Photoelectron Spectroscopy

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Photoelectron Spectroscopy

Principles and Applications

Third Revised and Enlarged Edition
With 461 Figures and 28 Tables

Springer

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Preface

Since the completion of the manuscript for the first edition of Photoelectron Spectroscopy, the field has undergone a steady growth.

Firstly, the theory has been refined and condensed into a manageable form. Secondly two important experimental developments have occurred. The resolution that can be obtained is now of the order of 3 meV, which corresponds approximately to an energy of 30 k_BK. This means that photoelectron spectroscopy can now obtain data with an accuracy similar to that achieved in standard thermodynamic experiments (such as specific heat experiments), thus facilitating a direct comparison of data from the two different types of experiment. The second important experimental advance is that one can now readily measure electron energy distributions over a solid angle of almost 2π. This yields valuable information whenever these electron energy distributions have anisotropies.

It was decided, in view of these developments, to rework and expand the volume so as to do justice to the full potential of today's photoelectron spectroscopy. I have benefitted very much from the help of my group namely R. de Masi, D. Ehm, B. Eltner, F. Müller, G. Nicolay, F. Reinert, D. Reinicke and in particular S. Schmidt. Without the dedicated effort of these collaborators the present edition could not have been produced. I am grateful to S. Neumann who typed the complete text with great skill. Thanks are due to the Springer Verlag for their expert help and patience.

Saarbrücken,
February 2003

Stefan Hüfner

Preface to the Second Edition

This new edition has provided me with the possibility to correct, with the assistance of R. Zimmermann (Saarbrücken), some errors that appeared in the previous edition and to prepare a somewhat more detailed subject index which was done with the help of Th. Engel (Saarbrücken). In addition, some references have been added from publications that appeared in 1994/1995 to give the reader the chance to find in some areas the most recent literature.

A word on the nomenclature should be added. The field treated with in this monograph is called photoelectron spectroscopy (if one wants to name it by the particle that is being detected) or photoemission spectroscopy (if one wants to name it by the primary process that takes place). Both names are and have been used in the literature on an equal footing, and in this book this practice has been adopted.

In preparing this second edition I have enjoyed the expert and friendly help of Dr. H. Lotsch from Springer Verlag.

Saarbrücken, November 1995 *Stefan Hüfner*

Preface to the First Edition

Molecules and solids can be characterized by two main types of qualities, namely their vibrational (elastic) properties and their electronic properties, which are of course intimately connected with each other. The study of vibrations in molecules and solids is mostly performed by means of optical spectroscopy. This spectroscopy can also determine the electronic excitations of molecules and solids. In solids, compared to molecules, the phonon and electron excitations depend on an additional quantum number, which originates from the periodicity of the crystal solid, namely the wave vector $\boldsymbol{k}$. In order to perform wave-vector-dependent measurements one has to work with exciting particles which can transmit or absorb wave vectors of the same magnitude as those present in a solid. Therefore the optical technique is no longer sufficient to scan the phonon or electron distributions over the whole Brillouin zone (except with the difficult technique of two-photon spectroscopy).

With respect to the elastic properties of solids, the neutron diffraction technique has provided much information on the phonon dispersion curves of a great number of systems. Today we have a fair understanding of these phonon dispersion curves. With respect to the electron dispersion curves the situation was different up to about 1980, when the first electron dispersion curves were measured by photoemission spectroscopy. In the meantime photoemission spectroscopy has been developed further and is now the method of choice to study the electron dispersion curves of solids. Of course such dispersion curves can be, and also have been, measured for electronic surface states.

This volume deals with some, although by no means all, aspects of photoemission spectroscopy. This technique has been developed in the last 25 years and, with the extensive use of synchrotron radiation, can now be employed for such diverse fields as the investigation of the chemical properties of specially treated surfaces of semiconductors or high polymers, for the study of the electronic structure of molecules absorbed on surfaces, and for the measurement of dispersion curves of bulk and surface electronic states. We have tried to write this volume at an elementary level such that the newcomer to the field can find some basic information that will then allow him to study recent reviews and the original literature.

After an introductory chapter, core levels, which are mostly used for chemical investigations, are treated in Chap 2. In Chaps. 3 and 4 the different final states that can arise in the photoemission process and the relation to the initial ground state are discussed. Chapters 5, 6 and 7 deal with valence bands in molecules and in particular solids, where we try to present in some detail the methods by which electron dispersion relations can be obtained by this kind of spectroscopy. Finally, in the last four chapters we discuss specific fields of photoemission spectroscopy, namely the study of surface effects and then three particular modes of this technique, namely inverse photoemission spectroscopy, spin polarized photoemission spectroscopy and photoelectron diffraction.

Saarbrücken,
February 1994

Stefan Hüfner

Acknowledgements

This book has profited tremendously from long standing cooperation and many discussions with colleagues in the field. My early interest in photoemission spectroscopy was stimulated by G.K. Wertheim of AT&T Laboratories more than twenty years ago. I enjoyed the collaboration with him over many years. Later, in Saarbrücken, R. Courths, A. Goldmann, H. Höchst, F. Reinert, and, in particular, P. Steiner, have worked with me and much of the material presented in this book derives from that collaboration.

A very successful collaboration that I have enjoyed during the last years was that with the group of L. Schlapbach (Zürich, now Fribourg), and with many of his colleagues, notably J. Osterwalder, T. Greber and A. Stuck. From that collaboration I have learned everything that I know about photoelectron diffraction.

Over the years I have profited from discussions with many people in the field, notably Y. Baer (Neuchâtel), A. Bradshaw (Berlin), P. Echenique (San Sebastian), P. Fulde (Stuttgart), A. Fujimori and A. Kotani (Tokyo), O. Gunnarsson (Stuttgart), K. Schönhammer (Göttingen), G. Kaindl (Berlin), F. Meier (Zürich), W.D. Schneider (Lausanne), G.A. Sawatzky (Groningen) and H.C. Siegmann (Zürich).

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The manuscript originated from a series of lectures given at the ETH Zürich in 1983 and repeated at the University of Fribourg and Lausanne in 1989. The first draft of the manuscript was written during the tenure of an Akademie Stipendium granted by the Volkswagen Foundation during the academic year 1986/87, which I spent at the Cavendish Laboratory in Cambridge. I thank the Volkswagen Foundation for the financial support and the mentioned institutions for their hospitality.

I thank the Deutsche Forschungsgemeinschaft, the Bundesministerium für Forschung und Technologie and the Volkswagen Stiftung for the financial support that kept my laboratory running and made the work reported in this volume possible.

I have to thank my secretary H. Waack for typing with great skill the various (many) drafts of the manuscript and for helping me in reading the proofs.

This book would not have been completed without the expert and friendly cooperation and help from Dr. A. Lahee and in particular Dr. H. Lotsch from Springer Verlag. I appreciate in particular that H. Lotsch worked intensively on the manuscript even under the most difficult personal conditions.

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