Electronic Structure Studies Using Resonant X-Ray and Photoemission Spectroscopy

BY

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Dissertation for the Degree of Doctor of Philosophy in Physics presented at Uppsala University in 1999

Abstract


This thesis addresses the electronic structure of molecules and solids using resonant X-ray emission and photoemission spectroscopy. The use of monochromatic synchrotron radiation and the improved performance of the instrumentation have opened up the possibility of detailed analyses of the response of the electronic systems under interaction with X-rays. The experimental studies are accompanied by numerical ab initio calculations in the formalism of resonant inelastic scattering. The energy selectivity has made it possible for the first time to study how the chemical bonds in a molecule break up during resonant inelastic X-ray scattering. In the conjugated polymer systems, the element selectivity of the X-ray emission process made it possible to probe the different atomic elements separately. The X-ray emission technique proved to be useful for extracting isomeric information, and for measuring the change in the valence levels at different degrees of doping.

In this thesis, spectral satellite features in transition metals were thoroughly investigated for various excitation energies around a core-level threshold. By measuring the relative spectral intensity of the satellites it was possible to extract information on the partial core-level widths. Using the nickel metal system as an example, it was shown that it is possible to probe the different core-excited states close to shake-up thresholds by measuring the relative spectral intensity variation of the Auger emission. Resonant photoemission measurements showed unambiguous evidence of interference effects. These effects were also thoroughly probed using angle-dependent measurements. The combination of X-ray emission and absorption were useful for studying buried layers and interfaces due to the appreciable penetration depth of soft X-rays. X-ray scattering was further found to be useful for studying low-energy excited states of rare earth metallic compounds and transition metal oxides.

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ISSN 1104-232X
ISBN 91-554-4463-6

Printed in Sweden by Eklundshofs Grafiska AB, Uppsala 1999
To my family
List of papers
This thesis is based on a collection of articles given below referred to by the Roman numerals. Reprints were made with permission from the publishers.

I. Competition between decay and dissociation of core-excited carbonyl sulfide studied by X-ray scattering
L. Yang, P. Salek and H. Ågren

II. Resonant and non-resonant X-ray scattering spectra of some poly(phenylenevinylene)s
J.-H. Guo, M. Magnuson, C. Såthe, J. Nordgren, L. Yang, Y. Luo, H. Ågren,
K. Z. Xing, N. Johansson, W. R. Salaneck, R. Daik and W. J. Feast

III. The electronic structure of poly(pyridine-2,5-diyli) investigated by soft X-ray absorption and emission spectroscopies
Ägren, N. Johansson, W. R. Salaneck, L. E. Horsburgh and A. P. Monkman

IV. Resonant inelastic soft-X-ray scattering spectra at the nitrogen and carbon K-edges of poly(pyridine-2,5-diyli)
Ägren, N. Johansson, W. R. Salaneck, L. E. Horsburgh and A. P. Monkman
J. Electron. Spec., 00, 00 (1999).

V. The electronic structure of polyaniline and doped phases studied by soft X-ray absorption and emission spectroscopies
M. Magnuson, J.-H. Guo, S. M. Butorin, A. Agui, C. Såthe, J. Nordgren and
A. P. Monkman

VI. Energy dependence of Cu L$_{2,3}$ satellite structures using synchrotron excited X-ray emission spectroscopy
M. Magnuson, N. Wassdahl and J. Nordgren

VII. Resonant Auger spectroscopy at the L$_{2,3}$ shake-up thresholds as a probe of electron correlation effects in nickel
M. Magnuson, N. Wassdahl, A. Nilsson, A. Föhlisch, J. Nordgren and N.
Mårtensson

VIII. Resonant photoemission at the 2p edges of Ni: resonant Raman and interference effects
Föhlisch, N. Mårtensson, J. Stöhr and M. Samant
IX. Angular dependent resonant photoemission processes at the 2p thresholds in nickel metal
M. Magnuson, A. Nilsson, M. Weinelt and N. Mårtensson

X. Coherent and incoherent processes in resonant photoemission
N. Mårtensson, M. Weinelt, O. Karis, M. Magnuson, N. Wassdahl, A. Nilsson,
J. Stöhr and M. Samant

XI. X-ray fluorescence spectra of metals excited below threshold
M. Magnuson, J.-E. Rubensson, N. Wassdahl, A. Föhlisch, A. Nilsson and N.
Mårtensson
To be submitted.

XII. Electronic structure of buried Si layers in GaAs(001) as studied by
soft x-ray emission
P. O. Nilsson, J. Kanski, J. V. Thordson, T. G. Andersson, J. Nordgren, J.
Guo, M. Magnuson

XIII. Electronic structure of Cu/Ni(100) Interfaces
and J. Stöhr
To be submitted.

XIV. Resonant inelastic soft-X-ray scattering at the 4d edge of Ce-based
heavy-fermion materials
S. M. Butorin, M. Magnuson, K. Ivanov, D. K. Shuh, T. Takahashi, S. Kunii,
J.-H. Guo and J. Nordgren
J. Electr. Spec., 00, 00 (1999).

XV. Soft X-ray scattering from CeB₆ at the 3d and 4d thresholds
and S. Kunii
Submitted to Phys. Rev. B

XVI. Resonant inelastic soft X-ray scattering from valence-band excita-
tions in 3d⁰ compounds
S. M. Butorin, J.-H. Guo, M. Magnuson, and J. Nordgren

XVII. Low-energy d-d excitations in MnO studied by resonant x-ray floures-
cence spectroscopy
S. M. Butorin, J.-H. Guo, M. Magnuson, P. Kuiper, and J. Nordgren
This list shows papers of relevance for the present thesis, but not included. They were omitted either since they essentially cover the same material as the other papers or because they are of internal report character.

Decay and dissociation of core-excited OCS studied by X-ray scattering
M. Magnuson, J. Guo, C. Sthe, J.-E. Rubensson, and J. Nordgren
ALS compendium of user abstracts and technical reports 1999.

Measurements of Zn L\textsubscript{2,3} satellites using X-ray emission spectroscopy
M. Magnuson and J. Nordgren
Hamburger Synchrotronstrahlungslabor HASYLAB am Deutschen Elektronen-Synchrotron
DESY, Jahresbericht 1997, I.

Resonant and nonresonant X-ray emission spectroscopy of poly(pyridine-2,5-diyl)

How the phenyle rings (benzene) act as building blocks in the $\pi$ conjugated polymers

Coherent and incoherent processes in resonant photoemission

Low-energy $d - d$ excitations in MnO studied by resonant X-ray fluorescence spectroscopy

Resonant photoemission and resonant inelastic X-ray scattering - coherent vs. incoherent processes, in Raman emission by X-ray scattering
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Preface

The present thesis includes the major part of the research which I carried out during the years 1993 to 1998 at the Department of Physics at the University of Uppsala. The outline of the thesis is the following: Chapter I comprises background information with an outline of the area of physics addressed in the scientific papers. Chapter II describes the basics for the techniques and the spectroscopic methods used in the measurements. Chapter III describes the computational methods used in some of the papers. In Chapter IV, the results of the studies are presented and discussed, summarizing the papers included in this thesis. The purpose of the work has been to contribute to the understanding of the behaviour of the electronic structure of the various systems, from both experimental and theoretical points of view.

All the experimental research presented here was performed with the aid of synchrotron radiation. The first two years of my doctoral studies I was involved full time in the assembly and testing of a new experimental station which had previously not been used for synchrotron radiation research. It was to be used for angular resolved electronic structure studies of surfaces, adsorbates and solids using a grazing incidence geometry, with integrated X-ray emission, X-ray absorption and photoemission spectrometers. The experimental station was designed and assembled at the Department of Physics as a joint research project between two research groups, the Dept. of Physics in Uppsala (J. Nordgren and N. Mårtensson), and IBM in Almaden (J. Stöhr). A picture of the experimental station is found in the appendix.

In the beginning, much time was thus spent on various technical tasks, such as assembling a so-called \( I_0 \) chamber with a gold evaporator and fixtures for translational feed-throughs for thin gold meshes and foils to be used for intensity-normalization of the spectra. I was also involved in the testing of a new cryostat, and in the design and planning for parts for a new NEXAFS detector. After the build-up and preliminary vacuum testing in Uppsala, the station was shipped to Berkeley and installed at beamline 8.0 at the Advanced Light Source. I was a Scholar in Residence at the Lawrence Berkeley National Laboratory (LBNL) at the University of California in Berkeley (UCB) during the academic year 1994/95. This was a tough experience, combining the experimental efforts with the new equipment at beamline 8.0 with attending the physics classes given at the UCB Campus. During the whole summer of 1994 we worked intensively with setting up the equipment to be ready when the beamtime started in the fall. Necessary preparations to make the planned experiments possible was to accomplish sufficient vacuum with baking (heating) of the vacuum chambers during long time periods (weeks), with continuous control of the temperatures in different parts. I used several months in Berkeley to assemble and test an electron beam evaporator for growing ultra-thin nickel films, which I later mounted in the preparation chamber of the experimental station.

Later, I was also involved in various smaller experiments at beamline 7.0 at ALS and at beamline BW3 at the Hamburger Synchrotronstrahlungslabor, (HASYLAB) at Deutschen Elektronen-Synchrotron (DESY). I assembled and tested
various electronic equipment such as the electronic gating unit used at HASYLAB to synchronize the X-ray emission detector with the bunches for removing unwanted background counts in the spectra. For the channeltron detector which we used in some of the absorption measurements I assembled a preamplifier. During the preparations of the dichroism experiments at the European Synchrotron Radiation Facility (ESRF), I built and tested a unit for the step-motor electronics used for controlling the magnets. I also worked with theoretical and numerical models, which were to be used for interpreting the experimental results. For simulations of resonant inelastic scattering spectra using calculated state densities as input, I made my own Fortran programs. In order to learn more about electronic structure theory I took computational physics courses and participated in a summer school in Århus, Denmark.
Comments on the contribution to the papers

As mentioned, in the beginning of my studies I worked mostly on the technical side with building up experimental equipment, and in the latter part I contributed mostly on the scientific, experimental side. The experimental work carried out at synchrotron radiation facilities is always the result of a teamwork. In general, the contribution to the articles is reflected by the position of the names in the author list.

In the molecular dissociation paper I, the gas cell measurements were done as a team work on beamline 7.0 at ALS. I analyzed the data, performed atomic Hartree-Fock calculations, and was responsible for co-ordinating the experimental and theoretical results as well as writing the paper together with the co-authors. In the polymer paper II, my main contribution was to take part in the interpretation of the spectra and writing the paper together with the co-authors. In the polymer papers III, IV, and V, I was responsible for the experimental work and wrote the papers together with the co-authors. In the copper and nickel papers VI and VII, I did all the analysis of the data and was responsible for writing the paper together with the co-authors. In the Fano paper VIII, I took part in the measurements, in the evaluation and the discussion of the data, and in writing the papers. In the angular resolved nickel paper IX, I was involved in the original experiments, analysed the data and was responsible for writing the paper. In the overview paper X, I helped to make some of the figures and contributed to the writing. In the detuning paper on both copper and nickel XI, I was actively involved in most of the experiments and did the numerical calculations of the spectra. In paper XII, I was actively involved in the experiments. In paper XIII, I made the figures and was responsible for the iterative procedure to finalize the text. In the cerium paper XIV, I took a major part in the measurements and to some extent contributed to the text. In paper XV, I was responsible for the measurements in Hamburg and the writing. In papers XVI and XVII, I contributed to the measurement work and to some extent in the writing.
Acknowledgments

This thesis includes work carried out during the period September 1993 to the end of 1998 at the Department of Physics at Uppsala University, Sweden. During this time many people influenced the work in different ways and, in particular, I would like to thank the following:

Prof. Joseph Nordgren and Prof. Nils Mårtensson for giving me the opportunity to work in the field of X-ray emission and photoemission spectroscopy in combination with theoretical calculations. I would like to express my gratitude to J.-E. Rubensson who, when returning from Jülich, created an inspiring scientific atmosphere in our group at the Ångström laboratory. I would also like to thank Sergei Butorin for introducing me to the field of strongly correlated rare earths systems and the Anderson impurity model. It has been interesting to share the office with Dr. Akane Agui and learn about all the Japanese traditions and customs. All the present and former members of the soft X-ray physics group including Nial Wassdahl, Per Skytt, Laurent Duda and Pieter Kuiper are also acknowledged for creating an interesting environment to work in.

I would also like to thank all the nice people that I had the pleasure of collaborating with during the last five years. Especially, Hans Ågren and his computational team at the University of Linköping, all the members of the electronic structure theory group, and the surface physics group at the Department of Physics in Uppsala.

Jinghua Guo is acknowledged for his patience in teaching me, between the beamtime shifts, how to cook Chinese food including lots of bamboo, soy sauce and vegetables both in Hamburg and in the Bay Area. Special thanks to Dr. Per Söderlind for introducing me to Fortran codes and teaching me how to perform self-consistent standard band-structure calculations. We shared some great times weight lifting at the Sports Palace in San Francisco and listening to the Beach Boys during our excursions to remote places in California.

I would also like to acknowledge the support I received from Miriam and Bengt, my mother and father.

Martin Magnuson
Uppsala, April 15, 1999.
Chapter 1
General Introduction

1.1 The nature of light

1.1.1 The wave-particle dualism

Mankind has always experienced and learned about the physical world by the sense of vision, using eyesight to observe how light is reflected and scattered by matter. Since ancient times, the enigmatous nature of light itself has attracted much interest. How should light be understood and explained; is it some kind of wave motion, or is it of corpuscular (particle) nature? In fact, this question was never resolved. Rather, in the twentieth century, it was understood that light can be defined either as a wave motion, or as a beam of particles - light travels as a wave but is emitted and absorbed as a particle. The subject of this thesis involves one of nature’s most fundamental processes, namely the interaction between light (photons) and matter. In the following, light refers to all kinds of electromagnetic radiation, not only visible light. In the seventeenth century the wave theory for light was accepted, being supported by prominent scientists such as the Italian Francesco Grimaldi (1618-63) in Bologna, and the Englishman Robert Hooke (1635-1703) in Oxford. Hooke discovered the phenomenon of diffraction, which is a clear sign of the wave property of light, and in 1665 he published his scientific work on optics in *Micrographia*. Grimaldi investigated the bending of light, and described the diffraction phenomena in his work *de Lumine* (1665), for the first time using wave theory. The first detailed description of the wave theory was given by Christian Huygens (1629-95) who to a large extent worked in Paris but originated from the Netherlands. In Huygens’ time it was clear that sound was a wave motion, and that matter was needed for the sound waves to propagate. Therefore, it was thought that light waves also need a medium in which to propagate; the ‘Ether’. The mechanism known as Huygens’ Principle, was successful in explaining the phenomena which were known at the time; reflection and refraction, but the theory could not explain why light did not turn around corners like sound waves do.

Isaac Newton (1643-1727), the grand experimentalist and theorist, published his optical findings in the book *Opticks* (1704). Newton studied the visual spectrum of light i.e., the rainbow of colors which appears when light is passing through a glass prism. Newton concluded that white light consists of different components which, when separated by the prism, make up the different colors, and thereby
he made an important step towards modern spectroscopy. Based on a series of experiments, Newton concluded that light is predominantly of corpuscular nature, but that the particles generate waves in the "Ether" by causing vibrations when hitting the surface of the glass prism.

1.1.2 Interference and diffraction

The particle theory prevailed during the eighteenth century, but the wave theory returned again in the beginning of the nineteenth century, when Thomas Young (1773-1829) in London used a slit experiment to produce interference patterns. The interference phenomenon can only be explained if light is of wave nature.

Figure 1.1: (a) Light with a wavelength comparable to the width of a slit appears to be a wave motion which is diffracted in the slit. (b) Light diffraction in two neighbouring slits interfere and develop a sharper pattern.

If the wavelength of the radiation is comparable to the width of the slit, the wave propagation is markedly modulated as illustrated in Fig. 1.1 (a). This phenomenon is known as diffraction. Young observed that light passing a narrow slit produced a symmetrical pattern of alternating dark and light fields with gradually decreasing separation and intensity. He observed that the distance between the symmetrical interference fringes were proportional to the wavelength of the light and inversely proportional to the width of the slit. The pattern thus became broader when the slit was made narrower. Within the slit, the light appears as if produced by a new source which emits coherent radiation, i.e., light from one part of the slit is always in phase with the light in the other parts of the slit. However, as the wave front

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1Much later, it turned out that interference patterns can occur with a beam of particles such as electrons or atoms, since they also exhibit wave nature.
propagates from the slit, intensity maxima are caused by constructive interference in directions where the radiation coming from all parts of the slit have a 'twin part' of the same phase which increase the intensity. If light is diffracted in two or more closely placed slits as illustrated in Fig. 1.1 (b), interference effects occur between the two different wave fronts. In this case light from one slit may be reduced by light having the opposite phase from other slits. The intensity is then modulated so that more structures in the interference pattern appear.

With the slit experiment, together with experiments performed by Augustin Fresnel (1788-1827), it was established that light was indeed a transverse wave motion and not longitudinal as earlier assumed. Fresnel also found that sound waves with short wavelength were less prone to turn around corners than were sound waves with longer wavelength. It was found that a beam of light can in fact also turn a corner and produce a diffraction pattern. In the beginning of the nineteenth century, extensive experiments were made by Joseph Fraunhofer (1787-1826) in München, who studied the characteristics of light scattered by several narrow slits. The interference pattern became sharper and had more lines than was the case of a single slit due to the strict geometrical rule for constructive interference. Within the interpretation of his diffraction experiments, Fraunhofer established the principle for diffraction in a transmission grating and, at a very early stage of the development of the field of spectroscopy, he introduced the technique to separate the different wavelengths of the radiation. Today, transmission and reflection gratings are important components in spectrometers, spectrographs and monochromators, and are thus used to analyze electromagnetic radiation, to measure wavelength, and to separate a certain wavelength needed for a specific experiment, as will be further discussed throughout this thesis.

1.2 Radiation interaction with matter

1.2.1 Absorption and emission lines

Among the various scientists who studied characteristic wave properties of radiation and its interaction with matter by means of spectroscopy was Anders Jonas Ångström (1814-1874), in Uppsala. In 1853 he measured the hydrogen spectrum. This observation later resulted in the Balmer formula and became the experimental foundation of the atomic model. Ångström studied the solar spectrum, especially the Fraunhofer lines, which were dark lines caused by the absorption of light in the different elements in the outer atmosphere of the sun. In 1868 he presented his results in *Recherches sur le spectre solaire*. He was also the first to do spectroscopical measurements of the northern light. In 1859, Gustav Robert Kirchhoff (1824-1887) in Heidelberg made an important step for the development of the spectroscopical research when he introduced general rules which govern absorption and emission of light interactions with matter. Together with Robert W. Bunsen (1811-1899), Kirchhoff identified several characteristic emission lines by comparison with the corresponding absorption lines in the solar spectrum. After these first measurements, a fast development of spectral analysis started. Kirchhoff and Bunsen showed that the Fraunhofer lines correspond to the light emission lines which some
metals display after being heated to gas phase in a flame. Since the atomic model was not developed at this time, thermodynamics was used to interpret the relation between the absorption and the emission lines.

During the eighteen-sixties, the Scottish physicist, James Clerk Maxwell (1831-79) showed with a set of equations that light could be described as a wave motion of a combined electrical and magnetic field. However, in the year 1900, when the German physicist Max Planck (1858-1947) derived the law for black body radiation, the particle nature of light reappeared once again. Earlier, most physicists regarded the classical world as a continuum, where various physical quantities, such as energy, momentum and angular momentum were thought to be continuous and could have any value. Planck tried to understand the nature of the black body radiation. The light from a heated piece of metal in a dark room displays a spectrum of colors which can be accurately measured. However, the empirical data could not be fitted by using the laws of classical thermodynamics and electrodynamics, especially for short wavelengths, which is known as the ultraviolet catastrophe. In the case of black body radiation it was apparent that the classical theories would not work, and that a new kind of physical theory was needed. Planck first reasoned that the reflections at the walls of a black body cavity resulted in radiation being absorbed and then quickly re-emitted by the atoms of the wall. Planck tried to find a way to reduce the number of standing waves in the cavity by reducing the number of short-wavelength oscillators in the walls of the cavity. He finally assumed that the black body radiation was constituted by quanta, or photons, each with the energy: \[ E = h\nu, \] where \( h \) is Planck's constant, and \( \nu \) is the frequency of the radiation. This hypothesis diverged sharply from the 'classical' wave theory of light, replacing it with the quantum theory, which Planck himself accepted with much reluctance, describing his own theory as a desperate move, something he was forced to introduce.

1.2.2 Photoelectrons and X-rays

The photoelectric effect was discovered in 1887 by Heinrich Hertz (1857-94) in Germany when it was observed that a spark was produced when a negative electrode was exposed to ultraviolet radiation [1]. The photoelectric effect was the subject of much speculation during the turn of the century and a number of investigations were made. The discovery of X-rays by Wilhelm Conrad Röntgen (1845-1923) in Würzburg in 1895 immediately had a large impact in science all over the world. The discovery was made when Röntgen was studying electrical currents in discharge tubes and found that beams (which he called X-rays) were emitted when cathode rays (later called electrons) in the glass tube hit the anti-cathode. During his experiments, photographic plates near the apparatus became exposed despite the opaque packaging, a very surprising result. By the discovery of X-rays, a large number of applications were founded in many research areas, such as physics, chemistry, biology, and medicine.

Shortly afterwards, in 1897, Joseph John Thomson (1856-1940) working at the Cavendish laboratory in Cambridge discovered the electron. The electrons were identified as particles that had escaped from the atoms by the photoelectric effect.
This phenomenon implies that some metal surfaces emit electrons when irradiated by light. This was a reciprocal phenomenon to Röntgen's discovery, and Pierre Curie and one of his co-workers were the first to discover that the photoelectric effect can also be induced by X-rays [2]. The photoelectric effect was theoretically explained in 1905 [3] by Albert Einstein (1879-1955).

Light of a particular color can be described by its wave character as having a specific frequency or, according to its particle character, as having a specific energy. It was clear that the emitted electrons from the metal all had the same energy as long as the frequency of the incoming light was constant. If the intensity of the incoming light was increased, the only result was that more electrons were emitted without any increase of the energy of the individual photons. Only if the energy (frequency) of the incident light was increased did the energy of individual photons increase. A minimum energy (cut-off energy) was needed to emit electrons from the metal, and if the frequency of the light was lower, no emitted electrons were observed. Einstein had now gone beyond Planck since he proposed that also visible light could appear as a beam of quantized particles. This was in sharp contrast to the experimental findings (interference, diffraction, reflection and refraction phenomena), and the theory that was established at the time - that light was a wave motion. With the quantum theory Planck and Einstein showed that the 'classical physics' of Newton was not as solid as it was thought to be.

Based on experimental data the British physicist Henry Moseley (1887-1915) derived a simple relationship between the frequency $\nu$ for transitions involving X-ray radiation and the atomic number (Z) for the elements known as Moseley's law: $\nu = A(Z - b)^2$. $A$ and $b$ are constants, which are characteristic for every X-ray transition i.e., $K_o$, $L_o$ etc. With this law, Moseley predicted new atomic numbers and the existence of unknown elements later confirmed by experiments and atomic theory.

The English physicists William Henry Bragg and William Lawrence Bragg, father and son (received the Nobel Prize together in 1915), studied how X-rays striking a crystal backscatter in a manner depending on the periodic structure of the crystal lattice. In what is now known as Bragg's law, the two scientists stated that the intensity of reflected radiation depends on three factors: the wavelength of the X-rays, the spacing of the atoms in the crystal, and the angle at which the X-rays strike the lattice. With the work of Manne Siegbahn (1886-1978, Nobel Prize 1924) who moved his research projects from Lund to Uppsala in 1922, exploration and accurate classification of X-ray emission and absorption spectra of many elements were obtained. He was also able to advance the field of X-ray spectroscopy through the development of more sophisticated methods to rule gratings [4].

1.2.3 The quantized theory of radiation

Niels Bohr (1885-1962) became the first to use a quantized atomic model for the interpretation of experimental emission and absorption lines. This model assumes that the electrons move around a tiny positively charged nucleus in quantized orbits. In contrast to the classical electrodynamic wave theory introduced by Maxwell and Fresnel the electron in its orbit emits no electromagnetic radiation. The atomic
model permits absorption and emission of characteristic energy quanta only when an electron makes a transition from one quantum state to another. The difference in energy between the quantum states is emitted as electromagnetic radiation (light) if the initial state has a higher energy than the final state or, in the opposite case, radiation energy is absorbed if the energy of the initial state has the lowest energy. The energy (or frequency) of the emitted or absorbed radiation is determined by the energy difference between the two states involved according to the relation: \( E_1 - E_2 = h\nu \), where \( E_1 \) and \( E_2 \) are the energies of the two states and \( h \) is Planck's constant.

With the quantized atomic model from 1913, Bohr managed to make use of the remarkable proposal by Planck and Einstein that light consists of quanta (quantized particles, photons). Thus, in the early years of the twentieth century the study of how light interacts with matter led to a completely new theory. This quantum theory of radiation developed by Planck, Einstein and Bohr contributed greatly to the understanding of the underlying phenomena of light scattering. The classical wave theory showed to be a special case of the quantum physics when the quantum numbers become infinitely large. In 1924, Louis de Broglie (1892-1987) proposed that the wave-particle dualism of light could also be valid for particles such as electrons. The idea of material waves led to a new and very fruitful theory called wave mechanics. At the same time, Max Born (1882-1970), together with his student Werner Heisenberg (1901-76), wanted to replace the old quantum theory with a new theory which they called quantum mechanics. However, Heisenbergs new theory was not based on the postulates by Bohr; rather, the quantum aspect was developed into the theory from the uncertainty principle. Erwin Schrödinger (1887-1961) also showed that quantum mechanics and wave mechanics were two different mathematical formulations of the same physics.

In the late 1927, it was shown by George Thomson, that electrons can also behave as waves. However, it was actually not until 1987 that the double-slit experiment was carried out with electrons by a Japanese team of researchers from the Hitachi research labs and Gakushuin University in Tokyo. The result of the experiment, producing an interference pattern, was exactly the same as the equivalent experiment with photons. Not until the beginning of the 1990s, the two-slit experiment was applied to atoms which also showed the familiar interference pattern. Under certain experimental conditions, atoms can thus also display a wave character.

In a short period (1925-1927) the modern quantum mechanics thus emerged from the work of Heisenberg, de Broglie, Schrödinger and Max Born, replacing the Newtonian mechanics and the first quantum theory by Planck, Einstein and Bohr. Quantum mechanics quickly became the standard theory for dealing with all microscopic phenomena. The mathematical formalism of quantum mechanics remains almost entirely today as it was established in the 1930s, although its interpretation has remained controversial. The official explanation of quantum reality became known as the Copenhagen Interpretation named after Bohr’s physics institute in Denmark which was founded in the 1920s. It is a set of ideas which provided the recipes brought forward by Bohr, Heisenberg and Born - including the combination of complementarity, probability waves, and the collapse of the wave function.
The principle of complementarity can be illustrated by the wave-particle duality; the wave and particle properties of a quantum object constitute complementary aspects of its behavior. Therefore, one should never encounter any experiments in which these two distinct behaviors conflict with each other. In a similar way there is a position-momentum complementarity, where we can choose to measure the position of a particle, in which case its momentum is uncertain, or vice versa, according to Heisenberg's uncertainty principle. Each quality - particle or wave, position or momentum - constitutes a complementary aspect of the quantum object. The equation which describes how a quantum particle moves is the wave equation derived by Schrödinger which states the probability of finding the photon or electron (or some other particle) at a particular place (and time). The collapse of the wave function explains why particles such as photons or electrons travel as waves but are emitted and absorbed as particles. It is the very act of observing the wave that makes it collapse to become a particle. In this picture, an electron that is not observed does not exist in the form of a particle at all and, in principle, it could turn up anywhere in the Universe. A new theory describing the interaction of light and matter, called Quantum Electrodynamics (QED), was developed by a number of physicists in 1929. The problems of how to calculate properties using QED was straightened out around 1948 by Julian Schwinger (1918-94), Shin'itiro Tomonaga (1906-79), and Richard Feynman (1918-88).

1.3 Soft X-ray physics

1.3.1 The electromagnetic spectrum

Figure 1.2 shows the electromagnetic spectrum as it extends from the infrared (IR) to the hard X-ray region. Wavelengths are shown at the top and photon energies at the bottom. Radiation ranging from a few tens of eV's up to about 5 keV is referred to as soft X-rays. The high-energy limit is due to the absorption in air (containing mostly nitrogen and oxygen). The low-energy limit is not as well defined and the overlap is large with the longer wavelength regions. The visible wavelength region represents only a very small part of a continuous wavelength range which spans over many orders of magnitude. The visible light and infrared (IR) spectrum extends to even longer wavelengths to short and long radio-waves. The shorter wavelengths, including ultraviolet (UV) radiation, ultra soft X-rays (USX) or extreme ultraviolet radiation (EUV), soft X-rays (SX), and hard X-rays, are used in many physics experiments to probe the electronic structure of matter. All experimental equipment operating in the energy range above 6 eV must be evacuated with vacuum pumps. This is the reason for using the term vacuum-ultraviolet (VUV) for photons in the wavelength region 6 eV to 50 eV.

The soft X-ray region can be regarded as the least explored or unused wavelength region of the electromagnetic spectrum. In the soft X-ray region, there are a large number of absorption resonances and absorption edges of many elements with low or intermediate atomic numbers. This leads to strong absorption of radiation in very short distances in all kinds of materials while at other photon energies some materials become transparent for the radiation. Historically, the strong ab-
Figure 1.2: The electromagnetic spectrum as it extends from the infrared (IR) to the hard X-ray region. Visible light, corresponding to the red, green and blue colors is shown on the left in different shades of gray.

Absorption has prohibited the investigation of the soft X-ray region. However, during the last decades, this energy region has become used extensively in several areas of research. The absorption resonances are now widely used for spectroscopic measurements giving both elemental and chemical information about the investigated materials. With the new kind of light sources, with their special characteristics, it is now possible to produce soft X-rays in large quantities which can be used for this purpose.

1.3.2 Spectroscopic tools and transition processes

The first spectroscopic tool for physics experiments was the prism spectrograph used already by Newton. As mentioned previously, Fraunhofer realized that grating diffraction could be used in order to improve the resolution in spectroscopic studies. Fraunhofer spent much effort to make his own gratings and used them to perform accurate measurements of the wavelengths of spectral lines, i.e., the absorption lines in the solar spectrum (Fraunhofer lines). A transmission grating is made up of a large number of closely spaced parallel slits where light can pass through. Fraunhofer’s first gratings were of the transmission type and were made of a large number of parallel silver threads. With this type of grating he resolved the term splitting of the yellow doublet in sodium corresponding to the wavelengths 5895.92 Å and 5889.95 Å, respectively. Fraunhofer also realized the advantage of reflection gratings in comparison to transmission gratings. By using a diamond to engrave periodic lines in a piece of flat glass, the accuracy of engraving a large number of lines was improved. The apparatus that Fraunhofer used for this purpose could make up to 3000 lines/cm. The development of grating spectroscopy was further improved in the middle of the nineteenth century when photographic methods were introduced to register the spectra. In the 1970’s, holographic and lithographic methods were also introduced to improve the rendering of lines in the grating. The American physicist Henry Augustus Rowland (1848-1901) further significantly improved the grating spectrometers by introducing a concave grating (instead of a flat surface), which was used to focus all the scattered light from the sample onto the
detector. The Rowland-type spectrometer will be further discussed in Chapter II. Later on, the interferometer introduced by, among others, the American physicist Albert Michelson (1852-1931) at the University of Chicago, significantly improved the accuracy of wavelength determination.

In the following, a brief review of some basic transition processes involved when radiation interacts with matter will be presented. Figure 1.3 shows schematically photoionization and accompanying excitation processes. The valence levels include the outer, least bound electrons in the electronic structure, which are responsible for the chemical bonding between the atoms in molecules. The core levels have a much larger binding energy and are not important for the chemical bond. Each element has a unique set of core levels and their energies are usually well separated from other elements. In Fig. 1.3 (a), an incident photon is interacting with a multielectron atomic system. If the incident photon energy is high enough, it will be possible to remove a core electron (excite or ionize) from one of the deeper electron shells with the photoelectric effect. At this photon energy, electrons are also removed from all the valence shells. If the photon energy is lower, as is the case in Fig. 1.3 (b), a valence electron can be removed from the valence shell without the removal of a core electron. In the photoionization process, the photon is absorbed by an atom and transfers the energy to the emitted photoelectron with a kinetic energy equal to that of the incident photon minus the binding energy of an electron in the particular shell. During the photoemission process and the creation of a core hole in an atom of the sample, the surrounding electron cloud of the remaining ion contracts (relaxes) in order to screen the positive charge. The relaxation may lead to so-called shake-up and/or shake-off as illustrated in Fig. 1.3 (c) and (d).

The electronic structure of the electron shells subsequently rearrange to minimize the total energy by two competing decay processes. The core hole can be filled by an electron from the valence shell which results in the emission of a photon or an electron of characteristic energy. Figure 1.4 (a) shows how the atomic system decays according to an X-ray emission process (fluorescence) in which the electron transition is accompanied by the emission of a photon of characteristic energy equal...
Figure 1.4: The Auger and X-ray emission decay processes.

to the difference between the initial and final atomic states. The inner core electron shells are (sufficiently) bound to the corresponding atom in a molecule so that radiation originating from different kinds of atoms can be separated and identified. This element specificity is an important aspect of X-ray radiation from matter. However, the atomic valence shells, are spread out over the different atoms which constitute the studied system. Since only some of the atomic shells are allowed to participate in an electron transition, according to quantum mechanical selection rules, the observed intensity of emitted radiation is determined by the local valence electron distribution around the core hole site. In a competing decay channel (b), the atom rearranges through the emission of an Auger electron [5]. Auger electrons have a characteristic energy and are commonly used in spectroscopic methods for elemental characterization in surface and interface analysis. The details of the spectroscopies and the interaction processes will be further discussed in Chapter 2.

In the 1940’s, Skinner and O'Brian used X-ray emission spectroscopy in their investigations of the valence electron band structure [6]. Solid state valence band theory was also applied for the interpretation of X-ray spectra by Arnold Sommerfeld (1868-1951) and Hans Bethe (f. 1906) in the 1930s [7] and by Seitz in the 1940s [8]. As will be further described in Chapter 3, the theoretical valence band theory was developed from the interpretation of soft X-ray emission spectra of solids. In the 1950’s, Kai Siegbahn (b. 1918), and co-workers, building on their experience from nuclear spectroscopy and radioactive decay, pointed out the much overlooked fact that electron spectroscopy (using the photoelectric effect) is a powerful alternative to X-ray spectroscopy. It was shown that electron spectra also appear as lines with the then newly developed high resolution magnetic double-focussing spectrometer, and that the electron lines were just as narrow as the X-ray emission lines. Spectroscopic measurements of the kinetic energy of photoelectrons as a function of the incident photon energy is known as photoemission spectroscopy. The instrumental development initiated comprehensive studies of electron energy levels of a large number of the elements in the periodic system. It was also observed that the core electron lines from an element displayed a shift in energy when the chemical state of the atom was changed, so-called chemical shifts. Hence, the
experimental method for electron spectroscopy became known as Electron Spectroscopy for Chemical Analysis (ESCA) [9]. This spectroscopy is widely used for elemental identification and analysis of chemical bonding of atoms, molecules and solids. In ESCA the sample is irradiated with an X-ray beam, and the ejected photoelectrons are analyzed in an electrostatic spectrometer.

In the 1960s and 70s, it was shown that valence band X-ray spectra of molecules can be interpreted by using molecular orbital theory [10]. Rolf Manne proposed that the relative intensities of the X-ray transitions from the molecular orbitals were related to a linear combination of atomic orbitals, as will be explained in Chapter 3. Atomic and molecular physics, i.e., the studies of free and non-interacting atoms or molecules, provides the basic understanding of more complex systems such as very large molecular systems, polymers and solids. Several investigators also showed that molecular orbital theory could be effectively used for the interpretation of chemical bonding of valence electrons. The molecular orbital structure theory does now fairly well describe the experimental observations.

1.3.3 X-ray scattering and selective excitation

Previously, X-ray physics experiments were performed by using either electron excitation or conventional X-ray tubes. Figure 1.5 is a general illustration of the different processes involved when a sample containing atoms in a cubic crystal lattice is irradiated and excited by a beam of photons, electrons or other particles. If the sample is relatively thick, there will be no transmitted radiation since everything will be absorbed by the atoms in the bulk. If the energy is sufficient, photoelectrons and scattered light will be re-emitted from the sample. In some cases, ions and neutral particles may also leave the surface. The scattered X-rays may be either elastic (reflected) or inelastic (fluorescence). Thus, X-ray spectroscopy can be simply thought of as a method for measuring inelastic X-ray scattering which is generally known for it's many applications in chemistry and medicine. It is also widely used in different experimental applications, as shown by the contents of this thesis.

When the photon energy of the exciting beam is close to a core excitation threshold of an inner shell, the inelastic part is dominated by so-called resonant X-ray fluorescence which is also sometimes referred to as resonant Raman scattering. The Raman effect was discovered in the 1920:s when the Indian physicist Sir Chandrasekhara Venkata Raman (1888-1970) in Calcutta found that monochromatic light in the visible (optical) wavelength region, when scattered from a material, could change its wavelength. In this case, X-ray inelastic scattering, or resonant fluorescence, is emitted, and the energy is changed corresponding to transitions between the bound states of the atoms in the sample. Thus, the photon looses some of it’s energy to the sample, or gains energy, and finally leaves the sample with a lower or a higher energy.

The Raman scattering concept was first used in the optical wavelength region, and was later applied to the X-ray region [11, 12]. The X-ray Raman scattering offers a means to obtain information of the electronic structure of the valence levels when the electrons are transferred to a core-level with the resulting emission
of either an electron or a photon. In addition, elastic scattering where no energy is lost in the collision process, is one of the earliest and most useful tools for investigating the properties of solids and molecules.

In contrast to the elastic X-ray scattering process, inelastic X-ray scattering is very weak at excitation energies far away from the core-level thresholds. However, when the excitation energy is close to an excitation threshold of an inner shell, the inelastic scattering part (the resonant X-ray Raman scattering) is dominating. Analogous to the important breakthrough of laser techniques in the optics of visible light in the 1960’s, synchrotron radiation has now become important for spectroscopy in the soft X-ray energy region. It is an invaluable tool for studies of all kinds of light-matter interactions. This has been particularly important in this energy range where in comparison to ordinary laboratory sources, the synchrotron source has much higher intensity, better energy resolution, and tunability. The synchrotron sources span energies from the IR-region all the way to the hard X-rays, which makes it possible to perform outer-shell excitations as well as deep inner-shell excitations. The excitation energy tunability makes it possible to select, for example, a core-ionization threshold and thus reduce the number of excited states from other thresholds. For these reasons, large national facilities have been built in many countries, where the users from different fields, such as biology, chemistry and physics, share the beamtime. The last two decades, as a result of the increased availability of dedicated facilities, photon and electron spectroscopy have become increasingly important tools for investigating fundamental physics interactions of
photons with matter. Performing experimental and theoretical development in parallel is particularly advantageous and has enabled sophisticated investigations of the atomic many-body systems. Numerical models are also developed to help in the interpretation of the experimental results and to predict properties of the studied systems. Some experimental achievements and numerical models are presented in this thesis. In particular, resonant processes of the fundamental interaction between light and matter close to core-ionization thresholds of inner shells have been studied. A richness of information can be obtained using core-level probes, such as X-ray emission, photoemission and X-ray absorption spectroscopies.
Chapter 2

Experimental Techniques and Interaction Processes

2.1 Introduction

As described in the previous chapter, spectroscopical methods are important tools in basic research as well as in applications where determination of the content and amount of different elements in a sample is of interest. Excitation of the studied system is achieved by supplying energy with either electrons or photons. The response to the excitation is studied by measuring the energy and intensity distribution of the emitted electrons and photons with photoelectron emission and X-ray emission spectroscopy. The emitted electrons or photons give rise to characteristic intensity patterns in the measured spectra.

When electron bombardment or X-ray radiation excites a core electron, creating a core hole in an inner electron shell, the subsequent decay from the valence levels may occur through different channels. Auger, X-ray, and Coster-Kronig decays\(^1\) are competing channels and the approximate branching ratios are tabulated in the literature [13]. The Auger and X-ray emission (fluorescence) decay channels are described in section 2.2 and 2.3, respectively. If a core hole is created in one of the deeper inner subshells, Coster-Kronig transitions between two inner core levels may also occur. In this case, the core hole is first filled by an electron from a more shallow core level, and the energy is then released by emitting one of the valence electrons.

The energy width \(\Gamma\) of a core-level is related to the lifetime \(\tau\) of the core hole by the Heisenberg uncertainty principle, \(\Gamma \tau = \hbar\), where \(\hbar\) is Planck’s constant. Typically, the core hole lifetime is about \(10^{-15}\) sec. In general, the transition rate of a decay process \(i\) filling the hole is \(S_i = 1/\tau_i = \Gamma_i/\hbar\), and the lifetime can be expressed as

\[
\tau = \hbar \frac{1}{\sum_{i=1}^{n} \Gamma_i}
\]

(2.1)

where \(\Gamma_i\) is the partial widths corresponding to the Auger, X-ray and Coster-Kronig processes that compete in filling the core hole. The total core level width \(\Gamma_{\text{tot}}\) is

\(^1\)Coster-Kronig decay is a special case of the Auger process.
then given by: $\Gamma_{tot} = \Gamma_A + \Gamma_X + \Gamma_{CK}$, where $\Gamma_A$ is the Auger width, $\Gamma_X$ is the X-ray width and $\Gamma_{CK}$ is the Coster Kronig width. The corresponding yields of the three processes are defined as: $\alpha = \Gamma_A/\Gamma_{tot}$ (Auger yield), $\omega = \Gamma_X/\Gamma_{tot}$ (fluorescence yield) and $f = \Gamma_{CK}/\Gamma_{tot}$ (Coster-Kronig yield) where $\alpha + \omega + f = 1$.

For light elements and shallow core levels, the Auger process dominates. In the soft X-ray wavelength region the fluorescence yield is generally very low, typically about 0.1 percent. For heavier elements and for deeper core-levels, the decay is instead dominated by the radiative X-ray emission decay channel. Each element in the periodic table has a unique set of core-levels at certain energies, which makes core-level spectroscopy suitable to determine what elements are present in a sample.

In section 2.4, the X-ray absorption method with the alternative electron and fluorescence yield techniques is described. When electrons or broadband photon sources are used in the excitation, the interpretation of the emission spectra is often obstructed by overlapping lines due to satellite transitions and close lying core levels. In addition, unwanted inner core transitions may fall into the studied wavelength region. The satellites and inner core transitions can be removed with the use of synchrotron radiation which provides a continuously tunable photon source which is described in section 2.5. When the energy is monochromatized, tuned to a specific resonance at an absorption threshold, the excitation is said to be resonant while, otherwise, it is non-resonant. The study of resonant excitations in emission spectra involving interference effects in the excited states is often treated in terms of scattering theory described in section 2.3.

2.2 X-ray photoelectron and Auger spectroscopy

2.2.1 The photoelectric effect

As described in Chapter 1, the photoelectric effect is used in Electron Spectroscopy for Chemical Analysis (ESCA). This spectroscopy is also known as X-ray Photoelectron Spectroscopy (XPS), since an X-ray source is used in the excitation of a bound electron which is excited to a free state in the continuum of available energy levels. The kinetic energy of the outgoing electron is well defined, and the uncertainty of its energy is only due to the width of the final state, the bandwidth of the energy of the incident characteristic X-ray beam and the experimental resolution. In the 1950s, the use of low energy excitation sources was developed, and the experimental electron spectroscopy technique in this energy region was therefore called Ultraviolet Photoelectron Spectroscopy (UPS).

As mentioned previously, when a sample is irradiated by photons there is a probability that a bound electron is excited or released from the sample through the photoelectric effect. The energy of the released photoelectron depends on the photon energy according to the energy conservation law

$$E_{kin} = h\nu - E_{bind} - \phi \quad (2.2)$$

where $h\nu$ is the energy of the incoming photon, $E_{bind}$ is the binding energy of the electron referred to the Fermi level, and $\phi$ is the work function. The kinetic energy
The electron mean-free path universal curve of photoemission. 

$E_{\text{kin}}$ of the electrons is often measured in an electrostatic hemispherical analyzer which will be described in the next subsection. With the Fermi level as a reference level for the electron binding energies, i.e., if the binding energy is zero at the Fermi level, the energy conservation also requires that

$$E_{\text{bind}} = E_{\text{final}} - E_{\text{initial}} = h\nu - E_{\text{kin}} - \phi. \quad (2.3)$$

This means that the measured binding energy of the electron corresponds to the energy difference between the initial ground state of the neutral atom and the final excited state of the ionized atom.

When the emitted photoelectron travels a distance in a material, it will quickly loose energy through interactions with other electrons through individual collisions or collective motion. Fig. 2.1 shows the electron mean-free path universal curve of photoemission [14]. The magnitude and energy dependence of the mean-free-path $\lambda(E_{\text{kin}})$ for electrons in solids is determined by the scattering mechanisms in the sample. It has been found that $\lambda(E_{\text{kin}})$ for different materials approximately follows the universal curve of mean-free-paths. A minimum of $\lambda$ generally occurs at an energy of approximately 50 to 100 eV. Below 10 eV, $\lambda$ increases rapidly, and above 100 eV it varies roughly as $E^{1/2}$. For electron energies lower than 100 eV, the rise in mean-free-path is due to the smaller number of energy allowed inelastic scattering mechanisms. With the photon energies which are characteristic for the soft X-ray spectral region, the photoelectron ranges will be in the order of 5-10 Å which makes the photoemission technique very surface sensitive.
2.2.2 Instrumentation

Figure 2.2 shows a cross section of the electron analyzer used in the present experiments. The analyzer basically consists of three parts: an electron lens, two electrostatic hemispheres and a detector. The relatively large radius of the hemisphere together with the detection system gives a high sensitivity combined with high resolution. The electron lens pre-retards the electrons to a suitable constant analyzing energy, the pass energy. The pass energy of the analyzer can be chosen in the range 1 - 1000 eV. By changing the acceleration voltage of the lens, a specific electron energy can be adjusted to fit the analyzing pass energy. The energy resolution is defined by a slit that is mounted between the lens and the analyzer. The most important factors which contribute to the resolution of the electron analyzer can be expressed as

$$\frac{\Delta E}{E_{\text{pass}}} = \frac{a}{2r} + \left(\frac{\alpha_m}{2}\right)^2$$  (2.4)

where $r = 200$ mm, $a$ = the width of the entrance slit, $E_{\text{pass}}$ = the pass energy of the electrons, and $\alpha_m$ is the half aperture angle. The resolving power $\frac{E_{\text{pass}}}{\Delta E}$ can be increased either by decreasing the size of the entrance slit or the pass energy [15]. The potential difference between the spheres and their relative separation determines the energy of the electrons which can pass along the mean radius. The analyzer and lens are shielded from external magnetic fields by two separate continuous layers of $\mu$-metal. Electrons with slightly different energies reach different spots on the detector. When the analyzer is operated at constant pass energy it
Figure 2.3: (a) Principle experimental set-up of photoemission (left), (b) Angular emission patterns with various $\beta$-values of photoelectrons (right).

gives a constant resolution over a large kinetic energy range. The kinetic energy is scanned by varying the acceleration/retardation potential of the lens, which defines the mean value of the analyzer sphere potentials. A spectrum of different electron energies is always obtained in a constant resolution mode by scanning the lens voltage while keeping the pass energy constant during the scan. The electrons are detected in a multichannel detection system with a channel plate and a phosphor screen. The spots on the screen generated by the electrons are registered by a CCD camera connected to the data acquisition system.

### 2.2.3 Angular distribution

In general, the energy position of an Auger line in a spectrum is independent of the incoming photon energy while photoemission lines are not. Thus, by progressively increasing the excitation energy it is possible to distinguish between these two kinds of processes. Another way is to measure their different angular distributions. Fig. 2.3 shows the angular dependence of the electron emission; (a) a set-up for angular resolved measurements; (b) the angular distribution pattern for some different $\beta$-parameters. The angular distribution of the differential photoionization cross section for linearly polarized photons can be expressed as

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_o}{4\pi} \left[ 1 + \frac{\beta}{2} (3\cos^2\Theta - 1) \right]$$

where $\sigma_o$ is the absolute photoelectron cross section for a certain excitation energy, $\beta$ is the angular asymmetry parameter and $\sigma$ is the angle between the polarization vector and the outgoing electron. $\beta=+2$ corresponds to a pure $\cos^2\Theta$ behaviour, whereas $\beta=0$ corresponds to an isotropic distribution. When the wavelength of the
soft X-ray radiation is larger than the atomic dimensions, it is possible to apply the dipole selection rules \((\Delta l = \pm 1, \Delta m = \pm 1 \text{ or } 0)\). For direct photoionization far from a core ionization threshold (non-resonant), the angular dependence of the photoelectrons can be predicted from the dipole character of the exciting photon which has an angular momentum of \(l = +1\). During the photoionization process, the angular momentum of the photon is transferred to an electron. For example, the photoionization of an electron occupying an \(s\)-orbital results in an angular momentum \(l=1\) of the outgoing electron wave (\(p\)-character, \(\beta = +2\)) i.e., an angular distribution with the intensity maxima parallel to the polarization plane as illustrated in Fig. 2.3. A photoionization of a \(p\)-orbital yields a photoelectron with angular momentum \(l=1 \pm 1\) which is a superposition of \(s\) and \(d\) waves. Due to interference between these waves, any \(\beta\)-value between -1 and 2 is possible.

The Auger process may also have a non-isotropic angular distribution. In a two-step description, with separated excitation and emission steps, the angular distribution of the Auger electrons are described by the product \(\beta_A = A \times C_A\). The alignment parameter, \(A\) is due to the dipole photoionization process and describes the alignment of the ion after the excitation step. The Auger decay parameter \(C_A\) describes the asymmetry of the second step i.e., the Auger transition, which involves the Coulomb matrix elements including the relative phases. For resonant Auger decay from a specific core-excited state, the \(C_A\)-parameter is assumed to be photon energy dependent in the two-step approximation.

2.2.4 Photoemission satellites

Photoionization generally leads to an excited final state. In the one-electron approximation, the ionic states are derived from the neutral ground state by removal of a one-particle state from the initial electronic configuration, while the other electrons remain fixed or frozen in their previous states. Fig. 2.4 shows a schematic core-level spectrum with an adiabatic peak due to the primary photoionization, with shake-up and shake-off satellite features included.

The adiabatic peak corresponds to the binding energy of a species where the nuclei are fixed or frozen, but where the electrons have had time enough to relax. This is the essence of the Born-Oppenheimer approximation, where the electronic and nuclear parts of the system are treated separately. This approximation is valid since the nuclear relaxation time is typically much longer than the time needed for a photoelectron to leave the system and the time for the remaining electrons to relax. The effect of relaxation and screening gives a shift of the absolute binding energy by \(\Delta E_{\text{relax}}\) towards lower binding energy.

A first approximation for the ionic state is given by the frozen-orbital approximation by removing the \(i\)th spin-orbital from the ground state and leaving the rest of the orbitals unchanged. In this simple picture, the remaining electrons do not relax when a photoelectron is removed, and the orbital energies are equal to the negative binding energies \(\epsilon_i \approx -E_{\text{bind}}\). This is the basis of the sudden approximation, or frozen orbital approximation according to Koopmans’ theorem where it is assumed that the core-level photoelectron is removed in an infinitely short time in the excitation process. The orbital energies \(\epsilon_i\) can be calculated using
2.2.5 Resonant photoemission

When a series of photoemission spectra are measured at various photon energies close to a core-level resonance, the emission from the resonating state is sometimes substantially modulated. The phenomenon is known as resonant photoemission and occurs when there is an interference between the direct valence band photoemission and a core assisted Auger-like process. These phenomena lead to pronounced effects for strongly interacting electron systems of transition metals, lanthanides and actinides where there is a huge enhancement (giant resonance) in the photoemission cross section at a resonance. The resonant photoemission process is most prominent for systems where the electrons of partially filled valence shells retain some of
its atomic-like properties while at the same time they may or may not contribute to the solid state bonding. This situation is often not well described neither by a traditional band theory nor by a model of weakly interacting atoms. The added atomic ingredient results in strong Coulomb interactions among the valence electrons. The resonant photoemission process can be viewed as resulting from two paths. In the Auger-type path, the photon excites the system into an intermediate state with a core hole, and the core hole decays via Coulomb interactions in an Auger-like autoionization process. When the core hole is filled by an electron and a second electron is ejected from the system it ends up in a state which is identical to that of the direct photoemission path. The intermediate state is often modelled as discrete while the final state is a continuum due to the wide range of kinetic energies of the ejected electron. In general, the resonant photoemission intensity is given by the following expression [17]

\[
w = 2\pi \cdot \sum_f \langle f \mid V_r^n \mid g \rangle + \sum_m \frac{\langle f \mid V_A \mid m \rangle \langle m \mid V_r \mid g \rangle}{E_f - E_m + \frac{\Gamma_m}{2}} \cdot \delta(E_f - E_g)
\]

i.e. a sum of a direct photoemission term and a set of threshold terms. The initial \((g)\) and final \((f)\) states contain the incoming photon and the outgoing electron, respectively, and \((m)\) denotes the intermediate core excited states. \(V_r\) and \(V_A\) denote the radiative and Coulomb (Auger) contributions to the interaction, respectively, and \(\Gamma_m\) is the life-time width of the core-excited state.

The simplest description of the resonant photoemission effect is provided by the Fano theory [18]. This model was first used in 1961 by Fano to describe the absorption spectrum of helium which is influenced by interference between the autoionizing resonances and the direct process. A similar model was used already in the 1930:s by Weisskopf and Wigner [19] to explain the shape of radiative linewidths. In the linewidth problem, the discrete state is an excited atomic state and the continuum is a lower atomic state and a photon. In the Fano theory, the Hamiltonian is diagonalized into a subspace which consists of one discrete core-excited state \(
\psi\n\) with energy \(E_\psi\) and one continuum \(\psi_E\) with states of energy \(E\), as schematically shown in Fig. 2.5 (a). The non-diagonal matrix elements \(V_E\) are between the discrete state and the continuum. In the resonant photoemission process, \(\psi\) is the core-excited intermediate state and \(V_E\) is the Auger matrix element for the decay step. The exact eigenfunctions of the continuum states \(\psi_E\) can be expressed as

\[
\psi = a_E \phi + \int dE' b_{EE'} \psi_{E'}
\]

where \(a_E\) and \(b_{EE'}\) are wave function coefficients. The transition matrix element \(T\) to excite the state \(\psi_E\) from the ground state \(\phi\) can then be expressed as

\[
\langle \psi_E | T | \phi \rangle = a_E^* \langle \phi | T | \phi \rangle + \int dE' b_{EE'}^* \langle \psi_{E'} | T | \phi \rangle.
\]
Figure 2.5: (a) The interaction between a discrete state and a continuum (left). (b) Characteristic Fano profiles for different q-values (right).

The ratio $f$ between the transition probability $|\langle \Psi_E | T | \Phi_g \rangle|^2$ and the probability of the transition to the unperturbed continuum $|\langle \Psi_E | T | \phi_g \rangle|^2$ gives the Fano resonance lineshape curves

$$f(\epsilon) = \frac{(q + \epsilon)^2}{\epsilon^2 + 1} = 1 + \frac{(q^2 - 1 + 2q\epsilon)}{\epsilon^2 + 1}. \quad (2.10)$$

The Fano resonance lineshape curves $f(\epsilon)$ are plotted in Fig. 2.5 (b) for a few different values of the asymmetry strength parameter, $q$. The $q$-value is defined as

$$q = \frac{\langle \Phi | T | \Phi_g \rangle}{\pi V_E \langle \Psi_E | T | \Phi_g \rangle} \quad (2.11)$$

where the discrete state $\phi$ is modified by an admixture of continuum states as

$$\Phi = \phi + P \int dE' V_{E'} \Psi_{E'} \frac{E' - E}{E - E'}. \quad (2.12)$$

The reduced energy variable $\epsilon$ is given by

$$\epsilon = \frac{E - E_\phi - F(E)}{\pi |V_E|^2}. \quad (2.13)$$

The definition of $\epsilon$ accounts for a shift of the discrete state $\phi$ at the resonance energy $E_\phi$ by the self-energy $F(E)$ defined as
\[ F(E) = P \int dE' \frac{|V_{E'}|^2}{E - E'} \]  

(2.14)

where \( P \) denotes the principal value. The self-energy is due to the interaction with the continuum which also causes the discrete state \( \phi \) to be diffused through the continuum states by a Lorenzian line shape forming a virtual bound state given by

\[ |a_E|^2 = \frac{|V_E|^2}{[E - E_\phi - F(E)]^2 + \pi^2|V_E|^4}. \]  

(2.15)

The Lorenzian half width of the discrete state \( \phi \) is given by \( \Gamma_m(E) = \pi|V_E|^2 \) as illustrated in Fig. 2.5 (a). This means that after excitation to the discrete state \( \phi \), the system will autoionize with a mean lifetime \( \tau = h/|V_E|^2 \).

The photoemission intensity in Fig. 2.5 (b) decreases below threshold and increases above due to the interference between the two channels. The asymmetric shape reflects the phases of the wave function coefficients \( a_E \) and \( b_E \).

A way is to measure the photon energy dependence of resonant photoemission is to use the constant initial state (CIS) technique, in which the incoming photon energy and the kinetic energy are simultaneously varied so that the ionization energy is constant. The CIS spectrum measures the cross section of a resonant photoemission lineshape. Another common technique to measure the photon energy dependence is to use the constant final state (CFS) technique where the incoming photon energy is varied while the detected electron kinetic energy is fixed. This type of measurement is related to the photon-absorption spectrum.

### 2.3 X-ray emission spectroscopy

#### 2.3.1 Instrumentation

Figure 2.6 (a) shows the principles of a Rowland-type spectrometer which combines dispersion and focussing properties. The grating is used as a dispersive component in the spectrometer to separate the different wavelength components of the incident light. The grating consists of a piece of glass or metal with a large number of parallel grooves (engravings). If light with a certain wavelength, \( \lambda \), is directed towards the grating and is reflected, a number of intensity maxima appears according to the grating equation

\[ n\lambda = d(sin\alpha - sin\beta) \]  

(2.16)

where \( d \) is the grating constant (distance between the grooves), \( \alpha \) and \( \beta \) are the angles of the incoming and outgoing photons measured with respect to the surface. The integer \( n = 0, \pm 1, \pm 2 \ldots \) is the spectral order of diffraction. The deflection
angle in the grating is larger for long wavelengths than for short wavelengths. The resolution of a grating is determined by the number of grooves, which is usually in the order of 300-3000 per mm. This can be understood from considering the distance between the observer and two successive grooves for two different wavelengths (exit angles).

With the Rowland spectrograph, the necessary condition implies that focussing is achieved if the source and the detector are placed on a circle with a radius of half the concave grating radius [20]. For the outgoing rays, the angle depends on the wavelength and the focussing condition is fulfilled. The principles of the concave grating theory was described by Rowland in 1882 [21]. Further improvements and refinements were made by Runge [22] and by Kayser [23]. The optimum Rowland condition can be derived mathematically by using Fermat’s principle. The limitations of the Rowland mounting become apparent when grazing incidence angles are used and an exceptionally large resolution is needed. Several different ways of arranging the components of a concave grating spectrograph have been developed. However, in most cases, these are modifications and variations of the original Rowland principle. In some cases, e.g., in monochromators where the wavelength separation is not as critical, the Rowland criterion is not used strictly in order to simplify the construction and operation of the equipment.

The Rowland condition is generally valid up to the fourth order approximation of the radiation path while the higher order terms limit the usable width and resolution of the grating. It has been shown that it is possible to obtain higher resolution by slightly displacing the slit and detector from the Rowland circle. This can be achieved so that the third order terms of the radiation path expansion vanish while the second order terms are brought to compensate those of the fourth order. Since the fourth order terms are the most dominant for the limitation of the grating width this implies that a greater width can be used and still obtain higher resolution than with the pure Rowland condition.

The X-ray emission spectra presented in this thesis were measured using a
grazing incidence spectrometer which is schematically shown in Fig. 2.7. Three fixed gratings are mounted together with the entrance slit on a precision ground slab used as a reference surface. The three gratings cover a total energy range of about 50 to 1000 eV in the first order of diffraction. The gratings have a spherical surface with respectively 5, 5 and 3 m radii with corresponding groove densities of 1200, 400 and 300 lines/mm. In order to improve the diffraction efficiency for specific energies the grooves on the gratings are blazed. The entrance slit is placed on the Rowland circle. The grazing incidence angles on the gratings are 1.9, 2.6 and 5.4 degrees, respectively. The entrance slit consists of two sharp edges which can be rotated so that the projected slit size, which determines the resolution of the instrument can be varied continuously between zero and 100 µm. The grating selector consists of two other separate adjustable edges which are used to select which grating be illuminated. Each grating together with the entrance slit and the detector forms a Rowland mounted instrument. The large two-dimensional detector can be accurately positioned and oriented in a three-axis coordinate system using motorized coordinate tables. Thus, the instrument can be looked upon as several different instruments with different grating radii which have the entrance slit and detector in common. By moving the detector it is possible to align with the different Rowland circles. By using gratings with different groove densities and radii, it is possible to achieve optimal performance over a large energy range. In order to obtain the desired angle of incidence of the gratings they are each mounted on precision pieces onto the ground slab. The detector is mounted so that it is also possible to rotate around an axis through the detector surface. The detector house is mounted on an x-y axis coordinate table which is used to accurately position the
detector on the Rowland circle defined by the different gratings. The tables are driven by computer controlled step motors.

In order to improve the resolution, it is possible to use the grating selector to illuminate only a small part of the grating. When the instrument is operated with a large slit at lower resolution, a larger area of the grating can be illuminated in order to increase the intensity. When grating is changed, the light path also changes and it is necessary to adjust the optical axis by rotating the spectrometer to maintain the Rowland criterion [24]. The movable and rotatable two-dimensional multichannel detector consists of a stack of 3 to 5 multichannel plates which are set on high voltages. The sensitivity of the detector, which normally is low for the soft X-rays is enhanced by a 3000 Å CsI coating in combination with an electrode with an electron capturing electric field. The emitted photoelectrons are then multiplied in the channel plates. At the end, the multiplied electron cascade hits a resistive anode and the coordinates of the spot on the anode where the event happened is recorded by a position analyzer. In this way an energy distribution of the detected photons is achieved. The two-dimensional detection results in curved line for the detected photons on the detector area and it is necessary to adjust a curvature for the different read-out channels.

In the case of slit limited resolution, the instrument is limited by a line broadening \( \Delta \lambda \), due to the geometrical factors

\[
\Delta \lambda = 1.1 \frac{wd}{mR} \tag{2.17}
\]

where \( w \) is the width of the entrance slit, \( d \) is the grating groove separation, \( R \) is the radius of curvature of the grating and \( m \) is the order of diffraction.

In order to maximize the resolution of the instrument, it is thus necessary to increase the order of diffraction and the radius of curvature of the grating, or alternatively, to decrease the width of the entrance slit and the groove separation. However, X-ray emission spectroscopy always involves a trade-off between intensity and energy resolution.

### 2.3.2 The X-ray emission process

In the following, the essential properties of the X-ray emission process is presented. The initial state of the X-ray emission transition is a core ionized state which is the same as the final state of the XPS process. The final state of the UPS transition which is a valence ionized state, is also related to the X-ray emission final state.

The X-ray emission process can be described as spontaneous emission of photons in a dipole transition between the core excited initial state and the valence excited final state. The interaction between the radiation field (photons) with electrons in an atom is determined by the interaction Hamiltonian

\[
H_{int} = \sum_i \left[ -\frac{e}{2mc} (p_i \cdot A(x_i, t) + A(x_i, t) \cdot p_i) + \frac{e^2}{2mc^2} A(x_i, t) \cdot A(x_i, t) \right] \tag{2.18}
\]
where the summation is over all electrons and $A(x_i, t)$ is a field operator which is a superposition of creation and annihilation operators from photons acting on electron $i$ with momentum $p_i$, which is located at $x_i$.

In a single emission (or absorption) event, the number of photons is changed by one. The $\mathbf{p} \cdot \mathbf{A}$ term in Eq. 2.18 does not contribute to lowest order of this process since it changes the total number of photons by 0 or ± 2. Due to the transversality of the field ($\nabla \cdot \mathbf{A} = 0$), the $\mathbf{p} \cdot \mathbf{A}$ operator can be replaced by $\mathbf{A} \cdot \mathbf{p}$ and vice versa. Thus only terms of the form $\mathbf{p} \cdot \mathbf{A}$ have to be considered to describe the process. For calculations of the transition probabilities, the vector potential $\mathbf{A}$ can be expressed as

$$A_{\text{emission}} = c\sqrt{\frac{(n_{q,\alpha} + 1)\hbar}{2\omega V}}\epsilon_\alpha e^{-i\mathbf{q} \cdot \mathbf{x} + i\omega t}$$

where $n_{q,\alpha}$ is the photon occupation number in the initial state, $\epsilon$ is the polarization vector for the photon of angular frequency $\omega$ in the transition and $V$ is the normalization volume. The photon is described by the quantum numbers $\mathbf{q}$ (wave vector) and $\alpha$ (polarization). If we assume that the transition is driven by a harmonic time dependent perturbation $V(t) = V_0 \times e^{-i\omega t}$, the transition probability per unit time can be expressed by Fermi’s ‘Golden rule’

$$w \propto \frac{\omega^2 \pi}{\hbar} \left| \langle f \mid e^{i\mathbf{k} \cdot \mathbf{x_i}} \epsilon_\alpha \mathbf{p} \mid i \rangle \right|^2 \delta(E_f - E_i + h\nu)$$

where $h\nu$ is the frequency of the fluorescence photon, $|i\rangle$ denotes the initial and $|f\rangle$ the final state wave functions. Since the wavelength of the soft X-ray photons is much larger than the atomic dimensions, the dipole approximation can be applied. In this case the $e^{i\mathbf{k} \cdot \mathbf{x_i}}$ term can be approximated using the dipole approximation, where only the first term in the expansion $e^{i\mathbf{k} \cdot \mathbf{x_i}} = 1 + i\mathbf{k} \cdot \mathbf{x_i} + \frac{1}{2}(i\mathbf{k} \cdot \mathbf{x_i})^2 + ...$ is taken into account. This approximation also assumes that $\mathbf{k} \cdot \mathbf{x} \ll 1$ or $|\mathbf{x}| \ll \frac{\lambda}{2\pi}$, where $\lambda$ is the X-ray wavelength. By angular integration of Eq. 2.20, the dipole selection rules emerge. The angular momentum has to change by one, $\Delta l = \pm 1$, the $z$-component of the orbital momentum has to change by $\Delta m = \pm 1, 0$ and the spin has to be conserved, $\Delta s = 0$. The transitions which takes place in a particular atom can be expanded in atomic-like wavefunctions around the atom of interest. The dipole selection rules apply to all kinds of systems, atoms, molecules and solids. For atoms, the selection rules are naturally well defined. In molecular systems, the wave functions are usually expressed as a linear combination of atomic orbitals (LCAO). The final state wavefunction can then be expanded into atomic valence orbitals as

$$\phi_f = \sum_{j=1}^{n} C_j \chi_i.$$  

If we only consider the one-center terms i.e., the contribution from the orbitals centered on the same atom as the core hole state, the intensities can easily be calculated.
In a solid sample, the discrete states in atoms are transformed into continuous bands. Even in this case, the transition takes place at one particular atom and the Bloch wavefunctions can be expanded in atomic-like wavefunctions around the atom of interest. Therefore, it is relevant to use $s$, $p$ and $d$ symmetry as in the atomic case. After summing over all final states, expressions for the transition rate can be obtained. From a $1s$ core hole where only final states of $p$-character can be reached, the intensity can be expressed as

$$I(h\nu) \propto \nu^3 pDOS(E)M_{sp}^2(E). \quad (2.22)$$

Accordingly, from a $2p$ core hole, only final states of $s$ and $d$ character are possible and the intensity can be written as

$$I(h\nu) \propto \nu^3 [ sDOS(E)M_{sa}^2(E) + \frac{2}{5} dDOS(E).M_{pd}^2(E) ] \quad (2.23)$$

Here $h\nu$ is the energy of the emitted photon while $E = h\nu - E_{bind}$ is the energy of the valence band electrons referred to the Fermi level. $DOS$ denotes the density of states of the indicated symmetry type and the $M(E)'s$ are the radial matrix elements for the particular transition. If the variation of the matrix elements over the energy range of interest can be neglected, the emission process directly maps the local partial density of states due to the atomic character of the core levels and the dipole selection rules. According to the initial and final state rules [25], the measured total X-ray emission intensity is approximately set by the occupation of the initial state which is a core-excited state in this case. However, the relative intensities of the peaks in the spectrum are approximately determined by the final states which in this case are valence excited states.

### 2.3.3 X-ray emission satellites

X-ray emission spectra are often divided into main transitions and satellite transitions. The main transitions can be explained in terms of a one-electron level diagram for a singly ionized state while the satellite transitions may have several different origins. In nonresonant spectra, satellite transitions can make up an essential part of the total spectrum and often fall into the same energy region as the main transitions. It is often desirable to separate the satellite contribution from the main lines. The most prominent X-ray emission satellites originate from transitions between doubly ionized states. This kind of transitions has been observed in hard X-ray spectra since the beginning of X-ray spectroscopy [26] and were identified in the 1920's by Wentzel and Druyvesteyn [27]. This kind of satellites are frequently observed also in emission spectra measured in the soft X-ray region.

Figure 2.8 shows a schematic energy level diagram of a single ionized state and double ionized Wentzel-Druyvesteyn satellites. The Wentzel-Druyvesteyn satellites are generally occurring in non-resonant X-ray emission spectra excited with broad band (non-monochromatic) excitation. Most of the satellites are generated by the shake-up/off transitions in the excitation step of the photoionization process.
described in section 2.2.4. The decay of the shake-up/off state produces X-ray emission lines with slightly different energies than the main emission line. The energy of a main X-ray emission line can be written as

$$\Delta E_{\text{main}} = E(c) - E(v)$$

(2.24)

where (c) and (v) are the core and valence ionized states, respectively. The doubly ionized states which appear in the satellite transitions have in addition a spectator vacancy (s). This leads to the satellite transition energy

$$\Delta E_{\text{sat}} = E(c, s) - E(v, s).$$

(2.25)

The satellite to main line displacement energy can then be written as

$$\Delta E_{\text{sat}} = E(c, s) - E(c) - [E(v, s) - E(v)]$$

(2.26)

i.e., the satellite shift is the difference between two ionization energies for the spectator electron. If (s) is instead a chemically different system of another type of atom then Eq. 2.26 denotes the chemical shift in X-ray emission spectra.

### 2.3.4 Resonant scattering

As mentioned previously, the use of tunable synchrotron radiation sources has opened up the possibility to study resonant processes in detail. During the last
decades, an inelastic scattering theory including resonance phenomena has been established for single atoms [28, 29]. The scattering theory has also been applied on solids implying that conservation of momentum \( \mathbf{k} \) is important in the overall process [30, 31]. The scattering process is schematically shown in Fig. 2.9 as an energy level diagram. An excitation is made from the initial state \( \mid i \rangle \) to the excited states \( \mid m \rangle \) with a well defined excitation energy. An interference between the excited states occurs due to the lifetime broadening of the different states. At this excitation energy, there are contributions from both states. For the scattering process, we once more consider the interaction Hamiltonian 2.18. In this case, the total number of photons does not change and the linear terms in \( \mathbf{A} \) do not contribute. The only contribution is from the \( \mathbf{A} \cdot \mathbf{A} \) term and the \( \mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p} \) term in second order. A calculation of the transition probability leads to the differential cross section [32]

\[
\frac{d\sigma}{d\omega_2 d\Omega} \propto \frac{\omega_2}{\omega_1} \sum_f \left| \frac{e^2}{2mc^2} \langle f \mid \mathbf{A}_2 \cdot \mathbf{A}_1 \mid i \rangle \right|^2 + \frac{e}{mc} \sum_m \left[ \frac{\langle f \mid \mathbf{p}_2 \cdot \mathbf{A}_2 \mid m \rangle \langle m \mid \mathbf{p}_1 \cdot \mathbf{A}_1 \mid i \rangle}{E_m - E_i - \hbar \omega_1 - \hbar \frac{\Delta m}{2}} \right] \times \delta(\omega_1 - \omega_2 - \omega_f)
\]

where the incident photon energy is \( \hbar \omega_1 \), and the scattered photon energy is \( \hbar \omega_2 \).

\( d\Omega \) is a solid angle, \( \Gamma_m \) is the lifetime of the intermediate states and \( \hbar \omega_{fi} = E_f - E_i \).

The first term is a first order \( \mathbf{A} \cdot \mathbf{A} \) interaction and the second and third terms describe the resonant and non-resonant 'anomalous' inelastic scattering [32]. The sums over \( m \) and \( f \) are for all intermediate and final states, respectively. Equation 2.27 was first obtained by H. A. Kramers and W. Heisenberg in 1925 [33] and is thus called the Kramers-Heisenberg formula. The only nonzero contributions come
from the $p_1 \cdot A_1$ term which acts on the excited electron and $p_2 \cdot A_2$, which acts on the electron filling the core vacancy. The second term is called the resonant term, since it resonates for $\hbar \omega_1 = E_m - E_i$. In a solid with a continuum of states this condition is fulfilled if $\hbar \omega_1$ is at or above an absorption threshold. On resonance, this term is enhanced by the order of $\hbar \omega_1/\Gamma_m$, which is typically a factor of $10^6$ [28]. This corresponds to excitation energies close to a core-ionization threshold i.e., when the resonant inelastic scattering cross section has a maximum. As mentioned previously, the quantum theory of unstable states known as radiation damping is a linewidth problem which was first solved by V. F. Weisskopf and E. P. Wigner [19].

The scattering processes are illustrated in Fig. 2.10 by space-time (Feynman) diagrams. The solid line represents an atomic state and the wavy line represents a photon. Fig. 2.10 (a) illustrates the normal elastic scattering contribution due to the $A_1 \cdot A_2$ interaction. Fig. 2.10 (b) is the resonant scattering where the atomic state $|i\rangle$ first absorbs the incident photon at time $t_1$ and becomes state $|m\rangle$. Subsequently, at $t_2$ the atomic state $|m\rangle$ emits the outgoing photon and transforms into the final state $|f\rangle$. Fig. 2.10 (c) illustrates the non-resonant scattering where state $|i\rangle$ first emits the outgoing photon at $t_1$ and transforms into state $|m\rangle$ and, subsequently, at $t_2$ state $|m\rangle$ absorbs the incident photon and transforms into state $|f\rangle$.

When the Kramers-Heisenberg formula is applied to inelastic scattering in atomic physics (when $\hbar \omega_1 \neq \hbar \omega_2$, $|i\rangle \neq |f\rangle$), it is often referred to as the Raman effect. The Raman scattering is described by the last two terms in the Kramers-Heisenberg formula. In resonant fluorescence, which is sometimes referred to as the resonant Raman effect, only the resonant term contributes. Since the process involves inelastic scattering of a photon, it looses (or gains) some of it’s energy to (or from) the atom or molecule. In the 1920s, the Indian physicist Sir Chandrasekhara Venkata Raman (1888-1970) in Calcutta observed a frequency shift of the radiation in the visible (optical) wavelength region, when light was scattered in liquid solutions. This had earlier been predicted by A. Smekal. The lower fre-
quency components of the scattered radiation are called the *Stokes lines* (red shift) and the higher frequency components are called the *anti-Stokes lines* (blue shift). As mentioned in Chapter 1, the concept of inelastic Raman scattering was first used in the optical wavelength region and was later applied to the hard and soft X-ray wavelength regions.

### 2.4 X-ray absorption spectroscopy

In X-ray absorption spectroscopy (XAS), the sample is irradiated with X-rays, but here the absorption of the X-ray beam is measured as a function of the incident X-ray energy. X-ray absorption occurs when a bound electron is promoted resonantly to an unoccupied level. The important characteristics of an absorption spectrum is the transition energies and their intensities. For a metallic sample, this will be levels in the valence band close to the Fermi level and for an insulator it will be levels in the conduction band. As the photon energy is increased, the excitation involves higher regions of the empty valence band and the absorption spectrum is determined by the structure of the outer, unoccupied levels [34]. To measure an X-ray absorption spectrum requires a continuously tunable photon source as will be described in section 2.5.

#### 2.4.1 The photoabsorption cross section

Calculations of absorption and scattering in metals are often based on the atomic scattering factors \( f_1 + i f_2 \) for the different atoms. These factors can be derived from experimental absorption data by using the Kramers-Kronig dispersion relations

\[
\begin{align*}
    f_1 &= Z + C \int_0^\infty \frac{e^2 \mu_a(\epsilon) d\epsilon}{E^2 - \epsilon^2} \quad (2.28) \\
    f_2 &= \frac{\pi}{2} C E \mu_a(\epsilon) \quad (2.29)
\end{align*}
\]

where \( Z \) is the total number of electrons; \( C = 1/(\pi r_0 hc) \) where \( r_0 \) is the classical electron radius, \( h \) is Planck's constant, \( c \) is the speed of light, \( \mu_a(\epsilon) \) is the atomic photoabsorption cross section and \( E \) the incident photon energy. If we consider a homogeneous material containing one element only, the photoabsorption cross section \( \mu_a(\epsilon) \) (cm\(^2\)/atom) is related to the mass absorption coefficient \( \mu \) (cm\(^2\)/g)

\[
\mu_a = \frac{A}{NA} \mu \quad (2.30)
\]

where \( A \) is the atomic weight and \( N_A \) is Avogadros number. The transition probability of X-ray absorption can be calculated in analogy with what was described for X-ray emission i.e., by using the interaction Hamiltonian in Eq. 2.18. The vector potential \( A \) can then be expressed as
\[ A_{\text{absorption}} = c \sqrt{\frac{n_{q,0} \hbar}{2 \omega V}} e^{i q \cdot \mathbf{x} - i \omega t} \]  

(2.31)

where \( n_{q,0} \) is the photon occupation number in the initial state, \( \epsilon_\alpha \) is the polarization vector for the photon of angular frequency \( \omega \) in the transition and \( V \) is the normalization volume. The photon is described by the quantum numbers \( q \) (wave vector) and \( \alpha \) (polarization). Similar to the X-ray emission process, we assume that the transition is driven by a harmonic time dependent perturbation \( V(t) = V_0 e^{-i \omega t} \), and the transition probability per unit time can be expressed by Fermi’s ‘Golden rule’ as

\[ w \propto \frac{2\pi}{\hbar \omega} \left| \langle f \mid e^{-i k \cdot \mathbf{x}} \epsilon_\alpha \mathbf{p} \mid i \rangle \right|^2 \delta(E_f - E_i - h\nu) \]  

(2.32)

where \( h \omega \) is the frequency of the absorbed photon and \( |i\rangle \) denotes the initial state and \( |f\rangle \) the final state wave functions. After normalization with the photon flux, the X-ray absorption cross section can be written as

\[ \sigma_x = \frac{4\pi^2 e^2}{m^2 c \omega} \left| \langle f \mid e \cdot p \mid i \rangle \right|^2 \rho_f(E). \]  

(2.33)

### 2.4.2 Electron and fluorescence yields

The experimental setup can be designed so that the absorption measurements can be performed either in a transmission mode or in an indirect way by measuring secondary processes (electron and photon emission) following the primary absorption process. Historically, absorption measurements were made by passing radiation through thin foils and measuring the decrease in intensity as a function of thickness. Thus, with an incremental increase of thickness \( \Delta x \) of the foil, an incremental decrease of the transmitted intensity \( I \) relative to the incident intensity \( I_0 \) can be expressed as

\[ \frac{\Delta I}{I_0} = -\rho \mu \Delta x \]  

(2.34)

where \( \rho \) is the density and \( \mu \) is the energy and material dependent mass-absorption coefficient. In the differential limit (\( \Delta x \rightarrow 0, \Delta I \rightarrow 0 \)), the equation integrates to an exponential form

\[ \frac{I}{I_0} = e^{-\rho \mu x}. \]  

(2.35)

In this expression, it is assumed that the number of decays are proportional to the number of excited core holes and that the thickness of the layer that produces the measured signal is small compared to the absorption length. Equation 2.35 can
also be expressed in terms of the atomic density $n_a$ and the photoionization cross section $\sigma_{abs}$ as

$$\frac{I}{I_0} = e^{-n_a\sigma_{abs}x}. \quad (2.36)$$

Equations 2.35 and 2.36 represent macroscopic and microscopic descriptions of the absorption process. The mass absorption coefficient $\mu$ is an experimentally derived parameter which depends on the studied material whereas the photoionization cross section $\sigma_{abs}$ (Mb/atom) can be calculated for each subshell for an isolated atom. However, X-ray absorption spectra are usually measured indirectly by observing the secondary processes since it is much easier to perform experimentally. If all emitted electrons are measured the technique is known as total electron yield (TEY) whereas if all the emitted photons are measured it is known as total fluorescence yield (TFY). Figure 2.11 shows the very different penetration depths in a solid sample associated with electron and photon decay processes. These differences determine the characteristics of the electron and fluorescence yield techniques. Soft X-rays have a penetration depth of typically 500-1000 Å into the sample. The escape depth of the photoelectrons emitted through the photoelectric effect (or Auger electrons) is rather shallow i.e. in the order of 50 Å (see also Fig. 2.1). This is due to the fact that the escaping electrons will scatter inelastically. The electrons escaping from the bulk (below the top-most layers of the surface) give rise to cascades of secondary electrons. Only those secondary electrons that reach the surface of the sample and have enough kinetic energy to overcome the work function of the material will leave the sample. Thus, the electron yield technique is surface sensitive.

With the total electron yield technique, the current of electrons leaving the electrically insulated sample can be measured either directly with a channeltron or a stack of multichannel plates directed towards the surface or indirectly by measuring the total current from the sample with a sensitive pico-ammeter. Photoelectrons (or Auger electrons) leaving the surface directly without being inelastically scattered originate from the topmost layers only. If the electrons are measured directly, the surface sensitivity can be further increased. This is done by applying a retarding voltage to the detector (so called partial electron yield mode) and only electrons with higher kinetic energy than the applied voltage can be detected. High energy photoelectrons (or Auger electrons) originating from the topmost atomic layer(s) of the sample can thereby be detected selectively. In the soft X-ray energy range, where the electron escape depth is much smaller than the penetration depth of photons, the electron yield signal is to a good approximation linearly related to the absorption coefficient. The electron yield mode has the advantage that the measurements are relatively easy to perform. The drawbacks of the electron yield technique are the restrictions related to its surface sensitivity and that the samples may exhibit charging effects if the conductivity of the studied material is low. Electron yield techniques are not well suited for studies of buried layers. In addition, saturation effects may occur if the incidence angle is very small (ideally it should be close to normal).
Fluorescence yield detection has recently shown to be a promising alternative for studies of bulk properties. As pointed out by Jaklevic et al. [35], the fluorescence technique for recording X-ray absorption spectra is especially useful for investigation of dilute samples and thin buried layers. In these cases, the signal is directly proportional to the absorption coefficient in question. In addition, the drawback with the surface sensitivity is not so severe. However, depending on the geometry, the fluorescence technique may also give rise to saturation which may deviate from a linear relation to the absorption coefficient as discussed in the next section.

2.4.3 Self absorption and saturation

As was illustrated in Fig. 2.11, the escape depth of the fluorescence photons is on the same order of magnitude as the penetration depth, i.e., about 1000 Å. The probing depth of fluorescence yield depends especially on the detection angle, i.e., at small detection angles less than a few degrees the detected photons originate on average from shallower layers than those detected at near normal exit angles.

Fig. 2.12 illustrates the influence of the experimental geometry on the saturation and self-absorption effects. If the incoming radiation enters the sample at a highly grazing incidence angle, nearly all the incoming photons are absorbed close to the surface. This means that all the outgoing photons can be detected. The signal is thus nearly independent of the absorption coefficient and the measured spectrum suffers from severe saturation effects due to the lack of self-absorption. If the incoming photons instead enter the sample at close to normal incidence the signal becomes much more proportional to the absorption coefficient. This is due
Figure 2.12: The influence of the experimental geometry on the saturation effects observed in fluorescence yield.

to the fact that the outgoing photons emitted from deep in the bulk do not reach the surface since they are to a very large extent self-absorbed in the sample [36, 37]. These drawbacks can be avoided by using a grazing-out normal-in geometry which reduces the bulk sensitivity of the fluorescence yield detection. Another drawback of both the electron and fluorescence yield measurements is that absolute measurements are generally not possible to obtain since the information depth (mean-free path) of the signals can only be estimated by calculations.

Additionally, the signal-to-background ratio of fluorescence yield detection is higher than in electron yield measurements of dilute samples and it can easily be used in the presence of magnetic fields. However, for concentrated bulk samples, the measured fluorescence yield is not proportional to the absorption coefficient and the experimental fluorescence yield spectra exhibit distortions due to the ‘self-absorption effects’. These distortions vary with the geometry of the experiment as shown in Fig. 2.12. They are caused by the absorption of the generated fluorescence radiation on its way out of the sample.

Let us consider photons with energy $E$ entering the sample with the incident angle $\alpha$ which produces a core hole in core level $X$. Then the core hole decays with the probability $\omega_X$ by emission of a photon with energy $E_f$. The total absorption coefficient is: $\mu_{\text{tot}} = \mu_X + \mu_{\text{other}}$, where $\mu_X$ is the absorption coefficient associated with the production of a core hole in the investigated level and $\mu_{\text{other}}$ is the absorption in the more shallow valence levels and other kinds of atoms. The measured intensity of a sample of thickness $d$ at a take-off angle $\beta$ may then be written as [35]

$$I^X(E) = \frac{A}{r^2} \omega_X I_0(E) \frac{\mu_X(E)}{\mu_{\text{tot}}(E) + \mu_{\text{tot}}(E_f) \frac{\sin \alpha}{\sin \beta}} [1 - e^{-\frac{\mu_{\text{tot}} (E_f)}{\sin \beta} d}]$$

(2.37)

where $I_0(E)$ denotes the intensity of the incoming radiation, $A$ is the active detector area, $r$ is the distance to the sample and $\kappa$ is the efficiency of the detector. In this formula, the incident radiation is absorbed according to $\mu_{\text{tot}}(E)$. The absorption of the produced fluorescence radiation with energy $E_f$ is characterized by $\mu_{\text{tot}}(E_f)$. Eq. 2.37 is derived by integrating Eq. 2.36 with the corresponding absorption coefficients over the path lengths which the photons travel through the sample.
2.5 Synchrotron radiation

The first experimental observation of what is now called synchrotron radiation was made at the 70 MeV synchrotron at the General Electric Research Laboratory in 1947 [38] where electromagnetic radiation was emitted by electrons moving in a circular orbit with highly relativistic velocities, close to the speed of light [39]. Historically, synchrotron radiation was first collected as energy loss in circular electron storage rings used for nuclear and particle physics experiments [40]. Later on, specially dedicated sources for synchrotron radiation experiments were constructed, so-called second-generation facilities. These early sources generally have an electron beam of relatively large cross section and angular divergence.

2.5.1 Storage rings

Figure 2.13 shows a general layout of one of the newest synchrotron radiation facilities, the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory (LBNL) at Berkeley, USA. It is a third generation radiation source, dedicated for broad scientific use and it consists of alternating curved and long straight sections specially optimized for producing radiation of very high intensity with the use of magnetic structures, so-called insertion devices, placed into the straight sections of the storage ring. An insertion device is a periodic array of magnets with alternating polarity of transversial or helical structure. Bending magnet radiation is also generated in the bent sections between the straight sections. The electrons injected into the storage ring are first pre-accelerated in a linear accelerator and a booster synchrotron. The relativistic electrons in a storage ring are guided by bending magnets and focussed by quadruple-, sextu- or octupole magnets in order to keep the mutually repelling electrons in a tightly focussed beam travelling in the desired trajectory. The arrangement of the magnets is referred to as the lattice of the machine and the movement of a particle in a beam is often described in the six-dimensional phase space with three space coordinates and three momentum coordinates. Synchrotron radiation is produced when the electrons pass through the bending magnets and insertion devices since in both cases the circulating electrons are centripetally accelerated towards the center of the circular motion by the Lorentz force and therefore emit radiation.

The energy lost in the electron beam due to synchrotron radiation is replenished with a radio-frequency accelerator cavity in one of the straight sections of the storage ring. The cavity accelerates the slowest electrons which leads to a grouping of the orbiting electrons into 'bunches'. The dimensions of the accelerator cavity, gives the resonant frequency of the bunches. The lengths and groupings of the bunches are also given by the wavelength of the radio-frequency field pumped into the cavity via a waveguide from a clystron which provides the energy of the system. Thus, the so-called harmonic number of the ring (electron orbital period) has to be an integral multiple of the wavelengths of the radio-frequency field in the cavity. The ALS facility consists of an ultrahigh vacuum electron storage ring of 197 m circumference optimized for electron energies of 1.5-1.9 GeV. The accelerating system (injection chain) at ALS consists of an electron gun, a linac, and a booster synchrotron. During an injection, a high-voltage source powers the electron gun at
120 kVolts, thereby creating a pulse of accelerated electrons. Acceleration of the electrons begins with the linac, and by the time the electrons emerge from the linac, they have been accelerated to an energy of 50 MeV, and are ready to go into the booster synchrotron. The booster synchrotron is a circular machine that accelerates the electrons to their final energy in about half a second. At the end, the electrons have an energy of 1.5 billion electron volts (1.5 GeV), are travelling at 99.99% of the speed of light, and are ready to be transported to the storage ring. The radio frequency fields in the two accelerating cavities of the storage ring oscillates at a frequency of 500 MHz forcing the electrons to travel at constant energy. Due to the slow exponential decrease of the circulating electron beam current in the storage ring, it is necessary to inject a new beam of electrons every 8-10 hours. This is due to the collisions between the electrons and the residual gas in the ultra-high vacuum tube of the storage ring. In general, however, the beam lifetime of the ring is largely defined by the original design of the operational energy of the electrons. If the energy is increased, the electrons move more closely to the speed of light and the interactions with the rest gas are decreased. The lifetime of the beam can be increased if positrons are used instead of electrons, since the interactions with the rest gas is largely reduced, although it is somewhat more costly to achieve. For example, at the HASYLAB synchrotron radiation facility in Hamburg, the beam lifetime has been increased in this way.
Direction of acceleration

Electron orbit

\[ \Theta \]

\[ v = c \]

2.5.2 Characteristic radiation parameters

Fig. 2.14 shows the characteristic emission patterns of electrons moving in a circular orbit in two different reference frames. In the frame of reference moving with the electron, the emitted radiation is that of a classical radiating dipole \([41]\), i.e., a point charge oscillating with an amplitude much smaller than the radiated wavelength. The radiation pattern has a \(\sin^2 \theta\) (doughnut-shape) angular distribution, since there is no radiation in the acceleration direction, \(\theta = 0\). However, due to the relativistic velocity of the circulating electrons, the radiated emission pattern in the laboratory frame of reference is pushed dramatically along the velocity vector into a narrow cone of light.

The pronounced forward direction of the radiation pattern of the synchrotron radiation arises from the relativistic effect (Lorentz contraction) when the motion of the electron in the rest frame of reference is transformed to that of the laboratory. It is also called a search light effect since an observer fixed in space can see the synchrotron light only for very short time intervals. The time interval \(\Delta t\) between two successive light flashes depends on the number of electron bunches in the storage ring and the repetition time of one bunch. In a single-bunch mode, \(\Delta t = R/2\gamma^3c\), where \(R\) is the circumference of the electron orbit, \(\gamma\) is the Lorentz function and \(c\) is the speed of light in vacuum. The inter-bunch period is typically in the \(\mu s\) range, whereas in multi-bunch mode pulse separations are usually in the order of \(1\ ns\). The timing properties gives the possibility to study time dependent processes and perform time-of-flight and coincidence experiments.

The Lorentz function which describes the relativistic relationship between the reference frames of the orbiting electron and the laboratory is defined as
\[ \gamma = \frac{1}{\sqrt{1 - \left(\frac{v}{c}\right)^2}} \]  
(2.38)

where \( v \) is the energy of the electron and \( c \) is the velocity of light in vacuum.

This can also be written as

\[ \gamma = \frac{E_e}{m_0 c^2} \approx 1957 \times E_e(GeV) \]  
(2.39)

where \( E_e \) is the kinetic energy and \( m_0 \) is the rest mass of the particle. The total emitted radiation per revolution by a relativistic electron in a circular orbit can be derived to be

\[ I = \frac{e^2}{3\epsilon_0 \rho} \cdot \frac{E^4}{(m_0 c^2)^4}. \]  
(2.40)

The total radiated power can then be expressed as

\[ P_r = \frac{1}{4\pi \epsilon_0} \cdot \frac{2}{3} \cdot \frac{e^2 c}{\rho^2} \cdot \frac{E^4}{(m_0 c^2)^4}. \]  
(2.41)

Since the emitted power is proportional to \( m_0^{-4} \), light particles like electrons or positrons emit much more radiation than heavier particles like protons.

The divergence \( \sigma \), of the relativistically focussed forward radiation cone in the laboratory frame of reference is defined as \( \sigma = 2\gamma^{-1} = 2\theta \). For example, at the ALS storage ring with 1.5 GeV electron energy, \( \gamma \approx 3000 \) and \( \sigma \approx 0.67 \) mrad which can be considered as highly collimated. The critical photon energy in a bending magnet is calculated as that for which half of the power of the radiation is distributed at higher energy photons, and half is distributed at lower energy photons.

\[ E_c(keV) = \hbar \omega_c = \frac{3eB\gamma^2}{2m} \approx 0.665 \times E_e^2(GeV) \times B(T) \]  
(2.42)

where \( E \) is the kinetic energy of the electrons and \( B \) the magnetic field of the bending magnet. The critical photon energy \( E_c \) has the corresponding critical wavelength

\[ \lambda_c = \frac{4\pi mc}{3eB\gamma^2} \approx \frac{1.86\text{nm}}{E^2(GeV) \times B(T)}. \]  
(2.43)

The critical photon energy is a useful parameter for characterizing synchrotron radiation from relativistic electrons as they pass through the magnetic field of a bending magnet. For example, the ALS which has a beam energy of 1.5 GeV and a bending magnet field of 1.0 Tesla has a critical photon energy of 1.6 keV, and a critical wavelength of 0.80 nm, whereas the Advanced Photon Source (APS) at the Argonne National Laboratory in Illinois, with a beam energy of 7.0 GeV and a magnet field strength of 0.60 Tesla, has a critical photon energy of 20 keV, and a critical wavelength of 0.064 nm.
2.5.3 Insertion devices

At a modern third generation synchrotron radiation facility, there are usually three different kinds of magnetic structures to produce synchrotron radiation: bending magnets, wigglers, and undulators. Bending magnets force the electrons into a single curved trajectory which results in a fan of radiation around the bend. Wiggler and undulator insertion devices increase the intensity (photon flux). Fig. 2.15 shows a schematic picture of an insertion device (undulator) which consists of an array of dipole magnets.

An electron which passes through an insertion device in one of the straight sections of a storage ring undergoes many small oscillations and, therefore radiate a lot more than a single bending magnet. The resulting radiation in the laboratory frame of reference is greatly reduced in wavelength $\lambda$ from that of the magnet period $\lambda_0$ by a factor of $\gamma$ due to the Lorentz contraction. A further reduction of the wavelength by a factor of $\gamma$ is due to the Doppler effect (blue shift) since the radiating electrons are moving close to the speed of light towards the observer in the laboratory frame of reference. Thus, the Lorentz contraction and the relativistic Doppler shift lead to a reduction of the radiated wavelength by a factor of $2\gamma^2$. Since $\gamma$ is usually in the order of several thousands, the magnet periods measured in centimeters lead to observed X-ray wavelengths measured in the order of Ångströms. For example, at the ALS storage ring $2\gamma^2 \approx 1.8 \times 10^7$. If the magnet period $\lambda_0$ is 5.0 cm, the wavelength will be relativistically shifted to an observed wavelength in the order of $\lambda = \frac{5.0}{(1.8 \times 10^7)} \approx 2.8$ nm. Thus, an insertion device (periodic magnet) generates radiation peaking in the X-ray region of the electromagnetic spectrum.

In contrast to the smooth spectral distribution of radiation from a bending magnet, the spectral radiation from an undulator (and to some extent from a wiggler) is
concentrated into a series of discrete energies (undulator peaks) at which the intensity is greatly increased. The peak maxima are generated by the periodic magnetic structure with \( N \) poles of length \( \lambda_u \) of the insertion device create an oscillatory (wiggling or undulating) path for the electrons. Undulator devices normally have more magnet poles, lower magnetic fields and the electron oscillations have smaller amplitudes than in a wiggler. Wigglers and undulators can be distinguished from each other by the magnitude of the dimensionless deflection parameter \( K \) which is defined as

\[
K = \frac{\alpha}{1/\gamma} = \frac{eB_0\lambda_u}{2\pi m_0 c} = 0.9337 \times B_0(T) \times \lambda_u (cm)
\]

where \( B_0 \) is the peak magnetic field (in Tesla) and \( \lambda_u \) the length of the magnetic period (in meters), \( \alpha \) is the maximum deflection angle of the electron path and \( 1/\gamma \) is the natural opening angle for the cone of the emitted radiation, where \( \gamma \) is the Lorentz function.

For \( K \gg 1 \), the cones from individual wiggles contribute separately to the intensity available in the horizontal plane which is the case of the wiggler device. The spectral shape of wiggler radiation is similar to bending magnet radiation, but due to the higher magnetic fields the emitted wavelength is shifted to higher photon energy and the photon flux is increased by a factor of 2 times the number of magnetic poles, \( N \). If \( K \leq 1 \), the cones from individual wiggles overlap and contribute coherently, and interference effects between electromagnetic waves emitted by the same electrons at different wiggles cause a constructive interference of the intensity. The result is an \( N^2 \)-fold (the squared number of magnet periods) increase of the angular density of the flux in the forward direction. The electromagnetic waves of radiation emitted at each pole in the magnet array of an undulator reinforce or cancel one another to enhance the emission of certain wavelengths (harmonics) according to the undulator equation

\[
\lambda_n = \frac{\lambda_u}{2n\gamma} \left[ 1 + \frac{K^2}{2} + \gamma^2(\theta^2 + \psi^2) \right]^{1/2}
\]

where \( \theta \) is the angle of observation within the plane of the undulations (or wiggles), \( \psi \) is the angle perpendicular to it, and \( \lambda_n \) is the wavelength of the \( n \)th harmonic radiation where \( n=1, 3, 5, \ldots \) is the order of interference (\( n=1 \) is the fundamental wavelength). The positions of the undulator peaks (wavelengths of the \( n \)th harmonic \( \lambda_n \)) for a given undulator can be tuned according to the experimental needs. This is done by vertically changing the gap between the opposing permanent magnets around the beam axis of the insertion device which changes the magnetic field strength \( B_0 \) and the deflection parameter \( K \).

Another important property of synchrotron radiation is the polarization. If the electrons circulate a storage ring in a clockwise direction, an observer in the laboratory frame of reference viewing the radiation from above (below) the orbit plane will see right (left) elliptically polarized radiation, whereas an observer in the orbit plane will see linearly polarized radiation. Here, a clockwise rotation of the electric field vector for an observer looking towards the light source gives right elliptically polarized light and vice versa.
2.5.4 Beamlines

When the synchrotron radiation leaves the storage ring it is guided to the experimental station via a beamline. A beamline consists of a series of precision optical elements (mirrors and gratings) which direct, monochromatize and focus the radiation to the sample. The optical components are generally kept in ultra-high vacuum \((\sim 10^{-10} \text{ Torr})\) so that the photons are not attenuated by air molecules. Another important reason that the beamline must be kept under constant high vacuum is to keep the reflecting surfaces of the mirrors clean from contamination e.g., by carbon and oxygen. In the soft X-ray region, at wavelengths below 300 Å, reflection from mirrors and gratings only occurs at grazing incidence angles. Monochromatized photons at these energies are obtained by diffraction of the synchrotron radiation either by crystals (hard X-rays) or reflection gratings (vacuum ultraviolet). Depending on the energy range of interest and the requirements of the experiments, the beamline designs vary significantly. Thus, there are many different ways to achieve monochromatization with the use of reflection and transmission gratings, Bragg reflection on crystals or multilayers and zone plates. However, the most common design in the soft X-ray range is the grazing-incidence reflection grating monochromator. The grating in a monochromator acts as a narrow bandpass filter of the radiation and the reflection is governed by the grating equation 2.16. Thus, there are several different orders of the diffracted light. The zero order light (when the grating acts as a mirror) also contains radiation in the visible energy range and is sometimes very useful for optical alignment of the samples. Usually the first or third order of diffraction is used for the experiments. The grazing incidence angle \(\alpha\) of the gratings and the mirrors is usually in the order of 3-5 degrees in order to increase reflection (and minimize absorption) in the surface material.

![Figure 2.16: Schematic layout of a spherical grating monochromator (SGM).](image)

Fig. 2.16 shows a schematic layout of a spherical grating monochromator (SGM). The first mirror (pre-focussing mirror) collects and focuses the divergent synchrotron radiation from the storage ring onto the entrance slit of the monochromator. From the entrance slit, the radiation again diverges and illuminates the grating. The grating diffracts (according to the grating equation) and focusses the radiation of the desired wavelength onto the exit slit of the monochromator. After the exit slit, the monochromatized radiation is again divergent and is refocussed in a second mirror onto the focal point where the sample is kept and the experiments performed. In order to tune the wavelength, the grating in the monochromator is slightly rotated so that another diffracted wavelength is focussed on the exit slit.
For example, the ALS beamlines 7.0 and 8.0 used in the experiments presented in this thesis consist of 5 m long undulators, having 89 magnetic periods with a length $\lambda_u$ of 5.0 cm. The spherical prefocus mirror in the beamline takes most of the heat load from the intense undulator radiation and is therefore water cooled in order to minimize deformation of the optical surface. The entrance slit further reduces the heat load on the grating surface. The spherical grating monochromator (SGM) covers a spectral range from 60 to 1300 eV. The monochromator includes three gratings which are holographically ruled, platinum coated, and have a radius of curvature of 70 meters. The components are precision mounted in an approximate grazing incidence Rowland circle geometry. The gratings are water cooled to eliminate possible deformation due to the heat load. The adjustable exit slit on the monochromator can open and close from 500 $\mu$m to 5 $\mu$m width and translate up and down the beamline through a distance of 0.7 m. In order to simplify the operation of the monochromator, usually only the exit slit is moved when the grating is rotated which implies that all the optical elements are not exactly on the Rowland circle except for one particular wavelength. However, the resolution of the beamline is not severely affected by this error. The refocusing mirrors after the monochromator do not need water cooling due to the much reduced heat load of the narrow bandpass monochromatized photon beam.

In addition to the spectral wavelength of interest, a monochromator always delivers a certain amount of higher-order light and stray light. Higher order suppression can be achieved in different ways depending on the monochromator design. For example, the disturbances by photons of higher energy can be suppressed by the insertion of suitable absorption foils (filters) in the photon beam after the refocusing mirrors. In this case the low values of the absorption coefficients at energies below an inner-shell absorption edge and the high values above this edge is used. Thus, by choosing the desired first-order light to an energy value below such an absorption edge, the small absorption coefficient leads to high transmission for the first-order light while the unwanted higher-orders are effectively suppressed. In the plane grating monochromator (PGM) which is installed at beamline BW3 at HASYLAB, higher order suppression is achieved in another way. This type of grazing incidence monochromator consists of a plane mirror, a plane grating and a plane-elliptical mirror. After the monochromator, the radiation passes an exit slit and a refocusing toroidal mirror from which it is focused into the experimental chamber. With this monochromator design, there is an option to choose a slightly smaller grazing incidence angle on the grating. This is done by changing the so-called C-value which is defined as; $C = \sin \alpha / \sin \beta$, where $\alpha$ is the incidence angle and $\beta$ the angle of the diffracted light relative to the grating surface. By changing the C-value from 2.25 to lower values e.g., 1.6, the higher orders are attenuated since the higher frequency radiation is less reflected (and more absorbed) in the surface material of the grating when the angle of incidence is increased. However, this also affects the so-called fixed-focus criterion and, in principle, it is necessary to move the exit slit along the beam axis in order to adjust to the new focal length.

The performance of a beamline may also be improved in other ways. One way is to try to minimize the amount of stray light by using baffles to restrict the area of illumination on the optical elements. However, stray light contributions
are usually difficult to eliminate completely since there are many different origins which produce a broad continuous wavelength distribution which essentially covers the whole spectral range of the monochromator.

A useful concept in the design of a beamline is the so-called resolving power criterion of a slit. When two waves coming from two distant sources pass through the same slit at different angles, they become distinguishable when the central maximum of one wave falls into the first minimum of the other. This resolving power criterion was first used by the English physicist Lord Rayleigh (1842-1919) and in the case of a slit it is defined as; \( R = \lambda / D \), where \( \lambda \) is the wavelength of the radiation and \( D \) is the width of the slit. The resolving power of a grating is defined as; \( R = \lambda / \Delta \lambda = E / \Delta E = N \cdot n \) where \( \lambda \) is the wavelength of the photons, \( \Delta \lambda \) is the minimum resolvable wavelength difference, \( n \) is the order of diffraction and \( N \) is the total number of lines of a grating. Thus, the resolving power of a grating is increased by a greater number of lines and a higher order of diffraction. The maximum resolving power of the two ALS beamlines is typically in the order of 8000-10000.

For experiments which require optimal conditions concerning the flux density of photons (e.g., X-ray emission spectroscopy from low-Z materials), the undulator radiation can be greatly improved if the source size, angular distribution and the bandpass are made as small as possible. These quantities are characterized by the spectral brilliance (or brightness), \( B \), which is an important parameter for the design of storage rings and beamlines, and is defined as

\[
B = \frac{(\text{spectral flux in 0.1 \% bandpass/s}) \times (100 \text{ nA ring current})}{(\text{source area/mm}^2) \times (\text{solid angle/mrad}^2)}.
\] (2.46)

Thus, the spectral brilliance takes into account the spatial distribution of the electrons circulating in the storage ring, the spatial distribution of the emission process, the optical components in the beamline to the experiment and the experimental equipment. However, according to the Liouville's theorem [43], which describes the invariance of the volume in phase space, the spectral brilliance \( B \) cannot be increased further by any optical system. For example, closing the exit slit of the monochromator in order to gain resolution inevitably decreases the photon flux.
Chapter 3

Computational methods

3.1 Introduction

The most important issue in electronic structure calculations of atoms, molecules and solids is to solve the Schrödinger equation. In this chapter, some of the most commonly used methods for calculating the electronic structure used in this thesis are introduced. These techniques are based on numerical schemes and rely substantially on the use of computers. Here some of the basic equations and approximations which are the basis of the computations will be described. In section 3.2, the fundamental Hartree-Fock (HF) method for calculating the quantum mechanical states of atoms and molecules is introduced [44]. This method is used in papers I, II, III and IV. In section 3.3, the Density Functional Theory used in papers XI and XIII is introduced. In section 3.4, the Single Impurity Anderson Model (SIAM) discussed in papers XIV, XV, XVI and XVII is briefly introduced.

3.2 The Hartree-Fock method

3.2.1 The Born-Oppenheimer approximation

The vibrational motion of a nucleus in an atom are relatively slow in comparison to the surrounding electrons due to the very large difference in mass. This means that the electrons respond very quickly to any perturbation of the atomic system, whereas the nuclei remain virtually fixed during different electronic transitions. Thus, the kinetic energy and the change of the Coulomb repulsion energy of the nuclei can be neglected when the Schrödinger equation is solved for the electronic wave functions. This provides the basis for a separation between the electronic and the nuclear degrees of freedom in the so-called Born-Oppenheimer approximation. This approximation is most often used for solving the Schrödinger equation to obtain the electronic wave functions and the energies needed to calculate a spectrum. Thus, the total wave function of a system containing $N$ electrons and $P$ nuclei can be separated into a product of an electronic and a nuclear part

$$\psi_{\text{tot}} = \psi_e \cdot \psi_n \quad (3.1)$$
and the Schrödinger equation for the electrons is

\[ H \Psi_e = E_0 \Psi_e. \]  

The solutions \( \Psi_e \) and \( E_0 \) are parametric functions of the nuclear positions. If relativistic effects are ignored, the Hamiltonian can be written as

\[
H = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N} \sum_{n=1}^{P} \frac{Z_n e^2}{|r_i - R_n|} + \sum_{i=1}^{N} \sum_{k>1}^{P} \frac{e^2}{|r_i - r_k|} + \sum_{i=1}^{P} \sum_{n>1}^{P} \frac{Z_l Z_n e^2}{|R_l - R_n|}
\]  

where the first term is the electron kinetic energy, the second term is the Coulomb electron-nuclear attraction, the third term is the Coulomb electron-electron repulsion and the fourth term is the nuclear-nuclear Coulomb repulsion term, \( m \) is the electronic mass, \( e \) the electronic charge, and \( Z_l e \) the charge of the \( l \)th nucleus. In molecular structure calculations, the nucleus-nucleus repulsion energy is often not included in the Hamiltonian but can be added as a classical term at the end of the calculation. The summations are over the electrons and the nuclei, separately. \( r_i \) and \( R_i \) denotes the position vectors for the electrons and the nuclei, respectively.

### 3.2.2 Excited states

An electronic dipole transition may occur from an initial state \( \Psi_i \) to a final state \( \Psi_f \) by absorption or emission of a photon with energy \( h \nu \). The induction of electronic transitions from the ground state require several electron volts. For transitions between vibrational and rotational states this energy is only about 0.1 and 0.001 eV, respectively. In a molecule, the vibrational energies of the harmonic oscillator are given by

\[
E_{\text{vib}}(n) = h \omega_{\text{vib}} (n + \frac{1}{2})
\]

where \( h \omega_{\text{vib}} \) is the vibrational energy and \( n=0,1,2 \ldots \) is the vibrational quantum number which can be obtained if the Schrödinger equation is instead solved as a function of the nuclear motion. The kinematics of the nuclear Schrödinger equation can be divided into translational, vibrational and rotational parts. The translational part is not quantized and is simply a free-particle motion of the center of mass of the whole system. For a diatomic molecule, the potential energy as a function of internuclear separation \( R \) is represented by a potential curve. If the function has a minimum, the curve is attractive, and in the opposite case repulsive. For polyatomic molecules both linear and bent vibrational modes are possible. This gives several vibrational quantum numbers to consider, for example, symmetric stretching, bending and anti-symmetric stretching.

For core excitations, the equilibrium internuclear distance of the electronic ground and excited states are usually slightly different. The vibrational structure
Figure 3.1: Vertical transitions according to the Franck-Condon principle.

gives rise to an intensity distribution which can be explained by the Franck-Condon principle. According to the Franck-Condon principle, the transitions between electronic states in a molecule occur so quickly that the relative positions of the nuclei can be considered as fixed. Only vertical transitions occur between vibrational levels of different potential curves. In a classical picture the vibrating nuclei spend most of the time at the turning points, except for the lowest vibrational modes in each electronic state where most of the time is spent at the equilibrium distance $R_e$. In the gas phase, at room temperature, the molecules are initially almost entirely in their vibrational ground states. The relative population of vibrational and rotational states is described by the Boltzmann distribution.

### 3.2.3 The variational principle

The total energy of the system is used for the determination of the optimum (lowest total energy) geometry of an atomic or molecular system and is defined as

$$E(R_A) = E_d(R_A) + \sum_{A} \sum_{B>A} \frac{Z_A Z_B}{|R_A - R_B|}.$$  \hspace{1cm} (3.5)

To obtain the HF wavefunctions for electrons in the ground state of atoms and molecules, the self-consistent-field (SCF) method is often used. The HF equations are then derived from the quantum mechanical variation principle. For the minimization of the total energy, the so-called Rayleigh-Ritz ratio

$$\epsilon = \frac{\int \Psi^*(x, R) H \Psi(x, R) dx}{\int \Psi^*(x, R) \Psi(x, R) dx}$$  \hspace{1cm} (3.6)
is applied. The total HF wavefunctions are constructed by an antisymmetrical product of one-electron wavefunctions in terms of a Slater determinant

\[ \Psi_e \propto \Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \ldots & \phi_N(x_1) \\ \ldots & \ldots & \ldots \\ \phi_1(x_N) & \ldots & \phi_N(x_N) \end{vmatrix} \]

where \( N \) is the number of electrons and \( \phi_i \) are the spin-orbitals which are eigenfunctions to the effective non-local Schrödinger equation arising from this ansatz of the many-body wave function. The expectation value can then be derived from the Rayleigh-Ritz ratio.

By variation of the \( \Psi_i \)'s, the total energy \( E_0 \) is minimized which result in \( N \) HF equations

\[ F\phi_i(x_1) = \sum_{k=1}^{N} \lambda_{ik} \phi_k(x_1) \quad (3.7) \]

and the Fock operator

\[ F = -\frac{\hbar^2}{2m} \nabla_i^2 - \sum_{n=1}^{P} \frac{Z_n e^2}{r_{in}} + \sum_{k=1}^{N} (J_k - K_k) \quad (3.8) \]

where the first term is the electron kinetic energy, the second term is the Coulomb attraction energy between the electrons and the nuclei. The two-electron operators \( J_j \) and \( K_j \) are called the Coulomb and exchange terms, respectively. The diagonal (or canonical) form of the HF equations is then given by

\[ F\phi_i(x_1) = E_i \phi_i(x_1) \quad (3.9) \]

where \( \phi_i \) are the canonical orbitals with orbital energies \( E_i \). Since both the Coulomb and exchange terms depend on all \( \phi_i \)'s, the diagonal HF equations are solved self-consistently which implies an evaluation of the matrix elements of the Fock operator

\[ E_i = \langle \phi_i(x_1) | F | \phi_i(x_1) \rangle = H_{ii} + \sum_{k=1}^{N} (J_{ik} - K_{ik}) \quad (3.10) \]

\[ H_{ii} = \int \phi_i^*(x_1)(-\frac{\hbar^2}{2m} \nabla_i^2 - \sum_{n=1}^{P} \frac{Z_n e^2}{r_{in}})\phi_i(x_1)dx_1 \quad (3.11) \]

\[ J_{ik} = \int \int \phi_i^*(x_1)\phi_k^*(x_2)\frac{e^2}{r_{12}}\phi_k(x_2)\phi_i(x_1)dx_1dx_2 \quad (3.12) \]
where \( J_{ik} \) is the two-electron Coulomb integral and \( K_{ik} \) is the two-electron exchange integral. The total energy is then given by

\[
E_0 = \sum_{i=1}^{N} H_{ii} + \frac{1}{2} \sum_{i=1}^{N} \sum_{k=1}^{N} (J_{ik} - K_{ik}) + \sum_{i=1}^{P} \sum_{n>i}^{P} \frac{Z_i Z_n e^2}{R_{in}}
\]  (3.14)

The self-consistent variational process is finished when the difference in the total energy between two consecutive iterations is less than some small predetermined value.

### 3.2.4 The Roothaan-Hall equations

The evaluation of the two-electron Coulomb and exchange integrals is the most time-consuming procedure of the Hartree-Fock self-consistent field (HF-SCF) calculation. For large molecular systems, the numerical iteration of the Fock matrix elements in each cycle of the iterative process is very time-consuming. The standard way to solve the HF equations is therefore to use the Roothaan-Hall method in which the wavefunctions are expanded in a basis set

\[
\phi_i = \sum_{l=1}^{M} a_{il} \chi_l
\]  (3.15)

The atomic orbitals \( \chi_l \) are themselves solutions of the HF equations for the individual atoms, and are regarded as fixed while the variation in the HF procedure is performed on the expansion coefficients \( a_{il} \). Thus, the HF equations are transformed into a set of approximate linear equations. For calculation of molecular orbitals (MO’s) it is often advantageous to utilize linear combinations of atomic orbitals (LCAO) for the basis set. In the limit of a complete basis set (\( M \rightarrow \infty \)), the molecular orbitals obtained are equal to the exact HF solution. The limiting energy is called the Hartree-Fock limit. However, in practice, a finite basis set is always used which limits the accuracy of the solution. Here, the introduction of Gaussian-type orbitals has played an important role for the computation. The correct choice of basis set is thus very important since it affects the quality of the solution and the time of the calculation. The simplest, called the minimum basis set, contains one type of basis function for each type of atomic orbital which is occupied by electrons in the ground state of the particular atom. The basis functions are usually of Slater type or Gaussian type. With the minimal basis set, usually only the qualitative properties of the particular system can be obtained. A better description is often obtained with the use of more sophisticated basis sets which consist of more independent basis functions for each occupied atomic orbital. Sometimes different basis sets are used for the inner (core) and the outer...
(valence) orbitals or for the occupied and virtual (empty) orbitals. Polarization and diffuse functions may also be added. The iteration procedure is repeated until convergence is reached which means that the difference between the two following sets of expansion coefficients is smaller than some predetermined value. When the convergence is reached, the solution is said to be self-consistent and the potential in which the single electron is moving is called the self-consistent field (SCF).

A more accurate wavefunction can be obtained by a linear combination of determinants each representing a different state of the system. This kind of wavefunctions are configuration interaction (CI) corrected. Using the variational principle, the coefficient for each determinant which builds up the total wavefunction is found by minimizing the energy in the Schrödinger equation with respect to the complete electronic Hamiltonian. The rapid development of computers and programs has simplified calculations using commercial software packages. The development of new methods to improve the calculational accuracy is usually performed in connection with new experimental techniques.

For very large molecular systems, even the Roothan-Hall HF method is very time consuming due to the large number of two-electron integrals which have to be calculated. One way to overcome this problem is to use empirical data to obtain the most important integrals and ignore the rest as is done with the use of semi-empirical methods. Examples of these methods are the Complete Neglect of Differential Overlap (CNDO) where only the valence electrons are explicitly considered and the Modified Neglect of Differential Overlap (MNDO).

### 3.2.5 Multiconfigurational self-consistent field

For the theoretical treatment of molecular dissociation in paper I, we consider a single determinant as an approximation to the electronic wave function in the Hartree-Fock theory. The orbitals can then be obtained by minimizing the electronic energy with the variational principle. However in this case, a multideterminant wave function can be used which contain a small number of determinants in what is known as the multiconfigurational self-consistent-field (MC-SCF) method. By taking into account the molecular symmetry in model calculations, it is possible to largely reduce the effort of calculating the electronic wavefunction. With the application of the Born-Oppenheimer approximation, the energy of the molecule can change either by a redistribution of the electrons or by a redistribution of the nuclei. In the former case, a transition occurs between two eigenstates of the electronic Schrödinger equation and in the latter case, there is a transition between two eigenstates of the nuclear Schrödinger equation. A redistribution of the electrons is often followed by a redistribution of the nuclei. Molecular spectra contain information about bond lengths and molecular geometry and is usually somewhat more complex than atomic spectra. In many small molecules, the absorption of a photon can be treated as a redistribution of electrons in a small group of atoms as building blocks. The MC-SCF wave function can be expressed as

\[ |\Psi_{MC-SCF}\rangle = \sum_l c_l |\Psi_l\rangle \quad (3.16) \]
where both the expansion coefficients $c_1$ and the orbitals $|\Psi_1\rangle$ are optimized. However, the equations used to obtain the MC-SCF wave functions are considerably more complicated than the Roothaan's equations in the Hartree-Fock theory. In the calculation of the potential energy surfaces of the dissociative states of a molecule, it is necessary to use an MC-SCF wave function. A multideterminantal wave function is needed to describe not only the bond stretching but also to describe the excited electronic states. A closed shell restricted Hartree-Fock model may be a rather good approximation close to the equilibrium geometry. However, at large internuclear distances, the bonding and antibonding orbitals become close to degenerate and several Slater determinants are very close in energy. This degeneracy problem can be removed by the use of a multideterminantal wave function which gives only one linear combination of determinants at the lowest energy. With the MC-SCF expansion, the inactive and active orbitals may be divided into two different groups in what is known as the complete active space self-consistent-field (CAS-SCF) wave function. All the inactive orbitals are doubly occupied in the determinants of the CAS-SCF expansion. The MC-SCF technique is the easiest method to calculate the shape of a potential surface accurately.

3.3 Density Functional theory

3.3.1 The Kohn-Sham equations

In atoms, molecules and solids, the interactions among the electrons and atomic nuclei constitute a complicated many-body problem. In the majority of systems, the electrons retain much of their independent particle behaviour. The major features of the electronic structure can thus be well described in one-electron models where the electrons move in an effective average potential from the nuclei and all the other electrons. Among all the different ab initio methods treating the many-body problem in electronic structure calculations, Density Functional Theory (DFT) is widely used for calculating ground state properties of solids. This fundamentally important theory gives an exact description of the electronic structure of the ground state. However, in reality, numerical calculations using DFT are often based on various kinds of approximations. In the mid 60's, Hohenberg, Kohn and Sham developed important concepts for the theory [45, 46]. All the ground state observables such as the total energy are functionals of the particle density $\rho(r)$. The exact ground-state electronic energy $E$ of an $n$-electron system may be written as

$$E[\rho] = -\frac{\hbar^2}{2m_e} \sum_{i=1}^n \int \Psi_i^*(r_1) \nabla_i^2 \Psi_i(r_1) dr_1 - \sum_{j=1}^N \int \frac{Z_j e^2}{4\pi\varepsilon_0 r_{j1}} \rho(r_1) dr_1 + \frac{1}{2} \int \frac{\rho(r_1)\rho(r_2)e^2}{4\pi\varepsilon_0 r_{12}} dr_1 dr_2 + E_{XC}[\rho]$$

(3.17)

where the one-electron spatial orbitals $\Psi_i$ are the so-called Kohn-Sham (K-S) orbitals. The first term in Eq. 3.17, represents the kinetic energy of the electrons.
The second term represents the electron-nucleus attraction with the sum over all \( N \) nuclei with index \( j \) and atomic number \( Z_j \). The third term represents the Coulomb interaction between the total charge distribution at \( r_1 \) and \( r_2 \). The last term \( E_{XC}[\rho] \) is the exchange-correlation energy of the system which is a functional of the density containing all many-body effects due to electron-electron interactions. However, the exchange-correlation energy is not possible to obtain exactly and has to be included in some approximate way. The ground-state electron charge density \( \rho \) of the interacting system at a point \( r \) is given by

\[
\rho(r) = \sum_{i=1}^{n} |\Psi_i(r)|^2
\]  

(3.18)

where the sum is over all occupied K-S orbitals. In expression 3.18, it is assumed that the potential \( V_{XC} \) is local (see below). By the application of the variational principle to the electronic energy \( E(\rho) \) (Eq. 3.17) with the charge density \( \rho(r) \), (Eq. 3.18) a set of effective one-electron Schrödinger-like equations called the Kohn-Sham equations can be obtained as

\[
\left\{ -\frac{\hbar^2}{2m_e} \nabla^2 - \sum_{j=1}^{N} \frac{Z_j e^2}{4\pi \epsilon_0 r_{j1}} + \int \frac{\rho(r_2) e^2}{4\pi \epsilon_0 r_{12}} dr_2 + V_{XC}(r_1) \right\} \Psi_i(r_1) = \epsilon_i \Psi_i(r_1) 
\]  

(3.19)

where the \( \epsilon_i \)'s are the K-S orbital energies. The term \( V_{XC}(r_1) \) is the exchange-correlation potential which is defined as the functional derivative of the exchange-correlation energy

\[
V_{XC}[\rho] = \frac{\delta E_{XC}[\rho]}{\delta \rho}.
\]  

(3.20)

If the exchange-correlation functional \( E_{XC}[\rho] \) is known, then \( V_{XC} \) can thus be easily obtained. The K-S equations are solved self-consistently by first guessing a charge-density \( \rho \). This is done by using a fixed approximate form for the functional dependence of \( E_{XC} \) on the density. In order to calculate the total energy functional of an interacting many-body system, the K-S equation has to be solved to obtain the charge density and the kinetic energy of the non-interacting system. However, to solve this equation in an efficient way, the problem has to be reformulated into some standard algebraic form possible to treat numerically. One common way is to use the variational Reighleigh-Ritz ratio, where the solution is expanded in some basis set. The \( V_{XC}(r) \) is then obtained and is used to solve the K-S equations to obtain an initial set of K-S orbitals. The obtained K-S orbitals can then be used to compute an improved density \( \rho(r) \) and the process is repeated until the density has converged. The total electron energy can then be computed from Eq. 3.17. The K-S orbitals can either be calculated or be expressed in some type of basis functions. If a basis set is used, the K-S equations are used to find the coefficients in the basis set expansion from which the electron density can be calculated. Different methods use different kinds of basis sets depending on the application. In the
early seventies, it was shown by O. K. Andersen [47] that the so-called Koringa, Kohn and Rostoker (KKR) method could be linearized into the linear muffin-tin orbital (LMTO) method which provides a highly efficient way of representing an energy dependent basis set. Slater's augmented plane wave method (APW) was also linearized in a similar way. The s, p, d and f basis functions are obtained from the solutions of the Schrödinger-like equation. This is often done for a potential which is spherically symmetric out to a certain distance from the atomic nucleus and constant in the interstitial regions, i.e., by using the so-called muffin-tin potential. The atomic sphere approximation (ASA), is used to approximate the Wigner-Seitz cell by a sphere.

3.3.2 The local density approximation

For the problem of obtaining an approximate form for the functional $E_{xc}[\rho]$ for the exchange-correlation energy, several different schemes have been developed. One way is to approximate the exchange-correlation part of the density functional locally at a point $r$ by the exchange-correlation functional of a homogeneous electron gas of density $\rho (r)$. This is done in the so-called local density approximation (LDA) within the K-S scheme for calculating the total energy in DFT. Using the LDA approach, the exchange-correlation energy can be written as

$$E_{xc} = \int \epsilon_{xc}[\rho(r)](\rho(r))dr \quad (3.21)$$

i.e., an integral over a function whose value in a local point only depends on the electron density in that point. The exchange-correlation energy $\epsilon_{xc}$ of the homogeneous electron gas can be parametrized in different ways depending on the particular problem. However, in a real system, neither the nuclear charge or the electronic charge are uniformly distributed. In order to improve the LDA approximation, it is also possible to use more elaborate Hartree-Fock approximations or general gradient corrections (GGA) to estimate $E_{xc} [\rho (r)]$.

3.3.3 Green's function methods

The development of field theory and Green's function methods in the 1950's rapidly advanced the understanding of fundamental issues concerning many-body problems. These methods were developed as an attempt to construct a theory that included both quantum mechanics and electrodynamics. It is of importance to understand the validity of the use of DFT (and LDA) eigenvalues for the interpretation of excitation spectra of solids. One of the central problems is that the exchange-correlation potential does not always take correlation effects into account sufficiently. This fundamental problem cannot be solved only by finding the exact exchange correlation functional. One way to describe the problem is to use Green's functions.

The Green's function $G$, and its spectral function $A$, provide information about the electronic structure of a medium e.g., the total ground state energy and the excitation energies which can be directly related to excitation spectra of solids. If
the spectral function $A$ is known, it implies that also the Green’s function $G$ of the system is known. The Green’s function describes the propagation of an electron or hole in a medium and is therefore also called a propagator. The Green’s function technique enables studies of both single-particle behaviour as well as collective phenomena. It allows calculation of the expectation value of all one-particle operators in the system, as well as the total energy. A common method or rather an approximation for the Green’s function is provided by using perturbation theory in which the interaction of the electrons is treated as a perturbation. Thus, in a similar way as the Hamiltonian operator $H$ is used in the Schrödinger equation, a Green’s function operator $G$, can be used variationally in DFT. The Green’s function Hamiltonian can be divided into an unperturbed reference part $H_0$ and a perturbation part $V$. The Schrödinger equation can then be written as

$$ (H_0 + E)\Psi_i = V\Psi_i \quad (3.22) $$

where the $V\Psi_i$-term is a so-called source term causing the perturbation. The unperturbed and full Green’s function operators, $G_0$ and $G$ are connected with the Dyson equation

$$ G = G_0 + G_0 V G \quad (3.23) $$

Due to the correlation interaction between the electrons, the Green’s function can normally not be calculated exactly and it is thus necessary to use approximate schemes to obtain $G$. The Green’s function $G$ can be calculated if the interaction between the electrons is viewed as a perturbation to a non-interacting system described by $G_0$ [48]. The Green’s function $G$ can then be expressed as an infinite sum in which each term contains contributions from the non-interacting Green’s function $G_0$ and from the Coulombic interactions $V$ of the system. The Dyson equation can thus be expanded in the Dyson series

$$ G = G_0 + G_0 V G_0 + G_0 V G_0 V G_0 + ... \quad (3.24) $$

The different terms can be represented by Feynman diagrams and interpreted as corrections of higher and higher complexity. The first term $G_0$ corresponds to propagation in an unperturbed reference medium. The perturbations which are introduced by the higher order terms appear as modified LDA eigenvalues (energies) which improve the exchange-correlation potential.

For a single, discrete excited state the Green’s function can be expressed as

$$ G_k(E) = \frac{1}{E - E_k} \quad (3.25) $$

where $E_k$ is the energy eigenvalue, including relaxation effects. The energy eigenvalues approximate the excitation energy when an electron is added to, or removed from the system. In the special case of the Hartree-Fock approximation, the result
is the Koopmans’ energy. The spectral function of an excited state observed in an experiment can then be expressed as

$$A_k(E) = -\frac{1}{\pi} \text{Im}[G(E)] = \delta(E - E_k)$$ (3.26)

where the electron with wave vector $k$ can only have the energies $E_k$. However, in a real system, the excited state is not a stable discrete state, but instead has a finite, average life-time $\tau$, corresponding to an energy level width $\Gamma$ according to Heisenberg’s uncertainty principle. The Green’s function and the spectral density may therefore be expressed as

$$G_k(E) = \frac{1}{E - E_k + i\Gamma}$$ (3.27)

and

$$A_k(E) = -\frac{1}{\pi} \text{Im}[G(E)] = \frac{\Gamma}{(E - E_k)^2 + \Gamma^2}.$$ (3.28)

In order to make a comparison to experimental results, the calculated spectral peaks $A_k(E)$ are often broadened by Gaussian and/or Lorenzian functions with a full-width-at-half-maximum chosen to match the core-hole width and resolution of the spectrometer.

### 3.3.4 Self energy corrections

In the following, the effects of an interaction between the electrons is considered. The presence of an electron or a hole in a medium produces a perturbation in its own surrounding. This perturbation results in a self-energy which may be viewed as if the electron or hole was interacting with itself. The self-energy can be expressed as a complex energy-dependent operator $\Sigma(E)$. $\text{Re} \Sigma(E)$ and $\text{Im} \Sigma(E)$ are related through the Kramers-Kronig dispersion relation

$$\text{Re}\Sigma(E) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\text{Im}\Sigma(E')dE'}{E - E'}.$$ (3.29)

The self-energy acts like a potential in the Dyson equation, the solution of which is a Greens function which shifts the spectral eigenvalues by a complex energy distribution [49]. It leads to mass enhancement of a virtual bound state at the Fermi level due to the dynamical effects or electron correlation, electron-phonon interaction. The Green’s function $G(E)$ is then modified for the interacting system by the self-energy as

$$G_k(E) = \frac{1}{E - E_k - \Sigma(E)}$$ (3.30)
and the spectral function of the density of states can then be expressed as

\[ A_k(E) = \frac{1}{\pi} \frac{|\text{Im}\Sigma(E)|}{|E - E_k - \text{Re}\Sigma(E)|^2 + |\text{Im}\Sigma(E)|^2}. \]  

(3.31)

The complex self-energy \( \Sigma(E) = \text{Re}\Sigma(E) + i\text{Im}\Sigma(E) \) includes the core hole decay as well as elastic and inelastic processes such as electron-electron scattering and plasmon excitations, and the eigenvalues give the excitation energies. The general structure of the spectral function \( A_k(E) \) is changed from a sharp peak at \( E_k \), into a smoother, positive function with a quasi-particle peak together with a background structure. The width of the quasi-particle peak defines the finite lifetime of the quasi-particle. The background contains small peaks, corresponding to collective excitations of the medium e.g., plasmons. The general structure of the imaginary part of the self-energy is such that it approaches zero for values of \( k \) close to the Fermi level which means that quasi-particles close to the Fermi surface can be regarded as stable with infinite lifetime. The spectral density function is thus a Lorenzian function which reflects the decay time of the excited state. The excited state may for example be a core-level in a photoemission experiment. Using calculated density-of-states eigenvalues, the spectral density function, \( A(E) \), can be written as

\[ A(E) = -\frac{1}{\pi} \cdot \text{Im} \int \frac{\text{DOS}(E_k)}{E - E_k - \Sigma(E)} dE_k \]  

(3.32)

where \( \text{DOS}(E_k) \) is the density of states obtained from the LDA calculation. The simplest approximation to \( \Sigma \) is the Hartree-Fock approximation where it is reduced to a non-local energy-dependent exchange potential. However, the Hartree-Fock approximation usually gives too much dispersion and too large band gaps.

An exact approach to the self-energy was presented in 1965 by L. Hedin [50] as a set of coupled equations which in principle can be solved self-consistently to obtain the following properties of the system exactly: the Green’s function \( G \), the screened interaction \( W \), the self-energy \( \Sigma \) and the so-called vertex-function, which couples the equations together. Since the potential of a particle in a medium with other charged particles is effectively shielded which shortens the range of the Coulomb potential, it is better to use the screened interaction \( W \), for the description of the potential of a particle in a medium. The coupled equations are then used to expand the properties \( \Sigma \) and \( G \) in terms of \( W \) instead of \( V \). The long range Coulomb interaction \( V \sim 1/r \) between the electrons is thus replaced by a the dynamically screened interaction \( W \). The coupled equations should in principle be solved iteratively to obtain the self-energy \( \Sigma \) as a function of \( G \). However, this process is computationally too complicated to perform even for a simple system due to the vertex-function. As an approximation, Hedin therefore suggested to keep the vertex fixed to one in the calculation of \( W \). This scheme of calculation is known as the GW-approximation (GWA) since the self-energy is a convolution over the Green’s function \( G \) and the screened interaction \( W \). In the GWA scheme, the self-energy is obtained as a convolution over the Green’s function \( G \) and the
Figure 3.2: The valence band of nickel metal as probed by the photoemission and X-ray emission techniques. The 6-eV correlation satellite in the Photoemission spectrum does not show up in the X-ray emission spectrum. Self-energy corrected LDA bandstructure calculations are shown at the bottom for comparison.

The GW approximation largely improves the excitation energies but its applications have been limited by the time consuming computations.

Figure 3.2 shows valence-band spectra of the correlated nickel metal system as an example. This metal system has a well-known correlation satellite situated...
at 6-eV binding energy in the photoemission spectrum. The satellite does not show up in X-ray emission spectra since the transition energies are due to the energy difference between the core-excited and the valence-band states including their shake-up structures, respectively. Standard LDA calculations are known to give a bandwidth which is 30% too broad compared to the experimental value. The GWA method has been successfully applied to the valence band of nickel metal [55] showing quasi-particles in the 6-eV binding energy region and a correct bandwidth. In Fig. 3.2 (bottom) a simple semi-empirical self-energy correction is shown. The self-energy is shown in the lower panel and is expressed by the analytical function

$$\Sigma(\omega) = \frac{g\omega}{(\omega + i\gamma)^2}$$  \hspace{1cm} (3.33)

where g and \( \gamma \) are adjustable parameters which are related to the Coulomb interaction \( U \) and the bandwidth \( W \) [57]. In this case the k-dependence of the self-energy is neglected which is a good approximation for short-range interactions. The real and imaginary parts of the \( \Sigma(\omega) \) are related through the Kramers-Kronig relation (above) and show Fermi-liquid behaviour, i.e., \( \text{Re}\Sigma(\omega) \propto -\omega \) (linear in binding energy) and \( \text{Im}\Sigma(\omega) \propto -\omega^2 \), near the Fermi level. For very large values of \( \omega \) well beyond the valence bandwidth \( \Sigma(\omega) \) approaches zero. The lifetime of the quasi-particle is given by the imaginary part of \( \Sigma(\omega) \) and its energy shift relative to the uncorrelated LDA eigenvalue is given by the real part of \( \Sigma(\omega) \). Thus, a short lifetime (large broadening) is found at the bottom of a valence band, whereas a long lifetime (small broadening) is found close to the Fermi level. The self-energy operator \( \Sigma(E) \) describing the exchange and correlation in the excited state and can be included in the Schrödinger equation as

$$\left\{ -\nabla^2 + V(r)\Psi_k(r) + \int \sum \langle r, E_k \rangle \psi_k(r)dr \right\} \psi_k(r) = E_k \psi_k(r)$$  \hspace{1cm} (3.34)

where \( V(r) \) is the sum of the Hartree potential and the electron-nuclear attraction. The cross section of the observed energy spectrum using core-level spectroscopies is then obtained by multiplying the spectral function \( A(E) \) by the transition probability

$$\frac{d\sigma(E)}{dE} \propto \int \langle f | \tilde{D} | i \rangle^2 A_i(E)$$  \hspace{1cm} (3.35)

where \( \tilde{D} \) is an operator connecting the initial state \(|i\rangle \) with the final state \(|f\rangle \). In the case of X-ray emission and photoemission spectroscopy, \( \tilde{D} \) is the dipole operator. Since \( \Sigma(E) \) is a functional of the density and a ground state property, the local density approximation for the ground state can be used. The exchange-correlation contribution \( V_{xc}(r) \) of the excited state can then be obtained with a self-consistent procedure.
3.4 The Anderson impurity model

3.4.1 Correlated systems

For correlated systems with strong intra-atomic Coulomb interactions, in for example some 3d transition metal elements, lanthanide and actinide compounds with a partially filled $d$ or $f$ shell, the one-electron picture often breaks down. In this situation, it is not sufficient to calculate the electronic self-energy in Green's function perturbation theory or to use approximations like the GW-approximation mentioned in the previous section. Due to the differences in treating the electronic correlation effects it is instead common to abandon the exact Hamiltonian and to introduce a simplified model containing only those interactions which are important for the particular system. Thus, a more atomic-like approach is needed to characterize the electronic structure. In such a model, the final state system without a core hole can be described in terms of intra-atomic excitations and inter-atomic charge-transfer excitations. The intra-atomic excitations gives a multiplet structure of the ground state electronic configuration due to electrostatic, exchange, crystal field, and spin-orbit interactions. The inter-atomic charge-transfer excitations are due to electron hopping from delocalized states to a localized state. In this case the single impurity Anderson model (SIAM) can be applied [58].

3.4.2 The Anderson Hamiltonian

The SIAM was first applied to transition metals by Anderson in 1961 [58]. Since then the model has been extended for the interpretation of core-level spectra of various mixed valence cerium compounds [59]. The SIAM has been successfully applied for interpretation of valence and core-level X-ray photoemission and X-ray absorption spectra in $f$ and $d$ electron systems. The $f$ and $d$ electronic states are treated from a single atomic site and hybridized with the valence and conduction electronic states, especially when a core hole is present in the final state. In rare earth compounds, the screening mechanism by the $f$ and $d$ electrons play an important role in core level spectroscopy. Recently, the SIAM has also been used for the interpretation of X-ray emission and Auger spectra [60]. The ground state of a system can be described by the following Hamiltonian

\[ H = \sum_{k,\alpha,\sigma} \epsilon_{k\alpha} n_{k,\alpha,\sigma} + \sum_{m,\sigma} \epsilon_m n_{m\sigma} + \sum_{k,\alpha,\sigma} (V_{k\alpha m,\sigma} \psi_{m,\sigma}^* \psi_{k,\alpha,\sigma} + H.c.) + U \sum_{m,m',\sigma,\sigma'} n_{m,\sigma} n_{m',\sigma'} \]  \hspace{1cm} (3.36)

where $\epsilon_{k\alpha}$ is the energy of the delocalized state, $\epsilon_m$ is the energy of the localized state, $V_{k\alpha m,\sigma}$ is the hopping matrix element and $U$ is the Coulomb interaction between the localized electrons. Here, $k$, $\alpha$, $\sigma$ and $m$ denote a wave vector, an index of the energy level in the valence band, a spin index, and an azimuthal quantum number, respectively. For the application of core-level spectroscopies, another term is added in the Hamiltonian to account for the coupling between the localized electron and the core hole.
The values of the model parameters are configuration dependent and are optimized by fitting both high-energy spectroscopic and low-energy transport data. After the optimization, the model parameters can for example be employed to describe various ground state properties and the nature of the band gap in insulators [61]. When different high-energy spectroscopies are used for the estimations of the model parameters, it is important to take into account the different number of electrons in the final states. Removing a valence electron may result in a decrease of the hybridization strength $V$ which may lead to renormalization effects for the Coulomb interaction $U$. 
Chapter 4

Applications and Results

4.1 Introduction

This chapter reviews the scientific results of the present thesis. A more detailed discussion is found in the papers but brief overviews are presented here. As discussed in Chapter 3, quantum mechanics, the outstanding theory for the structure of matter, is based on the assumption that a physical system is built up from a few basic particles interacting through fundamental forces. For simple systems i.e., systems built from a small number of particles, and systems with a high symmetry, the results of experiments can be accurately predicted by quantum mechanical calculations. For the more complicated systems of daily life, many observations can be qualitatively described within this framework by using various approximations. The particles that build up the system are not observable, and they are mostly not attributable to non-contradictory common sense analogies. However, all information on a quantum mechanical system can be contained in a wave function, and macroscopic analogies to the microscopical particles often work quite well, depending on the specific process and the level of approximation. Protons, electrons and photons can be viewed either as particles or waves. The atomic nucleus can be regarded as a point-like structure-less particle with a certain mass and electric charge. The prevailing conception of matter, on this level of approximation, comprises nuclear particles held together by the electrostatic Coulomb interaction through the distribution of electrons. The properties of matter, in this picture, thus largely depend on how the electrons are distributed, and how the nuclei are arranged. The investigation of the electronic structure is the topic of atomic, molecular and solid state physics.

The present studies address the electronic structure of molecules and solids probed by resonant X-ray emission and photoemission. Detailed analyses of the response of the electronic systems under interaction with X-rays were made using monochromatic synchrotron radiation and sophisticated spectroscopical techniques.
4.2 Molecular studies

When a molecule absorbs a photon it is brought into an excited state. After a very short time, the electron cloud responds by for example releasing energy in the form of radiation (X-rays in this case). The energy of the emitted photons depend on the excitation energy and the energy of the final state, whereas the intensity distribution is influenced by the properties of the intermediate core-excited state. Thus, a study of the electronic decay spectra may reveal important information about the excited electronic states. In paper I of this thesis an interesting molecular system is presented, namely the carbonyl sulphide (OCS) molecule. The X-ray emission after excitation of a sulfur 2p core-electron to one of the empty valence levels is studied. A complicating factor, which is particularly studied in the case of the OCS molecule in paper I, is that the molecule may 'fall apart', dissociate, after the absorption of X-rays. The importance of the energy selectivity in the excitation is emphasized; the selectivity makes it possible to study how the chemical bond in a molecule breaks up during the X-ray scattering process, leading to emission from neutral fragments. This provides fascinating views on the dynamics of molecular dissociation occurring on the femtosecond time scale. The experimental study was accompanied by numerical model calculations in the formalism of resonant inelastic scattering.

4.2.1 Experimental set-up

![Figure 4.1: Schematic illustration of the experimental set-up for measurements with the gas-cell.](image)

Fig. 4.1 shows schematically the experimental set-up for molecular gas-phase experiments which was used for the measurements of the OCS molecule. Pressures in the range 0.1 to 10 Torr (0.13 to 13 mbar) are usually necessary for most gases to sufficiently absorb the radiation within the length of the gas cell. This can be accomplished by using thin transmission windows (foils) to keep the sample gas in a restricted volume. The beam entered the experimental vacuum chamber via a small aperture which is used to protect the beamline in the case of an accidental
breakage of a window in the gas cell. The OCS gas was kept at a constant pressure in the gas cell. For the OCS measurements, a gas pressure of ~2 mbar was used. The radiation entered the gas cell through a small entrance window, about 250 µm in diameter. The region where the photon beam interacts with the gas was viewed by the X-ray emission spectrometer through a long rectangular 160 nm thick polyimide (C_{22}H_{10}N_{2}O_{5}) exit window. In Fig. 4.2 the transmission curves show that polyimide and carbon windows transmit a large fraction of the radiation in the energy range 100 to 250 eV [62]. For absorption measurements, an electrode was used to measure the electron yield current of the gas.

The experiments were performed at the undulator beamline 7.0 at the Advanced Light Source [63]. This beamline has good resolution, high photon flux, and the beam can be highly collimated and is well focussed onto a small spot.

4.2.2 The dissociation process

In general, resonant X-ray emission of molecules can give important information about the fundamental processes and interactions which appear in the chemical bond between the constituent atoms. Different molecular orbitals contribute in different ways to the chemical bonding between the atoms. Some orbitals are bonding, others antibonding and some are nonbonding. In some particular cases, electronic excitation may weaken the molecular bonds so much that the molecule breaks up in fragments i.e., dissociates. For instance, the excitation of a core electron to a strongly anti-bonding orbital may result in fast dissociation. The
Figure 4.3: The resonant X-ray emission process for OCS in the case of dissociation. On the left, an X-ray photon with energy $h\nu_1$ is absorbed and a 2p core electron in sulfur is excited to an antibonding level. A fast dissociation occurs where the core-excited sulfur atom separates from the rest of the molecule. The core-excited sulfur atom then decays with the emission of an X-ray photon with energy $h\nu_2$.

dissociation time of OCS after resonant S 2p excitation was found to be very short i.e., in the $10^{-15}$ s range which is on the same time scale as the decay processes. In the OCS molecule, the two lowest unoccupied molecular orbitals (LUMO's) are strongly antibonding, while the higher lying empty levels, the so-called Rydberg levels, are more or less non-bonding. The excitation of a S 2p electron to the LUMO leads to dissociation of the OCS molecule, which in this case is so fast that it competes with the de-excitation channel. From Fig. 4.3 it is clear that the final state does not only involve two particles as in the case of X-ray emission from atoms. Instead it is three: one neutral sulphur atom, one neutral CO molecule and one X-ray photon.

In a simplified picture, the resonant X-ray emission may in this case be described as occurring in three steps. In the first step, the absorption of an X-ray photon of energy $h\nu_1$ occurs when a S 2p electron is excited to an empty valence level. Thereafter, the excited sulfur molecule dissociates in a few femtoseconds to an excited sulphur atom and a free CO molecule. In the last step which may occur during the dissociation, the decay occurs with the emission of a photon with energy $h\nu_2$ according to the dipole selection rules. The emission process is atomic, although there was a molecule which was excited in the beginning of the process.

If we instead excite an electron from a 2p core-level to one of the higher levels which are non-bonding there will be no dissociation. The energy of the final state can be thought of as separated into the energy of the neutral molecule and the photon which can be determined due to energy conservation since the incoming photon energy can be accurately determined from the monochromator.
A fast dissociation results in sharp atomic lines in X-ray emission (or Auger) spectra governed by the different dissociation channels involved, while slower dissociation results in broad molecular features. This is illustrated in Fig. 4.4 by a set of potential energy curves. The core-excited molecule may fragment before de-excitation (dissociation channel prior), leading to atomic decay lines, or the de-excitation is followed by dissociation (de-excitation channel prior), which leads to broad molecular features. The time for dissociation and the lifetime of the core hole have pronounced effects on line positions, line widths, transition rates, and vibrational fine structures in the spectra. If both molecular and atomic features are observed with similar intensities, the dissociation and the core-hole decay processes occur on the same time scale, i.e. typically in the $10^{-15}$ s range. The core-hole lifetime can be looked upon as a reference time (core-hole clock) which can be used to determine the dissociation time. The dissociative core-excitation processes have until now been studied in the Auger decay channel, while no results for the X-ray emission channel have been presented previously. The advantage of using the X-ray emission channel is the application of the dipole selection rules. This makes it possible to more accurately determine the final states of the dissociation products than what can be achieved in the non-radiative channel. In paper I, this was done by comparison to calculations.

For future experiments it would be very interesting to try to shorten the duration time of the scattering process [64] (adjusting the core-hole clock) by detuning i.e., by slightly lowering the excitation energy below the sulfur $2p_{3/2} \rightarrow \pi^*$ resonance. This will lower the relative atomic contribution in the X-ray emission
spectra. This may contribute to a better understanding of the dissociation process. For soft X-ray emission spectroscopy it is obvious that gas-phase studies have a large potential, since the resolution has so far been too limited for studies of spectral fine structure.

4.3 Conjugated polymers

The interest in the field of conjugated polymers has grown dramatically since it was discovered in 1977 that polymers can be doped to become good conductors [65]. Presently, different kinds of conjugated polymers are used as active materials in different kinds of prototype applications. Examples of these are light emitting diodes [66], batteries [67], and photodiodes [68]. The linear polymer chain (backbone) is a macromolecule comprising a large number of repeat units (unit cells) of monomers. In a three-dimensional structure, the individual chains may cross each other to form a complex structure with improved mechanical properties. The overlap between the electron clouds of the neighbouring polymer chains is always much longer ($\sim 3 - 4 \text{ Å}$) than between the carbon atoms within a chain ($\sim 1.4 \text{ Å}$).

4.3.1 The $\pi$-band structure

The electron configuration of the six electrons in a carbon atom is $1s^22s^22p^2$. The core orbitals in the $1s^2$ level do not contribute to the chemical bonding. The four electrons in the $2s^22p^2$ shells forms a hybridized structure in the conjugated polymers which is denoted $sp^2$ hybridization. The hybridization gives three orbitals which form a linear combination of the two $s$-orbitals and one $p$-orbital. The remaining $p_z$ orbital contains one electron for each carbon atom. Figure 4.5 (a) shows how the $sp^2$ hybridization results in three $\sigma$ bonding orbitals ($2s$, $2p_z$ and $2p_x$) and (b) a remaining $2p_z$ orbital. The $2p_z$ orbitals which are located next to each other form the $\pi$ bonds if they overlap. In a $\pi$ conjugated polymer, the $2p_z$ orbitals significantly overlap along the backbone which give rise to a delocalization of the $\pi$-electrons. The three hybridized orbitals give the covalent chemical $\sigma$ bond which defines the geometry of the carbon chain. The remaining $p_z$ electron gives the conduction properties of the chain since it is the least bound delocalized electron. A conjugated polymer can therefore be looked upon as a one-dimensional system.
of carbon atoms, where each carbon atom contains a delocalized $p_z$ electron. Each unit cell thus has an unfilled shell containing only one unpaired electron. The polymer becomes conducting (metallic-like) since there are unoccupied states just above the Fermi level.

### 4.3.2 Building blocks and symmetry

From the symmetry point of view, a conjugated polymer can be looked upon as a molecular building block of repeat units in a one-dimensional linear chain of carbon atoms which are covalently bonded with their neighbours. The unit cell may be synthesized so that it contains a dimer, instead of a monomer, with two different bond lengths between the carbon atoms (single and double bonds). If this is done, the symmetry of the system is lowered: the unit cell becomes larger and there are now two delocalized electrons in the unit cell. The polymer thus becomes a semiconductor or an insulator. The dimerization was predicted and studied by Sir Rudolph Peierls and is thus called the Peierls transition [69]. In such a one-dimensional semiconductor, the $p$-electrons from each carbon atom contribute and form the valence band while the conduction band is empty. A band gap is formed between the filled $\pi$ and empty $\pi^*$ levels. For the interpretation of the transitions in the band gap of the polymer chains, quantum mechanics can be applied. It is now possible to make polymer materials with a desired bandgap. This can be accomplished by producing short polymers (oligomers) which can contain 3-10 monomers. It is also possible to combine two different types of monomers, to build a polymer chain. The bandgap can also be controlled by steric methods by attaching side groups to the backbone. The polymer chain can then be forced from a plane geometry to a certain torsional angle.

Conjugated polymers used in various applications often contain benzene rings which are polymerized into a linear structure. These types of polymers are often synthesized by first producing a non-conjugated pre-polymer (precursor) which is then transformed to a conjugated polymer by heating or radiation. The precursor can be contained in a solution and formed into thin films. Alternatively, the luminescent polymer can be synthesized in soluble form and be directly applied as a thin film on an electrode. These films are often prepared by spreading a polymer solution on a rotating surface (spin coating). Then the solution is spread out and the solvent evaporates. The net result is a thin film of the polymer on the surface.

In paper II, some different polymers containing the benzene ring as a building block were studied with X-ray emission spectroscopy. Figure 4.6 shows the geometry of the set of poly(phenylenevinylene)s studied: (a) a single benzene ring, (b) poly(phenylenevinylene) (PPV), (c) poly(4,4'-diphenylenediphenyl-vinylene) (PDPV) and (d) poly(1,3-phenylenediphenylvinylene) (PMPV). The compounds (b), (c) and (d) are made up of benzene rings connected by short hydrocarbon bridges. The PPV compound is one of the most commonly used polymers used in light emitting diodes. The repeat unit of PPV consists of a benzene ring and a vinylene group. Fig. 4.7 shows nonresonant (a) and resonant (b) X-ray emission spectra of the poly(phenylenevinylene)s. The nonresonant spectra can roughly be divided into 6 bands. The band structure of the different polymer spectra are sim-
Figure 4.6: Schematic geometries of poly-phenylene-vinylene compounds.

Similar to that of the spectrum of the benzene ring at the bottom of the figure. For a simple qualitative understanding of the transitions involved, we first consider the benzene ring. In the benzene ring, the ground state has high symmetry ($D_{6h}$) with 9 outer valence molecular orbital levels. The six bands ($A - F$) in the nonresonant benzene spectrum involves the $1e_{1g}, 3e_{2g} + 1a_{2u}, 3e_{1u} + 1b_{2u} + 2b_{1u}, 3a_{1g}, 2e_{2g}, 2e_{1u}$ valence molecular orbitals, respectively. The $2e_{2g}$ and $2e_{1u}$ orbitals corresponding to the $E$ and $F$ bands are weak due to the $2s$ character of the corresponding molecular orbitals.

In the benzene ring, the lowest unoccupied (empty) molecular orbital (LUMO) is $1e_{2u}$ in the $D_{6h}$ symmetry. When the incident X-ray photon energy is tuned to this orbital, only electrons occupying the ungerade ($u$) molecular orbitals can fill the core hole according to the gerade-gerade ($g - g$) and ungerade-ungerade ($u - u$) parity selection rule for resonant inelastic X-ray scattering. In particular, the highest occupied molecular orbital $1e_{1g}$ level corresponding to band $A$ will be symmetry forbidden and is thus depleted in the resonant spectrum. Band $B$ in the nonresonant spectrum corresponding to the $3e_{2g} + 1a_{2u}$ levels should in principle also be depleted in the resonant case due to symmetry selection. However, although band $B$ show a large reduction of intensity in the resonant case, there is still significant intensity left due to the $1a_{2u}$ ungerade orbital and probably also due to the final state vibronic coupling effect [70].

For the PPV, PDPV and PMPV polymers the situation is more complex than for the benzene ring. Comparing the resonant and nonresonant spectra of the polymers in Fig. 4.7, one would expect the depletion of the $A$-band to be smaller in comparison to the spectrum of the benzene ring due to the symmetry reduction. However, since the vinylene groups only give small perturbations of torsion angles between the neighbouring benzene rings, the local electronic structure in each unit cell is expected to remain essentially intact. Since the X-ray emission process is local, the symmetry selection is thus largely conserved for polymers. The polymer
spectra in Fig. 4.7 thus all show benzene-like features with a large reduction of intensity of the A-band in the resonant case. The conservation of the symmetry selectivity in the case of polymers can be ascribed to ‘channel interference’. This means that the X-ray scattering of the different close-lying core-hole states interfere so that the total signal is depleted. In paper II we also noted that the band gap of the polymers can be obtained by combining the resonant and the nonresonant X-ray emission spectra. The band gap is equal to the energy difference between the position of the elastic peak in the resonant spectrum and the high-energy cut-off in the non-resonant X-ray emission spectrum. The bandgap is \( \sim 2.8 \) eV for the PPV, PMPV and PDPV polymers which is in fairly good agreement with optical absorption spectroscopy [71] and ultraviolet photoelectron spectroscopy [72].

### 4.3.3 Isomeric dependence

In papers III and IV, the poly(pyridine-2,5-diyl) (PPy) polymer was investigated for both the nitrogen and carbon contents. The geometrical structures of PPy are shown in Fig. 4.8. PPy can contain four different types of isomers: head-to-tail (HT) and head-to-head (HH) with two different steric positions denoted by the letter \( T \) and \( C \) for the relative positions between the adjacent nitrogen atoms (\( \text{trans} \) and \( \text{cis} \)). In principle, one could expect the polymer chain to be in a constant head-to-tail backbone configuration. However, due to the synthesis process, it also contains the head-to-head isomers. The energy barriers between the different isomers is very low and due to this fact one can expect an almost random distribution of zero and \( 180^\circ \) torsion angles. As demonstrated in papers III and IV, by using X-ray emission spectroscopy, it is possible to obtain information about the relative isomer content of PPy. Figure 4.9 (a) and (b) shows nonresonant and
Figure 4.8: The isomeric head-to-tail (HT) and head-to-head (HH) geometries of PPy. The letter T and C denotes the relative positions between adjacent nitrogen atoms.

Figure 4.9: (a) X-ray emission and absorption spectra of PPy at the nitrogen 1s threshold. (b) X-ray emission and absorption spectra of PPy at the carbon 1s threshold.
resonant X-ray emission spectra of nitrogen and carbon of PPy. The dashed lines show the corresponding absorption spectra. Five features (A - E) are identified in both the nonresonant and resonant emission spectra. Peak A corresponds to \( \pi \) electron and \( n \)-lone pair (nonbonding) electron states, peak B is due to both \( \pi \) and \( \sigma \), with \( \sigma \) dominating, while the other features C, D and E are all related to \( \sigma \) electronic states. At the bottom of the figures, a molecular orbital Hartree-Fock calculation of the different isomers is shown. The calculated spectra were obtained by taking the repeat unit as a model molecule and the transition intensities were broadened to match the experimental resolution. By comparing the peak structures in the measured and calculated spectra, the agreement was found to be best for the head-to-head-trans and head-to-tail-trans isomers.

### 4.3.4 The effect of doping

The Peierls transition in conjugated polymers also occurs when the polymer is doped i.e., by providing or removing extra charge. The process is called reduction or oxidation, but in analogy with the doping of semiconductors it is called doping also in this context. However, the doping levels of polymers are generally much larger than for inorganic semiconductors. Doping can be accomplished in different ways; chemically, electronically, and by injection of charge. The process transforms the polymer from a semiconducting state to a state which can almost be characterized as a metal.

![Geometrical structure of polyaniline](image)

Figure 4.10: Geometrical structure of polyaniline. The studied emeraldine form has \( y=0.5 \).

When the polymer is doped, a charge-transfer is introduced through oxidation (p-type doping) or reduction (n-type doping) in which electrons are added to the conduction band or holes are added to the valence band. The electrical conductivity of doped \( \pi \)-conjugated polymers extends over a large range anywhere between an insulator and a metallic-like system depending on the doping level. In paper V, the effect of doping through protonation on the nitrogen sites was studied for the poly-aniline (PANi) polymer. In this case the doping can be looked upon as adding holes to the valence band (p-type doping). The basic geometry of PANi is shown in Fig. 4.10. PANi exist in three different forms depending on the oxidation state. In paper V, the emeraldine form with \( y=0.5 \) which is the only conducting form of PANi was studied both for the undoped and protonated phases. PANi is particularly interesting to study since, in comparison to other polymers, it has a rather high electrical conductivity in the doped phases. Fig. 4.11 shows nonresonant spectra of the undoped and doped phases for both the nitrogen and carbon
Figure 4.11: Non-resonant nitrogen and carbon X-ray emission spectra of polyaniline.

The effect of doping with protonation on the spectra is clearly seen at peak A on the carbon spectra and the enhancement of peak B in the nitrogen spectra in the doped phases. The protonated phases of polyaniline were found to have less occupied states at the uppermost π-levels as a result of the charge-transfer from the protonated nitrogen sites. A comparison between the nitrogen and carbon spectra show that the orbitals have different relative intensities. The non-bonding (lone-pair) levels which are mixed into the π-levels are particularly emphasized in peak B of the nitrogen spectra.

4.4 Correlation satellites

4.4.1 Shake-up and Coster-Kronig satellites

In paper VI, the energy dependence of Wentzel-Druyvesteyn satellites was investigated in metallic copper using soft X-ray emission spectroscopy. As explained in section 2.3.3, these type of satellites typically end up on the high-energy side of the main line in X-ray emission spectra. The origin of these satellites has earlier been debated in the literature. The energy dependence of the intensity increase around the $L_{2,3}$ thresholds is here of particular interest; especially the transition from the adiabatic to the sudden core-electron excitation.

Figure 4.12 shows a comparison between an X-ray emission spectrum excited resonantly at the $L_3$ threshold and a nonresonant spectrum excited at 1088.5 eV. The spectra were aligned to the low-energy flanks. The difference spectrum (dashed area) is the satellite contribution due to both shake-up/off and Coster-Kronig contributions. The separation clearly shows the energy shift between the main line and the satellite. Fig. 4.13 shows the growth curve of the relative satellite intensity as function of excitation energy close to the $L_3$, $L_2$ and $L_1$ thresholds. For excitation
energies below the $L_2$ threshold, the satellite contribution is slowly increasing due to the shake-up/off processes. As the Coster-Kronig channel is opened at the $L_2$ threshold, there is a step of large intensity increase. Above the $L_2$ threshold, the intensity is again slowly increasing due to additional shake-up/off processes towards the $L_1$ threshold. As extensively discussed in paper VI, the intensity increase at the $L_1$ threshold is much smaller than at the $L_2$ threshold due to additional decay channels. The Coster-Kronig decay was proven to be much more important than the charge-transfer effect for the satellite contribution in X-ray emission spectra of copper metal.

Figure 4.12: Separation of Coster-Kronig proceeded satellite contribution between spectra excited at 1088.5 and 932.5 eV photon energies. The dashed area represents the difference spectrum.

Figure 4.13: Growth curve for shake-up processes in metallic Cu.
For large excitation energies above a core level threshold, the sudden approximation is valid for shake processes. As described in section 2.2.4, this assumes that the removed electron leaves the system so quickly that the other orbitals do not have time to relax. An interesting question which has been debated is how large the photoelectron energy must be for the sudden approximation to be applicable. It has thus been interesting to investigate how the shake intensity depends on the photoelectron energy in the near threshold energy regime. For a shake-up process, the excited electron ends up in a bound state whereas, for a shake-off process, the electron is ionized into the continuum. It has been shown experimentally and theoretically that with increasing excitation energy, the shake probability approaches the sudden-approximation limit. This applies both for shake-off as well as shake-up processes. For shake-up processes, the sudden limit is reached very quickly within a few eV above threshold. Shake-off processes reach the sudden limit at much higher energies i.e., in the energy range 100-200 eV above threshold [73]. Thus, the photon energy dependence behaviour of shake-up and shake-off processes close to a threshold is very different. Our experimental results indicate that the onset of the sudden limit appears to be rather abrupt and close to the threshold.

In paper VII, resonant Auger spectroscopy was applied to the nickel metal system. In nickel metal, the excitation and decay mechanisms are more complicated than in the copper system due to the configuration interaction in the ground and core-excited states. This gives rise to interesting many-body effects. A controversial issue of the interpretation of the well-known 6-eV feature present at the $L_{2,3}$ edges in the X-ray absorption spectrum in nickel was addressed. Figure 4.14, shows an X-ray absorption spectrum of the nickel metal measured at the $L_{2,3}$ thresholds together with calculated atomic multiplets of the $2p^63d^9$ and $2p^53d^8$ core-excited configurations. Figure 4.15 (a) shows a set of Auger spectra measured at the $L_{2,3}$ thresholds. The high-energy cutoff in each spectrum corresponds to the Fermi level.
Figure 4.15: (a) A set of Auger spectra for different excitation energies around the $L_3$ and $L_2$ thresholds. (b) Difference spectra of Auger satellites in Auger spectra showing the energy dependence of the shake-up and Coster-Kronig contributions at excitation energies between 11.1 - 19.8 eV.

At the bottom, the localized $3d^8$ multiplets are schematically shown. The threshold spectrum excited at 852.8 eV can be considered as essentially free from $3d^7$ satellite structures. In Auger spectra, the $3d^7$ three-hole satellites end up on the low kinetic energy side of the main line. At higher photon energies, the satellite structures are clearly observed on the low kinetic energy side of the main line. Figure 4.15 (b) shows difference spectra between Auger spectra measured at different photon energies around the $L_{2,3}$ thresholds. The large satellite structure at about 845 eV corresponds to shake-up transitions. It is interesting to note that there is a new feature at about 841 eV which has an onset at the $L_2$ threshold. This feature corresponds to the Coster-Kronig contribution to the satellite intensity. Based on the relative intensity increase of the three-hole satellites in Auger spectra, it was shown in paper VII that it is possible to obtain quantitative information about the population of the shake-up states in the nickel absorption spectrum seen in Fig. 4.14. This gives insight into the origin of the 6-eV spectral feature, which had earlier been discussed both in terms of delocalized band states and localized multiplet states. Fig. 4.16 shows the integrated satellite intensity of nickel metal as function of photon energy above the $L_3$ and $L_2$ thresholds. The integrated satellite intensity reveals a maximum at 5 eV above both the $L_3$ and $L_2$ thresholds. The 6 eV feature in the X-ray absorption spectrum in Fig. 4.14 was explained to be due to a critical point in the unoccupied band structure (at the $L$ symmetry point).
while the strength of the localized states had a maximum about 5 eV above the threshold.

4.4.2 Resonant photoemission and Fano profiles

One of the most studied spectroscopical effects has been the 6-eV satellite in nickel metal. Since the discovery of a Fano-type lineshape by Dietz et al. [74] in 1974 in the electron energy loss spectrum at the 3p threshold in nickel metal, the effect has been extensively studied. Resonant photoemission on Ni metal was first used in 1977 by Guillot et al. [75] and in 1978 for certain rare-earth materials by Lenth et al. [76] Allen et al. [77] Johansson et al. [78] and Gudat et al. [79] Theoretical formulations of the resonant photoemission process have been made by Penn [80] and by Davis and Feldkamp [81].

In the nickel metal system studied in papers VII, VIII, IX, X, the excitation energy is tuned to the 2p core level, which results in an interaction between the $2p^5[3d^{10}4s]$ autoionization channel and the direct photoemission process. This is illustrated in Fig. 4.17, where the thick arrows indicates the majority channels and the thin arrows are the minority channels.

As explained in section 2.2.5, the shape of a Fano profile is determined by the asymmetry parameter $q$, if there is an interaction between one discrete state and one continuum. Fig. 4.18 shows experimental data in comparison to a calculated Fano profile for the valence band of nickel metal. In this case the simulated Fano lineshape $\Gamma = 0.35$ eV and $q = 2$. This can be compared with the measured $2p$
core level width of nickel metal obtained by Nyholm et al. \[82\] which was found to be 0.31 eV.

\[\langle f | \hat{V}_c | g \rangle \]

\[\langle m | \hat{V}_d | g \rangle \]

\[\langle f | \hat{V}_A | m \rangle \]

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Figure 4.17: Schematic diagram of the interference between the direct valence-band photoemission channel and the core-assisted Auger channel at the 2p thresholds in Ni.

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Figure 4.18: A Fano-like profile in the nickel valence band. The markers are the experimental data and the dashed line represents the Fano model for \( q = 2 \) and \( \Gamma = 0.35 \) eV.

In paper VIII, a very strong intensity enhancement \( (q \sim 9) \) was observed for the 6-eV satellite. The measured spectral profiles for the 6-eV satellite could not be accurately fitted within the simple Fano model. This is probably due to the fact that there are interactions between several discrete states and continua. Thus, the basic assumption for the Fano model i.e., one discrete state and one underlying
continuum is no longer valid in this case. It was observed that the profiles were different in two angular orientations which give strong evidence for interference effects. In paper IX, the resonantly enhanced interference effects in the nickel metal were accurately probed with the use of angle-dependent measurements.

4.5 Subthreshold excitations of metals

In paper XI, subthreshold X-ray fluorescence excitation of metals was discussed within the context of energy conservation which determined the main features of the spectra. Resonant inelastic scattering, sometimes denoted X-ray resonant Raman scattering, was first observed by Sparks using a Cu $K_\alpha$ source to irradiate different samples [11]. Later, this effect was investigated using synchrotron radiation by Eisenberger et al. [12] and Briand et al. [83]. The process has been theoretically described in terms of resonant scattering theory by Tulkki and Åberg [28] based on the Kramers-Heisenberg equation (2.27) described in section 2.3.4. In this case the Kramers-Heisenberg expression is essentially a convolution of two terms which represents the excitation and emission steps. The Lorenzian in the excitation term represents a broadening of the core-excited states corresponding to a distribution of photoelectron energies. The photoelectron energy distribution is weighted by the intermediate density-of-states. The emission term represents a distribution of energies of the final states. The core-excited density-of-states can be obtained by for example a deconvolution of absorption spectra or using calculated density-of-states.

![Diagram of subthreshold excitations](image)

Figure 4.19: An illustration of how Lorenzian tails of continuum states with a core vacancy are excited below threshold. The uncertainty of the intermediate state is transferred to the excited electron in the final state.

In paper XI, we use the Kramers-Heisenberg equation to interprete the spec-
tra in a two-step model neglecting interference effects which provides a sufficient understanding of the experimental spectra. The width of the characteristic fluorescence which follows from excitation well above threshold is a sum of the natural widths of the intermediate and final states.

Figure 4.19 shows a schematic energy level diagram to illustrate how Lorenzian tails of continuum states with a core vacancy are excited below threshold. An electron is excited in the system from the ground state of energy $E_0$ to a final state with a core hole of energy $E_h$ with an electron of energy $E_e$. Due to energy conservation, the outgoing photon will have an energy $E_{\text{out}} = E_{\text{in}} - (E_h + E_e - E_0)$. The uncertainty of the intermediate state is transformed to the excited electron in the final state. This results in a high-energy cut-off in the spectra for excitation energies below a core-level threshold and a linear dispersion is observed. By varying the excitation energy, the access to the intermediate density of states is varied which results in a modulation of the fluorescence intensities. The intensity variations of the fluorescence spectra essentially reflects the absorption profiles following the transition amplitudes from the ground to the intermediate states. It was shown in paper XI, that for excitations far below threshold, the intensity of the emission spectra are proportional to a convolution of the occupied and unoccupied local partial density-of-states.

4.6 Layered materials and buried interfaces

The ability to control thin-film growth at the atomic level to artificially grow epitaxial and heteroepitaxial semiconductor structures has more recently been extended to magnetic nanostructures, including metallic, oxide, and semiconducting phases. This makes it possible to custom-make magnetic properties to be used in different applications. In many ways research in magnetic materials is therefore experiencing a renaissance enabled by developments in the last decades in the fields of semiconductor physics and materials science. Many examples can be found to illustrate the close link between fundamental physics of magnetic phenomena and their technological applications. The first observation of an oscillatory magnetic interlayer coupling was done in 1986 by Grünberg et al. [84]. Since then much research has been focussed on studying magnetic interlayer coupling both from an experimental and theoretical point of view. A layered system with an anti-ferromagnetically aligned coupling has higher electrical resistivity than a ferromagnetically aligned system. This effect is usually referred to as the giant magneto-resistance (GMR) effect. The GMR effect can be used to construct highly sensitive and compact sensors which for example, can be used to read magnetically stored data of high density. Examples are recording heads that uses a spin-valve read transducer based on the GMR effect. With the ability to synthesize novel magnetic films and nanostructures exhibiting a variety of magnetic properties, prospects for new generation devices are made possible, with applications based on magnetoelectronics, such as magnetic random-memory cells.

The diversity of interactions underlying magnetic phenomena and semiconductor structures require measuring probes which are sensitive to the local atomic and extended electronic structure in thin film systems. It is also necessary to probe the
geometric structure in materials of different thickness where the bulk symmetry is broken in both the lateral and vertical (depth) dimensions. Knowledge of the electronic structure of buried layers and their interfaces represents a key concept for the understanding of the properties of semiconductor and magnetic devices. Since the probing depth of photoelectron spectroscopy and related techniques is limited to a few atomic layers, these methods are generally not suitable for studying buried layers.

In papers XII and XIII, it was demonstrated that it is possible to investigate details of the electronic structure of internal atomic layers by using X-ray emission and absorption spectroscopy. In paper XII, the local and partial density-of-states of bulk silicon, bulk gallium-arsenide, one monolayer and three monolayers of silicon, deeply embedded below a gallium-arsenide(001) surface was measured at the silicon \(L_{2,3}\) threshold. Unambiguous differences of the density-of-states of bulk silicon in the different situations were observed. In paper XIII, the electronic structure of a single buried copper monolayer in bulk nickel was investigated. X-ray emission and absorption spectra were compared with band structure calculations using a LMTO-Green's function method. The advantage of the Green’s function technique is that it efficiently takes into account the loss of translational symmetry perpendicular to the interface. The calculations were performed for bulk copper, bulk nickel and a nickel/copper/nickel triple-layer. The triple-layer consisted of two semi-infinite crystals of nickel, separated by a single monolayer of copper. This allowed a direct comparison between the spectral properties of the absorption and emission spectra and the calculated, partial density-of-states of the ground state. The spectral variations of the occupied and empty 3d-bands were found to be well described within the one-electron band structure picture. In comparison to bulk copper, an X-ray emission spectrum of a buried copper monolayer revealed a band narrowing and a small intensity enhancement close to the Fermi level. The results showed a different behavior of the d-band and the sp-band regions. The sp-band structure probed by the X-ray absorption technique was strongly influenced by the chemical surrounding due to hybridization. The characteristics of the more localized d-electron states were dominated by the properties of the individual atoms. The effects of the core-hole in the final state were found to be very small for the sp-band structure. It was interesting to observe that the 6-eV feature in the X-ray absorption spectrum of the nickel metal also appeared in the same energy regime in the buried copper layer. This result led to the conclusion that the 6-eV feature mainly originates from flat regions of the \(L\) symmetry point in the band structure rather than from multi-electron correlation effects as previously assumed.

It has recently been proposed theoretically and shown experimentally that the spin-dependent density-of-occupied-states can be obtained from X-ray emission spectroscopy, following the creation of a spin-polarized core-hole through absorption of circularly polarized X-rays. With the use of circularly polarized synchrotron radiation in the excitation, the X-ray emission dichroism spectrum is the difference in emission intensity obtained with opposite relative orientations of the photon spin (helicity) of the incident X-rays and magnetization direction of the sample. The difference spectrum shows all components that depend on the polarization of the radiation and can therefore show details of the electronic structure of ferro-
magnets. This is known as circularly X-ray emission dichroism, where the magnetic order induces an anisotropy in the electronic structure of the system. These type of measurements are expected to provide useful information about the mechanism of oscillatory exchange coupling in magnetic multilayers and half-metallic ferromagnets (heusler alloys) where only one sub-band contributes to the electron transport. In order to fully understand the influence of magnetic interlayer coupling, it is necessary to make detailed quantitative comparison to band-structure calculations. However, a complicating factor in this context is that the measured layered structures are not in equilibrium and the experimental conditions may not be fully known. Another uncertainty of comparing the experimental data with theory is to what extent an observed discrepancy is due to roughness and diffusion of the interface layers.

4.7 X-ray studies of low-energy excited states

Strongly electron correlated systems are interesting both from an experimental and theoretical point of view. The physical properties of these materials are determined by the competition between atomic-like properties and the orbital overlap on neighbouring sites leading to a delocalized band-like behaviour. A comparison between the on-site Coulomb correlation energy ($U$) and the bandwidth ($W$), provides a measure of the relative strength of the localization tendency. If $W$ is much larger than $U$, the conduction electrons are delocalized and can be described in a band model. In the opposite case, which applies to the 4f-electrons in many rare-earths systems, an atomic-like approach is more appropriate. The intermediate regime between the localized and delocalized limits is relevant for many interesting materials.

The electronic properties of strongly correlated systems are often interpreted within the framework of the Anderson impurity model (SIAM) described in section 3.4. The SIAM provides a satisfactory description of various properties of many systems with localized states. In this model, the localized states of the metal ion with the on-site Coulomb interaction $U$ are treated as a degenerate impurity level coupled to the hybridization strength $V$ to the valence band separated by the charge-transfer energy $\Delta$. The ground state can then be described using the relationships between $\Delta$, $U$ and $V$ as parameters in the model Hamiltonian. The model parameters are normally derived from the analysis of core-level X-ray photoemission and X-ray absorption data although it is expected a priori that the hybridization $V$ and the on-site Coulomb interaction $U_{dd}$ are different in the presence of a core-hole. However, the validity of the SIAM for heavy fermions has been questioned based on the inconsistency of experimental data obtained with electron spectroscopies. In particular, the existence or lack of the Kondo resonance in valence-band photoemission spectra of heavy fermion materials has been debated [85]. The large surface contribution in the spectra often complicates the analysis of the temperature dependent behaviour of the bulk component.

It has been shown that it is possible to gain access to low-energy loss spectra by the application of the X-ray scattering technique in metallic systems. Resonant inelastic X-ray scattering experiments on e.g., cerium compounds and transition
metal oxides can be performed by tuning the incident photon energy to specific energies close to a core level threshold. The bulk sensitivity, element and symmetry selectivity of the X-ray scattering technique makes it a powerful tool for studying the electronic structure of correlated systems. The ground state values of the charge-transfer energy and the hybridization strength which are used as model parameters to characterize charge-transfer excitations can be estimated directly from the X-ray scattering spectra.

Figure 4.20: Schematic picture of (a) single-particle approach; (b) many-body approach to describe inelastic X-ray scattering of rare earth metals and compounds.

Figure 4.20 (a) and (b), schematically shows how inelastic X-ray scattering spectra can be interpreted in two different ways. Above a core-ionization threshold, where there is a competition between normal emission and the X-ray scattering process, it is possible to distinguish between the two contributions by progressively changing the incident photon energy. This is due to the fact that the X-ray scattering contribution disperses on a photon-emission energy scale, and the normal fluorescence signal does not. In a single-particle picture (a), the X-ray scattering and normal emission contributions are not energetically separable. The elastic peak follows the excitation energy but there is also some contribution of momentum conserved X-ray inelastic scattering intensity superimposed on the normal emission part. In a many-body picture (b), the X-ray scattering contribution essentially follows the excitation energy while the normal emission stays at the same emitted photon energy with increasing intensity. For many strongly correlated systems, the many-body picture provides the best agreement with the experimental observations.

Using the many-body approach, the peaks can be assigned to structures of three different categories: the elastic peak, the resonating loss structures and the normal X-ray emission lines. At a metal core-level threshold, as a result of the creation-annihilation of a core-hole, there are radiative transitions back to the ground and low-lying excited states so that the final states of the spectroscopic process can be described as eigenvalues of the ground state Hamiltonian.

In paper XIV, resonant inelastic soft X-ray scattering spectra are presented at different photon energies close to the cerium 4d threshold of CeB6, CeAl, γ-Ce and α-Ce. A pronounced inelastic scattering feature was observed at about 4 eV
(loss energy) below the elastic peak. The origin and character of this structure was discussed in terms of charge-transfer excitations. It is very interesting to note that a simulation of the X-ray scattering spectra within the SIAM can give ‘true’ (not renormalized) values of the model parameters of the ground state. The SIAM predicts a significant temperature dependence of the $f$ occupancy for the cerium systems. This value is crucial for the description of various physical properties.

In paper XV, the electronic structure of the CeB$_6$ metal compound was studied both at the cerium 3d and 4d thresholds. The elastic peak was found to be a dominant feature at both thresholds due to the strong localization of the 4f electrons. Different contributions from the inelastic scattering and the normal fluorescence could be identified in the scattering spectra.

The 4-eV low-energy loss structures in papers XIV and XV which were assigned to charge-transfer excitations to the 4f$^0$ state in the X-ray scattering spectra of the cerium compounds were found to be higher in energy than the corresponding 4f$^0$ peak at 2.5 eV in valence band photoemission spectra. The difference between the energy positions of the 4f$^0$ state between the two techniques can be the result of probing the systems with different numbers of electrons. The X-ray scattering process can be considered as charge neutral while in the photoemission final state one electron has been removed. The present interpretation from the X-ray scattering measurements indicate that absolute values of both the energy of the 4f states and the hybridization matrix element $V$, which contribute to the energy separation between the $f^1$ and $f^0$ configurations, can be larger than previously obtained from photoemission data.

In paper XVI, low-energy excited states of titanium and manganese X-ray scattering spectra of FeTiO$_3$ and KMnO$_4$ were presented. By progressively changing excitation energy over the $L_{2,3}$ thresholds of both compounds the energy positions of the charge-transfer satellites with respect to the recombination peak, the transition metal 3d - ligand 2p hybridization strength in the ground state of the system could be estimated.

In paper XVII, low-energy $d$-$d$ and charge-transfer excitations were studied by resonant X-ray scattering from manganese oxide. By using a two-step approximation, the varying energies and intensities of the $d$-$d$ excitations were well reproduced by simple atomic model calculations. The $d$-$d$ excitations in transition metal compounds are dipole forbidden and have previously been observed with electron energy loss spectroscopy (EELS). Since there are two dipole transitions involved in the excitation-emission process, the final state has the same parity as the initial state, and the $d$-$d$ excitations become allowed. Charge-transfer excitations in MnO were observed as a result of transitions involving the transfer of an electron from the ligand O$^{2-}$ site to the metal ion. Although the charge-transfer process plays an important role in these types of spectra, it cannot be reproduced by a simple atomic calculation.

It is important to gain further experimental knowledge about the charge-transfer and low-energy excited states, and the hybridization parameters which are indispensable for the model calculations. In this case, the bulk sensitivity and elementspecific nature of resonant inelastic scattering spectroscopy is particularly useful. Another important aspect, yet unaddressed by scattering experiments, concerns
magnetic properties. These questions are currently receiving much attention internationally.
Bibliography


Appendix I

Figure 4.21: The experimental station at beamline BW3 at the Hamburger Synchrotronstrahlungslabor (HASYLAB) am Deutschen Elektronen-Synchrotron (DESY). The picture shows the event of the first rotational tests of the chamber under vacuum.

Figure 4.22: The experimental station at beamline 8.0 at the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory (LBNL) in Berkeley.