

# Topics in Applied Physics Volume 27



# Topics in Applied Physics

Founded by Helmut K. V. Lotsch

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Editor: H.-J. Queisser
  - 23 **Optical Data Processing**. Applications  
Editor: D. Casasent
  - 24 **Acoustic Surface Waves**  
Editor: A. A. Oliner
  - 25 **Laser Beam Propagation in the Atmosphere**  
Editor: J. W. Strohbehn
  - 26 **Photoemission in Solids I**  
General Principles  
Editors: M. Cardona and L. Ley
  - 27 **Photoemission in Solids II**. Case Studies  
Editors: L. Ley and M. Cardona
  - 28 **Hydrogen in Metals I**. Basic Properties  
Editors: G. Alefeld and J. Vökl
  - 29 **Hydrogen in Metals II**  
Application-Oriented Properties  
Editors: G. Alefeld and J. Vökl
  - 30 **Excimer Lasers** Editor: Ch. K. Rhodes
  - 31 **Solar Energy Conversion**. Solid-State  
Physics Aspects. Editor: B. O. Seraphin
  - 32 **Image Reconstruction from Projections**  
Implementation and Applications  
Editor: G. T. Herman
  - 33 **Electrets** Editor: G. M. Sessler
  - 34 **Nonlinear Methods of Spectral Analysis**  
Editor: S. Haykin
  - 35 **Uranium Enrichment**  
Editor: S. Villani
  - 36 **Amorphous Semiconductors**  
Editor: M. H. Brodsky
  - 37 **Thermally Stimulated Relaxation in Solids**  
Editor: P. Bräunlich
  - 38 **Charge-Coupled Devices**  
Editor: D. F. Barbe
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# Photoemission in Solids II

Case Studies

Edited by L. Ley and M. Cardona

With Contributions by

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With 214 Figures

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## Preface

This book constitutes the continuation of Volume 26 of the series Topics in Applied Physics (*Photoemission in Solids I*). In the first volume we discussed the general principles underlying the phenomena of photoemission and photoelectron spectroscopy, including a brief review of the experimental techniques. Such topics as the general formal theory of photoemission, the three-step model, the theory of photoionization cross sections, one-electron excitations and phenomena beyond the one-electron approximation were treated by some of the leading specialists in the field. The emphasis of the present volume lies on the discussion of photoelectron spectra of specific families of materials and the information that can be obtained from such spectra about their electronic structure. The largest contribution, Chap. 2, refers to semiconductors. It contains extensive background discussion on the band structures of the most common types of semiconductors. The vast amount of knowledge accumulated for these materials, due in part to their practical applications, makes them ideal to exemplify the methodology and the scope of photoelectron spectroscopy. Successive chapters cover transition metals and their compounds, rare earths, organic molecular crystals of the type which show characteristic solid-state effects and, last but not least, simple metals. In addition, Chap. 6 discusses photoemission experiments for which the use of synchrotron radiation is of the essence. For convenience of the users we have reproduced in this volume the periodic table with work functions and the table of binding energies which already appeared in TAP 26.

The range of information obtained with photoelectron spectroscopy is so wide that this book should be of interest to both students and practitioners of solid-state physics interested in the electronic structure of solids. While it would be impossible to compile an exhaustive materials bibliography within the space limitations of the volume (such compilation would anyway make the volume rather dull), we believe enough references are included to help the research worker muddle his way through the literature of specific types of solids.

We have found the task of editing these volumes an extremely rewarding experience. The exchange of ideas and information with the various authors has been rather intensive. We thank them all once more for their cooperation and patience. We would also like to thank again the colleagues of the institutions to whom we owe our expertise in the field, the Max-Planck-Institut für Festkörperforschung, the Deutsches Elektronen-Synchrotron (DESY), and the University of California, Berkeley. We should also thank the staffs of various

companies involved in the manufacturing of photoelectron spectrometers, especially those whose equipment we use. Without them the enormous development which has taken place in the field within the past ten years would not have been possible.

Stuttgart, December 1978

*Lothar Ley*  
*Manuel Cardona*

# Contents

<b>1. Introduction.</b> By L. Ley and M. Cardona . . . . .	1
1.1 Survey of Previous Volume . . . . .	4
1.2 Contents of Present Volume . . . . .	8
References . . . . .	9
<b>2. Photoemission in Semiconductors</b>	
By L. Ley, M. Cardona, and R.A. Pollak (With 97 Figures) . . . . .	11
2.1 Background . . . . .	11
2.1.1 Historical Survey . . . . .	13
2.2 Band Structure of Semiconductors . . . . .	15
2.2.1 Tetrahedral Semiconductors . . . . .	15
2.2.2 Semiconductors with an Average of Five Valence Electrons per Atom . . . . .	28
2.2.3 Selenium, Tellurium, and the $V_2VI_3$ Compounds . . . . .	30
2.2.4 Transition Metal Dichalcogenides . . . . .	32
2.3 Methods Complementary to Photoelectron Spectroscopy . . . . .	40
2.3.1 Optical Absorption, Reflection, and Modulation Spectros- copy . . . . .	40
2.3.2 Characteristic Electron Energy Losses . . . . .	43
2.3.3 X-Ray Emission Spectroscopy . . . . .	45
2.4 Volume Photoemission: Angular Integrated EDC's from Valence Bands . . . . .	47
2.4.1 Band-Structure Regime: Germanium . . . . .	51
2.4.2 XPS Regime: Tetrahedral Semiconductors . . . . .	55
2.4.3 XPS Regime: IV-VI Compounds . . . . .	62
2.4.4 Partial Density of Valence States: Copper and Silver Halides; Chalcopyrites; Transition Metal, Rare Earth, and Actinide Compounds . . . . .	67
2.4.5 Layer Structures: Transition Metal Dichalcogenides . . . . .	72
2.4.6 Layer Structures: $SnS_2$ , $SnSe_2$ , $PbI_2$ , $GaS$ , $GaSe$ . . . . .	75
2.5 Photoemission and Density of Conduction States . . . . .	78
2.5.1 Secondary Electron Tails . . . . .	79
2.5.2 Partial Yield Spectroscopy . . . . .	79
2.6 Angular Resolved Photoemission from the Lead Salts . . . . .	80

2.7	Amorphous Semiconductors . . . . .	85
2.7.1	Tetrahedrally Coordinated Amorphous Semiconductors . . . . .	87
a)	Amorphous Si and Ge . . . . .	87
b)	Amorphous III–V Compounds . . . . .	100
2.7.2	Amorphous Semiconductors with an Average of Five Valence Electrons per Atom . . . . .	104
2.7.3	Amorphous Group VI Semiconductors . . . . .	111
2.7.4	Gap States in Amorphous Semiconductors . . . . .	114
2.8	Ionicity . . . . .	118
2.8.1	An Ionicity Scale Based on Valence Band Spectra . . . . .	121
2.8.2	Binding Energy Shift and Charge Transfer . . . . .	126
2.9	Photoemission Spectroscopy of Semiconductor Surfaces . . . . .	130
2.9.1	Semiconductor Surface States . . . . .	131
2.9.2	Silicon Surface States . . . . .	133
a)	Photoemission from Si(111) $2 \times 1$ and $7 \times 7$ Surfaces . . . . .	135
b)	Electronic Structure Theory of Si(111) Surfaces . . . . .	141
2.9.3	Surface States of Group III–V Semiconductors . . . . .	148
2.9.4	Surface Chemistry of Semiconductors — Si(111): H and Si(111): SiH <sub>3</sub> . . . . .	151
2.9.5	Interface States: Metal-Semiconductor Electrical Barriers . . . . .	154
	References . . . . .	158

### 3. Unfilled Inner Shells: Transition Metals and Compounds

	By S. Hüfner (With 25 Figures) . . . . .	173
3.1	Overview . . . . .	173
3.2	Transition Metal Compounds . . . . .	176
3.2.1	The Hubbard Model . . . . .	176
3.2.2	Final State Effects in Photoemission Spectra . . . . .	177
a)	Satellites . . . . .	177
b)	Multiplet and Crystal-Field Splitting . . . . .	179
3.2.3	Transition Metal Oxides . . . . .	183
a)	MnO, CoO, NiO: Mott Insulators . . . . .	183
b)	VO <sub>2</sub> : A Nonmetal-Metal Transition . . . . .	188
c)	ReO <sub>3</sub> : A Typical Metal . . . . .	189
3.2.4	Miscellaneous Compounds . . . . .	191
3.2.5	The Correlation Energy U . . . . .	191
3.3	<i>d</i> -Band Metals: Introduction . . . . .	192
3.3.1	The Noble Metals: Cu, Ag, Au . . . . .	194
3.3.2	The Ferromagnets: Fe, Co, Ni . . . . .	200
3.3.3	Nonmagnetic <i>d</i> -Band Metals . . . . .	205
3.4	Alloys . . . . .	206
3.4.1	Dilute Alloys: The Friedel-Anderson Model . . . . .	206
3.4.2	Concentrated Alloys: The Coherent Potential Approximation . . . . .	210
3.5	Intermetallic Compounds . . . . .	212
3.6	Summary, Outlook . . . . .	212
	References . . . . .	213



<b>4. Unfilled Inner Shells: Rare Earths and Their Compounds</b>	
By M. Campagna, G.K. Wertheim, and Y. Baer (With 35 Figures)	217
4.1 Background	217
4.1.1 Where Are the $4f$ Levels Located?	217
4.1.2 Multiplet Intensities Versus Total Photoelectric Cross Sections at 1.5 keV	218
4.1.3 Renormalized Atom Scheme and Thermodynamics	221
4.1.4 Multiplet and Satellite Structure in Photoemission from Core Levels Other than $4f$	226
4.2 Techniques	227
4.2.1 The Need of High Resolution in Rare-Earth Studies	227
4.2.2 Sample Preparation	228
a) Pure Metals	228
b) Chalcogenides, Borides, and Alloys	229
4.3 Results	229
4.3.1 Metals	229
a) Identification of the Outermost Levels	229
b) The Light Rare Earths	230
c) The Heavy Rare Earths	233
d) Cerium	235
e) The $4f$ Promotion Energy	237
4.3.2 Compounds and Alloys: Stable $4f^n$ Configurations	237
a) Rare-Earth Halides	237
b) Chalcogenides and Pnictides	238
c) Phonon Broadening in EuO	243
d) Interatomic Auger Transitions in Rare-Earth Borides	245
e) Rare-Earth Intermetallics	249
f) $4s$ and $5s$ Multiplet Splittings	250
g) Spectra of $3d$ and $4d$ Electrons of Rare-Earth Solids	251
h) $4f$ and $4d$ Binding Energy: Atom Versus Solid	253
4.3.3 Intermediate Valence (IV) Compounds	254
a) The Intra-Atomic Coulomb Correlation Energy $U_{\text{eff}}$	257
4.4 Conclusions and Outlook	257
References	258
<b>5. Photoemission from Organic Molecular Crystals</b>	
By W. D. Grobman and E. E. Koch (With 14 Figures)	261
5.1 Some Experimental Aspects of Photoemission from Organic Molecular Crystals	262
5.1.1 Charging Effects	262
5.1.2 Secondary Electron Background	264
5.1.3 Electron Attenuation Length (Escape Depth) $\lambda_c(E)$	264
5.1.4 Vacuum Requirements	265
5.1.5 Effects of the Transmission Function of the Electron Energy Analyzer	265
5.2 Band Formation in Linear Alkanes	266

5.3	Aromatic Hydrocarbons . . . . .	267
5.3.1	Acene . . . . .	268
5.3.2	Organometallic Phenyl Compounds . . . . .	270
5.3.3	Anthracene . . . . .	272
5.4	Photoemission Induced by Exciton Annihilation . . . . .	275
5.5	Photoemission from Biological Materials . . . . .	278
5.5.1	Phthalocyanines . . . . .	278
5.5.2	Nucleic Acid Bases . . . . .	280
5.6	Valence Orbital Spectroscopy of Molecular Organic Conductors . . . . .	280
5.6.1	Valence Bands of TTF-TCNQ and Related Compounds . . . . .	280
5.6.2	Valence Bands of $(\text{SN})_x$ . . . . .	285
5.6.3	The Absence of a Fermi Edge in Photoemission Spectra of Organic "Metals" . . . . .	287
5.7	Core Orbital Spectroscopy of Organic Molecular Crystals . . . . .	288
5.7.1	Solid-State Effects on Core Levels in Charge Transfer Salts . . . . .	288
5.7.2	Core Level Spectroscopy and Charge Transfer in TTF-TCNQ . . . . .	292
5.7.3	Conclusions . . . . .	293
	References . . . . .	294
<b>6.</b>	<b>Synchrotron Radiation: Overview.</b> By C. Kunz (With 33 Figures) . . . . .	<b>299</b>
6.1	Overview . . . . .	300
6.2	Properties of Synchrotron Radiation . . . . .	301
6.2.1	Basic Equations . . . . .	301
6.2.2	Comparison with Other Sources . . . . .	305
6.2.3	Evolution of Synchrotron Sources . . . . .	306
6.3	Arrangement of Experiments . . . . .	310
6.3.1	Layout of Laboratories . . . . .	310
6.3.2	Monochromators . . . . .	311
6.4	Spectroscopic Techniques . . . . .	313
6.4.1	Spectroscopy of Directly Excited Electrons . . . . .	313
6.4.2	Energy Distribution Curves (EDC) . . . . .	314
6.4.3	Constant Final-State Spectroscopy (CFS) . . . . .	316
6.4.4	Constant Initial-State Spectroscopy (CIS) . . . . .	317
6.4.5	Angular Resolved Photoemission (ARP, ARPES) . . . . .	319
6.4.6	Secondary Processes . . . . .	319
6.4.7	Photoelectron Yield Spectroscopy (PEYS) . . . . .	322
6.4.8	Yield Spectroscopy at Oblique Incidence . . . . .	323
6.5	Applications of Yield Spectroscopy . . . . .	326
6.5.1	Anisotropy in the Absorption Coefficient of Se . . . . .	326
6.5.2	Investigation of Alloys . . . . .	328
6.5.3	Investigation of Liquid Metals . . . . .	329
6.6	Experiments Investigating Occupied and Empty States . . . . .	330
6.6.1	Valence Bands in Rare-Gas Solids . . . . .	330
6.6.2	Conduction Band State from Angular Dependent Photoemission . . . . .	333

6.7 Experiments on Relaxation Processes and Excitons . . . . .	335
6.7.1 Phonon Broadening of Core Lines . . . . .	335
6.7.2 Exciton Effects with Core Excitations . . . . .	337
6.7.3 Energy Transfer Processes . . . . .	339
6.8 Surface States and Adsorbates . . . . .	341
6.8.1 Surface Core Excitons on NaCl . . . . .	341
6.8.2 Adsorbates and Oxidation . . . . .	343
References . . . . .	344
<b>7. Simple Metals</b>	
By P.Steiner, H.Höchst, and S.Hüfner (With 10 Figures) . . . . .	349
7.1 Historical Background . . . . .	349
7.2 Theory of the Photoelectron Spectrum . . . . .	351
7.3 Core Level Spectra . . . . .	357
7.4 Valence Band Spectra . . . . .	364
7.5 Summary . . . . .	369
References . . . . .	370
<b>Appendix: Table of Core-Level Binding Energies</b> . . . . .	373
<b>Additional References with Titles</b> . . . . .	385
<b>Subject Index</b> . . . . .	389

# Contents of **Photoemission in Solids I**

General Principles (Topics in Applied Physics, Vol. 26)

- 1. Introduction.** By M. Cardona and L. Ley (With 26 Figures)
  - 1.1 Historical Remarks
    - 1.1.1 The Photoelectric Effect in the Visible and Near uv: The Early Days
    - 1.1.2 Photoemissive Materials: Photocathodes
    - 1.1.3 Photoemission and the Electronic Structure of Solids
    - 1.1.4 X-Ray Photoelectron Spectroscopy (ESCA, XPS)
  - 1.2 The Work Function
    - 1.2.1 Methods to Determine the Work Function
    - 1.2.2 Thermionic Emission
    - 1.2.3 Contact Potential: The Kelvin Method  
The Break Point of the Retarding Potential Curve  
The Electron Beam Method
    - 1.2.4 Photoyield Near Threshold
    - 1.2.5 Quantum Yield as a Function of Temperature
    - 1.2.6 Total Photoelectric Yield
    - 1.2.7 Threshold of Energy Distribution Curves (EDC)
    - 1.2.8 Field Emission
    - 1.2.9 Calorimetric Method
    - 1.2.10 Effusion Method
  - 1.3 Theory of the Work Function
    - 1.3.1 Simple Metals
    - 1.3.2 Simple Metals: Surface Dipole Contribution
    - 1.3.3 Volume and Temperature Dependence of the Work Function
    - 1.3.4 Effect of Adsorbed Alkali Metal Layers
    - 1.3.5 Transition Metals
    - 1.3.6 Semiconductors
    - 1.3.7 Numerological and Phenomenological Theories
  - 1.4 Techniques of Photoemission
    - 1.4.1 The Photon Source
    - 1.4.2 Energy Analyzers
    - 1.4.3 Sample Preparation  
Cleaning Procedures
  - 1.5 Core Levels
    - 1.5.1 Elemental Analysis

- 1.5.2 Chemical Shifts
    - Theoretical Models for the Calculation of Binding Energy Shifts
    - Core Level Shifts of Rare Gas Atoms Implanted in Noble Metals
    - Binding Energies in Ionic Solids
    - Chemical Shifts in Alloys
  - 1.5.3 The Width of Core Levels
  - 1.5.4 The Core Level Cross Sections
  - 1.6 The Interpretation of Valence Band Spectra
    - 1.6.1 The Three-Step Model of Photoemission
    - 1.6.2 Beyond the Isotropic Three-Step Model
- References

## **2. Theory of Photoemission: Independent Particle Model**

By W.L.Schaich (With 2 Figures)

- 2.1 Formal Approaches
    - 2.1.1 Quadratic Response
    - 2.1.2 Many-Body Features
  - 2.2 Independent Particle Reduction
    - 2.2.1 Golden Rule Form
    - 2.2.2 Comparison With Scattering Theory
    - 2.2.3 Theoretical Ingredients
  - 2.3 Model Calculations
    - 2.3.1 Simplification of Transverse Periodicity
    - 2.3.2 Volume Effect Limit
    - 2.3.3 Surface Effects
  - 2.4 Summary
- References

## **3. The Calculation of Photoionization Cross Sections: An Atomic View**

By S.T.Manson (With 16 Figures)

- 3.1 Theory of Atomic Photoabsorption
  - 3.1.1 General Theory
  - 3.1.2 Reduction of the Matrix Element to the Dipole Approximation
  - 3.1.3 Alternate Forms of the Dipole Matrix Element
  - 3.1.4 Relationship to Density of States
- 3.2 Central Field Calculations
- 3.3 Accurate Calculations of Photoionization Cross Sections
  - 3.3.1 Hartree-Fock Calculations

- 3.3.2 Beyond the Hartree-Fock Calculation: The Effects of Correlation
- 3.4 Concluding Remarks
- References

#### **4. Many-Electron and Final-State Effects: Beyond the One-Electron Picture.** By D. A. Shirley (With 10 Figures)

- 4.1 Multiplet Splitting
  - 4.1.1 Theory
  - 4.1.2 Transition Metals
  - 4.1.3 Rare Earths
- 4.2 Relaxation
  - 4.2.1 The Energy Sum Rule
  - 4.2.2 Relaxation Energies
    - Atomic Relaxation
    - Extra-Atomic Relaxation
- 4.3 Electron Correlation Effects
  - 4.3.1 The Configuration Interaction Formalism
    - Final-State Configuration Interaction (FSCI)
    - Continuum-State Configuration Interaction (CSCI)
    - Initial-State Configuration Interaction (ISCI)
  - 4.3.2 Case Studies
    - Final-State Configuration Interactions: The  $4p$  Shell of Xe-Like Ions
    - Continuum-State Configuration Interaction: The  $5p^6 6s^2$  Shell
    - Initial-State Configuration: Two Closed-Shell Cases
- 4.4 Inelastic Process
  - 4.4.1 Intrinsic and Extrinsic Structure
  - 4.4.2 Surface Sensitivity
- References

#### **5. Fermi Surface Excitations in X-Ray Photoemission Line Shapes from Metals.** By G. K. Wertheim and P. H. Citrin (With 22 Figures)

- 5.1 Overview
- 5.2 Historical Background
  - 5.2.1 The X-Ray Edge Problem
  - 5.2.2 X-Ray Emission and Photoemission Spectra
- 5.3 The X-Ray Photoemission Line Shape
  - 5.3.1 Behavior Near the Singularity
  - 5.3.2 Extrinsic Effects in XPS
  - 5.3.3 Data Analysis

- 5.4 Discussion of Experimental Results
  - 5.4.1 The Simple Metals Li, Na, Mg, and Al
  - 5.4.2 The Noble Metals
  - 5.4.3 The *s-p* Metals Cd, In, Sn, and Pb
  - 5.4.4 The Transition Metals and Alloys
- 5.5 Summary

References

**6. Angular Dependent Photoemission.** By N. V. Smith  
(With 14 Figures)

- 6.1 Preliminary Discussion
  - 6.1.1 Energetics
  - 6.1.2 Theoretical Perspective
- 6.2 Experimental Systems
  - 6.2.1 General Considerations
  - 6.2.2 Movable Analyzer
  - 6.2.3 Modified Analyzer
  - 6.2.4 Multidetectoring Systems
- 6.3 Theoretical Approaches
  - 6.3.1 Pseudopotential Model
  - 6.3.2 Orbital Information
  - 6.3.3 One-Step Theories
- 6.4 Selected Results
  - 6.4.1 Layer Compounds
  - 6.4.2 Three-Dimensional Band Structures
  - 6.4.3 Normal Emission
  - 6.4.4 Nonnormal CFS

References

**Appendix:** Table of Core-Level Binding Energies

Contents of **Photoemission in Solids II**

**Additional References with Titles**

**Subject Index**

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# 1. Introduction

L. Ley and M. Cardona

*Caminante, no hay camino  
sino estelas en la mar*

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This is the second of a series of two volumes devoted to photoemission in solids with particular emphasis on photoelectron spectroscopy. Photoelectron spectroscopy is one of a number of spectroscopic techniques involving photons and electrons (see [Ref. 1.1, Fig. 1.1]): monochromatic, possibly polarized photons impinge on a sample and, as a result, electrons are ejected. Their energy is then measured with a suitable analyzer. The photoelectron spectrum yields information about the electronic levels of the solid in its photoexcited states. Thus photoelectron spectroscopy is mainly a technique for the investigation of the electronic structure. Recently, however, it has also become possible to observe effects of the vibronic structure (phonons) in the photoelectron spectra of solids, (see [Ref. 1.1, Sect. 1.4.3]).

Photoelectron spectroscopy has undergone an unprecedented development within the past ten years and has become one of the most popular areas of research in solid state physics. The reason for this development is to be found mainly in the increasing improvement of experimental techniques and the commercial availability of photoelectron spectrometers. Measurements are nowadays performed in a routine way under ultrahigh vacuum, thus eliminating one of the main sources of unreliability of photoelectron spectra: the surface contamination. The escape depth of the photoelectrons is very small (5–50 Å) and it becomes imperative to work with ultraclean surfaces.

It is customary to subdivide the field of photoelectron spectroscopy into two categories depending on the type of photon source used. When lamps are used for excitation with uv photons one speaks of ultraviolet photoelectron spectroscopy or UPS. If X-ray tubes are used one calls it XPS (X-ray photoelectron spectroscopy). A table of the gas discharge and X-ray lines conventionally used can be found in [Ref. 1.1, Table 1.7]. Because of the high work functions of most materials ( $\phi \gtrsim 4 \text{ eV}$ ) little data can be obtained in the wavelength region where air is transparent. Hence UPS is usually performed in the vacuum ultraviolet. The upper limit of 11.8 eV on the photon energy is imposed in some spectrometers by the use of a LiF window between the lamp and the sample. The modern trend, however, is to disregard the region below 11.8 eV and to operate without a window, mostly by using the He I (21.2 eV) and the He II (40.8 eV) lines. XPS is presently done mainly with AlK $_{\alpha}$  (1486.6 eV) radiation. A particularly annoying problem, the natural linewidth of the AlK $_{\alpha}$  line and its satellite structure, can be solved with an X-ray monochromator.

The increasing availability of electron synchrotrons and storage rings for spectroscopic work using synchrotron radiation seems to be changing the trends of work in photoelectron spectroscopy (see Chap. 6). Synchrotron radiation as produced in storage rings is ideal for photoelectron spectroscopy work. It is intense, linearly (or circularly) polarized, produced in ultrahigh vacuum and covers the photon energy range from photoelectric thresholds to the hard X-rays for big machines (electron energies 2 GeV). Smaller machines, which can be built as “dedicated” sources of synchrotron radiation at a moderate cost, cover the region up to  $h\nu \sim 1000$  eV. Thus synchrotron radiation, after suitable monochromatization, can be used advantageously in photoelectron spectroscopy, especially in experiments which require the continuous variation of the exciting photon energy. Synchrotron radiation bridges the traditional gap between XPS and UPS making the distinction, based on the source used, basically meaningless.

The number of parameters at our disposal for variation in a photoelectron spectroscopy experiment is very large. The photon energy, polarization and angle of incidence of the exciting source can be varied while for the emitted electrons the energy and the spin polarization can be analyzed as a function of polar and azimuthal angles of emergence. The sample orientation, or actually that of the photoemitting surface, can be changed, provided we know how to prepare such a surface with the required cleanliness and perfection. The number of parameters and the volume of data obtained by varying them is actually prohibitively large so that an intelligent choice must be made in order to make the analysis possible. Thus arise the various techniques discussed in our two volumes. The conventional EDC's (energy distribution curves) are run for photons of a given energy at fixed polarization, and angle of incidence, as a function of the electron energy with the electrons being collected either over a wide solid angle (angular integrated) or angular resolved. In the latter case the EDC's are taken using the azimuthal and polar take-off angles as parameters, (see [Ref. 1.1, Chap. 6]). Measurements can also be performed for a fixed electron energy and varying the energy of the exciting photon (constant final-state or CFS spectroscopy, see Chap. 6) if synchrotron radiation is available. Another alternative is to vary both, photon and electron energies keeping their difference constant. Thus one obtains the technique of constant initial-state spectroscopy (CIS) which also requires the use of synchrotron radiation. The technique of spin-polarized photoemission, in which the spin of the photoelectrons is analyzed, has been left out of our two volumes as it is covered elsewhere [1.2].

The traditional emphasis of photoelectron spectroscopy lies in the investigation of the electronic structure of valence electrons and core levels. It is generally believed that for sufficiently big photon energies ( $\geq 25$  eV) the angular *integrated* EDC's represent the density of occupied (valence) states somewhat modulated by the appropriate matrix elements (see Chap. 7). At lower photon energies the spectra are also affected by the properties of the final state: the

EDC's corresponding to the energy distribution of the joint density of states (EDJDOS) are obtained (see [Ref. 1.1, Chaps. 1 and 6]). The matrix elements mentioned above depend on the exciting photon energy. This fact can be advantageously used to extract the partial densities of valence states, i.e., to split the density of states into components of a given atomic parentage (see Chap. 2). The angular resolved EDC's yield, in principle, the complete energy versus wavevector curves in the case of two-dimensional solids (layer structures or surface states, see [Ref. 1.1, Chap. 6]).

The investigation of core levels lies usually in the domain of XPS although a few of the outermost *d* core levels can be also excited with uv radiation (in particular HeII). Core level XPS can be used for qualitative or quantitative chemical analysis (electron spectroscopy for chemical analysis "ESCA", see [Ref. 1.1, Sect. 1.5.1]). The core levels, in particular their chemical shifts, contain also information about the electronic structure and bonding (see [Ref. 1.1, Sect. 1.2.2]). The line shape of the core levels contains additionally a number of interesting effects, especially the asymmetry due to low-energy electron excitations near the Fermi surface, the so-called Mahan, Nozières, De Dominicis effect (see [Ref. 1.1, Chap. 5]). The linewidths of the core lines reflect the lifetime of the core holes plus a contribution due to phonon broadening, see [Ref. 1.1, Sect. 1.5.3]. Core levels can be accompanied by a number of satellites due to simultaneous excitations of other electronic levels (shake up, shake off [Ref. 1.1, Sect. 4.3]) and single or multiple excitation of plasmons, see Chap. 7. Also, central to the photoelectron spectroscopy of core levels is the matter of electronic *relaxation*: the binding energies being measured are not those of the one-electron core states corresponding to the ejected electron, but those of the atom left behind with a core hole. The difference in these energies is produced by the remaining electrons "relaxing" upon the creation of the core hole (see [Ref. 1.1, Sects. 1.5, 4.2]). The main part of this relaxation ( $\sim 20$  eV typically) is of atomic origin and thus the same in the solid as in an isolated atom (intra-atomic relaxation). Part of the relaxation, however, is produced by the valence electrons and thus affected by solid-state bonding (extra-atomic relaxation). Extra-atomic relaxation can amount to a few eV.

As already mentioned, the phenomenon of photoemission takes place within a depth which varies between  $\sim 5$  Å (UPS) and  $\sim 50$  Å (XPS) (see [Ref. 1.1, Fig. 4.10]). Hence it is expected to be strongly sensitive to the condition and properties of the surface. In the XPS case 50 Å suffice to observe bulk properties provided the surface is clean. For UPS with escape depths of 5 Å, typically two monolayers, the electronic properties of these two monolayers, which can differ significantly from those of the bulk, are usually measured. Hence UPS is particularly appropriate for the investigation of the electronic properties of surfaces, in particular surface states. With the exception of Chap. 2 (surfaces of semiconductors) we have not dealt with the question of photoemission from surface states since it is adequately covered by another recent monograph [1.3]. We should point out, however, that besides specific surfaces the bulk electronic