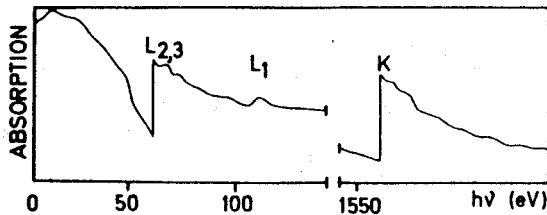


# 1. INTRODUCTION

If an x-ray enters a solid it can be absorbed and in this absorption process a core electron is excited to an empty state. If the energy of the x-ray is much larger than the binding energy of the core state the excited electron behaves like a 'free' electron in the solid. If however the x-ray energy is just enough to excite a core electron it will occupy the lowest available empty state. The probability for these edge absorption processes is large. If the x-ray energy is too small to reach an empty state no excitation can occur. Thus if the x-ray energy is varied from below the binding energy of the core state to about 100 eV above the edge, a spectrum as given in figure 1.1 is observed.



**Figure 1.1:** X-ray absorption edges of aluminium. The K edge corresponds to an electron excitation from the  $1s$  core state.  $L_1$  corresponds to  $2s$  and  $L_{2,3}$  to  $2p$  core states. (Figure taken from Ref. 1).

An edge jump is followed by a slowly decaying structure, which can be related to the variations in the number of empty states which can be reached from the core state. An alternative picture to identify this structure originates from the idea that the 'free' electron, created in the absorption process at a specific site in the solid, is subject to scattering due to the core potentials of neighbouring atoms. It can be shown that both viewpoints, if worked out rigorously in their mathematical frameworks, predict equivalent x-ray absorption spectra [25]. Close to the edge the created electron has low energy and the density of states picture is more appealing but for electrons created some 50 eV or more above the edge the scattering picture is preferred because in that energy region (the so-called extended x-ray absorption fine structure, EXAFS, region) the spectrum is dominated by single-scattering events which yield useful structural information [3]. However in this thesis the emphasis will be completely on the first 30 eV of the spectrum. As a result of the experimental progress in the soft x-ray monochromators, the attainable resolution has improved to about  $1 : 10^4$  [4]. This resulted in high resolution metal  $2p$  and oxygen  $1s$  x-ray absorption edges of  $3d$ -metal compounds, which showed a large amount of structure at the edge and which thereby made a detailed analysis possible. The analysis of the high resolution spectra is a main subject of

this thesis.

## Scope

Section 1.1 discusses the electron-electron interactions which are important for the electronic structure and consequently for the interpretation of the x-ray absorption results. The impact of the x-ray, that is the electron-photon interaction, is discussed in section 1.2. In chapter 2 the experimental aspects of the x-ray absorption process are discussed and chapter 3 deals with the detailed theoretical analysis of the x-ray absorption spectral shape. Chapter 4 focuses on the electronic structure of 3d-metal oxides, which because of their intermediate character in between the weakly correlated and strongly correlated limits, are as yet only partially understood. Chapter 5 gives examples of novel applications of the x-ray absorption technique to material science, mineralogy, bioinorganics and surface studies. An important subject which is left out of this thesis is the use of x-ray absorption for the study the magnetic structure of materials [5].

### 1.1. The electron-electron interaction

The general starting point for describing electron-electron interactions is the quantum mechanical formalism. The system is described with a wavefunction ( $\Phi_N$ ), which is dependent on the position of all electrons. An observable can be found by acting on the wavefunction with the corresponding operator. The eigenvalue problem of the energy operator, the Hamiltonian ( $\mathcal{H}$ ), is known as the Schrödinger equation [6]:

$$\mathcal{H}\Phi_N = E_N\Phi_N \tag{1.1}$$

The most important ingredient of the quantum mechanical description of electrons is the Pauli principle, which states that the wavefunction of a system consisting of a collection of electrons must be antisymmetric for the interchange of two electrons [7]. The next step is to define the system and usually a molecule or a solid is visualized as a collection of atomic nuclei surrounded by electrons. As the mass of the proton is 1860 times that of the electron, the wavefunctions of the nuclei are decoupled from the wavefunctions of the electrons: the Born-Oppenheimer approximation [8]. The system which will be described with the wavefunction  $\Phi$  is thus the collection of all electrons in a particular atom, molecule or solid with the nuclei in fixed positions.

The Hamiltonian consists of the kinetic ( $T$ ) and potential ( $V$ ) energy of the electrons. The potential energy includes the interactions between the electrons and the nuclei ( $V_N$ ) and the electron-electron interactions ( $V_{ee}$ ). Though relativistic effects are not treated explicitly, one of their consequences, the spin-orbit coupling, will prove to be essential for a proper description of x-ray absorption. Inclusion of relativistic effects results in three additional terms in the Hamiltonian [9] of which the coupling between the angular momentum and the spin ( $V_{LS} \sim l_i \cdot s_i$ ) is essential. For many electron systems also consideration must be given to the inter-electronic couplings  $l_i \cdot l_j$ ,  $l_i \cdot s_j$  and  $s_i \cdot s_j$ . Though these couplings possibly can have some effect on the ground state they will be neglected throughout this thesis.

Also the coupling to the spin of the nucleus, used in nuclear magnetic resonance (NMR) techniques, will be neglected as it is too small to influence the electronic structure as far as x-ray absorption is concerned.

From these considerations the Hamiltonian to solve is:

$$\mathcal{H} = T + V_N + V_{LS} + V_{ee} \quad (1.2)$$

For a system with more than one electron the Schrödinger equation 1.1 is not exactly solvable because the  $V_{ee}$ -term in equation 1.2 is dependent on two electrons. To find the optimum numerical solution of a system with more than one electron a number of methods have been developed. Central to all is matrix calculation [10]: the wavefunction  $\Phi$  is developed in a series of basis functions. For a full description of  $\Phi$  an infinite series of basis functions is necessary, thus the specific choice of a certain limited basis set introduces an approximation intrinsic to matrix calculation. Important for the success of the numerical matrix methods is the variation principle which states that any approximate wavefunction  $\Psi$  will yield an energy which is larger than the ground state energy obtained with the ground state wavefunction.

### single particle wavefunctions

To solve the electron-electron interactions in an atom or a solid it is useful to rewrite the many-particle wavefunction  $\Phi$  in terms of single-particle wavefunctions  $\phi(i)$ . This problem was dealt with by Hartree who simply rewrote the wavefunction  $\Phi$  as the product function of the single-particle wavefunctions [11]:

$$\Phi(1, n) = \phi(1) \cdot \phi(2) \cdot \dots \cdot \phi(n) \quad (1.3)$$

The antisymmetrization of the wavefunctions  $\Phi$  was accomplished by Fock and Slater [10,12], and the method which resulted is called Hartree-Fock. The result is that the single particle wavefunctions are described by a so-called Slater determinant, build from the chosen basis functions. As the Hamiltonian is dependent on the wavefunctions and vice-versa, the problem is solved with a self-consistent iterative procedure. The energies ( $\varepsilon_i$ ) of these Slater determinants have in principle no physical meaning, but it is an appealing picture to identify them with the binding energy of a single electron: Koopmans' theorem states that if an electron is removed from the system, the ionization energy ( $E^i$ ) is equal to ( $\varepsilon_i$ ) under the assumption that the remaining electron wavefunctions are not modified [13].

The Hartree-Fock method does not treat electron correlations, apart from a partial effect due to the Pauli principle. The straightforward way to include the correlation effects is to form a linear combination of the Slater determinants: the configuration interaction method. This method will yield, within the chosen basis set, the correct many electron ground state energy. For a two-electron system a full configuration interaction calculation is still feasible [14], but for three or more electrons a specific subset of configurations has to be chosen.

### Local potentials for atoms

An enormous simplification and reduction of the computational time can be achieved if the two-electron integrals are reduced to effective single particle integrals, or in other words if the potential  $V_{ee}$  is reduced to a local potential  $V_i$ . The simplest local potential is obtained if the original Hartree method is used [11, 15]. Instead of inclusion of the exchange by the use of Slater determinants, as in the non-local Hartree-Fock potential, a statistical exchange term can be included [16]. Because the Hartree term excludes self-interaction, self-exchange effects have to be excluded too. In further developments correlation corrections have been added [15], and the resulting Hartree plus statistical exchange method has been in the atomic multiplet calculations discussed in chapter 3. As far as atomic core level binding energies are concerned the correlation corrected Hartree plus statistical exchange calculations are superior to Hartree-Fock results as well as to the results from density functional theory [17].

### Local potentials for solids

The situation for solids is far more complicated as the number of electrons is effectively infinite. Thomas considered an electron  $j$  as interacting with a spherical symmetric density distribution function, representing all other electrons [18]. Though the Thomas-Fermi potential [19, 20] gives a rather poor agreement with experiment, it is historically important as it concentrates on the electron density instead of the wavefunctions. Dirac included a statistical exchange-term into the Thomas-Fermi potential [21] and later Slater combined this statistical exchange term with the direct interaction term of the Hartree-Fock method [22]. It has been found that agreement with experiment was improved by rescaling the statistical exchange term to a value  $\alpha$  in between 2/3 and 1: the so-called  $X\alpha$ -method [23].

For solids an important step was taken when Hohenberg and Kohn introduced their density functional theorems [24, 25], which state that the ground state energy of a system can be expressed as functionals of the electron density alone. The practical implementation of the density functional theorems was greatly enhanced after Kohn and Sham introduced their local density approximation (LDA) [26], in which the energy is equal to:

$$E[n] = T_0[n] + E_H[n] + E_{xc}[n] \quad (1.4)$$

In the local density approximation both exchange and correlation are combined in a total exchange correlation potential  $V_{xc}$ . As all terms except the exchange correlation potential can be calculated exactly, this equation can be viewed as the definition of the exchange correlation potential. The former identification of the exchange potential with the Pauli principle and the correlation term with the effect of the electron under consideration on the electron density is lost. In fact the exchange correlation potential includes also part of the kinetic energy. There are several different formulations of the exchange correlation potential and also a whole range of numerical methods to solve the local density equations. (See the review of Jones and Gunnarsson and references therein [25]). The local density approximation is basically valid for weakly correlated systems, hence its limitations are more evident if correlation effects are important.

### Limitations of local density calculations

In contrast to the atomic Hartree plus statistical exchange calculations with which the Slater integrals are calculated explicitly [17], the local spin density calculations do not include the effects due to the non-spherical symmetry of the wavefunctions [25, 27, 28]. These effects are important if the ground state consists of a partly filled  $d$  or  $f$  band. Recently they were included in the local spin density calculations under the heading of orbital polarization [29, 30].

A second drawback is, as discussed before, the incomplete cancelation of the self-interactions. For local spin density calculations this was studied by Perdew and Zunger [31–33]. Recently Svane and Gunnarsson performed self-interaction corrected density functional calculations for the  $3d$ -metal oxides; their results yield band gaps as well as magnetic moments in close agreement with experiment [16]. The self-interaction causes problems only if the states are localized, as its limit for extended states is zero [17].

A final drawback of density functional methods is the neglect of many body effects as far as excitations are concerned. Many body calculations invoke a clever selection of the most important effects. For example in the  $GW$ -approach a series expansion of the screened potential  $W$  is used [36, 37]. The main effort of the  $GW$ -approach is to transform the non-observable  $N$ -particle density of states to an occupied  $N-1$  plus an unoccupied  $N+1$  description.

### Model Hamiltonians

In cases which are as yet not tractable with the *ab-initio* methods of the weakly correlated limit, one has to rely on a model Hamiltonian<sup>1</sup> designed for the specific problem of interest. A successful model Hamiltonian for the description of the electronic structure of systems with highly correlated valence electrons has been found in the Anderson impurity model [38]. In this impurity model some dominating many body effects are included explicitly. For example for the rare earths the  $4f$ -band is approximated as a set of distinct  $4f^N$ -configurations which are separated by the 'Hubbard  $U$ ' [39]. The localized ground state is then found by performing a configuration interaction calculation [40]. In the chapters 3 and 4 the Zaanen-Sawatzky-Allen (ZSA) model will be discussed because as yet it is the most direct model to interpret the x-ray and electron spectroscopies of the  $3d$ -metal compounds [41].

## 1.2. The electron-photon interaction

The second basic ingredient for the analysis of x-ray absorption spectra is the interaction of electromagnetic radiation with matter. The probability for absorption of a photon is (in the dipole approximation) equal to a transition matrix element squared times a delta function

<sup>1</sup>The usage of the term model Hamiltonian is rather arbitrary; for example the local density method uses in principle also a 'model Hamiltonian', valid for the weakly correlated limit.

describing the conservation of energy; Fermi's golden rule [43]:

$$W_{abs} = \frac{8\pi e^2 \omega^3 n}{hc^3} \cdot |\langle \Phi_f | \mathbf{p}_q | \Phi_i \rangle|^2 \cdot \delta(E_f - E_i + E_{h\nu}) \quad (1.5)$$

The momentum operator  $\mathbf{p}_q$  ( $q$  accounts for the polarization degrees of freedom) can be replaced by the position operator  $\mathbf{r}$  as  $[\mathbf{r}, \mathcal{H}] = (i\hbar/m) \cdot \mathbf{p}$ . This replacement is correct only if the same Hamiltonian is used in initial and final states. Equation 1.5 in principle refers to a final state with infinite lifetime. If the finite lifetime is accounted for the  $\delta$ -function is replaced by a Lorentzian [42].

In theoretical treatments of the x-ray absorption cross section it is customary to reformulate equation 1.5 in terms of a correlation function [40,41]. Though the golden rule notation is used throughout this thesis, the correlation function is given for convenience. The squared matrix element  $|\langle \Phi_f | \mathbf{r} | \Phi_i \rangle|^2$  is rewritten as  $\langle \Phi_i | \mathbf{r} | \Phi_f \rangle \cdot \langle \Phi_f | \mathbf{r} | \Phi_i \rangle$ . The radial operator  $\mathbf{r}$  is rewritten in second quantization as  $T = \sum_v W_v \phi_v^\dagger \phi_c$ .  $\phi_c$  annihilates a core electron and  $\phi_v^\dagger$  creates a valence electron. The finite lifetime of the excited state ( $\Gamma$ ) is included and the delta function  $\delta(E_f - E_i + E_{h\nu})$  is rewritten as (one over  $\pi$  times) the imaginary part of a Green's function  $\mathcal{G}$ :

$$\mathcal{G} = \frac{1}{\mathcal{H} - E_i + E_{h\nu} - \frac{1}{2} \cdot i\Gamma} \quad (1.6)$$

After these modifications the total equation takes the shape of a correlation function:

$$W_{abs} \sim -\frac{1}{\pi} \Im \langle \phi_i | T^\dagger \mathcal{G} T | \phi_i \rangle \quad (1.7)$$

$T$  and  $T^\dagger$  project the initial state wavefunction on a series of final states for which the Green's function is evaluated.

### Selection Rules for x-ray absorption

In case of an atom the wavefunctions in equation 1.5 can be given  $J$  and  $M$  (or  $M_J$ ) quantum numbers. The matrix element  $\langle \phi(JM) | \mathbf{r}_q | \phi(J'M') \rangle$  can be separated into a radial and an angular part according to the Wigner-Eckart theorem [44]:

$$\langle \phi(JM) | \mathbf{r}_q | \phi(J'M') \rangle = (-1)^{J-M} \begin{pmatrix} J & 1 & J' \\ -M & q & M' \end{pmatrix} \langle \phi(J) || \mathbf{r}_q || \phi(J') \rangle \quad (1.8)$$

The triangle relations of the 3J-symbol [45] give directly the selection rules for x-ray absorption. They read as follows: because the x-ray has an angular momentum of  $l_{h\nu} = +1$ , conservation of angular momentum gives  $\Delta l_i = +1$  or  $-1$ ; the angular momentum of the excited electron differs by 1 from the original core state. As x-rays do not carry spin, conservation of spin gives  $\Delta s_i = 0$ . Given these restrictions the overall momentum quantum number cannot be changed by more than 1, thus  $\Delta J = +1, 0$  or  $-1$ , with  $J + J' \geq 1$ . The magnetic quantum number  $M$  is changed according to the polarization of

the x-ray, i.e.  $\Delta M = q$ . The x-ray absorption experiments are performed with linearly polarized synchrotron radiation (see chapter 2). Thus if the x-ray impinges on a sample under normal incidence  $q = +1$  or  $-1$ , while for grazing incidence  $q = 0$ . This can give rise to angular dependent x-ray absorption spectra if the sample under consideration has a non-cubic symmetry [46]. In section 3.6 these polarization dependent effects will be dealt with in more detail.

### Extended final states

For extended final states (the Bloch-like wavefunctions in density functional methods)  $J$  and  $M$  are not good quantum numbers and the only selection rules are  $\Delta l_i = +1$  or  $-1$  and  $\Delta s_i = 0$ . Thus in case of an excitation from a  $1s$  core state only  $p$ -final states can be reached and from a  $p$  core state  $s$  and  $d$  final states can be reached. The absorption cross section is reformulated as the matrix element squared times the local projected density of states [47, 48]:

$$W_{abs} \sim |\langle \Phi_{l-1} | \mathbf{r}_q | \Phi_l \rangle|^2 \cdot \mathcal{P}_{l-1} + |\langle \Phi_{l+1} | \mathbf{r}_q | \Phi_l \rangle|^2 \cdot \mathcal{P}_{l+1} \quad (1.9)$$

This approximation assumes that both the extra valence electron and the core hole do not modify the calculated density of states significantly. Thus it is assumed that  $\mathcal{P}_N \approx \mathcal{P}_{N+1}$ , which is a rather valid approximation for weakly correlated systems like simple metals, but which can give problems for strongly correlated narrow band systems like the  $3d$ -metal oxides. Additionally it is assumed that  $\mathcal{P}_N \approx \mathcal{P}_{eN}$ . The complete neglect of the core hole is a rather drastic assumption, as will become evident in chapters 3 and 4.

## 1.3. X-ray absorption in relation to other spectroscopies

In this section the x-ray absorption technique is compared with related spectroscopies. Discussed are the relation to other photon absorption techniques, the equivalence of electron energy loss spectroscopy (EELS) and the relation to other core level spectroscopies.

### X-rays versus UV, visible and IR radiation

The absorption of electromagnetic radiation is generally divided into a number of energy regions. Originally the division has been made into infrared (IR), visible (VIS) and ultraviolet (UV) radiation, on the basis of the sensitivity of the human eye. This division is still dominant, but a conceptually clearer division is to separate the electromagnetic spectrum into the kind of excitations they produce: x-rays produce core level excitations, UV/VIS light produces valence band excitations and IR radiation produces roto-vibrational excitations. Optical absorption (absorption of UV/VIS light) excites a valence state to an empty state, hence the spectral shape has to be described as the joint density of states. Because the excited electron interacts with the hole, the optical transition can generate an exciton (electron hole pair) with an energy below the bandgap.

Though the main transition in x-ray absorption is that of a core state to an unoccupied state, this by no means excludes additional vibrational effects. For example the  $1s \rightarrow 2p$  x-ray absorption spectra of simple molecules like  $N_2$  or CO have fine structure originating from vibrational effects [49, 50]. In general any low energy excitation can accompany the main excitation (if allowed for by selection rules, etc). A technique which makes specific use of optical transitions accompanying the main x-ray transition is x-ray excited optical luminescence (XEOL). After the decay of the core hole a system will in general not be back at its ground state. It is possible that an intermediate state is reached which is optically active, hence its luminescence can be measured [51].

### Equivalence of x-ray absorption with EELS

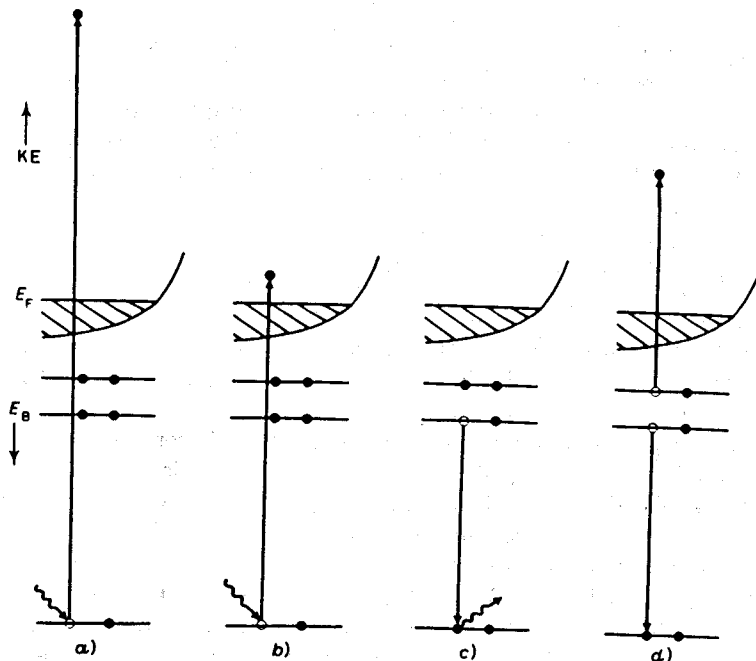
It has been shown that (core level) electron energy loss spectroscopy (EELS) can result in identical spectra to x-ray absorption. In EELS the electronic transition is caused by a high energy electron, typically several hundreds of keV [52]. The spectrum is measured in transmission mode and the detector is placed at an angle  $\Theta$  to the normal. For example the Karlsruhe spectrometer uses 170 keV electrons and the detector is placed at an angle of 4 mrad. Under these conditions the wave vector  $|\vec{q}| \simeq q_{\perp} \simeq k\Theta$ . The interaction Hamiltonian for electrons contains the term  $e^{-i\vec{q}\vec{r}}$ , instead of  $e^{i\vec{e}\vec{p}}$  for photons. For small  $|\vec{q}|$  this term can be expanded as  $1 - i\vec{q}\vec{r} - (\vec{q}\vec{r})^2/2$ . If the wave vector  $|\vec{q}|$  is much smaller than the inverse of the core wave function mean diameter ( $1/\langle R_c \rangle$ ), all terms except  $i\vec{q}\vec{r}$  vanish and the dipole approximation retains its validity. A disadvantage of a transmission mode experiment is the necessity to use thin samples. An advantage of EELS is the possibility to modify the wave vector in order to allow for non-dipole transitions. Additionally it is possible to use an electron microscope, to allow for a spatial resolution of the order of nanometers. The present status of the detectors used in EELS makes possible a resolution of about 0.2 eV at the oxygen edge (500 eV). This is in the same order of magnitude as the presently used x-ray absorption monochromators (see chapter 2).

### Core level spectroscopies

X-ray absorption excites an electron from a core state to an empty state and because the core level binding energies are specific to a certain chemical element, x-ray absorption (as well as all other core level spectroscopies) is element specific [53]. Other core level spectroscopies are x-ray photo-emission (XPS) x-ray emission (XES) and Auger electron spectroscopy (AES). Figure 1.2 sketches schematically the four core level spectroscopies.

The nomenclature of core level spectroscopies is not uniformly used. Historically the main quantum number is given a letter in alphabetic order starting with K [54]. Within this main quantum number the levels are numbered from high energy to low energy (the numbers are given either in roman or arabic). In electronic structure calculations the orbital names are used for the core states, i.e. the main quantum number  $n$  is given a number and the angular quantum number  $l$  is denoted as respectively  $s$ ,  $p$ ,  $d$ ,  $f$  and thereafter alphabetically. For instance absorption from a  $2p$  core state is called the  $L_{2,3}$  edge. Table 1.1 makes a comparison of both nomenclatures.





**Figure 1.2:** Core level spectroscopies; from left to right (a) x-ray photoemission, (b) x-ray absorption, (c) x-ray emission and (d) Auger electron spectroscopy.

Core state	Spectroscopic name
1s,	K
2s, 2p	L <sub>1</sub> , L <sub>2,3</sub>
3s, 3p, 3d	M <sub>1</sub> , M <sub>2,3</sub> , M <sub>4,5</sub>
4s, 4p, 4d, 4f	N <sub>1</sub> , N <sub>2,3</sub> , N <sub>4,5</sub> , N <sub>6,7</sub>

**Table 1.1:** Nomenclature as used in x-ray spectroscopies.

Throughout this thesis both notations will be used. X-ray absorption and x-ray photoemission can be completely described with this notation. However as there can be many different Auger and x-ray emission decay processes, these spectroscopies need more complex identifications. The Auger process consists of three core or valence states, one in the initial state and two in its final state. An Auger process which transfers a  $2p$  core electron to a  $1s$  core hole with the simultaneous ejection of another  $2p$  core electron is called  $1s2p2p$ -Auger or alternatively  $KL_{2,3}L_{2,3}$ -Auger. Valence electrons are given the symbol V in both notations, i.e.  $KL_1V$ , etc. X-ray emission processes are possible from any core state above the core

hole present, given that they are allowed to couple from symmetry arguments. In principle therefore a two core state notation could be used, i.e.  $KL_{2,3}$  x-ray emission. However for historical reasons the usual notation has developed into a rather complicated set of names. For instance the transition from  $L_2$  to  $K$  is denoted as  $K\alpha$  and the transition  $M_3 \rightarrow L_2$  is called  $L_{II}\beta_{17}$ , etc. The full table of historical notations is given in Ref. 125.

### Decay spectroscopies

An important division which can be made is between spectroscopies which create excited states, like x-ray absorption and x-ray photoemission, and spectroscopies which monitor the decay of an excited state like Auger electron spectroscopy and x-ray emission spectroscopy. Neglecting finite temperature, the initial state in x-ray absorption is clearly defined as the ground state of the system. On this ground state a specific perturbation is applied, which creates a core hole and brings the system into an excited state. In contrast for Auger electron spectroscopy the initial state is in general not be a single core hole state, but a specific set of core hole states depending on the x-ray energy of the core hole creation process and the reaction of the system under consideration to the core hole creation. For instance in cases where the lowest energy core hole state does not significantly couple to the ground state the majority of states generated will consequently be of higher energy. These states can relax to the lowest ground state with the core hole present, or alternatively they can decay directly via an Auger or an x-ray emission decay process depending on the subsequent transition probabilities. For a detailed description of the decay spectroscopies these effects should be known or at least kept in mind if a specific approximation is made. For example in Auger electron spectroscopy it is often tacitly assumed that the initial state is uniquely defined, which must surely lead to errors in some cases.

### Spectral functions

The ground state density of states ( $\mathcal{P}_N$ ) does in itself not have any real (i.e. observable) meaning as it presents the optimized distribution of effective one particle states and the occupied states yield the correct ground state total energy of the system. For x-ray absorption the spectral function is equal to  $\mathcal{P}_{\bar{e}N+1}^-$  ( $\bar{e} \equiv$  the unoccupied part). Under the assumption that  $\mathcal{P}_{\bar{e}N+1}^- \approx \mathcal{P}_N^-$ , the spectral shape is approximated with the density of states as calculated with a ground state calculation. For this assumption to be valid two conditions must be met: (1) the core hole should not influence the spectral shape and (2) the extra valence electron should not be correlated with the other valence electrons. These conditions however are in general not met for strongly correlated systems like  $3d$ -metal compounds. It should be noted that the core hole and the extra valence electron are, from an electrostatic viewpoint, counteracting effects. In other words the total charge is conserved locally and consequently the disturbance on the system is not large.

The overall charge is not conserved in photoemission and inverse photoemission. Thus as can be checked in table 1.2 inverse photoemission relates to the  $(N+1)$ -particle density of empty states and because the counteracting effect of the core hole is not present, the inverse photoemission spectrum will be more sensitive to correlation effects. The last column of

Spectroscopy	Spectral Function	Ground state DOS
x-ray absorption	$\mathcal{P}_{cN+1}^-$	$\approx \mathcal{P}_N^-$
inverse photoemission	$\mathcal{P}_{N+1}^-$	$\approx \mathcal{P}_N^-$
photoemission	$\mathcal{P}_{N-1}^+$	$\approx \mathcal{P}_N^+$
x-ray emission	$\mathcal{P}_N^+$	$= \mathcal{P}_N^+$
optical	$\mathcal{P}_{N-1}^+ \cdot \mathcal{P}_{N+1}^-$	$\approx \mathcal{P}_N^+ \cdot \mathcal{P}_N^-$
core XPS	$\mathcal{P}_c$ (relaxed)	$\mathcal{P}_c$

**Table 1.2:** Spectral functions of the different spectroscopies. All spectroscopies have to be multiplied with their respective matrix elements.

table 1.2 is the spectral shape if correlation is not important as is met closest for free electron metals. Thus for free electron metals one can expect the spectral shapes to be closely related to the ground state density of states. For correlated systems this condition is not met; thus the 'amount of disagreement' between ground state density of states and the spectral shape indicates the importance of correlations in the system. Because the 'amount of disagreement' is a highly qualitative concept, model calculations are required for a quantitative discussion. From the table it is found that the XPS spectrum should correspond to a single peak, representing the core level binding energy. This makes core level XPS a good candidate to study correlation effects: if the spectrum does not correspond to a single peak some sort of correlation effect is important. Important correlation effects are, depending on the specific system, (1) multiplets, (2) charge transfer satellites, (3) electron hole pairs and (4) plasmon satellites. For x-ray absorption of 3d-metal oxides specifically multiplets and charge transfer are important, as will be discussed in chapter 3.

## Resonant techniques

If the electron and photon spectroscopies discussed are combined, a whole series of novel possibilities arise. The x-ray energy can be changed through an x-ray absorption edge and for every x-ray energy the corresponding photoemission and/or Auger spectrum can be measured. Figure 1.3 sketches the energy positions of some Auger and photoemission peaks as a function of the x-ray energy. For simplicity, level splittings, correlations and core hole effects are neglected. As they resemble a core state of a specific binding energy, the photoemission peaks vary linearly with the x-ray energy. The Auger peaks have a constant kinetic energy as they relate to the energy difference between three core states, which is independent of the x-ray energy.

In the schematic example of figure 1.3 the  $2p$  binding energy is 30 eV and the  $1s$  binding energy is 100 eV, i.e. the  $2p$ -photoemission peak has a kinetic energy of the x-ray energy minus 30 eV and the  $1s2p2p$  Auger peak has a kinetic energy of  $100 - 60 = 40$  eV. An interesting phenomena occurs if an Auger process interferes with a photoemission process. At the x-ray energy indicated with the arrow the  $2p$ -photoemission process ( $1s^22p^6V^N \rightarrow 1s^22p^5V^N + e^-$ ) interferes with the Auger process ( $1s^22p^6V^N \rightarrow 1s^12p^6V^{N+1} \rightarrow 1s^22p^5V^N +$

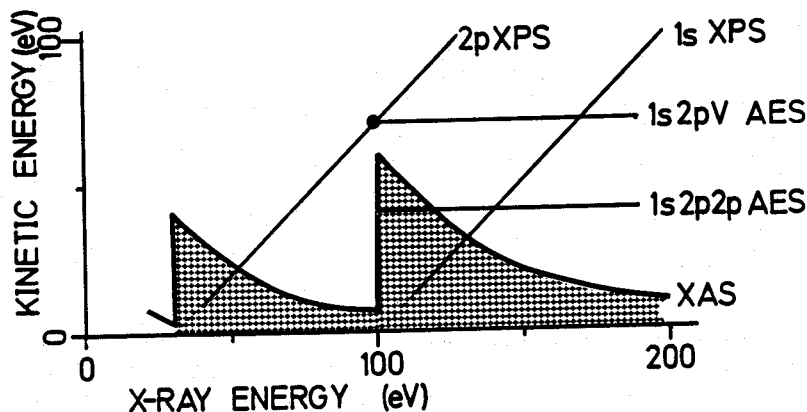


Figure 1.3: Energy dependence of Auger and photoemission peaks.

$e^-$ ). In case of resonant enhancement of valence band photoemission, information concerning the partial density of states in the valence band can be obtained [52]. If for example the valence band of CuO is measured with the x-ray energy varying through the copper  $3p$  edge, the spectrum is clearly modified [167]. However because the overall process can be complicated the interpretation is in general not straightforward [81].

### Spin polarization, x-ray polarization and angular dependence

The techniques discussed can be extended if use is made of extra degrees of freedom, for example the electron spin and the polarization of the x-ray. All electron spectroscopies can be modified to a spin-polarized version, with detection and/or creation of spin dependency. Also the x-rays can be used in a linear or circular polarized fashion, selecting only specific transitions. This can yield an overwhelming amount of extra obtainable information, specifically concerning the magnetic structure of materials [59].

Another degree of freedom is the angular variation of the material of investigation with respect to the incoming/outgoing electron/photon. For example angular resolved photoemission (ARPES) gives information concerning the  $\mathbf{k}$ -dependence of the states and from the spectral shapes an 'experimental band structure' can be obtained. X-ray diffraction (XD) gives information concerning the bulk structure whereas (low energy) electron diffraction (LEED) gives information concerning the surface structure. Photo-electron diffraction (PED) and Auger electron diffraction (AED) use an internal electron source. [60]. In this thesis the possibilities of spin polarization and diffraction are not considered. The use of the polarization of the x-ray is discussed in section 3.6 and an application concerning surfaces is discussed in section 5.4.1.

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