
Contents

Part I Basic Mathematics

1	Basic Mathematical Background: Introduction	3
1.1	Definition of a Group	3
1.2	Simple Example of a Group	3
1.3	Basic Definitions	6
1.4	Rearrangement Theorem	7
1.5	Cosets	7
1.6	Conjugation and Class	9
1.7	Factor Groups	11
1.8	Group Theory and Quantum Mechanics	11
2	Representation Theory and Basic Theorems	15
2.1	Important Definitions	15
2.2	Matrices	16
2.3	Irreducible Representations	17
2.4	The Unitarity of Representations	19
2.5	Schur's Lemma (Part 1)	21
2.6	Schur's Lemma (Part 2)	23
2.7	Wonderful Orthogonality Theorem	25
2.8	Representations and Vector Spaces	28
3	Character of a Representation	29
3.1	Definition of Character	29
3.2	Characters and Class	30
3.3	Wonderful Orthogonality Theorem for Character	31
3.4	Reducible Representations	33
3.5	The Number of Irreducible Representations	35
3.6	Second Orthogonality Relation for Characters	36
3.7	Regular Representation	37
3.8	Setting up Character Tables	40

3.9	Schoenflies Symmetry Notation	44
3.10	The Hermann–Mauguin Symmetry Notation	46
3.11	Symmetry Relations and Point Group Classifications	48
4	Basis Functions	57
4.1	Symmetry Operations and Basis Functions	57
4.2	Basis Functions for Irreducible Representations	58
4.3	Projection Operators $\hat{P}_{kl}^{(\Gamma_n)}$	64
4.4	Derivation of an Explicit Expression for $\hat{P}_{k\ell}^{(\Gamma_n)}$	64
4.5	The Effect of Projection Operations on an Arbitrary Function	65
4.6	Linear Combinations of Atomic Orbitals for Three Equivalent Atoms at the Corners of an Equilateral Triangle	67
4.7	The Application of Group Theory to Quantum Mechanics	70

Part II Introductory Application to Quantum Systems

5	Splitting of Atomic Orbitals in a Crystal Potential	79
5.1	Introduction	79
5.2	Characters for the Full Rotation Group	81
5.3	Cubic Crystal Field Environment for a Paramagnetic Transition Metal Ion	85
5.4	Comments on Basis Functions	90
5.5	Comments on the Form of Crystal Fields	92
6	Application to Selection Rules and Direct Products	97
6.1	The Electromagnetic Interaction as a Perturbation	97
6.2	Orthogonality of Basis Functions	99
6.3	Direct Product of Two Groups	100
6.4	Direct Product of Two Irreducible Representations	101
6.5	Characters for the Direct Product	103
6.6	Selection Rule Concept in Group Theoretical Terms	105
6.7	Example of Selection Rules	106

Part III Molecular Systems

7	Electronic States of Molecules and Directed Valence	113
7.1	Introduction	113
7.2	General Concept of Equivalence	115
7.3	Directed Valence Bonding	117
7.4	Diatomic Molecules	118
7.4.1	Homonuclear Diatomic Molecules	118
7.4.2	Heterogeneous Diatomic Molecules	120

7.5	Electronic Orbitals for Multiatomic Molecules	124
7.5.1	The NH ₃ Molecule	124
7.5.2	The CH ₄ Molecule	125
7.5.3	The Hypothetical SH ₆ Molecule	129
7.5.4	The Octahedral SF ₆ Molecule	133
7.6	σ - and π -Bonds	134
7.7	Jahn–Teller Effect	141
8	Molecular Vibrations, Infrared, and Raman Activity	147
8.1	Molecular Vibrations: Background	147
8.2	Application of Group Theory to Molecular Vibrations	149
8.3	Finding the Vibrational Normal Modes	152
8.4	Molecular Vibrations in H ₂ O	154
8.5	Overtones and Combination Modes	156
8.6	Infrared Activity	157
8.7	Raman Effect	159
8.8	Vibrations for Specific Molecules	161
8.8.1	The Linear Molecules	161
8.8.2	Vibrations of the NH ₃ Molecule	166
8.8.3	Vibrations of the CH ₄ Molecule	168
8.9	Rotational Energy Levels	170
8.9.1	The Rigid Rotator	170
8.9.2	Wigner–Eckart Theorem	172
8.9.3	Vibrational–Rotational Interaction	174

Part IV Application to Periodic Lattices

9	Space Groups in Real Space	183
9.1	Mathematical Background for Space Groups	184
9.1.1	Space Groups Symmetry Operations	184
9.1.2	Compound Space Group Operations	186
9.1.3	Translation Subgroup	188
9.1.4	Symmorphic and Nonsymmorphic Space Groups	189
9.2	Bravais Lattices and Space Groups	190
9.2.1	Examples of Symmorphic Space Groups	192
9.2.2	Cubic Space Groups and the Equivalence Transformation	194
9.2.3	Examples of Nonsymmorphic Space Groups	196
9.3	Two-Dimensional Space Groups	198
9.3.1	2D Oblique Space Groups	200
9.3.2	2D Rectangular Space Groups	201
9.3.3	2D Square Space Group	203
9.3.4	2D Hexagonal Space Groups	203
9.4	Line Groups	204

9.5 The Determination of Crystal Structure and Space Group . . . 205

9.5.1 Determination of the Crystal Structure 206

9.5.2 Determination of the Space Group 206

10 Space Groups in Reciprocal Space and Representations . . . 209

10.1 Reciprocal Space 210

10.2 Translation Subgroup 211

10.2.1 Representations for the Translation Group 211

10.2.2 Bloch's Theorem and the Basis
of the Translational Group 212

10.3 Symmetry of \mathbf{k} Vectors and the Group of the Wave Vector . . 214

10.3.1 Point Group Operation in \mathbf{r} -space and \mathbf{k} -space 214

10.3.2 The Group of the Wave Vector $G_{\mathbf{k}}$ and the Star of \mathbf{k} . . 215

10.3.3 Effect of Translations and Point Group Operations
on Bloch Functions 215

10.4 Space Group Representations 219

10.4.1 Symmorphic Group Representations 219

10.4.2 Nonsymmorphic Group Representations
and the Multiplier Algebra 220

10.5 Characters for the Equivalence Representation 221

10.6 Common Cubic Lattices: Symmorphic Space Groups 222

10.6.1 The Γ Point 223

10.6.2 Points with $\mathbf{k} \neq 0$ 224

10.7 Compatibility Relations 227

10.8 The Diamond Structure: Nonsymmorphic Space Group 230

10.8.1 Factor Group and the Γ Point 231

10.8.2 Points with $\mathbf{k} \neq 0$ 232

10.9 Finding Character Tables for all Groups of the Wave Vector . . 235

Part V Electron and Phonon Dispersion Relation

11 Applications to Lattice Vibrations 241

11.1 Introduction 241

11.2 Lattice Modes and Molecular Vibrations 244

11.3 Zone Center Phonon Modes 246

11.3.1 The NaCl Structure 246

11.3.2 The Perovskite Structure 247

11.3.3 Phonons in the Nonsymmorphic Diamond Lattice 250

11.3.4 Phonons in the Zinc Blende Structure 252

11.4 Lattice Modes Away from $\mathbf{k} = 0$ 253

11.4.1 Phonons in NaCl at the X Point $\mathbf{k} = (\pi/a)(100)$ 254

11.4.2 Phonons in BaTiO₃ at the X Point 256

11.4.3 Phonons at the K Point in Two-Dimensional Graphite . 258

11.5	Phonons in Te and α -Quartz Nonsymmorphic Structures	262
11.5.1	Phonons in Tellurium	262
11.5.2	Phonons in the α -Quartz Structure	268
11.6	Effect of Axial Stress on Phonons	272
12	Electronic Energy Levels in a Cubic Crystals	279
12.1	Introduction	279
12.2	Plane Wave Solutions at $\mathbf{k} = 0$	282
12.3	Symmetrized Plane Solution Waves along the Δ -Axis	286
12.4	Plane Wave Solutions at the X Point	288
12.5	Effect of Glide Planes and Screw Axes	294
13	Energy Band Models Based on Symmetry	305
13.1	Introduction	305
13.2	$\mathbf{k} \cdot \mathbf{p}$ Perturbation Theory	307
13.3	Example of $\mathbf{k} \cdot \mathbf{p}$ Perturbation Theory for a Nondegenerate Γ_1^+ Band	308
13.4	Two Band Model: Degenerate First-Order Perturbation Theory	311
13.5	Degenerate second-order $\mathbf{k} \cdot \mathbf{p}$ Perturbation Theory	316
13.6	Nondegenerate $\mathbf{k} \cdot \mathbf{p}$ Perturbation Theory at a Δ Point	324
13.7	Use of $\mathbf{k} \cdot \mathbf{p}$ Perturbation Theory to Interpret Optical Experiments	326
13.8	Application of Group Theory to Valley–Orbit Interactions in Semiconductors	327
13.8.1	Background	328
13.8.2	Impurities in Multivalley Semiconductors	330
13.8.3	The Valley–Orbit Interaction	331
14	Spin–Orbit Interaction in Solids and Double Groups	337
14.1	Introduction	337
14.2	Crystal Double Groups	341
14.3	Double Group Properties	343
14.4	Crystal Field Splitting Including Spin–Orbit Coupling	349
14.5	Basis Functions for Double Group Representations	353
14.6	Some Explicit Basis Functions	355
14.7	Basis Functions for Other Γ_8^+ States	358
14.8	Comments on Double Group Character Tables	359
14.9	Plane Wave Basis Functions for Double Group Representations	360
14.10	Group of the Wave Vector for Nonsymmorphic Double Groups	362

15 Application of Double Groups to Energy Bands with Spin . 367

15.1 Introduction 367

15.2 $E(k)$ for the Empty Lattice Including Spin–Orbit Interaction . 368

15.3 The $\mathbf{k} \cdot \mathbf{p}$ Perturbation with Spin–Orbit Interaction 369

15.4 $E(\mathbf{k})$ for a Nondegenerate Band Including Spin–Orbit Interaction 372

15.5 $E(\mathbf{k})$ for Degenerate Bands Including Spin–Orbit Interaction . 374

15.6 Effective g -Factor 378

15.7 Fourier Expansion of Energy Bands: Slater–Koster Method . . . 389

15.7.1 Contributions at $d = 0$ 396

15.7.2 Contributions at $d = 1$ 396

15.7.3 Contributions at $d = 2$ 397

15.7.4 Summing Contributions through $d = 2$ 397

15.7.5 Other Degenerate Levels 397

Part VI Other Symmetries

16 Time Reversal Symmetry 403

16.1 The Time Reversal Operator 403

16.2 Properties of the Time Reversal Operator 404

16.3 The Effect of \hat{T} on $E(\mathbf{k})$, Neglecting Spin 407

16.4 The Effect of \hat{T} on $E(\mathbf{k})$, Including the Spin–Orbit Interaction 411

16.5 Magnetic Groups 416

16.5.1 Introduction 418

16.5.2 Types of Elements 418

16.5.3 Types of Magnetic Point Groups 419

16.5.4 Properties of the 58 Magnetic Point Groups $\{A_i, M_k\}$. 419

16.5.5 Examples of Magnetic Structures 423

16.5.6 Effect of Symmetry on the Spin Hamiltonian for the 32 Ordinary Point Groups 426

17 Permutation Groups and Many-Electron States 431

17.1 Introduction 432

17.2 Classes and Irreducible Representations of Permutation Groups 434

17.3 Basis Functions of Permutation Groups 437

17.4 Pauli Principle in Atomic Spectra 440

17.4.1 Two-Electron States 440

17.4.2 Three-Electron States 443

17.4.3 Four-Electron States 448

17.4.4 Five-Electron States 451

17.4.5 General Comments on Many-Electron States 451

18	Symmetry Properties of Tensors	455
18.1	Introduction	455
18.2	Independent Components of Tensors Under Permutation Group Symmetry	458
18.3	Independent Components of Tensors: Point Symmetry Groups	462
18.4	Independent Components of Tensors Under Full Rotational Symmetry	463
18.5	Tensors in Nonlinear Optics	463
	18.5.1 Cubic Symmetry: O_h	464
	18.5.2 Tetrahedral Symmetry: T_d	466
	18.5.3 Hexagonal Symmetry: D_{6h}	466
18.6	Elastic Modulus Tensor	467
	18.6.1 Full Rotational Symmetry: 3D Isotropy	469
	18.6.2 Icosahedral Symmetry	472
	18.6.3 Cubic Symmetry	472
	18.6.4 Other Symmetry Groups	474
A	Point Group Character Tables	479
B	Two-Dimensional Space Groups	489
C	Tables for 3D Space Groups	499
	C.1 Real Space	499
	C.2 Reciprocal Space	503
D	Tables for Double Groups	521
E	Group Theory Aspects of Carbon Nanotubes	533
	E.1 Nanotube Geometry and the (n, m) Indices	534
	E.2 Lattice Vectors in Real Space	534
	E.3 Lattice Vectors in Reciprocal Space	535
	E.4 Compound Operations and Tube Helicity	536
	E.5 Character Tables for Carbon Nanotubes	538
F	Permutation Group Character Tables	543
	References	549
	Index	553