4.5.1 Extracting Term Symbols Using Russell–Saunders Coupling 100
4.5.2 Extracting Term Symbols Using jj Coupling 102
4.5.3 Correlation Between RS (LS) Coupling and jj Coupling 104
4.6 Shielding and Effective Nuclear Charge 105

Exercises 107

Bibliography 108

Chapter 5 | Periodic Properties of the Elements 109
5.1 The Modern Periodic Table 109
5.2 Radius 111
5.3 Ionization Energy 118
5.4 Electron Affinity 121
5.5 The Uniqueness Principle 122
5.6 Diagonal Properties 124
5.7 The Metal–Nonmetal Line 125
5.8 Standard Reduction Potentials 126
5.9 The Inert-Pair Effect 129
5.10 Relativistic Effects 130
5.11 Electronegativity 133

Exercises 136

Bibliography 137

Chapter 6 | An Introduction to Chemical Bonding 139
6.1 The Bonding in Molecular Hydrogen 139
6.2 Lewis Structures 140
6.3 Covalent Bond Lengths and Bond Dissociation Energies 144
6.4 Resonance 146
6.5 Polar Covalent Bonding 149

Exercises 153

Bibliography 154

Chapter 7 | Molecular Geometry 155
7.1 The VSEPR Model 155
7.2 The Ligand Close-Packing Model 170
7.3 A Comparison of the VSEPR and LCP Models 175

Exercises 176

Bibliography 177

Chapter 8 | Molecular Symmetry 179
8.1 Symmetry Elements and Symmetry Operations 179
8.1.1 Identity, E 180
8.1.2 Proper Rotation, C_n 181
8.1.3 Reflection, σ_v 182
8.1.4 Inversion, i 183
8.1.5 Improper Rotation, S_n 183
8.2 Symmetry Groups 186
8.3 Molecular Point Groups 191
8.4 Representations 195
8.5 Character Tables 202
8.6 Direct Products 209
8.7 Reducible Representations 214

Exercises 222

Bibliography 224
## CONTENTS

**Chapter 9 | Vibrational Spectroscopy**  
9.1 Overview of Vibrational Spectroscopy 227  
9.2 Selection Rules for IR and Raman-Active Vibrational Modes 231  
9.3 Determining the Symmetries of the Normal Modes of Vibration 235  
9.4 Generating Symmetry Coordinates Using the Projection Operator Method 243  
9.5 Resonance Raman Spectroscopy 252  
Exercises 256  
Bibliography 258

**Chapter 10 | Covalent Bonding**  
10.1 Valence Bond Theory 259  
10.2 Molecular Orbital Theory: Diatomics 278  
10.3 Molecular Orbital Theory: Polyatomics 292  
10.4 Molecular Orbital Theory: $\pi$ Orbitals 305  
10.5 Molecular Orbital Theory: More Complex Examples 317  
10.6 Borane and Carborane Cluster Compounds 325  
Exercises 334  
Bibliography 336

**Chapter 11 | Metallic Bonding**  
11.1 Crystalline Lattices 339  
11.2 X-Ray Diffraction 345  
11.3 Closest-Packed Structures 350  
11.4 The Free Electron Model of Metallic Bonding 355  
11.5 Band Theory of Solids 360  
11.6 Conductivity in Solids 374  
11.7 Connections Between Solids and Discrete Molecules 383  
Exercises 384  
Bibliography 388

**Chapter 12 | Ionic Bonding**  
12.1 Common Types of Ionic Solids 391  
12.2 Lattice Enthalpies and the Born–Haber Cycle 398  
12.3 Ionic Radii and Pauling’s Rules 404  
12.4 The Silicates 417  
12.5 Zeolites 422  
12.6 Defects in Crystals 423  
Exercises 426  
Bibliography 428

**Chapter 13 | Structure and Bonding**  
13.1 A Reexamination of Crystalline Solids 431  
13.2 Intermediate Types of Bonding in Solids 434  
13.3 Quantum Theory of Atoms in Molecules (QTAIM) 443  
Exercises 449  
Bibliography 452

**Chapter 14 | Structure and Reactivity**  
14.1 An Overview of Chemical Reactivity 453  
14.2 Acid–Base Reactions 455  
14.3 Frontier Molecular Orbital Theory 467
<table>
<thead>
<tr>
<th>Chapter 14</th>
<th>Oxidation–Reduction Reactions 473</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.5</td>
<td>A Generalized View of Molecular Reactivity 475</td>
</tr>
<tr>
<td>Exercises</td>
<td>480</td>
</tr>
<tr>
<td>Bibliography</td>
<td>481</td>
</tr>
<tr>
<td>Chapter 15</td>
<td>An Introduction to Coordination Compounds 483</td>
</tr>
<tr>
<td>15.1</td>
<td>A Historical Overview of Coordination Chemistry 483</td>
</tr>
<tr>
<td>15.2</td>
<td>Types of Ligands and Nomenclature 487</td>
</tr>
<tr>
<td>15.3</td>
<td>Stability Constants 490</td>
</tr>
<tr>
<td>15.4</td>
<td>Coordination Numbers and Geometries 492</td>
</tr>
<tr>
<td>15.5</td>
<td>Isomerism 498</td>
</tr>
<tr>
<td>15.6</td>
<td>The Magnetic Properties of Coordination Compounds 501</td>
</tr>
<tr>
<td>Exercises</td>
<td>506</td>
</tr>
<tr>
<td>Bibliography</td>
<td>508</td>
</tr>
<tr>
<td>Chapter 16</td>
<td>Structure, Bonding, and Spectroscopy of Coordination Compounds 509</td>
</tr>
<tr>
<td>16.1</td>
<td>Valence Bond Model 509</td>
</tr>
<tr>
<td>16.2</td>
<td>Crystal Field Theory 512</td>
</tr>
<tr>
<td>16.3</td>
<td>Ligand Field Theory 525</td>
</tr>
<tr>
<td>16.4</td>
<td>The Angular Overlap Method 534</td>
</tr>
<tr>
<td>16.5</td>
<td>Molecular Term Symbols 541</td>
</tr>
<tr>
<td>16.5.1</td>
<td>Scenario 1—All the Orbitals are Completely Occupied 546</td>
</tr>
<tr>
<td>16.5.2</td>
<td>Scenario 2—There is a Single Unpaired Electron in One of the Orbitals 546</td>
</tr>
<tr>
<td>16.5.3</td>
<td>Scenario 3—There are Two Unpaired Electrons in Two Different Orbitals 546</td>
</tr>
<tr>
<td>16.5.4</td>
<td>Scenario 4—A Degenerate Orbital is Lacking a Single Electron 547</td>
</tr>
<tr>
<td>16.5.5</td>
<td>Scenario 5—There are Two Electrons in a Degenerate Orbital 547</td>
</tr>
<tr>
<td>16.5.6</td>
<td>Scenario 6—There are Three Electrons in a Triply Degenerate Orbital 547</td>
</tr>
<tr>
<td>16.6</td>
<td>Tanabe–Sugano Diagrams 549</td>
</tr>
<tr>
<td>16.7</td>
<td>Electronic Spectroscopy of Coordination Compounds 554</td>
</tr>
<tr>
<td>16.8</td>
<td>The Jahn–Teller Effect 564</td>
</tr>
<tr>
<td>Exercises</td>
<td>566</td>
</tr>
<tr>
<td>Bibliography</td>
<td>570</td>
</tr>
<tr>
<td>Chapter 17</td>
<td>Reactions of Coordination Compounds 573</td>
</tr>
<tr>
<td>17.1</td>
<td>Kinetics Overview 573</td>
</tr>
<tr>
<td>17.2</td>
<td>Octahedral Substitution Reactions 577</td>
</tr>
<tr>
<td>17.2.1</td>
<td>Associative (A) Mechanism 578</td>
</tr>
<tr>
<td>17.2.2</td>
<td>Interchange (I) Mechanism 579</td>
</tr>
<tr>
<td>17.2.3</td>
<td>Dissociative (D) Mechanism 580</td>
</tr>
<tr>
<td>17.3</td>
<td>Square Planar Substitution Reactions 585</td>
</tr>
<tr>
<td>17.4</td>
<td>Electron Transfer Reactions 593</td>
</tr>
<tr>
<td>17.5</td>
<td>Inorganic Photochemistry 606</td>
</tr>
<tr>
<td>17.5.1</td>
<td>Photochemistry of Chromium(III) Ammine Compounds 607</td>
</tr>
<tr>
<td>17.5.2</td>
<td>Light-Induced Excited State Spin Trapping in Iron(II) Compounds 611</td>
</tr>
<tr>
<td>17.5.3</td>
<td>MLCT Photochemistry in Pentaammineruthenium(II) Compounds 615</td>
</tr>
<tr>
<td>17.5.4</td>
<td>Photochemistry and Photophysics of Ruthenium(II) Polypyridyl Compounds 617</td>
</tr>
<tr>
<td>Exercises</td>
<td>622</td>
</tr>
<tr>
<td>Bibliography</td>
<td>624</td>
</tr>
<tr>
<td>Chapter 18</td>
<td>Structure and Bonding in Organometallic Compounds 627</td>
</tr>
<tr>
<td>18.1</td>
<td>Introduction to Organometallic Chemistry 627</td>
</tr>
<tr>
<td>18.2</td>
<td>Electron Counting and the 18-Electron Rule 628</td>
</tr>
</tbody>
</table>
### Chapter 18: Ligands and Complexes

18.3 Carbonyl Ligands 631  
18.4 Nitrosyl Ligands 635  
18.5 Hydride and Dihydrogen Ligands 638  
18.6 Phosphine Ligands 640  
18.7 Ethylene and Related Ligands 641  
18.8 Cyclopentadiene and Related Ligands 645  
18.9 Carbenes, Carbynes, and Carbidos 648  

#### Exercises 651  
Bibliography 654

### Chapter 19: Reactions of Organometallic Compounds

19.1 Some General Principles 655  
19.2 Organometallic Reactions Involving Changes at the Metal 656  
19.2.1 Ligand Substitution Reactions 656  
19.2.2 Oxidative Addition and Reductive Elimination 658  
19.3 Organometallic Reactions Involving Changes at the Ligand 664  
19.3.1 Insertion and Elimination Reactions 664  
19.3.2 Nucleophilic Attack on the Ligands 667  
19.3.3 Electrophilic Attack on the Ligands 669  
19.4 Metathesis Reactions 670  
19.4.1 Π-Bond Metathesis 670  
19.4.2 Ziegler–Natta Polymerization of Alkenes 671  
19.4.3 Σ-Bond Metathesis 671  
19.5 Commercial Catalytic Processes 674  
19.5.1 Catalytic Hydrogenation 674  
19.5.2 Hydroformylation 674  
19.5.3 Wacker–Smidt Process 676  
19.5.4 Monsanto Acetic Acid Process 677  
19.6 Organometallic Photochemistry 678  
19.6.1 Photosubstitution of CO 678  
19.6.2 Photoinduced Cleavage of Metal–Metal Bonds 680  
19.6.3 Photochemistry of Metallocenes 682  
19.7 The Isolobal Analogy and Metal–Metal Bonding in Organometallic Clusters 683  

#### Exercises 689  
Bibliography 691

### Appendix: A Derivation of the Classical Wave Equation 693  
Bibliography 694

### Appendix: B Character Tables 695  
Bibliography 708

### Appendix: C Direct Product Tables 709  
Bibliography 713

### Appendix: D Correlation Tables 715  
Bibliography 721

### Appendix: E The 230 Space Groups 723  
Bibliography 728

### Index 729