Contents

1 Operations 1
1.1 Operations and Points 1
1.2 Operations and Functions 4
1.3 Operations and Operators 8
1.4 An Aide Mémoire 10
1.5 Problems 10
References 10

2 Function Spaces and Matrices 11
2.1 Function Spaces 11
2.2 Linear Operators and Transformation Matrices 12
2.3 Unitary Matrices 14
2.4 Time Reversal as an Anti-linear Operator 16
2.5 Problems 19
References 19

3 Groups 21
3.1 The Symmetry of Ammonia 21
3.2 The Group Structure 24
3.3 Some Special Groups 27
3.4 Subgroups 29
3.5 Cosets 30
3.6 Classes 32
3.7 Overview of the Point Groups 34
Spherical Symmetry and the Platonic Solids 34
Cylindrical Symmetries 40
3.8 Rotational Groups and Chiral Molecules 44
3.9 Applications: Magnetic and Electric Fields 46
3.10 Problems 47
References 48

4 Representations 51
4.1 Symmetry-Adapted Linear Combinations of Hydrogen Orbitals in Ammonia 52
4.2 Character Theorems 56
4.3 Character Tables 62
4.4 Matrix Theorem 63
4.5 Projection Operators 64
4.6 Subduction and Induction 69
4.7 Application: The sp^3 Hybridization of Carbon 76
4.8 Application: The Vibrations of UF_6 78
4.9 Application: Hückel Theory 84
Cyclic Polyenes 85
Polyhedral Hückel Systems of Equivalent Atoms 91
Triphenylmethyl Radical and Hidden Symmetry 95
4.10 Problems 99
References 101
5 What has Quantum Chemistry Got to Do with It? 103
5.1 The Prequantum Era 103
5.2 The Schrödinger Equation 105
5.3 How to Structure a Degenerate Space 107
5.4 The Molecular Symmetry Group 108
5.5 Problems 112
References 112
6 Interactions 113
6.1 Overlap Integrals 114
6.2 The Coupling of Representations 115
6.3 Symmetry Properties of the Coupling Coefficients 117
6.4 Product Symmetrization and the Pauli Exchange-Symmetry 122
6.5 Matrix Elements and the Wigner–Eckart Theorem 126
6.6 Application: The Jahn–Teller Effect 128
6.7 Application: Pseudo-Jahn–Teller interactions 134
6.8 Application: Linear and Circular Dichroism 138
Linear Dichroism 139
Circular Dichroism 144
6.9 Induction Revisited: The Fibre Bundle 148
6.10 Application: Bonding Schemes for Polyhedra 150
Edge Bonding in Trivalent Polyhedra 155
Frontier Orbitals in Leapfrog Fullerenes 156
6.11 Problems 159
References 160
7 Spherical Symmetry and Spins 163
7.1 The Spherical-Symmetry Group 163
7.2 Application: Crystal-Field Potentials 167
7.3 Interactions of a Two-Component Spinor 170

7.4 The Coupling of Spins . . . 173
7.5 Double Groups . . . 175
7.6 Kramers Degeneracy . . . 180
Time-Reversal Selection Rules . . . 182
7.7 Application: Spin Hamiltonian for the Octahedral Quartet State . . 184
7.8 Problems . . . 189
References . . . 190

Appendix A Character Tables . . . 191
A.1 Finite Point Groups . . . 192
C_1 and the Binary Groups C_s, C_i, C_2 . . . 192
The Cyclic Groups C_n $(n = 3, 4, 5, 6, 7, 8)$ . . . 192
The Dihedral Groups D_n $(n = 2, 3, 4, 5, 6)$ . . . 194
The Conical Groups C_{nv} $(n = 2, 3, 4, 5, 6)$ . . . 195
The C_{nh} Groups $(n = 2, 3, 4, 5, 6)$ . . . 196
The Rotation–Reflection Groups S_{2n} $(n = 2, 3, 4)$ . . . 197
The Prismatic Groups D_{nh} $(n = 2, 3, 4, 5, 6, 8)$ . . . 198
The Antiprismatic Groups D_{nd} $(n = 2, 3, 4, 5, 6)$ . . . 199
The Tetrahedral and Cubic Groups . . . 201
The Icosahedral Groups . . . 202
A.2 Infinite Groups . . . 203
Cylindrical Symmetry . . . 203
Spherical Symmetry . . . 204

Appendix B Symmetry Breaking by Uniform Linear Electric and Magnetic Fields . . . 205
B.1 Spherical Groups . . . 205
B.2 Binary and Cylindrical Groups . . . 205

Appendix C Subduction and Induction . . . 207
C.1 Subduction $G \downarrow H$ . . . 207
C.2 Induction: $H \uparrow G$ . . . 211

Appendix D Canonical-Basis Relationships . . . 215

Appendix E Direct-Product Tables . . . 219

Appendix F Coupling Coefficients . . . 221

Appendix G Spinor Representations . . . 235
G.1 Character Tables . . . 235
G.2 Subduction . . . 237
G.3 Canonical-Basis Relationships . . . 237
G.4 Direct-Product Tables . . . 240
G.5 Coupling Coefficients . . . 241

Solutions to Problems . . . 245

References . . . 261

Index . . . 263