Contents

| Preface to Third Edition | | | |
|--------------------------|---|--|--|
| 1 | | Introduction The ammonia molecule 1.2.1 The atomic orbital model 1.2.2 The hybrid orbital model 1.2.3 The electron-repulsion model 1.2.4 The electron-spin-repulsion model 1.2.5 Accurate calculations | 1 1 1 2 3 4 6 7 |
| 2 | 2.1 2.2 2.3 2.4 | Symmetry of the water molecule Symmetry operations and symmetry elements Multipliers associated with symmetry operations Group multiplication tables Character tables Summary | 11 11 19 36 40 43 |
| 3 | 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.8 3.9 3.10 | The orthonormal properties of irreducible representations. The transformation properties of atomic orbitals in the water molecule. A reducible representation. Symmetry-adapted combinations. The bonding interactions in H ₂ O and their angular dependence. The molecular orbital energy level diagram for H ₂ O. Comparison with experiment. The Walsh diagram for triatomic dihydrides. Simple models for the bonding in H ₂ O. A rapprochement between simple and symmetry models. Summary | 45 45 47 51 54 59 65 67 68 70 73 |
| 4 | Vibra 4.1 4.2 4.3 | (| 75 76 80 92 |

| vi | | CONTENTS | |
|----|------------|---|------------|
| | 4.4 4.5 | Direct products and quantum mechanical integrals Spectroscopic selection rules | 96 99 |
| | 4.6 | The vibrational spectroscopy of the water molecule | 103 |
| | 4.7 | Optical activity | 107 |
| | 4.8 | Summary | 108 |
| 5 | | character table and the electronic structures of ethene | |
| | • | ylene) and diborane | 109 |
| | 5.1 | The symmetry of the ethene molecule | 109 |
| | 5.2 | The character and multiplication tables of the D_{2h} group | 112 |
| | 5.3 | Direct products of groups | 114 |
| | 5.4 5.5 | Nodal patterns of the irreducible representations of the D_{2h} group | 117 121 |
| | 5.6 | The symmetries of the budgegen 1s orbitals in ethene | 121 |
| | 5.7 | The symmetries of the hydrogen 1s orbitals in ethene The projection operator method | 128 |
| | 5.8 | Bonding in the ethene molecule | 134 |
| | 5.9 | Bonding in the diborane molecule | 136 |
| | | Comparison with other models | 141 |
| | | Summary | 144 |
| 6 | The | electronic structure of bromine pentafluoride, BrF₅ | 145 |
| | 6.1 | Symmetry operations of the C_{4y} group | 147 |
| | 6.2 | Problems in using the C_{4v} group | 150 |
| | 6.3 | Orthonormality relationships | 152 |
| | 6.4 | The derivation of the C_{4v} character table using the orthonormality theorems | 155 |
| | 6.5 | Nodal patterns of the irreducible representations of C_{4v} | 160 |
| | 6.6 | The bonding in the BrF ₅ molecule | 162 |
| | 6.7 | Summary | 171 |
| 7 | The | electronic structure of the ammonia molecule | 173 |
| | 7.1 | The symmetry of the ammonia molecule | 173 |
| | 7.2 | Nodal patterns of the irreducible representations of \mathcal{C}_{3v} | 178 |
| | 7.3 | The bonding in the ammonia molecule | 180 |
| | 7.4 | Summary | 187 |
| 8 | The | electronic structures of some octahedral molecules | 189 |
| | 8.1 | The symmetry operations of the octahedron | 190 |
| | 8.2 | Nodal patterns of the irreducible representations of the o_{h} group | 199 |
| | 8.3 | The bonding in the SF ₆ molecule | 204 |
| | 8.4 | Octahedral transition metal complexes | 218 |
| | 8.5 | Summary | 229 |
| 9 | | t groups and their relationships | 231 |
| | 9.1 | The determination of the point group of a molecule | 231 |
| | 9.2 | The relationships between point groups | 235 |

| | CONTENTS | vii |
|----|---|----------|
| | 9.3 Correlation tables | 240 |
| | 9.4 Summary | 244 |
| 10 | Tetrahedral, icosahedral and spherical symmetries | 245 |
| | 10.1 An overview | 245 |
| | 10.2 The tetrahedron | 247 |
| | 10.3 The icosahedron | 251 |
| | 10.4 Spherical symmetry | 254 |
| | 10.5 Linear molecules | 261 |
| | 10.6 Summary | 262 |
| 11 | π -Electron systems | 263 |
| | 11.1 Square cyclobutadiene and the C_4 point group | 263 |
| | 11.2 Working with complex characters ⁴ | 268 |
| | 11.3 The π orbitals of cyclobutadiene | 269 |
| | 11.4 The energies of the π orbitals of cyclobutadiene | |
| | in the Hückel approximation | 271 |
| | 11.5 Symmetry and chemical reactions | 276 |
| | 11.6 Summary | 280 |
| 12 | The group theory of electron spin | 281 |
| | 12.1 The problem of electron spin | 281 |
| | 12.2 More about the symmetry of product functions | 288 |
| | 12.3 Configurations and terms | 289 |
| | 12.4 The inclusion of electron spin | 294 |
| | 12.5 Summary | 297 |
| 13 | Space groups | 299 |
| | 13.1 The crystal systems | 299 |
| | 13.2 The Bravais lattices | 308 |
| | 13.3 The crystallographic point groups | 311 |
| | 13.4 The symmorphic space groups | 317 |
| | 13.5 The non-symmorphic space groups | 322 |
| | 13.6 Unit cells | 325 |
| | 13.7 Wigner-Seitz unit cells | 327 |
| | 13.8 Summary | 330 |
| 14 | Spectroscopic studies of crystals | |
| | 14.1 Translational invariance | 331 |
| | 14.2 The factor group and unit cell group models | 333 |
| | 14.3 Examples of use of the factor and unit cell group models | 336 |
| | 14.3.1 The $\nu(CO)$ spectra of crystalline $(C_6H_6)Cr(CO)_3$ 14.3.2 The vibrational spectrum of a $M(C=O)_3$ species crystallizing | 336 a |
| | in the C2/c (C_{2h}^{6}) space group using the unit cell model | 340 |
| | 14.4 Summary | 344 |

viii

| Appendix 1 Groups and classes: definitions and examples | 345 |
|--|-----|
| A1.1 Groups | 345 |
| A1.2 Some examples of groups | 347 |
| A1.3 The classes of a group | 349 |
| A1.4 Class algebra | 352 |
| Appendix 2 Matrix algebra and group theory | 355 |
| A2.1 Matrix algebra and symmetry operations | 355 |
| A2.2 Direct products | 363 |
| Appendix 3 Character tables of the more important point groups | 369 |
| Appendix 4 The fluorine group orbitals of π symmetry in SF_6 | 391 |
| A4.1 Ligand group orbitals of complex ions | 397 |
| Appendix 5 The Hermann-Mauguin notation | 404 |
| Appendix 6 Non-symmorphic relatives of the point group D_2 | 407 |
| A6.1 The space group $P2_1/c(C_{2h}^5)$ | 416 |
| Index | 421 |

CONTENTS