Contents

1. Introduction and Basic Principles 1
1.1 Historical Development 1
1.2 The Electron Mean Free Path 9
1.3 Photoelectron Spectroscopy and Inverse Photoelectron Spectroscopy 14
1.4 Experimental Aspects 20
1.5 Very High Resolution 27
1.6 The Theory of Photoemission 39
1.6.1 Core-Level Photoemission 42
1.6.2 Valence-State Photoemission 45
1.6.3 Three-Step and One-Step Considerations 50
1.7 Deviations from the Simple Theory of Photoemission 51
References 57

2. Core Levels and Final States 61
2.1 Core-Level Binding Energies in Atoms and Molecules 63
2.1.1 The Equivalent-Core Approximation 63
2.1.2 Chemical Shifts 65
2.2 Core-Level Binding Energies in Solids 69
2.2.1 The Born–Haber Cycle in Insulators 69
2.2.2 Theory of Binding Energies 71
2.2.3 Determination of Binding Energies and Chemical Shifts from Thermodynamic Data 76
2.3 Core Polarization 83
2.4 Final-State Multiplets in Rare-Earth Valence Bands 92
2.5 Vibrational Side Bands 99
2.6 Core Levels of Adsorbed Molecules 100
2.7 Quantitative Chemical Analysis from Core-Level Intensities .. 103
References 104

3. Charge-Excitation Final States: Satellites 109
3.1 Copper Dihalides; 3d Transition Metal Compounds 110
3.1.1 Characterization of a Satellite 110
3.1.2 Analysis of Charge-Transfer Satellites 115

3.1.3 Non-local Screening . . . 126
3.2 The 6-eV Satellite in Nickel . . . 130
3.2.1 Resonance Photoemission . . . 133
3.2.2 Satellites in Other Metals . . . 143
3.3 The Gunnarsson–Schönhammer Theory . . . 148
3.4 Photoemission Signals and Narrow Bands in Metals . . . 152
References . . . 166

4. Continuous Satellites and Plasmon Satellites: XPS Photoemission in Nearly Free Electron Systems . . . 173
4.1 Theory . . . 181
4.1.1 General . . . 181
4.1.2 Core-Line Shape . . . 182
4.1.3 Intrinsic Plasmons . . . 183
4.1.4 Extrinsic Electron Scattering: Plasmons and Background . . . 185
4.1.5 The Total Photoelectron Spectrum . . . 187
4.2 Experimental Results . . . 187
4.2.1 The Core Line Without Plasmons . . . 187
4.2.2 Core-Level Spectra Including Plasmons . . . 190
4.2.3 Valence-Band Spectra of the Simple Metals . . . 195
4.2.4 Simple Metals: A General Comment . . . 200
4.3 The Background Correction . . . 201
References . . . 206

5. Valence Orbitals in Simple Molecules and Insulating Solids . . . 211
5.1 UPS Spectra of Monatomic Gases . . . 212
5.2 Photoelectron Spectra of Diatomic Molecules . . . 214
5.3 Binding Energy of the H_2 Molecule . . . 221
5.4 Hydrides Isoelectronic with Noble Gases . . . 222
Neon (Ne) . . . 223
Hydrogen Fluoride (HF) . . . 223
Water (H_2O) . . . 223
Ammonia (NH_3) . . . 224
Methane (CH_4) . . . 224
5.5 Spectra of the Alkali Halides . . . 225
5.6 Transition Metal Dihalides . . . 232
5.7 Hydrocarbons . . . 233
5.7.1 Guidelines for the Interpretation of Spectra from Free Molecules . . . 238
5.7.2 Linear Polymers . . . 238
5.8 Insulating Solids with Valence d Electrons . . . 244
5.8.1 The NiO Problem . . . 254
5.8.2 Mott Insulation . . . 268

5.8.3 The Metal–Insulator Transition; the Ratio of the Correlation Energy and the Bandwidth; Doping 274
5.8.4 Band Structures of Transition Metal Compounds 283
5.9 High-Temperature Superconductors 286
5.9.1 Valence-Band Electronic Structure; Polycrystalline Samples 287
5.9.2 Dispersion Relations in High Temperature Superconductors; Single Crystals 303
5.9.3 The Superconducting Gap 310
5.9.4 Symmetry of the Order Parameter in the High-Temperature Superconductors 312
5.9.5 Core-Level Shifts 315
5.10 The Fermi Liquid and the Luttinger Liquid 317
5.11 Adsorbed Molecules 324
5.11.1 Outline 324
5.11.2 CO on Metal Surfaces 324
References 337

6. Photoemission of Valence Electrons from Metallic Solids in the One-Electron Approximation 347
6.1 Theory of Photoemission: A Summary of the Three-Step Model 349
6.2 Discussion of the Photocurrent 357
6.2.1 Kinematics of Internal Photoemission in a Polycrystalline Sample 357
6.2.2 Primary and Secondary Cones in the Photoemission from a Real Solid 365
6.2.3 Angle-Integrated and Angle-Resolved Data Collection . 366
6.3 Photoemission from the Semi-infinite Crystal: The Inverse LEED Formalism 374
6.3.1 Band Structure Regime 381
6.3.2 XPS Regime 381
6.3.3 Surface Emission 383
6.3.4 One-Step Calculations 385
6.4 Thermal Effects 387
6.5 Dipole Selection Rules for Direct Optical Transitions 401
References 407

7. Band Structure and Angular-Resolved Photoelectron Spectra 411
7.1 Free-Electron Final-State Model 413
7.2 Methods Employing Calculated Band Structures 415
7.3 Methods for the Absolute Determination of the Crystal Momentum 418

7.3.1 Triangulation or Energy Coincidence Method 421
7.3.2 Bragg Plane Method: Variation of External Emission Angle at Fixed Photon Frequency (Disappearance/Appearance Angle Method 425
7.3.3 Bragg Plane Method: Variation of Photon Energy at Fixed Emission Angle (Symmetry Method) 433
7.3.4 The Surface Emission Method and Electron Damping 437
7.3.5 The Very-Low-Energy Electron Diffraction Method .. 439
7.3.6 The Fermi Surface Method 443
7.3.7 Intensities and Their Use in Band-Structure Determinations 445
7.3.8 Summary 450
7.4 Experimental Band Structures 453
7.4.1 One- and Two-Dimensional Systems 453
7.4.2 Three-Dimensional Solids: Metals and Semiconductors 472
7.4.3 UPS Band Structures and XPS Density of States 481
7.5 A Comment 493
References 495

8. Surface States, Surface Effects 501
8.1 Theoretical Considerations 503
8.2 Experimental Results on Surface States 513
8.3 Quantum-Well States 529
8.4 Surface Core-Level Shifts 535
References 546

9. Inverse Photoelectron Spectroscopy 551
9.1 Surface States 555
9.2 Bulk Band Structures 560
9.3 Adsorbed Molecules 563
References 571

10. Spin-Polarized Photoelectron Spectroscopy 575
10.1 General Description 575
10.2 Examples of Spin-Polarized Photoelectron Spectroscopy 575
10.3 Magnetic Dichroism 586
References 593

11. Photoelectron Diffraction 597
11.1 Examples 601
11.2 Substrate Photoelectron Diffraction 607
11.3 Adsorbate Photoelectron Diffraction 619
11.4 Fermi Surface Scans 626
References 633

Appendix 635
A.1 Table of Binding Energies 636
A.2 Surface and Bulk Brillouin Zones of the Three Low-Index Faces of a Face-Centered Cubic (fcc) Crystal Face 642
A.3 Compilation of Work Functions 650
References 651

Index 653