1 with the site-symmetry D_{4h} . The $2s$ -functions of an oxygen atom transform over a_{1g} irrep of the point group D_{4h} . Thus, the induced representation in \mathbf{q} basis (c, a_{1g}) is three-dimensional at each \mathbf{k} point ($d^{(\beta)} = a_{1g}, n_\beta = 1, n_{\mathbf{q}} = 3$).

3.2.3 Induced Representations of Space Groups in \mathbf{k} -basis. Band Representations

In Sect. 3.1 we have considered the space-group irreps $D^{(\mathbf{k}, \alpha)}(g)$ defined by stars $^* \mathbf{k}$ of wavevectors \mathbf{k} from the first Brillouin zone and by irreps $D^{(\alpha)}$ of little groups $G_{\mathbf{k}}$. Let us construct in the space of induced rep (\mathbf{q}, β) new basis functions that span the space of irreps of the translation group T (Bloch functions)

$$\Psi_{ij}^{(\beta)}(\mathbf{k}, \mathbf{r}) = \sum_{\mathbf{n}} \exp(i\mathbf{k}\mathbf{a}_n) W_{ij}^{(\beta)}(\mathbf{r} - \mathbf{a}_n), \quad (i = 1, 2, \dots, n_\beta; \quad j = 1, 2, \dots, n_{\mathbf{q}}) \quad (3.60)$$

and *vice versa*

$$\begin{aligned} W_{ij}^{(\beta)}(\mathbf{r} - \mathbf{a}_n) &= \frac{V_a}{(2\pi)^3} \int \exp(-i\mathbf{k}\mathbf{a}_n) \Psi_{ij}^{(\beta)}(\mathbf{k}, \mathbf{r}) d\mathbf{k} \\ W_{ij}^{(\beta)}(\mathbf{r} - \mathbf{a}_n) &= N^{-1} \sum_{\mathbf{k}} \exp(-i\mathbf{k}\mathbf{a}_n) \Psi_{ij}^{(\beta)}(\mathbf{k}, \mathbf{r}) \end{aligned} \quad (3.61)$$

for infinite and cyclic models of a crystal, respectively. Using (3.24), (3.28) and (3.59) one obtains

$$t_{v_R} R \Psi_{ij}^{(\beta)}(\mathbf{k}, \mathbf{r}) = \exp(-iR\mathbf{k} \cdot \mathbf{a}_{jj'}) \sum_{i'} d_{i'i}^{(\beta)} \left(R_j^{-1} R R_j \right) \Psi_{i'j'}(R\mathbf{k}, \mathbf{r}) \quad (3.62)$$

Let the wavevector \mathbf{k} be fixed and $t_{v_R} R \in G_{\mathbf{k}}$. Then $p = n_{\beta} n_q$ functions $\Psi_{ij}^{(\beta)}(\mathbf{k}, \mathbf{r})$ span the space of the small representation of the little group $G_{\mathbf{k}}$ with the character

$$\chi_{\mathbf{k}}^{(\beta)}(g) = \sum_{j=1}^{n_q} \exp(-i\mathbf{k} \cdot \mathbf{a}_{jj'}) \tilde{\chi}^{(\beta)}(R_j^{-1} R R_j) \quad (3.63)$$

where

$$\tilde{\chi}^{(\beta)}(R_j^{-1} R R_j) = \begin{cases} 0, & \text{if } R_j^{-1} R R_j \neq R_q \\ \chi^{(\beta)}(R_q), & \text{if } R_j^{-1} R R_j = R_q \end{cases} \quad (3.64)$$

Knowing the characters (3.63) of the induced rep one can easily calculate the number of times the small irrep $D^{(\mathbf{k}, \gamma)}$ of the group $G_{\mathbf{k}}$ with characters $\chi^{(\mathbf{k}, \gamma)}(g), g \in G_{\mathbf{k}}$ is contained in the induced rep (\mathbf{q}, β) .

This procedure gives the labels of the induced rep (\mathbf{q}, β) in the \mathbf{k} basis corresponding to those in the \mathbf{q} basis, *i.e.* the results of the reduction of the induced rep over irreps of the group $G_{\mathbf{k}}$. All the information obtained can be specified by listing the symmetry (the labels of irreps) of the Bloch states with wavevectors \mathbf{k} corresponding only to a relatively small number of \mathbf{k} points in the Brillouin zone forming a set K . The set K contains the inequivalent symmetry points of the Brillouin zone and one representative point from each inequivalent symmetry element (symmetry line or symmetry plane) if the latter does not contain the points of higher symmetry.

The symmetry properties of basis functions with other vectors \mathbf{k} can be determined with the use of the compatibility relations.

The set K for the space groups with high-symmetry classes consists only of the symmetry points. For instance, the set K for the space groups O_h^5, O_h^7 contains the points Γ, X, L, W (Fig. 3.2); for the space group O_h^4 - the points Γ, X, M, R (Fig. 3.2). The symmetry points can be absent in the Brillouin zone of space groups with low symmetry classes.

The symmetry properties of basis functions of an induced rep are described by the full group irreps $(*\mathbf{k}, \gamma)$ or by the small irreps (\mathbf{k}, γ) of the wavevector groups $G_{\mathbf{k}}$ unambiguously related to them. Thus, as an index of an induced rep we shall use the symbols of those small irreps of the little groups $G_{\mathbf{k}}$ with wavevectors from the set K that correspond to basis functions of a given induced rep

$$\mathbf{k}_1(\gamma_1^{(1)}, \gamma_2^{(1)}, \dots), \mathbf{k}_2(\gamma_1^{(2)}, \gamma_2^{(2)}, \dots), \dots, \mathbf{k}_i \in K \quad (3.65)$$

The index of the induced rep (3.65) can also be considered as the set of so-called subduction frequencies $r_{(*\mathbf{k},\gamma)}^{(\mathbf{q},\beta)}$. The latter give the number of times the irrep $(*\mathbf{k},\gamma)$ of G is contained in the induced rep (\mathbf{q},β) . From the Frobenius theorem the subduction frequencies $r_{(*\mathbf{k},\gamma)}^{(\mathbf{q},\beta)}$ are equal to the number of times the irrep $(*\mathbf{k},\gamma)$ subduces the irrep β of $G_{\mathbf{k}}^{(*\mathbf{k},\gamma)}$

$$r_{\beta}^{(*\mathbf{k},\gamma)} = r_{(*\mathbf{k},\gamma)}^{(\mathbf{q},\beta)} = \sum_{g \in G_{\mathbf{q}}} \left(\chi^{(\beta)*}(g) \right) \chi^{(*\mathbf{k},\gamma)}(g) \quad (3.66)$$

where $\chi^{(*\mathbf{k},\gamma)}(g)$ and $\chi^{(\beta)}(g)$ are the characters of the irreps $(*\mathbf{k},\gamma)$ of G and β of $G_{\mathbf{q}}$, respectively.

To calculate the subduction frequencies (3.66) one may use different procedures [13]. The first uses (3.63) and does not require knowledge of the full irrep $(*\mathbf{k},\gamma)$ characters. Indeed, one obtains, according to (3.63), the characters $\chi_{\mathbf{k}}^{(\beta)}(g)$ of the rep of a little group $G_{\mathbf{k}}$. Reducing this rep requires the characters of the irreps of the little group $G_{\mathbf{k}}$ (tabulated in [17] and on site [16]) and gives the induced rep index (3.66) in the \mathbf{k} -basis. The second procedure for calculating subduction frequencies uses (3.66) and requires the character $\chi^{(*\mathbf{k},\gamma)}$ of full irreps of space groups.

Comparing the two ways of finding the induced rep index in the \mathbf{k} basis one may conclude:

1. the first one is more appropriate for \mathbf{q} sets consisting of only one Wyckoff position in the unit cell (this is possible only in symmorphic space groups);
2. the second one is more appropriate for those wavevector stars that consist of one ray so that the full and small irreps coincide.

In [39] the concept of a band rep of a space group, which may be an induced rep, was introduced. Band reps were used to define the symmetry of an electron energy band as a whole entity.

From the group-theoretical point of view a band rep of a space group is a direct sum of its irreps that have the following properties:

- 1) the space of the band rep contains the basis vectors with all the \mathbf{k} vector stars in the Brillouin zone;
- 2) the compatibility relations are fulfilled throughout the Brillouin zone in the model of an infinite crystal or for N points in the cyclic model.

It is obvious that at every \mathbf{k} point there is the same number p of Bloch-type basis states.

In a cyclic model of a crystal with N primitive cells in the main region a band rep is an Np dimensional reducible rep of a space group. An induced rep is a particular case of a band rep as it satisfies both properties 1 and 2 with $p = n_{\mathbf{q}}n_{\beta}$ (n_{β} is the dimension of the site-symmetry group irrep for a point \mathbf{q} belonging to the set of $n_{\mathbf{q}}$ points in the unit cell).

The index of a band rep in the \mathbf{k} basis has the form given by (3.65). By analogy with the same index for an induced rep, all informaton about the band rep can be given by specifying the symmetry (the labels of irreps) of the basis vectors with wavevectors $\mathbf{k} \in K$.

It is seen now that band reps (induced reps included) of space groups can be specified by the index (3.65) in the \mathbf{k} basis, and only those band reps that are induced ones can also be specified in the \mathbf{q} basis in the form (\mathbf{q},β) .

Let us return to our example of the induced representation (c, a_{1g}) of the space group O_h^1 formed by 2s functions of oxygen atoms in the perovskite structure. Using the full group irreps from the site [16] we calculate the subduction frequencies (3.66) for belonging to K set points of Brillouin zone and write the induced band representation (c, a_{1g}) in the \mathbf{k} basis in the form $\Gamma(1^+3^+)\text{R}(5^+)\text{M}(4^+5^-)\text{X}(1^+3^-4^-)$. The labels of the small irreps of the little groups are taken from [17].

3.2.4 Simple and Composite Induced Representations

The use of the \mathbf{q} basis of induced reps allows one to introduce the concept of simple induced reps, that facilitates the analysis of all possible types of induced reps for a given space group. An induced rep is called simple if it is impossible to split up the space of this rep into subspaces that are invariant under operators \hat{g} ($g \in G$) and are also the spaces of some induced reps.

By definition, a composite induced rep is a direct sum of the simple ones. As a group rep, a simple induced rep is reducible, so we prefer to avoid the expression “irreducible induced rep” used in [39]. The term introduced in [40], “elementary induced rep”, is equivalent to the term simple induced rep used in this book.

All simple induced reps may be generated by induction from the irreps of site-symmetry groups $G_{\mathbf{q}'}$, of a relatively small number of \mathbf{q}' points forming the set Q in the Wigner–Seitz unit cell of the direct lattice. The set Q consists of

- 1) all the inequivalent symmetry points of the Wigner–Seitz unit cell;
- 2) one representative point from all the inequivalent symmetry lines and symmetry planes that do not contain the symmetry points.

The site groups $G_{\mathbf{q}}$ for all $\mathbf{q} \in Q$ are called maximal isotropy subgroups in [40]. The set Q in the Wigner–Seitz unit cell is determined in the same way as the set K in the Brillouin zone. However, the action of symmetry operations in the direct and reciprocal spaces is different.

A reducible rep $d(g) = \sum_{\beta} r_{\beta} d^{(\beta)}(g)$ of the site group $G_{\mathbf{q}}$ induces a composite induced rep that is the direct sum of reps induced by the irreps $d^{(\beta)}(g)$. As an example, we can consider a composite rep induced by d functions of a transition metal atom (Wyckoff position a) in the perovskite structure: these functions span the reducible 5-dimensional rep of the the site-symmetry group O_h subducing t_{2g} and e_{2g} irreps. Therefore the induced irrep in \mathbf{q} basis is composite: $b(e_g) + b(t_{2g})$.

Now let us show that if the \mathbf{q} -point does not belong to the set Q , the rep (\mathbf{q}, β) induced from the irrep of the site group $G_{\mathbf{q}}$ is composite.

Let \mathbf{q}' be one of the points in the set Q for which the site group $G_{\mathbf{q}'}$ contains $G_{\mathbf{q}}$ as a subgroup ($G_{\mathbf{q}} \subset G_{\mathbf{q}'}$).

This condition may be satisfied for several points \mathbf{q}' of the set Q . The decomposition of the site group $G_{\mathbf{q}'}$ into left cosets with respect to the subgroup $G_{\mathbf{q}}$ has the form

$$G_{\mathbf{q}'} = \sum_{j=1}^n t_{\mathbf{v}_j} R_j G_{\mathbf{q}} \quad (3.67)$$

If the functions $W_{i1}^{(\beta)}(\mathbf{r}) (i = 1, 2, \dots, n_{\beta})$ span the space of an irrep β of the group $G_{\mathbf{q}}$ then $n \cdot n_{\beta}$ functions

$$W_{ij}^{(\beta)}(\mathbf{r}) = t_{v_j} R_j W_{i1}^{(\beta)}(\mathbf{r}) \quad (3.68)$$

form the space of the site group $G_{\mathbf{q}}$ rep $\beta \uparrow G_{\mathbf{q}}$ induced from the irrep β of its subgroup $G_{\mathbf{q}'}$. Let us decompose the rep $\beta \uparrow G_{\mathbf{q}'}$ into the irreps α' of the group $G_{\mathbf{q}'}$

$$\beta \uparrow G_{\mathbf{q}'} = \sum_{\alpha'} r_{\alpha'} \alpha' \quad (3.69)$$

The irrep β of the group $G_{\mathbf{q}'}$ and rep $\beta \uparrow G_{\mathbf{q}'}$ of the group $G_{\mathbf{q}'}$ generate the same induced rep

$$(\mathbf{q}, \beta) = (\mathbf{q}', \beta \uparrow G_{\mathbf{q}'}) = \sum_{\alpha'} r_{\alpha'}(\mathbf{q}', \alpha') \quad (3.70)$$

which is obviously composite. Thus, we have proved that all the possible simple induced reps of a given space group G may be generated by induction from the irreps of the subgroups $G_{\mathbf{q}'}$ for $\mathbf{q}' \in Q$.

In [40] a complete classification of the inequivalent simple induced reps is given and all the cases when the reps induced from the irreps of maximal isotropy subgroups can be equivalent to one another are considered. First, equivalent induced reps at the same site $\mathbf{q}' \in Q$ arise.

1) by induction from one-dimensional irreps forming an orbit of the normalizer $N_G(G_{\mathbf{q}'})$; there are 23 pairs of them belonging to 15 space groups; and

2) four types of isotropy subgroups (C_{2v}, D_2, D_{2h}, T) may generate reps induced by irreps that do not form an orbit of $N_G(G_{\mathbf{q}'})$. There are 34 pairs of them belonging to 25 space groups.

Second, there are 17 pairs of different maximal isotropy subgroups (belonging to 14 space groups) yielding 63 pairs of equivalent induced reps by induction from one-dimensional irreps. When inducing from two-dimensional irreps of isotropy subgroups, 33 pairs of equivalent induced reps are obtained, belonging to 23 space groups. In total, there are 153 pairs of equivalent induced reps (57 at the same site and 96 at different sites) induced from different irreps of maximal isotropy subgroups. In [40] it was also shown that 40 reps belonging to 25 space groups and induced from irreps of maximal isotropy groups are composite.

There is a formal analogy between simple induced reps and reps irreducible in the usual group-theoretical sense. However, this analogy is not complete. Indeed, the composite induced rep decomposition into simple ones is not always unique. This occurs whenever the site-symmetry group $G_{\mathbf{q}}$ is not the maximal isotropy one ($\mathbf{q} \notin Q$). In this case, the group $G_{\mathbf{q}}$ is a subgroup of several maximal isotropy groups $G_{\mathbf{q}'} (\mathbf{q}' \in Q)$. Consequently, the induced rep decomposition (3.70) will be different for different points.

The theory of induced representations of space groups gives the answer to the question of whether it is possible to generate in the space of states of a given energy band the basis of localized functions? The answer to this question allows the symmetry connection between delocalized Bloch-type and localized Wannier-type crystalline orbitals to be obtained. This point is discussed in Sect. 3.3.

The following qualitative discussion should explain some features of band reps corresponding to real energy bands in crystals. Let a crystal be formed from isolated constituent atoms by decreasing the interatomic distances from very large ones to those corresponding to real crystalline structure. The crystal field may split the degenerate one-electron atomic levels due to symmetry requirements, leading to quite

narrow energy bands, because of the interatomic interactions. The interatomic distances are sufficiently large that the crystalline orbitals corresponding to these bands are localized quite well at the atomic sites and are close to atomic functions. The Bloch states of these narrow energy bands span the spaces of some band reps that certainly have \mathbf{q} basis, *i.e.* are induced representations. These reps are induced by those irreps of site-symmetry groups of atoms that describe the transformation properties of atomic states generating the energy bands. The further decrease of the interatomic distances may considerably transform the energy bands (join them together into more complicated ones and later split them up again into other simple ones) but a new electronic state of arbitrary symmetry cannot arise nor can any state disappear. At the same time, the wavefunctions of all possible symmetry types may change and corresponding one-electron energies may shift along the energy scale. Thus, an energy band corresponding to a band rep without a \mathbf{q} basis (*i.e.* that is not an induced rep) may arise. However, this band, in joining with one or several neighboring ones, forms an energy band corresponding to a composite induced rep with \mathbf{q} basis. In the joint space of these band states one can generate the basis of localized functions. Thus, the calculated one-electron energy band spectra of crystals may always be divided into bands connected with some simple or composite induced reps. When the interatomic distances are decreased to those in a real crystal the atomic functions undergo more or less extensive modifications and become the Wannier functions of a crystal (see Sect. 3.3). When the latter arise directly from atomic functions one can use for them the same notation (*s, p, d* and so on). Let the atoms be at Wyckoff positions with the site symmetry group $G_{\mathbf{q}}$. Localized functions transforming according to irreps of the group $G_{\mathbf{q}}$ correspond to the bands arising from atomic levels split by a crystalline field. If these Wyckoff positions belong to the set Q , the band states usually form the space of a simple induced rep. When atoms are at positions that do not belong to the set Q the band states form the basis of a composite induced rep. If, when the interatomic distances are decreased, the energy bands cross one another then the states of the resultant composite band also span the space of a composite induced rep. However, it may happen that this new band splits into several subbands related to localized functions that have centers of localization somewhat displaced from the atomic positions for further decreases in the interatomic distances. This case is typical for the electronic structure of crystals with covalent chemical bonding.

The information about the simple induced representations of the space groups can be given in the form of tables, shown in the next section for the space groups O_h^5 , O_h^7 and O_h^1 .

3.2.5 Simple Induced Representations for Cubic Space Groups O_h^1 , O_h^5 and O_h^7

The correspondence between symbols of simple induced reps in \mathbf{q} - and \mathbf{k} -basis for $\mathbf{q} \in Q$ and $\mathbf{k} \in K$ is usually given in tables of simple induced reps having the following structure (*e.g.* Tables 3.8–3.10 for the space groups O_h^1 , O_h^5 and O_h^7 , respectively).

The first two columns of the table contain the labels of the induced reps in the \mathbf{q} -basis (these labels number the rows of the table): the international symbols (Roman letters *a, b, c* and so on) of the Wyckoff positions (sites in direct space) and the Mulliken symbols of the irreps of the site-symmetry groups for these Wyckoff positions. For example, $d(a_{2u})$ and $d(e_u)$ are the labels of induced reps in \mathbf{q} -basis for space

Table 3.8. Simple induced representations of the $O_h^1 - Pm\bar{3}m$ space group

q	β	Γ	R		M		X	
			a	b	a	b	a	b
a	a_{1g}	1^+	1^+	2^-	1^+	4^+	1^+	3^-
	a_{1u}	1^-	1^-	2^+	1^-	4^-	1^-	3^+
	a_{2g}	2^+	2^+	1^-	2^+	3^+	2^+	4^-
	a_{2u}	2^-	2^-	1^+	2^-	3^-	2^-	4^+
	e_g	3^+	3^+	3^-	1^+2^+	3^+4^+	1^+2^+	3^-4^-
	e_u	3^-	3^-	3^+	1^-2^-	3^-4^-	1^-2^-	3^+4^+
	t_{1g}	4^+	4^+	5^-	3^+5^+	2^+5^+	3^+5^+	1^-5^-
	t_{1u}	4^-	4^-	5^+	3^-5^-	2^-5^-	3^-5^-	1^+5^+
	t_{2g}	5^+	5^+	4^-	4^+5^+	1^+5^+	4^+5^+	2^-5^-
	t_{2u}	5^-	5^-	4^+	4^-5^-	1^-5^-	4^-5^-	2^+5^+
c	a_{1g}	1^+3^+	5^+	4^-	4^+5^-	1^+5^-	$1^+3^-4^-$	$1^+2^+3^-$
	a_{1u}	1^-3^-	5^-	4^+	4^-5^+	1^-5^+	$1^-3^+4^+$	$1^-2^-3^+$
	b_{1g}	2^+3^+	4^+	5^-	3^+5^-	2^+5^-	$2^+3^-4^-$	$1^+2^+4^-$
	b_{1u}	2^-3^-	4^-	5^+	3^-5^+	2^-5^+	$2^-3^+4^+$	$1^-2^-4^+$
	a_{2g}	4^+	2^+3^+	1^-3^-	$2^+3^-4^-$	$1^-2^-3^+$	3^+5^-	1^-5^+
	a_{2u}	4^-	2^-3^-	1^+3^+	$2^-3^+4^+$	$1^+2^+3^-$	3^-5^+	1^+5^-
	b_{2g}	5^+	1^+3^+	2^-3^-	$1^+3^-4^-$	$1^-2^-4^+$	4^+5^-	2^-5^+
	b_{2u}	5^-	1^-3^-	2^+3^+	$1^-3^+4^+$	$1^+2^+4^-$	4^-5^+	2^+5^-
	e_g	4^+5^+	4^+5^+	4^-5^-	$1^-2^-5^+5^-$	$3^-4^-5^+5^-$	$1^-2^-5^+5^-$	$3^+4^+5^+5^-$
	e_u	4^-5^-	4^-5^-	4^+5^+	$1^+2^+5^-5^+$	$3^+4^+5^-5^+$	$1^+2^+5^-5^+$	$3^-4^-5^-5^+$

In (aaa) units: $\mathbf{a}_1(100)$, $\mathbf{a}_2(010)$, $\mathbf{a}_3(001)$

$Q: O_h(m\bar{3}m) - a(000)$, $b(1/2, 1/2, 1/2)$;

$D_{4h}(4/mmm) - c(1/2, 1/2, 0)$, $d(1/2, 0, 0)$

In $(2\pi/a, 2\pi/a, 2\pi/a)$ units: $\mathbf{b}_1(100)$, $\mathbf{b}_2(010)$, $\mathbf{b}_3(001)$

$K: O_h - \Gamma(000)$, $R(1/2, 1/2, 1/2)$; $D_{4h} - M(1/2, 1/2, 0)$, $X(1/2, 0, 0)$

group O_h^1 (Table 3.8). The remaining columns give the labels of induced reps in the \mathbf{k} -basis, with the symbols of \mathbf{k} -points (wavevectors) in the first row of the table and the indices of small irreps of little groups in subsequent rows. For example, 4^- in the column Γ means small irrep Γ_{4^-} . Below the table supplementary information is given – the primitive translations, the coordinates and site-symmetry groups of Wyckoff positions in the direct lattice and the analogous data for the reciprocal lattice. The correspondence between small representations of little groups for symmetry points in BZ is given in Table 3.11 (space group O_h^1) and in Table 3.12 (space group O_h^5).

In Tables 3.8–3.10 of simple induced reps the labeling of the space-group irreps is that of [17], the labeling of the point group irreps is that of [30] and the site points \mathbf{q} are indexed as Wyckhoff positions from [19].

Table 3.9. Simple induced representations of the $O_h^5 - Fm\bar{3}m$ space group

q	β	Γ	L		X	W	
			a	b		a	b
a	a_{1g}	1^+	1^+	2^-	1^+	1	2
	a_{1u}	1^-	1^-	2^+	1^-	1	2
	a_{2g}	2^+	2^+	1^-	2^+	2	1
	a_{2u}	2^-	2^-	1^+	2^-	2	1
	e_g	3^+	3^+	3^-	1^+2^+	1	2
	e_u	3^-	3^-	3^+	1^-2^-	3	4
	t_{1g}	4^+	2^+3^+	1^-3^-	3^+5^+	3	5
	t_{1u}	4^-	2^-3^-	1^+3^+	3^-5^-	2	5
	t_{2g}	5^+	1^+3^+	2^-3^-	4^+5^+	4	5
t_{2u}	5^-	1^-3^-	2^+3^+	4^-5^-	1	5	
c	a_1	1^+2^-	1^+2^-		4^+3^-	5	
	a_2	2^+1^-	2^+1^-		3^+4^-	5	
	e	3^+3^-	3^+3^-		$3^+4^+3^-4^-$	5	
	t_1	4^+5^-	$2^+3^+1^-3^-$		$2^+5^+1^-5^-$	1	2
	t_2	5^+4^-	$1^+3^+2^-3^-$		$1^+5^+2^-5^-$	1	2
d	a_g	$1^+3^+5^+$	$1^+3^+2^-3^-$		$1^+4^+3^-4^-5^-$	1	2
	a_u	$1^-3^-5^-$	$1^-3^-2^+3^+$		$1^-4^-3^+4^+5^+$	3	4
	b_{1g}	$2^+3^+4^+$	$2^+3^+1^-3^-$		$2^+3^+3^-4^-5^-$	1	2
	b_{1u}	$2^-3^-4^-$	$2^-3^-1^+3^+$		$2^-3^-3^+4^+5^+$	3	4
	b_{2g}	4^+5^+	$1^+3^+1^-3^-$		$1^-2^-5^+5^-$	1	3
	b_{2u}	4^-5^-	$1^-3^-1^+3^+$		$1^+2^+5^-5^+$	1	2
	b_{3g}	4^+5^+	$2^+3^+2^-3^-$		$5^+1^-2^-5^-$	2	3
	b_{3u}	4^-5^-	$2^-3^-2^+3^+$		$5^-1^+2^+5^+$	1	2

In (aaa) units: $\mathbf{a}_1(0, 1/2, 1/2)$, $\mathbf{a}_2(1/2, 0, 1/2)$, $\mathbf{a}_3(1/2, 1/2, 0)$

Q : $O_h(m\bar{3}m) - a(000)$, $b(1/2, 1/2, -1/2)$;

$T_d(\bar{4}3m) - c(1/4, 1/4, 1/4)$; $D_{4h}(mmm) - d(1/2, 0, 0)$.

In $(2\pi/a, 2\pi/a, 2\pi/a)$ units: $\mathbf{b}_1(-111)$, $\mathbf{b}_2(1-11)$, $\mathbf{b}_3(11-1)$

K : $O_h - \Gamma(000)$; $D_{4h} - X(0, 1/2, 1/2)$

$D_{3d} - L(1/2, 1/2, 1/2)$; $D_{2d} - W(1/4, 1/2, 3/4)$.

According to the theory developed in previous sections, all the information about the induced reps of a given space group is contained in the table of its simple induced reps. Using these tables one can solve the following two purely mathematical problems:

1) Finding the irreducible components of the space-group reps induced by the irreps of all the possible site-symmetry subgroups for a given space group.

2) Finding the irreducible components of the site-symmetry group reps subduced by the irreps of the corresponding space group.

To solve these two problems one also needs:

a) the compatibility relation tables for the irreps of space groups [17];

b) tables of induced reps of crystallographic point groups [13].

Table 3.10. Simple induced representations of the $O_h^7 - Fd\bar{3}m$ space group

q	β	Γ	X	L		W	
a	a_1	1^+2^-	1	1^+2^-		a	b
	a_2	1^-2^+	2	1^-2^+		1	2
	e	3^+3^-	1 2	3^+3^-		2	1
b	t_1	4^+5^-	2 3 4	$1^-2^+3^+3^-$		1 2	1 2
	t_2	4^-5^+	1 3 4	$1^+2^-3^+3^-$		1 1 2	1 2 2
				c	d		
c	a_{1g}	1^+5^+	1 3	$1^+2^-3^-$	$1^+2^-3^+$	1 2	
	a_{1u}	1^-5^-	2 3	$1^-2^+3^+$	$1^-2^+3^-$	1 2	
	a_{2g}	2^+4^+	2 4	$1^-2^+3^-$	$1^-2^+3^+$	1 2	
d	a_{2u}	2^-4^-	1 4	$1^+2^-3^+$	$1^+2^-3^-$	1 2	
	e_g	$3^+4^+4^+$	1 2 3 4	$1^-2^-3^+3^-3^-$	$1^-2^+3^+3^+3^-$	1 1 2 2	
	e_u	$3^-4^-4^-$	1 2 3 4	$1^+2^+3^-3^+3^+$	$1^+2^-3^-3^-3^+$	1 1 2 2	

For the direct and reciprocal lattice translation vectors and coordinates of K -set points see Table 3.9.

Q : $T_d(\bar{4}3m) - a(000), b(1/2, 1/2, -1/2)$;

$D_{3d}(\bar{3}m - c(1/8, 1/8, 1/8), d(-3/8, -3/8, 5/8))$.

Table 3.11. Space group O_h^1 : correspondence between small representations of little groups G_Γ, G_R, G_X and G_M and irreducible representations of point groups O_h and D_{4h}

Γ, R	O_h	X, M	D_{4h}
1^+	a_{1g}	1^+	a_{1g}
1^-	a_{1u}	1^-	a_{1u}
2^+	a_{2g}	2^+	a_{2g}
2^-	a_{2u}	2^-	a_{2u}
3^+	e_g	3^+	b_{1g}
3^-	e_u	3^-	b_{1u}
4^+	t_{1g}	4^+	b_{2g}
4^-	t_{1u}	4^-	b_{2u}
5^+	t_{2g}	5^+	e_g
5^-	t_{2u}	5^-	e_u

We consider now in more detail the application of the tables of simple induced reps for the solution of the two problems mentioned above. Suppose one needs to find, for a given space-group, the irreducible components of the space group reps induced by some irrep of the site-symmetry subgroup $G_q \subset G$. One has to consider four cases.

la) $q \in Q$ and $k \in K$. All the irreps in question can be found immediately from the table of simple induced reps. For example, all the irreps $(*k, \beta)$ of the space group O_h^1 with $k \in K$ contained in the simple induced rep $d(a_{1g})$ are enumerated in the row $d(a_{1g})$ of Table 3.8: $\Gamma(1^+3^+)R(4^-)M(1^+5^-)X(1^+2^+3^-)$.

Table 3.12. Space group O_h^5 : correspondence between small representations of little groups Γ, G_x, G_L, G_w and irreducible representations of point groups O_h, D_{4h}, D_{3d} and D_{2d}

Γ	O_h	X	D_{4h}	L	D_{3d}	W	D_{2d}
1^+	a_{1g}	1^+	a_{1g}	1^+	a_{1g}	1	a
1^-	a_{1u}	1^-	a_{1u}	1^-	a_{1u}	2	b
2^+	a_{2g}	2^+	a_{2g}	2^+	a_{2g}	3,4	e
2^-	a_{2u}	2^-	a_{2u}	2^-	a_{2u}		
3^+	e_g	3^+	b_{1g}	3^+	e_g		
3^-	e_u	3^-	b_{1u}	3^-	e_u		
4^+	t_{1g}	4^+	b_{2g}				
4^-	t_{1u}	4^-	b_{2u}				
5^+	t_{2g}	5^+	e_g				
5^-	t_{2u}	5^-	e_u				

lb) $q \in Q$ and $k \notin K$. After using the table of simple induced reps it is necessary to use the tables of compatibility relations. As an example the latter are given in Table 3.13 for the R and M points of the BZ. For example, the simple induced rep $d(a_{1g})$ of the group O_h^1 contains the irreps R_{4-} and, according to Table 3.13 of compatibility relations, the irreps A_1, A_2 with $k \notin K$ since $R_{4-} \downarrow G_d = A_1 + A_2$.

Table 3.13. Compatibility relations for space group O_h^1 . For the Γ and X points the compatibility relations for the space group O_h^1 coincide with those for the space group O_h^5 (see Table 3.12)

R	1^+	1^-	2^+	2^-	3^+	3^-	4^+	4^-	5^+	5^-
$\Lambda (\Gamma L)$	1	2	2	1	3	3	2,3	1,3	1,3	2,3
$S (R X)$	1	2	4	3	1,4	2,3	2,3,4	1,3,4	1,2,3	1,2,4
$T (R M)$	1	2	4	1,3	2,4	2,5	1,5	4,5	3,5	
M	1^+	1^-	2^+	2^-	3^+	3^-	4^+	4^-	5^+	5^-
$\Sigma (\Gamma M)$	1	2	4	3	4	3	1	2	2,3	1,4
$Z (X M)$	1	2	4	3	1	2	3	4	2,4	1,3
$T (R M)$	1	2	2	1	3	4	4	3	5	5

1c) $q \notin Q$ and $k \in K$. First, the table of induced representations of point groups is used to obtain the decomposition (3.75) and then the table of simple induced reps may be used.

1d) $q \notin Q$ and $k \notin K$. All three tables (simple induced reps of a space group, induced representations of point groups and compatibility relations) are necessary. All the four cases are considered in detail in [13] on the example of the space group D_{4h}^{14} (symmetry group of rutile structure). If we now seek the irreducible components of the site-symmetry group reps subduced by a given space group irrep $(*k, \gamma)$ (problem 2) we also have four cases to consider.

2a) $\mathbf{k} \in K$ and $\mathbf{q} \in Q$. One finds the irrep $(*\mathbf{k}, \gamma)$ in question in the rows of the table of simple induced reps corresponding to the irreps of the site group. According to the Frobenius reciprocity theorem the irrep β is contained in the reducible rep of the group $G_{\mathbf{q}}$ subduced by the irrep $(*\mathbf{k}, \gamma)$ of the space group G as many times as the symbol $(*\mathbf{k}, \gamma)$ is repeated in the corresponding row of the table of simple induced reps. For example, the rep of the site group $G_d = D_{4h}$ subduced by the irrep M_{5-} of the space group O_h^1 consists of the irreps a_{1g} and e_u (Table 3.13).

2b) $\mathbf{k} \in K$ and $\mathbf{q} \notin Q$. First one finds the irreps α' contained in the decomposition of the rep of the group $G_{\bar{q}}$ ($G_{\mathbf{q}} \subset G_{\bar{q}}$ subduced by the irrep $(*\mathbf{k}, \gamma)$ (as is done in 2a)). Then, using the table of induced representations of point groups one decomposes the reps of the group $G_{\bar{q}}$ subduced by the irreps α' of the group $G_{\bar{q}}$.

2c) $\mathbf{k} \notin K$ and $\mathbf{q} \in Q$. Using the compatibility-relations perovskite table one completes the simple induced reps table by one additional column only in the rows corresponding to the irreps of the group $G_{\bar{q}}$. Then one proceeds as in case 2a.

2d) $\mathbf{k} \notin K$ and $\mathbf{q} \notin Q$. The irreducible components of the subduced rep can be found in two steps: first, the compatibility-relations table is used as in case 2c, and then the table of induced representations of point groups as in case 2b.

Unfortunately simple induced reps for 230 space groups can not be found on any Internet site. One can find them in the book by Kovalev [31], but the irreps notations in this book sometimes differ from those used by Miller and Love [17] and on the site [16]. The latter notations are introduced in tables of simple induced reps of 25 frequently used space groups given in [13]. In this section we reproduce from [13] the simple induced tables for three cubic space groups belonging to the crystal class O_h : O_h^1 (simple cubic lattice, see the Brillouin zone in Fig. 3.1) and O_h^5 , O_h^7 (face-centered cubic lattices, the Brillouin zone in Fig. 3.2). The symmetry of the perovskite form of SrZrO_3 , MgO and silicon crystals is described by the groups O_h^1 , O_h^5 and O_h^7 , respectively. These crystals are examples of systems with different types of chemical bonding: the mixed ionic-covalent bonding (in SrZrO_3 the Sr atom is in the Sr^{2+} state, the Zr–O bonding is essentially covalent), ionic bonding (MgO) and covalent bonding (Si). In the next subsection we illustrate the use of the simple induced representations in the electronic-structure theory for these relatively simple structures.

3.2.6 Symmetry of Atomic and Crystalline Orbitals in MgO, Si and SrZrO_3 Crystals

The space symmetry of crystalline orbitals generated by atomic orbitals of the LCAO basis can be found from the tables of induced representations of space groups considered in previous section. The knowledge of space symmetry of crystalline orbitals allows the pictures of electronic bands given as a result of electronic-structure calculations to be understood. It is also useful in localized crystalline orbitals generation (see Sect. 3.3). As an example, we show the energy bands for MgO (Fig. 3.4), silicon (Si) (Fig. 3.5) and SrZrO_3 crystals (Fig. 3.3). The LCAO calculations of these crystals were made using the Hartree–Fock LCAO method (see Chap. 4). MgO crystal has rocksalt structure with symmorphic space group O_h^5 , Si crystal has diamond structure with nonsymmorphic space group O_h^7 and SrZrO_3 crystal has perovskite structure with symmorphic space group O_h^1 , see Sect. 2.3.2. The translation symmetry of the first two crystals is described by the same face-centered cubic lattice, of

the third one – by the simple cubic lattice. The point group $F = O_h$ of all the three crystals is holosymmetric (coincides with point group F^0 of the cubic lattice). For the first two crystals the wavevector belongs to the same Brillouin zone (Fig. 3.2), the representation domain coincides with the basic domain, the symmetry points of BZ are the same: $\Gamma(0, 0, 0)$, $X(1/2, 1/2, 0)$, $L(1/2, 1/2, 1/2)$ and $W(1/4, 1/2, 3/4)$ with the wavevector point groups O_h, D_{4h}, D_{3d} and D_{2d} , respectively. For the third crystal, the wavevector belongs to the simple cubic lattice Brillouin zone (Fig. 3.1), the representation domain also coincides with basic domain, the symmetry points of BZ are: $\Gamma(0, 0, 0)$, $R(1/2, 1/2, 1/2)$, $X(1/2, 0, 0)$ and $M(1/2, 1/2, 0)$ with the wavevector point groups O_h, O_h, D_{4h} and D_{4h} , respectively. For the symmorphic space groups O_h^5 and O_h^1 the small representations of little groups of symmetry points of BZ coincide with the ordinary (vector) irreducible representations of the corresponding wavevector point groups. For nonsymmorphic space group O_h^7 the small representations of little groups G_Γ, G_X, G_L and G_W were considered in Sect. 3.1.4. For the Γ and L points the notations given in Table 3.12 are used as the corresponding small representations are p -equivalent to ordinary representations of point groups O_h and D_{3d} . For the X and W points the small representations are not p -equivalent to ordinary irreducible representations of point groups D_{4h} and D_{2d} , respectively. The notations for these representations were given in Sect. 3.4.

Let us connect the pictures of the calculated band structures with the symmetry of crystalline orbitals. As for MgO and silicon crystals the dimensions of the corresponding small representations are different at the X and W points, the splitting of the valence band to one-sheet and three-sheet subbands takes place for MgO, but for *Si* crystal the valence band is not split. In the symmetry directions of the Brillouin zone the compatibility relations are used to explain the energy-level splittings. The compatibility relations for space groups O_h^5 and O_h^7 are given in Table 3.14 and in Table 3.13 for space group O_h^1 .

For the symmetry directions in the Brillouin zone $\Delta(\Gamma X)$, $A(\Gamma L)$, Σ (see Fig. 3.2) the small representations of both space groups are p -equivalent to ordinary irreducible representations of point groups C_{4v}, C_{3v} and C_{2v} . The notations of these representations are taken from [17]. For symmetry directions on the surface of the Brillouin zone $Z(XW)$, S small representations of space group O_h^5 are p -equivalent to ordinary irreducible representations of point group C_{2v} , for the symmetry direction Q – to ordinary irreducible representations of group C_s . For the nonsymmorphic space group O_h^7 small representations in the symmetry direction Z are not p -equivalent to ordinary irreducible representations of point group C_{2v} (see Sect. 3.2.2).

In Tables 3.15 and 3.16 we give the notations of induced representations in \mathbf{k} -basis for symmetry points of the Brillouin zone. We include only the band representations for upper valence bands of all the crystals under consideration.

These bands are induced by the oxygen atom $2s, 2p$ states in MgO, by the silicon atom $3s, 3p$ states in silicon, by the strontium atom $4p$ states and oxygen atom $2s, 2p$ states in SrZrO_3 . The symmetry of the corresponding crystalline orbitals is given in Figures 3.3–3.5 and was extracted directly from the tables of the simple induced representations of the corresponding space groups given in Sect. 3.2.5 as the Wyckoff positions occupied by atoms belong to the Q sets in all three structures under consideration. For all three crystals the short symbol of the BR in \mathbf{k} -basis contains only the indices of the small IRs for the most symmetrical points of the BZ, because the

Table 3.14. Compatibility relations for space groups O_h^5 and O_h^7

$\Gamma(O_h^5, O_h^7)$	1 ⁺	1 ⁻	2 ⁺	2 ⁻	3 ⁺	3 ⁻	4 ⁺	4 ⁻	5 ⁺	5 ⁻
$\Delta(\Gamma X)$	1	2	3	4	1,3	2,4	2,5	4,5	1,5	3,5
$\Delta(\Gamma L)$	1	2	2	1	3	3	2,3	1,3	1,3	2,3
Σ	1	2	4	3	1,4	2,3	2,3,4	1,3,4	1,2,3	1,2,4
$X(O_h^5)$	1 ⁺	1 ⁻	2 ⁺	2 ⁻	3 ⁺	3 ⁻	4 ⁺	4 ⁻	5 ⁺	5 ⁻
Δ	1	2	2	1	3	4	4	3	5	5
$Z(XW)$	1	2	3	4	1	2	4	3	2,3	1,4
S	1	2	4	3	4	3	1	2	2,3	1,4
$X(O_h^7)$	1	2	3	4						
Δ	1,4	2,3	5	5						
$Z(XW)$	1	1	1	1						
S	1,3	2,4	3,4	1,2						
$L(O_h^5, O_h^7)$	1 ⁺	1 ⁻	2 ⁺	2 ⁻	3 ⁺	3 ⁻				
A	1	2	2	1	3	3				
Q	1	1	2	2	1,2	1,2				
$W(O_h^5)$	1	2	3	4	5	$W(O_h^7)$	1	2		
Z	1	2	2	1	3,4		1	1		
Q	1	2	1	2	1,2		1,2	1,2		

Table 3.15. Band representations of space groups O_h^5 and O_h^7 for upper valence bands of MgO and Si crystals

	Γ	X	L	W	
MgO – O_h^5					
$b(1/2, 1/2, 1/2)$	a_{1g}	1 ⁺	1 ⁺	2 ⁻	4
	t_{1u}	5 ⁻	2 ⁻ 5 ⁻	1 ⁺ 3 ⁺	1 5
Si – O_h^7					
$a(0 0 0)$	a_1	1 ⁺ 2 ⁻	1	1 ⁺ 2 ⁻	1
	t_2	4 ⁻ 5 ⁺	1 3 4	1 ⁺ 2 ⁻ 3 ⁺ 3 ⁻	1 2 2

Table 3.16. Band representations of upper valence bands in SrZrO₃ crystal induced from Sr 4*p*-, O 2*s*- and O 2*p*- atom-like states

Atom states	q -basis	Γ	R	M	X
Sr 4 <i>p</i> -	(b, t_{1u})	4 ⁻	5 ⁺	2 ⁻ 5 ⁻	1 ⁺ 5 ⁺
O 2 <i>s</i> -	(d, a_{1g})	1 ⁺ 3 ⁺	4 ⁻	1 ⁺ 5 ⁻	1 ⁺ 2 ⁺ 3 ⁻
O 2 <i>p</i> _z -	(d, a_{2u})	4 ⁻	1 ⁺ 3 ⁺	1 ⁺ 2 ⁺ 3 ⁻	1 ⁺ 5 ⁻
O 2 <i>p</i> _{x,y} -	(d, e_u)	4 ⁻ 5 ⁻	4 ⁺ 5 ⁺	3 ⁺ 4 ⁺ 5 [±]	3 ⁻ 4 ⁻ 5 [±]

indices for all other IRs contained in the BR are determined with the help of compatibility relations. These are the states responsible for four-sheet valence bands in the first two crystals (Fig. 3.4 and Fig. 3.5) and for the 6- and 9-sheet valence bands in $SrZrO_3$ crystal (Fig. 3.3)

Due to the considered symmetry difference of crystalline orbitals in MgO and Si crystals the nature of chemical bonding in these crystals is also different. Indeed, in ionic MgO crystal the splitting of the valence band allows the crystalline orbitals localized on an oxygen atom to be generated and transformed over a_{1g} and t_{1u} irreducible representations of the oxygen site-symmetry group O_h . In covalent Si crystal all four sheets of the valence band have to be included in localization so that the localized orbitals found are centered at the middle of the Si – Si bond.

In $SrZrO_3$ crystal oxygen $2s$ functions transform according to $\beta = a_{1g}$ IR of the oxygen site-symmetry group $G_{\mathbf{q}} = D_{4h}$ and generate a 3-sheeted BR. The symmetry of states in this band is fully determined by the $2s$ function of one of three oxygens in the primitive cell and may be labeled by the symbol (d, a_{1g}) as oxygen atoms occupy Wyckoff position d in space group O_h^1 . In Table 3.16 this band, with the symbol of the BR (d, a_{1g}) , is given in \mathbf{k} -basis (Γ, R, M, X are the symmetry points of the BZ).

In Sect. 3.2.4 we defined simple and composite BRs. A BR is simple if it does not consist of two or more BRs of a smaller dimension. All simple BRs for a given space group are generated by the IRs of site-symmetry groups of just a few points in the Wigner–Seitz cell of the direct lattice.

In our examples, all the induced irreps are simple, excluding the BR corresponding to the 6-sheeted lower valence subband (see Fig. 3.3). This band representation is a composite one as it is formed by two simple band representations (d, a_{1g}) and (b, t_{1u}) induced by O $2s$ - and Sr $4p$ states, respectively. Analysis of the space symmetry of crystalline orbitals is used to consider the possible centers of localization of chemical bonding in crystals. This task requires the Wannier-function definition and is considered in the next section.

3.3 Symmetry of Localized Crystalline Orbitals. Wannier Functions

3.3.1 Symmetry of Localized Orbitals and Band Representations of Space Groups

The localized molecular orbitals (LMO) are extensively used not only for the chemical-bonding analysis in molecules but also in the local correlation methods [41] (we consider the problem of electron correlation in molecules and crystals in Chap. 5). The LMO are generated from the canonical MO occupied by electrons and found in the Hartree–Fock or DFT calculations. This generation is based on one or other localization criteria [42].

Localized crystalline orbitals (LCO) are generated from a canonical delocalized Bloch functions (CO). As in the case of the molecules one or other localization criteria is used. The orthonormalized LCO in crystals are known as Wannier functions. Wannier functions (WFs) have attracted much attention in solid-state physics since their first introduction in 1937 [43] and up to now. The analytical behavior of Bloch