INTERPRETATION AND RELATIVISTIC SIMULATION OF SELECTED ELECTRONIC TRANSITIONS: DECAYS OF M-SHELL HOLE STATES IN ATOMIC Cr, Br AND Rb

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Abstract

In this thesis electronic structure of atomic chromium, rubidium and bromine are studied experimentally and theoretically through transitions and decay processes originating from selected $M$-shell hole states. The experiments are conducted with traditional methods of electron spectroscopy as well as more recent multicoincidence methods using pulsed synchrotron radiation and a magnetic bottle spectrometer. The observed electronic transitions are theoretically simulated with multiconfiguration Dirac-Fock method. Finally, the calculations are used to interpret the measured spectra to investigate the energy level structure and electron dynamics of the studied elements.

Key words: atomic structure, Auger decay, coincidence, Coster-Kronig, electronic transition, HF, krypton, magnetic bottle, MCDF, photoionization, spectroscopy, super-Coster-Kronig, synchrotron, X-ray
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Oulu, November 2019

Juho Keskinen
LIST OF ORIGINAL PUBLICATIONS

The presented thesis contains an introductory part and the following articles, which will be referred in the text by their Roman numerals (I–III).


The publications listed above are results of teamwork. The author has handled and analyzed the data, performed the theoretical computations to evaluate the data, and been the main contributor in writing the articles.

Reprints of the original articles are not included in the electronically distributed version of the thesis.
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CHAPTER 1

Introduction

Atoms are the building blocks of everything around us. By joining together into molecules, ions, clusters, liquids and solids they form all the matter we interact with in our everyday lives. The atom gets its name from Ancient Greek, in which ἀτόμος means indivisible, though back then it existed merely as a philosophical concept. The modern idea of atoms as small building blocks for the matter was brought up by John Dalton in 1805 [1]. Evidence for the divisibility of atoms was discovered by the end of the century in 1897. Sir Joseph Thomson was able to provide the evidence by measuring the mass of cathode rays that negatively charged particles lighter than hydrogen atom exist [2]; nowadays we know these particles as electrons. Later in 1911 Sir Ernest Rutherford proposed, based on scattering experiments, that the positive charge to balance the opposite charge of the electrons is concentrated in a small region of space, a nucleus, at the centre of the atom [3]. This discovery inspired Antonius van den Broek to suggest that the placement of each element in the periodic table was determined by its nuclear charge [4]. This was later confirmed experimentally by Henry Moseley [5,6]; prior to this the order of the elements on the table was not thought to be physical in nature. The amount of charge was later linked to the number of positively charged particles, which Rutherford started to call protons [7]. The advancements in mass spectrometry finally paved way for the detection of neutron in 1932 by James Chadwick [8].

The principles of classical physics could be used to describe the electromagnetic attraction between the electrons and the positively charged nucleus. To prevent the electrons from falling into the nucleus it had to be assumed that they orbit the nucleus. Charged particles in acceleration were however known to emit electromagnetic radiation and thus electrons orbiting this way would eventually anyway spiral into the nucleus. Niels Bohr suggested a model in which the electrons orbit the nucleus in stationary orbits, which have discrete energies [9,11]. The model gives rise to the concept of quantum numbers and explains why atoms can only absorb and emit certain
wavelengths of electromagnetic radiation. The idea that electromagnetic radiation itself can be considered as quantized packets of energy had already been coined by Max Planck in the beginning of the 20th century \[12\]. Later Albert Einstein built on this idea suggesting that these packets could be considered particles called photons in his theoretical study on photoelectric effect \[13\], which had already been experimentally discovered by Heinrich Hertz by the end of the 19th century \[14\]. All these ideas and discoveries had made the time ripe for the advent of quantum mechanics, which in the following years was conceived by Werner Heisenberg, Max Born, and Erwin Schrödinger among many others \[15–22\]. The theories were further developed and generalized by Paul Dirac \[23–25\] to take into account the special theory of relativity \[26\].

We tend to shine light upon objects we wish to examine closer. Thus it is especially fitting that particles of light, photons, can be used according to the photoelectric effect to probe the qualities of atoms. Such application of the effect has led to the development of the field of photoelectron spectroscopy (PES), in which photons of appropriate energy are used to detach electrons from the target. The kinetic energies of the ejected electrons are measured and depicted as spectra, which reveal the characteristic discrete energy level structure of the binding energies of the electrons of the sample. Methods utilizing X-ray energy range photons to study the binding energies of core electrons of atoms were developed by Kai Siegbahn \[27,28\], and less energetic ultraviolet range photons were used to probe valence electrons by Feodor Vilesov and David Turner \[29,30\]. Nowadays many applications use radiation from synchrotrons, in which charged particles are moving at relativistic speed in a circular path. The electromagnetic radiation emitted by these charged particles in radial acceleration has high intensity and brilliance and on top of that can be tuned to match a specific wavelength from infrared to hard X-rays. The emitted radiation also has a time structure so it can be used for time-of-flight type of experiments. The electronic structure of atoms and the transitions taking place within the electron cloud are covered in chapter 2 and the relevant experimental methods used to record these transitions and collect the studied spectra are discussed in chapter 4.

In order to be able to interpret measured spectra, one has to simulate the ionization and other processes that take place within the electron cloud of an atom. Running a simulation for a quantum mechanical object requires solving the associated Schrödinger, or in cases of heavier atoms, the relativistic Dirac equation. The Schrödinger equation can be solved analytically for hydrogen-like atoms, but numerical methods have to be used for other cases with more than one electron. To prevent the computations from getting too heavy, iterative methods, in which each electron moves in a spherically symmetrical effective potential caused by all the other electrons of the atom, are used. One such is the self-consistent field method developed by Douglas Hartree \[31,32\]
and refined by John Slater [33, 34] and Vladimir Fock [35]. The code of Cowan [36], used to calculate energies in some of the studies in this thesis, is based on this method. With heavier elements it becomes important to take into account the increasing spin-orbit interaction between the angular momentum and spin of an electron. This can be accounted for by solving the atomic energy levels from the Dirac equation instead of using the Schrödinger equation. In practice the Dirac equation is often solved using the relativistic multiconfiguration Dirac-Fock method [37, 38], which also accounts for the electron correlations. This method in the form of GRASP2K [39–41] and the flexible atomic code (FAC) packages [42] has been utilized in the studies presented in this thesis. Chapter 3 describes the theoretical background of the simulations used in the studies of this thesis in more detail.

The focus in this thesis is on the interpretation of recorded atomic spectra with the help of relativistic calculations. In article I the 3p photoelectron spectrum and the subsequent Auger electron spectrum of atomic chromium were studied and interpreted. Multielectron coincidence methods were used to record the 3d photoionization in atomic rubidium with all the associated satellite lines and the following Auger decay in article II. This enabled the extraction of initial-state-selected Auger final state distribution graphs through means of data handling. The graphs could be used to unambiguously detect and identify shake-up processes happening during normal Auger decay for the first time. In article III the decay following the creation of a 3d hole in the isoelectronic series of excited bromine, singly ionized krypton and doubly ionized rubidium atoms was studied by interpreting the measured spectra. The traditional high resolution Auger spectrum together with multielectron coincidence measurement and theoretical simulation made it possible to study the features of the Auger cascade decay in the case of bromine with high accuracy. More detailed summaries of the included articles, their results and findings are presented in chapter 5 and conclusions with a future outlook in chapter 6.
Chapter 1. Introduction
CHAPTER 2

Electronic structure of atoms and transitions

Atoms consist of a nucleus and an electron cloud surrounding it. Positively charged nucleons, protons, each carrying the positive elementary charge, are concentrated in the nucleus of an atom, whereas each electron in the cloud around it carries the negative elementary charge. The nucleus also houses the neutrons, which have no charge but contribute to the total mass of the atom. In a neutral atom the number of protons and electrons is the same, so the multiples of positive and negative elementary charges cancel each other out. The nucleus houses almost all the mass of the atom, but for the scope of research presented in this thesis, it is enough to treat it as a point charge in space.

The number of protons in an atom is called its atomic number and denoted with the letter \( Z \) characteristic to each element. The sum of all nucleons in the nucleus is called the mass number and denoted with the letter \( A \). Atoms of same \( Z \) but different \( A \) are called isotopes due to them differing in the number of neutrons. When the number of electrons in the cloud does not match the atomic number, the atom has a non-zero total electric charge and is called an ion.

2.1 Electron shells and configurations

Atoms as quantum mechanical objects, as well as particles they consist of, are subject to the effects of quantization. Because of this the configuration of electrons in the cloud is best described as if the electrons are located in discrete shells around the nucleus. Each shell is described by its principal quantum number \( n = 1, 2, 3, \ldots \). Due to historical reasons these shells are occasionally denoted with letters \( K, L, M \), and so on respectively in the vein of the X-ray notation \([43]\).

The shells are further divided into a number of subshells characterized by their orbital angular momentum quantum number, also called the secondary
Chapter 2. Electronic structure of atoms and transitions

quantum number, $\ell = 0, 1, 2, 3, \ldots, n - 1$. The different subshells $\ell$ are often denoted with letters $s, p, d, f$, and so on respectively in alphabetical order from $d$ onward. A specific subshell is commonly designated with the combination $n\ell$, in which $n$ is written using numerals and $\ell$ with alphabets, for example $3d$ ($n = 3$ and $\ell = 2$).

Each subshell consists of one or more orbitals, which differ from each other in shape and spatial distribution. The magnetic quantum number $m_{\ell} = -\ell, \ldots, \ell$ is used to identify the different orbitals, which each can house two electrons, each of which can be thought as spinning tops that can spin either clockwise or counter-clockwise. The magnitude of the angular momentum generated by this spin is always the same $s = \frac{1}{2}$, but its direction can be either up (+) or down (-) and can be described with the spin magnetic quantum number $m_s = \pm \frac{1}{2}$. Two electrons, which have their spins anti-aligned, occupying the same orbital are said to be paired with the total spin of the pair being zero forming a rather stable configuration [44].

Following the Pauli exclusion principle [45], which requires each electron to have a unique set of quantum numbers $n, \ell, m_{\ell}$ and $m_s$, it is possible to determine that the maximum number of electrons each shell can host is $2(2\ell+1)$. The number of electrons in a specific subshell can be written as a superscript in the upper right corner of the $n\ell$ designation, for example $3d^9$. This way it is possible to write out the particular way the electrons occupy the subshells; the electron configuration. The Pauli exclusion principle together with the Aufbau principle [46] can be used to figure out the electron configuration of an atom in its ground state; for example the configuration of electrons in a neutral rubidium atom can be written as $1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^1$ or in a simpler fashion as [Ar]5s by replacing the fully filled subshells with the square-bracketed chemical symbol of a noble gas of the same configuration and omitting superscripts for singly occupied subshells.

### 2.2 Total angular momentum of an atom

Each electron of an atom can be considered having two different angular momenta. The orbital angular momentum $\ell_i$ is caused by the electron circling around the nucleus and the spin angular momentum $s_i$ by the electron revolving around itself. Because of the quantum mechanical nature of electrons these angular momenta are however quantized in magnitude along a chosen quantization axis, usually taken to be the z-direction [47]. The magnitudes of the orbital angular momentum and the spin angular momentum vectors are

$$|\ell_i| = \hbar \sqrt{\ell_i(\ell_i + 1)}$$  \hspace{1cm} (2.1)

$$|s_i| = \hbar \sqrt{s_i(s_i + 1)}$$  \hspace{1cm} (2.2)
2.3. Coupling schemes for angular momenta

respectively. The z-components of these momenta are quantized in such a manner that the possible values \[47\] for them are

\[l_{zi} = m_{li} \hbar\] (2.3)

\[s_{zi} = m_{si} \hbar = \pm \frac{1}{2} \hbar.\] (2.4)

The orbital and spin angular momenta of an electron interact respectively with those of other electrons of an atom due to the Coulomb interaction, which originates from the electromagnetic repulsive force the electrons exert on each other. It causes the individual orbital angular momenta \(\ell_i\) to couple together into total orbital angular momentum \(L\) of the atom; the corresponding quantum number is \(L = \sum \ell_i\). The same interaction together with the purely quantum mechanical exchange interaction \[23,48\] make also individual spin angular momenta \(s_i\) of all the electrons to sum up and form the total spin angular momentum \(S\) for which the corresponding quantum number is \(S = \sum s_i\). The two different total angular momenta \(L\) and \(S\) couple via spin-orbit interaction \[49,50\] into the total angular momentum of the atom \(J\), which as the vector sum of \(L\) and \(S\) is also quantized. Its magnitude is given by

\[|J| = \hbar \sqrt{J(J + 1)},\] (2.5)

in which \(J = |L - S|, |L - S| + 1, \ldots, |L + S| - 1, |L + S|\). The related magnetic quantum number is \(M_j = -J, \ldots, J\) and can be used to write out the quantized z-component

\[J_z = M_j \hbar\] (2.6)

of the total angular momentum. The same total angular momentum can be deduced by first coupling each \(\ell_i\) and \(s_i\) together into the total angular momentum \(j_i\) of an individual atom. The quantum number \(j_i = \ell_i \pm s_i\) is used to describe the corresponding z-component in a similar fashion to Eq. 2.6. For fully occupied subshells the total angular momenta \(L, S\) and \(J\) are always zero, so it is enough to take into account only the electrons on partially filled subshells, when determining the total angular momentum of an atom. Determination of these angular momenta helps to understand and interpret the energy structure of the electron cloud.

2.3 Coupling schemes for angular momenta

The order in which the different angular momenta are summed plays an integral role in different coupling schemes. If the Coulomb interaction between the electrons is stronger than the spin-orbit effect, as is usually the case for lighter elements and valence orbitals, then the so-called \(LS\)-coupling, which
is also sometimes called Russell-Saunders-coupling, should be used. The relative strength of the spin-orbit interaction increases with heavier elements and orbital depth. For these cases the so-called \( jj \)-coupling often gives better results.

### 2.3.1 \( LS \)-coupling

In the \( LS \)-coupling scheme the Coulomb interaction is considered dominant and thus the individual orbital angular and spin angular momenta of all the electrons are coupled together into total orbital \( L = \sum l_i \) and total spin angular momenta \( S = \sum s_i \), respectively. These two then further couple into the total angular momentum \( J = L + S \), as discussed in the previous section \[47\]. If the orbital is more than half-full, it is easier to couple electron holes, which are vacancies of electrons, with each other and, if necessary, electrons of other subshells. This is because for coupling, a hole in a particular subshell has same properties as an electron of the same subshell. The same term symbols are acquired regardless of whether the coupling was done for electrons, holes or a mix of both.

Describing the different energy levels of an atom can be done with the help of the so-called term \( 2S+1L_J \) symbol, in which \( S \), \( L \) and \( J \) are the aforementioned quantum numbers associated with \( S \), \( L \) and \( J \) respectively. The term symbols of a particular configuration can be organized in energy using a set of so-called Hund’s rules \[44\]. The applicability of these three rules is however limited to cases, in which the assumption about the Coulomb interaction prevailing over spin-orbit effect holds true.

### 2.3.2 \( jj \)-coupling

The \( jj \)-coupling scheme is best suited for describing the states of heavier elements, for which the spin-orbit effect can be considered to be significantly stronger than the Coulomb interaction. In the \( jj \)-coupling the orbital \( l_i \) and spin angular momentum \( s_i \) of a single electron are first coupled to form the total angular momentum \( j_i \) for this particular electron. By coupling together all the individual total angular momenta \( j_i \) of electrons or holes in unfilled subshells the total angular momentum \( J = \sum j_i \) of the atom can be determined. When coupling two electrons, holes, or a hole with an electron the resulting levels can be denoted with the term \((j_1, j_2)J\), in which \( j_1 \) and \( j_2 \) are the quantum numbers associated with the total angular momenta \( j_1 \) and \( j_2 \) of individual electrons respectively: the quantum number \( J \) can be determined from \( j_1 \) and \( j_2 \) while respecting the Pauli exclusion principle. \[51\]

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2.3.3 Intermediate coupling and configuration interaction

In practice the atomic energy levels can rarely be described in the terms of pure $LS$- or $jj$-coupling but as something intermediate, as atoms of most elements and cases, in which transitions in and from different orbitals are studied, fall somewhere between the optimal applicability region of either coupling scheme.

In more sophisticated models, like configuration interaction, the atomic energy levels are not considered being represented by any single configuration, but rather by a linear combination of different $LS$- or $jj$-coupled levels of the same $J$ value. [51]

2.4 Electronic transitions

The ground state of an atom can be disturbed by bombarding the target atom with other particles. The incident particles can interact with the electrons of the atom and the resulting electronic transitions can be utilized to extract information about the structure of the electron cloud and the interaction itself. Though at least in principle any particles can be used to bombard the target, the most convenient way, regarding the research discussed in this thesis, is to use photons. This is because as particles without rest mass they are like packets of energy or energy quanta that are absorbed by the particles they collide with.

In photoelectric effect, which was first discovered in 1887 by Heinrich Hertz [14] and theoretically explained by Albert Einstein in 1905 [13], incident electromagnetic radiation of high enough energy can detach electrons from a material. This situation is described by the equation

\[ E_{kin} = h\nu - W_0, \]  

in which $E_{kin}$ is the kinetic energy of the detached electron, $h\nu$ the energy of the incident radiation and $W_0$ the work function of the irradiated material i.e. the minimum amount of energy required to remove an electron from the material. The analogous phenomenon for gas phase is known as photoionization.

2.4.1 Photoionization

Photoionization is a phenomenon in which an electron of an atom absorbs a photon in a process called photoabsorption and escapes from the electron cloud into the continuum, where the energy levels are not quantized. The target atom is left in an ionized state, and the ejected electron is called a photoelectron. The process can be expressed with the following reaction equation

\[ A + h\nu \rightarrow A^+ + e^{-}_{\text{photo}}, \]  

in which $A$ is the atom, $h\nu$ is the energy of the photon, $A^+$ is the ionized atom, and $e^{-}_{\text{photo}}$ is the detached electron.
Chapter 2. Electronic structure of atoms and transitions

in which $A$ is the target atom and $\epsilon_{\text{photo}}$ the photoelectron [52]. As the total energy of the system formed by the atom, the photon and emitted electron is conserved, the kinetic energy of the electron is

$$E_{\text{kin}} = h\nu - (E_f^+ - E_i), \hspace{1cm} (2.9)$$

in which $E_f^+$ and $E_i$ are the total energies of the system in its final (ionized) and initial (neutral) state respectively. The difference $(E_f^+ - E_i)$ is often called the binding energy $E_b$ of the electron and corresponds to the amount of energy required to detach the electron from the atom. For photoionization to occur, the energy $h\nu$ of the photon has to be greater than the binding energy $E_b$ of the electron. The binding energy is characteristic for each of the electrons in the atom.

$$A + h\nu \rightarrow A^*, \hspace{1cm} (2.10)$$

in which $A^*$ is the atom in its excited state. Photoexcitation is most likely if the photon energy $h\nu$ closely matches the difference $(E_f^+ - E_i) = E_{\text{ex}}$ the initial and final levels have in energy [17]. Generic illustration of the photoexcitation process is presented in Fig. 2.1(b).
2.4. Electronic transitions

2.4.3 Auger decay

After photoionization or phoexcitation the atom is potentially left in an energetically higher, excited state. According to the principle of minimum energy such systems are unstable and prefer to decay into an energetically lower state. In the case of excited atoms the lower states can be reached through decay processes which are either radiative or non-radiative. During radiative decay the atom decays into an energetically lower state by emitting a photon \[54\].

The Auger effect, which was independently discovered by Lise Meitner \[55\] and Pierre Auger \[56\] in the 1920s, is a non-radiative decay. During the process a vacancy in the electron cloud is filled by an electron from an energetically higher level. The energy released from this transition is transferred to another electron, which then escapes from the cloud. This ejected electron is called an Auger electron and its kinetic energy

\[
E_{\text{kin}} = E_i - E_f
\]

is defined by a distribution mainly dependent on the energy difference dictated by the lifetimes of the initial hole and final states of the atom. The kinetic energy of the Auger electron is characteristic to the levels involved in the specific transition. The effect of the method of the initial hole state creation on the Auger decay is insignificant, if the energy of the incident radiation is well above the ionization threshold of the target. When the energy used for ionization is only slightly above the binding energy of the detached electron, the photoelectron and Auger electron can interact with each other through so-called post-collision interaction (PCI) \[57\], which changes their perceived kinetic energies.

It is customary to categorize Auger transitions depending on the type of the electron vacancy created in the first step. If the hole state was created through ionization the subsequent process is called normal Auger decay to differentiate it from the resonant Auger decay, in which the initial hole is the result of an excitation process. The resonant Auger transition is even further divided into participator and spectator variants: the decay is called a participator resonant Auger, if the excited electron takes part in the Auger process – otherwise it is called a spectator resonant Auger. The participator transition is also called autoionization. The three Auger decay variants can be summarized with the following reaction equations

Normal: \[A^{+\ast} \rightarrow A^{2+\ast} + \epsilon_{\text{Auger}}\] \hspace{1cm} (2.12)

Participator/spectator: \[A^\ast \rightarrow A^{+\ast} + \epsilon_{\text{Auger}}\] \hspace{1cm} (2.13)

in which \(\epsilon_{\text{Auger}}\) is the ejected Auger electron and the various superscripts of \(A\) denote the states and potential states of the atom. If the electron hole is
still in the core shells, the atom is left in an excited state and may undergo a subsequent Auger decay. Such a chain of decays is called an Auger cascade and consists of two or more steps with the degree of ionization increasing and the electron vacancies accumulating in the outer, more loosely bound orbitals with each step.

Auger transitions are often named using the X-ray notation \( XYZ \) by giving them a three-letter combination, in which the first letter \( X \) corresponds to the shell of the initial hole and the two others, \( Y \) and \( Z \), to those of the shells of the two holes in the final state. Special cases of Auger decay are Coster-Kronig decay, in which the final state electron vacancy is
2.4. Electronic transitions

in the same shell as the initial hole, and super-Coster-Kronig, which has all the holes in the same shell. M-shell hole Auger decay was studied in articles I, II and III. The discussed Auger processes are presented as schematic illustrations in Fig. 2.2.

2.4.4 Satellite transitions

Photoexcitation and photoionization are not mutually exclusive processes and can occur upon the absorption of a single photon. The emitted photoelectron has less kinetic energy as some of the energy of the photon is spent on excitations in the following manner

\[ E_{\text{kin}} = h\nu - E_b^*, \quad (2.14) \]

in which \( E_b^* > E_b \). This is commonly referred to as a shake-up process as the affected electron is shaken upwards onto a Rydberg level. It can also happen simultaneously with for example an Auger decay likewise lowering the kinetic energy the ejected electron has. The opposite process is called shake-down, as during the transition an already excited electron decays to an energetically lower level releasing energy that is taken up by the emitted electron, thus increasing its kinetic energy. [58]

The third shake process, shake-off, is different from the other two transitions as it results in an emission of an additional electron. In this process the electron receives enough energy to get ejected from the cloud [58]. The amount of absorbed energy is not discrete, as the transition happens into the continuum. The total excess energy of the process, during which shake-off took place, is shared by the two emitted electrons. A shake-off transition happening during a photoionization is called also a direct double photoionization (DPI). In this process the two photoelectrons share the excess energy \( E_{\text{kin}} \) in Eq. 2.9 when \( E_f^+ \) represents the doubly ionized final state) in all proportions. In a similar fashion, when shake-off takes place during an Auger decay, the whole process is often called a double-Auger decay: the sum of the kinetic energies of the two electrons stays constant as it equals the energy released by the Auger transition. Shake-up and shake-down processes were studied in article I. The shake processes are collectively called satellite transitions and are presented as electron chart illustrations in Fig. 2.3.
Chapter 2. Electronic structure of atoms and transitions
The studies discussed in this thesis deal with many-electron atoms. This chapter introduces and covers different ways to theoretically model the energy states of such atoms and the transitions between their states. The energy levels, Auger transition energies and rates associated with the studied states of the atoms were simulated with the multiconfiguration Dirac-Fock-based (MCDF) GRASP2K \cite{39,40} package augmented with the RATIP program \cite{59,60}. In article I the energy level computations were supplemented by predictions from the Hartree-Fock-based (HF) code of Cowan \cite{36}. The calculations in article III were also run with the MCDF-based flexible atomic code (FAC) \cite{42}.

### 3.1 Schrödinger equation

Any stationary state \( k \) of an atom is a quantum mechanical system and thus can be mathematically described by a wave function \( \Psi_k \). Its energy can be determined from the time-independent Schrödinger equation

\[
\hat{H}\Psi_k = E_k \Psi_k, \tag{3.1}
\]

in which \( \hat{H} \) is the Hamiltonian and \( E_k \), as the solution of this eigenvalue equation, the total energy of the state \( k \). The Hamiltonian consists of operators related to the kinetic and potential energies of all the particles of the system. In many-electron atoms the energy is affected not just by the attractive Coulomb force between the electrons and the nucleus but also the repulsive one between the electrons as well as the spin-orbit interaction \cite{36}. The appropriate Hamiltonian can be presented as

\[
\hat{H} = \hat{H}_{\text{kin}} + \hat{H}_{\text{elec-nucl}} + \hat{H}_{\text{elec-elec}} + \hat{H}_{\text{spin-orbit}}
\]

\[
= -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_i \sum_{i>j} \frac{1}{r_{ij}} + \frac{1}{2} \sum_i \xi_i(r_i)(l_i \cdot s_i), \tag{3.2}
\]
Chapter 3. Theoretical background of the calculations

where $r_i$ is the distance between the electron number $i$ and the nucleus and $r_{ij}$ the distance between electrons $\epsilon_i$ and $\epsilon_j$; the function $\xi_i$ in the spin-orbit term is a proportionality factor and its form depends on the type of atom in question. The operator in Eq. 3.2 is, for the sake of brevity, given in so-called atomic Hartree units, in which the elementary charge, reduced Planck constant, electron mass and Coulomb constant are all unity ($e = \hbar = m_e = k_e = 1$ and $c \approx 137$) and energies are measured in hartrees ($1 E_H \approx 27.2$ eV).

It is not possible to solve the Schrödinger equation (see Eq. 3.1) analytically for systems with more than one electron. This is due to the potential caused by the interactions between all the electrons not being spherically symmetric, which prevents the separation of the wave function into angular and radial parts as is possible for hydrogen-like atoms [61]. Approximate and numerical methods have to be used when solving Eq. 3.1.

3.2 Central-field approximation

In an atom with $N$ electrons the Coulomb interactions can be taken into account by assuming that an arbitrary electron $\epsilon_i$ is moving in an effective potential $\phi_{\text{eff}}(r)$. This potential is caused by the nuclear charge $Ze$ and the time-averaged charge distribution of the other $N - 1$ electrons. The movement of this electron $\epsilon_i$ in this central-field is not dependent on the momentary location of any other electron and thus the effective potential $\phi_{\text{eff}}(r)$ is spherical in shape reducing the problem to a one-electron case for any given electron $\epsilon_i$. Inserting such potential into the Schrödinger equation gives the one-electron wave function $\psi_i$ and the total energy $E_i$ of the electron $\epsilon_i$ [61].

While this wave function can be separated into radial and angular parts, it is not analytically solvable as the effective potential, though spherically symmetric, is not Coulombic in form [36].

It is possible to determine the effective potential for the electron $\epsilon_i$ from

$$\phi_{\text{eff}}(r_i) = \frac{-e}{4\pi\varepsilon_0} \left[ \frac{Z}{r_i} - \sum_{j \neq i} \int \frac{1}{r_{ij}} |\psi_j(r_j)|^2 d\tau_j \right], \quad (3.3)$$

in which the first term denotes the attractive interaction caused by the nuclear charge $Ze$ and the second term describes the repulsive interaction due to all the other electrons in the cloud. As the integration in the second term is done over all angular coordinates, the distance $r_{ij}$ between electrons $\epsilon_i$ and $\epsilon_j$ becomes averaged, and the potential can be determined, if all the one-electron wave functions $\psi_j$ ($j \neq i$) are known. Determination of the best possible effective potential is dependent on obtaining the optimal one-electron wave functions. This approach requires an approximate potential to be first inserted into the Schrödinger equation in order to calculate the required wave functions.
3.3 Hartree-Fock method

In 1927 Douglas Hartree proposed an approach, which he called the self-consistent field method (SCF), for obtaining the optimal one-electron wave functions through iteration [31, 32]. The procedure starts as an ab-initio (“from the beginning” in Latin) method by inserting a crudely guessed spherically symmetric potential \( \phi_i^{(0)} \), obtained for example from screened hydrogenic orbitals, into the Schrödinger equation (see Eq. 3.1), and solving the zeroth order one-electron wave function \( \varphi_i^{(0)} \) and energy eigenvalue \( E_i^{(0)} \) for the electron \( \epsilon_i \). Once the procedure has been done for all the electrons in the cloud, the energy states \( E_i \), each defined by a unique set of quantum numbers \( (n_i, l_i, m_l, m_s) \), can be filled starting from the lowest until all the electrons have been assigned. The obtained one-electron wave functions are then used to calculate an improved effective potential \( \phi_i^{(1)} \) from Eq. 3.3 for each of the \( N \) electrons. The improved potentials are then used to calculate the first order wave functions \( \varphi_i^{(1)} \) and energy eigenvalues \( E_i^{(1)} \), which in turn are compared with their zeroth order counterparts. If they differ from each other more than the predetermined limits, then the procedure is repeated with \( \varphi_i^{(1)} \) and \( E_i^{(1)} \) as the new inputs. Convergence has been reached, once subsequent rounds of iteration do not change the values of the effective potential and energy significantly.

The optimized one-electron wave functions \( \varphi_i(r_i) \) obtained through this iterative process can be written as a Hartree product

\[
\psi(r_1, r_2, \ldots, r_N) = \varphi_1(r_1)\varphi_2(r_2)\ldots\varphi_N(r_N) \tag{3.4}
\]

to express the total wave function \( \psi(r_1, r_2, \ldots, r_N) \) of a level in an atom with \( N \) electrons [36]. All atomic states observed in the nature are described by total wave functions that are antisymmetric to interchange of two electrons. Therefore the wave function to describe an atomic state should be expressed as a linear combination of product functions like the one in Eq. 3.4 while following the symmetry condition [61]. This requirement can be conveniently fulfilled when the wave function is expressed as the determinant

\[
\psi(r_1, r_2, \ldots, r_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\varphi_1(r_1) & \varphi_1(r_2) & \ldots & \varphi_1(r_N) \\
\varphi_2(r_1) & \varphi_2(r_2) & \ldots & \varphi_2(r_N) \\
\vdots & \vdots & \ddots & \vdots \\
\varphi_N(r_1) & \varphi_N(r_2) & \ldots & \varphi_N(r_N)
\end{vmatrix} \tag{3.5}
\]

which is called a Slater determinant after John Slater [62].

The method can be adjusted to account for the electron spin by considering that the total wave function can be expressed as a product \( \psi = \varphi(r)\chi(s) \) of the spatial part and spin function respectively. This is reflected accordingly in the corresponding Slater determinant (see Eq. 3.5) making the iteration
process considerably heavier. The separation of spatial and spin part is valid, when the spin-orbit interaction is considerably weaker than the Coulomb interaction. This Hartree-Fock (HF) method can be further amended to account for the main relativistic effects such as its mass increase due to high velocity and the non-localizability of the electron [63]. This is done in the relativistic Hartree-Fock (HFR) method by adding mass-velocity and Darwin terms respectively to the Hamiltonian. The code of Cowan used for some of the calculations in article I takes the relativistic effects into account by using the Cowan-Griffin operator [64]; the spin-orbit effect is treated as a perturbation with the Blume-Watson method [65,66].

### 3.4 Configuration interaction and multiconfiguration methods

The repulsive Coulomb effect between the electron of interest $\epsilon_i$ and the other electrons, sometimes called electron correlation, can be included in the calculations through the method of configuration interaction (CI). In the matrix method of the Slater-Condon theory a wavefunction representing the state $k$ in an atom is expanded into a linear combination of the Slater determinants (see Eq. 3.5) as its basis set:

$$\Psi_k = \sum_i y_i \psi_i,$$

in which $\Psi_k$ is called the configuration state function (CSF) and $y_i$ the expansion coefficient. By presenting the coefficients collectively as a column vector $Y_k$ the expanded wave function in Eq. 3.6 can be inserted into the Schrödinger equation (see Eq. 3.1) in its matrix form

$$HY_k = E_k Y_k,$$

in which $E_k$ is the eigenvalue matrix and $H$ the Hamiltonian matrix consisting of elements of the form $H_{ij} = \langle \psi_i | \hat{H} | \psi_j \rangle$. The vector $Y_k$ can be solved by diagonalizing the Hamiltonian matrix: numerical methods are used to find the matrix $T$ that diagonalizes $H$. Now the $i$th diagonal element of the diagonalized Hamiltonian matrix is the eigenvalue $E_i$, whereas the corresponding eigenvector $Y_k$ can be found as the $i$th column of $T$ [36]. If the average energy $E_k = \langle \Psi_k | \hat{H} | \Psi_k \rangle$ is calculated, the final value is dependent also on terms of the form $\langle \psi_i | \hat{H} | \psi_j \rangle$ ($i \neq j$), which correspond to the interaction between different configurations. The linear combination in Eq. 3.6 contains only configurations of the same total angular momentum $J$ and parity $\Pi = (-1)^{J_m}$, in which $l_i$ is the orbital quantum number and the summation is done over all the electrons in the configuration [61].
3.5. Dirac-Fock method

The different atomic states can be further described as linear combinations of CSFs (see Eq. 3.6) in the following manner

\[ \Psi = \sum_i c_i \Psi_{k_i}, \]  

(3.8)

in which \( \Psi \) is the atomic state function (ASF) and \( c_i \) is the mixing coefficient. The number of constructed ASFs is the same as the number of CSFs \([41]\). It can be shown with variational theorem that average state energies calculated with the approximate wave functions are always higher than or equal to the true energies, thus it is possible to approach the optimal ASF by finding such mixing coefficients \( c_i \) and one-electron wave functions \( \varphi_n(r_i) \) that yield the lowest possible ASF energy \([67]\).

In CI schemes the wave functions are first obtained through the HF method, after which the CSF coefficients \( y_i \) are determined by diagonalizing the Hamiltonian matrix. Multiconfiguration (MC) methods take the concept further by varying both the mixing coefficients and the one-electron wave functions during the iteration to find the optimal ASFs. The code of Cowan used in article \([I]\) utilizes the CI, sometimes also called superposition of configurations \([68]\), method for solving the wave functions and level energies. The GRASP2K suite \([39–41]\), while capable of MC, was used in CI mode in all of the articles. The FAC package \([42]\) utilized in article \([III]\) was used in CI mode.

3.5 Dirac-Fock method

The spin-orbit interaction and relativistic effects become more significant the heavier the atom is and when dealing with core shells, and thus it is appropriate to take them into account in a more intrinsic way than as mere corrections and adjustments. This can be done by replacing the Hamiltonian in Eq. 3.2 in the SCF method for an \( N \)-electron atom with the so-called Dirac-Coulomb Hamiltonian, which in atomic Hartree units \((e = \hbar = m_e = k_e = 1 \text{ and } c \approx 137)\) takes the form

\[ \hat{H}_{DC} = \sum_{i=1}^{N} \left( c \sum_{j}^{3} \alpha_j \cdot \hat{p}_j + (\beta - 1) e^2 - \frac{Z}{r_i} \right) + \sum_{i \neq j}^{N} \frac{1}{r_{ij}}, \]  

(3.9)

in which \( c \) is the speed of light, \( r_i \) the distance of electron \( \epsilon_i \) from the point nucleus, \( r_{ij} \) the distance between electrons \( \epsilon_i \) and \( \epsilon_j \) and \( \hat{p}_i \) the momentum operator \([69]\). This Hamiltonian includes the Dirac matrices

\[ \alpha_j = \begin{pmatrix} 0 & \sigma_j \\ \sigma_j & 0 \end{pmatrix}, \text{ and } \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \]
Chapter 3. Theoretical background of the calculations

in which \( \sigma_{j=1,2,3} \) are the Pauli spin matrices while 0 and 1 are \( 2 \times 2 \) matrices, to satisfy the relativistic relation \( E^2 = p^2 c^2 + m^2 c^4 \) between energy and momentum while only having first-order time derivatives. The first term in Eq. 3.9 represents the contributions from the kinetic energy of the electrons and their interaction with the nucleus whereas the second term describes the effect of interelectronic interactions on the energy.

As with the SCF iteration in the HF method the central-field approximation is used to estimate the initial wave functions to be used as the starting point of the iteration. For this, the one-electron wave functions are expressed as four-component spin-orbitals, Dirac spinors

\[
\psi_{n\kappa m}(r, \theta, \varphi) = \frac{1}{r} \left[ \frac{P_{n\kappa}(r)\chi_{\kappa m}(\theta, \varphi)}{iQ_{n\kappa}(r)\chi_{-\kappa m}(\theta, \varphi)} \right], \tag{3.10}
\]

in which \( P_{n\kappa}(r) \) and \( Q_{n\kappa}(r) \) are radial wave functions and the spin-angular functions \( \chi_{\kappa m} \) are two-component Pauli spherical spinors [70]. The quantum numbers \( n \) and \( m \) are the principal quantum number and the eigenvalue of \( j_z \) respectively. The relativistic quantum number \( \kappa \) combines the orbital angular momentum quantum number \( \ell \) and the total angular momentum \( j \) into \( \kappa = -(2j + 1)(j - \ell) \). The bispinor in Eq. 3.10 is simultaneously an eigenfunction of the parity operator \( \hat{\Pi} \), the square of the total angular momentum operator \( \hat{\jmath} = \hat{\ell} + \hat{s} \) and its z-component [71]. The one-electron wave functions \( \psi_{n\kappa m}(r, \theta, \varphi) \) as defined in Eq. 3.10 are laid into a Slater determinant as their non-relativistic counterparts in Eq. 3.5. The CSFs \( \Psi(\Pi JM) \) are constructed as linear combinations of these determinants, and finally the ASFs \( \Psi(\Pi JM) \) are built as linear combinations of CSFs of the same total angular momentum \( J \), its projection \( M \) and parity \( \Pi \).

The Grasp2K suite [39–41] (articles I, II, III) and FAC package [42] (article III) are based on the Dirac-(Hartree)-Fock (DHF) method making them inherently relativistic. The codes minimize the average energies of the ASFs through SCF iteration to find the optimal wave functions and level energies.

3.6 Transition probabilities

The probabilities of transitions, discussed in general in section 2.4, also called transition rates, depend on the coupling between the initial and final states of the atom. The rates can be computed based on Wentzel’s ansatz later known as Fermi’s Golden Rule No. 2

\[
w_{i \rightarrow f} = \frac{2\pi}{\hbar} |M_{i \rightarrow f}|^2 \rho(E_f) \tag{3.11}
\]

where \( M_{i \rightarrow f} \) is the matrix element of the transition and \( \rho(E_f) \) the density of final states. The matrix element can be written as an integral \( \langle \Psi_f | \hat{V} | \Psi_i \rangle \),

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3.6. Transition probabilities

in which $\Psi_i$ and $\Psi_f$ respectively are the wave functions of the initial and final states and $\hat{V}$ is the operator describing the interaction, which causes the transition. 

### 3.6.1 Photoexcitation rates

Photoexcitation process discussed in section 2.4.2 is caused by interaction between a photon and an electron. This interaction can be expressed in atomic units with the operator

$$\hat{V}_{\text{photon-elec}} = e^{ik \cdot r} \varepsilon \cdot \hat{p}$$

(3.12)

where $\hat{p}$ is the momentum operator, $k$ the wave vector and $\varepsilon$ the direction of the polarization of the incident photon. The integration in the matrix element $M_{i \rightarrow f}$ is done over the entire space $r$, but because the bound electron state $\Psi_i$ has significant amplitude only around the origin, the exponent in Eq. 3.12 can be expanded into a Taylor series at $r = 0$

$$e^{ik \cdot r(0)} \approx 1 + ik \cdot r - \frac{(k \cdot r)^2}{2} + \ldots$$

(3.13)

If the wavelength of the incident photon is considerably larger than the spatial dimensions of the region of the affected electron, the scalar product $k \cdot r \ll 1$ and it is sufficient to approximate the operator in Eq. 3.12 with the first term of the series in Eq. 3.13. When this condition is satisfied the dipole approximation is said to hold true, and the operator in Eq. 3.12 becomes

$$\hat{V}_{\text{photon-elec}} \approx \varepsilon \cdot \hat{p}.$$ (3.14)

The selection rules for the quantum numbers of transitions within the dipole approximation are

$$\Delta L = 0, \pm 1, \Delta J = 0, \pm 1, \Delta S = 0,$$

though a transition $J = 0 \leftrightarrow 0$ is prohibited and when only a single electron is involved $\Delta L \neq 0 \text{ [47]}$. The parity of the state also has to change so $\Pi_i = -\Pi_f$.

### 3.6.2 Auger decay rates

The transitions in Auger effect, discussed in section 2.4.3, arise from the Coulomb interaction between the involved electrons. In the two-step model the initial and final states of the Auger decay are treated as two distinct atomic states. The model is valid when the interaction of the initially removed electron with the Auger electron as well as the one between the vacancy and the Auger continuum are weak. When these conditions apply the Auger decay probabilities can be obtained from Eq. 3.11.
Chapter 3. Theoretical background of the calculations

The Coulombic interaction between the two electrons $\epsilon_j$ and $\epsilon_k$, which participate in the Auger decay, can be expressed in the matrix element in atomic units with the operator

$$\hat{V}_{\text{elec-elec}} = \frac{1}{r_{jk}}, \quad (3.15)$$

in which $r_{jk}$ is the interelectronic distance [75]. The same final state is reached even, if the places of the ejected electron and the electron, which transitioned onto an energetically lower level, are exchanged as can be seen from Fig. 2.2(a). Therefore the process consists of two indistinguishable cases represented in the matrix element $M_{i \rightarrow f}$ (see Eq. 3.11) by the terms $D$ and $E$ respectively for direct and exchanged transitions expressed as

$$D = \langle \psi_f(r_j)\psi_\epsilon(r_k)|r_{jk}^{-1}|\psi_i(r_j)|\psi_\epsilon(r_k)\rangle,$$

$$E = \langle \psi_f(r_k)\psi_\epsilon(r_j)|r_{jk}^{-1}|\psi_i(r_j)|\psi_\epsilon(r_k)\rangle, \quad (3.16)$$

in which $\psi_f$ is the filled electron hole, $\psi_\epsilon$ the continuum state of the ejected electron and $\psi_i$ together with $\psi_i'$ are wave functions describing the initial states of electrons $\epsilon_j$ and $\epsilon_k$. With Eq. 3.16 the matrix element of the Auger transition can be written out as $M_{i \rightarrow f} = D - E$, which with Eq. 3.11 gives

$$w_{\text{Auger}} = \frac{2\pi}{\hbar} |D - E|^2 \rho(E_f). \quad (3.17)$$

When pure LS-coupling scheme is applied, the total quantum numbers of the initial and final states of the Auger decay are required to adhere to the following selection rules

$$\Delta L = \Delta S = \Delta M_L = \Delta M_S = \Delta J = \Delta M = 0.$$ 

The final state quantum numbers are for the system consisting of the ion and the Auger electron. Because of the scalarity of the Coulomb operator, $\Delta J = \Delta M = 0$ in any coupling scheme while the parity also has to remain unchanged: $\Pi_i = \Pi_f$ [75].
Overview of experimental methods

Measurements of kinetic energies of electrons ejected from atoms or other targets is called electron spectroscopy. The electron can escape the sphere of influence of the nucleus in various ways discussed from a conceptual point of view in section 2.4. The studies in this thesis are based on simulation and interpretation of collected spectra resulting from such electronic transitions. This chapter gives an overview of the experimental methods and instruments relevant to these studies. In practice, before the spectra can be recorded, analyzed and interpreted, the target samples have to be prepared so that inducing the desired transitions using appropriate equipment becomes possible, after which the emitted electrons can be detected and separated in kinetic energy with a suitable experimental set-up.

4.1 Sample preparation

The properties and dynamics of electrons of the elements covered in this thesis, chromium (article I), rubidium (articles II and III), krypton and bromine (article III), have been studied in their atomic forms. In this work Cr and Rb atoms were obtained from respective solids through heating and Br atoms from HBr molecules through dissociative photoexcitation, whereas Kr already exists as single free atoms at room temperature.

In general, many sample elements can be brought into their atomic forms through evaporation at high enough temperatures. This is often done with a resistively or inductively heated oven [76]. The evaporation is done in a vacuum chamber to enable long enough free path for the emitted electrons, making electron spectroscopy possible in the first place, and to prevent the atomic samples from reacting with any atmospheric gases. The vacuum, upheld with a series of pumps, also protects the various sensitive devices, necessary for the measurements, from contamination.
4.2 Inducing electronic transitions

In general, the different electronic transitions studied in this thesis are initiated by disturbing the ground electronic state of the target atom. This can be done by bombarding the target with photons or other electrons. The term *photoelectron spectroscopy* (PES) is often associated with the former case, in which the kinetic energy of the ejected electron is given by Eq. 2.9, because photons as particles without rest mass get absorbed entirely, which makes the process highly selective. Bombardment with other electrons results in an elastic collision between two electrons, after which the kinetic energy of the incident electron is shared by these two electrons, so the method is best suited for studying transitions such as Auger decays, which are not highly dependent on the way the initial electron vacancy was created.

4.2.1 Synchrotron radiation

In principle the transitions studied with the PES methods can be induced with any light source with the right energy. For practical purposes though it is desirable that the utilized source is *monochromatic*, that is emits photons at a very narrow distribution around a single energy, and has high brilliance. Conventional lasers do exhibit these qualities but are difficult to tune in energy and the emitted photons are not energetic enough to ionize most atomic targets. On the other hand X-ray tube sources have the sufficient energy but lack in intensity for gas phase studies after monochromatization [77]. Though these devices can be useful due to their relatively compact size, many modern applications of PES use synchrotron light sources to provide users with tunable monochromatic photon beam with high brilliance.

Synchrotron is a circular particle accelerator, a *storage ring*, in which charged particles, usually electrons, move in a loop close to the speed of light. Charged particles emit electromagnetic radiation as they are being accelerated. Electrons in a storage ring are radially accelerated to keep them in a circular path, which causes them to emit photons tangentially. The phenomenon was first discovered in 1940s as an undesired side-effect in cyclic particle accelerators as it set a practical upper limit to the energy of the electron beam [78]. It was soon discovered that this intense synchrotron radiation was optimal for studying electronic transitions. To increase the intensity of the photon beam, modern synchrotrons are polygonal loops that consist of multiple straight sections, in which discrete bunches of electrons are accelerated using electric fields. Depending on the operation mode there might be multiple bunches or just a single bunch looping in the storage ring. The straight sections are connected to each other with angled connectors, in which the electrons are subjected to immense radial acceleration using *bending magnets*. The intensity of the emitted conical photon beam can be further
4.2. Inducing electronic transitions

Figure 4.1: The working principle of an undulator depicted. The insertion device consists of two arrays of dipole magnets of alternating polarity (1). An electron beam (2) is depicted entering the space between the arrays. The alternating magnetic field forces the electrons into an oscillating path, which has a characteristic wavelength $\lambda_U$ and subjects the electrons to high radial acceleration. A sharp cone of electromagnetic radiation (3) is shown exiting the array configuration. Adapted from Ref. [79] under CC BY-SA 3.0 license.

increased by using insertion devices such as wigglers or undulators between two adjacent bending magnets. Both wigglers and undulators consist of periodic array of dipole magnets, which cause the electron beam to oscillate and emit a cone of electromagnetic radiation. Whereas a wiggler produces a wider cone of continuous spectrum of wavelengths of a specific range, only very intense radiation in narrow bandwidths around certain wavelengths are emitted from an undulator as a sharp cone [80]. The oscillating electrons moving in the undulator at relativistic speed emit photons almost simultaneously causing an interference pattern to appear in the resulting spectrum of electromagnetic radiation. The intervals of high intensity result from the constructive interference between the emitted photons. The wavelengths of the intensity maxima can be tuned by adjusting the gap between the magnetic arrays of the undulator. The principle of the structure of undulators is shown as a schematic depiction in Fig. 4.1. Monochromators, which are used to allow only the selected wavelengths to eventually pass into the sample region, and other devices such as focusing lenses and mirrors are chained together tangentially to the curvature of the storage ring to form a beamline. Synchrotron radiation from differently optimized beamlines [81,82] in various laboratories were used to induce the transitions studied in this thesis.
4.2.2 Electron gun

Electron guns are devices, in which electrons are in one way or another provided enough energy through external means to overcome the work function of the material and break free. This is usually achieved via thermionic or field emission but also photoemission of electrons from materials with low work functions such as metals is used.

In this work only thermionic emission was used. In such electron guns a thin metal wire is heated by running an electrical current through it. The energy from the heat detaches electrons from this filament and the detached electrons are accelerated using a high electrical potential. The intensity of the produced electron beam is proportional to the temperature of the filament, which can be controlled by adjusting the current passing through the wire. Each filament material has its characteristic saturation point, after which increasing the temperature does not result in emission of more electrons [77]. The Auger electron spectra in article [1] has been measured after inducing the initial hole state by electron impact.

4.3 Energy analyzers

The electrons originating from the different energy levels of the studied sample differ from each other in kinetic energy and relative numbers. This is also reflected in the experimental set-up, which has to be able to not just detect the emitted electrons but also separate them in energy.

4.3.1 Hemispherical electron energy analyzer

The kinetic energy of an emitted electron can be measured using a hemispherical electron energy analyzer. The analyzer consists of two conductive hemispheres with the one of larger radius covering the other one leaving a space in the shape of a hemispherical shell between them as shown in Fig. [4.2]. The hemispheres are set in different electric potentials creating an electric field between the two halves. The potentials are chosen so that the charged particles entering the space between the hemispheres via the entrance slit (see Fig. [4.2]) with a certain amount of kinetic energy can travel through this chamber without colliding with its walls. The chosen energy is called the pass energy of the hemispherical analyzer [83]. Electrons are allowed to enter this space, which is kept in a vacuum, through an electron lens, which focuses them into the slit and also decelerates or accelerates them to closely match the selected pass energy of the analyzer. By adjusting the retardation at the lens, it is possible to choose, which electrons will be able to pass through the analyzer into the detector as depicted in Fig. [4.2]. The feedback caused by a single electron is too weak to be reliably detected, so amplifiers such as...
arrays of stacked micro-channel plates, which release a deluge of electrons for each electron to hit the plate, are used. Once these electrons hit a detector the signal is converted into digital format for storage and further analysis. In practice, because of the dimensions of the entrance slit, the pass energy of the analyzer is actually an energy interval. This can be taken into account by using a position sensitive detector such as a charge-coupled device also known as CCD, because the electrons arriving at different kinetic energies around the selected pass energy hit different spots on the detector.

The data collected with a hemispherical analyzer is often most conveniently presented visually as a histogram with energy as the horizontal and the number of detection events or intensity as the vertical axis. The measurements carried out in article I were recorded with modified Scienta SES-100 [84] and SES-200 [85] hemispherical electron energy analyzers, and in article III the high-resolution Auger spectra was recorded with a hemispherical MBS-A1 analyzer [86].

### 4.3.2 Magnetic bottle

Sometimes a single induced transition in the sample works as a catalyst for other transitions. This results in the emission of multiple electrons originating from different non-radiative decay processes. In the case of an Auger decay following a photoionization, the energy of the incident radiation can
be chosen so that the Auger and photoelectrons appear at different kinetic energies and are easy to separate from each other. In the case of Auger cascades, that is multiple subsequent Auger transitions, the kinetic energies of the emitted electrons are fixed and may appear overlapped. This creates a need to detect the emitted electrons in such a way that it is possible to deduce from the results the process, from which they originated.

This is possible with time-of-flight (TOF) type of coincidence measurements, which can be performed for electrons using a set-up called a magnetic bottle. This spectrometer has two magnetic field regions: the interaction region, in which the sample is placed, and the flight tube. The magnetic field in the interaction region is created by a strong conical permanent magnet acting as a magnetic mirror deflecting nearly all the emitted electrons into the flight tube. The flight region consists of a long solenoid, which has an electric current running through it inducing a longitudinal magnetic field inside the tube. This forces the electrons entering the flight region into spiral paths, which ensures that they can traverse all the way to the detector at the end of the tube without hitting the walls [87]. The structure of a typical magnetic bottle energy analyzer is presented in Fig. 4.3. A discretely enough pulsed radiation source, such as a synchrotron in single-bunch mode, is needed to enable the study of transitions and decays originating from a single ionization or excitation event. In addition, it provides the start signal for the flight time measurement. The kinetic energies of the detected electrons can be solved from the measured flight times.

Figure 4.3: A typical magnetic bottle electron spectrometer (MBES): sample preparation with pulsed radiation happens in the vacuum of the test chamber, in which a conical permanent magnet directs emitted electrons through the lens chamber, containing an electron lens, into the drift tube housing the solenoid. The flight times are measured based on the signal given by the detector in the detector chamber. Adapted from the internal MBES assembly manual of NANOMO with the permission of L. Hautala and P. Turunen.
4.4 Data handling

Magnetic bottles offer several advantages compared to conventional hemispherical energy analyzers. The bottle set-up is capable of collecting almost all the electrons emitted from the sample due to the spatial collection angle of nearly $4\pi$. The use of TOF type of measurements makes it possible to trace the electrons detected in coincidence back to a single photoionization or excitation event. Magnetic bottles cannot however match the energy resolution provided by conventional hemispherical analyzers at higher kinetic energies. The current geometry of bottle analyzers also limits their usage to experiments with gas phase samples, and the study of angular distribution of emitted electrons is difficult.

The results from measurements with a magnetic bottle are often presented as a density map with kinetic energies of fast and slow electron as horizontal and vertical axes respectively. The fast electron corresponds to the first detection event and slow to the second detection, which was detected in coincidence with the fast electron. The relative number of detection events at each point of the map corresponds with the likelihood of such coincidence. The multielectron coincidence experiments in articles [II] and [III] were carried out using the HERMES magnetic bottle set-up [88].

4.4 Data handling

The measured spectra have to be calibrated and fitted with appropriate line profiles so that the collected data can be refined for making interpretation and conclusions about the studied samples. Energy calibration is usually done with the help of reference lines from well-known transitions in noble gases, which can be measured simultaneously with the sample. The whole spectrum is moved in energy so that the energies of the reference lines match their literature values. Transmission calibration for data measured with hemispherical analyzers is performed, because the electron lenses used are not equally effective at converting electrons of different kinetic energies to match the pass energy of the spectrometer. The relative transmission rates are resolved by moving reference photolines, peaks originating from photoionization, through the studied energy interval and mapping their relative intensities at different kinetic energies. Detector calibration addresses the varying levels of sensitivity to electron hitting the used detector at different positions.

Spectral features are commonly fit with Voigt lineshapes, which are convolutions of Gaussian and Lorentzian profiles, to determine their energies and relative intensities. The Gaussian part takes into account the broadening caused by the instruments used in the experiment as well as Doppler effect due to the thermal motion of the sample particles. The Lorentzian contribution originates from the lifetime of the involved electronic states. Energies of the lines in the studied spectra are determined from the fitted peak maxima and areas correspond to the relative intensities.
Chapter 4. Overview of experimental methods

Figure 4.4: The electron coincidence map collected after the 3d photoionization of atomic Rb. The solid lines on the left and above are respectively results of vertical and horizontal integrations of electron counts and correspond to traditional PES and AES respectively. The map is discussed in more detail in section 5.2.

The aforementioned data handling methods are for traditional one-dimensional spectra, whereas multielectron correlation density maps can be considered multidimensional spectra. Coincidences of two electrons, as studied in this thesis, are conveniently represented as two-dimensional spectra. These can be binned and integrated along a chosen axis depending on the desired result to extract one-dimensional graphs depicting different distributions of electronic states. This graph can then be processed with the same methods as any one-dimensional spectrum. Examples of vertical and horizontal integrations resulting in a conventional PES and AES respectively are depicted in Fig. 4.4. Diagonal integration gives a graph depicting the distribution of final states of the observed process. As such integration is performed along the total excess energy, the resulting graph is free of the PCI effect. Any integration can also be performed for only a chosen slice of the map to achieve state-selectivity.
Summary of the included articles

This chapter gives an overview and summarizes the studies, their results and conclusions on selected $M$-shell decay of the included original articles I, II, III.

5.1 Article I: $3p$ photoionization of atomic Cr and the following Auger decay

In article I the properties of the $M$-shell hole decay of chromium were studied. The $3p$-subshell of atomic chromium was photoionized using synchrotron radiation with a photon energy of $h\nu = 120$ eV and the resulting spectra were recorded. In a separate experiment the following Coster-Kronig and super-Coster-Kronig type Auger decays were initiated using electron impact excitation and the spectra were recorded in high resolution. The aim of the study was to continue, supplement, and complete the earlier studies on the structure of core shells of chromium [89–94] and other industrially important metals [95–99] by determining the decay pathways from the ground state to the doubly ionized final states in detail. The spectra were measured with a position sensitive detector at the so-called magic angle of 54.7° and interpreted with the aid of multiconfiguration Dirac-Fock (MCDF) and pseudo-relativistic Hartree-Fock (HF) calculations. By theoretically simulating the whole process following pathways from the photoionization until the final states of the Auger decay enabled us to interpret both the photoelectron and the Auger electron spectra in more detail than would have been possible by studying them separately.

5.1.1 $3p$ photoelectron spectrum

Atomic chromium is described by the non-relativistic electron configuration of $3p^63d^54s$ in its ground CrI state. Following the $3p$ ionization the atom is left in a CrII state defined by the configuration $3p^53d^54s$. The prominent
Figure 5.1: The collected Cr 3p photoelectron spectrum measured at $h\nu = 120$ eV and the theoretical predictions based on MCDF computations. Refer to sections 5.1.1 and 5.1.2 for the labels A, B, C, and G and Table 1 of the article for the rest.

Lines of the collected Cr 3p photoelectron spectrum presented and labeled in Fig. 5.1 were fitted with lineshapes described by Voigt functions to obtain the binding energies, relative intensities, and linewidths to be compared with the results of our MCDF and HF calculations. The overall agreement with earlier studies on Cr 3p photoionization by von dem Borne et al. [91] as well as our calculations was found to be good enabling us to identify peaks in the photoelectron spectrum. We were able to extract the energy separation of the singly ionized states (final states of the photoionization) within the observed linegroups of the photoelectron spectrum with very high accuracy from the subsequent high-resolution Auger electron spectrum. This enabled us to determine the binding energies of the associated singly ionized CrII states with higher accuracy than earlier studies especially in the case of groups C: $3p^5(3d^5 4D)(5D)4s\ 6P_{3/2,5/2,7/2}$ and G: $3p^5(3d^5 6S)(7S)4s\ 6P_{3/2,5/2,7/2}$. We were also able to provide both simulated and measured linewidths for the observed peaks. In addition, we were able to obtain high-accuracy widths (in the meV scale) for the peaks in the well-defined linegroup A: $3p^5(3d^5 6S)(7S)4s\ 6P_{9/2,7/2,5/2}$ in Fig. 5.1 with the help of the recorded high-resolution Auger spectrum.

5.1.2 MMM and MMN Auger spectrum

After the 3p photoionization process the chromium atom is left in an excited CrII state described by the non-relativistic configuration $3p^53d^5 4s$. The ex-
5.1. Article 3p photoionization of atomic Cr and the following Auger decay

Figure 5.2: The collected electron impact induced Cr $M_{2,3}M_{4,5}M_{4,5}$ and $M_{2,3}M_{4,5}N_1$ Auger electron spectrum and the theoretical predictions for energies and intensities based on MCDF computations. Refer to the section 5.1.2 for the labels.

citation decays through Auger process after which the Cr atom is left in a doubly ionized CrIII state. These final states are defined by configurations $3d^4$ and $3d^34s$ in our MCDF simulation. The collected high-resolution electron impact induced Auger decay spectrum is presented in Fig. 5.2 and most prominently features three distinct linegroups in the kinetic energy region below 25 eV mark. The groups, labeled Aa, Ab and Ac in the order of ascending kinetic energy, all originate from the singly ionized states within the A designation and represent the decay of those states into the doubly ionized states within the designations a: $3p^6(3d^3\,^4P)(^5P)4s\,^5P_{3,2,1}$, b: $3p^6(3d^3\,^4F)(^5F)4s\,^5F_{5,4,3,2,1}$, and c: $3p^6(3d^4\,^5D)\,^5D_{4,3,2,1,0}$ respectively. The decay between the intermediate CrII and final CrIII states defined by the aforementioned configurations is forbidden in a pure LS-coupling scheme, as the multiplicity of the CrII states is 8 whereas for CrIII it is 5. This means that the values of respective total spin angular momentums are $S_i = 7/2$ and $S_f = 2$, so in order to comply with the $\Delta S = 0$ selection rule an electron has to undergo a spinflip during the Auger decay process. We could see the consequences of this in our measurements and calculations as extremely narrow lines denoting long-lived atomic states in the A group with widths below 1 meV as predicted by the theory.

The other distinguishable linegroups, which correspond to decays from states B: $3p^5(3d^5\,^6S)(^5S)4s\,^6P_{7/2,5/2,3/2}$ and C, in the Auger electron spectrum have less intensity and wider profiles as predicted by our calculations. The higher kinetic energy side of the spectrum features asymmetric peaks
that according to earlier studies result from autoionization. The high resolution of the collected spectra enabled us to determine the energies of the peaks with higher accuracy than before, as well as the binding energies of the doubly ionized CrIII states. This was made possible by careful examination of the decay pathways based on the calculations, which in addition gave grounds for suggesting a new interpretation for one of the observed line-groups. Earlier studies have identified the group Cb as a decay between the states \(3p^53d^54s^8P_{9/2}\) and \(3p^63d^43D\) whereas, based on our theoretical computations, we suggested this should rather be interpreted to be arising from the Auger decay of the states \(3p^5(3d^54D)(5D)4s^6P\) into \(3p^6(3d^34F)(5F)4s^5F\).

### 5.2 Article II: Initial-state-selected MNN Auger spectroscopy of atomic Rb

Multi-electron coincidence methods were used in article II to study the Auger decay processes that originate from the creation of an \(M\)-shell hole in atomic rubidium, which in its ground state has the electron configuration of \([Ar]3d^{10}4s^24p^65s\). Photon energy of \(h\nu = 142\) eV from a synchrotron radiation source was used to ionize rubidium from its 3\(d\)-subshell and all the ejected electrons were collected with a time-of-flight type magnetic bottle setup resulting in a photoelectron-Auger electron coincidence map shown in Fig. 5.3. The ionization energy was chosen so that the photoelectron appears just below the subsequent Auger decay spectra in kinetic energy, so the horizontal axis gives the kinetic energy of the Auger electron (fast electron) whereas the vertical axis corresponds to the energy of the photoelectron (slow electron).

During the ionization process, the loosely bound 5\(s\) valence electron can get excited to an energetically higher Rydberg state in a process called shake-up transition. This phenomenon creates a satellite spectrum, which consists of about 20% of the total studied photoionization cross-section. Each of the initial ionic satellite states can undergo a MNN Auger decay, which all appear overlapped in the same kinetic energy range creating a spectrum that is difficult to interpret. The study aimed to complete and refine earlier research on Rb [100] and other alkali atoms [101-104] by showing that using the satellite state structure combined with multi-electron coincidence measurements and utilizing elaborate handling of the collected data, it is possible to individually follow and inspect the Auger decay processes starting from selected satellite states – even the ones with low cross-section. The significant reduction of overlapping features enabled also unambiguous detection of shake-down lines during normal Auger process for the first time.
5.2. Article II: Initial-state-selected MNN Auger spectroscopy of atomic Rb

Figure 5.3: The raw two-dimensional electron correlation map of atomic Rb collected in coincidence after the 3d photoionization ($h\nu = 142$ eV) and the subsequent Auger decay.

5.2.1 Auger decay of satellite states

The satellite spectral structure in the 3d photoelectron spectrum of atomic Rb appears on the lower kinetic energy side of the main $3d_j^{-1}5s$ lines. This is due to the valence electron going through a $5s \rightarrow n\ell$ excitation absorbing the energy needed for the transition leaving the ejected photoelectron with less excess energy. In the correlation map (see Fig. 5.3) the different $3d_j^{-1}n\ell$ final states of the photoionization process can be seen as horizontal lines; integrating along the vertical axis results in a traditional photoelectron spectrum. The final states of the subsequent MNN Auger decay are shown as spots of high intensity within these lines; integration along the horizontal axis gives a traditional Auger decay spectrum. The selection of an initial state could be performed by counting only the coincidences within a certain horizontal slice. The integrated photoelectron spectrum was used to determine the limits of the slices, so that excited ionic satellite states $5s$, $5p$, $5d$, $6s$, $6p$, and $7s$ could be separated. It was possible to generate the post-collision free MNN decay final state population distribution graphs starting from these valence states (initial-state-selected Auger decay spectra, see Fig. 5.4) by integrating along the diagonal of the selected slices. The decay from each studied state was separately simulated with the MCDF based atomic structure code 35.
Chapter 5. Summary of the included articles

Figure 5.4: The measured (left) and MCDF-simulated (right) $M_5N_{2,3}N_{2,3}$ Auger decay of Rb $3d_{3/2}^{-1}n\ell$ from selected valence states presented as a function of kinetic energy of the ejected electron.

GRASP2K for the $M_{4,5}N_{2,3}N_{2,3}$ and $M_{4,5}N_{1}N_{2,3}$ cases. The calculations made it possible to interpret the features of the extracted Auger spectra.

The most noticeable change in the initial-state-selected $MNN$ Auger spectra is the general trend of the whole spectrum moving towards lower kinetic energies as orbital of the valence electron gets higher as shown with the selected $5\ell$ cases for $M_5N_{2,3}N_{2,3}$ in Fig. 5.4. In the case of $M_{4,5}N_{1}N_{2,3}$, which features peaks representing states $4s^{-1}4p^{-1}{}^1Pn\ell$ and $4s^{-1}4p^{-1}{}^3Pn\ell$ in the order of ascending kinetic energy as seen in the Fig. 4 of the article [11] the energy shift is the only observable difference. Contrarily in the $M_{4,5}N_{2,3}N_{2,3}$ decay, which shows peaks $4p^{-2}{}^1S \! n\ell$, $4p^{-2}{}^1D \! n\ell$ and $4p^{-2}{}^3P \! n\ell$, few other subtle changes are also present. The $ns$ and $nd$ cases of the decay have an additional line, which is a result of the $ns$ orbitals of the final states mixing with $5d$, just on the lower kinetic energy side of $4p^{-2}{}^1S \! n\ell$. It can also be seen that the $4p^{-2}{}^1D \! n\ell$ peak has a wider profile when $\ell \neq 0$, because it actually consists of two lines caused by the spin-orbit splitting of the valence electron. The splitting is absent in the $ns$ cases and the largest in $5d$.

5.2.2 Shake-down

All the initial-state-selected spectra except the $5s$ case feature some minor spectral lines in the higher kinetic energy side of the main peaks. The lines are caused by a so-called shake-down process, in which the excited valence electron transitions into an energetically lower valence state during the Auger decay. The released energy is absorbed by the ejected Auger electron thus
5.3 Article III: 3d Auger decay in the isoelectronic series of Br*, Kr+ and Rb2+

The Auger decays following the creation of an M-shell hole were studied in the isoelectronic series of atomic excited bromine, singly ionized krypton and doubly ionized rubidium. Multicoincidence methods were used with synchrotron radiation to study the process starting from the configuration [Ar]3d−14s24p6 in the series. Bromine atoms were also studied through traditional electron spectroscopic methods in higher resolution. The Br 3d5/2 and 3d3/2 hole states could be studied independently by taking advantage of the σ* resonance in HBr molecule. Earlier studies on processes following
Figure 5.6: The resonant Auger decay spectrum resulting from the creation of a 3d hole via 3p → 4p excitation in atomic Br presented separately for \( j = \frac{5}{2}, \frac{3}{2} \) as well as both states together in the emboldened frames (i), (ii), and (iii) respectively. In each frame the upper panel (blue) depicts the collected spectrum whereas the lower (red) shows the results of the theoretical simulation with the contribution of the subsequent Auger decay to the width added; the dotted lines represent simulated spectra without the contribution of the subsequent decay. Refer to section 5.3.1 for the labels.
3d Auger decay in the isoelectronic series of Br\textsuperscript{*}, Kr\textsuperscript{+} and Rb\textsuperscript{2+}

Figure 5.7: The Auger electron-Auger electron correlation map (top) recorded following the decay of the 3d\textsubscript{5/2} hole state in atomic Br and the extracted population distribution graph (bottom) of the identified Br\textsuperscript{2+} states.

Figure 5.8: The measured Auger spectra resulting from the decay of the 3d\textsubscript{1/2} state presented for the isoelectronic series consisting of Br\textsuperscript{*}, Kr\textsuperscript{+}, and Rb\textsuperscript{2+}. Refer to section 5.3.1 for the labels.

the creation of a 3d hole in Kr\textsuperscript{[88, 105, 109]} have shown it to decay via an $M_{4,5,NN}$ Auger process; studies on $3p \rightarrow 4p$ excited Br\textsuperscript{[110, 112]} have hinted towards similar behavior. The decays in the isoelectronic series were simulated with the flexible atomic code (FAC) and GRASP2K, which are both MCDF-based. The extensive calculations made it possible to follow various
decay pathways, identify the peaks of the resonant Br* Auger spectrum, and study trends in spectral features within the series as a function of the atomic number Z.

5.3.1 Auger decay and the subsequent processes in Br*

The resonant Auger decay spectrum (see Fig. 5.6) of atomic Br following the 3d hole state bears such a resemblance to its isoelectronic Kr⁺ counterpart that it is possible to identify many of the corresponding linegroups by visual comparison. The MCDF computations with FAC confirm that starting from about 16 eV the groups b₁: 4s4p⁴(5s, 6/7/9d), a: 4p⁶, b₂: 4s4p⁴4d, c₁: 4s²4p³4d, d: 4s4p⁵, and e: 4s²4p⁴ have clear equivalents in the Kr⁺ 3d Auger decay spectrum [88,108]. The groups b₁ and a(b₂) in the lower kinetic energy region below 30 eV feature an increased mixing with d-orbitals compared to the Kr⁺ case. Considerable contribution of d-orbitals all the way up to 9d is also present in the group c₂x: 4s²4p³(5s, nd) between 30 and 37 eV.

The calculations predict an intense line of label a at around 10 eV. The peak is not visible in the collected Auger spectrum, but can be seen as a diagonal line starting at about 49 eV in the recorded coincidence map (see Fig. 5.7). Such line with a rather even distribution of detected coincidences along its length usually represents a direct double ionization, but in this case it is interpreted as a very fast N₁N₂N₃ super Coster-Kronig type Auger decay, because it only appears when measured on-resonance. The short-lived, and thus indistinguishable from the Auger spectrum background, intermediate Br⁺ state of this decay is described by 4p⁶, which correlates strongly with 4s4p⁴(5s, nd) (n = 5...9) enabling the fast pathway for the decay into Br²⁺ states dominated by configuration 4s4p⁴εℓ, in which εℓ denotes the Auger electron.

5.3.2 Trends within the isoelectronic series

The studied MNN decay spectra depicted in Fig. 5.8 all have visually identifiable equivalent features that become simpler in structure when moving from Br⁺ to Rb²⁺. This is especially evident with the group c₂x in Br* as it features considerable contribution from configurations in which d-subshell is singly occupied; the equivalent groups in Kr⁺ and Rb²⁺ are much simpler in structure and less mixed with significantly lower contribution of d-orbitals. The linegroups below 40 eV in Br* and their equivalents in the series move lower in kinetic energy as Z increases: the group e equivalents move higher in energy while barely any shift occurs in the d group. The observed trends can be attributed to the increasing effective nuclear charge as it can be seen that the states dominated by configurations, which have the 4s-subshell occupied, are affected by the change in Z more than the other studied states.
Conclusions and future outlook

Electronic transitions originating from a vacancy in $M$-shell were studied in atomic chromium, rubidium, krypton and bromine. The synchrotron radiation induced photoionization and Auger decay processes were measured using traditional electron spectroscopy as well as multi-electron coincidence methods. The observed transitions were meticulously simulated with MCDF-based atomic structure packages augmented with HF calculations where appropriate. Results of these calculations were used for careful and detailed interpretation of the collected spectra and coincidence maps.

In atomic Cr the $3p$ photoelectron spectrum was interpreted with higher accuracy than before. This was made possible, not only because of the higher resolution of the photoelectron spectrum compared to earlier studies, but also by the very high resolution electron impact induced measurements of the subsequent $MMM$ and $MMN$ Auger spectra. Through comprehensive theoretical calculations based on HF and MCDF methods the features seen in the photo and Auger electron spectra could be linked together, so that lifetimes and energy splittings of the photolines could be accurately extracted from the Auger spectrum.

The photoelectron-Auger electron multicoincidence study on the initial atomic Rb $3d$ hole state showed the versatile nature of multi-electron coincidence experiments, as proper data handling and MCDF calculations made it possible to study the following $MNN$ Auger decay as a function of $j$ of the initial hole state and $n\ell$ of the valence electron. Also for the first time shake-down transitions could be unambiguously identified during normal Auger decay.

The Auger electron-Auger electron multicoincidence study of $3d \rightarrow 4p$ excited atomic Br and its isoelectronic Kr and Rb counterparts and their MCDF simulations revealed that the lighter the element, the stronger the configuration interaction is within the isoelectronic series resulting in a more complex spectral structure. Br* was measured also with a traditional hemispherical analyzer to obtain a higher resolution spectrum, which together
with the extensive calculations and the coincidence experiment enabled the identification of the very fast super-Coster-Kronig type $NNN$ Auger decay. The feature was found to be present only in Br*, and with the theoretical calculations it could be shown that this decay channel becomes unavailable in heavier elements due to the changes in the relative energies of the corresponding levels.

This thesis continues the fundamental research on atomic structure, which has long traditions in the Nano and Molecular Systems Research Unit (NA-NOMO) and its predecessor Electron Spectroscopy Research Group (ELSP). The work presented here is an example that by combining results from multiple measurements, or just a single multicoincidence experiment, with thorough data analysis and comprehensive simulations it is possible to gain a deeper understanding of the electronic structure of the studied samples than it would be by just concentrating on a single traditional electron spectroscopic experiment. Synchrotron radiation has been an essential tool for inducing the studied electronic transitions, and modern\[113\] as well as future beamlines are expected to provide high enough brilliance for faster multi-electron coincidence measurements while at the same time the development on the magnetic bottle analyzers aims to improve their energy resolution. The reignited interest in modernizing established atomic structure packages\[114\] to be run on modern multi-core computers and developing new ones\[115\] is anticipated to pave way for slicker and more accurate calculations.
Bibliography


Bibliography


