
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

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	Incremental 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	Atomic Orbital Laplace-transformed MP2 Theory for Periodic 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 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	Semiempirical LCAO Methods for Molecules and Periodic Systems	193
6.1	Extended 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-differential Overlap Approximations for Molecules and Crystals .	203
6.2.1	Zero-differential Overlap Approximations for Molecules.....	203
6.2.2	Complete and Intermediate Neglect of Differential Overlap for Crystals	208
6.3	Zero-differential overlap Approximation in Cyclic-cluster Model	211
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 and Hartree–Fock LCAO Methods	220
7	Kohn–Sham LCAO Method for Periodic Systems	231
7.1	Foundations of the Density-functional Theory	231
7.1.1	The Basic Formulation of the Density-functional Theory	231
7.1.2	The Kohn–Sham Single-particle Equations	234
7.1.3	Exchange and Correlation Functionals in the Local Density Approximation	237
7.1.4	Beyond the Local Density Approximation	240
7.1.5	The Pair Density. Orbital-dependent Exchange-correlation Functionals	244

7.2	Density-functional LCAO Methods for Solids	249
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	Basis Sets 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	Nonrelativistic 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	Relativistic 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	LCAO Calculations of Perfect-crystal Properties	327
9.1	Theoretical 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 Crystals	369
9.2	Electron Properties of Crystals in LCAO Methods	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: Magnetic Phases of LaMnO_3 and ScMnO_3 Crystals	383
9.3	Total Energy and Related Observables in LCAO Methods for Solids	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 of Vibrational Frequencies	403
10	Modeling and LCAO Calculations of Point Defects in Crystals	409
10.1	Symmetry 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 and Charged Point Defects	417
10.1.4	Molecular-cluster Models of Defective Solids	421
10.2	Point Defects in Binary Oxides	426
10.2.1	Oxygen Interstitials in Magnesium Oxide: Supercell LCAO Calculations	426
10.2.2	Neutral and Charged Oxygen Vacancy in Al_2O_3 Crystal: Supercell and Cyclic-cluster Calculations	429
10.2.3	Supercell Modeling of Metal-doped Rutile TiO_2	435
10.3	Point Defects in Perovskites	438
10.3.1	Oxygen Vacancy in SrTiO_3	438
10.3.2	Supercell Model of Fe-doped SrTiO_3	445
10.3.3	Modeling of Solid Solutions of $\text{La}_c\text{Sr}_{1-c}\text{MnO}_3$	452
11	Surface Modeling in LCAO Calculations of Metal Oxides	459
11.1	Diperiodic 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	Surface LCAO Calculations on TiO_2 and SnO_2	482
11.2.1	Cluster Models of (110) TiO_2	482
11.2.2	Adsorption of Water on the TiO_2 (Rutile) (110) Surface: 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

XIV Contents

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 Bravais Lattices	521
B Reciprocal Matrices of the Symmetric Supercell Transformations of the Three Cubic Bravais Lattices	525
C Computer Programs for Periodic Calculations in Basis of Localized Orbitals.....	527
References	531
Index	553