Wolfgang Schattke, Michel A. Van Hove (Eds.)

Solid-State Photoemission and Related Methods

Theory and Experiment

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Library of Congress Card No.: applied for
British Library Cataloging-in-Publication Data:
A catalogue record for this book is available from the British Library

Bibliographic information published by Die Deutsche Bibliothek
Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is available in the Internet at <http://dnb.ddb.de>.

Cover Picture
Photoelectron angular distributions of 1T-$TiTe_2$ taken at 100 eV photon energy (showing the momentum resolved electronic structure over several Brillouin zones). Top sheet: Fermi level. Sheets to higher binding energies separated by 100 meV.

Printed in the Federal Republic of Germany
Printed on acid-free paper

Composition Uwe Krieg, Berlin
Printing Strauss Offsetdruck GmbH, Mörlenbach
Bookbinding Litges & Dopf Buchbinderei GmbH, Heppenheim

ISBN 3-527-40334-5

Preface

The objective of this volume is to provide a comprehensive review of the state and progress of solid-state photoemission, including closely-related methods, both from a theoretical and from an experimental point of view. This material should be of particular interest to a wide range of theoretical and experimental physicists, materials scientists, and chemists, from graduate students to experts, dealing especially with surfaces and other nanostructures.

Many excellent treatments of major aspects of this field have appeared in the last decade: we mention in particular Inglesfield and Plummer's 1992 review article[1], which focused on the fundamental principles of valence-level angle-resolved photoemission, and the 1995 book by Hüfner[2], which adopted a more experimental perspective.

This field has continued to grow at a fast pace on many fronts, greatly expanding its capabilities and achievements. We thus felt that it was necessary and timely to bring together diverse developments in a single monograph, in an attempt to provide a degree of up-to-date completeness of the current state of the art.

Given that photoemission is intimately tied to ground and excited electronic states, this book starts with an exposition of contemporary theory of such states. It then provides a unified overview of the theoretical principles of core and valence photoemission. This is then followed by a much more thorough treatment of the theory of core level photoemission.

Turning to valence photoemission, a chapter is devoted to valence bands and VUV spectra, while another addresses actual development of spatial imaging of valence levels besides the traditional spectroscopic analysis. The very important application to the study of magnetic materials is covered in the following chapter. In the subsequent chapter, recent progress towards a compact photoemission program based on an all-electron ab-initio representation is described in the context of band structure theory.

Several very exciting novel developments with two-particle spectroscopies and their inherent access to many-particle properties such as lifetime and correlation are introduced in three separate chapters dealing with: time-resolved two-photon photoemission; low-energy (e,2e) spectroscopy; and one-photon two-electron transitions at surfaces.

The book next shifts the attention toward the use of core levels, in particular for surface structure determination. For that purpose, an overview of the known structures of surfaces is offered, being fundamental to many surface processes, including photoemission itself.

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[1] J. E. Inglesfield and E. W. Plummer, *The physics of photoemission* in S. D. Kevan (ed.) *Angle-resolved photoemission*, (Elsevier 1992)

[2] S. Hüfner, *Photoelectron spectroscopy* in Springer Series in Solid State Sciences, Vol. 82 (Springer, Berlin 1995)

This is followed by a very recent application of core-level angle resolved photoelectron spectroscopy to surface structural analysis; its implications for the valence band structure are also discussed. Then, new holographic approaches to obtaining surface structure are addressed.

Several related methods of surface analysis are covered next. One is X-ray absorption fine structure and its derivative techniques. Another is the use of X-rays and their properties in photoemission and X-ray emission. Finally, developments in low-energy electron diffraction are addressed in the last chapter, covering the important issue of surface vibrations.

Wolfgang Schattke and *Michel A. Van Hove, Editors*

August 2003

In memoriam Lars Hedin (1930–2002)

Tragically, soon after completing his chapter for this Handbook, Professor Lars Hedin passed away.

Lars was born in 1930 and raised in Örebro, Sweden. He met and within one year married his lifetime companion Hillevi in 1953. They now have three daughters and six grandchildren. His higher education was at the Royal Institute of Technology in Stockholm, Uppsala University, and finally Chalmers University of Technology in Gothenburg, from which he obtained his Ph.D. in 1965. He then became Professor of Physics at Linköping University (1970–71), and subsequently at Lund University (1971–95), where he spent most of his career. During his years in Lund, he made extended visits to Stanford, Nijmegen, and Yokohama. He was head of a theory group at the Max Planck Institute in Stuttgart from 1994-98, at which time he returned to Lund as Professor Emeritus, and continued to maintain an active research program until his death. Beyond this, Lars was an editor of Solid State Communications (1971–90), played a leading role in the organization of the International Conferences on Vacuum Ultraviolet Radiation Physics (1977–92), and was a member of many other committees and editorial boards in Sweden and abroad.

The field of condensed matter theory has been enriched by Lars' many outstanding and fundamental contributions over the last half century. He is responsible for various important advances, particularly in the theory of interacting electron systems. These began in the 1960s, the fascinating period during which many of the analytical tools of many body theory were being developed. His contributions took place in parallel with the development of various powerful spectroscopic tools for studying complex electronic systems, and Lars provided crucial insights for linking theory with experiment, as illustrated in his chapter for this Handbook. His theoretical developments demonstrate his unique ability to combine mathematical rigor and physical intuition within formal analytical frameworks which he designed. A multitude of scientific milestones testify to his profound impact. In particular, Lars' theories paved the way for a quantitative understanding of electronic excitations, in particular in photoemission and X-ray absorption spectra. These theories provide the basis for many calculations of electronic structure and for a quantitative understanding of experimental investigations that now dominate the science of the microscopic world.

Those who personally know him will agree that Lars combined a most friendly and engaging personality with an exacting scientific attitude that made him a great researcher, teacher, and friend. We are most grateful for having received Lars' manuscript in time for inclusion in this Handbook. It reflects most of the topics he was devoted to, especially in the last few years of his very productive life. As such it represents one of his last scientific achievements, and it also provides a solid foundation for many of the topics covered in the Handbook. By dedicating this Handbook to Lars Hedin, we hope to show how very much alive his influence will remain within the scientific community.

Wolfgang Schattke and *Michel A. Van Hove*

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Solid-State Photoemission and Related Methods
Wolfgang Schattke, Michel A. Van Hove (Eds.)

1 Electronic structure theory for ground and excited state properties of materials

Arthur J. Freeman, Ryoji Asahi, Alessandra Continenza, and Ruqian Wu

1.1 Introduction

It is now well recognized that recent major advances in the quantitative computation of ground-state properties in solids are essentially related to the development of density-functional theory (DFT) in the local density approximation (LDA) and the local spin density approximation (LSDA). [1, 2] These efficient approximation schemes give the electronic ground-state energy and density distribution as a function of the position of the atomic nuclei, which in turn determine the molecular and crystal structure and give the forces acting on the atomic nuclei when they are not at their equilibrium positions. The LDA (or LSDA) has been widely used to solve problems in atomic, molecular, and condensed matter physics, such as phase transitions, vibration spectra, chemical reactions, and magnetic properties.

Recent advances in experimental techniques such as X-ray absorption and inverse photoemission strongly require understanding of unoccupied states by first-principles calculations in addition to the occupied states. Although excitation properties are outside the domain of DFT, LDA eigenvalues have been frequently interpreted as quasiparticle states. This is because LDA is so widely used and much easier to perform than full many-body theories. In practice, LDA band structures successfully give an account of experiment including some excitation properties, *e.g.*, photoemission spectra of metals. This procedure, however, is certainly not valid for all the eigenvalues and excitation properties.

One of the major problems in describing excitation properties is that the LDA gives a substantial underestimate of the band gap in semiconductors and insulators, typically by 40–50% in comparison with experiment. This problem, the so-called band gap problem, is so serious when considering fundamental properties in semiconductors for instance, that it has been intensively discussed over 20 years. A complication of the problem comes from the difficulty to access an exact form of the exchange-correlation functional or the corresponding exchange-correlation potential in the Kohn Sham (KS) scheme.

Several attempts have been undertaken to set up alternatives to LDA in order to improve LDA and to extend its applicability to excitation properties. These can be divided into mainly two groups. One is to obtain the quasiparticle energies, which directly correspond to the excitation energies of a many-body Dyson equation, by the perturbation expansion of the self-energy. A comprehensive discussion including a more realistic approximation, known as the GW approximation, to the self-energy was given by Hedin [3]. Another theoretical approach in going beyond LDA is to attempt to find better energy functionals by modeling the exchange-correlation hole but still within DFT framework; this includes the self-interaction correction

Solid-State Photoemission and Related Methods: Theory and Experiment. Edited by Wolfgang Schattke, Michel A. Van Hove

ISBN: 3-527-40334-5

(SIC), [4] the LDA+U, [5] and the optimized effective potential (OEP) method, [6–8] the generalized density functional theory, [9–11] and the generalized Kohn-Sham (GKS) scheme with the screened-exchange LDA method [12, 13] (sX-LDA).

The simplification of the GW calculation, called the model GW method, [14, 15] is one way to reduce the numerical effort of the GW calculations. Although the accuracy should be limited by the neglect of local-field effects and dynamic screening, the results for various nonmagnetic semiconductors [14] and for transition metal oxides [15–18], give mostly good agreement with experiment and the results of full GW calculations. While the method gives self-consistent eigenvalues and wavefunctions with respect to the perturbed self-energy corrections, the reliability of the total energy, and therefore of the ground states obtained, has not been established.

The applicability of the SIC and the LDA+U approaches is relatively limited to the particular systems where localized states are involved. The LDA+U works reasonably well for the Mott-Hubbard insulators or rare-earth metal compounds, where the partially filled $3d$ or $4f$ bands are split by the Coulomb interaction, forming the upper and lower Hubbard bands. The SIC also describes the Mott-Hubbard insulators and the $3d$ monoxides. However, these methods fail to give satisfactory results for more itinerant systems; in particular, the SIC does not yield good band gaps of sp semiconductors, *e.g.*, Si and Ge. [19]

The basic idea of the OEP method was proposed [6] by Sharp and Horton in 1953, showing the way to obtain a local exchange potential exactly from the Hartree-Fock potential. The method was revised to improve the LDA description. Kotani [7] used the OEP with the correlation energy in the random-phase approximation (RPA) and presented results for Cu, Fe, Co, Ni, Si, and MnO. The results for metals are very close to those of LDA, and a good agreement with experiment is obtained for MnO. However, the band gap of Si is improved by only 0.2 eV. Städele *et al.* suggested [8] that a main effect for improvement of the band gap by the OEP method is a self-interaction reduction, not including the discontinuity of the exchange-correlation potential which is supposed to be dominant for Si. [20]

The screened-exchange LDA method (sX-LDA) was first proposed [12] by Bylander and Kleinman in order to obtain a better band gap. Seidl *et al.*showed [13] that the method is actually described in the framework of the generalized Kohn-Sham scheme (GKS), and that the discontinuity of the exchange-correlation potential is introduced through the nonlocal screened potential. Encouraging results for the band gaps, structural properties, and optical properties were demonstrated for several bulk semiconductor materials. [12, 13, 21–23] The method was also applied to surface and superlattice. [24] The advantages of the sX-LDA over the GW calculations are that it is much less computationally demanding, and that it permits the self-consistent determination of ground-state properties.

In this chapter, after a short introduction to density functional theory and its most precise implementation via the full-potential linearized augmented plane wave (FLAPW) method, we present a brief discussion on the general aspects of the band gap problem and its prescriptions, theoretical frameworks of the model GW and the sX-LDA are presented. The former is derived from the quasiparticle picture through the GW approximation, and the latter is introduced as a particular case of the generalized KS scheme. These two methods have a capability to obtain self-consistent properties including band gaps in a wide range of semiconductors. Moreover, rather light computational demands allows us to implement them into an all-electron methods, the FLAPW method. The applications of these method are also demonstrated in the case of semiconductor and magnetic properties.

1.2 Density functional theory and the FLAPW method

1.2.1 Introduction

The full-potential spin-polarized linear augmented plane wave (FLAPW) method is considered to be the most accurate electronic structure calculation scheme. It has its origin in the augmented plane wave (APW) method introduced by Slater [25] (details about this method can also be found in Ref. [26]). In this approach, real space is partitioned into spherical regions around atoms ("muffin-tins" or "atomic spheres") and interstitial regions between the spheres. Computationally, the APW method is demanding since the basis functions are energy dependent and the eigenvalue problem non-linear. The subsequent linearization of the APW method (LAPW) [27, 28], where the energy dependence is removed by selecting a fixed set of suitable muffin-tin radial functions and their energy derivatives, represented an important development. In the full-potential (F)LAPW method there is no shape approximation for either the charge density or the potential, and all electrons are treated in the self-consistent process; the core electrons are treated fully relativistically and the valence electrons are treated semi-relativistically. Further details can be found in original papers [29, 30] and in recent reviews [31, 32].

Aside from the early important introduction of a total energy capability [33], recent improvements and extensions to the present FLAPW calculation scheme include: (i) evaluation of forces on the atoms, which affords automatic optimization of the atomic geometry [34–36], (ii) methodological developments resulting in significant speed-ups [37], (iii) spin-orbit coupling affording calculation of magnetic properties, namely, magnetocrystalline anisotropy (MCA), surface magneto-optic Kerr effect (SMOKE), and magnetic circular X-ray dichroism (MCD), (iv) optical properties, (v) the option of several different exchange-correlation functionals, i.e., the local density approximation (LDA) and the generalized gradient approximation (GGA) and (vi) the treatment of excited states via screened exchange (sX), as well as model GW treatments, and (vii) the calculation of vibrational frequencies. A very recent and important break-through is the successful implementation of a parallelized version of the code.

1.2.2 Density-functional theory

The FLAPW method employs density-functional theory (DFT), introduced by Hohenberg and Kohn [38] and Kohn and Sham [39]. The underlying theorem (Hohenberg-Kohn-Sham theorem) on which this theory rests is that the total energy, E, of an atomistic system can be expressed as a functional of its electron density, ρ, namely, $E = E[\rho]$, that E is at its minimum for the ground-state density, and is stationary with respect to first-order variations in the density.

Typically, the Born-Oppenheimer approximation [40] is employed which assumes that the motion of the nuclei are negligible with respect to that of electrons. This implies that the electronic structure is calculated for a given atomic geometry; the nuclei are then moved according to classical mechanics.

The Kohn-Sham equations

To obtain the ground-state density, the variational principle is applied with respect to the one-particle wave functions:

$$\left[(-\hbar^2/2m)\nabla^2 + V_{eff}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}), \tag{1.1}$$

where

$$V_{eff}(\mathbf{r}) = V_C(\mathbf{r}) + \mu_{xc}[\rho(\mathbf{r})] \tag{1.2}$$

is the effective potential and ε_i the effective one-electron eigenvalues. Equations (1.1) are the "Kohn-Sham equations" and the solutions, $\psi_i(\mathbf{r})$, form an orthonormal set,
i.e., $\int \psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\, d\mathbf{r} = \delta_{ij}$. The Coulomb or electrostatic potential is given as:

$$V_C(\mathbf{r}) = -e^2 \sum_\alpha \frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|} + e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \tag{1.3}$$

which can also be calculated using Poisson's equation, i.e.,

$$\nabla^2 V_C(\mathbf{r}) = -4\pi e^2 q(\mathbf{r}) \quad , \tag{1.4}$$

where $q(\mathbf{r})$ represents the electronic charge distribution *and* the positive point charges at position $\mathbf{R}_\alpha$. The exchange-correlation potential is given by

$$\mu_{xc} = \partial E_{xc}[\rho]/\partial\rho \quad . \tag{1.5}$$

Because the exchange-correlation potential (and energy) are not known, approximations have to be made.

Spin-polarized density functional theory

The generalization of density-functional theory to spin-polarized systems has been made within the local spin density approximation (LSD) [41, 42]. The important quantity, in addition to the electron density $\rho(\mathbf{r})$, is the spin density $\sigma(\mathbf{r})$ which is the density difference between the spin-up and spin-down configurations, i.e., $\sigma(\mathbf{r}) = \rho_\uparrow(\mathbf{r}) - \rho_\downarrow(\mathbf{r})$; the total density being given by $\rho(\mathbf{r}) = \rho_\uparrow(\mathbf{r}) + \rho_\downarrow(\mathbf{r})$. Because the exchange-correlation potential for spin-up and spin-down electrons is in general different, the spin-polarized form of the Kohn-Sham equations are:

$$\left[(-\hbar^2/2m)\nabla^2 + V^\sigma_{eff}(\mathbf{r})\right]\psi^\sigma_i(\mathbf{r}) = \varepsilon^\sigma_i\psi^\sigma_i(\mathbf{r}), \quad \text{where}\, \sigma = \uparrow \text{ or } \downarrow \quad , \tag{1.6}$$

and

$$V^\sigma_{eff}(\mathbf{r}) = V_C(\mathbf{r}) + \mu^\sigma_{xc}[\rho(\mathbf{r}), \sigma(\mathbf{r})] \quad . \tag{1.7}$$

Thus there are two sets of single-particle wave functions, one for spin-up (or "majority") electrons and one for spin-down ("minority") electrons, each with corresponding one-electron eigenvalues.

Exchange-correlation functions

Local-density approximation (LDA) A very successful and widely used approximation for the exchange-correlation energy is the local-density approximation (LDA). Here the exchange-correlation energy is assumed to depend only on the local electron density of each volume element $d\mathbf{r}$:

$$E_{xc}[\rho] \approx \int \rho(\mathbf{r})\varepsilon_{xc}[\rho(\mathbf{r})]d\mathbf{r} \quad . \tag{1.8}$$

$\varepsilon_{xc}[\rho]$ is the exchange-correlation energy per electron of a *homogeneous* electron gas and is expressed as an analytic function of the electron density, as is the exchange-correlation potential, μ_{xc}. There are various forms of the LDA in the literature; we refer to those of Hedin-Lunqvist [43] and Wigner (non-spin-polarized forms), and Barth-Hedin [41] (spin-polarized form) since they are the ones implemented in the present FLAPW program version.

Generalized gradient approximation (GGA) In recent years, the generalized gradient approximation (GGA) is being considered as a possible improvement over the LDA. The GGA has been found to generally improve the description of total energies, ionization energies, and electron affinities of atoms, atomization energies of molecules [44–46] and some solid state properties [47–50]. Adsorption energies of adparticles on surfaces are also reported to be improved [51, 52] as are reaction energies [53, 54]. Furthermore, the GGA leads to significantly better activation energy barriers for H_2 dissociation [55, 56] and also the relative stability of structural phases appears to be better described for magnetic [57] and non-magnetic systems [58, 59].

There are a number of GGA approaches in the literature. The generic form of the GGA exchange-correlation energy may be written as:

$$E_{xc}^{\mathrm{GGA}}[\rho] = \int \rho(\mathbf{r})\varepsilon_{xc}^{\mathrm{GGA}}\big(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})\big)\, d\mathbf{r} \tag{1.9}$$

so that it depends locally on the electronic density $\rho(\mathbf{r})$ and its gradient.

The GGA developed by Perdew and Wang (PW) [44] is derived essentially from first principles, combining the gradient expansions of the exchange and correlation holes of a non-uniform electron gas with real-space truncations to enforce constraints imposed by properties of the physical exchange-correlation hole. The GGA developed by Becke and Perdew [60] on the other hand relies on fitted parameters. In the present program version of the FLAPW program the GGA implemented is that proposed by Perdew, Burke and Ernzerhof (PBE) [61]. This functional is regarded to be conceptually more concise than the PW GGA but appears to yield very similar results [62].

1.2.3 The FLAPW basis-set

In the FLAPW method, in bulk material, real space is partitioned into spherical regions around atoms ("muffin-tins" or "atomic spheres") and interstitial regions between the spheres. In the spherical region, the basis functions are products of radial functions and spherical harmonics, and in the interstitial region plane waves are used. For the film geometry, there is a number

of atomic layers surrounded by vacuum, thus in addition to spherical and interstitial regions, one defines a vacuum region, which starts at $\pm D/2$ and ends at $\pm\tilde{D}/2$ (see Fig. 1.1), where the wave functions are products of two-dimensional (2D) plane waves and z-dependent functions which are solutions of the one-dimensional Schrödinger equation of the (x, y)-averaged potential in the vacuum region.

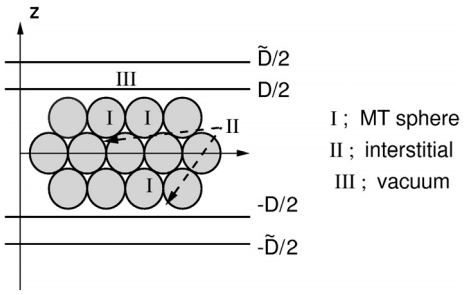

Figure 1.1: Geometry for a film calculation showing division of space in a film geometry.

Specifically, the FLAPW one-particle wave functions in the film geometry are:

$$\psi_i(\mathbf{r}, \mathbf{k}_\parallel) = \sum_j c_{ij}\phi(\mathbf{r}, \mathbf{K}_j); \quad \mathbf{K}_j = \mathbf{k}^\parallel + \mathbf{G}_j \quad , \tag{1.10}$$

where $\mathbf{k}^\parallel$ is an arbitrary vector of the 2D BZ and $\mathbf{G}_j$ is a three-dimensional (3D) reciprocal lattice vector (in the z-direction an artificial periodicity between the boundaries at $\pm\tilde{D}/2$ is imposed). The basis functions are:

$$\phi(\mathbf{r}, \mathbf{K}_j) = \begin{cases} \Omega^{-1/2} e^{i\mathbf{K}_j \cdot \mathbf{r}} & \text{interstitial} \\ \sum_{lm}[A^\alpha_{lm}(\mathbf{K}_j)u_l(E^\alpha_l, r_\alpha) + B^\alpha_{lm}(\mathbf{K}_j)\dot{u}_l(E^\alpha_l, r_\alpha)]Y_{lm}(\hat{r}_\alpha) & \text{sphere} \\ \sum_q [A_q(\mathbf{K}_j)u_{\mathbf{k}q}(E_\nu, z) + B_q(\mathbf{K}_j)\dot{u}_{\mathbf{k}q}(E_\nu, z)]e^{i(\mathbf{k}^\parallel + \mathbf{K}^\parallel_q)\cdot\mathbf{r}} & \text{vacuum} \end{cases} \tag{1.11}$$

The Coulomb potential $V(\mathbf{r})$ is obtained by solving Poisson's equation in each of the three regions. At infinity the potential is gauged equal to zero in the case of the film geometry. The effective single-particle potential is constructed by adding the exchange-correlation potential, which is determined by the charge density in real space and transformation of it into each representation. The core electrons are treated fully relativistically and are updated at each iteration using a scheme for *free* atoms (only the spherical part of the potential is used). The valence electrons are expanded in a variational basis set and are treated scalar-relativistically.

1.3 Electronic structure theory for excited states

1.3.1 Band gaps and derivative discontinuities

The band gap is rigorously defined as the difference between the lowest conduction-band energy and the highest valence-band energy: the latter is the energy required to remove an electron from the insulating N-particle ground state to infinity, *i.e.*, the ionization potential, I;