## **Contents**

## Part I Theory

l	Intro	duction		3		
2	Spac	Space Groups and Crystalline Structures				
	2.1		ation 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	17		
		2.2.1	Space Groups of Bravais Lattices.			
			Symmorphic and Nonsymmorpic Space Groups	17		
		2.2.2	Three-Periodic Space Groups	19		
		2.2.3	Site Symmetry in Crystals. Wyckoff Positions	23		
	2.3	Crysta	Iline Structures	27		
		2.3.1	Crystal-Structure Types: Structure			
			Information for Computer Codes	27		
		2.3.2	Cubic Structures: Diamond, Rock Salt,			
			Fluorite, Zincblende, Cesium Chloride,			
			and Cubic Perovskite	30		
		2.3.3	Tetragonal Structures: Rutile, Anatase, and La <sub>2</sub> CuO <sub>4</sub>	35		
		2.3.4	Orthorhombic Structures: LaMnO <sub>3</sub> and YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	39		
		2.3.5	Hexagonal and Trigonal Structures: Graphite,			
			Wurtzite, Corundum, and ScMnO <sub>3</sub>	42		
3	Sym	metry a	nd Localization of Crystalline Orbitals	47		
	3.1	Transl	ation and Space Symmetry of Crystalline			
		Orbita	ls: Bloch Functions	47		
		3.1.1	Symmetry of Molecular and Crystalline Orbitals	47		
		3.1.2	Irreducible Representations of Translation			
			Group: Brillouin Zone	5		

xii Contents

		3.1.3	Stars of Wave Vectors. Little Groups. Full	
			Representations of Space Groups	59
		3.1.4	Small Representations of a Little Group:	
			Projective Representations of Point Groups	62
	3.2	Site Sy	mmetry and Induced Representations of Space Groups	67
		3.2.1	Induced Representations of Point Groups:	
			Localized Molecular Orbitals	67
		3.2.2	Induced Representations of Space Groups	
		3,2,2	in <b>q</b> -Basis	72
		3.2.3	Induced Representations of Space Groups	
		5.2.5	in k-Basis: Band Representations	74
		3.2.4	Simple and Composite Induced Representations	77
		3.2.5	Simple Induced Representations for Cubic	
		3.2.3	Space Groups $O_h^1$ , $O_h^5$ , and $O_h^7$	80
		3.2.6	Symmetry of Atomic and Crystalline Orbitals	
		5.2.0	in MgO, Si, and SrZrO <sub>3</sub> Crystals	85
	3.3	Symme	etry of Localized Crystalline Orbitals.	05
	5.5	-	er Functions	89
		3.3.1	Symmetry of Localized Orbitals and Band	0,
		3.3.1	Representations of Space Groups	89
		3.3.2	Localization Criteria in Wannier-Function	0,
		3.3.2	Generation	93
		3.3.3	Localized Orbitals for Valence Bands: LCAO	75
		3.3.3	Approximation	97
		3.3.4	Variational Method of Localized Wannier-	91
		3.3.4	Function Generation on the Base of Bloch	
			Functions	99
			ruictions	77
4	Hart	ree-Foc	k LCAO Method for Periodic Systems	109
	4.1	One-El	lectron Approximation for Crystals	110
		4.1.1	One-Electron and One-Determinant	
			Approximations for Molecules and Crystals	110
		4.1.2	Symmetry of the One-Electron Approximation	
			Hamiltonian	115
		4.1.3	Restricted and Unrestricted Hartree-Fock	
			LCAO Methods for Molecules	117
		4.1.4	Specific Features of the Hartree–Fock Method	
		•	for a Cyclic Model of a Crystal	123
		4.1.5	Restricted Hartree–Fock LCAO Method for Crystals	125
		4.1.6	Unrestricted and Restricted Open-Shell	
			Hartree–Fock Methods for Crystals	129
	4.2	Specia	l Points of Brillouin Zone	131
	_	4.2.1	Supercells of Three-Dimensional Bravais Lattices	131
		4.2.2	Special Points of Brillouin-Zone Generating	

Contents xiii

		4.2.3	Modification of the Monkhorst–Pack	127
	4.0	ъ .:.	Special-Points Meshes	137
	4.3		Matrix of Crystals in the Hartree–Fock Method	140
		4.3.1	Properties of the One-Electron Density Matrix	140
		4.3.2	of a Crystal	140
		4.3.2	, and the second	145
		422	Crystal in the LCAO Approximation	143
		4.3.3	Interpolation Procedure for Constructing an Approximate Density Matrix for Periodic Systems	149
5	Elect	ron Cor	relations in Molecules and Crystals	157
	5.1		n Correlations in Molecules:	15,
	*		artree–Fock Methods	157
		5.1.1	What Is the Electron Correlation?	157
		5.1.2	Configuration Interaction and	
			Multiconfiguration Self-Consistent Field Methods	161
		5.1.3	Coupled-Cluster Methods	165
		5.1.4	Many-Electron Perturbation Theory	167
		5.1.5	Local Electron Correlation Methods	170
	5.2	Increm	ental Scheme for Local Correlation in Periodic	
			S	176
		5.2.1	Weak and Strong Electron Correlation	176
		5.2.2	Method of Increments: Ground State	179
		5.2.3	Method of Increments: Valence-Band	
			Structure and Bandgap	183
	5.3	Atomic	Orbital Laplace-Transformed MP2 Theory for	
		Periodi	c Systems	188
		5.3.1	Laplace MP2 for Periodic Systems:	
			Unit-Cell Correlation Energy	188
		5.3.2	Laplace MP2 for Periodic Systems: Bandgap	191
	5.4	Local I	MP2 Electron Correlation Method	
		for Nor	nconducting Crystals	194
		5.4.1	Local MP2 Equations for Periodic Systems	194
		5.4.2	Fitted Wannier Functions for Periodic Local	
			Correlation Methods	199
		5.4.3	Symmetry Exploitation in Local MP2 Method	
			for Periodic Systems	204
6			al LCAO Methods for Molecules	
			Systems	207
	6.1		ed Hückel and Mulliken-Rüdenberg Approximations	208
		6.1.1	Nonself-Consistent Extended Hückel-Tight-	
			Binding Method	208
		6.1.2	Iterative Mulliken–Rüdenberg Method for Crystals	214

xiv Contents

	6.2	Zero [	Differential Overlap Approximations	
		for Mo	plecules and Crystals	219
		6.2.1	Zero Differential Overlap Approximations	
			for Molecules	219
		6.2.2	Complete and Intermediate Neglect of	
			Differential Overlap for Crystals	225
	6.3	Zero [	Differential Overlap Approximation	
			lic-Cluster Model	228
		6.3.1	Symmetry of Cyclic-Cluster Model of Perfect	
			Crystal	228
		6.3.2	Semiempirical LCAO Methods in	
			Cyclic-Cluster Model	233
		6.3.3	Implementation of the Cyclic-Cluster Model	
		0.0.0	in MSINDO and Hartree–Fock LCAO Methods	239
7	Koł		LCAO Method for Periodic Systems	251
	7.1	Founda	ations of the Density-Functional Theory	252
		7.1.1	The Basic Formulation of the Density-	
			Functional Theory	252
		7.1.2	The Kohn–Sham Single-Particle Equations	255
		7.1.3	Exchange and Correlation Functionals	
			in the Local-Density Approximation	259
		7.1.4	Beyond the Local-Density Approximation	262
		7.1.5	The Pair Density: Orbital-Dependent	
			Exchange-Correlation Functionals	266
	7.2	Densit	y-Functional LCAO Methods for Solids	272
		7.2.1	Implementation of Kohn–Sham LCAO	
			Method in Crystal Calculations	272
		7.2.2	Linear-Scaling DFT LCAO Methods for Solids	276
		7.2.3	Heyd-Scuseria-Ernzerhof Screened Coulomb	
			Hybrid Functional	283
		7.2.4	Are Molecular Exchange-Correlation	
			Functionals Transferable to Crystals?	287
		7.2.5	Density-Functional Methods for Strongly	-0.
		,	Correlated Systems: SIC-DFT and DFT+U	
			Approaches	294
			Approaches	~ / ·
Par	t II	Applicat	tions	
o	D	:- C-4	d Boundary described in Book 21 d CAO CA Late	201
8			d Pseudopotentials in Periodic LCAO Calculations	305
	8.1		Sets in the Electron-Structure Calculations of Crystals	305
		8.1.1	Plane Waves and Atomic-Like Basis Sets:	200
		0	Slater-Type Functions	305
		8.1.2	Molecular Basis Sets of Gaussian-Type Functions	-310

Contents xv

		8.1.3	Molecular Basis-Set Adaptation for Periodic	
			Systems	316
	8.2		ativistic Effective Core Potentials and Valence	
		Basis S	ets	324
		8.2.1	Effective Core Potentials: Theoretical	
			Grounds	324
		8.2.2	Gaussian Form of Effective Core Potentials	
			and Valence Basis Sets in	
			Periodic LCAO Calculations	329
		8.2.3	Separable Embedding Potential	331
	8.3		istic Effective Core Potentials and Valence Basis Sets	338
		8.3.1	Relativistic Electronic-Structure Theory:	
			Dirac-Hartree-Fock and Dirac-Kohn-Sham	
			Methods for Molecules	338
		8.3.2	Relativistic Effective Core Potentials	342
		8.3.3	One-Center Restoration of Electronic	
			Structure in the Core Region	344
		8.3.4	Basis Sets for Relativistic Calculations of Molecules	346
		8.3.5	Relativistic LCAO Methods for Periodic Systems	349
9	LCA	O Calcul	lations of Perfect-Crystal Properties	357
	9.1		tical Analysis of Chemical Bonding in Crystals	357
		9.1.1	Local Properties of Electronic	
			Structure in LCAO HF	
			and DFT Methods for Crystals and Post-HF	
			Methods for Molecules	357
		9.1.2	Chemical Bonding in Cyclic-Cluster Model:	
			Local Properties of Composite Crystalline Oxides	363
		9.1.3	Chemical Bonding in Titanium Oxides:	
			Periodic and Molecular-Crystalline Approaches	373
		9.1.4	Wannier-Type Atomic Functions and	
			Chemical Bonding in Crystals	381
		9.1.5	The Localized Wannier Functions for Valence	
			Bands: Chemical Bonding in Crystalline Oxides	390
		9.1.6	Projection Technique for Population	
			Analysis of Atomic Orbitals: Comparison of	
			Different Methods of the Chemical-Bonding	
		•	Description in Crystals	401
	9.2	Electro	n Properties of Crystals in LCAO Methods	408
		9.2.1	One-Electron Properties: Band Structure,	
			Density of States, and Electron Momentum Density	408
		9.2.2	Magnetic Structure of Metal Oxides in LCAO	
			Methods: Magnetic Phases of LaMnO <sub>3</sub> and	
			ScMnO2 Crystals	417

xvi Contents

	9.3	Total E	nergy and Related Observables in LCAO	
		Method	Is for Solids	427
		9.3.1	Equilibrium Structure and Cohesive Energy	427
		9.3.2	Bulk Modulus, Elastic Constants, and Phase	
			Stability of Solids: LCAO Ab Initio Calculations	432
		9.3.3	Lattice Dynamics and LCAO Calculations	
			of Vibrational Frequencies	438
		9.3.4	Calculations on Cubic Ba(Ti, Zr, Hf)O <sub>3</sub> and	
			Noncubic BaTiO <sub>3</sub>	443
		9.3.5	First-Principles Calculations of the	
			Thermodynamic Properties of BaTiO <sub>3</sub> of	
			Rhombohedral Phase	454
		9.3.6	Quantum Mechanics-Molecular Dynamics	
			Approach to the Interpretation of X-Ray	
			Absorption Spectra	466
	9.4	LCAO	Calculations on Tungstates MeWO <sub>4</sub> (Me: Zn,Ni)	475
		9.4.1	Electron and Phonon Properties of ZnWO <sub>4</sub>	475
		9.4.2	Magnetic Ordering in NiWO <sub>4</sub>	480
10		_	LCAO Calculations of Point Defects in Crystals	489
	10.1		etry and Models of Defective Crystals	489
		10.1.1	Point Defects in Solids and Their Models	489
		10.1.2	Symmetry of Supercell Model of Defective Crystals	494
		10.1.3	Supercell and Cyclic-Cluster Models of	
			Neutral and Charged Point Defects	497
		10.1.4	Molecular-Cluster Models of Defective Solids	502
	10.2		Defects in Binary Oxides	507
		10.2.1	Oxygen Interstitials in Magnesium Oxide:	
			Supercell LCAO Calculations	507
		10.2.2	Neutral and Charged Oxygen Vacancy in	
			Al <sub>2</sub> O <sub>3</sub> Crystal: Supercell	
			and Cyclic-Cluster Calculations	510
		10.2.3	Supercell Modeling of Metal-Doped Rutile TiO <sub>2</sub>	517
	10.3	Point D	Defects in Perovskites	520
		10.3.1	Oxygen Vacancy in SrTiO <sub>3</sub>	520
		10.3.2	Supercell Model of Fe-Doped SrTiO <sub>3</sub>	528
		10.3.3	Modeling of Solid Solutions of	
		•	$La_cSr_{1-c}MnO_3$	535
11	ÇF			541
11			leling in LCAO Calculations of Metal Oxides	541
	11.1	_	odic Space Groups and Slab Models of Surfaces	541
		11.1.1	Diperiodic (Layer) Space Groups	541
		11.1.2	Oxide-Surface Types and Stability	548
		11.1.3	Single- and Periodic-Slab Models of MgO	550
			and TiO <sub>2</sub> Surfaces	553

Contents xvii

	11.2	Surface	LCAO Calculations on TiO <sub>2</sub> and SnO <sub>2</sub>	565
		11.2.1	Cluster Models of (110) TiO <sub>2</sub>	565
		11.2.2	Adsorption of Water on the TiO <sub>2</sub> (Rutile)	
			(110) Surface: Comparison of Periodic	
			LCAO-PW and Embedded-Cluster	
			LCAO Calculations	570
		11.2.3	Single-Slab LCAO Calculations of Bare	
			and Hydroxylated SnO <sub>2</sub> Surfaces	577
	11.3	Slab M	lodels of SrTiO <sub>3</sub> , SrZrO <sub>3</sub> , and LaMnO <sub>3</sub> Surfaces	589
		11.3.1	Hybrid HF-DFT Comparative Study of	
			SrZrO <sub>3</sub> and SrTiO <sub>3</sub> (001) Surface Properties	589
		11.3.2	F Center on the SrTiO <sub>3</sub> (001) Surface	596
		11.3.3	Slab Models of LaMnO <sub>3</sub> Surfaces	597
12	LCA	n Calcul	lations on Uranium Nitrides	603
	12.1		rystals	603
	12.1	12.1.1	•	603
		12.1.2	Uranium Nitrides UN,U <sub>2</sub> N <sub>3</sub> ,UN <sub>2</sub>	614
	12.2		e and Point-Defect Modeling in Uranium Nitrides	621
	12.2	12.2.1	•	621
		12.2.2	First-Principles Calculation of Point Defects	021
		12.2.2	in Bulk Uranium Nitride and on (001) Surface	626
4.0	<u> </u>		, ,	
13			d Modeling of BN, TiO <sub>2</sub> , and SrTiO <sub>3</sub> Nanotubes	631
	13.1		roups of One-Periodic Systems	631
		13.1.1	Rod Groups as Subperiodic Subgroups of	(21
			Space Groups	631
		12.1.2	I Comme	()(
	12.2	13.1.2	Line Groups	636
	13.2	Nanotu	be Rolling Up from Two-Dimensional Lattices	640
	13.2	Nanotu 13.2.1	be Rolling Up from Two-Dimensional Lattices  General Procedure	640 640
	13.2	Nanotu 13.2.1 13.2.2	be Rolling Up from Two-Dimensional Lattices	640 640 643
	13.2	Nanotu 13.2.1 13.2.2 13.2.3	be Rolling Up from Two-Dimensional Lattices  General Procedure  Hexagonal Lattice  Square Lattices	640 640 643 645
	13.2	Nanotu 13.2.1 13.2.2 13.2.3 13.2.4	be Rolling Up from Two-Dimensional Lattices General Procedure Hexagonal Lattice Square Lattices Rectangular Lattices	640 640 643 645 647
	13.2	Nanotu 13.2.1 13.2.2 13.2.3 13.2.4 13.2.5	be Rolling Up from Two-Dimensional Lattices General Procedure Hexagonal Lattice Square Lattices Rectangular Lattices Symmetry of Double- and Multiwall Nanotubes.	640 640 643 645 647 648
		Nanotu 13.2.1 13.2.2 13.2.3 13.2.4 13.2.5 13.2.6	be Rolling Up from Two-Dimensional Lattices General Procedure Hexagonal Lattice Square Lattices Rectangular Lattices Symmetry of Double- and Multiwall Nanotubes. Use of Symmetry in Nanotube LCAO Calculations	640 640 643 645 647
	13.2	Nanotu 13.2.1 13.2.2 13.2.3 13.2.4 13.2.5 13.2.6 LCAO	be Rolling Up from Two-Dimensional Lattices General Procedure Hexagonal Lattice Square Lattices Rectangular Lattices Symmetry of Double- and Multiwall Nanotubes Use of Symmetry in Nanotube LCAO Calculations Calculations on BN and TiO <sub>2</sub> Nanotubes	640 640 643 645 647 648 650
		Nanotu 13.2.1 13.2.2 13.2.3 13.2.4 13.2.5 13.2.6 LCAO with He	the Rolling Up from Two-Dimensional Lattices  General Procedure  Hexagonal Lattice  Square Lattices  Rectangular Lattices  Symmetry of Double- and Multiwall Nanotubes  Use of Symmetry in Nanotube LCAO Calculations  Calculations on BN and TiO <sub>2</sub> Nanotubes  exagonal Morphology	640 640 643 645 647 648 650
		Nanotu 13.2.1 13.2.2 13.2.3 13.2.4 13.2.5 13.2.6 LCAO with He 13.3.1	the Rolling Up from Two-Dimensional Lattices General Procedure Hexagonal Lattice Square Lattices Rectangular Lattices Symmetry of Double- and Multiwall Nanotubes Use of Symmetry in Nanotube LCAO Calculations Calculations on BN and TiO <sub>2</sub> Nanotubes exagonal Morphology Single-Wall BN and TiO <sub>2</sub> Nanotubes	640 643 645 647 648 650
	13.3	Nanotu 13.2.1 13.2.2 13.2.3 13.2.4 13.2.5 13.2.6 LCAO with He 13.3.1 13.3.2	the Rolling Up from Two-Dimensional Lattices  General Procedure  Hexagonal Lattice  Square Lattices  Rectangular Lattices  Symmetry of Double- and Multiwall Nanotubes  Use of Symmetry in Nanotube LCAO Calculations  Calculations on BN and TiO <sub>2</sub> Nanotubes  exagonal Morphology  Single-Wall BN and TiO <sub>2</sub> Nanotubes  Double-Wall BN and TiO <sub>2</sub> Nanotubes	640 643 645 647 648 650
		Nanotu 13.2.1 13.2.2 13.2.3 13.2.4 13.2.5 13.2.6 LCAO with He 13.3.1 13.3.2 LCAO	the Rolling Up from Two-Dimensional Lattices General Procedure Hexagonal Lattice Square Lattices Rectangular Lattices Symmetry of Double- and Multiwall Nanotubes Use of Symmetry in Nanotube LCAO Calculations Calculations on BN and TiO <sub>2</sub> Nanotubes exagonal Morphology Single-Wall BN and TiO <sub>2</sub> Nanotubes Double-Wall BN and TiO <sub>2</sub> Nanotubes Calculations of TiO <sub>2</sub> Nanotubes	640 643 645 647 648 650 653 662
	13.3	Nanotu 13.2.1 13.2.2 13.2.3 13.2.4 13.2.5 13.2.6 LCAO with He 13.3.1 13.3.2 LCAO with Re	the Rolling Up from Two-Dimensional Lattices General Procedure Hexagonal Lattice Square Lattices Rectangular Lattices Symmetry of Double- and Multiwall Nanotubes Use of Symmetry in Nanotube LCAO Calculations Calculations on BN and TiO <sub>2</sub> Nanotubes exagonal Morphology Single-Wall BN and TiO <sub>2</sub> Nanotubes Double-Wall BN and TiO <sub>2</sub> Nanotubes Calculations of TiO <sub>2</sub> Nanotubes ectangular Morphology	640 640 643 645 647 648 650
	13.3	Nanotu 13.2.1 13.2.2 13.2.3 13.2.4 13.2.5 13.2.6 LCAO with He 13.3.1 13.3.2 LCAO with Re LCAO	the Rolling Up from Two-Dimensional Lattices General Procedure Hexagonal Lattice Square Lattices Rectangular Lattices Symmetry of Double- and Multiwall Nanotubes Use of Symmetry in Nanotube LCAO Calculations Calculations on BN and TiO <sub>2</sub> Nanotubes exagonal Morphology Single-Wall BN and TiO <sub>2</sub> Nanotubes Double-Wall BN and TiO <sub>2</sub> Nanotubes Calculations of TiO <sub>2</sub> Nanotubes ectangular Morphology Calculations on SrTiO <sub>3</sub> Nanotubes with Square	640 640 643 645 647 648 650 653 662
	13.3	Nanotu 13.2.1 13.2.2 13.2.3 13.2.4 13.2.5 13.2.6 LCAO with He 13.3.1 13.3.2 LCAO with Re LCAO Morphe	the Rolling Up from Two-Dimensional Lattices General Procedure Hexagonal Lattice Square Lattices Rectangular Lattices Symmetry of Double- and Multiwall Nanotubes Use of Symmetry in Nanotube LCAO Calculations Calculations on BN and TiO <sub>2</sub> Nanotubes exagonal Morphology Single-Wall BN and TiO <sub>2</sub> Nanotubes Double-Wall BN and TiO <sub>2</sub> Nanotubes Calculations of TiO <sub>2</sub> Nanotubes ectangular Morphology Calculations on SrTiO <sub>3</sub> Nanotubes with Square ology	640 640 643 645 647 648 650 653 662 672
	13.3	Nanotu 13.2.1 13.2.2 13.2.3 13.2.4 13.2.5 13.2.6 LCAO with He 13.3.1 13.3.2 LCAO with Re LCAO	the Rolling Up from Two-Dimensional Lattices General Procedure Hexagonal Lattice Square Lattices Rectangular Lattices Symmetry of Double- and Multiwall Nanotubes Use of Symmetry in Nanotube LCAO Calculations Calculations on BN and TiO <sub>2</sub> Nanotubes exagonal Morphology Single-Wall BN and TiO <sub>2</sub> Nanotubes Double-Wall BN and TiO <sub>2</sub> Nanotubes Calculations of TiO <sub>2</sub> Nanotubes ectangular Morphology Calculations on SrTiO <sub>3</sub> Nanotubes with Square	640 640 643 645 647 648 650 653 662

xviii Contents

A	Matrices of the Symmetrical Supercell Transformations of 14 Three-Dimensional Bravais Lattices	691
В	Reciprocal Matrices of the Symmetric Supercell	
	Transformations of the Three Cubic Bravais Lattices	695
C	Computer Programs for Periodic Calculations	
	in Basis of Localized Orbitals	697
Ref	ferences	701
Ind	lex	729