

Università degli Studi Roma Tre

Dottorato in Fisica XIX ciclo

CORRELATION EFFECTS IN TWO ELECTRON RESONANT EMISSION: A MULTIPLE SCATTERING APPROACH

Fabiana Da Pieve

Chairperson of the Ph.D. School prof. Orlando Ragnisco

Supervisors

prof. Giovanni Stefani prof. C.R. Natoli

A.A. 2005 - 2006

Ciao Papá !

Contents

Introduction				
1	Elec	tronic correlations studied by coincidence spectroscopy	9	
	1.1	Electron emission spectroscopies: second order processes	9	
	1.2	Recent interesting results from resonant photoemission	11	
	1.3	Coincidence spectroscopy as a probe of electron correlations	12	
		1.3.1 A tribute to pioneers: coincidence spectroscopy in atomic physics	13	
		 1.3.2 Coincidence spectroscopy in solid state physics	20	
		emission	26	
2	Fun	damentals of Multiple Scattering Theory	29	
	2.1	Introduction	29	
	2.2	Use of MS theory in several spectroscopies	30	
	2.3	Approaches to the MS problem	31	
	2.4	General expression of the cross section	32	
	2.5	Cross section for incoming photons	33	
	2.6	Cross section for the atomic case	37	
		2.6.1 Connection with the Green's function formalism	40	
		2.6.2 The free Green's function $G_0 \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots$	42	
	2.7	Emission from a cluster: the multiple scattering problem	42	
		2.7.1 The free Green's function G_0^+ in the multicenter problem	43	
		2.7.2 Resolution of the Lippmann-Schwinger equation in the multicenter		
		$problem \dots \dots$	44	
		2.7.3 The multiple scattering equations	47	
	2.8	The Rehr-Albers formulation	50	
	2.9	Calculational details	53	
	2.10	Use of general potential in MS theory	57	
	2.11	Multichannel MS theory	58	
	2.12	Magnetic and natural dichroism in photoemission and absorption	58	
3	Mul	tiple Scattering approach to two electrons resonant emission	61	
	3.1	Importance of the angular correlation between photoelectron and Auger electron	61	
	3.2	Calculation of the cross section	62	
	3.3	One and two step model	64	

	3.4	Second quantization form of the cross section	67	
		3.4.1 First step: photoionization	69	
		3.4.2 Second step: Auger decay	71	
		3.4.3 The coincidence cross section	75	
	3.5	The coincidence cross section in the atomic limit	80	
	3.6	Light polarization dependence	81	
		3.6.1 Kinematic dependence of the atomic cross section for different light		
		$polarization \dots \dots$	83	
		3.6.2 Linearly polarized photon beam	84	
		3.6.3 Circularly polarized photon beam: circular natural dicroism	86	
4	The	eory vs. Experiment	89	
	4.1	Introduction	89	
	4.2	Generation of phase shift and radial matrix elements (PHAGEN)	90	
	4.3	Calculation of the Coulomb integrals	91	
	4.4	Implementation of the cross section in the multiple scattering code (SPEC) .	93	
	4.5	Tests on atomic targets: the case of Ar and Xe	95	
	4.6	Multiple scattering calculation of Auger and coincidence diffraction pattern	99	
C	Conclusions and future developments			
A	Acknowledgements			
B	Bibliography			

Introduction

Today one of the focus point in condensed mater physics is the study of the microscopic origin of several effects caused ed by strong electronic correlations, which sometimes represent the boundaries between atomic and solid state properties. Effects like superconductivity, colossal magnetic resistance, perpendicular magnetic anisotropy, magnetic dichroism, and the enhanced correlations in nanoscale structures have attracted a great deal of interest, both from a fundamental physics point of view and as resources for practical applications. To understand the nature of such phenomena, it is highly desiderable to have informations about the localized electronic properties and the atomic magnetic structure of systems which display such behaviours.

For example, in investigating the physics behind superconductivity, the study of the spin character of the first ionization states is important to understand the behaviour of the charge carriers in the doped materials [1], and the estimation of such spin polarization of the conduction band are very interesting for basic research in the field of spintronics [2]. Stimulated by the discovery of cuprate superconductors, many studies have been done on the electronic structure of late transition metal (TM) oxides since they provide oppurtunities for a better understanding of the electronic structure of highly correlated materials. The attention is mainly focused on understanding the nature of their energy gap, through the analysis of multiplet and satellite structure observed in core level spectroscopies. The Mott Hubbard correlation, charge transfer energy and band gaps obtained from the analysis of spectroscopic data do not unambiguosly address towards a final assessment of the nature of the energy gap.

In low-dimensional magnetic systems spin-orbit coupling effects are important. In atoms, Hund's rules predict maximum orbital angular momenum L compatible with the maximum spin multiplicity, while in transition metals solids, electron delocalization and band formation result in an almost complete quenching of $\langle L \rangle$. Such intrinsic differences between atomic and bulk behaviours are characteristic of systems developing itinerant electron magnetism. Thus, whereas the orbital moments in bulk materials of high symmetry are strongly reduced due to orbital quenching, they may attain large values in low dimensional systems [3]. Consequently, investigations of orbital magnetism on TM clusters, in the way from atom to solid, should reveal novel size-dependent phenomena. These general considerations indicate that $\langle L \rangle$ should be very sensitive to the local environment of the atoms. TM compounds have been also studied in low dimensions, like nanometer-sized structures, ultra-thin films, which also have attracted a great interest. Their magnetic properties can be drastically different from those of bulk materials. Surface contributions to magnetic anisotropy, which are related to under-coordination of atoms at the interface, become more relevant. The orbital moment of delocalized electron states should, to a large extent, depend on the shape and width of the density of states (DOS) [4]. At surfaces the d bands become more narrow causing larger spin moments which, due to spin orbit coupling produces enhanced orbital moments. Moreover, at the surface the crystal field partitioning of the electronic levels is modified due to reduced symmetry, thus at surfaces there is a lower crystal field quenching of the orbital moment.

All these considerations about some examples concerning electronic correlations at the atomic scale lead to the conclusion that powerful techniques are needed in order to deeply understand phenomena like magnetic dichroism, colossal magnetoresistance, perpendicular magnetic anisotropy, high T_c superconductivity. In particular, over the timespan of two decades magnetic dichroism has evolved into a powerful standard technique to separate spin and orbital contributions to the magnetic moments, giving insight into the microscopic origin of several effects. Also in photoemission spectroscopy, magnetic dichroism has become a powerful probe to measure different kinds of correlations between the angular moments of core and valence electrons. Chirality is not only introduced through the helicity vector of the light but also by the experimental geometry spanned by the directions of light polarizations, sample magnetization and photoemission direction. Recently, scientific interest has moved towards second-order processes; with the intermediate state created either by excitation of the electron to an upper bound level or by photoemission, followed by a decay process. The polarized (oriented) or aligned intermediate state breaks the selection rules for direct transitions and allow forbidden transition, e.g. spin-flip, and gives sensitivity to the local environment. Moreover, the decay process acts as a core hole clock, allowing a determination of the time scale of the electron screening and spin dependent screening. Examples of second order processes are found in photon in-photon out techniques, such as Raman scattering or resonant inelastic x-ray scattering. Another example is resonant photoemission, in which one electron is excited by photon absorption to an upper level and then it goes back down to fill the core hole while another electron is emitted. Sum rules for the magnetic circular dichroism in resonant processes can give information about the higher multipole moments in the ground state [5, 6, 7].

During the last years another resonant process has gained more and more attention: Auger-photoelectron emission studied by time coincidence spectroscopy. This process can be considered the general case of resonant photoemission: the electron is excited into the continuum and then another electron from an upper level fills the core hole. The energy gained in the hole decay is given to another electron which is emitted (the Auger electron). Coincidence spectroscopy consists in detecting in time coincidence the Auger electron and the corresponding photoelectron. The whole process of photoionization and Auger decay has been studied for a long time in atomic physics and several coincidence experiments have been performed. In the last decade some groups also tried to perform such experiments in the solid state, but yet no one has studied from the theoretical point of view the emission of two correlated electrons from a solid sample. A theoretical interpretation is completely missing, and the aim of this thesis is to fill this gap and to give a strong input to further studies.

It has been demonstrated that coincidence detection of the Auger and the parent photoelectron allows to physically discriminate Coster-Kronig transitions (originated by different core hole states) even if they largely overlap in energy [8] and beyond natural lifetime limits [9] and that its surface sensitivity allows to study systems with reduced symmetry, like thin films. In many cases, Auger-photoelectron coincidence spectroscopy (APECS) has demonstrated to be of crucial relevance in studying multiplet structure; however, a further discrimination capability in resolving the contribution from different magnetic sublevels is still available by detecting the Auger-photoelectron correlated pairs in angle as well as in energy and time, i.e., performing an angle resolved APECS (AR-APECS) experiment. Feasibility of this latter kind of spectroscopy has been demonstrated by a pioneering experiment on Ge(100) [10] where the angular distribution of the correlated Auger-photoelectron pairs have been measured in for different fixed emissione direction of the photoelectron, which means to measure Auger electrons originating from core hole states whose polarization is different, since it can be controlled by varying the mutual directions of the light polarization and momentum vectors of the two final electrons. In this case chirality is not introduced by the helicity vector of the photon beam or by the magnetization of the sample, but the electron pair shows to have an intrinsic natural chirality which forces the two electrons in determined emission directions. The energy and angular correlation of the continuum electrons (Auger and photoelectrons) is determined mainly by the occupation of the magnetic sublevels of the intermediate hole ion state (polarization). Thus this kind of spectroscopy allows to have access on the state multipoles of the systems under investigation, as well as other spectroscopies like absorption, photoemission, resonant photoemission, but the difference is that APECS allows to be sensitive to higher state multipoles and different combinations of them with respect to the other techniques.

In the first chapter we mainly review the topic of coincidence spectroscopy in atomic physics and then we describe the recent results from APECS experiments from solids. In the second chapter we describe the theory (multiple scattering theory) which is the fundamental approach to treat electron emission from solid sample. In the third one we derive, within the multiple scattering theory, the cross section for Auger-photoelectron emission from a cluster and from an isolated atom, and we then also analyze the dependence of the cross section on the light polarization of the photon beam. In the fourth chapter we talk about the implementation of the new formulas into the computer codes and we present the numerical calculations performed on both atomic targets (as first tests) and on a Ge(100) surface. In the conclusions we summerize the results obtained and we make suggestions for the future work.

Chapter 1

Electronic correlations studied by coincidence spectroscopy

1.1 Electron emission spectroscopies: second order processes

During the last decade several experimental techniques have been developed or improved to study the electronic correlations at the atomic scale. Great progress in understanding the properties of magnetic (and also macroscopically non magnetic) materials has been achieved using magnetic dichroism in absorption and photoemission, Auger emission and their spin polarized related techniques. These different kinds of spectroscopic techniques allow to access to different informations on both ground and excited states of the systems under investigation. We can briefly review their advantages and their limitations. Absorption dichroism probes directly the valence polarized states, while the core level photoemission dichroism probes the polarized valence states only indirectly through the exchange interaction with the core but offers the additional benefit of intrinsic surface sensitivity. Essential requirement to observe magnetic dichroism is to energetically discriminate contributions from different non degenerate sublevels, whose transition probabilities are different depending on the relative orientations between the light polarization and the magnetization. The big success of the absorption magnetic dichroism is due to the spin [11] and orbital sum rules [12], which, in a one electron-model, allow to estimate the contribution of the spin and orbital ground state moment. The case of localized orbitals such as $M_{4,5}$ edges of rare earths (probing 4f states) or, to a lesser extent, $L_{2,3}$ edges of light transition metals (probing 3d states), was investigated with great success [13, 14, 15]. The theoretical interpretation of the effect is now clear: MXD is due to the effect of selection rules governing transitions from the ground state to the multiplets obtained by coupling the ion state with the core hole. The effects is present if the spin orbit interaction is present in the ground state or in the final state, or when there is a breaking of the time reversal symmetry. If the influence of the crystal field is taken into account, the agreement between experiments and theory is very satisfactory. However, deviations from sum rules can be observed due to core valence interactions which can induce a transfer of spectral weight between the different edges [16, 17, 18].

The magnetic dichroism in photoemission from core levels is sensitive to the exchange effects at the core but only probes indirectly the interaction with the valence shells; the magnetic dichroism and spin resolved photoemission from the polarized valence states can provide very incisive information regarding the density of states and band dispersions, but the results cannot be associated with given species.

Auger spectroscopy (AES) deals with detection of the Auger electrons, which are emitted following a second order process. AES has prooved to be one of the most powerful tool to study local electronic correlations. The excitation of Auger electrons is element specific and is a probe of the short range order of atoms. The Auger process is due to Coulomb interaction between electrons, and the final state is given by a doubly ionized ion. It consists in the decay of a core hole, which can be produced by photon or electron impact, which is filled by an electron from an upper level; then the system autoionizes giving the energy gained during the process to an electron which is emitted and is called Auger electron.

Both energy and angular patterns have been studied extensively and can provide informations on atomic scale correlations in extended systems. The Auger lineshape is strongly influenced by electronic correlations and the case which involves valence band holes can be predicted with the use of the Cini-Sawatsky [19, 20] model, who derived the Auger intensity from a two particle Green function within the framework of Hubbard-type Hamiltonians. The lineshape depends on the ratio between the bandwidth W and the repulsion energy U. When U/W >> 1 a singularity appears in the spectrum in the high energy region, similar to a quasi atomic structure, which is called two holes resonance and is caused by a localized state on a single atomic site in which the two holes are related to each other by a quantistic localization. Thus the analysis of the Auger lineshape can allow an insight into the atomic correlations both within the levels of the two final holes, and between core and valence levels.

Also the angular distributions of Auger electrons can give important informations on the electronic correlations. From the determination of the anisotropy, information can be obtained on both Auger decay and primary ionization [21]. Moreover, in the solid state, the striking sensitivity to bond length and atomic type of scattering atoms of Auger diffraction (AED) makes it a very powerful structural tool, similar to LEED, but with additional chemical discrimination. Both XPS and AES valence spectra are related to the local density of states and can tell us much about bond strenght, polarization and symmetry. AES is a widely used method for surface analysis. The Auger electrons have energies in the range 10-1000 eV and are superimposed on a background of inelastically scattered electrons. Any Auger electron suffering an energy loss will be scattered out of the Auger peak and becomes part of the background. Thus the range of detected Auger electrons from a solid will be approximately the mean free path for the strongest electron-electron energy loss process, generally plasmon generation or excitation of interband transitions. Measurements of the escape depths of Auger electrons show that the mean depths of emission of collected Auger electrons are of the order of a few atomic layers [22].

Recently, also the spin polarization of Auger electron has been considered. Spin resolved Auger spectroscopy is in principle a powerful probe of local element properties, but the information is always given by an average over intermediate core hole states that is inherently associate with this process. Spin resolved photemission and spin resolved Auger spectroscopy both from magnetic and non magnetic systems can provide informations on the magnetic sublevels structure of the systems, but such measurements are always affected by loss of intensity and often the interplay between exchange and spin orbit interaction makes the features in the spectrum not so easily distinguishable. The Auger decay is based on Coulomb interaction, thus spectroscopies which probe such effect are very powerful tools to study particle correlation. However, in conventional Auger spectra the core hole intrinsic linewidth is responsible for a wider Auger lineshape and spin orbit separation, often of the same order of magnitude of the Auger multiplet splitting, gives rise to overlapping contributions. As a result, spectroscopic features sensitive to electron correlation effects, such as multiplet energy splitting and relative intensity of the individual components, remain hidden in the resulting broad, almost featureless, lineshape. Conventional Auger spectroscopy is unable to resolve these overlapping features and for such reason the rich information contained in CK spectroscopy is usually overlooked. It would then be of general relevance to develop a methodology that allows to disentangle spectroscopic details of the Auger spectrum. Missing from these spectroscopies is a way to probe the local valence electronic structure of magnetic species in both a spin- and element-selective manner. Such studies are interesting especially for those systems with reduced symmetry, like thin films, or without long range order, like antiferromagnets, where an atomic probe of both core and valence states and their interaction is necessary to go deeper in understanding their properties.

Resonant photoemission and Auger-photoelectron coincidence spectroscopy are gaining more and more attention and they are proving to be very powerful techniques which allow to gain more informations with respect to usual techniques.

1.2 Recent interesting results from resonant photoemission

Resonant photoemission spectroscopy (RPES) is a technique which combines the possibility to obtain informations about the valence levels probing their interaction with the core levels through the autoionization effect. The process of resonant photoemission consists in exciting a photoelectron to a valence level, then this electron decays to fill the core hole and another electron from the valence level is emitted. Recently a spin resolved circularly polarized resonant photoemission has been performed [23]. The authors showed that it is possible to obtain spin resolved valence band of macroscopically non magnetic transition metal materials by doing the resonant photoemission with spin orbit split core levels. At the resonance the behaviour of satellites due to two holes states allows the separation of the spectra into singlet and triplet states. They analyzed the L_3 resonant photoemission on Ni below and above the Curie temperature with the aim of studing the spin polarization in 3d level. Direct photoemission from such level would produce little spin signal, since the spin orbit interaction (0.1 eV) is too little and circularly polarized light can only be effective if a strong spin orbit splitting is present in one of the atomic subshells under study, because then angular momenta will govern the selection rules. Circularly polarized light produce a spin polarized hole, then the subsequent Auger decay give rise to photoelectrons which are also spin polarized (with a polarization depending on the final state). Essential is the fact that the photoelectron carries information concerning the local moment on the ground state, since the probability and degree of spin polarization with which the core hole is created depends on the spin and multiplet character of the valence hole in the ground state, and since the core excited electron is a participator in the Auger decay. The resulting degree of spin polarization of the photoelectron is determined by selection rules. Analysis of the spin polarization (the difference between spectra taken with parallel and antiparallel alignment of the photon and electron spins) for the different multiplet terms allow to assign the multiplet terms to the structures observed in the spectra. The results demonstrate that the singlet states of the valence band are located at much higher binding energy than the triplets. This indicated that despite the strong band formation the on site Coulomb and exchange matrix elements, and in particular the Hund's rule (triplets lower in energy than singlets), still play an important role in determining the energetics of the valence states. Above T_c the local 3d spin polarization doesn't change, thus the local moments are still present. Thus the observed polarization does not depend on the orientation of the local moment, but only on the magnitude of the local moment. Upon crossing T_c , the high spin states continue to dominate at low energy, indicating the local moments and short range magnetic order persits above T_c . This is one of the shortcomings of the mean field theory which predict the disappearence of local moments above T_c . The neglects of Hund's first rule and coulomb correlations causes mean field theories to underestimate the gain in potential energy obtained by keeping the 3d electrons localized relative to the gain in kinetic energy related to band formation.

The authors also performed the same experiment at L_3 edge of CuO [24], which is generally considered a model compound for high T_c cuprates. The characteristics of the first ionization states in CuO (the two holes final state in photoemission) may be representative for the behaviour of the doped hole in cuprates (ground state). The spin polarization results to be quite large, which is quite remarkable considering a system with randomly oriented local moments. the highest spin polarization is observed at high binding energy, and analysis of the selection rules indicate that the highest spin polarization is expected for singlets. Thus states located at the top of the valence band are singlets, which provides strong supports for the existence and stability of Zhang-Rice singlets in cuprates.

1.3 Coincidence spectroscopy as a probe of electron correlations

Auger-photoelectron coincidence spectroscopy is another technique which is attracting much attention during the last years. As already said, the information contained in Auger (and also in resonant photoemission) spectra are often obscured by the complexity of the spectra. Decay spectra related to different spin-orbit partner edges or to different initial state (due to possible shake up or shake off in the photoionization process) may strongly overlap and quantitative analisys are difficult [8]. Moreover the Auger spectra have a complex structure given by several multiplet terms and satellites originating by many body effects, which extend over several eV. Coincidence spectroscopy consists in detecting in time coincidence the decay products of a certain process. This technique has a long history in atomic and nuclear physics, but only recently it is becoming a relevant technique also for solid state physicists. In atomic physics coincidence spectroscopy has been applied to several processes, like Auger-photoelectron emission, Auger cascades, electron-fluorescent photon emission and direct double emission (in which two electrons are directly emitted due to one photon absorption). In this dissertation we will focus our attention to Auger-photoelectron emission spectroscopy (APECS), which, together with direct double photoemission (DPI), constitutes a technique which is now used also in condensed matter studies.

Auger-photoelectron coincidence spectroscopy exploits the relationship between the initial photoionization and Auger decay, which are related by the respective creation and annihilation of the same core hole, and enables the photoemission and Auger spectra to be examined with unprecedented discrimination [8, 120, 26]. In APECS, a photoelectron and its associated Auger electron are detected in time coincidence: within the experimental resolution, the two particles are considered as emitted simultaneously, i.e. they come from the same ionization event. The photoelectron selects a specific atomic site and the APECS spectrum is determined only by those electrons originated by the decay of the selected core hole state [27]. The discrete state with one hole is energetically degenerate with the continuum of final states with two holes and a free particle thus in principle the process interferes with the direct double photoionization, but interference between the two processes can be neglected since the probability for DPI is lower than the resonant process. Since both these electrons are generated in the same ionization event, only features characteristic of that event contribute to the coincidence spectrum [27]. Double direct ionization and ionization followed by Auger decay, studied using coincidence techniques, may be also used to investigate respectively the important question of entanglement and coherence, whose exploration is a topic of strong current interest.

During the last years Auger-photoelectron coincidence spectroscopy has proved to be a very powerful tool to obtain detailed information on electronic correlations. Both angular and energy correlations between the two electrons have been analyzed and several interesting results have been published regarding both atomic and solid state physics experiments. We now review some of the main results in atomic and condensed matter physics.

1.3.1 A tribute to pioneers: coincidence spectroscopy in atomic physics

In atomic physics APECS constitutes what is called the *complete experiment* [28, 29, 30, 31, 32, 33, 34], i.e. the experimental determination of all the transition amplitudes and phases necessary for the complete description of the process. Today it is possible to perform different kinds of equivalent complete experiments, e.g. spin-resolved photoelectron spectroscopy [28, 35], electron-electron coincidence spectroscopy [36], electron-fluorescent photon coincidence spectroscopy [37], and photoelectron spectroscopy of polarized atoms [38], linear dichroism (LD) in photoionization of laser-aligned atoms [39, 40]. Moreover, in some particular transitions and geometries the linear dichroism of the Auger electron from aligned atoms allows to obtain the same kind of dynamical information which can be extracted from LD in direct photoionization [40].

In the case of APECS, much information about the dynamics of ionization and decay can be obtained by the angular correlation between the Auger and the photoelectrons. Such correlations depend strongly on the initial and final state symmetries such as parity, angular momentum, spin, anisotropy created in the magnetic sublevels of the intermediate ion and also on the interference between the different open decay channels.

When analyzing the single Auger process, it is generally treated as independent on the initial state. Hence the lineshape and angular distribution are treated as being independent of the method of the hole production. This is not possible in coincidence experiment. This means that it has no sense to calculate the cross section as the product of two modulus squares, one related to the ionization event and the other to the decay process. Generally photoelectron emission+Auger decay are treated as a two step process and the link between photoionization and Auger decay is made via the intermediate hole state only. Essential prerequisites for the two step model are: the intermediate state lifetime must be bigger than the relaxation time of the system (thus, the Auger decay begins from a completely relaxed state; no influence of the many body effects due to multiple excitations are observed), a well defined angular momentum JM and parity, no overlapping with neighbours states, neglect of DPI as well as final channel interactions, different energies for the two continuum electrons. The two step model leads to a convenient factorization of the observables into quantities belonging to the first and second step. If the strength of the Auger transition is considered, these factors are the partial cross section σ_{ph} for photoionization and the Auger yield; if the angular distribution of the Auger electron is considered, these factors are the so called alignment tensor of the photoionized state and the Auger decay parameter. Because the alignment tensor and the Auger decay parameter contain the occurring matrix elements in different combinations as compared to the photoionization cross section and the Auger yield, the angle dependence of photon induced Auger electron emission provides supplementary informations on photoionization and Auger decay [41].

Angular distributions

Examples of complete experiments using APECS have been performed on Xenon [42] and Argon [43]. The photoionization dynamical parameters (i.e. radial matrix elements and their phase shifts) have been extracted from the coincidence angular distributions and compared with numerical calculations. The angular distributions of the Auger (photoelectron) in coincidence with the photoelectron (Auger) at different fixed angles are different and they show different a degree of anisotropy.

In single emission spectroscopy on randomly oriented atoms, the angular distribution of the emitted electrons have axial symmetry with respect to the electric field vector, which is the only direction of preference in the initial system. In a coincidence experiment, the introduction of another quantization axis (the axis of detection of one of the two electrons) makes the angular distribution to rotate with respect to an axis which is neither the electric field or the detection axis. Thus the axial symmetry is broken, and the angular pattern shows a geometrically induced anisotropy, i.e. terms depending on azimuthal angle do not vanish. The axial symmetry is retained only if the detected electron is revealed along the polarization vector; thus the angular distribution follows the same behaviour as it has in single electron emission. Thus Auger-photoelectron coincidence spectroscopy allows an insight into the interplay between symmetry reduction and interparticle correlation. An example of the rotation of the coincidence angular distribution can be seen in figure 1.1, where the angular distribution of the $L_3M_{23}M_{23}$ (1S_0) Auger electron is detected in coincidence with the corresponding photoelectron emitted by absorption of linearly polarized light and detected at 0 degrees (i.e. along the light polarization), at 30 degrees, and at 60 degrees from the light polarization. Both electrons are detected in the plane perpendicular to the beam direction. The angular distribution related to the photoelectron detected at 0 degree is peaked along the light polarization, while the others are shifted by an angle which is not the new direction of detection of the photoelectron.



Figure 1.1: Experimental coincidence angular distributions and related fit curves of the Ar $L_3M_{23}M_{23}$ (1S_0) transition. The full circles curve corresponds to detection of the photoelectron along the light polarization, the lonzangenes curve to detection of the photoelectron at 30 degree from the polarization vector and the empt circles curve to detection of the photoelectron at 60 degree from the light polarization vector [43]

The photoelectron-Auger electron angular distribution for closed shell atoms can be found in [44, 45, 46] where standard techniques from angular correlation theory are applied within the two step model. A tensorial form of the cross section can be derived where the tensors which determine the angular distribution are connected to the charge cloud distribution of the intermediate ion. The inclusion of the spin observation for both ejected electrons in order to get the differential cross section for the energy-, angle- and spinresolved photo and Auger electron emission which fully describes the fragmentation pattern can be found in [42]. Here we briefly review the quantities which are relevant in the study of Auger photoelectron coincidence angular distributions. The angular correlation between the photoelectron and the Auger electron is given by (for linearly polarized light):

$$\frac{d^3\sigma}{d\Omega_1 d\Omega_2 d\epsilon_2} \bigg|^{2-step} \sim \left[1 + \sum_{k=2,4,\dots}^{k_{max}} \sqrt{\frac{4\pi}{2k+1}} \alpha_k \sum_{q=-k}^k \mathcal{A}_{kq}(\alpha J) Y_{kq}(\Omega_2) \right]$$
(1.1)

where α_k is the Auger parameter which contains the Auger matrix elements, and $\mathcal{A}_{kq}(\alpha J)$ is the alignment tensor, which describes how the populations in the magnetic sublevels of the intermediate state are distribuited. For single Auger emission (or when the photoelectron is detected along the light polarization vector) the axial symmetry with respect to the z axis is retained, only the component q = 0 is different from zero. Then the Auger electrons are emitted following the well known expression $P_2(\cos(\theta))$, where θ is the angle with respet to the z axis. In a coincidence experiment, due to the detection of the first electron, the axial symmetry is broken, and also the other components of the tensor contribute to the cross section. The way the magnetic sublevels are distributed in the intermediate state depends on the polarization of the impact beam. For linearly polarized light, this polarization is called alignment, which is characterized by equal population of the magnetic sublevels with opposite projection quantum number, i.e.:

$$a(JM_i) \neq \text{constant} \text{ and } a(J - M_i) = a(JM_i).$$

For circularly polarized light, one can also have a different kind of polarization, called orientation, which is characterized by populations which increase or decrease with M, i.e.

$$a(JM_i) \neq \text{costant} \text{ and } a(JM_i) \geq a(JM_i - 1) \text{ or } a(JM_i) \leq a(JM_i - 1)$$

A spatial vision of the isotropy, alignment and orientation condition is given in fig 1.3.1.

The alignment and the orientation of the system are due to the parity conservation in electromagnetic interaction. The parity operation is given by a reflection through a plane perpendicular to the symmetry axis and a rotation of π around an axis perpendicular to this plane. The parity conservation requires that a process and it specular image have the same probability. If the symmetry axis is a polar vector, defined for example by the electric field for linearly polarized light or the incidence direction of an electron beam, then the angular distribution of the emitted particles is symmetric with respect to this axis. Each polar vector remain inaltered for reflections through a plane which contains the vector while the precession of the angular momentum (which is an axial vector) keep its direction. Thus, with an initial isotropic state, the total system must remain invariant for such operations, since the interaction between two different symmetries (in this case SO(3) and SO(2)) gives as resultant the lower symmetry for the total system (SO(2)). Since



Figure 1.2: Schematic representation of isotropy, alignment [induced by linear polarization] and orientation [induced by circular polarization] [47]

states $|JM_j\rangle$ are transformed in $|J - M_j\rangle$ states, it follows from the parity conservation that states characterized by opposite M_j are necessarily equally populated and the system is aligned. If the symmetry axis is defined by an axial vector (as the incidence direction for circularly polarized light) states with opposite M_j are populated in a different way and in general both orientation and alignment can be created. The total angular momentum of an aligned state is null while an oriented system has a non zero total angular momentum.

Generally, the anisotropy of the angular correlation pattern is determined by the interplay between two sources of anisotropy: the alignment due to photon absorption and the alignment appearing as a result of a specific emission direction of one of the two electrons [48].

The angular correlation technique relies on density matrix and statistical tensors [49] theory, which allows a multichannel treatment of the decay, in which all the possible intermediate states and all the possible couplings between continuum channels and bound states are considered. The statistical tensor approach is very powerful since it gives a complete description of the process at least from the angular momentum correlation point of view, i.e. it allows to treat all the possible couplings between quantum numbers of intermediate or residual final ion with continuum electrons. It has been applied both to closed and open shell systems and different coupling scheme can be adopted depending on the relative strenght of spin orbit and Coulomb interaction. The Wigner-Eckart theorem leads to a factorization of the cross section in a dynamical and kinematical part, which is very convenient for analyzing the influence of the geometry of different experimental conditions. A more general form of the cross section (1.1) can be derived starting from the scalar product between the tensor which describes the properties of the light and the tensor describing the properties of the system under investigation. The general expression for the cross section for Auger-photoelectron coincidence emission is given by [50]:

$$\frac{d^2\sigma}{d\mathbf{k}_a d\mathbf{k}_p} = \sum_{k_1 k_2 k_q} 4\pi (\hat{k}_1 \hat{k}_2)^{-1} B(k_1, k_2, k) \left\{ Y_{k_1}(\mathbf{k}_p) \otimes Y_{k_2}(\mathbf{k}_a) \right\}_{kq} \rho_{kq}^{\gamma}(1, 1)$$
(1.2)

where $\hat{k} = \sqrt{2k+1}$, \mathbf{k}_p , \mathbf{k}_a are unit vectors determining the escaping direction of the outgoing electrons, $\rho_{kq}^{\gamma}(1,1)$ is a dipole photon statistical tensor carrying a total momentum

 $j_{\gamma} = 1$, and $B(k_1, k_2, k)$ are coefficients which contain all the informations concerning the double photoionization dynamics. When also interference effects like post collision interaction (PCI) are considered, then a correlation factors which modifies the angle dependent cross section (1.2) must be included [51]. For the radial matrix elements very detailed calculations are possible today. Many works [52] implemented the multiconfiguration Dirac-Fock (MCDF) model with or without QED corrections to calculate radial functions. Coincidence calculations performed within MCDF approach show rather good agreement with experimental data, both in reproducing the energy distribution and the angular correlation patterns, even if sometimes a satisfying agreement in terms of the anisotropy is missing and would require the inclusion of several higher electronic configurations. Several computers code are now available to deal with such approach. Among them, GRASP92 and the related suite of programs RATIP [53] have been used in the interpretation of many experiments performed by different groups all over the world.

Energy distributions

When the two electrons have nearly the same energies, they becomes indistinguishable. Then the process must be described as a resonance embedded in the double-ionization continuum [54, 55] (one-step model). It has been predicted [56] that depending on the spin of the electron pair and on the direction of each electron with respect to the polarization axis of the incident photon, the interference is constructive or destructive. Experimental confirmations have been reported for double photoionization of Neon [57] and inner-shell double photoionization of Xenon [58]. The symmetry property of the electron-pair wavefunction manifests itself in the interference affecting the angular correlation between coincident photoelectrons and Auger electrons of equal energies. Moreover, angle and energy distributions can be seriously distorted by Coulomb interaction in the final state (post collision interaction (PCI)) [59], given by spatial interference effects may lead to rather complicated energy and angle dependent pattern of the cross section, as predicted theoretically by Sheinerman and Schmidt [60, 61] (see [62] for the one step model).

An example of the distortion given to the cross section by PCI effects can be observed in figure 1.3. The figure shows the experimental data and theoretical curves (in which PCI effects have been included) of the Auger coincidence angular distribution coming from Xe $N_5O_{2,3}O_{2,3}$. The correlation factor which takes into account for the PCI effect collapses to zero for small relative angles between the photoelectron and the Auger electron. Within a time picture one might think then of the Auger deacy as a continuum emission and reabsorption process, the emission of the Auger electron in the final state being inhibited if it is ejected in the direction of the photoelectron [51].

Dichroism in two electrons emission

Dichroism in two electrons emission has been treated mostly in direct double photoionization, even if circular dichroism has been also studied for APECS in a paper [63]. For single photoionization of an atom the polarization of the incident light enters only kinematically



Figure 1.3: Experimental data and theoretical curves for Xe $N_5O_{2,3}O_{2,3}$ coincidence distribution. The dotted line is the cross section without PCI effects [51]

into the spin-unpolarized differential cross section, while it enters dynamically in two electrons emission cross section. The dicroism signal persists even if the magnetic substates of the photoion and/or the spin of the electrons are not resolved [64] in contrast to the case of single photoionization. In DPI it has been shown that the circular dichroism vanishes when the two electrons are emitted with the same energy, or when they are emitted parallel or antiparallel to each other, i.e. when the two electrons are indistinguishable, since no chirality can be associated to the three vectors (light polarization, two electrons directions) and also in other conditions in which the electronic correlations within the two electrons state are particularly stronger [64].

In the case of circular dicroism in auger-photoelectron emission, it has been shown [63] that in the two step model dichroism doesn't disappear even if the two electrons have the same energy since they are distinguishable particles. Moreover, it was shown that the circular dichroism in Auger-photoelectron measurements is more symmetric with respect to the one in DPI since a determined intermediate state put some restrictions on the alignment tensor which describe the anisotropy. The authors also found that the circular dichroism is equivalent to spin polarization measurements. The chirality related to the electrons pair is a direct manifestation of the electronic correlations [65].

Coincidence specroscopy on polarized atoms

Coincidence spectroscopy on polarized atoms could allow to obtain even more informations. Theoretical calculations have shown promising perspectives in using this method similarly to the well known autoionization studies with crossed laser and synchrotron radiation beams. Excitation of the laser-excited atoms is advantageous in investigating the autoionizing states which are not coupled optically with the ground state. On the other hand, strong dependence of the angular distribution of the ejected electrons on the polarization of the laser-excited intermediate state, allows one to obtain more detailed informations on excitation of autoionizing states from anisotropic targets [66].

Dichroism in direct double emission from polarized atoms has been analyzed also [67]. The authors showed that the circular dichroism carries information on the properties of the phase of the bound two particle wavefunction and can be an indicator for a broken time reversal symmetry. This finding is of special importance for the investigation of systems

with spontaneous time reversal symmetry breaking, such as p- and d- wave superconductors. The superconductor ground state is non-invariant for a change of sign of the phase of the wavefunction of the two electrons [68].

About Auger-photoelectron coincidence spectroscopy, recently the case of linear dichroism from polarized atoms has been considered [69]. Analyzing simple particular geometries the authors show that such measurements, in principle, can provide a complete information about the density matrix of the polarized electrons in the target. Full-numerical *ab initio* calculations for the particular case of photoionization of laser oriented or/and aligned Sn atoms and the following Auger decay has shown that the dichroic effects are significantly dependent on the chosen geometry of experiment. The value of the dichroism as well as the complexity of the dichroic pattern strongly variate in different experimental conditions. The authors suggest that the APECS measurements on magnetized targets will provide important information about site-specific local magnetic properties of surfaces and solids.

1.3.2 Coincidence spectroscopy in solid state physics

Advantages of APECS with respect to one-arm measurements

The first APECS experiment in the solid state [8] have been performed on Cu $L_{23}M_{45}M_{45}$ transition and demonstrated that it is possible to separate some features which are generally overlapped in the conventional AES spectra. The authors also observed the elimination of the lineshape broadening due to finite lifetime of the intermediate hole. This effect is predicted by theoreticians [70] and it is very important since the short lifetime of core holes in the solid state can lead to a broadening of several eV, obscuring interesting features due to chemical shift, many body effects [71, 72]. This effect is due to energy conservation:

$$E_0^N - E^{N-2} + \omega = \epsilon_1 + \epsilon_2 \tag{1.3}$$

where ω is the photon energy, ϵ_1 and ϵ_2 are the energy of the photoelectron and the Auger electron respectively, E_0^N is the energy of the N particle initial state and E^{N-2} is the energy of one of the possible final state with N-2 particles. Assuming that the state E^{N-2} does not provide any broadening due to the decay to other possible states, then the left part of (1.3) is a well defined with energy value with small indetermination. For the right side ϵ_1 is considered as to be measured with infinite precision and thus terms depending on the lifetime of the N-1 electron states do not influence on the measurements of ϵ_2 . One can do the same with exchanging ϵ_1 and ϵ_2 : the limit of the precision of the energies is given by the experimental resolution. The sum of the energies is fixed, even if in the two step model the two energies are determined independently within the uncertainty of the intermediate state energy. This effect has been observed by Jensen et al [73] on the Cu MVV transition. For certain Auger electron energies the spectral lines of the coincidence photoemission spectra have major resolution, and thus show less broadening than the peaks of the usual single spectra. The uncertainty of the sum of the two energies is determined only by the uncertainty of the photon energy and of the energy of the final two holes state; the broadening due to the intermediate states do not contribute.

Jensen et al [73], also observed that the energies of the two electrons are correlated in a way to conserve the sum of the energies. They observed a shift of the peaks in the coincidence photoemission spectra within the natural width when changing little the Auger energy. Thurgate and Jiang [74] have measured a shift of the photoelectron line Cu L_3 towards low kinetic energy when measured in coincidence with the ${}^{3}F L_{3}VV$ Auger line and towards higher kinetic energy when in coincidence with the ${}^{1}G$ term, but the centroid is unshifted. The centroid remains at the same energy, even when the Auger electron analyser is set 1.0 eV above or below the ${}^{1}G$ line. The explanation for a reduced kinetic energy of the outgoing photoelectron for the ${}^{3}F$ state compared to the photoelectron associated with the ${}^{1}G$ state was that the effective hole-hole interaction energy for the ${}^{3}F$ state is lower than that for ${}^{1}G$ state. Then the band-like contribution is larger for the ${}^{3}F$ state than for the ${}^{1}G$ state. The ionic core hole is less screened by the ${}^{3}F$ bandlike extended wavefunction, while the ${}^{1}G$ wavefunction is more tightly bound to the ion core, allowing the ion's charge to be screened better by valence-band electrons. They decomposed the L_3 XPS spectral line of Cu metal into two Gaussian lineshapes, separated by 0.5 eV, i.e. the separation energy they observed by APECS. They proposed the presence of both well screened and poorly screened core-hole states upon the L_3 core electron ionization in Cu metal. The generally used two step model is not longer valid if, when the hole is created, there is a finite probability that the ion is formed in an excited state. This happens for example when the energy of the photon is near the ionization threshold. If the lifetime of the hole state is short and there is superposition between the screening process and the hole decay, the excitations created in the emission of the first electron can transfer their energy to the Auger electron. Such additional peaks are called shake down peaks and are a typical example of the inedequacy of the two step model description.

The discrimination provided by APECS spectroscopy allows to reduce the background of the secondary electrons, since the electron pairs come from the same ionization event and must not be inelastically scattered by the potentials of the surrounding atoms. This effect can be clearly seen comparing the coincidence Auger spectra with usual single Auger spectra. The effects of the elastic and inelatic scattering on the lineshape have been studied by Werner et al [75]. Several types of inelastic collisions can obscure the Auger or photoelectron lineshape. In [75] a simplified description of the effects of multiple scattering in APECS has been presented that allows to model the surface sensitivity of the technique. Within the limits imposed by the inherent depth resolution of n-fold scattered signal electrons [76], the depth sampled in APECS can be selected by measuring the Auger electron spectrum in coincidence with energy loss features in the photoelectron peak. An effective procedure to decompose the spectrum into contributions due to bulk and surface excitations is presented and successfully tested. The total energy-loss background encountered in conventional spectroscopy is due to contributions from electrons coming from atoms at various distances from the surface. If, however, one of the coincidence energies is set at the zero energy-loss peak, only atoms close to the surface are selected and the loss contributions in the coincidence spectrum are suppressed [77]. By APECS one is able to resolve the Auger peaks originating from the main photoelectron lines from those originating from the satellites [78]. The unique capability of such technique to increase the surface sensitivity and to separate overlapping features make this spectroscopy a promising tool to study surfaces,

nanostructured materials and adsorbates.

Recent results from angular and energy coincidence distributions

Recent APECS experiments [10] show that the angular distributions of the coincidence Auger electrons are different when the photoelectron is observed at different fixed angles. This can be clearly seen in fig. 1.4 where the angular distribution of the Auger electrons coming from Ge(100) $L_3M_{4,5}M_{4,5}$ is measured in coincidence with five different detection angles of the photoelectron.



Figure 1.4: Angular distribution of Auger electrons $L_3M_{45}M_{45}$ from Ge(100) in coincidence with photoelectrons detected at different directions [10]

Such changes, which in the atomic theory are ascribed to a different degree of the alignment of the intermediate ion state, could suggest that the effects of the polarization of the intermediate state are visible also in the solid state. In particular, the authors interpreted these changes in the angular distributions as due to the angle resolution of the experiment, which allows to discriminate the degree of alignment induced in the intermediate state by revealing the first electron at certain angles. The alignent is given by an imbalance between the population in the magnetic sublevels in the intermediate state, which, in a simple closed shell model, is given only by the quantum numbers of the core hole. At different detection

angles, the sublevels m_l contributions related to the inner core hole are weighted in a different way. For specific geometries the intensities from orbitals with different symmetries (i.e. spatial orientations) can be different, especially in the case of decreased symmetry at the surface [79]. Here, the sublevels of the inner core are further related, through the selection rules of the process, to the magnetic sublevels of the two holes final state. Thus, detecting the first electron at different angles, i.e. weighting the contributions of the inner core m_l sublevels in a different way, it means that one observes the angular distribution related only to specific sublevels of the second electrons (see fig. 1.4)

The effects of multiple scattering on the angular distributions of coincidence Auger electron seem not to destroy the influence of a different degree of alignment due to a particular direction of the first electron, even if it must be noted that large error bars are present and only a qualitative discussion can be given.

Also the coincidence Auger lineshape changes varying the detection angles of the two electrons [80]. This means that the symmetry properties (both orbital and spin symmetries) of the two electrons wave function influence the energy distributions also in the solid state. This can be observed in figure 1.5 where the Auger coincidence spectrum related to $M_5N_{4,5}N_{4,5}$ from a $(\sqrt{3}x\sqrt{3})R30^\circ$ -Sn/Ge(111) surface have been reported for different detection angles of the photoelectron. The right part of the spectrum, which is composed by triplet states, seems to be suppressed when the photoelectron is detected along the light polarization, while in other kinematic conditions it does not happen.

Since the multiplet terms which give the peaks in the Auger spectrum are given by combinations of the magnetic sublevels of the two final holes, different geometries allow to weight in a different way the multiplet terms, and thus the coincidence Auger spectrum changes depending on the detection angles of the photoelectron. The fact that for different kinematic conditions the intensities from orbitals with different spatial orientations can be different determines the spin coupling of the two final holes. The authors concluded that the coincidence spectroscopy in angle-resolved mode allows one to study the influence of the angular components of the source wave function which describe contributions from different magnetic sublevels. In particular, since the angular components of the continuum wave function are related to the population in the outer levels which are involved in the Auger transitions, APECS can be a powerful tool to study the imbalance between m_l sublevels and the spin polarization in valence bands, which is essential to understand microscopic properties of strongly correlated materials.

A very recent APECS experiment performed on CoO on both paramagnetic and antiferromagnetic phase reveals different behaviour of the coincidence Auger lineshape in the two phases. This is in contrast to what observed by various authors in the past in XPS spectra, from CoO and other transition metal oxides, which was identical below and above the transition temperature. These results are in contrast to a simple itinerant band model which predicts a clear difference in the total DOS above and below the transition temperatures due to the exchange splitting [81]. A simple model was suggested by many authors where a local moment is formed on each atom, which persist but it is disordered above the critical temperature [82, 83, 84, 85]. The difference in the total DOS should be of the order





Figure 1.5: Auger coincidence spectrum related to $M_5N_{4,5}N_{4,5}$ from a $(\sqrt{3}x\sqrt{3})R30^\circ$ -Sn/Ge(111) surface for different detection angles of the photoelectron. The weight given to triplet states is suppressed in particular geometries. For further details see [80]

of kT_c rather than the exchange splitting, hence no change of the total DOS should be expected. However, non angle resolved data and non spin polarized results must be considered with caution, since they are not sensitive to the spin order. For example, in [86] no LEED superstructure was observed when the CoO sample went from the paramagnetic to antiferromagnetic state. Angle resolved photoemission experiments on Ni [87] showed some changes in the spectra above and below the Curie temperature. But this experiment also confirmed a non vanishing exchange splitting above the transition temperature, which is in contrast to the long range order models which predict that the exchange splitting disappears above the Curie temperature. Also spin resolved experiments confirmed the short range magnetic order persists which allows the definition of "local bands" which are exchange split with respect to the local direction of magnetization. The same happens for antiferromagnetic compounds, as several experiments have demonstrated.

Thus a persisting short range magnetic order seems to exist above the critical temperature, both for ferromagnetic and antiferromagnetic compounds. The sensitivity that angle resolved APECS has on the contributions of the magnetic sublevels of the two holes (in this case in the d level) can be used to study the possible imbalance in the population of magnetic sublevels which give an orbital contribution to the total moment. For CoO such studies could clarify the nature of the insulating gap. CoO is not well described by one electron theory such as LDA-DFT. The ground state for CoO and FeO is predicted to be metallic. It has been argued that one of the problems in such calculations is an underestimation of the orbital moment [91]. Ideed an orbital polarization induced by exchange interaction in the t_{2g} band, i.e. a preferential occupation of $m_l = 1$ states over $m_l = -1$ states in the t_{2q} manifold, could lead to an insulating gap in CoO [92, 93, 94]. Indeed the measured magnetic moment in CoO ($3.4\mu_B$ [95]) is larger than can be predicted by spin alone. In [93] the authors concluded that LSDA is not adequate for treating the symmetry breaking in the charge distribution and that one must go beyond LSDA formalism in order to deal with an unquenced orbital momentum properly. However, a self interaction corrected LSDA approximation, which removes the unphysical interaction of the electron with itself present in LSDA, predicts the insulating state of transition metal oxides correctly and the substantial role of the orbital moment in CoO and FeO, for which reason the authors included the spin orbit coupling in the calculation [96, 97]. But yet this theory does not reproduce the observed photoemission results [98]. Improvement of the quasiparticle energies in NiO [99] has been achieved using the GW approximation [100, 101], but the satellite structure is not reproduced. This shortcoming is ascribed to the fact that the GW takes into account of bubble type diagrams but not of ladder ones, which give rise to satellite intensities. The nature of the insulating gap in CoO and the contribution of the orbital moment are still controversial and major efforts are needed to fully understand the properties of the late pure transition metals and their compounds. Some new results about CoO from Auger-photoelectron coincidence spectroscopy will be published in the near future.

The encouraging results from APECS make this spectroscopy a promising tool to study the microscopic origin of several interesting effects which appear in the solid state. The presented results all rely on the angular resolution of the experiments, which, as suggested by the authors, allows to discriminate the different contribution from levels with different orbital symmetry. The idea is that detecting also the photoelectron, then one is sensitive also to the orientation of the local moment and not only to its magnitude. Then combining experimental data on and off resonance one should be able to map the magnetic state of single atomic sites.

The present status of the coincidence spectroscopy is still far from being completely understood. The excitation of atoms involves non isotropic excited states with several magnetic substates. A standard differential or total cross section experiment averages over the magnetic substates, and thus does not determine the shape and inherent momentum of the exited atom. Avoiding such averaging procedures, one has access to detailed informations which were not available before. In favourable cases a complete set of excitation amplitudes for the excited atomic states, including their relative phases, can be derived. The essential ingredient necessary for such studies is coincidence electronic for simultaneous detection of the decay products, which carries the information on the magnetic substates population amplitudes [102]. The angular dependence of the intensity of photoelectrons and Auger electrons may be a source of valuable information on the atomic and magnetic structure of solids.

1.3.3 Inherent angular anisotropy and multiple scattering effects in electron emission

It is important to consider not only the process which gives rise to the electron emission at the atomic site (photoionization or Auger decay) but also the effects of the crystal potential on the propagation of the two electrons. The anisotropy of diffraction patterns is determined by: an intrinsic anisotropy due to non spherical emission at the emitting atom, the different interaction (for different orbital momenta) with the atomic potentials and the interference with the direct wave and the elastically scattered waves. At high energies, the differential cross elastic scattering cross sections are dominated by forward scattering amplitudes. The character of the source wave, i.e. the wave of the excited electron prior to crystal diffraction, is of minor importance in this regime [103]. At low kinetic energy the multiple scattering effects are dominant and for this reason, many past works assumed a spherically symmetric initial emission also in this regime [104, 105, 106, 107], neglecting the possibility of inherent angular dependence. The amplitude of the emitted waves of different magnetic quantum numbers m corresponding to a particular l was taken to be equal. For Auger diffraction, this was consistent with the usual assumption that the final ejected electron has lost any memory of the initial excitation, and thus has an overall initial isotropic angular distribution [108]. These works show rather poor agreement with the experimental data [104, 105, 106, 107]. Detailed studies show that the effects of diffraction over different angular momentum components of the initial wave function, both for Auger and photoelectrons, are different. Calculations of multiple scattering [109] show the sensibility of the diffraction process to the orbital character of the impinging initial wave: for Cu $M_{23}VV \ l=0$ and l=1 resulted to have a maximum at normal emission, the intensities for l = 2, 4 show a minimum along this direction. The strong dependence of the AED patterns on the value of l requires to take into account Auger transition matrix elements because they determine amplitudes of different Auger electron waves contributing to the total emission intensity. In the case of one dominating angular momentum in the Auger electron emission then the value of the matrix element for the corresponding transition will have only a weak effect on the angular distribution. However, in the case of interference of different Auger electron waves (if they have amplitudes of the same order of magnitudes) an interpretation of the measured AED pattern cannot be possible without involving of Auger transition matrix elements.

Other theorethical results show a breakdown of the assumed spherical symmetry of the initial Auger wave due to an irregular occupation of the m sublevels for a given angular momentum l [111, 113, 110, 114]. It has been found [105] for Ni(100), that along direction (001) and (011) the m = 0 component of an f wave at 62 eV reproduces well the experimental pattern near the normal to the surface while it does not reproduce the data far away. Along the azimuth between the two directions, the m = 0 component of the p wave reproduce well the behaviour far from the normal and not near the grazing direction. The l-dependence of the angular distributions is due to a different interaction of the partial waves with the potential and to a strong anisotropy of the individual magnetic sublevel waves. The potential is given by an attractive Coulomb potential and a repulsive centrifugal barrier, whose heigh is related to the orbital momentum of the incoming electron. For high l the potential barrier is not negligible and thus electrons which pass by the outer region are rejected by the barrier. This effect is negligible if the kinetic energy of the electrons is sufficiently high. Moreover, important scattering atoms in the electron near field can be either illuminated by or are near a node of the sublevel waves, and contribute accordingly to the total wave interference. The angular momentum character of the photoelectron and Auger electron depends on the particular transition involved: parity as well as total angular momentum have to be conserved. Selection rules cause the source wave to be anisotropic for photoelectrons as well as for Auger electrons which do not form a pure s wave and whose initial ion (before the Auger recombination) is not spherically symmetric, i.e. does not have a total angular momentum of J = 1/2 [21]. Emission from particular sublevels can be due to an initial non statistical population of the sublevels (like in magnetic materials) or to a sublevel selection by the exciting probe [111]. The spherical symmetry of the wave of the outgoing electron is broken, and this is due to an irregular occupation of the magnetic sublevels. Moreover even if the intensity is obtained by summing over all the projections, the angle-resolved technique could enhance contributions from particular sublevels. At different angles, the waves of the outgoing electron which give the total intensity give a different contribution, weighting in a different way the contributions from the magnetic sublevels of the core hole.

Thus at low kinetic energy it is necessary to take into account both the multiple scattering and the fact that the wavelength of the electrons is of the same order of the atomic dimension, then the features of the source wave function [112] become important.

A realistic description of the intrinsic anisotropy of the source and the incorporation of multiple scattering effects are both essential features of a model for the description of Auger emission [106].

About coincidence spectroscopy, a treatment of the propagation of the two electrons is still lacking. Because of the growing interest in this spectroscopic technique and of the encouragin results obtained by APECS experiments, there is the need to study in more detail the effects of diffraction on the possible waves of the emitted electrons, and to develop a multiple scattering theory of the two correlated electrons, i.e. to consider the two electrons angular correlations in the solid state. It is essential to perform such studies since the multiple scattering effects could complicate or obscure the atomic features of the two electrons emission, but maybe more detailed structural informations can be gained with respect to one electron conventional experiments.

In order to deal with the propagation of the two electrons keeping their initial correlation at the atomic site, the density matrix and statistical tensor approach [49] is not suited. Such approach is based on a many body theory, which takes into account all the possible angular momenta of the open shell system under investigation. Summations over several indexes are present. These summations should be added to those given by the multiple scattering formulation, making this approach not very suitable for fast computer calculations. Moreover, the density matrix approach is not very intuitive, since it makes loose contact with wavefunctions, which have an important role in the multiple scattering theory, since they contain the modifications due to non spherical environment of the absorber. Multiple scattering theory relies on a single particle approach, which is a semplification and allows to make the number of summations a value which can be acceptable for reliable calculations.

Chapter 2

Fundamentals of Multiple Scattering Theory

2.1 Introduction

The multiple scattering (MS) theory deals with the excitation of an electron in an extended system. It allows to express the cross section in terms of the states which are probed by the excited electron, which are not eigenstates of the angular momentum due to spherical symmetry breaking. MS theory is used extensively to calculate the electronic structure of materials [115, 116], the optical and x-ray response of solids. Within the single particle approach, these properties can be calculated in terms of the Green's function $G = 1/(E - H + i\Gamma)$ where H is the Hamiltonian and Γ accounts for inelastic losses and lifetime effects. There is a direct connection between G and electronic structure. For example, the angular momentum projected density of electron states at a given site is given by the imaginary part of the Green's function [117].

There are many approaches to the MS problem. In ground state electronic structure calculations, the problem is reduced to an exact diagonalization based upon some assumed wave function basis set. In x-ray Absorption Fine Structure (XAFS), however, at energies high above the absorption edge, the description of the excited electron requires either many plane waves or many orbital angular momentum components. This dramatically increases the size of the matrices that need to be diagonalized, for which the computational time scales as the cube of the matrix size. An alternative approach to the MS problem consists of a perturbative expansion in the strength of the scattering potential, which is expressed in terms of the hypothetical paths that the electron follows as it scatters and propagates from atom to atom. This is the basis for the standard XAFS and photoelectron diffraction (PHD) formalism used for structural analysis and is called the path formalism.

MS theory describes altogether the elastic channel, that provides the structural informations, and the inelastic ones, that modify the elastic channel and give informations on the electronic correlations [118]. It provides a unified and accurate scheme for the calculation of unoccupied electronic states which are probed by various synchrotron spectroscopies such as x-ray absorption, resonant elastic and inelastic x-ray scattering.

The MS theory relies on the single-particle picture, thus it neglects electron correlation

effects. In an effective one-electron theory the excited electron, as it traverses the solid, behaves as a quasiparticle that moves in an effective complex-valued optical potential. Such a lossy potential is needed to calculate the phase shifts, the scattering, and also the damping of the electron. Dyson's self-energies are calculated using the local density approximation. Correlation effects can be taken into account in an average way in the framework of the local density scheme through the introduction of an exchange-correlation potential [119].

2.2 Use of MS theory in several spectroscopies

MS theory has been widely used to interpret the modulations of X-ray absorption spectra, the photo- and Auger electron diffraction patterns in a variety of systems.

• The basic physical process for the explanation of the fine structure in the absorption cross section and of the anisotropy in the PHD angular patterns is the elastic scattering. Core-level absorption gives origin to an l - defined outgoing electron wave. The interference effect among the direct wave and the elastically scattered waves depends essentially on the difference in path lengths, so that the diffraction pattern is strictly bound to the geometry of the system. The amplitude of all the reflected waves at the absorbing atom add either constructively or destructively to the outgoing wave and hence modulate the matrix element between the initial and final states that controls the strength of the transition. This interference pattern changes with the energy of the photoelectron, thus the matrix element, and consequently the absorption, exhibits similar oscillations. What is observed in XAFS is essentially the projected density of the final states onto the absorbing site for the final angular component selected by the dipole selection rules, via a generalized optical theorem for wave function amplitudes. In the EXAFS regime, far from the absorption edge, the dominant single scattering term, due to paths from the absorbing atom to near neighbours and back, is used to determine near neighbours distances. In this region the MS expansion can be assumed to be convergent. In contrast, the region closer to an edge (NEXAFS) is often dominated by strong scattering processes and the path approach cannot be used. In this case all contributions from the different paths must be considered and the series cannot be truncated at a certain term.

The excited photoelectron state decays as a function of time and distance because of inelastic losses by interacting with and exciting other electrons in the solid, or by creating collective excitations. In addition, the intrinsic lifetime of the core-hole state must be considered. The original outgoing wave of the excited photoelectron dies away as it moves further away from the absorbing atom. Ultimately it becomes too weak to significantly reflect any waves off of distant atoms. The returning reflected waves also suffer this same type of extinction. Thus XAFS can only measure the local atomic structure over a range limited by the net lifetime (or effective mean free path) of the excited photoelectron. The absorption cross section, apart from a background, in general slowly varying in energy in the region of interest, due to inelastic scatterings, can be identified with the photoemission cross section integrated over angles and summed over final spin and over initial degeneracies of the completely filled core level. • Angular resolved photoemission studies are very useful to determine the surface structure, especially when the energy of the emitted electron lies in the 20-200 eV range, ensuring a short enough wavelength for good resolving power and a short mean free path for surface sensitivity. MS theory provides the square modulus of the wave function amplitude on the photoabsorber as a function of energy and direction of the outgoing photoelectron, giving a sort of holographic reconstruction of the short range geometrical environment of the absorbing atom. Thus photoemission provides a fine structure in a three dimensional space (energy and emission angles of the escaping photoelectron). The cross section for emission of a photoelectron along \mathbf{k}_e is the result of an interference process in which all composite amplitudes of all possible events describing the propagation of the photoelectron interfere to create the final total amplitude whose modulus square is proportional to the intensity of the photocurrent along \mathbf{k}_{e} . Holographic inversion methods can be applied to photoelectron diffraction data to directly yield atomic structures in three dimensions [120, 121, 122, 123, 124]. Auger electron diffraction and x-ray photoelectron diffraction give straightforward identification of the crystalline order of the first atomic layers. Since all elements have a unique photoelectron spectum, it is almost always possible to find a kinetic energy specific for each element of the system under consideration, and to localize the origin of the signal in different sites of the crystal. XAFS, PED, AED probe the short-range order and this makes these methods complementary to LEED and x-ray diffraction, which are sensitive to the long range order.

2.3 Approaches to the MS problem

MS calculations in the path approach are truncated at a certain order, which depends essentially on the energy of the excited electron. One might expect that a path formalism would always be inferior relative to the diagonalization approaches in (low-energy) regimes where the usual basis sets converge well. In that case diagonalization is virtually exact and hence is equivalent to summing the path formalism to infinite order, while a direct calculation using the path formalism must necessarily be truncated at some finite order. Final state lifetime effects allow to truncate the MS expansion such that only path lengths less than a few mean free paths are retained. The size of the cluster needed is determined by the effective mean free paths. Once clusters are bigger than a few mean free paths, the broadened results of cluster calculations converge to a fixed answer, independent of size, and hence only a finite size-cluster is required. An exact cluster approach is equivalent to carrying the path formalism to infinite order under the restriction that the paths only involve atoms in the cluster (instead of all the atoms in the infinite solid). This difference is usually of little concern, provided the MS expansion converges, since any additional fine details of a cluster calculation would be washed out by lifetime effects. It is possible that the MS expansion will fail to converge, then lifetime effects will still smear out sharp features of the spectrum, but some differences between the two approaches may remain. The path formalism is thus complementary to exact or cluster approach in that convergence of the MS expansion is implicitly assumed. When carried to all orders, this theory is equivalent to exact treatments based on wave functions and Hamiltonian diagonalizations [125].

The formal MS theory [126] of XAFS has been derived based on both the Green's function method [127, 128] and the wave-function approach [129]. The two approaches are equivalent [129]. The Green's-function formulation is particularly advantageous for XAFS, since it can naturally incorporate inelastic losses and other quasiparticle effects and avoids the necessity of explicit calculations of wave functions. The cross section is given by the imaginary part of the Green's function, which is the density matrix. Then the absorption from a given final state 1 is proportional to the projected density of final states (in the presence of an appropriately screened core hole).

The path approach works well in the high energy region, where MS corrections are weaker and where a simplifying plane wave approximation (PWA) becomes quite accurate. At large distances from the center of a wave, the curvature of a spherical wave front lessens, and it becomes more plane-wave-like, which is a great simplification. However, it was shown [130, 131] that curved-wave corrections are actually important at all energies both in backscattering and MS terms. In the next sections we will review the MS theory in the curved waves approach and we will focus our attention particularly on photoelectron diffraction.

2.4 General expression of the cross section

The Hamiltonian of the full system is given by:

$$H = H_{mat} + H_{rad} + H_{int} = H_0 + H_{int}$$
(2.1)

where H_{mat} and H_{rad} are the hamiltonian of the system and the hamiltonian of the radiation field respectively, and H_{int} is the potential describing the interaction. The eigenstates of the unperturbed hamiltonian H_0 are then simply $|\Phi\rangle = |\varphi\rangle |\phi\rangle$, i.e. the direct product between the matter states and the radiation states.

If H_{int} is sufficiently small, we can treat it as a perturbation of the system described by H_0 . In this case, standard perturbation theory tells us that we can approximate the eigenstates $|\psi\rangle$ of the total hamiltonian H in terms of the eigensolutions $|\Phi\rangle$ of the unperturbed hamiltonian $H_0 = H_{mat} + H_{rad}$. These eigensolutions can be written as

$$H_0 | \Phi_i \rangle = E_i | \Phi_i \rangle \text{ with } E_i = \epsilon_i + \xi_i$$

$$H_0 | \Phi_f \rangle = E_f | \Phi_f \rangle \text{ with } E_f = \epsilon_f + \xi_f$$

where ϵ, ξ are the eigenvalues associated to $|\varphi\rangle$ and $|\phi\rangle$ respectively. We are interested here in transitions from an initial state $|\Phi_i\rangle$ of H_0 to a final state $|\Phi_f\rangle$ of the same hamiltonian that can result from the action of the interaction term H_{int} . From time dependent perturbation theory, we know that the transition probability per unit time from state $\Phi_i \rangle$ to state $|\Phi_f\rangle$ under the effect of the perturbation H_{int} is given by:

$$W_{if} = \frac{2\pi}{\hbar} \sum_{f} |\langle \Phi_f | T_I | \Phi_i \rangle |^2 \delta(E_i - E_f)$$
(2.2)

where T_I is the transition operator associated to to the interaction potential $V_I = H_{int}$. Transition operators are introduced in scattering theory as a convenient way to describe the effect of a given perturbation on the eigenstates of the unperturbed system. Following their usual definition, T_I can be expressed by the relation:

$$T_I = V_I + V_I G(E_i) V_I \tag{2.3}$$

where $G(E_i)$ is the resolvent of the total hamiltonian H at the energy of the initial state (or of the final state as the energy E of the total system is conserved). This resolvent is defined by

$$G(E_i) = \lim_{\epsilon \to 0^+} \frac{1}{E_i - H \pm i\epsilon}$$
(2.4)

An infinitesimal imaginary part is introduced in order to impose apporpriate boundary conditions when required. The action of $G(E_i)$ on any eigenstates $|\Psi_n\rangle$ of H gives

$$G(E_i)|\Psi_n\rangle = \frac{|\Psi_n\rangle}{E_i - E_n} \tag{2.5}$$

There are two fundamental equations in quantum scattering theory. One is the Dyson equation which allows the calculation of $G(E_i)$ from the knowledge of $G_0(E_i)$ and V. The second expands $|\Psi_n\rangle$ in terms of known solutions which are the asymptotical states of the hamiltonian. this is referred as Lippmann-Schwinger equation. The Green's function $G(E_i)$ is related to its free counterpart $G_0(E_i)$ by the Dyson equation:

$$G(E_i) = G_0(E_i) + G_0(E_i)VG(E_i)$$
(2.6)

At the lowest order in V_I , the transition operator (2.3) can be approximated by the pertubration V_I . When inserted in (2.2), this gives the Fermi's Golden rule. To second order in V_I , it can be replaced by

$$T_I \approx V_I + V_I G_0(E_i) V_I \tag{2.7}$$

where $G_0(E_i)$ is the unperturbed resolvent and is obtained from (2.4) by replacing H by H_0 . The cross section is then obtained from (2.2) by dividing by the flux I_0 of incoming particles.

2.5 Cross section for incoming photons

The hamiltonian of the whole system is given by:

$$H_{tot} = H_{mat} + H_{rad} + H_{int} = \sum_{i}^{N} \frac{1}{2m} (\mathbf{p}_{i} - \frac{e}{c} \mathbf{A}(\mathbf{r}_{i}))^{2} + \sum_{i} V_{ext}(\mathbf{r}_{i}) + \sum_{i < j} V(\mathbf{r}_{i} - \mathbf{r}_{j}) \quad (2.8)$$

where

$$H_{rad} = \sum_{q\epsilon_q} \hbar \omega (a_{q\epsilon_q}^+ a_{q\epsilon_q} + \frac{1}{2})$$
(2.9)

$$H_{int} = V_I = -\frac{e}{mc} \sum_i \mathbf{p}_i \cdot \mathbf{A}(\mathbf{r}_i) + \sum_i \frac{e^2}{2mc^2} \mathbf{A}^2(\mathbf{r}_i)$$
(2.10)

where \mathbf{p} is the electron momentum and \mathbf{A} is the vector potential of the electromagnetic field which is given by:

$$\mathbf{A}(\mathbf{r}_i) = \sqrt{\frac{2\pi\hbar c^2}{V\omega_q}} \sum_{\mathbf{q},\boldsymbol{\epsilon}_q} (a_q \boldsymbol{\epsilon}_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}_i} + a_q^+ \boldsymbol{\epsilon}_{\mathbf{q}}^* e^{-i\mathbf{q}\cdot\mathbf{r}_i})$$
(2.11)

The fields, or more precisely $|e|\mathbf{A}/c$, is treated as a perturbation so the term corresponding to A^2 in (2.10) can generally be dropped for weak fields. Thus in our case $V_I = -\frac{e}{mc}\sum_i \mathbf{p}_i \cdot \mathbf{A}(\mathbf{r}_i)$. The transition probability for unit time is given by:

$$W_{if} = \frac{2\pi}{\hbar} \sum_{f} |\langle \Phi_{f} | T_{I} | \Phi_{i} \rangle |^{2} \delta(\hbar\omega_{q} + E_{i} - E_{f}) = \frac{2\pi}{\hbar} |\langle \Phi_{f} | T_{I} | \Phi_{i} \rangle |^{2} \rho(E_{f}) \quad (2.12)$$

where $\rho(E_f)$ is the density of possible final states. $|\Phi_i\rangle$ is the system initial state, given by the tensor product of a photon state $a_q^+|0\rangle$ times a matter electronic ground state $|\phi_i\rangle$, whereas $|\Phi_f\rangle$ is given by the product of the photon vacuum state times an electronic final state $|\phi_f^-\rangle$, time reversed solution of the Schrödinger equation with scattering boundary conditions at infinity.

The cross section is given by $\sigma = \frac{W_{if}}{I_0}$, where $I_0 = \frac{c}{V}$ is calculated considering the vector potential normalized to one photon per volume [132]. Then we have

$$\frac{d\sigma}{d\Omega} = \frac{dW_{if}}{d\Omega} \frac{1}{I_0}$$
(2.13)

Only the destruction operator in equation (2.11) acts in the photoabsorption or photoemission process, then the matrix element becomes:

$$<\Phi_f|\sum_i \mathbf{p}_i \cdot \boldsymbol{\epsilon} e^{i\mathbf{q}\cdot\mathbf{r}_i}|\Phi_i>$$
 (2.14)

The initial and final state should be described by multielectron states. However, it is possibile to explain the main features of x-ray absorption through the change of state of a single electron (single particle approach). Use of the sudden approximation, within the framework of a Hartree Fock Slater treatment of the states describing the initial and the
final atoms, enables the factorisation of those states reducing the many body amplitude to a single particle amplitude. Then the final state is calculated for a completely relaxed (i.e. the lowest energy configuration of the passive Z-1 electrons in the presence of the core hole) ionised absorbing atom. The single particle approach works nicely at energies away from the threshold, in the EXAFS region, where the active electron scarcely interacts with the other electrons of the system. Close to the threshold, in the XANES region, x-ray absorption from deep core levels is still dominated by single electron transitions, however, many body effects appear. The interaction of the photoelectron with the passive electrons becomes strong and the probability for the excitation or ionisation (shake up-shake off) of other electrons becomes sizeable.

The multielectron matter electronic ground state can be written as $|\phi_i\rangle = |\psi_0\rangle \otimes |\psi^{N-1}\rangle$ and the final state as $|\phi_f^-\rangle = |\psi_k^-\rangle \otimes |\psi^{N-1}\rangle$. Thus the matrix element (2.14) becomes:

$$<\psi_k^-|\mathbf{p}\cdot\boldsymbol{\epsilon}e^{i\mathbf{q}\cdot\mathbf{r}}|\psi_0>$$
 (2.15)

where $|\psi_0\rangle$ is the electron in the ground state and ψ_k^- is its excited state. The sum over the different electrons \sum_i has been eliminated in this approximation. The excited state satisfies incoming wave boundary conditions [133]. It is connected to the physical state ψ^+ , which obeys outgoing wave boundary conditions, through time reversal invariance [134]: $\psi^-(k_f, r) = \psi^{+*}(-k_f, r)$, neglecting spin.

The density of free photoelectron final states per unit energy and solid angle $\sum_k \delta(\hbar\omega + E_i - E_k) = \rho_k(E_k)$ can be written counting the number of the states in the quantization volume:

$$dE_k\rho(E_k) = \frac{V}{(2\pi)^3} d^3k$$
 (2.16)

This is correct when the box dimension are much bigger than the wavelength of the mode, then one can do the continuum approximation. k is given by p/\hbar .

$$\rho_k = \frac{V}{(2\pi)^3} \frac{d^3k}{dE_k} = \frac{V}{(2\pi\hbar)^3} p^2 dp \frac{d\Omega_k}{dE_k} = \frac{V}{(2\pi\hbar)^3} pm d\Omega_k$$
(2.17)

since $\frac{p^2}{2m} = E$ and thus $\frac{pdp}{m} = dE$. Thus, the factor for the density of states is $k/16\pi^3$ (in atomic units and V = 1).

It is costumary to incorporate this factor into the normalization of the photoelectron wavefunction passing from a plane wave normalization

$$\int d\mathbf{r} \psi_{\mathbf{k}}^*(\mathbf{r}) \psi_{\mathbf{k}'}(\mathbf{r}) = \frac{(2\pi)^3}{V} \delta(\mathbf{k} - \mathbf{k}')$$
(2.18)

to a normalization to one state per unit energy interval

$$\int d\mathbf{r}\psi_k^*(\mathbf{r})\psi_{k'}(\mathbf{r}) = \frac{2m}{\hbar^2}\delta(k^2 - k'^2)\delta\Omega_k$$
(2.19)

In fact, calling N the normalization factor such that $\sqrt{N}\phi_{\mathbf{k}} = \phi_k$, we find

$$\frac{2m}{\hbar^2}\delta(k^2 - k'^2)\delta(\hat{\mathbf{k}} - \hat{\mathbf{k}}') = N\frac{(2\pi)^3}{V}\delta(\mathbf{k} - \mathbf{k}') = N\frac{(2\pi)^3}{V}\delta(\hat{\mathbf{k}} - \hat{\mathbf{k}}')\frac{\delta(k^2 - k'^2)2k}{k^2}$$
(2.20)

so that

$$N = \frac{V}{(2\pi)^3} \frac{k}{2} \frac{2m}{\hbar^2} = \frac{k}{16\pi^3}$$
(2.21)

which is identical to $\rho(E_k)$, the last equality holding in atomic units of lengths and Rydberg units of energy $(2m/\hbar^2 \rightarrow 1)$. Thus, normalizing to one state per Rydberg, the normalization factor is given just by $\sqrt{\rho_k(E_k)}$ and we can include it in the definition of the final state wavefunction. Then the cross section is given by:

$$\frac{d\sigma}{d\Omega} = \frac{2\pi}{\hbar} \frac{e^2}{c^2} \frac{2\pi\hbar c^2}{\omega V} \frac{V}{c} | < \psi_k^- | \frac{\mathbf{p}}{m} \cdot \boldsymbol{\epsilon} e^{i\mathbf{q}\cdot\mathbf{r}} | \psi_0 > |^2$$
(2.22)

For X-ray radiation, the inverse of $q(\text{angstrom}) = 0.5 \cdot 10^{-3} \hbar \omega_q (\text{eV})$ can be large compared to the extension of the core orbitals involved in the transition. In this case, $\mathbf{q} \cdot \mathbf{r} \ll 1$ and the exponential can be replaced either by 1 (dipolar approximation) or by $1 + i\mathbf{qr}$ (quadrupolar approximation).

Moreover one can use the fact that $[\mathbf{r}, H_0] = \frac{i\hbar}{m}\mathbf{p}$:

$$<\psi_{k}|\mathbf{p}|\psi_{0}>=\frac{m}{i\hbar}<\psi_{k}|(\mathbf{r}H_{0}-H_{0}\mathbf{r})|\psi_{0}>=im\frac{E_{k}-E_{0}}{\hbar}<\psi_{k}|\mathbf{r}|\psi_{0}>=$$
$$=im\omega_{k}<\psi_{k}|\mathbf{r}|\psi_{0}>$$
(2.23)

Thus one easily obtains:

$$\frac{d\sigma}{d\Omega} = \frac{2\pi}{\hbar} \frac{e^2}{c^2} \frac{2\pi\hbar c^2}{\omega V} \frac{V}{c} \omega^2 |\langle \psi_k | \boldsymbol{\epsilon} \cdot \mathbf{r} | \psi_i \rangle|^2 = 4\pi^2 \alpha \hbar \omega |\langle \psi_k | \boldsymbol{\epsilon} \cdot \mathbf{r} | \psi_0 \rangle|^2$$
(2.24)

where $\alpha = \frac{e^2}{\hbar c}$ is the fine structure costant, which defines the coupling strength of the radiation-matter interaction. Its small value $(\alpha = \frac{1}{137})$ ensures that the spectroscopies using radiation as probe slightly perturb the system.

2.6 Cross section for the atomic case

In principle one should solve the time dependent Schrödinger equation describing the initial and final state as wave packets. However, yhe same result is obtained by solving the static 3D Schrödinger equation

$$(\nabla^2 + k^2 - V(\mathbf{r}))\psi_k^+(\mathbf{r}) = 0$$
(2.25)

with the appropriate boundary conditions. In what follows we shall assume that the potential vanishes faster than 1/r for large r. In this case, the scattering wave function $\psi_k^+(\mathbf{r})$ satisfies at large r the free-particle Schrödinger equation:

$$r \to \infty$$
 $(\nabla^2 + k^2)\psi_k^+(\mathbf{r}) = 0$ (2.26)

and in this region we can write $\psi_k^+(\mathbf{r}) \approx \psi_{inc}(\mathbf{r}) + \psi_{sc}(\mathbf{r})$, where $\psi_{inc}(\mathbf{r})$ represents the incident beam of particles and $\psi_{sc}(\mathbf{r})$ the scattered particles. The incident particles are monoenergetic and are travelling in the direction \mathbf{k} , thus the beam can be represented by a plane wave $\psi_{inc}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}$. A plane wave is of infinite extent in the transverse direction, but in any real experiment, the beam is collimated and has a finite transverse extension. However the transverse dimensions of the beam, which may be of the order 1 cm to 1 mm, are sufficiently large for the corresponding uncertainty in momentum to be negligible and for the wave function to be described accurately by a plane wave over the scattering region (which, for atoms, is of the order $\approx 10^{-8}$ cm). Far from the scatterer, the scattered wave function must represent an outward flow of particles from the scattering center. It has the form of an outgoing spherical wave, the amplitude of which depends on the direction of \mathbf{r} and on the energy $k = \sqrt{E}$. Then the scattered wave function can be written as $\psi_{sc}(\mathbf{r}) = f(\mathbf{k}, \mathbf{r}) \frac{e^{iqr}}{r}$.

In principle, the photoemission process is the time reversal of this one, since it is at positive times that one has a plane wave. The connection between scattering theory and experiment is described most easily in terms of the behaviour of wave packets. The physical interpretation of the stationary states $\psi_k^{\pm}(\mathbf{r})$ with such asymptotic behaviour is most easily obtained by constructing a wave packet of such states to represent a localized electron and then examining the time evolution of the wave packet. However, it is mathematically simpler to use the exact eigenstates:

$$\psi_k^{\pm}(\mathbf{r}) \simeq e^{\pm i\mathbf{k}\cdot\mathbf{r}} - f(\pm\mathbf{k},\mathbf{r})\frac{e^{\pm iqr}}{r}$$
(2.27)

rather then linear combination of such states.

The out states $\psi_k^-(\mathbf{r})$ are the proper ones to use for the final state electron wave function in a photoionization experiment. At positive infinite times it reduces to what is measured experimentally: a localized wave function with linear momentum equal to \mathbf{k} . That is, one requires that the final state wave function satisfies the so called incoming wave boundary condition. Namely, at large r the wave function has the form of a plane wave plus incoming spherical waves [133]. Due to this, the photoemission process can be seen as the time reversal of LEED spectroscopy.

The function $f(\mathbf{k}, \mathbf{r})$ is called the scattering amplitude, it represents the probability amplitude for scattering between the momentum states \mathbf{k} and \mathbf{k}' , where in the case of potential scattering \mathbf{k}' has the same magnitude as \mathbf{k} but is directed along $\hat{\mathbf{r}}$, i.e. $\mathbf{k}' = \mathbf{k}\hat{\mathbf{r}}$.

Thus let us suppose that the potential is given by V(r) for $r \leq r_s$ (which will be called the I zone) and 0 for $r > r_s$ (which will be called the II zone). The basic idea of scattering theory is to solve the wave equation separately in the region inside the scatterer and in the region outside and then to match these partial solutions together into a solution that is acceptable over all of space by matching the pieces at the boundaries of the region. The wave functions in the I and II zone must match smoothly and continuously at the boundaries between regions [135]. In the MS theory generally one makes a partition of the whole space V into nonoverlapping spheres Ω_j centered about the atomic site j and a remaining interstitial region $\Delta\Omega$; in that case the problem will be of the same kind: to match the solution at the boundary between the sphere and the interstitial region. Then one seeks the solution of the Schrödinger equation inside each sphere Ω_j .

In the atomic case, we can consider a central potential, which allows the separation between the radial and angular part of the Schrödinger equation. Then the Schrödinger equation becomes a radial equation and it reads: $(\nabla^2 + k^2 - V(r))\psi_k^+ = 0$. Writing the laplacian in spherical coordinates, the Schrödinger equation becomes:

$$\left(\frac{1}{r^2}\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{L^2}{r^2} + E - V(r)\right)\psi_k^+ = 0$$
(2.28)

The operators H, L^2, L_z commute, so one can take the scattering final state function as eigenstate of the L, L_z operator. In the first zone (i.e. inside the sphere with radius r_s) the solution can be written as

$$\psi_k^I = \sum_{lm} R_l(r) Y_L(\hat{\mathbf{r}}) 4\pi i^l Y_L(\hat{\mathbf{k}}) c_L \frac{1}{4\pi} \sqrt{\frac{k}{\pi}}$$
(2.29)

where we have used the notation L = (l, m). Unless explicitly stated we shall use real spherical harmonic, otherwise in (2.29) it would be $Y_L^*(\hat{\mathbf{k}})$. Outside the sphere one has V = 0 and should solve the equation (2.28) without V(r):

$$\left(\frac{1}{r^2}\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{L^2}{r^2} + E\right)\psi_k^{II} = 0$$
(2.30)

we use the spherical waves expansion of the plane wave for $r \to \infty$:

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{L} i^{l} j_{l}(kr) Y_{L}(\hat{\mathbf{r}}) Y_{L}(\hat{\mathbf{k}}) = 4\pi \sum_{L} i^{l} J_{L}(\mathbf{r}) Y_{L}(\hat{\mathbf{k}})$$
(2.31)

The Bessel function $j_l(kr)$ is a solution for the free-particle equation (2.30). Thus the Bessel function has the behaviour of a plane wave. The function $j_l(kr)$ is regular at the origin and everywhere. The Hankel function is an irregular solution to the free-particle equation and it can be written in terms of the Neumann functions: $h_l^+ = j_l + in_l$. It represents a spherical wave for $r \to \infty$. For Bessel, Hanckel and Neumann functions see [136]. Defining $H_L(\mathbf{r}) = h_l^+(kr)Y_L(\hat{\mathbf{r}})$, the solution outside the potential can then be written as:

$$\psi_k^{II} = \sum_L 4\pi i^l Y_L(\hat{\mathbf{k}}) [J_L(\mathbf{r}) - ikt_l H_L^+(\mathbf{r})] =$$

$$= \sum_L 4\pi i^l Y_L(\hat{\mathbf{k}}) j_l(kr) Y_L(\hat{\mathbf{r}}) - \sum_L 4\pi i^l Y_L(\hat{\mathbf{k}}) ikt_l h_l^+(kr) Y_L(\hat{\mathbf{r}}) =$$

$$= e^{i\mathbf{k}\cdot\mathbf{r}} - f(\mathbf{k}, \hat{\mathbf{r}}) \frac{e^{ikr}}{kr}$$
(2.32)

If the tails of the potentials are not truncated, then this fact has influence on the form of the continuum wavefunction, i.e. Coulomb functions must be used instead of j_l and h_l^+ . Now we have to match the two solutions at r_s . We impose the continuity of the function and the continuity of the first derivative (the latter by using the logarithmic derivative):

• continuity of the logarithmic derivative:

$$\frac{\psi^{I'}}{\psi^{I}}|_{r=r_s} = \frac{\psi^{II'}}{\psi^{II}}|_{r=r_s}$$
(2.33)

where $\psi^I \propto R_l$ and $\psi^{II} \propto j_l(kr) - ikt_l h_l^+(kr)$. From this condition one obtains the expression for t_l :

$$t_{l} = -\frac{1}{k} \frac{W[j_{l}(kr), R_{l}(r)]}{W[-ih_{l}^{+}, R_{l}]} = -\frac{1}{k} \frac{W[j_{l}, R_{l}]}{W[n_{l}, R_{l}] - iW[j_{l}, R_{l}]} = -\frac{1}{k} e^{i\delta_{l}} sin\delta_{l}$$
(2.34)

The last passage holds since it is a quantity which is always smaller than 1. Equation (2.34) holds if the potential is real; if not, then δ_l becomes complex and a damping factor arises in its expression. The t_l indicate the strength of the interaction of the electron with the potential.

• continuity of the function:

$$c_l R_l(r_s) = j_l(kr_s) - ikt_l h_l^+(kr_s)$$
(2.35)

Using the fact that the wronskian of a regular solution and an irregular solution is $W \propto \frac{1}{r^2}$, then one obtains

$$c_L = \frac{t_l}{r_s^2 W[j_l, R_l]|_{r_s}}$$
(2.36)

We can define a renormalized wave function $\tilde{R}_l = \frac{R_l}{r_s^2 W[j_l, R_l]}|_{r_s}$. With this renormalization the ψ^I becomes:

$$\psi^{I}(\mathbf{r}) = \sum_{L} \tilde{R}_{l} r_{s}^{2} W[j_{l}, R_{l}]|_{r_{s}} Y_{L}(\hat{\mathbf{r}}) \frac{t_{l}}{r_{s}^{2} W[j_{l}, R_{l}]|_{r_{s}}} i^{l} Y_{L}(\hat{\mathbf{k}}) \frac{\sqrt{k}}{\pi} = \sum_{L} \tilde{R}_{l} Y_{L}(\hat{\mathbf{r}}) t_{l} i_{l} Y_{L}(\hat{\mathbf{k}}) \frac{\sqrt{k}}{\pi} (2.37)$$

Then the cross section is given by:

$$\frac{d\sigma}{d\Omega} = 4\pi^2 \alpha \hbar \omega \sum_{m_0} |\langle \psi_k^I(\mathbf{r}) | \boldsymbol{\epsilon} \cdot \mathbf{r} | R_{l_0}(r) Y_{l_0 m_0}(\hat{\mathbf{r}}) \rangle|^2 = 4\pi^2 \alpha \hbar \omega \sum_{m_0} |\sum_{lm} \langle \tilde{R}_l(r) Y_{lm}(\hat{\mathbf{r}}) t_l 4\pi i^l Y_L(\hat{\mathbf{k}}) | r Y_{1m_r}(\hat{\mathbf{r}}) | R_{l_0} Y_{l_0 m_0}(\hat{\mathbf{r}}) \rangle|^2$$
(2.38)

where we have averaged over m_0 since we don't know from which substate the process takes place. In polar coordinates, the integration over the angles gives a Gaunt coefficient:

$$\frac{d\sigma}{d\Omega} = 4\pi^2 \alpha \hbar \omega \sum_{m_0} |\sum_{lm} M_{ll_0} C^{l_0 m_o}_{l_0 + 1m, 1m_r} i^l Y_{lm}(\hat{\mathbf{k}}) t_l(E)|^2$$
(2.39)

where M_{ll_0} is the radial matrix element, which is a smooth function of the energy. The structure of the cross section at varying energy are due to the t_l . The Gaunt coefficient gives the selection rules for the orbital momentum. If the photon is absorbed by an electron charcaterized by $l_0 = 0$ then $m = m_{\gamma}$ and $Y_{lm} = Y_{1m_{\gamma}}$, i.e. the electron is emitted preferentially along the polarization vector.

This is the photoemission atomic cross section. If one integrates over the emission angle then the total cross section is obtained, i.e. the photoabsorption cross section:

$$\int \frac{d\sigma}{d\Omega} d\Omega = 4\pi^2 \alpha \hbar \omega \sum_{m_0} \sum_{lm} (M_{ll_0})^2 (C_{lm1m_r}^{l_0m_0})^2 |t_l(E)|^2$$
(2.40)

Then one can write that $\sigma_{tot} \propto |t_l|^2$. If the potential is real $(t_l = e^{i\delta_l} \sin\delta_l = \cos\delta_l \sin\delta_l + i\sin^2\delta_l)$ then one has that $Im[t_l] = |t_l|^2$ and thus $\sigma_{tot} = Imt_l$ which is the optical theorem. When the potential is complex then the optical theorem doesn't hold anymore, and the Imt_l gives both the elastic and inelastic channels $(Imt_l - |t_l|^2 = \text{total absorption} - \text{diffused}$ particles=lost particles). In this case $k|t_l|^2 < Imt_l$, implying that δ_l is complex and the difference $Imt_l - k|t_l|^2$ is related to the loss of flux due to absorptive part of the potential, which becomes the source of the damping of the electronic wave.

2.6.1 Connection with the Green's function formalism

One can also write the cross section in terms of the Green function:

$$\sigma_{tot}(E_k) = 4\pi^2 \alpha \hbar \omega \sum_f |\langle \psi_f | \boldsymbol{\epsilon} \cdot \mathbf{r} | \psi_i \rangle|^2 \delta(\hbar \omega + E_i - E_f) = = -\frac{1}{\pi} 4\pi^2 \alpha \hbar \omega Im(\sum_f \frac{\langle \psi_i | \boldsymbol{\epsilon} \cdot \mathbf{r} | \psi_f \rangle \langle \psi_f | \boldsymbol{\epsilon} \cdot \mathbf{r} | \psi_i \rangle}{\hbar \omega + E_i - E_f + i\Gamma})$$
(2.41)

This expression is valid for $\Gamma \to 0$. In the coordinates space the Green function is given by:

$$G^{+}(\mathbf{r}, \mathbf{r}', E) = \sum_{f} \frac{\psi_{f}(\mathbf{r})\psi_{f}^{*}(\mathbf{r}')}{E - E_{f} + i\Gamma}$$
(2.42)

and is such that (E-H)G(E) = I i.e. $(E+\nabla^2 - V(\mathbf{r}))G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')$, i.e. the Green function is the solution to the associated equation with the delta function. With $V(\mathbf{r}) = 0$ the *G* function only depends on the difference between \mathbf{r} and \mathbf{r}' .

Then using the Green function the equation (2.41) becomes:

$$\sigma_{tot}(E_k) = -\frac{1}{\pi} 4\pi^2 \alpha \hbar \omega Im \int \psi_n(\mathbf{r}) \boldsymbol{\epsilon} \cdot \mathbf{r} G(\mathbf{r}, \mathbf{r}', E) \boldsymbol{\epsilon} \cdot \mathbf{r}' \psi_n(\mathbf{r}') d^3 r d^3 r'$$
(2.43)

Since the wave functions are localized, it is reasonable to put $\mathbf{r} = \mathbf{r}'$. In this case we are measuring

$$-\frac{1}{\pi}Im\int d^3r G(\mathbf{r},\mathbf{r}',E) = \sum_n \int |\psi_n(\mathbf{r})|^2 \delta(E-E_n) d^3r = \sum_n \delta(E-E_n)$$
(2.44)

which means that $-\frac{1}{\pi}ImTrG(\mathbf{r}, \mathbf{r}', E) = \rho(E)$, i.e. (supposing that *n* is a continuos variable) one measures the density of non occupied states above the Fermi surface for a certain energy. The oscillations in EXAFS signal are structures in the density of states. Where the density of states is higher (i.e. a higher number of free states) the absorption is stronger (more electrons go to an upper level and occupy it). Thus one sees the density of states projected on a determined symmetry and projected on the direction of the light polarization.

In the presence of a spherical potential the Green function can be written as

$$G(\mathbf{r}, \mathbf{r}', E) = \sum_{L} Y_L(\hat{\mathbf{r}}) g_l(\mathbf{r}, \mathbf{r}', E) Y_L(\mathbf{r}')$$
(2.45)

If the potential has no spherical symmetry then there is a double sum $\sum_{LL'}$. The Green function (2.45) inserted in (2.28) gives (when projected on the *L* component):

$$\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r + E - \frac{l(l+1)}{r^2} - V(r)\right)g_l(r,r',E) = \frac{1}{r^2}\delta(r-r')$$
(2.46)

Following Green's functions theory, the solution is given by the product between a regular solution and an irregular solution $R_l(r_<)R_l^+(r_>)/r^2W[R_l, R_l^+]$, where we have further divided by a costant quantity. The regular solution must be calculated always at the smaller r between r and r'. For $V(\mathbf{r}) = 0$ then $R_l(r_<)$ coincide with j_l and $R_l^+(r_>)$ coincide with h_l^+ . For $r = r' g_l$ is continuos, and the difference between right and left first derivative is the Wronskian, which gives a unitary jump; to the second derivative it gives the $\delta(r - r')$. At $r = r_s$ the denominator becomes $r^2W[R_l, R_l^+] = r_s^2W[R_l, -ih_l^+]_{r=r_s}$. Thus multiplying for $W[j_l, R_l]$ and dividing by the same quantity one can write

$$\frac{R_l(r_{<})R_l^+(r_{>})}{r^2 W[R_l, R_l^+]} = k\bar{R}_l(r_{<})t_l R_l^+(r_{>})$$
(2.47)

We can now remember that $t_l \bar{R}_l = j_l - ikt_l h_l^+$; multiplying by t_l^{-1} we obtain $\bar{R}_l = t_l^{-1} j_l - ikh_l^+$. This is true at $r = r_s$, and also in the region inside if one continues the solutions $kR_l^+ = \bar{R}_l(r) - t_l^{-1}J(r)$ then the Green function becomes $k\bar{R}_l(r)t_l\bar{R}_l(r') - \bar{R}_l(r_c)J_l(r_c)$. If one inserts this expression for the Green function in the cross section and taking its imaginary part then \bar{R}_l and J_l are real, thus the singular part does not contribute; we have contributions only from the first part. The radial part gives $M_l^2 Imt_l(E)$. The $Imt_l(E)$ gives the density of the states of l type projected on the specific site.

2.6.2 The free Green's function G_0

For V(r) = 0 the Green function G_0^+ can be calculated in the following way. G_0^+ is given by $G_0^+ = \sum_k \frac{\psi_k(\mathbf{r})\psi_k^*(\mathbf{r}')}{E-k^2}$. The wavefunction ψ_k for $V(\mathbf{r}) = 0$ is given by a plane wave $\psi_k = \frac{1}{\sqrt{V}}e^{i\mathbf{k}\mathbf{r}}$; \sum_k can be transformed using the continuum approximation in $\frac{V}{(2\pi)^3}\int d^3k$. Thus one has to evaluate the integral

$$G_0^+ = \frac{1}{V} \frac{V}{(2\pi)^3} \int d^3k \frac{e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}}{E-k^2}$$
(2.48)

Then using standard integration in the complex plane with the Cauchy theorem and choosing only the contribution for outcoming waves for the poles, one has

$$G_0^+(\mathbf{r} - \mathbf{r}', E) = -\frac{1}{4\pi |\mathbf{r} - \mathbf{r}'|} e^{ik|\mathbf{r} - \mathbf{r}'|}$$
(2.49)

 $G_0^+(\mathbf{r} - \mathbf{r}', E)$ is nothing elese than the amplitude at \mathbf{r} of a spherical wave created at \mathbf{r}' . G_0^+ describes outgoing waves while the time reversed G_0^- (with $e^{-ik|\mathbf{r}-\mathbf{r}'|}$ will correspond to ingoing waves.

Another way to calculate the G_0^+ is using the partial wave expansion. Indeed, the numerator $e^{i\mathbf{k}\cdot\mathbf{r}}$ inside the integral (2.48) can be written as (2.31). Using again standard integration techniques in the complex plane one obtains

$$G_0^+(\mathbf{r} - \mathbf{r}', E) = -ik \sum_L J_L(k\mathbf{r}_{<}) H_L^+(k\mathbf{r}_{>})$$
(2.50)

where $J_L(k\mathbf{r}) = j_l(kr)Y_L(\hat{\mathbf{r}})$ and $H_L(k\mathbf{r}) = h_l(kr)Y_L(\hat{\mathbf{r}})$ which converges absolutely as can be seen from the asymptotic expressions of $J_L(k\mathbf{r}_{<})$ and $H_L^+(k\mathbf{r}_{>})$ for high values of L. In performing the integration one easily see that the h_l^+ function must be calculated at the bigger r between r and r' to ensure outgoing waves.

2.7 Emission from a cluster: the multiple scattering problem

The essence of the MS method relies on the partition of the space in Voronoi polyhedrons (equivalent to Wigner-Seitz cells for periodic systems) such that their maximum radius is

always smaller than the nearest distance between their centers. In each such polyhedron a local solution $\psi_k^+(\mathbf{r})$ of the Schrödinger equation is obtained behaving like $J_L(\mathbf{r}) = j_l(kr)Y_L(\hat{\mathbf{r}})$ near the origin. These functions are used to expand locally in the *i*-th cell the overall solutions of class C^1 (continuous together with first derivatives) in the whole space, satisfying the boundary condition (2.27).

2.7.1 The free Green's function G_0^+ in the multicenter problem

Since now we have dealt with Green's functions in which r and r' were both referred to the same center. One of the key of the MS theory is to rewrite the Green's function referring to coordinates of two different reference centers. One can consider two spheres, i and j with radius r_i and r'_j , whose centers are distant \mathbf{R}_i and \mathbf{R}_j from the origin O of the reference system. Then it is possible to write $\mathbf{r} - \mathbf{r}' = \mathbf{r} - \mathbf{R}_i + \mathbf{R}_i - \mathbf{r}' + \mathbf{R}_j - \mathbf{R}_j = \mathbf{r}_i - \mathbf{r}'_j + R_{ij}$. Using (2.31) one has

$$G_{0}^{+} = \frac{1}{V} \frac{V}{(2\pi)^{3}} \int d^{3}k \frac{e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}}{E-k^{2}+i\epsilon} = \frac{1}{(2\pi)^{3}} \int d^{3}k \frac{e^{i\mathbf{k}\cdot(\mathbf{r}_{i}-\mathbf{r}'_{j}+\mathbf{r}_{ij})}}{E-k^{2}+i\epsilon} =$$

$$= 8 \sum_{LL'L''} i^{l-l'+l''} C(L,L';L'') Y_{L}(\hat{\mathbf{r}}_{i}) Y_{L'}(\hat{\mathbf{r}}_{j}) Y_{L''}(\hat{\mathbf{R}}_{ij}) \cdot$$

$$\int_{0}^{\infty} d^{3}k \frac{k^{2}}{E-k^{2}+i\epsilon} j_{l}(kr_{i}) j_{l}(kr'_{j}) j_{l}(kR_{ij}) \qquad (2.51)$$

where C(L, L'; L'') is a Gaunt coefficient. Then there are different cases which must be considered:

• $R_{ij} > r_i + r'_j$ (sites *i* and *j* do not overlap). In this case one transforms the last j_l in (2.51) in half of the sum of the corresponding Hankel functions. The Green's function is then given by:

$$G_0^+(\mathbf{r} - \mathbf{r}', E) = \tilde{k} \sum_{LL'} J_L(\tilde{k}\mathbf{r}_i) G_{LL'}^{ij} J'_L(\tilde{k}\mathbf{r}'_j)$$
(2.52)

where

$$G_{LL'}^{ij} = 4\pi i \sum_{L''} i^{l-l'+l''} C(L,L';L'') H_{L''}^+(\tilde{k}\mathbf{R}_{ij})$$
(2.53)

where $\tilde{k} = \sqrt{E}$.

• $\mathbf{r} \in \Omega_i$, and \mathbf{r}' on S_{Ω_0} , which is the surface of the outer sphere S_{Ω_0} which contains all the spheres and is centered in 0 (j = 0): $r'_0 > r_i + R_{i0}$. Transforming the Bessel function which depends on r'_0 , then the Green's function is given by

$$G_0^+(\mathbf{r} - \mathbf{r}', E) = -ik \sum_{LL'} J_L(\tilde{k}\mathbf{r}_i) J_{LL'}^{i0} H'_L(\tilde{k}\mathbf{r}'_0)$$
(2.54)

where

$$J_{LL'}^{i0} = 4\pi i \sum_{L''} i^{l-l'+l''} C(L, L'; L'') J_{L''}^+(k\mathbf{R}_{i0})$$
(2.55)

• **r** is external to Ω_0 , **r**' is on S_{Ω_i} , thus $\mathbf{r}_0 > \mathbf{r}'_i + \mathbf{R}_{0i}$. Then in this case

$$G_0^+(\mathbf{r} - \mathbf{r}') = G_0(\mathbf{r}_0 - \mathbf{r}'_i + \mathbf{R}_{i0}) = -ik\sum_{LL'} H_L^+(\tilde{k}\mathbf{r}_0)J_{LL'}^{0i}J_{LL'}(\tilde{k}\mathbf{r}'_i)$$
(2.56)

where

$$J_{LL'}^{i0} = 4\pi \sum_{L''} i^{l-l'+l''} C(L, L'; L'') J_{L''}(\tilde{k} \mathbf{R}_{0i})$$
(2.57)

• **r** belongs to the interstitial region $\Delta\Omega$, **r**' is on S_{Ω_i} , **r**_i > **r**'. Thus writing the Green's fuction with respect to the only centre *i*, one has

$$G_0^+(\mathbf{r} - \mathbf{r}') = G_0(\mathbf{r}_i - \mathbf{r}'_i) = -i\tilde{k}\sum_{LL'}J_L(\tilde{k}\mathbf{r}'_i)H_L^+(\tilde{k}\mathbf{r}_i)$$
(2.58)

• **r** belongs to the interstitial region, \mathbf{r}' is on S_{Ω_0} , $\mathbf{r}'_0 > \mathbf{r}_0$. then writing the Green's function with respect to the centre 0 one has:

$$G_0^+(\mathbf{r} - \mathbf{r}') = G_0(\mathbf{r}_0 - \mathbf{r}'_0) = -i\tilde{k}\sum_{LL'} H_L^+(\tilde{k}\mathbf{r}'_0)J_L(\tilde{k}\mathbf{r}_0)$$
(2.59)

2.7.2 Resolution of the Lippmann-Schwinger equation in the multicenter problem

Our aim is to solve the Schrödinger equation $(\nabla^2 + k^2 - V(\mathbf{r}))\psi_k^+ = 0$ with the boundary conditions $\psi_k^+ \simeq e^{i\mathbf{k}\cdot\mathbf{r}} - f(\mathbf{k},\mathbf{r})\frac{e^{ikr}}{r}$. The general solution of this equation may be written as:

$$\psi_k(\mathbf{r}) = \phi(k, \mathbf{r}) + \int_V d^3 r' G_0^+(\mathbf{r}, \mathbf{r}'; k) V(\mathbf{r}') \psi_k(\mathbf{r}')$$
(2.60)

The superscript + of the free Green's function indicates outgoing wave boundary conditions. The equation can be iterated leading to its Born series expansion. The eigenstates $\phi(k, \mathbf{r})$ are called asymptotical states. The wave function $\phi(k, \mathbf{r})$ in equation (2.60) is given by $\phi(k, \mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}$ and it is the solution of the homogeneous equation

$$(\nabla^2 + k^2)\phi(k, \mathbf{r}) = 0 \tag{2.61}$$

and $G_0^+(\mathbf{r}, \mathbf{r}'; k)$ is the Green's function such that

$$(\nabla^2 + k^2)G_0^+(\mathbf{r}, \mathbf{r}'; k) = \delta(\mathbf{r} - \mathbf{r}')$$
(2.62)

Equation (2.60) is called Lippmann-Schwinger equation. It satisfies automatically the boundary conditions. The Lippmann-Schwinger equation and the Schrödinger equation are are equivalent, but numerically it is easier to cope with integral equations. One can see that equation (2.60) represents a solution to the Schrödinger equation:

$$(\nabla^2 + k^2)\psi_k(\mathbf{r}) = 0 + \int_V d^3r'\delta(\mathbf{r} - \mathbf{r}')V(\mathbf{r}')\psi_k(\mathbf{r}') = V(\mathbf{r})\psi_k(\mathbf{r})$$
(2.63)

Another thing which should be emphasized is the following. Using equation (2.49) for the expression of G_0^+ one has that equation (2.60) becomes:

$$\psi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{1}{4\pi} \int_V d^3 r' \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} V(\mathbf{r}')\psi_k(\mathbf{r}')$$
(2.64)

This is equivalent to the Schrödinger equation 2.25, together with the boundary condition 2.27, which is satisfied automatically. To verify the asymptotic behaviour of $\psi_k(\mathbf{r})$, we note that for r large and $r' \ll r$,

$$|\mathbf{r} - \mathbf{r}'|(r \to \infty) \to r - \hat{\mathbf{r}} \cdot \mathbf{r}' + \dots$$
 (2.65)

so that

$$\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}(r\to\infty)\to\frac{e^{ikr}}{r}e^{-i\mathbf{k}_f\cdot\mathbf{r}'}+\dots$$
(2.66)

where terms of higher order in 1/r have been neglected (this is allowed if the potential outside the sphere is null or goes to zero faster than 1/r). Moreover we have introduced the final wave vector $\mathbf{k}_f = k\hat{\mathbf{r}}$, which points in the direction of the detector and has spherical polar coordinates (k, θ, ϕ) . Thus one has:

$$\psi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{e^{ikr}}{4\pi} \int_V d^3r' e^{-i\mathbf{k}_f\mathbf{r}'} V(\mathbf{r}')\psi_k(\mathbf{r}')$$
(2.67)

This gives an integral representation of the scattering amplitude:

$$f(\mathbf{k}, \mathbf{r}) = \int_{V} d^{3}r' e^{-i\mathbf{k}_{f}\mathbf{r}'} V(\mathbf{r}')\psi_{k}(\mathbf{r}')$$
(2.68)

Thus the Lippmann-Schwinger equation allows to incorporate automatically the boundary conditions.

To perform the volume integration which appears in the Lippmann-Schwinger equation 2.60, we first partition the space in atomic non overlapping spheres S_k included in an outer sphere S_0 . Each cell is centered on the atomic nucleus. We use the Green's theorem, which allows to transform the integral over the volume in an integral over the surface:

$$\int_{V} d^{3}r [F(\nabla^{2} + E)G - G(\nabla^{2} + E)F] = \int_{S} (F\vec{\nabla}G - G\vec{\nabla}F) \cdot \vec{n}d\sigma \qquad (2.69)$$

It is valid for continuos functions which have continuos first derivatives. \vec{n} is the outward normal to the boundary S_V . Inside the atomic spheres $\psi_k(\mathbf{r})$ can be written in terms of basis function chosen to be the local radial regular solutions of the Schrödinger equation at the chosen energy. These functions are a complete set. For each cell, the wave function of the cell can be written as combination of local functions ϕ_L , which are regular for $r \to 0$:

$$\psi_k^i(\mathbf{r}_i) = \sum_i A_L^i(\mathbf{k})\phi_L(\mathbf{r}_i)$$

$$\phi_L(\mathbf{r}_i) \simeq (r \to 0)J_L(\mathbf{r}_i)$$
(2.70)

The coefficients $A_L^i(\mathbf{k})$ of such expansion are vectors and are determined imposing that the local solution inside the sphere matches the solution in the outer region at the boundary radius. The Green's theorem ensures such continuity and it allows to calculate this coefficients. Let us consider the interstitial region Δ_{Ω} , i.e. the region between the outer sphere and the atomic cells. In this region, where $V(\mathbf{r}) = 0$, $G = G_0$ and F can be taken equal to $F = e^{i\mathbf{k}\cdot\mathbf{r}} - f(\mathbf{k},\mathbf{r})\frac{e^{\pm iqr}}{r}$. In order to perform the surface integrals, one needs various one and two center expressions of the free Green's function, which have been treated in the previous two paragraphs.

The left side of (2.69) is

$$\int_{V_{\Delta\Omega}} d^3 r' [\psi_k(\mathbf{r}')(\nabla^2 + E)G_0 - G_0(\nabla^2 + E)\psi_k(\mathbf{r}')] = \int_{\Delta\Omega} d^3 r' \psi_k(\mathbf{r}')\delta(\mathbf{r} - \mathbf{r}') - \int_{\Delta\Omega} d^3 r' G_0(\mathbf{r} - \mathbf{r}')(\nabla^2 + E)\psi_k(\mathbf{r}') = 0$$
(2.71)

the first term is null since **r** never coincides with the integration variable **r**' and the second term is zero since $(\nabla^2 + E)\psi_k(\mathbf{r}') = 0$. This means that for the right hand side of (2.69) one has that $\int_{S_0} ... \vec{n} d\sigma - \int_{S_\Omega} ... \vec{n} d\sigma = 0$ i.e. $\int_{S_0} ... \vec{n} d\sigma = \int_{S_\Omega} ... \vec{n} d\sigma = \sum_i \int_{S_{\Omega_i}} ... \vec{n} d\sigma$. Taking **r** inside Ω_i then the left hand side of (2.69) is equal to

$$\sum_{j} \int_{\Omega_i} [\psi_k(\mathbf{r}'_j)(\nabla^2 + E)G_0^+(\mathbf{r} - \mathbf{r}') - G_0(\mathbf{r} - \mathbf{r}')\nabla^2 + E)\psi_k(\mathbf{r}'_i)]d^3r'_j$$
(2.72)

About the first term, one has $(\nabla^2 + E)G_0^+(\mathbf{r} - \mathbf{r'}) = \delta(\mathbf{r} - \mathbf{r'})$. Thus if $\mathbf{r'}$ is inside the *j* cell, then this term is null, if $\mathbf{r'}$ is inside the *i* cell then it is equal to $\psi_k(\mathbf{r}_i)$. If $\mathbf{r'}$ belongs to Ω_i then the second term in expression (2.72) is given by two terms

$$-\int_{V_{\Omega_i}} G_0(\mathbf{r} - \mathbf{r}')\nabla^2 + E)\psi_k(\mathbf{r}'_i)]d^3r'_i + \sum_{j\neq i}\int_{V_{\Omega_j}} G_0(\mathbf{r} - \mathbf{r}')\nabla^2 + E)\psi_k(\mathbf{r}'_i)]d^3r'_j.$$
(2.73)

Thus the integral appearing in the left side of eqn (2.71) can be written as the sum of the contribution from the *i* cell and from all the other cells $j \neq i$ and then one can use the Green's theorem for these contributions:

$$\int_{\Omega_{i}} \psi_{k}(\mathbf{r}'_{j})(\nabla^{2} + E)G_{0}^{+}(\mathbf{r} - \mathbf{r}') - \int_{V_{\Omega_{i}}} G_{0}(\mathbf{r} - \mathbf{r}')(\nabla^{2} + E)\psi_{k}(\mathbf{r}'_{i})d^{3}r'_{i} +
\sum_{j \neq i} \int_{\Omega_{j}} d^{3}r'_{j}\psi_{k}(\mathbf{r}'_{j})(\nabla^{2} + E)G_{0}^{+}(\mathbf{r} - \mathbf{r}') - \sum_{j \neq i} \int_{\Omega_{i}} G_{0}(\mathbf{r} - \mathbf{r}')(\nabla^{2} + E)\psi_{k}(\mathbf{r}'_{i})d^{3}r'_{j} =
\int_{S_{\Omega_{i}}} [\psi_{k}^{i}(\mathbf{r}'_{i})\vec{\nabla}G_{0}^{+}(\mathbf{r} - \mathbf{r}') - G_{0}^{+}(\mathbf{r} - \mathbf{r}'_{i})\vec{\nabla}\psi_{k}^{i}(\mathbf{r}'_{i})] \cdot \vec{n}_{i}d\sigma'_{i} +
\sum_{j \neq i} \int_{S_{\Omega_{j}}} [\psi_{k}(\mathbf{r}')\vec{\nabla}G_{0}^{+}(\mathbf{r} - \mathbf{r}') - G_{0}^{+}(\mathbf{r} - \mathbf{r}'_{i})\vec{\nabla}\psi_{k}(\mathbf{r}')] \cdot \vec{n}_{j}d\sigma'_{j}$$
(2.74)

The last term in eqn (2.74) corresponds to the fourth case in the previous paragraph, while the term before the last corresponds to the first case. The integrals on the internal "walls" of the cells do not contribute, only the contributions from integrals on the external surfaces remain:

$$S_{\Omega} = \int_{S_{\Omega}} (\psi_k \vec{\nabla} G - G \vec{\nabla} \psi_k) \cdot \vec{n} d\sigma = \int_{S_0} [\psi_k^0(\mathbf{r}') \vec{\nabla} G_0^+(\mathbf{r} - \mathbf{r}') - G_0^+(\mathbf{r} - \mathbf{r}') \vec{\nabla} \psi_k^0(\mathbf{r}')] \vec{n}_0 d\sigma_0' 2.75)$$

Terms in (2.75) are evaluated with \mathbf{r} belonging to Ω_i and $\mathbf{r'}$ on S_0 , thus they correpond to the second case in the previous chapter. Thus equation (2.75) and equation (2.74) are equivalent. One must substitute the correct expressions for G_0 which are written in the previous section and the correct expressions for ψ_k , i.e. $\psi_k^i(\vec{r_i}) = \sum_i A_L^i(\vec{k})\phi_L(\mathbf{r}_i)$ and $\psi_k(\mathbf{r}_0) = \sum_L 4\pi i^l Y_L(\hat{\mathbf{k}})[J_L(\mathbf{r}_0) + \sum_{L'} H_{L'}^+(\mathbf{r}_0)T_{L'L}]$ for the outer region $(T_{L'L}$ corresponds to $t_{lm,l'm'}$ which is the generalization of t_l in the case of non spherical potential). From the equivalence between (2.74) and (2.75) one obtains an equation for the coefficients of the basis functions:

$$\sum_{j} \sum_{L'} A^{i}_{L'}(\mathbf{k}) E^{i}_{LL'} + \sum_{j \neq i} \sum_{L'L''} G^{ij}_{LL''} S^{j}_{L''L'} A^{j}_{L'}(\mathbf{k}) = A^{0}_{L}(\mathbf{k}) = 4\pi i^{l} Y_{L}(\hat{\mathbf{k}}) e^{i\mathbf{k}\cdot\mathbf{r}_{i0}}$$
(2.76)

where

$$E_{LL'}^{i} = \int_{S_{\Omega_{i}}} \left[-i\tilde{k}\phi_{L'}(\mathbf{r}_{i}')\vec{\nabla}_{\mathbf{r}_{i}}H_{L}^{+}(\tilde{k}\mathbf{r}_{i}') + i\tilde{k}H_{L}^{+}(\tilde{k}\mathbf{r}_{i}')\vec{\nabla}_{\mathbf{r}_{i}}\phi_{L'}(\mathbf{r}_{i}') \right] \cdot \vec{n}_{j}d\sigma_{i}$$

$$S_{L''L'''}^{j} = \int_{S_{\Omega_{i}}} \left[\phi_{L'''}(\mathbf{r}_{j}')\vec{\nabla}_{\mathbf{r}_{j}}J_{L''}(\tilde{k}\mathbf{r}_{j}') - J_{L''}(\tilde{k}\mathbf{r}_{j}')\vec{\nabla}_{\mathbf{r}_{j}}\phi_{L'''}(\mathbf{r}_{j}') \right] \cdot \vec{n}_{j}d\sigma_{j} \qquad (2.77)$$

2.7.3 The multiple scattering equations

In solids, as a first approximation, the potential is given by the superposition of atomic potentials; in an atom the charge is practically spherically symmetric, i.e. only valence states have no spherical symmetry, but one can do the spherical average on the atomic potential itself plus the tails of potentials due to other atoms $V_0(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}' = \sum_i V_i(\mathbf{r}_i)$. Thus the potential is spherically symmetric. We now consider that the potential in each atomic cell is spherically simmetric and a constant potential in the interstitial region. This is the so called muffin tin approximation. Thus we have spheres around each atomic site and then an interstitial region which is the region between the outer sphere and the atomic spheres. In the interstitial region the the interstitial potential is generally taken as $V_0(\mathbf{r})$.

We deal with atoms embedded in an interstitial space of constant potential. This (muffin tin zero) level determines our zero of energy. The atoms are supposed to be fully screened so that the photoelectron feels finite range spherically symmetric non overlapping local potentials. Let us call ρ_i the radius of the muffin tin spheres. In each single sphere, if the potential is spherically symmetric, for $r \to 0$, one has $\phi_L(r) \simeq J_L(r) = R_l(r)Y_L(\hat{\mathbf{r}})$ (for non spherically simmetric potentials one should have $\sum_L R_l(\mathbf{r})Y_L(\hat{\mathbf{r}})$). In this case the two integrals $E_{LL'}^i$ and $S_{L''L''}^j$ become diagonal in L, L':

$$E_{LL'}^{i} = -\tilde{k}W[R_{l}^{i}(r_{i}'), h_{l}^{+}(\tilde{k}r_{i}')]_{r_{i}'=\rho_{i}}\rho_{i}^{2}\delta_{LL'}$$

$$S_{L''L'''}^{j} = W[R_{l}^{j}(r_{j}'), j_{l}(\tilde{k}r_{j}')]_{r_{j}'=\rho_{i}}\rho_{j}^{2}\delta_{LL'}$$
(2.78)

Then equation (2.76) becomes:

$$\sum_{jL'} \left\{ W[\tilde{h}_{l}^{+}(\tilde{k}r'_{i}), R_{l}^{i}(r'_{i})]_{r'_{i}=\rho_{i}}\rho_{i}^{2}\delta_{LL'}\delta_{ij} + G_{LL'}^{ij}W[j_{l'}(\tilde{k}r'_{j}), R_{l'}^{j}(r'_{j})]_{r'_{j}=\rho_{i}}\rho_{j}^{2}\delta_{LL'} \right\} \qquad A_{L'}(\mathbf{k}) = A_{L}^{0}(\mathbf{k})(2.79)$$

Let us define:

$$W[j_{l'}, R_{l'}^j]\rho_i^2 A_L(\mathbf{k}) = B_L(\mathbf{k})$$
(2.80)

such that the local wave functions are $\psi_k^i(\mathbf{r}_i) = \sum_L A_L^i(\mathbf{k})\phi_L(\mathbf{r}) = \sum_L B_L(\mathbf{k})\bar{\phi}_L(\mathbf{r})$ where $\bar{\phi}_L(\mathbf{r} = \phi_L(\mathbf{r}))/W[j_l, R_l^j]\rho_i^2$. Then the equation (2.79) can be written as:

$$\sum_{j} \sum_{L'} \left\{ (t_l^i)^{-1} \delta_{LL'} \delta_{ij} - G_{LL'}^{ij} \right\} B_{L'}^j = A_L^0(\mathbf{k})$$
(2.81)

which are known as the multiple scattering equations. t_l^i is the dynamical part (it represents the scattering at the *i* atomic site) and $G_{LL'}^{ij}$ represents the structural part (propagators from site *i* to site *j*). Thus the MS treatment allows to write an equation in which the two contributions are separated. The matrix $\{(t_l^i)^{-1}\delta_{LL'}\delta_{ij} - G_{LL'}^{ij}\}$ is called the MS matrix. The B_L are the scattering amplitudes.

To find the B_L let us introduce the inverse of the scattering matrix:

$$\left(\left\{(t_l^i)^{-1}\delta_{LL'}\delta_{ij} - G_{LL'}^{ij}\right\}\right)^{-1} = \tau_{LL'}^{ij}$$
(2.82)

which is known as the scattering path operator, giving the total amplitude of propagation from site *i* to site *j*, starting with angular momentum *L* and arriving with angular momentum L'. Then the B_L can be written as:

$$B_{L}^{i}(\mathbf{k}) = \sum_{jL'} \tau_{LL'}^{ij} i^{l'} Y_{L'}(\mathbf{k}) e^{i\mathbf{k}\mathbf{R}_{j0}} \sqrt{\frac{k}{\pi}} = \sum_{jL'} \tau_{LL'}^{ij} A_{L}^{0}$$
(2.83)

Thus the scattering wave function can be written as combinations of local solutions of the Schrödinger equation:

$$\psi_k^i(\mathbf{r}) \simeq \sum_L B_L^i(\mathbf{k}) R_l^i(r_i) Y_L(\hat{\mathbf{r}})$$
(2.84)

The photoemission cross section from a cluster can be written as follows:

$$\frac{d\sigma}{d\Omega} = 4\pi^2 \alpha \hbar \omega \frac{k}{\pi} \sum_m |\sum_L M_{L'L} B_L^0(\mathbf{k})|^2 = 4\pi^2 \alpha \hbar \omega \frac{k}{\pi} \sum_m |\sum_L M_{L'L} \sum_{L'j} \tau_{LL'}^{0j} i^{l'} Y_{L'}(\hat{\mathbf{k}}) e^{i\mathbf{k} \cdot \mathbf{R}_{j0}})|^2$$
(2.85)

where

$$M_{LL_c} = \int_0^{\rho_0} r^3 dr R_l(r) R_{l_c}(r) \int d\Omega Y_{L'} Y_{1m_\gamma} Y_L$$
(2.86)

The cross section is then given by the modulus square of composite amplitudes which are obtained as the product of the amplitude (the matrix element) for the creation of the electron at site 0 (the origin) in angular momentum L, times the amplitude of propagation (the τ matrix) from site 0 to any other site j with final angular momentum L', times the amplitude $Y_L(\hat{\mathbf{k}})$ for emission along the direction \mathbf{k} as seen from site j, times the phase factor $e^{i\mathbf{k}\cdot\mathbf{R}_{j0}}$ that takes into account the phase relation of the electronic wave between sites 0 and j. This form of the cross section follows very closely the usual three-step model for the photoemission process.

Regarding the scattering path operator it is possible to rewrite its expression as:

$$\tau_{LL'}^{ij} = [(T_a^{-1} + G)^{-1}]_{LL'}^{ij} = [T_a(I + GT_a)^{-1}]_{LL'}^{ij} = T_a \sum_n (-1)^n (GT_a)^n$$
(2.87)

where $T_a = [T_{LL'}^i \delta_{ij}]$. The scattering path operator describes all the possibilities for an electron to travel from atom i to atom j, with the initial and final scattering by these two atoms included. This simple interpretation makes multiple scattering theory in the scattering path operator formalism a very convenient tool to describe spectroscopies involving a probe electron. Equation (2.87) is nothing elese than a sum over all the pathways the probe electron can follow. This series converges only if the maximum eigenvalue of GT_a is less than 1. When n = 0 one has only atomic scattering (i.e. atomic cross section). For n = 1one has the single scattering approximation, for n = 2 two scattering events and so on. This way is the standard procedure to compute the cross section of electron spectroscopies in the high kinetic energy range. But for kinetic energies lower than about 50 eV, as discussed by Natoli and Benfatto [137], this expansion does not necessarily converge. So for low energies, the scattering path operator is usually computed in a more accurate way, i.e. totally inverting the $(T_a^{-1} + G)$ matrix. This corresponds to the summing of the series expansion up to infinity. It is therefore exact from the point of view scattering theory, contrarily to (2.87), which has to be truncated somewhere. In practice, however, the use of the inversion to compute the scattering path operator is restricted to small size clusters and low kinetic energies as the size of the matrix which has to be stored prior to inversion increases very rapidly.

Before finishing this section, it is important to quote an interesting relation connecting the square modulus of the scattering amplitude $B_L^i(\mathbf{k})$ with the imaginary part of the scattering path operator $\tau_{LL'}^{ij}$. More generally, in the case of a real potential one can show that as a consequence of the multiple scattering equations the following relation holds [138]:

$$\int d\hat{\mathbf{k}} [B_L^i(\mathbf{k})]^* B_{L'}^j(\mathbf{k}) = -\frac{1}{\pi} Im \tau_{LL'}^{ij}$$
(2.88)

This relation is the optical thereom for the scattering amplitude and is a consequence of the conservation of the particle flux and is not valid in the case of losses (complex potential). It can be used to connect the integrated photoemission cross section with the photoabsorption cross section derived from the Green's function expression. Indeed, from expression (2.85) one obtains:

$$\int d\hat{\mathbf{k}} \frac{d\sigma(\omega)}{d\hat{\mathbf{k}}} = -8\pi\alpha\hbar\omega\sum_{m_c}\sum_{LL'}M_{LL_c}(\hbar\omega)Im\tau^{ii}_{LL'}M_{L'}$$
(2.89)

2.8 The Rehr-Albers formulation

In the path approach only relatively low order terms can be calculated exactly in an efficient way. Since Clebsch-Gordan coefficients proliferate for higher-order scattering, an exact treatment of curved-wave contributions based on angular momentum algebra [139] is computationally demanding. Iterative methods for going to even higher order were developed [140], but they are generally limited to small clusters or low energies due to the large angular momenta. Moreover, the inclusion of thermal vibrations and disorder in such exact methods is nontrivial. Moreover l_{max} is usually large except at low energies; typically $l_{max} \approx k_{max} r_s$ is between 10 and 30. These difficulties are in contrast with the asymptotic high energy form, where all the outgoing spherical waves can be approximated by plane waves (PWA) [129], in which all couplings between different partial waves and hence all the coupled l and m sums are eliminated. Then the contribution from a MS path is given by a simple product over scattering amplitudes in which the summation over angular momenta that is carried out at each site combines with the t matrix to produce ordinary scattering amplitudes. But PWA fails rapidly as one approaches the absorption edge, where curved wave effects become important. Maybe the best one can do is to replace the $f(\theta)$ in the PWA with effective curved wave scattering amplitudes. Such result is equivalent to the point scattering approximation (PSA) [129, 141, 142]. But the PSA is not reliable at low energy for general θ , it works well only for collinear paths. For these reasons, neither the plane-wave approximation, the spherical wave approximation, nor exact methods provide practicable schemes for accurate MS calculations. A strategy that overcomes all computational problems was developed by Rehr and Albers [143], which is based on a rapidly convergent separable representation of the electron propagator, which permits fast, accurate calculations of any MS path to arbitrary order.

Each scattering amplitude is replaced by a scattering amplitude matrix and the method can be improved by varying the dimensionality of the matrices. The lowest term is a (1x1) matrix or scalar function which is just the effective curved wave scattering amplitude; the (1x1) case corresponds to point scattering approximation. This MS matrix formalism than permits independent summations at each site over all intermediate angular momentum variables (l, m), as in the calculation of $f(\theta)$, avoiding the computational bottleneck posed by large l_{max} . This approach is rapidly convergent at all energies, leading to essentially exact results, provided the MS expansion converges. The approach adopted for calculating the Green's function matrix elements $G_{L,L'}(\rho)$ ($\rho = k(\mathbf{R} - \mathbf{R}')$) is to seek a convergent separable representation, like

$$G_{L,L'}(\boldsymbol{\rho}) = \frac{e^{i\rho}}{\rho} \sum_{\lambda} \tilde{\Gamma}_{\lambda}^{L}(\boldsymbol{\rho}) \Gamma_{\lambda}^{L'}(\boldsymbol{\rho})$$
(2.90)

where successive terms in λ are of decreasing significance. This approach becomes exact when summed over its full (finite) range of indices. This separable representation is achieved in two steps:

(1) in the first step one applies to $G_{L,L'}(\rho)$ rotation matrices $R^l_{mm'}(\Omega_{\hat{\rho}})$ which rotate the bond direction $\hat{\rho}$ onto the z axis. These rotation operations separate $G_{L,L'}(\rho)$ exactly into energy dependent radial and purely angular dependent terms as follows:

$$G_{L,L'}(\boldsymbol{\rho}) = \frac{e^{i\rho}}{\rho} \sum_{\mu=-l}^{l} R^{l}_{m\mu}(\Omega_{\hat{\boldsymbol{\rho}}}^{-1}) g^{(|\mu|)}_{ll}(\rho) R^{l'}_{\mu m'}(\Omega_{\hat{\boldsymbol{\rho}}})$$
(2.91)

where $g_{ll}^{(|\mu|)}(\rho)$ is a reduced, dimensionless, z-axis propagator given by:

$$g_{ll'}^{(|\mu|)}(\rho) = \rho e^{-i\rho} G_{l\mu,l'\mu}(\rho) = N_{l\mu} N_{l'\mu} \int_0^\infty \frac{dx}{z} e^{-x/z} P_l^\mu (1-x) P_{l'}^\mu (1-x)$$
(2.92)

where $N_{l\mu}$ are spherical harmonic normalization factors, $z = 1/I\rho$ and $P_l^{\mu}(1-x)$ are associated Legendre polynomials in $cos(\theta) = (1-x)$. The authors found that truncating the sum over μ yields accurate approximations ($\mu_{max} \leq 2$ is usually sufficient). With step (1) alone, the summation of the MS expansion requires only $l_{max}\mu_{max}$ intermediate terms at each site, rather than $l_{max}(l_{max}+1)$ terms in the exact case. While this reduction works well for paths of low scattering order, it is still insufficient to make arbitrarily high order MS calculations practicable, as successive l's are still coupled. The next step in the separation of $G_{LL'}(\rho)$ overcomes this limitation.

(2) in the second step a separable representation for the z-axis propagator is derived. It is possible to express it as:

$$g_{ll'}^{(|\mu|)}(\rho) = \sum_{\nu=0}^{\min[l,l'-\mu]} \tilde{\gamma}_{\mu\nu}^{l}(\rho) \gamma_{\mu\nu}^{l'}(\rho)$$
(2.93)

where $\tilde{\gamma}_{\mu\nu}^{l}(\rho), \gamma_{\mu\nu}^{l'}(\rho)$ can be expressed by series of inverse powers of ρ . Examining the convergence properties, one finds that each term in (2.93) converges roughly as $(l^2/\rho)^{2\nu+\mu}$. Generally ρ is greater than unity even at smallest bong lengths and energies above threshold, as the near neighbour distance R_{nn} is always several atomic units and $k \geq k_F$, the Fermi momentum, which is of order of unity in atomic units. Convergence with respect to l is controlled by the partial wave t matrix elements. The mean value of l suitably averaged over t_l , which we call \bar{l} , is characteristic of the size r_0 of the scatterer and is generally much smaller than l_{max} . This maximum value of l may be defined as that for which the classical turning point is outside the range of the scattering potential, i.e., $L_{max}(k) \approx kr_s$. For $l > l_{max}, \delta_l$

becomes exponentially small. Provided \bar{l} is sufficiently small, the expansion parameter \bar{l}^2/ρ will also be small. It is sufficient to retain in (2.93) only the leading terms, e.g., $\mu \leq 2$ and $\nu \leq 1$. Barton and Shirley argue that the physical reason for the convergence of such expansions is that the higher magnetic sublevels μ have less overlap with the scattering potential; they also suggest that the number of sublevels needed for convergence is related to r_0/R . To see this one can also see $g_{ll'}^{(\mu)}$ as the overlap $\langle j_{l\mu}(\mathbf{r} - R\hat{\mathbf{z}})|h_{l'\mu}(\mathbf{r}) \rangle$ of an outgoing wave at the origin and a scattering state at $R\hat{\mathbf{z}}$; the outgoing wave has angular lobes at $\sin|\theta| \approx \mu/l'$ and the scattering state has a mean radius of roughly $r_l \approx l/k$. Thus there is significant overlap when $\mu < ll'/kR$. For scattering to be significant , $l < \bar{l}$ and hence $\mu < \bar{l}^2/kR$ which is just the small expansion parameter noted above. The truncated expansion is also accurate at low energies, even if the expansion parameter varies inversely with ρ . The reason is that only a few partial waves are significant at low energies and all expansion coefficients $\gamma_{\mu\nu}^l$ must vanish for $|\mu|, \nu > l$. It follows that only the indices $|\mu|$, $\nu \leq l_{max}(k)$ are important. Denoting with $\lambda = (\mu\nu)$ the explicit form of the factors $\tilde{\Gamma}_{\lambda}^L(\rho)$ and $\Gamma_{\lambda}^L(\rho)$ in $G_{L,L'}$ are given by

$$\tilde{\Gamma}^{L}_{\lambda}(\boldsymbol{\rho}) = R^{l}_{m\mu}(\Omega_{\hat{\boldsymbol{\rho}}}^{-1})\tilde{\gamma}^{l}_{\mu\nu}(\rho), \gamma^{l'}_{\mu\nu}(\rho)$$

$$\Gamma^{L'}_{\lambda}(\boldsymbol{\rho}) = R^{l}_{\mu m}(\Omega_{\hat{\boldsymbol{\rho}}})\gamma^{l}_{\mu\nu}(\rho)$$
(2.94)

The separable representation in eqn 2.90 with these coefficients is exact. Truncations at small $(\mu\nu)$ are accurate both at large energies or at large bond lengths. The lowest order terms are sufficient to obtain the point scattering approximation, and in the limit $\rho \to \infty$ to recover the PWA.

In this way, with the separable representation of $G_{L,L'}(\rho)$ presented above, the MS expansion can be reexpressed in terms of scattering matrices. Considering for example a path with N-1 scattereres, it is given by the exact MS expansion

$$G_{L_NL_0}^{(N-1)}(\mathbf{R}_1, ..., \mathbf{R}_N) = \sum_{L_i} G_{L_N, L_{N-1}}(\boldsymbol{\rho}_N), ..., t_{l_2}(\mathbf{R}_2) G_{L_2, L_1}(\boldsymbol{\rho}_2) t_{l_1}(\mathbf{R}_1) G_{L_1, L_0}(\boldsymbol{\rho}_1) \quad (2.95)$$

where L_0, L_N denote fixed initial and final angular momenta. Substitution of the explicit expression for $G_{L,L'}(\rho)$ in eqn (2.90) leads to the exact equivalent form:

$$G_{L_{N}L_{0}}^{(N-1)}(\mathbf{R}_{1},...,\mathbf{R}_{N}) = \frac{e^{\rho_{1}+\rho_{2}+...\rho_{N}}}{\rho_{1}\rho_{2}...\rho_{N}} \sum_{\lambda_{I}} M_{\lambda_{1},\lambda_{N}}^{L_{0},L_{N}}(\boldsymbol{\rho}_{1}\boldsymbol{\rho}_{N})F_{\lambda_{N},\lambda_{N-1}}(\boldsymbol{\rho}_{N}\boldsymbol{\rho}_{N-1})X...F_{\lambda_{3},\lambda_{2}}(\boldsymbol{\rho}_{3},\boldsymbol{\rho}_{2})F_{\lambda_{2},\lambda_{1}}(\boldsymbol{\rho}_{2},\boldsymbol{\rho}_{1})$$

this formula represents an exact formula for curved wave MS. The scattering amplitude matrices $F_{\lambda\lambda'}(\rho, \rho')$ at each site are defined by the partial wave expansion

$$F_{\lambda\lambda'}(\boldsymbol{\rho}, \boldsymbol{\rho}') = \sum_{L} t_l \Gamma^L_{\lambda}(\boldsymbol{\rho}) \tilde{\Gamma}^L_{\lambda'}(\boldsymbol{\rho}') = \sum_{l} t_l \gamma^l_{\mu\nu}(\rho) R^l_{\mu\mu'}(\Omega_{\hat{\rho}\hat{\rho}'}) \tilde{\gamma}^l_{\mu'\nu'}(\rho')$$
(2.97)

where ρ, ρ' are the bonds leading to and from the site in question. The separable angular momentum dependent termination matrix is

$$M_{\lambda_0,\lambda_N}^{L_0,L_N}(\boldsymbol{\rho}_1\boldsymbol{\rho}_N) = \Gamma_{\lambda_0}^{L_0}(\rho_1)\tilde{\Gamma}_{\lambda_N}^{L_N}(\rho_N)$$
(2.98)

The dependence of the coefficients $\tilde{\gamma}^l_{\mu\nu}(\rho)$ and $\gamma^l_{\mu\nu}(\rho)$ on ρ implies

that $F_{\lambda\lambda'}(\boldsymbol{\rho}, \boldsymbol{\rho}') \approx \rho^{-(2\nu+\mu)} \rho'^{-(2\nu'+\mu')}$ for large ρ, ρ' , and hence, the dominant matrix element is generally $F_{00,00}$. This is precisely the effective, curved wave scattering amplitude $F_{00,00}(\boldsymbol{\rho}, \boldsymbol{\rho}') = f_{00,00}(\rho, \rho', \beta) \ (\beta = \cos^{-1}(\hat{\boldsymbol{\rho}} \cdot \hat{\boldsymbol{\rho}}'))$. Keeping only this dominant term is equivalent to point scattering approximation, and yields the same contribution of PWA but with an effective scattering amplitude $f_{00,00}(\rho, \rho', \beta)$ replacing $f(\theta)$. The next level of approximation consists of keeping all terms up to first order in $1/\rho$. This yields a (3x3) matrix containing only the terms $(\mu\nu) = (0,0), (\pm 1,0)$. The second order expression correct to $O(1/\rho^2)$ is a (6x6) matrix that, in addition, contains the terms (0,1) and $(\pm 2,0)$.

2.9 Calculational details

• Scattering potential. The nature of the effective one-particle scattering potential V has been considered by several authors [145, 146, 147, 148]. The photoelectron potential differs significantly from that used in ground-state calculations based on the LDA familiar from band-structure theory. The optical potential V appears in the non- Hermitian but otherwise Schrödinger-like, one-particle Dyson equation for the photoelectron (quasiparticle) states ψ ,

$$[-\frac{1}{2}\nabla^{2} + V(E)]\psi = E\psi$$
 (2.99)

(in atomic units), or its relativistic generalization in terms of the Dirac equation. Here the operator

$$V(E) = V_{coul} + \Sigma(E) \tag{2.100}$$

consists of the net Coulomb potential V_{coul} felt by the photoelectron and a self-energy $\Sigma(E)$, which is analogous to the exchange-correlation potential V_{xc} in ground-state calculations [149] for the excited electron. A local approximation for the functional form of $\Sigma(E)$ is an excellent approximation for high energy excited states, partly due to the decrease of the de Broglie wavelength with increasing energy. Also the energy dependence of $\Sigma(E)$ must be considered. This variation corresponds physically to turning off the exchange interaction with increasing energy. V(E) also depends on the particular N-particle final state being considered [119].

• Charge densities and potential. The atomic scattering centers are described completely by atomic phase shifts, calculated from spherically symmetric atomic-like potentials inside the muffin tins. Green's-function propagators are employed to connect the scattering centers. Accurate calculations depend on good potentials, since they determine the strength of the scattering at each site. Near the center of each atom, the charge density of the atomic core will be large and dominate the potential, i.e. the potential is approximately atomic-like very close to the nucleus, where the spherical approximation is highly accurate. In the outer regions of the atom and between the atoms, the bonding properties of a material determine the distribution of charge,

and the potential is generally anisotropic and the anisotropy depends on the type of bonding present and the types of atoms. In close-packed metals, the electronic wave functions overlap so strongly that the bonding is quite flat and isotropic while in other systems there can be strong spatial variations. In EXAFS and photoemission spectroscopy the kinetic energy of the excited electron is large, and the electron is less sensitive to the details of the potential at the outer edges of the atom and in the regions between the atoms. The electron is mainly scattered by the inner parts of the atomic potential and moves more or less freely in the average potential within the flat interstitial region. It is essential to use approximations that conserve overall charge neutrality for an accurate determination of the energy reference. The most often used approach is the Mattheiss prescription [150], based on overlapping, neutral, atomiccharge densities. It is a very good approximation to the total ground-state charge distribution. It requires placing the charge density from a neutral-atom calculation on each atomic center and then using a direct superposition of these charges to obtain the total charge distribution around any given atom. A muffin tin mainly has the charge density due to the central atom. At the edges of the muffin tin, however, some charge density from neighboring atoms spills in, thus removing the spherical symmetry. Generally the charge density is spherically averaged, using, for example, the efficient Loucks [151] algorithm. The Coulomb potential is easily calculated for such spherically symmetric charge densities [151]. The neutral atomic-charge density may be calculated in several ways. In standard electronic-structure calculations a groundstate LDA exchange-correlation potential is typically used for crystalline solids, while a Hartree-Fock exchange is often used for molecular calculations. It is important to take into account the energy dependence of the exchange-correlation potential, which includes the quasiparticle character of the excited electron and reflects the decreasing importance of the Pauli principle with increasing energy.

- Mean free path. The mean free path is calculated by ab initio theoretical calculations of inelastic losses [147], based on the complex, energy-dependent, electron gas self-energy of Hedin and Lundqvist [152] in the local-density approximation. The use of a complex, energy-dependent self-energy provides a more accurate, system-dependent description of the damping of the electronic waves in a material. The Hedin-Lundqvist model is the most widely used self-energy for XAFS calculations.
- Atomic configuration. In determining the muffin-tin scattering potential, the question of the appropriate atomic configuration for the final state with the core hole is not unambiguous. For the absorbing atom a reasonable approximation is a neutral atomic configuration of a free atom of atomic number Z + 1 with a missing electron in a given core level, corresponding to the fully relaxed primary channel [153].
- Interstitial potential. The most efficient multiple-scattering treatments assume that the interstitial potential has no spatial variation (i.e., is constant); this is generally not true. For excited-state calculations the interstitial region is lossy and energy dependent. The critical parameter for determining structural information (the wave number k of the excited photoelectron) depends on the choice made for the average

value of the potential in the interstitial region. the spatial variation of the charge density in the interstitial region is called *warping* of the potential or charge density. Methods that include this effect are called fullpotential techniques (since the muffintin potential captures only the spherical part of the potential and misses the spatial dependence in the interstitial region).

• Excited-state effects-energy reference. The photoelectron of energy E moves in a uniform (lossy) optical potential, which is conventionally taken to be the average value $V_{int}(E) = \langle V(E) \rangle$ in the interstitial region. In general this uniform potential is energy dependent and complex valued, and hence the concept of a fixed inner potential is not well defined. With $V_{int}(E)$ as an energy reference, the inelastic loss in a system is mostly accounted for by the uniform mean-free-path term calculated at the interstitial density. The scattering perturbation is then defined as the difference with respect to the uniform potential, which we denote by a lower-case v. This potential is usually expressed as a sum over a set of local potentials v_i relative to atomic sites \mathbf{r}_i , i.e.,

$$v = V(E) - V_{int} = \sum_{j} v_j (\mathbf{r} - \mathbf{r}_j)$$
(2.101)

Some treatments, for example [154], use a real muffin-tin zero. The variation of $V_{int}(E)$ over the range of XAFS energies roughly amounts to the magnitude of the groundstate exchange hole, i.e., $V_{xc} \approx k_F/\pi$ in atomic units, where k_F is the Fermi momentum and is typically about 10 eV. To circumvent this ambiguity in the comparison of theoretical XAFS standards with experiment, it is useful to define a fixed energy reference E_0 , the photoabsorption energy threshold. Experimentally, this threshold corresponds to the energy at the onset of an absorption edge. However, values of E_0 that are typically valid to within a few eV may be estimated from the chemical potential μ of a homogeneous electron gas at the average interstitial-charge density. The errors introduced by the electron-gas approximation and the averaging of the interstitial potential and charge density are such that these estimates are typically a few eV higher than those from self-consistent calculations [155, 156, 157, 158].

• Relativistic effects. In atomic theory it has long been recognized that relativistic effects are only important for very heavy atoms, where the kinetic energy of the electrons becomes quite large near the nucleus of the atom and relativistic corrections are essential. These corrections modify the wave functions and energy eigenvalues of the electronic states, and change the self-consistent potential. In contrast, at large distances from the atom the kinetic energy of the outermost electrons responsible for bonding properties and the photoejected electrons are usually well into the nonrelativistic regime. Thus relativity can strongly affect the production of the photoelectron through the dipole matrix elements, but have a weak effect on the propagation of a photoelectron [151]. Clearly the electron propagators, which vary as $\exp(ikR)$, are essentially nonrelativistic (assuming spin-independent potentials), and thus most of the propagation involves knowledge of the electron's behavior at large distances from the nucleus where relativistic effects are usually negligible, even for heavy atoms. Thus

the only place where relativity can play a substantial role is in the phase shifts themselves. A conventional approach in many electronic-structure methods has been to use semirelativistic solutions for the wave function [159, 160]. Such an approach solves the Dirac equation, but averages the spin-orbit term over the two j components for each 1. Then the semirelativistic wave function is matched onto its nonrelativistic form in the outer part to find the phase shifts appropriate for a nonrelativistic regime, one can form the correct linear superposition (using Clebsch-Gordan coefficients) of the nonrelativistic Green's-function propagators to form propagators of the correct relativistic symmetry [161].

• Many body effects. Inelastic losses give the final photoelectron state a finite lifetime and hence lead effectively to a broadened one-electron spectrum. They divide in intrinsic and extrinsic processes. Extrinsic losses are those in the propagation of the photoelectron and include excitations of plasmons, electron-hole pairs, and inelastic scattering. They are described in terms of a complex, energy-dependent self energy $\Sigma(E)$, which gives both a real energy shift and a decay. $\Sigma(E)$ arises from the dynamically screened exchange interaction between the photoelectron and the system and is generally treated in the LDA ($\Sigma(E, \rho)$). The real part of $\Sigma(E)$ accounts for the energy dependence of the exchange and causes systematic shifts of location of the peaks compared to the positions obtained for the ground state, while the imaginary part gives rise to the mean free path. A generalization of the local-density approximation for excited states is the Hedin-Lundqvist GW/ plasmon-pole self-energy $\Sigma_{HL}(E,\rho)$ [146, 162], again based on a uniform electron-gas model. The advantage of this formulation over other approximations, such as the nonlocal Hartree-Fock or the analogous LDA Dirac-Hara self-energies [163], is that extrinsic losses are represented fairly accurately in terms of the imaginary part of $\Sigma(E,\rho)$. The effect of the imaginary part of the self-energy is similar to Lorentzian broadening of the XAFS spectrum with a half-width $Im\Sigma$ [127] and accounts for extrinsic losses. As noted above, the Hedin-Lundqvist [152] self-energy $\Sigma_{HL}(E)$ yields a good approximation for these losses [156] for EXAFS.

Intrinsic losses refer to excitations in response to creation of the core hole (e.g., shakeup or shakeoff processes). The quantum-mechanical amplitudes of the different processes can in principle interfere, and hence one cannot simply add their transition rates. However, they are accounted for phenomenologically by a constant many-body amplitudereduction factor S_0^2 which is a many body integral given by $S_0 = |\langle \psi_0^{(N-1)} | \psi_0^{N-1} \rangle|$ where $\psi_0^{(N-1)}$ is the N-1 final state calculated in presence of a hole and a photoelectron. This is reasonable approximation at high energies, when the sudden approximation is valid. Then the dominant contribution to the many-body dipole matrix element is given by $M_{fi} = \langle \psi_{phe} | \boldsymbol{\epsilon} \cdot \mathbf{r} | \psi_c \rangle \langle \psi_0^{(N-1)} | \psi_0^{N-1} \rangle$ where the prime refers to states calculated in the presence of the core hole. Thus the intensity in the lowest energy or primary channel is reduced in magnitude from the one-particle expression by the square modulus of the many body overlap integral. If $S_0^2 \neq 1$, there must be contributions from multielectron transitions in which the (N-1) state is excited $|\psi_n^{N-1}\rangle$

with excitation energy E_n . The reduction S_n should be energy dependent; it is usually small (for $n \neq 0$) and would vanish by orthogonality in the absence of relaxation. Due to completeness of the ψ'^{N-1} states, the sum of the weights S_n^2 is unity. They can be interpreted in the sudden approximation as the probabilities that the ion, initially in the ground state, finds itself in the *nth* final excited state, $|\psi_n^{N-1}\rangle$. According to the Manne-Aberg theorem, the centroid of the excitation spectrum corresponds to Koopman's theorem for the transition energy [164]. The difference between the centroid and the onset of absorption is defined as the relaxation energy. Since Koopman's theorem involves the groundstate wave functions, if the excitation spectrum were a d-function spectrum, the initial-state rule would be valid. The initial-state rule states that the photoelectron should be calculated with the ground-state charge density (i.e., in the absence of a core hole). Such a photoelectron would then have a Koopman's energy given by the difference between one-electron eigenvalues. At low energies close to threshold, no additional excitations are allowed (by conservation of energy, the photoexcited electron needs sufficient energy to cause the additional excitations), and only the primary channel is available. This is consistent with the final-state rule, in which the core hole is fully relaxed, since such a photoelectron energy would include a relaxation energy. Conversely, at high energy all the possible channels are active, and the average energy of the excitation spectrum is centered around the Koopman's theorem value.

2.10 Use of general potential in MS theory

MS theory is generally restricted to muffin-tin potentials, which are spherically symmetric inside the atomic spheres and constant in the interstitial region. The difference between the true potential and its muffin-tin form can be quite serious when there is a building up of charge density along a bond or when most of the charge lies in the interstitial region. A general formulation of the MS equations for any (local) potential has been given by Natoli et al [138]. The final result will turn out to be a straightforward generalization of the equations valid for the muffin tin case, and is easily amenable to computer programming. The derivation of the MS equations in the general case follows the Green's function approach as used by Beleznay and Lawrence [165] to introduce nonzero interstitial potentials in the calculation of electronic band structure. For the interstitial region, a local potential simplify greatly the solution, like the Hedin and Lungvist potential [152], which is based on the freeelectron gas approximation of the Dyson self-energy of the real system under study. This potential is energy dependent and incorporates the effect of the free electron gas exchange, the Coulomb correlation hole, and the screened exchange. Its complex part describes the inelastic processes that damp the photoelectron wave. Simpler version, within the local density approximation, are the $X\alpha$ potential and the Dirac-Hara free electron gas exchange potential [166]. An improvement on this approach is the time dependent LDA [167] which incorporates in a self consistent way the effect of the time dependent field induced by the external radiation field on the photoionization cross section and takes into account polarization-type many-body effects influencing the response of the electronic system.

2.11 Multichannel MS theory

MS theory is based on an effective one particle scheme. Correlation effects can be taken into account in an average way in the framework of the local density scheme through the exchange-correlation potential, but in certain cases this approximation is not sufficient. All dynamical phenomena like screening, polarization, relaxation, autoionization, and decay, especially in the presence of a certain degree of electronic localization, fall outside the realm of effective one-electron theory. Correlation effects are essential to understand both the electronic properties of these systems, and the structural information which tends to be distorted or obscured by them. Core-level x-ray spectra are often strongly modified by electron correlation, in particular by the Coulomb and exchange interaction of the valence electrons with the core hole. The multichannel generalization [119] of MS theory incorporates both the description of the geometrical arrangement of the system and the electronic dynamics of the excitation process. The structure of the MS theory is unchanged, provided the propagation vector of the photoelectron between successive scattering events is changed according to the energy loss suffered. It is also possible to include collective excitations in the multichannel formalism. The mathematical formalism used is equivalent to the close-coupling scheme used in the field of electron-molecule collisions and to the configuration interaction methods used by Fano [168] and Davis and Feldkamp [169, 170] to describe interaction effects between bound and continuum configurations in photoemission and photoabsorption. The multichannel theory enables one to take a quantitative account of all possible outcomes of the photoemission process. The final state wavefunction represents the photoelectron leaving the system in a different state.

2.12 Magnetic and natural dichroism in photoemission and absorption

MS theory offers a unified view also to natural and magnetic dichroism in absorption and photoemission from core states, that brings to the fore similarities and differences of these two spectroscopies and their intimate connection via a generalized optical theorem. Before finishing this chapter, it is important to spend a few words about the light polarization dependence of the photoabsorption and photoemission croos section from a cluster. This topic will be treated again in the case of two electrons emission.

In the case of absorption of circularly polarized light from a non magnetic material, the only way to observe a dichroic effect in the X-ray energy region is via an interference effect between the dipole and quadrupole transition operators, the interference with magnetic dipole operator being depressed by roughly three orders of magnitude [171]. The effect is small ($\Delta \sigma / \sigma \approx 10^{-2} - 10^{-3}$) but definitely measurable on third generations synchrotron radiation rings. In a MS approach, it can be shown that the effect is proportional to the imaginary part of the amplitude of creating the final state photoelectron into an angular momentum state selected by the electric dipole operator at the photoabsorbing site, times the full MS amplitude for returning at the same site to be annihilated in an angular momentum

tum state selected by the quadrupole operator (or viceversa). An absorption experiment conserves parity, therefore it is invariant in particular to a mirror reflection containing the incident photon direction. Since this operation interchanges the hands of circular polarization, if the system is invariant to it, the absorption does not depend on the helicity of the photon and therefore there is no dichroism. If instead the system as a whole is not invariant, it may well happen that a subset of MS paths transform into itself under the reflection, thus they don't contribute to the dichroic signal. This is the case of signal scattering paths. Hence the dichroic absorption reflects only pure MS processes and only those processes that involve subsets of atoms not invariant under reflection. Therefore in a path analysis the dichroic measurement brings about a drastic simplification that can be exploited to advantage in structural analysis. As in the case of magnetic circular dichroism (MCD), a sum rule can be established that measures the degree of mixing of even and odd parity components in the ground state wavefunction of the system. In photoemission the escape direction of the photoelectron constitues a new degree of freedom. Considering also the incident photon direction and a third direction describing the orientation of the system under study (a molecular axis in case of oriented molecules on a surface, the normal to a surface, etc..), the combined system of photon plus target can exhibit a definite handedness. More important, since the final state wave function is complex, the argument used in the case of photoabsorption to show that dipole only transitions do no give rise to CD, does not apply here, so that one can observe CD in the angular dependence of photoemission with the sole dipole operator. Obviously the angle integrated signal averages to zero. All the symmetry arguments described above can be applied here. Adding spin in the above analysis does not require a major modification of the formalism [118]. If a spin dependent atomic t-matrix is introduced in the MS equations due to the presence of spin dependent potentials (whether by internal exchange or spin-orbit interaction) and an additional spin index is added to the wavefunction amplitudes $(B^i_{L\sigma})$ all the above consideration carry through to this case, with due regard taken for the spin degree of freedom. In particular one can show that MCD in absorption is proportional to the average of the operators L, S and T in the final state integrated over all directions of the photoelectron at each energy, from which a sum rule derives in a way similar to natural CD. Moreover magnetic dichroic photoemission brings about a similar selective power, in that the signal is proportional to the average of the same operators over a single final state labeled by the photoelectron wave vector along the direction of detection. A further selectivity and probing power into the electronic properties of the system under study is provided by the detection of the photoelectron spin. In case of non magnetic materials the measure of the photo spin yield provides a further insight into the spin-orbit interaction, both in the initial and the final state. the use of the combined elemental selectivity and spin sensitivity of these core level spectroscopies has the potentiality to probe element-specific magnetic moments, exchange and spin-orbit splitting, and atomic-scale magnetic structure. To properly address such problems, it is essential to use probes which are capable to combine elemental selectivity with sensitivity to local order, both geometric and magnetic, spin specificity with sensitivity to atomic scale magnetic structure. The interpretation of these spectroscopies will pose a further challenge to future research. In fact the reduced dimensionality causes a general increase of electron correlation phenomena. At present one of the schemes for calculating X-ray absorption spectra and

photoelectron diffraction patterns from inner core levels in condensed matter is based on the reduction of the many-body problem to the problem of one-electron moving in an effective optical potential given by the local density approximation of the electron self-energy (Hedin-Lundqvist exchange-correlation potential). Despite the substantial success of this approach much remains to be done in the way of eliminating the various approximations (muffin-tin approximation for the potential, the local density approximation for the electron self-energy, the neglect of intrinsic relaxation processes) in order to forge a more reliable tool for extracting structural and electronic informations from the experimental spectra.

Chapter 3

Multiple Scattering approach to two electrons resonant emission

3.1 Importance of the angular correlation between photoelectron and Auger electron

In a coincidence experiment the photoelectron and the Auger electron coming from the decay of the core hole corresponding to that photoelectron are detected in time coincidence. This means that within the time reolution of the experimental apparatus, these two electrons can be considered as emitted simultaneously. Many informations about the dynamics of the decay and on core hole polarization induced by photon absorption can be obtained by the angular correlation between the Auger and the photoelectrons, i.e. the angular distribution of one of the electron measured in coincidence with the other one at a fixed position in space. For example one could think to detect the photoelectron in the plane perpendicular to the beam, along the light polarization or not, and to make a scan of the other electron in a particular plane (again it can be the plane perpendicular to the beam) or to scan over all the solid angle. The correlations between the two electrons leads to changes in the angular distribution of the scanning electron depending on the position of the fixed electron. Thus detecting the fixed electron at different position, the angular distribution of the second one varies, and it is interesting to study how it varies. This happens in all coincidence experiments: photon-photon, electron-electron, electron-photon and for every source one can use (photon beam, electron beam, ion impact,..). It is interesting to study such angular distributions since there are some parametrized expression which can be used to fit the data to extract the radial matrix elements, which contains the dynamic of the process. The importance of photoelectron-Auger spectroscopy over the other coincidence technique is in the fact that the Auger decay is only due to Coulomb interaction, and thus it allows to study the many body properties of the system and moreover can probe the interaction between core and valence states. The correlation between photoelectron and Auger electron since it depends strongly on the initial and final state symmetries such as parity, angular momentum, spin and also on the interference between the different open decay channels.

The importance of this technique in atomic physics relies in the possibility to study:

i) the so called 3-body problem, which one of the fundamental topics in scattering theory (2 electrons in the field of the ion)

ii) extraction of the matrix elements (the aim is to find experimental condition for which the cross section can give all the dynamical parameters necessary to describe the process within a certain model)

iii) the interference between the two electrons when for example they have the same energy or when the photoelectron is slower than the Auger electron (in this case the Auger electron overpass the photoelectron and there is a strong interference effects which make the angular distribution distorted). This gives rise to constructive/destructive intereference effects, as already described in the first chapter.

The importance of this technique in solid state physics relies in the possibility to:

i) to separate features which are generally overlapped in common auger spectra (this can be due to the fact that different spin-orbit partners edges can have Auger decay that overlap in energy); by the coincidence technique you choose a particular energy for the photoelectron and you detect only Auger electrons in time coincidence with those photoelectrons, so you can separate such overlapping features

ii) the only electrons pairs which are considered are those which can be considered as simultaneosly emitted; the electrons cannot come from a very deep layers, otherwise many losses could bring decoherence and they would not be detected as significant data. So the coincidence spectra are given by electrons which do not come from a very deep layer in the sample. Thus the technique has a big surface sensitivity. Scuh sensitivity has been verifies by expriments and should also be reproduced by theory

iii) since it can probe the interaction between core and valence levels, it can be used to study the deviations observed from the well known sum rules in dichroism experiments, which anyway relies on a single particle approach.

iv) it allows to eliminate the contribution of secondary electrons

3.2 Calculation of the cross section

A description of the emission of the two electrons, which takes into account the multiple scattering effects through the crystal potential, is still lacking, and this work aims to formulate such an approach. We aim at describing the process using the MS eleone electron approach, which is versatile and useful in our case to cope with the scattering problem. The idea is to demonstrate that even in presence of scattering effects, the core hole polarization still has the leading role in determining the angular correlation between the two electrons. We will consider core-core transitions, thus the final two holes wavefunctions are written as localized states. Such description can also be used as a first approximation for core-valence-valence transitions in materials where the valence levels are narrow and strictly localized on a single atomic site.

We want to calculate the differential cross section for the double ionization process: photoemission+Auger decay. The Hamiltonian of the system is given by:

$$H_{tot} = H_0 + V = H_{mat} + H_{\gamma} + V$$
(3.1)

Generally one can avoid to consider the term H_{γ} (as mentioned in section 2.5) and consider $H_0 = H_{mat}$. In our case the V operator contains both the interaction between matter and radiation field and the Coulomb interaction between electrons, which gives rise to the Auger decay. Thus, in the non relativistic limit, by minimal substitution for the electron impulse $p \rightarrow p + \frac{e}{c} \mathbf{A}(\mathbf{r}_i, t)$ in the presence of the radiation field and using the Coulomb gauge, we have:

$$V = V_{I1} + V_{I2} = \sum_{i=1}^{n} \frac{e}{mc} \vec{p}_i \cdot \mathbf{A}(\mathbf{r}_i) + \frac{e^2}{2mc^2} \mathbf{A}^2 + \sum_{i < j} V(|\mathbf{r}_i - \mathbf{r}_j|)$$
(3.2)

Thus we will retain only the first and the last term in eqn. (3.2), and we will call them V_{I1}, V_{I2} to indicate the two ionization potentials.

We can start from the golden rule. The transition probability per unit time can be written as:

$$W_{i\to f} = \frac{2\pi}{\hbar} \sum_{f} |\langle f|T|i\rangle|^2 \,\delta(\hbar\omega + E_i - \xi_a - \xi_b - E_f) \tag{3.3}$$

The energy conservation is assured by the δ function where E_i, E_f are the energy of the initial atom and of final state doubly charged ion, ξ_a, ξ_b are the energies of the two outgoing electrons.

The cross section is given by $W_{i\to f}$ normalized to the incident flux $I_0 = c/V$, where c is the speed of the light and V is the normalization volume for photons. The cross section will depend on all the fixed quantum numbers in the experiment (i.e. the initial core level, the final multiplet term, and so on). The T transition operator is given in terms of the Green's operator $G(E) = \lim_{\epsilon \to 0^+} \frac{1}{E-H+i\epsilon}$, where $H = H_{mat} + V_{I1} + V_{I2}$.

The relation between the transition operator and the Green's function is given by (see eqn. 2.3):

$$T = V + VGV = V_{I1} + V_{I2} + (V_{I1} + V_{I2})G(V_{I1} + V_{I2})$$
(3.4)

thus

$$< f|T|i> = < f|V|i> + < f|VG(E)V|i> = < f|V|i> + \sum_{n} < f|VG|n> < n|V|i> = < f|V|i> + \sum_{n} \frac{< f|V|n> < n|V|i>}{E-E_{n}}$$
(3.5)

At the lowest order in V, the transition operator can be approximated by the perturbation V. The emission of two subsequent electrons (photoelectrons and Auger electrons) happens through the second order interaction, i.e. it is described by the second term on the right hand side of eqn. (3.5). In the numerator, only V_{I1} acts on the initial state $|i\rangle$ while in the second step only the Coulomb interaction V_{I2} acts on the intermediate state $|n\rangle$. Using the Dyson expansion for the Green function we can replace the second order term in eqn (3.4):

$$T \approx V + V G_0 V \tag{3.6}$$

where G_0 is the resolvent operator of the unpertubed Hamiltonian H_{mat} .

Thus at the second order in the interaction potential V we have for the transition amplitude:

$$\langle f|T|i\rangle = \langle f|V + VG_0 V|i\rangle \tag{3.7}$$

The energy E in the denominator in (3.5) is equal to $E_i + \hbar \omega$, whether G is approximated with G_0 or not.

3.3 One and two step model

In principle one should consider the interference between the direct process (DPI) when two electrons are directly emitted following one photon absorption and the photoelectron-Auger electron emission, which is the corresponding resonant process. The two emitted electrons are indistinguishable, and one should treat them as such. This is the so called one step model. Neglecting the direct process, the matrix element for the resonant process can be written as:

$$< f|T|i> = \sum_{n} \int_{0}^{\infty} \frac{< f|V_{I2}|n> < n|V_{I1}|i>}{E - E_n + \frac{i\Gamma_n}{2}} d\tau$$
 (3.8)

In our case the initial state is given by the electronic system in the ground state plus the photon field and the final state is given by a double ionized residual ion plus two continuum electrons. This transition amplitude takes into account *resonances* in the ionization continuum described by the intermediate states n. These resonances are not only produced by

discrete excitations, but also by the interacting continua; each intermediate state n together with the characteristic (resonance) energy denominator, links the photoionization amplitude with Coulomb amplitude. The summation over n imply the sum over the discrete quantum numbers and the integration over τ exhausts the whole ionization continua of the intermediate states, including a summation over negative τ values (inner shell excitations and subsequent spectator Auger decay). The sum over n is a sum over j_c, j_{cz} of the possible core hole intermediate states; then the energy denominator is $\hbar \omega + E_i - E_{j_c(j_{cz})} + \frac{\Gamma_n}{2}$; the dependence on j_{cz} which is indicated in brackets is only for magnetic systems, where the polarization of the core levels is induced by the interaction with the polarized valence levels and the magnetic sublevels j_{cz} are not degenerate.

The one step model can be applied even in the case of a particular resonant state. Indeed, usually the sum over n can be limited to one defined state. Such state must be characterized by well defined energy, angular momentum and parity. Moreover, the natural level width must not be too large, since the core hole state must live enough to establish an intermediate state. The energy separation with neighbouring states must be large compared to the respective level widths Γ in order to avoid overlapping states. Thus, if it is possible to separe decays coming from different spin-orbit partner edges, then the sum is only over the projection number j_{cz} . In a non magnetic system, there is no dependence on j_{cz} and the complex energy E_{j_c} can be written as:

$$E_{j_c} \approx E_{j_c}^+ + \tau - \frac{i\Gamma_{j_c}}{2} \tag{3.9}$$

where τ is the energy of the excited electron in the intermediate state. The intermediate state, given by the ion and the excited (in the continuum or in an upper level) electron, will transform, through the Coulomb interaction, in the final state with a doubly ionized ion and two continuum electrons.

If one then neglects possible final state interactions, and takes into account explicitly the antisymmetrization of the scattering wave functions with respect to the exchange of excited electrons it is possible to write:

$$T = \frac{\langle \psi_{\beta e_2}^- | V | \Phi_r \rangle \langle \Phi_{re_1} | D | \psi_g \rangle}{\epsilon_2 + E_{\beta}^{++} - E_r^{+} - \frac{1}{2} i \Gamma_r} - \frac{\langle \psi_{\beta e_1}^- | V | \Phi_r \rangle \langle \Phi_{re_2} | D | \psi_g \rangle}{\epsilon_1 + E_{\beta}^{++} - E_r^{+} - \frac{1}{2} i \Gamma_r}$$
(3.10)

where $\psi_g, \psi_{\beta e_2}$ are the ground state and the final state wave function, the latter given by the doubly ionized ion and the outgoing electron; Φ_{re_1} is the wave function for the intermediate ion plus the outgoing electron. We have explicitly written V_{I1} and V_{I2} . Finally, if one assumes that the energies of the two electrons are different, then only one term will contribute, and one obtains the conventional two step formulation of the process photoionization + Auger decay:

$$T = \frac{\langle \psi_{\beta e_2}^- | V | \Phi_r \rangle \langle \Phi_{re_1} | D | \psi_g \rangle}{\epsilon_2 + E_{\beta}^{++} - E_r^{+} - \frac{1}{2} i \Gamma_r}$$
(3.11)

In the following we will use a single particle approach: this means that we describe the states as the state of the only particle strictly involved in the transition. Then the initial state is identified with the core wave function related to the electron that will be excited.

In the dipole excitation we make use of the sudden approximation, thus no relaxation effects are considered, and the electrons not involved in the transition are frozen. Again for the Auger decay, only the two final holes created by the process will be considered for the total angular momentum of the final ion. This means that no further recoupling with possible outer empty levels is considered. Also the intermediate state is simply identified with the core hole quantum numbers. These considerations imply that we are using two approximations: we are treating with a closed shell system, and we are considering the single particle approach. the identification of the intermediate state quantum numbers with the ones related to the core hole is appropriate in case of closed shell atoms but it can be considered valid in more general cases if the spin orbit interaction of the core hole exceeds the lifetime broadening of the two spin-orbit edges. In presence of core-outer shell interactions, this approximation is still valid if the energy splitting due to interaction with outer shells does not exceed the lifetime broadening. In our model, the photoelectron is considered as a pure spectator in the Auger decay neglecting interactions between photoelectron and the core hole state left behind. This is not longer valid if the experiment is performed only a little above threshold (photoelectron energy ≈ 20 meV), in this case recoupling between the ougoing electron and the intermediate ion must be considered.

Now, using an ELECTRON PICTURE, the cross section can be written as:

$$\frac{d^{3}\sigma}{d\mathbf{k}_{a}d\mathbf{k}_{b}}(\hbar\omega,\epsilon,l_{c},l_{1},l_{2},L,S,J) \propto \tilde{\Gamma}(\xi) \sum_{\sigma_{b}\sigma_{a}J_{z}} |\sum_{j_{cz}} < n_{c}l_{c}j_{c}m_{c},\psi_{a}|V_{I2}|(n_{1}l_{1},n_{2}l_{2})LSJ > <\psi_{p}|V_{I1}|n_{c}l_{c}j_{c}m_{c}>|^{2} (3.12)$$

where the intial state is given by a core electron which is excited thorugh dipole operator to a photoelectron continuum state. The state $(n_1l_1, n_2l_2)LSJ$ describe two electrons which interact and give rise to the Auger decay. the final state for the Auger decay is one electron that has gone down to refill the core hole and one Auger continuum electron. The factor $\tilde{\Gamma}(\xi)$ is given by $\tilde{\Gamma}(\xi) = \left| \frac{1}{\hbar \omega + E_i - E_{jc}^+ - \xi_a + \frac{i\Gamma_{jc}}{2}} \right|^2 = \frac{1}{(\xi_a^0 - \xi_a)^2 + \frac{\Gamma_{jc}^2}{4}} = \frac{1}{(\xi_b^0 - \xi_b)^2 + \frac{\Gamma_{jc}^2}{4}}$ where we have used the energy conservation. The factor $\tilde{\Gamma}(\xi)$ is proportional to the Lorentzian function. The sum over σ_b, σ_a, J_z are the sum over the spin projection of the Auger electron and photoelectron, and the sum over the total momentum of the residual ion, which are not observed. The sums over projections of the initial state are internal sums, differently from single photoemission cross section, where different initial state contribute incoherently to the intensity.

Using a HOLE PICTURE, the cross section can be written as:

$$\frac{d^3\sigma}{d\mathbf{k}_a d\mathbf{k}_b}(\hbar\omega,\epsilon,l_c,l_1,l_2,L,S,J) \propto \tilde{\Gamma}(\xi) \sum_{\sigma_b \sigma_a J_z} |\sum_{j_{cz}} < (n_1 l_1, n_2 l_2) LSJ |V_{I2}| n_c l_c j_c m_c, \psi_a > < n_c l_c j_c m_c |V_{I1}| \psi_p > |^2 \quad (3.13)$$

In the HOLE PICTURE, the initial state is given by the hole in the continuum space which will be fullfilled by the photoelectron, the intermediate state is given by the core hole plus the Auger continuum hole which will be fullfilled by the Auger electron, and the final state is given by the two final holes. The proportionality constants are given by the photon-matter interaction term, by the normalization of the transition rate to the incoming flux. Generally, also the density of the states enters in such constants, but in our case we will include the density of the states factors in the outgoing electrons wavefunctions, since such factors correspond exactly to the normalization costants to one state per Rydberg. In the following we will suppose that the quantum numbers $l_c, j_c, l_1, l_2, L, S, J$ are known. The result is the same both if we write the cross section using the electron or the hole picture. In the following we will refer to the electron picture.

3.4 Second quantization form of the cross section

To derive the proportionality costants in eqn. 3.13 let's write the matrix elements involved in second quantization form.

The interaction potential can be expressed as:

$$\mathbf{A}(\mathbf{r}_i) = \sqrt{\frac{2\pi\hbar c^2}{V\omega_q}} \sum_{\mathbf{q},\boldsymbol{\epsilon}_q} (a_q \boldsymbol{\epsilon}_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}_i} + a_q^+ \boldsymbol{\epsilon}_{\mathbf{q}}^* e^{-i\mathbf{q}\cdot\mathbf{r}_i})$$
(3.14)

$$V_{I2} = \sum_{j,l,k} V_{i,j,l,k} a_k^+ a_l^+ a_j a_i$$
(3.15)

where $\epsilon_{\mathbf{q}}$ is the complex light polarization, and \mathbf{q} is the wavenumber vector given by $q = \omega/c = 2\pi/\lambda$; moreover $V_{i,j,l,k} = \langle \phi_k \phi_l | \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} | \phi_i \phi_j \rangle$.

Now we indicate with ψ_{2e^-} the electrons involved in the Auger decay, with ψ_{e_1}, ψ_c the photoelectron and the core hole respectively. n_{γ} is the photon state with n photons with \mathbf{q}, ϵ_q . Then the photoionization matrix element becomes:

$$<\psi_{e_{1}},\psi_{2e^{-}}|\otimes<\dots n_{\gamma}-1\dots|\frac{e}{mc}\sum_{\mathbf{q},\boldsymbol{\epsilon}_{q}}\sqrt{\frac{2\pi\hbar c^{2}}{V\omega_{\mathbf{q}}}}\sum_{i}[a_{q}\boldsymbol{\epsilon}_{\mathbf{q}}e^{i\mathbf{q}\cdot\mathbf{r}_{i}}+a_{q}^{+}\boldsymbol{\epsilon}_{\mathbf{q}}^{*}e^{-i\mathbf{q}\cdot\mathbf{r}_{i}}]\cdot\mathbf{p}_{i}$$

$$|\psi_{c},\psi_{2e^{-}}>\otimes|\dots n_{\gamma}\dots>=$$

$$\frac{e}{mc}\sum_{\mathbf{q},\boldsymbol{\epsilon}_{q}}\sqrt{\frac{2\pi\hbar c^{2}}{V\omega_{k}}}<\dots n_{\gamma}-1\dots|a_{q}|n_{\gamma}>\cdot<\psi_{e_{1}}|\sum_{i}\epsilon_{\gamma}\cdot\mathbf{p}_{i}\cdot|\psi_{c}>$$
(3.16)

The two particle state which will give rise to Auger decay have been simply factorized since the dipole operator doesn't act on them. We choose the most common case, with only one photon $n_{\gamma} = 1$ in the initial state. Then we use the dipole approximation, i.e. we assume that the spatial variations of the electric field in atomic scale regions can be neglected; thus we can approximate $e^{ik \cdot r_i} \approx 1$. Moreover, we can transform the matrix elements from impulse to spatial coordinate representation using $[\sum_i \mathbf{r}_i, H_0] = \frac{i\hbar}{m} \sum_i \mathbf{p}_i$; then we have:

$$<\psi_{e_{1}}|\sum_{i}\mathbf{p}_{i}|\psi_{c}>=\frac{m}{i\hbar}<\psi_{e_{1}}|\sum_{i}(\mathbf{r}_{i}H_{0}-H_{0}\mathbf{r}_{i})|\psi_{c}>=im\frac{E_{e_{1}}-E_{c}}{\hbar}<\psi_{e_{1}}|\sum_{i}\mathbf{r}_{i}|\psi_{c}>=im\omega_{k}<\psi_{e_{1}}|\sum_{i}\mathbf{r}_{i}|\psi_{c}>$$
(3.17)

As discussed by [172], equality in (3.17) holds only for exact eigenstates of H. For approximate wavefunctions, the expressions on the right and left side of 3.17 will differ in general. The length form tends to weight the large r part of the wavefunctions, the acceleration form the small r part and the velocity form the intermediate range. Hence for wavefunctions determined variationally to give good energy expectation values, the intermediate range of r is probably best determined, and hence velocity form for the electric dipole matrix element would seem to give best results. However, for a certain class of approximate wavefunctions, namely, those obtained as the exact solutions of a model Hamiltonian, justifications may be given for using the length formula exclusively [173, 174].

Thus for the photoionization matrix elements we have:

$$im\omega_k \frac{e}{mc} \sqrt{\frac{2\pi\hbar c^2}{V\omega_k}} < \psi_{e_1} |\epsilon \cdot \sum_i \mathbf{r}_i|\psi_c >$$
(3.18)

As already discussed in the second chapter in the single particle approximation we can remove the \sum_i , i.e. the sum over all electrons in the system/ For Coulomb matrix elements:

$$<\psi_{e_1};\psi_{e_2};\psi_c|V|\psi_{e_1},\psi_{2e^-}> = <\psi_{e_2};\psi_c|V|\psi_{2e^-}>$$
(3.19)

where the photoelectron wave function has been factorized. Thus the cross section (3.13) can be rewritten as:

$$\frac{d^{3}\sigma}{d\mathbf{k}_{a}d\mathbf{k}_{p}}(\hbar\omega,\epsilon,l_{c},j_{c},l_{1},l_{2},L,S,J) = \frac{dW_{i\rightarrow f}}{dI_{0}} = \frac{V}{c}\frac{2\pi}{\hbar}\omega_{k}^{2}\frac{e^{2}}{c^{2}}\frac{2\pi\hbar c^{2}}{V\omega_{k}} \times \tilde{\Gamma}(\xi)\sum_{\sigma_{b}\sigma_{a}J_{z}}|\sum_{j_{cz}} < n_{c}l_{c}j_{c}m_{c},\psi_{a}^{-}|\frac{e^{2}}{|\mathbf{r}_{1}-\mathbf{r}_{2}|}|(n_{1}l_{1},n_{2}l_{2})LSJ > <\psi_{p}^{-}|\epsilon\cdot\mathbf{r}|n_{c}l_{c}j_{c}m_{c}\rangle|^{2} = 4\pi^{2}\alpha\hbar\omega\tilde{\Gamma}(\xi)\sum_{\sigma_{a}\sigma_{p}J_{z}}|\sum_{j_{cz}} < n_{c}l_{c}j_{c}m_{c},\psi_{a}^{-}|\frac{e^{2}}{|\mathbf{r}_{1}-\mathbf{r}_{2}|}|(n_{1}l_{1},n_{2}l_{2})LSJ > <\psi_{p}^{-}|\epsilon\cdot\mathbf{r}|n_{c}l_{c}j_{c}m_{c}^{-}3\approx0^{2}$$

where the minus superscript has been added to the outgoing electrons wavefunctions to indicate that they are solutions of the Schrödinger equation with incomincg boundary wave conditions, i.e. they are time reversed scattering states. The sum over the azimuthal quantum numers of the initial core is in this case an intermediate sum, while for conventional photoelectron studies this sum should be incoeherent. This is so since the intermediate state would be a photoelectron in the continuum and a hole in the residual ion, but the hole is written as an initial state for convenience; in photoemission the photoelectron+the hole constitues the final state, thus one sum incoherently over the quantum numbers of the hole; here the hole, though written as an initial state, it constitutes an intermediate state. If it is not possible to discriminate a particular j_c then the formula will contain an energy denominator, which cannot be factorized out as in (3.20):

$$\frac{d^{3}\sigma}{d\mathbf{k}_{a}d\mathbf{k}_{b}}(\hbar\omega,\epsilon,l_{c},j_{c},j_{c}',l_{1},l_{2},L,S,J) = 4\pi^{2}\alpha\hbar\omega \cdot \sum_{\sigma_{a}\sigma_{p}J_{z}}|\sum_{j_{cz}}\frac{\langle n_{c}l_{c}j_{c}m_{c},\psi_{a}^{-}|\frac{e^{2}}{|\mathbf{r}_{1}-\mathbf{r}_{2}|}|(n_{1}l_{1},n_{2}l_{2})LSJ\rangle\langle\psi_{p}^{-}|\boldsymbol{\epsilon}\cdot\mathbf{r}|n_{c}l_{c}j_{c}m_{c}\rangle}{\hbar\omega+E_{i}-E_{j_{c}}^{+}-\xi_{a}+\frac{i\Gamma_{j_{c}}}{2}}|^{2} (3.21)$$

3.4.1 First step: photoionization

The core hole state can be written as spin-orbit coupled state:

$$|\psi_c(\mathbf{r})\rangle = |l_c, \frac{1}{2}j_c j_{cz}\rangle = R_{nl_c}(r) \sum_{m_c \sigma_c} C^{j_c j_{cz}}_{l_c m_c \frac{1}{2}\sigma_c} Y_{l_c m_c}(\hat{\mathbf{r}}) \chi_{\sigma_c}$$
(3.22)

where the R_{nl_c} is the radial function and $Y_{l_cm_c}(\hat{r})$ are the spherical harmonics; we have used the standard notation for the Clebsch Gordan coefficient [Varshalovich] (In the case of magnetic systems also the exchange interaction must be considered-such interaction leads to a mixing of the two spin-orbit partner states with the same projection j_{cz}). Due to localization of the initial core state at site *i*, we need only the expression for the final state wavefunction at site *i*, i.e. the continuum wavefunctions for the photoelectron is given by the solution of the MS problem inside the *i*th atomic muffin tin sphere is given by:

$$\psi_{\mathbf{k}_{p}}^{+}(\mathbf{r}_{i}) = \frac{1}{4\pi} \sqrt{\frac{k_{p}}{\pi}} \sum_{l_{p}m_{p}\sigma_{p}} B_{l_{p}m_{p}}^{i}(\mathbf{k}_{p}) R_{\epsilon l_{p}}(r_{i}) Y_{l_{p}m_{p}}^{*}(\hat{\mathbf{r}}_{i}) \chi_{\sigma_{p}}$$
(3.23)

The wavefunctions are normalized to one state per Rydberg (the factor deriving by density of the states is incorporated in the normalization of the wavefunction). The radial part are normalized to:

$$R_l = \frac{R_l}{r_s^2 W[j_l, R_l]} \tag{3.24}$$

where $W[j_l, R_l]$ is the wronskian of Bessel function and the radial solution inside the muffin tin sphere.

The scattering amplitude are given by:

$$B_{l_p m_p}^{i}(\mathbf{k}_p) = \sum_{j l'_p m'_p} \tau_{l_p m_p l'_p m'_p}^{oj} i^{l'_p} Y_{l'_p m'_p}(\hat{\mathbf{k}}_p) e^{i\mathbf{k}_p \cdot \mathbf{R}_{j0}}$$
(3.25)

The scattering amplitude obey the MS equations:

$$\sum_{jlm} [(t^{-1})^{ij}_{l'm'l''m''} + G^{ij}_{l'm'l''m''}]B^{j}_{l''m''} = i^l e^{i\mathbf{k}\cdot\mathbf{R}_{i0}} \sqrt{\frac{k}{\pi}} Y_{lm}(\hat{\mathbf{k}})$$
(3.26)

Eq. (3.26) states the fact that the total scattering amplitude $B^i_{l'm'}$ at site i is given by the sum of the atomic scattering amplitude plus the amplitude of all the waves that come from all other sites with any angular momentum, propagate to site *i*, and are scattered by the atom located there.

The scattering matrix in (3.25) is given by:

$$\tau_{l_p m_p l'_p m'_p}^{ij} = \left(\left\{ (t_{l_p m_p l'_p m'_p}^{ij})^{-1} \delta_{ij} \delta_{l_p m_p l'_p m'_p} + G_{l_p m_p l'_p m'_p}^{ij} \right\} \right)^{-1}$$
(3.27)

where t^{ij} is the atomic scattering matrix and $G^{ij}_{l_p m_p l'_p m'_p}$ are the Green functions which describe the propagation of the electron from an atomic site to another.

The time reversed state is:

$$\psi_p^- = \Theta \psi_{\mathbf{k}_p}^+(\mathbf{r}_i) = \frac{1}{4\pi} \sqrt{\frac{k_p}{\pi}} \sum_{l_p m_p \sigma_p} B_{l_p m_p}^{i*}(\mathbf{k}_p) R_{\epsilon l_p}(r_i) Y_{l_p m_p}(\hat{\mathbf{r}}_i) \Theta \chi_{\sigma_p}$$
(3.28)

If the spin is neglected $\psi^- = \Theta \psi^+ = (\psi^+)^*$. However here we have also inserted the spin part, though not coupled to the orbital one. Thus the time reversal operation does not simply coincide with complex conjugation, but an extra phase is needed. However we will not write such factor but just indicate with $\Theta \chi_{\sigma}$ the time reversal of the spinor.

The bra is given by:

$$\langle \psi_p^- | = \langle \Theta \psi_{\mathbf{k}_p}^+(\mathbf{r}_i) | = \frac{1}{4\pi} \sqrt{\frac{k_p}{\pi}} \sum_{l_p m_p \sigma_p} B^i_{l_p m_p}(\mathbf{k}_p) R^*_{\epsilon l_p}(r_i) Y^*_{l_p m_p}(\hat{\mathbf{r}}_i) < \Theta \chi_{\sigma_p} |$$
(3.29)

The transition operator in the dipole approximation can be written as:

$$\boldsymbol{\epsilon} \cdot \mathbf{r} = \frac{4\pi}{3} r \sum_{\mu} Y_{1\mu}^*(\hat{\boldsymbol{\epsilon}}) Y_{1\mu}(\hat{\mathbf{r}})$$
(3.30)

where $\hat{\epsilon}$, $\hat{\mathbf{r}}$ are given by $\theta_{\epsilon}\phi_{\epsilon}$ and $\theta_{r}\phi_{r}$ respectively. The dipole matrix elements then is given by:

$$<\psi_{p}^{-}|\boldsymbol{\epsilon}\cdot\mathbf{r}|l_{c}\frac{1}{2}j_{c}j_{cz}>=\frac{4\pi}{3}\frac{1}{4\pi}\sqrt{\frac{k_{p}}{\pi}}\sum_{\mu}\sum_{l_{p}m_{p}\sigma_{p},m_{c},\sigma_{c}}Y_{1\mu}^{*}(\hat{\boldsymbol{\epsilon}})R(nl_{c},El_{p})C_{l_{c}m_{c}\frac{1}{2}\sigma_{p}}^{j_{c}j_{cz}}$$
$$B_{l_{p}m_{p}}^{i}(\mathbf{k}_{p})\int_{0}^{\pi}Y_{l_{c}m_{c}}(\hat{\mathbf{r}})Y_{1\mu}(\hat{\mathbf{r}})Y_{l_{p}m_{p}}^{*}(\hat{\mathbf{r}})\sin\theta d\theta\int_{0}^{2\pi}d\phi$$
(3.31)

The scalar product between the spin functions gives $\delta_{\sigma_c,\sigma_p}$; the radial integral is given by

$$R(nl_c, El_p) = \int_0^\infty R^*_{El_p}(r) r^3 R_{nl_c}(r) dr$$
(3.32)

The integral $\int_0^{\pi} Y_{l_c m_c}(\hat{r}) Y_{1\mu}(\hat{r}) Y_{l_p m_p}^*(\hat{r}) \sin \theta d\theta \int_0^{2\pi} d\phi$ is the Gaunt coefficient and it can be written in terms of Clebsch Gordan coefficient. Thus we obtain:

$$<\psi_{p}^{-}|\epsilon \cdot \mathbf{r}|l_{c}\frac{1}{2}j_{c}j_{cz}>=$$

$$=\frac{4\pi}{3}\frac{1}{4\pi}\sqrt{\frac{k_{p}}{\pi}}\sum_{\mu}\sum_{l_{p}m_{p}\sigma_{p}m_{c}}Y_{1\mu}^{*}(\hat{\epsilon})R(nl_{c},El_{p})C_{l_{c}m_{c}\frac{1}{2}\sigma_{p}}^{j_{c}j_{cz}}B_{l_{p}m_{p}}^{i}(\mathbf{k}_{p})\sqrt{\frac{3}{4\pi}}\frac{\hat{l}_{c}}{\hat{l}_{p}}C_{l_{c}010}^{l_{p}m_{p}}C_{l_{c}m_{c}M}^{l_{p}m_{p}}(3.33)$$
3.4.2 Second step: Auger decay

The final state is given by the Auger electron in the continuum and the electron that has refilled the primary hole; the photoelectron wave functions can be factorized in the Auger matrix element. As in photoemission, the final state representing the auger electron must consist asymptotically of an outgoing plane wave plus incoming spherical waves. The main difficulty in such calculations for solids is that most transitions of interest involve valence states so that generally band structure of the system needs to be taken into account. The total final wave function can be written as (the sum over σ_a is external in the expression of the cross section):

$$<\psi_{a}^{-}, l_{c}\frac{1}{2}j_{c}j_{cz}| = = \frac{1}{4\pi}\sqrt{\frac{k_{a}}{\pi}}\sum_{l_{a}m_{a}}R_{El_{a}}(r_{1})Y_{l_{a}m_{a}}^{*}(\hat{\mathbf{r}}_{1})B_{l_{a}m_{a}}^{i}(\mathbf{k}_{a})\chi_{\sigma_{a}}^{+}\sum_{m_{c}\sigma_{c}}C_{l_{c}m_{c}\frac{1}{2}\sigma_{c}}^{j_{c}j_{cz}}R_{nl_{c}}(r_{2})Y_{l_{c}m_{c}}^{*}(\hat{\mathbf{r}}_{2})\chi_{\sigma_{c}}^{+} = \frac{1}{4\pi}\sqrt{\frac{k_{a}}{\pi}}R_{nl_{c}}(r_{2})\sum_{l_{a}m_{a}\sigma_{c}m_{c}}R_{El_{a}}(r_{1})B_{l_{a}m_{a}}^{i}(\mathbf{k}_{a})\chi_{\sigma_{a}}^{+}\chi_{\sigma_{c}}^{+}C_{l_{c}m_{c}\frac{1}{2}\sigma_{c}}^{j_{c}j_{cz}}\times \sum_{L_{ac}M_{ac}}C_{l_{a}m_{a}l_{c}m_{c}}^{L_{ac}M_{ac}}[Y_{l_{a}}^{*}(\hat{\mathbf{r}}_{1})\otimes Y_{l_{c}}^{*}(\hat{\mathbf{r}}_{2})]_{L_{ac}M_{ac}}$$
(3.34)

where the scattering amplitude for the Auger electron is given by:

$$B_{l_a m_a}^i(\mathbf{k}_a) = \sum_{y l'_a m'_a} \tau_{l_a m_a l'_a m'_a}^{iy} i^{l'_a} Y_{l'_a m'_a}(\hat{\mathbf{k}}_a) e^{i\mathbf{k}_a \cdot \mathbf{R}_y}$$
(3.35)

We have introduced the bipolar spherical harmonic $[Y_{l_a}^*(\hat{\mathbf{r}}_1) \otimes Y_{l_c}^*(\hat{\mathbf{r}}_2)]_{L_{ac}M_{ac}}$ [176]. We have assumed that there is no correlation between the two escaping electrons and that their common boundary condition applies separately to each continuum electron wavefunction. The final state with two holes (nl_1, nl_2) in an electron picture represents the two electrons which interact and give rise to the Auger decay. This state can be represented by a Slater determinant, so that the Auger matrix element contains the coulomb direct integral and the corresponding exchange integral.Let's consider the wave function for these two electrons:

$$\psi(l_1(1)l_2(2)) = |((l_1(1)l_2(2))LS)JJ_z \rangle =$$

$$\sum_{MS_z} C_{LMSS_z}^{JM} \sum_{m_1m_2\sigma_1\sigma_2} C_{l_1m_1l_2m_2}^{LM} C_{\frac{1}{2}\sigma_1\frac{1}{2}\sigma_2}^{SS_z} \psi_{n_1l_1m_1\sigma_1}(1)\psi_{n_2l_2m_2\sigma_2}(2)$$
(3.36)

$$\psi(l_1(2)l_2(1)) = |((l_1(2)l_2(1))LS)JJ_z \rangle = \sum_{MS_z} C_{LMSS_z}^{JM} \sum_{m_1m_2\sigma_1\sigma_2} C_{l_1m_1l_2m_2}^{LM} C_{\frac{1}{2}\sigma_1\frac{1}{2}\sigma_2}^{SS_z} \psi_{n_1l_1m_1\sigma_1}(2)\psi_{n_2l_2m_2\sigma_2}(1)$$
(3.37)

where $\psi_{n_1 l_1 m_1 \sigma_1}$ is given by the product of the radial, angular, and spin part. The total function is given by the antisymmetric combination of the functions (3.36),(3.37):

$$\psi = \frac{1}{\sqrt{2}} \left\{ \psi(l_1(1)l_2(2)) - \psi(l_1(2)l_2(1)) \right\}$$
(3.38)

From the symmetries properties of Clebsch-Gordan coefficients:

$$C_{l_1m_1l_2m_2}^{LM} = (-1)^{l_1+l_2-L} C_{l_2m_2l_1m_1}^{LM}$$
(3.39)

$$C_{\frac{1}{2}\sigma_{1}\frac{1}{2}\sigma_{2}}^{SS_{z}} = (-1)^{1-S} C_{\frac{1}{2}\sigma_{2}\frac{1}{2}\sigma_{1}}^{SS_{z}}$$
(3.40)

Then it follows that:

$$\psi(l_1(2)l_2(1)) = (-1)^{l_1+l_2+1-L-S}\psi(l_2(1)l_1(2))$$
(3.41)

Therefore

$$\psi = \frac{1}{\sqrt{2}} \left\{ \psi(l_1(1)l_2(2)) + (-1)^{l_1 + l_2 - L - S} \psi(l_2(1)l_1(2)) \right\}$$
(3.42)

For equivalent holes $(n_1 = n_2, l_1 = l_2)$ the second term in (3.42) is equal to the first one and thus L + S must be even. In this case the second part in eqn. (3.42) is equal to the first part. However in this case particular attention must be given to the normalization factor, i.e. another $\frac{1}{\sqrt{2}}$ is needed.

It is convenient in a number of cases to represent the wave function ψ in the form of the product of the independent coordinate and spin functions, each of which do not have to be antisymmetric but must be combined in order to give a total antisymmetric wavefunction. Thus there are two cases:

$$\psi = \Phi_{LM}^+ Q_{SS_z}^- \tag{3.43}$$

$$\psi = \Phi_{LM}^- Q_{SS_z}^+ \tag{3.44}$$

where

$$\Phi^{+} = \frac{1}{\sqrt{2}} \left\{ \Phi_{LM}(l_{1}(1)l_{2}(2)) + \Phi_{LM}(l_{1}(2)l_{2}(1)) \right\} = \frac{1}{\sqrt{2}} \left\{ \Phi_{LM}(l_{1}(1)l_{2}(2)) + (-1)^{l_{1}+l_{2}-L} \Phi_{LM}(l_{2}(1)l_{1}(2)) \right\}$$
(3.45)

$$\Phi^{-} = \frac{1}{\sqrt{2}} \left\{ \Phi_{LM}(l_1(1)l_2(2)) - \Phi_{LM}(l_1(2)l_2(1)) \right\} = \frac{1}{\sqrt{2}} \left\{ \Phi_{LM}(l_1(1)l_2(2)) - (-1)^{l_1+l_2-L} \Phi_{LM}(l_2(1)l_1(2)) \right\}$$
(3.46)

$$Q_{SS_z}^+ = \frac{1}{\sqrt{2}} \left\{ Q_{SS_z}(\sigma_1(1)\sigma_2(2)) + (-1)^{1-S} Q_{SS_z}(\sigma_2(1)\sigma_1(2)) \right\}$$
(3.47)

$$Q_{SS_z}^+ = \frac{1}{\sqrt{2}} \left\{ Q_{SS_z}(\sigma_1(1)\sigma_2(2)) - (-1)^{1-S} Q_{SS_z}(\sigma_2(1)\sigma_1(2)) \right\}$$
(3.48)

Thus the total wave function can be written as:

$$\psi = \frac{1}{\sqrt{2}} \left\{ \Phi_{LM}(l_1(1)l_2(2)) \pm (-1)^{l_1+l_2-L} \Phi_{LM}(l_2(1)l_1(2)) \right\} Q_{SS_z}^{\mp}$$
(3.49)

where the upper signs are for triplet states.

Thus in LS coupling

$$\begin{aligned} &|((l_{1}\frac{1}{2}l_{2}\frac{1}{2})LS)JJ_{z} > = \\ &\sum_{MS_{z}} C_{LMSS_{z}}^{JJ_{z}} \sum_{m_{1}m_{2}\sigma_{1}\sigma_{2}} \frac{1}{\sqrt{2}} [C_{l_{1}m_{1}l_{2}m_{2}}^{LM}R_{n_{1}l_{1}}(r_{1})R_{n_{2}l_{2}}(r_{2})Y_{l_{1}m_{1}}(\hat{\mathbf{r}}_{1})Y_{l_{2}m_{2}}(\hat{\mathbf{r}}_{2})C_{\frac{1}{2}\sigma_{1}\frac{1}{2}\sigma_{2}}^{SS_{z}}\chi_{\sigma_{1}}(1)\chi_{\sigma_{2}}(2) - \\ &(-1)^{l_{1}+l_{2}-L+1-S}C_{l_{2}m_{2}l_{1}m_{1}}^{LM}R_{n_{1}l_{1}}(r_{2})R_{n_{2}l_{2}}(r_{1})Y_{l_{1}m_{1}}(\hat{\mathbf{r}}_{2})Y_{l_{2}m_{2}}(\hat{\mathbf{r}}_{1})C_{\frac{1}{2}\sigma_{2}\frac{1}{2}\sigma_{1}}\chi_{\sigma_{1}}(2)\chi_{\sigma_{2}}(1)] = \\ &\frac{1}{\sqrt{2}}\sum_{MS_{z}} C_{LMSS_{z}}^{JJ_{z}}\sum_{\sigma_{1}\sigma_{2}} [R_{n_{1}l_{1}}(r_{1})R_{n_{2}l_{2}}(r_{2})\left\{Y_{l_{1}}(\hat{\mathbf{r}}_{1})\otimes Y_{l_{2}}(\hat{\mathbf{r}}_{2})\right\}_{LM}C_{\frac{1}{2}\sigma_{1}\frac{1}{2}\sigma_{2}}\chi_{\sigma_{1}}(1)\chi_{\sigma_{2}}(2) + \\ &(-1)^{l_{1}+l_{2}-L-S}R_{n_{1}l_{1}}(r_{2})R_{n_{2}l_{2}}(r_{1})\left\{Y_{l_{2}}(\hat{\mathbf{r}}_{1})\otimes Y_{l_{1}}(\hat{\mathbf{r}}_{2})\right\}_{LM}C_{\frac{1}{2}\sigma_{2}\frac{1}{2}\sigma_{1}}\chi_{\sigma_{1}}(2)\chi_{\sigma_{2}}(1)\right]$$

$$(3.50)$$

For equivalent electrons we have:

$$|((l_1 l_2) LS) J J_z \rangle = \frac{1}{2} R_{n l_1}(r_1) R_{n l_2}(r_2) \sum_{M S_z} C_{LM S S_z}^{J J_z} \left[Y_{l_1}(\hat{\mathbf{r}}_1) \otimes Y_{l_2}(\hat{\mathbf{r}}_2) \right]_{LM} \left[\chi_{\frac{1}{2}} \otimes \chi_{\frac{1}{2}} \right]_{S S_z} (3.51)$$

In (3.50),(3.51) we have considered that the two electrons are in a closed shell and we have ignored all possible couplings with other open shells; in other words, we have considered that the interaction between the two final holes is stronger than Coulomb interaction between the electrons in the electronic level of the two holes and the electrons of other eventually not closed shells. The Coulomb interaction can be written as a scalar product between spherical harmonics [177]:

$$\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} = 4\pi e^2 \sum_{k=0}^{\infty} \frac{1}{2k+1} \frac{r_{<}^k}{r_{>}^{k+1}} [Y_k(\hat{\mathbf{r}}_1) \otimes Y_k(\hat{\mathbf{r}}_2)]_{00} (\sqrt{2k+1}) (-1)^{-k}$$
(3.52)

Thus we obtain for the Auger decay matrix elements:

$$< \psi_{a}^{-}, l_{c}, \frac{1}{2} j_{c} j_{cz} | \frac{e^{2}}{|\mathbf{r}_{1} - \mathbf{r}_{2}|} | ((l_{1}l_{2})LS)JJ_{z} > = = \frac{4\pi e^{2}}{\sqrt{2}} \sqrt{\frac{k_{a}}{\pi}} \sum_{L_{a}kL_{ac}M_{ac}M\sigma_{1}\sigma_{2}S_{z}} \frac{(-1)^{-k}}{\hat{k}} [\int_{0}^{\infty} \int_{0}^{\infty} R_{n_{c}l_{c}}(r_{2})R_{El_{a}}(r_{1})\frac{r_{<}^{k}}{r_{>}^{k+1}}R_{n_{1}l_{1}}(r_{1})R_{n_{2}l_{2}}(r_{2})r_{1}^{2}dr_{1} r_{2}^{2}dr_{2} \int d\Omega_{1}d\Omega_{2}[Y_{l_{1}}(\Omega_{1})\otimes Y_{l_{2}}(\Omega_{2})]_{LM}[Y_{k}(\Omega_{1})\otimes Y_{k}(\Omega_{2})]_{00}[Y_{l_{a}}^{*}(\Omega_{1})\otimes Y_{l_{c}}^{*}(\Omega_{2})]_{L_{ac}M_{ac}}C_{\frac{1}{2}\sigma_{1}\frac{1}{2}\sigma_{2}} \chi_{\sigma_{1}}(1)\chi_{\sigma_{2}}(2)\chi_{\sigma_{a}}^{+}(1)\chi_{\sigma_{c}}(2) - (-1)^{l_{1}+l_{2}-L+1-S} \int_{0}^{\infty} \int_{0}^{\infty} R_{n_{c}l_{c}}(r_{2})R_{El_{a}}(r_{1})\frac{r_{<}^{k}}{r_{>}^{k+1}}R_{n_{2}l_{2}}(r_{1})R_{n_{1}l_{1}}(r_{2}) r_{1}^{2}dr_{1}r_{2}^{2}dr_{2} \int d\Omega_{1}d\Omega_{2}[Y_{l_{2}}(\Omega_{1})\otimes Y_{l_{1}}(\Omega_{2})]_{LM}[Y_{k}(\Omega_{1})\otimes Y_{k}(\Omega_{2})]_{00}[Y_{l_{a}}^{*}(\Omega_{1})\otimes Y_{l_{c}}^{*}(\Omega_{2})]_{L_{ac}M_{ac}} C_{\frac{1}{2}\sigma_{2}\frac{1}{2}\sigma_{1}}\chi_{\sigma_{1}}(2)\chi_{\sigma_{2}}(1)\chi_{\sigma_{a}}^{+}(1)\chi_{\sigma_{c}}(2)] \sum_{m_{c}\sigma_{c}} C_{l_{c}m_{c}\frac{1}{2}\sigma_{c}}C_{LMSS_{z}}L_{am_{a}l_{c}m_{c}}B_{l_{a}m_{a}}^{i}(\mathbf{k}_{a})$$

$$(3.53)$$

We can couple the first two bipolar spherical harmonics [178]:

$$[Y_{l_1}(\Omega_1) \otimes Y_{l_2}(\Omega_2)]_{LM} [Y_k(\Omega_1) \otimes Y_k(\Omega_2)]_{00} = \sum_{L'M'} C_{L'M'00}^{LM} \sum_{l_1al_2a} Q_{l_1l_2Lkk0}^{l_1al_2aL'} [Y_{l_1a}(\Omega_1) \otimes Y_{l_2a}(\Omega_2)]_{L'M'}$$
(3.54)

where $Q_{l_1 l_2 L k k 0}^{l_{1a} l_{2a} L}$ is given by

$$Q_{l_1 l_2 L k k 0}^{l_{1a} l_{2a} L} = \frac{\hat{l}_1 \hat{l}_2 \hat{L} (2k+1)}{4\pi} C_{l_1 0 k 0}^{l_{1a} 0} C_{l_2 0 k 0}^{l_{2a} 0} \left\{ \begin{array}{ccc} l_1 & k & l_{1a} \\ l_2 & k & l_{2a} \\ L & 0 & L \end{array} \right\}$$
(3.55)

From eqn 3.54 we have $\delta_{L'L}$ and $\delta_{M'M}$.

Thus in eqn. 3.53 we will have the integral of the product of two bipolar spherical harmonics:

$$\sum_{LM} C_{LM00}^{LM} \sum_{l_{1a}l_{2a}} Q_{l_{1}l_{2}Lkk0}^{l_{1a}l_{2a}L} \times \int [Y_{l_{1a}}(\Omega_{1}) \otimes Y_{l_{2a}}(\Omega_{2})]_{LM} [Y_{l_{a}m_{a}}^{*}(\Omega_{1}) \otimes Y_{l_{c}m_{c}}^{*}(\Omega_{2})]_{LacMac} d\Omega_{1} d\Omega_{2} = \sum_{LM} \sum_{l_{1a}l_{2a}} Q_{l_{1}l_{2}Lkk0}^{l_{1a}l_{2a}L} \delta_{l_{1a},l_{a}} \delta_{l_{2a},l_{c}} \delta_{L,L_{ac}} \delta_{M,M_{ac}} = \sum_{L} \sum_{l_{a}} \frac{\hat{l}_{1}\hat{l}_{2}\hat{L}(2k+1)}{4\pi} C_{l_{1}0k0}^{l_{a}0} C_{l_{2}0k0}^{l_{c}0} \left\{ \begin{array}{c} l_{1} & k & l_{a} \\ l_{2} & k & l_{c} \\ L & 0 & L \end{array} \right\} = \sum_{L} \sum_{l_{a}} \frac{(-1)^{l_{c}+l_{1}+k+L}}{\hat{k}\hat{L}} \frac{\hat{l}_{1}\hat{l}_{2}\hat{L}(2k+1)}{4\pi} C_{l_{1}0k0}^{l_{a}0} C_{l_{2}0k0}^{l_{c}0} \left\{ \begin{array}{c} l_{2} & l_{c} & k \\ l_{a} & l_{1} & L \end{array} \right\}$$
(3.56)

where in the last expression we have reduced the 9j symbol with one zero to a 6j symbol. Moreover, in our case we do not sum over L since L is known. The same happens for the exchange term, which gives:

$$\int d\Omega_1 d\Omega_2 [Y_{l_2}(\Omega_1) \otimes Y_{l_1}(\Omega_2)]_{LM} [Y_k(\Omega_1) \otimes Y_k(\Omega_2)]_{00} [Y_{l_a}^*(\Omega_1) \otimes Y_{l_c}^*(\Omega_2)]_{L_{ac}M_{ac}} = = \sum_{l_a} \frac{(-1)^{l_c+l_2+k+L}}{\hat{k}\hat{L}} \frac{\hat{l}_1 \hat{l}_2 \hat{L}(2k+1)}{4\pi} C_{l_20k0}^{l_a0} C_{l_10k0}^{l_c0} \left\{ \begin{array}{cc} l_1 & l_c & k\\ l_a & l_2 & L \end{array} \right\}$$
(3.57)

Thus we can write the Auger matrix elements in the following way:

$$<\psi_{a}^{-}, l_{c}\frac{1}{2}j_{c}j_{cz}|\frac{e^{2}}{|\mathbf{r}_{1}-\mathbf{r}_{2}|}|((l_{1}l_{2})LS)JJ_{z}> = \frac{e^{2}}{\sqrt{2}}\frac{1}{4\pi}\sqrt{\frac{k_{a}}{\pi}}\hat{l}_{1}\hat{l}_{2}(-1)^{l_{c}+L}\sum_{l_{a}k}(-1)^{l_{1}}[D_{k}(n_{1}l_{1}n_{2}l_{2},\epsilon l_{a}n_{c}l_{c})C^{l_{a}0}_{l_{1}0k0}C^{l_{c}0}_{l_{2}0k0}\left\{\begin{array}{cc}l_{2}&l_{c}&k\\l_{a}&l_{1}&L\end{array}\right\} + (-1)^{-L-S}$$

$$E_{k}(n_{2}l_{2}n_{1}l_{1},\epsilon l_{a}n_{c}l_{c})C^{l_{a}0}_{l_{2}0k0}C^{l_{c}0}_{l_{1}0k0}\left\{\begin{array}{cc}l_{1}&l_{c}&k\\l_{a}&l_{2}&L\end{array}\right\}]\sum_{m_{a}m_{c}\sigma_{c}MS_{z}}C^{JJ_{z}}_{LMSS_{z}}C^{j_{c}j_{cz}}_{l_{c}m_{c}\frac{1}{2}\sigma_{c}}$$

$$C^{LM}_{l_{a}m_{a}l_{c}m_{c}}C^{SS_{z}}_{\frac{1}{2}\sigma_{a}\frac{1}{2}\sigma_{c}}B_{l_{a}m_{a}}(\mathbf{k}_{a})$$

$$(3.58)$$

where $D_k(n_1l_1n_2l_2, \epsilon l_an_cl_c)$ and $E_k(n_2l_2n_1l_1, \epsilon l_an_cl_c)$ are the direct and exchange radial integrals.

3.4.3 The coincidence cross section

The amplitude of the process can be written in terms of the scattering amplitudes as the following:

$$\begin{aligned} A_{k_{a}k_{p}}(l_{c}, j_{c}, l_{1}, l_{2}, L, S, J) &= \\ \sum_{j_{c_{z}}} < \psi_{a}^{-}, l_{c}\frac{1}{2}j_{c}j_{cz}|\frac{e^{2}}{|\mathbf{r}_{1} - \mathbf{r}_{2}|}|((l_{1}l_{2})LS)JJ_{z} > <\psi_{p}^{-}|\epsilon \cdot \mathbf{r}|l_{c}\frac{1}{2}j_{c}j_{cz} > = \\ \frac{e^{2}}{\sqrt{2}}\hat{l}_{1}\hat{l}_{2}\hat{l}_{c}(-1)^{l_{c}+l_{1}+L}\frac{4\pi}{3}\sqrt{\frac{3}{4\pi}\frac{1}{4\pi}}\sqrt{\frac{k_{a}}{\pi}\frac{1}{4\pi}}\sqrt{\frac{k_{p}}{\pi}}\sum_{l_{p}l_{a}\mu k}\frac{1}{\hat{l}_{p}}Y_{1\mu}^{*}(\hat{\epsilon})R(n_{c}l_{c},El_{p})} \\ [D_{k}(n_{1}l_{1}n_{2}l_{2},\epsilon l_{a}n_{c}l_{c})d_{kl_{a}} + (-1)^{-L-S}E_{k}(n_{2}l_{2}n_{1}l_{1},\epsilon l_{a}n_{c}l_{c})e_{kl_{a}}]\sum_{m_{a}m_{c}\bar{m}_{c}\bar{\sigma}_{c}MS_{z}}C_{l_{c}010}^{l_{p}0}C_{l_{c}m_{c}1\mu}^{l_{p}m_{p}} \\ C_{LMSS_{z}}^{JJ_{z}}C_{l_{c}m_{c}\frac{1}{2}\sigma_{p}}^{j_{c}j_{c}j_{c}z}C_{l_{a}m_{a}l_{c}\bar{m}_{c}}C_{\frac{1}{2}\sigma_{a}\frac{1}{2}\bar{\sigma}_{c}}^{SS_{z}}B_{l_{a}m_{a}}(\mathbf{k}_{a})B_{l_{p}m_{p}}(\mathbf{k}_{p}) \end{aligned}$$

$$(3.59)$$

where

$$d_{kl_a} = C_{l_10k0}^{l_a0} C_{l_20k0}^{l_c0} \left\{ \begin{array}{cc} l_2 & l_c & k \\ l_a & l_1 & L \end{array} \right\}$$
(3.60)

$$e_{kl_a} = C_{l_20k0}^{l_a0} C_{l_10k0}^{l_c0} \left\{ \begin{array}{cc} l_1 & l_c & k \\ l_a & l_2 & L \end{array} \right\}$$
(3.61)

and where we have supposed that the spin correlation between the photoelectron and the core hole left behind is kept also in the second step. Indeed, in the Coulomb matrix elements the photoelectron state can be factorized since the Coulomb interaction doesn't involve this continuum electron. In our case the sum over j_c does not exist since we have supposed a well defined resonance state, but, in general, one should sum over the whole set of quantum numbers characterizing the intermediate state.

For the intensity we sum incoherently over the projection numbers of the final electron spin states, σ_p and σ_a , and over the possible final state of the two final holes state J_z .

The intensity is given by:

$$\frac{d^{2}\sigma}{d\mathbf{k}_{a}d\mathbf{k}_{p}}(l_{c}, j_{c}, l_{1}, l_{2}, L, S, J) = 4\pi^{2}\alpha\hbar\omega\Gamma(\xi)\sum_{\sigma_{a}\sigma_{p}J_{z}}|A|^{2} = 4\pi^{2}\alpha\hbar\omega\Gamma(\xi)\sum_{\sigma_{a}\sigma_{p}J_{z}}|\frac{e^{2}}{\sqrt{2}}\sqrt{\frac{4\pi}{3}}(\frac{1}{4\pi})^{2}\sqrt{\frac{k_{a}}{\pi}}\sqrt{\frac{k_{p}}{\pi}}\hat{l}_{1}\hat{l}_{2}\hat{l}_{c}(-1)^{l_{c}+l_{1}+L}\sum_{l_{p}l_{a}\mu k}\frac{1}{\hat{l}_{p}}Y_{1\mu}^{*}(\hat{\epsilon})R(n_{c}l_{c}, El_{p})$$

$$[D_{k}(n_{1}l_{1}n_{2}l_{2}, \epsilon l_{a}n_{c}l_{c})d_{kl_{a}} + (-1)^{-L-S}E_{k}(n_{2}l_{2}n_{1}l_{1}, \epsilon l_{a}n_{c}l_{c})e_{kl_{a}}]\sum_{m_{a}m_{c}m_{p}MS_{z}\bar{m}_{c}\bar{\sigma}_{c}j_{cz}}C_{l_{c}m_{c}}^{l_{p}0}(1-\beta)e_{kl_{a}}|L_{MSS_{z}}C_{l_{c}m_{c}}\frac{1}{2}\sigma_{p}}C_{l_{c}\bar{m}_{c}}^{j_{c}j_{c}}B_{l_{a}m_{a}}(\mathbf{k}_{a})B_{l_{p}m_{p}}(\mathbf{k}_{p})|^{2}$$

$$(3.62)$$

Now, since the index $l'_p m'_p$ and $l'_a m'_a$ have been already used for inside the definition of the scattering amplitudes, in writing the cross section we will write for the *bra* states $l''_p m''_p, l''_a m''_a$ as denoting the complex conjugate state of $l_p m_p, l_a m_a$. The indexes $l''_p m''_p, l''_a m''_a$ then will be used to denote the sum contained in the complex conjugate of the scattering amplitude $(B^i)_{l''_a m''_a}^*(\mathbf{k}_p)$ and $(B^i)_{l''_a m''_a}^*(\mathbf{k}_a)$. Writing explicitly the modulus square:

$$\frac{d^{2}\sigma}{d\mathbf{k}_{a}d\mathbf{k}_{p}}(l_{c}, j_{c}, l_{1}, l_{2}, L, S, J) =
4\pi^{2}\alpha\hbar\omega\Gamma(\xi)e^{4}\hat{l}_{1}^{2}\hat{l}_{2}^{2}\hat{l}_{c}^{2}(-1)^{2l_{c}+2L+2l_{1}}\frac{2}{3\pi}k_{a}k_{p}\frac{1}{(16\pi^{2})^{2}}\sum_{l_{p}l''_{p}l_{a}l''_{a}\mu\mu'kk'}\frac{1}{\hat{l}_{p}\tilde{l}''_{p}}Y_{1\mu}^{*}(\hat{\epsilon})Y_{1\mu'}(\hat{\epsilon}^{*})R(n_{c}l_{c}, El_{p})$$

$$R^{*}(n_{c}l_{c}, El''_{p})[D_{k}(n_{1}l_{1}n_{2}l_{2}, \epsilon l_{a}n_{c}l_{c})d_{kl_{a}} + (-1)^{-L-S}E_{k}(n_{2}l_{2}n_{1}l_{1}, \epsilon l_{a}n_{c}l_{c})e_{kl_{a}}]$$

$$[D^{*}_{k'}(n_{1}l_{1}n_{2}l_{2}, \epsilon l''_{a}n_{c}l_{c})d_{k'l''_{a}} + (-1)^{-L-S}E^{*}_{k'}(n_{2}l_{2}n_{1}l_{1}, \epsilon l'_{a}n_{c}l_{c})e_{k'l''_{a}}]C^{l_{p}0}_{l_{c}010}C^{l''_{p}0}_{l_{c}010}$$

$$\sum_{\sigma_{a}\sigma_{p}J_{z}m_{c}m'_{c}\bar{m}_{c}\bar{m}_{c}\bar{\sigma}_{c}\bar{\sigma}'_{c}MM'S_{z}S'_{z}j_{cz}j'_{cz}m_{a}m''_{a}m_{p}m''_{p}}C^{j_{c}j_{cz}}_{l_{c}m_{c}\frac{1}{2}\sigma_{p}}C^{j_{c}j_{c}j_{cz}}_{l_{c}m'_{c}\frac{1}{2}\sigma_{p}}C^{j_{c}j'_{cz}}_{l_{c}m'_{c}\frac{1}{2}\sigma_{p}}C^{j_{c}j'_{cz}}_{l_{c}m'_{c}\frac{1}{2}\bar{\sigma}'_{c}}C^{l_{p}m_{p}}_{l_{c}\bar{m}'_{c}\frac{1}{2}\bar{\sigma}'_{c}}C^{l_{p}m_{p}}_{l_{c}m'_{c}1\mu'}C^{l''_{p}m''_{p}}_{l_{c}m'_{c}1\mu'}$$

$$C^{JJ_{z}}_{LMSS_{z}}C^{JJ_{z}}_{LM'SS'_{z}}C^{LM}_{a}m_{a}l_{c}\bar{m}_{c}C^{LM'}_{l''_{a}m''_{a}l_{c}\bar{m}'_{c}}C^{SS_{z}}_{\frac{1}{2}\sigma_{a}\frac{1}{2}\bar{\sigma}_{c}}C^{SS'_{z}}_{\frac{1}{2}\sigma_{a}\frac{1}{2}\bar{\sigma}'_{c}}$$

$$B^{i}_{l_{a}m_{a}}(\mathbf{k}_{a})B^{i}_{l_{p}m_{p}}(\mathbf{k}_{p})B^{i*}_{l''_{a}m''_{a}}(\mathbf{k}_{a})B^{i*}_{l''_{p}m''_{p}}(\mathbf{k}_{p})$$
(3.63)

We can now sum over dummy projection variables $j_{cz}, j'_{cz}, \sigma_a, J_z$ [179]:

$$\sum_{j_{cz}} C_{l_c m_c \frac{1}{2} \sigma_p}^{j_c j_{cz}} C_{l_c \bar{m}_c \frac{1}{2} \bar{\sigma}_c}^{j_c j_{cz}} = \sum_{c\gamma} (-1)^{c+j_c + \bar{m}_c - \sigma_p} \hat{j}_c^2 C_{l_c m_c l_c - \bar{m}_c}^{c\gamma} C_{\frac{1}{2} - \sigma_p \frac{1}{2} \bar{\sigma}_c}^{c\gamma} \left\{ \begin{array}{cc} l_c & l_c & c \\ \frac{1}{2} & \frac{1}{2} & j_c \end{array} \right\}$$
(3.64)

$$\sum_{j_{cz}'} C_{l_c m_c' \frac{1}{2} \sigma_p}^{j_c j_{cz}'} C_{l_c \bar{m}_c' \frac{1}{2} \bar{\sigma}_c'}^{j_c j_{cz}'} = \sum_{gh} (-1)^{g+j_c + \bar{m}_c - \sigma_p} \hat{j}_c^2 C_{l_c m_c' l_c - \bar{m}_c'}^{gh} C_{\frac{1}{2} - \sigma_p \frac{1}{2} \bar{\sigma}_c'}^{gh} \left\{ \begin{array}{cc} l_c & l_c & g \\ \frac{1}{2} & \frac{1}{2} & j_c \end{array} \right\}$$
(3.65)

$$\sum_{\sigma_{a}} C_{\frac{1}{2}\sigma_{a}\frac{1}{2}\bar{\sigma}_{c}}^{SS_{z}} C_{\frac{1}{2}\sigma_{a}\frac{1}{2}\bar{\sigma}_{c}}^{SS_{z}'} = \sum_{\sigma_{a}} (-1)^{1+\bar{\sigma}_{c}+\bar{\sigma}_{c}'} \frac{\hat{S}^{2}}{2} C_{S-S_{z}\frac{1}{2}\bar{\sigma}_{c}}^{\frac{1}{2}-\sigma_{a}} C_{S-S_{z}\frac{1}{2}\bar{\sigma}_{c}}^{\frac{1}{2}-\sigma_{a}} = \frac{\hat{S}^{2}}{2} \sum_{\sigma_{a}} (-1)^{1+\bar{\sigma}_{c}+\bar{\sigma}_{c}'+2(S+\frac{1}{2}-\frac{1}{2})} C_{SS_{z}\frac{1}{2}-\bar{\sigma}_{c}}^{\frac{1}{2}\sigma_{a}} C_{SS_{z}\frac{1}{2}-\bar{\sigma}_{c}}^{\frac{1}{2}\sigma_{a}} = \frac{\hat{S}^{2}}{2} \sum_{f\varphi} (-1)^{1+\bar{\sigma}_{c}+\bar{\sigma}_{c}'} (-1)^{f+\frac{1}{2}-\bar{\sigma}_{c}-S_{z}'} 2C_{\frac{1}{2}-\bar{\sigma}_{c}\frac{1}{2}\bar{\sigma}_{c}'}^{f\varphi} C_{SS_{z}S-S_{z}'}^{f\varphi} \left\{ \begin{array}{cc} S & S & f \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{array} \right\}$$
(3.66)

$$\sum_{J_z} C_{LMSS_z}^{JJ_z} C_{LM'SS_z}^{JJ_z} = \sum_{ax} (-1)^{a+J+M'-S_z} \hat{J}^2 C_{LML-M'}^{ax} C_{S-S_zSS_z}^{ax} \left\{ \begin{array}{cc} L & L & a \\ S & S & J \end{array} \right\}$$
(3.67)

Then :

$$\begin{aligned} \frac{d^{2}\sigma}{d\mathbf{k}_{a}d\mathbf{k}_{p}}(l_{c}, j_{c}, l_{1}, l_{2}, L, S, J) &= 4\pi^{2}\alpha\hbar\omega\Gamma(\xi)\hat{j}_{c}^{2}\hat{j}_{c}^{2}\hat{J}^{2}\hat{S}^{2}l_{c}^{2}\hat{l}_{1}^{2}\hat{l}_{2}^{2}e^{4}\frac{2k_{a}k_{p}}{3\pi(16\pi^{2})^{2}}\sum_{\mu\mu'l_{a}l_{a}''}\frac{1}{l_{p}l_{p}''}K_{a}''}\frac{1}{l_{p}l_{p}''}Y_{1\mu}^{*}(\hat{\epsilon})\\ Y_{1\mu'}(\hat{\epsilon^{*}})R(n_{c}l_{c}, El_{p})R^{*}(n_{c}l_{c}, El_{p}'')[D_{k}(n_{1}l_{1}n_{2}l_{2}, \epsilon l_{a}n_{c}l_{c})d_{kl_{a}} + (-1)^{-L-S}E_{k}(n_{2}l_{2}n_{1}l_{1}, \epsilon l_{a}n_{c}l_{c}) \cdot\\ e_{kl_{a}}][D_{k'}^{*}(n_{1}l_{1}n_{2}l_{2}, \epsilon l_{a}'''n_{c}l_{c})d_{k'l_{a}''} + (-1)^{-L-S}E_{k'}^{*}(n_{2}l_{2}n_{1}l_{1}, \epsilon l_{a}'''n_{c}l_{c})e_{k'l_{a}''}]\\ &\sum_{\sigma_{p}m_{c}m_{c}'MS_{z}m_{a}m_{a}''m_{p}m_{p}''gcfa\bar{m}_{c}\bar{m}_{c}c\bar{\sigma}_{c}}(-1)^{c+j_{c}+\bar{m}_{c}+g+j_{c}+\bar{m}_{c}'+a+J+M'-S_{z}+f+\frac{1}{2}-S_{z}'+\bar{\sigma}_{c}'+1}C_{l_{c}010}^{l_{p}0}C_{l_{c}010}^{l_{p}''0}\\ C_{l_{c}m_{c}lc}^{c\gamma}-\bar{m}_{c}C_{\frac{1}{2}-\sigma_{p}\frac{1}{2}\bar{\sigma}_{c}}C_{l_{c}m_{c}'lc}^{gh}-\bar{m}_{c}'C_{\frac{1}{2}-\sigma_{p}\frac{1}{2}\bar{\sigma}_{c}'}C_{\frac{1}{2}-\bar{\sigma}_{c}\frac{1}{2}\bar{\sigma}_{p}'}C_{S-S_{z}SS_{z}'}C_{LML-M'}C_{S-S_{z}SS_{z}'}C_{l_{c}m_{c}1\mu}\\ C_{l_{c}m_{c}'1\mu'}^{l_{p}m_{p}''}C_{l_{a}m_{a}l_{c}\bar{m}_{c}}C_{l_{a}''m_{a}''l_{c}\bar{m}_{c}'}\left\{\begin{array}{lc}l_{c}&l_{c}&c\\ \frac{1}{2}&\frac{1}{2}&j_{c}\end{array}\right\}\left\{\begin{array}{lc}l_{c}&l_{c}&g\\ \frac{1}{2}&\frac{1}{2}&j_{c}\end{array}\right\}\left\{\begin{array}{lc}L&L&a\\ \frac{1}{2}&\frac{1}{2}&j_{c}\end{array}\right\}\\ B_{l_{a}m_{a}}(\mathbf{k}_{a})B_{l_{p}m_{p}}(\mathbf{k}_{p})B_{l_{a}''m_{a}''}^{i*}(\mathbf{k}_{a})B_{l_{p}''m_{p}''}^{i*}(\mathbf{k}_{p})\end{array}\right\}$$

We can sum over the spin projections of the residual doubly charged ion \mathcal{S}_z :

$$\sum_{S_z, (-S_z)} C_{S-S_z S S'_z}^{f\varphi} C_{S-S_z S S'_z}^{ax} = \delta_{a,f} \delta_{x,\varphi}$$
(3.69)

where we have rotated the first Clebsch Gordan coefficient. We can also sum over the spin projections of the photoelectron [180]:

$$\sum_{\sigma_{p},\bar{\sigma}_{c},\bar{\sigma}_{c}'} (-1)^{\frac{1}{2}+\bar{\sigma}_{c}'} C^{c\gamma}_{\frac{1}{2}-\sigma_{p}\frac{1}{2}\bar{\sigma}_{c}} C^{gh}_{\frac{1}{2}-\sigma_{p}\frac{1}{2}\bar{\sigma}_{c}'} C^{f\varphi}_{\frac{1}{2}-\bar{\sigma}_{c}\frac{1}{2}\bar{\sigma}_{c}'} = (-1)^{\frac{1}{2}+c+\frac{1}{2}+f} \hat{g} \hat{f} C^{c-\gamma}_{g-hf\varphi} \left\{ \begin{array}{cc} \frac{1}{2} & \frac{1}{2} & g\\ c & f & \frac{1}{2} \end{array} \right\}$$
(3.70)

Now we can couple the following Clebsch Gordan coefficients [181]:

$$C_{l_{c}m_{c}l_{c}-\bar{m}_{c}}^{c\gamma}C_{l_{c}m_{c}1\mu}^{l_{p}m_{p}}C_{l_{c}-\bar{m}_{c}l_{a}-m_{a}}^{L-M} = C_{l_{c}m_{c}l_{c}\bar{m}_{c}}^{c\gamma}C_{l_{c}m_{c}1\mu}^{l_{p}m_{p}}(-1)^{l_{c}+\bar{m}_{c}}\frac{\hat{L}}{\hat{l}_{a}}C_{l_{c}-\bar{m}_{c}LM}^{l_{a}m_{a}} = (-1)^{l_{c}+\bar{m}_{c}}\frac{\hat{L}}{\hat{l}_{a}}\sum_{pqL_{1}M_{1}}\hat{p}\hat{c}\hat{l}_{p}\hat{l}_{a}C_{1\mu LM}^{pq}C_{l_{p}m_{p}l_{a}m_{a}}^{LM_{1}M_{1}}C_{c\gamma pq}^{LM_{1}M_{1}} \begin{cases} L & 1 & p \\ l_{c} & l_{c} & c \\ l_{a} & l_{p} & L_{1} \end{cases} \end{cases}$$
(3.71)

The same for interference quantum numbers:

$$C^{gh}_{l_c m'_c l_c - \bar{m}'_c} C^{l''_p m''_p}_{l_c m'_c 1 \mu'} C^{L-M'}_{l_c - \bar{m}'_c l''_a - m''_a} = (-1)^{l_c + \bar{m}'_c} \frac{\hat{L}}{\hat{l}''_a} \sum_{rsL_2M_2} \hat{r} \hat{g} \hat{l}''_p \hat{l}''_a C^{rs}_{1\mu'LM'} C^{L_2M_2}_{l''_p m''_p l''_a m''_a} C^{L_1M_1}_{ghrs} \left\{ \begin{array}{cc} L & 1 & r \\ l_c & l_c & g \\ l''_a & l''_p & L_2 \end{array} \right\}$$
(3.72)

The one can couple some of the coefficients contained in (3.71) and (3.72) [181]:

$$C_{LML-M'}^{f\varphi}(-1)^{1+L-p}C_{LM1\mu}^{pq}C_{L-M'1-\mu'}^{r-s} = (-1)^{1+L-p}\sum_{L_0M_0L_eM_e} \hat{L}_0 \hat{f} \hat{p} \hat{r} C_{1\mu1-\mu'}^{L_0M_0}C_{pqr-s}^{L_eM_e}C_{f\varphi L_0M_0}^{L_eM_e} \left\{ \begin{array}{ccc} 1 & 1 & L_0\\ L & L & f\\ r & p & L_e \end{array} \right\}$$
(3.73)

We can now recouple the spherical harmonics of the light to build a tensor. Thus we can use the phase factor $(-1)^{\mu'}$ to recouple the spherical harmonics:

$$(-1)^{-\mu'} C^{L_0 M_0}_{1\mu 1 - \mu'} Y^*_{1\mu}(\epsilon) Y_{1\mu'}(\epsilon^*) = \sum_{\mu\mu'} (-1)^{\mu'} C^{L_0 M_0}_{1\mu 1\mu'} Y^*_{1\mu}(\epsilon) Y_{1-\mu'}(\epsilon^*) = \sum_{\mu\mu'} C^{L_0 M_0}_{1\mu 1\mu'} Y^*_{1\mu}(\epsilon) Y^*_{1\mu'}(\epsilon^*) = \rho^*_{L_0 M_0} = (-1)^{M_0} (-1)^{1+1-L_0} \rho_{L_0 - M_0}$$

$$(3.74)$$

Now we can consider the following recoupling [181]:

$$(-1)^{-h+\varphi}C_{g-hf\varphi}^{c-\gamma}C_{c\gamma pq}^{L_{1}M_{1}}C_{ghrs}^{L_{2}M_{2}} = (-1)^{-h+\varphi}(-1)^{f+\varphi+c-\gamma+g+r-L_{2}}\frac{\hat{c}}{\hat{g}}\frac{\hat{g}}{\hat{f}}C_{c\gamma g-h}^{f-\varphi}$$

$$C_{c\gamma pq}^{L_{1}M_{1}}C_{g-hr-s}^{L_{2}-M_{2}} = (-1)^{-\varphi-\gamma-\gamma+f+c+g+r-L_{2}}\frac{\hat{c}}{\hat{f}}\sum_{xyL'_{e}M'_{e}}\hat{L}'_{e}\hat{f}\hat{L}_{1}\hat{L}_{2}C_{pqr-s}^{L'_{e}M'_{e}}$$

$$C_{L_{1}M_{1}L_{2}-M_{2}}^{xy}C_{f\varphi L'_{e}M'_{e}}^{xy} \left\{ \begin{array}{cc} r & p & L'_{e} \\ g & c & f \\ L_{2} & L_{1} & x \end{array} \right\}$$

$$(3.75)$$

Now we can sum over q, s:

$$(-1)^{f-\varphi+f+L_e-L_0} \sum_{qs} C^{L_eM_e}_{pqr-s} C^{L'_eM'_e}_{pqr-s} = (-1)^{f-\varphi+f+L_e-L_0}$$
(3.76)

Now we can sum over φ, M_e

$$(-1)^{f-\varphi+f+L_e-L_0}\frac{\hat{L}_e}{\hat{L}_0}\sum_{\varphi M_e} C^{xy}_{f-\varphi L_e M_e} C^{L_0 M_0}_{f-\varphi L_e M_e} = (-1)^{f-\varphi+f+L_e-L_0}\frac{\hat{L}_e}{\hat{L}_0}\delta_{xL_0}\delta_{yM_0}$$
(3.77)

Then the cross section for two electrons resonant emission from a cluster using spin unsensitive detectors results

$$\frac{d^{2}\sigma}{d\mathbf{k}_{a}d\mathbf{k}_{p}}\left(l_{c}, j_{c}, l_{1}, l_{2}, L, S, J\right) = 4\pi^{2}\alpha\hbar\omega\Gamma(\xi)\hat{j}_{c}^{2}\hat{j}_{c}^{2}\hat{J}^{2}\hat{S}^{2}\hat{l}_{c}^{2}\hat{l}_{1}^{2}\hat{l}_{2}^{2}e^{4}|k_{a}||k_{p}|\frac{2}{3\pi}\frac{1}{(16\pi^{2})^{2}} \times \\
\sum_{\mu\mu' l_{a}l'_{a}l'_{p}l''_{p}kk'}\frac{1}{l_{p}l''_{p}}Y_{1\mu}^{*}(\hat{\epsilon})Y_{1\mu'}(\hat{\epsilon}^{*})R(n_{c}l_{c}, El_{p})R^{*}(n_{c}l_{c}, El''_{p})C_{l_{c}010}^{l_{p}0}C_{l_{c}010}^{l''_{p}0}[D_{k}(n_{1}l_{1}n_{2}l_{2}, \epsilon l_{a}n_{c}l_{c})d_{kl_{a}} + \\
\left(-1\right)^{-L-S}E_{k}(n_{2}l_{2}n_{1}l_{1}, \epsilon l_{a}n_{c}l_{c})e_{kl_{a}}][D_{k'}^{*}(n_{1}l_{1}n_{2}l_{2}, \epsilon l''_{a}n_{c}l_{c})d_{k'l''_{a}} + \\
\left(-1\right)^{-L-S}E_{k'}^{*}(n_{2}l_{2}n_{1}l_{1}, \epsilon l''_{a}n_{c}l_{c})e_{kl_{a}}][D_{k'}^{*}(n_{1}l_{1}n_{2}l_{2}, \epsilon l''_{a}n_{c}l_{c})d_{k'l''_{a}} + \\
\left(-1\right)^{-L-S}E_{k'}^{*}(n_{2}l_{2}n_{1}l_{1}, \epsilon l''_{a}n_{c}l_{c})e_{k'l''_{a}}]\sum_{cgfprL_{1}M_{1}L_{2}M_{2}L_{0}M_{0}L_{e}}\left(-1\right)^{-p+g+r-L_{2}+M_{2}+L_{e}-L_{0}} \\
\hat{g}^{2}\hat{f}^{2}\hat{p}^{2}\hat{c}^{2}\hat{r}^{2}\hat{L}_{e}^{2}\hat{L}_{1}\hat{L}_{2}C_{L_{1}M_{1}L_{2}-M_{2}}\left\{\frac{1}{2}\frac{1}{2}\frac{1}{2}g\\c&f&\frac{1}{2}\frac{1}{2}\frac{1}{2}j_{c}\right\}\left\{l_{c}c&c\\\frac{1}{2}\frac{1}{2}\frac{1}{2}j_{c}\right\}\left\{l_{c}LLf\\S&S&J\right\}\left\{LLf\\l_{a}l_{p}L_{1}\right\}\left\{l_{c}Llf\\l_{a}l_{p}L_{1}\right\}\left\{l_{a}lf\\l_{a}l_{p}L_{1}\right\}\left\{l_{a}lf\\$$

This is the spin-unpolarized Auger-photoelectron coincidence cross section from a cluster. Due to dipole approximation the rank of light tensor can be 0,1,2. It can be written separating the light properties, the kinematical and the dynamical properties:

$$\frac{d^{2}\sigma}{d\mathbf{k}_{a}d\mathbf{k}_{p}} = 4\pi^{2}\alpha\hbar\omega\Gamma(\xi)\sum_{L_{0}M_{0}l_{a}l_{a}^{\prime\prime}l_{p}l_{p}^{\prime\prime}L_{1}M_{1}L_{2}M_{2}}(-1)^{M_{2}}C_{L_{1}M_{1}L_{2}-M_{2}}^{L_{0}M_{0}}$$

$$\rho_{L_{0}M_{0}}^{*}\left\{B_{l_{p}m_{p}}^{i}(\mathbf{k}_{p})\otimes B_{l_{a}m_{a}}^{i}(\mathbf{k}_{a})\right\}_{L_{1}M_{1}}\left\{B_{l_{p}^{\prime\prime}m_{p}^{\prime\prime}}^{i*}(\mathbf{k}_{p})\otimes B_{l_{a}m_{a}^{\prime\prime}}^{i*}(\mathbf{k}_{a})\right\}_{L_{2}M_{2}}A_{L_{1}L_{2}L_{0}}^{l_{p}l_{p}^{\prime\prime\prime}l_{a}l_{a}^{\prime\prime\prime}}$$
(3.79)

where

$$\begin{split} A_{L_{1}L_{2}L_{0}}^{l_{p}l_{p}''_{la}l_{a}''} &= \hat{j}_{c}^{2}\hat{j}_{c}^{2}\hat{J}^{2}\hat{S}^{2}\hat{l}_{c}^{2}\hat{l}_{1}^{2}\hat{l}_{2}^{2}e^{4}|k_{a}||k_{p}|\frac{2}{3\pi}\frac{1}{(16\pi^{2})^{2}}\times\\ &\sum_{\mu\mu'l_{a}l_{a}''_{lp}l_{p}''_{kk'}}\frac{1}{l_{p}l_{p}''}Y_{1\mu}^{*}(\hat{\epsilon})Y_{1\mu'}(\hat{\epsilon^{*}})R(n_{c}l_{c},El_{p})R^{*}(n_{c}l_{c},El_{p}'')C_{l_{c}010}^{l_{p}0}C_{l_{c}010}^{l_{p}''0} \end{split}$$

$$\begin{bmatrix} D_{k}(n_{1}l_{1}n_{2}l_{2},\epsilon l_{a}n_{c}l_{c})d_{kl_{a}} + (-1)^{-L-S}E_{k}(n_{2}l_{2}n_{1}l_{1},\epsilon l_{a}n_{c}l_{c})e_{kl_{a}} \end{bmatrix} \\ \begin{bmatrix} D_{k'}^{*}(n_{1}l_{1}n_{2}l_{2},\epsilon l_{a}''n_{c}l_{c})d_{k'l'_{a}''} + (-1)^{-L-S}E_{k'}^{*}(n_{2}l_{2}n_{1}l_{1},\epsilon l_{a}''n_{c}l_{c})e_{k'l'_{a}'} \end{bmatrix} \\ \sum_{cgfprL_{e}}(-1)^{-p+g+r-L_{2}+L_{e}-L_{0}}\hat{g}^{2}\hat{f}^{2}\hat{p}^{2}\hat{c}^{2}\hat{r}^{2}\hat{L}_{e}^{2}\hat{L}_{1}\hat{L}_{2} \left\{ \begin{array}{c} \frac{1}{2} & \frac{1}{2} & g \\ c & f & \frac{1}{2} \end{array} \right\} \left\{ \begin{array}{c} l_{c} & l_{c} & c \\ \frac{1}{2} & \frac{1}{2} & j_{c} \end{array} \right\} \left\{ \begin{array}{c} l_{c} & l_{c} & g \\ \frac{1}{2} & \frac{1}{2} & j_{c} \end{array} \right\} \left\{ \begin{array}{c} L & 1 & p \\ l_{c} & l_{c} & c \\ l_{a} & l_{p} & L_{1} \end{array} \right\} \left\{ \begin{array}{c} L & 1 & r \\ l_{c} & l_{c} & g \\ l''_{a} & l''_{p}'' & L_{2} \end{array} \right\} \left\{ \begin{array}{c} 1 & 1 & L_{0} \\ L & L & f \\ r & p & L_{e} \end{array} \right\}$$
(3.80)

3.5 The coincidence cross section in the atomic limit

In the atomic limit, the scattering matrix becomes:

$$\tau_{lml'm'}^{ij} \longrightarrow (t_{ll'}^{ij})\delta_{ij}\delta_{lml'm'} \tag{3.81}$$

where the atomic scattering matrix is defined by:

$$t_l^i = -\frac{1}{k} e^{i\delta_l} \sin(\delta_l) \tag{3.82}$$

Then the scattering amplitudes for the photoelectron and the Auger electron become:

$$B_{l_p m_p}(\mathbf{k}_p) = t_{l_p} i^{l_p} Y_{l_p m_p}(\hat{k}_p)$$
(3.83)

$$B_{l_a m_a}(\mathbf{k}_a) = t_{l_a} i^{l_a} Y_{l_a m_a}(\hat{k}_a) \tag{3.84}$$

In some cases the factor $sin\delta_l$ is included in the definition of the radial wavefunction. In the atomic case the two bipolar spherical harmonics can be recoupled further:

$$\left\{ Y_{l_p}(\mathbf{k}_p) \otimes Y_{l_a}(\mathbf{k}_a) \right\}_{L_1 M_1} (-1)^{M_2} (-1)^{l'_a + l'_p - L_2} \left\{ Y_{l'_p}(\mathbf{k}_p) \otimes Y_{l'_a}(\mathbf{k}_a) \right\}_{L_2 - M_2} = (-1)^{l'_a + l'_p - L_2 + M_2} \sum_{L_3 M_3} C_{L_1 M_1 L_2 - M_2}^{L_3 M_3} \sum_{l_p p l_{aa}} \frac{\hat{l}_p \hat{l'}_p \hat{l}_a \hat{l'}_a \hat{L}_1 \hat{L}_2}{4\pi} C_{l_p 0 l'_p 0}^{l_p p 0} C_{l_a 0 l'_a 0}^{l_{aa} 0} \left\{ \begin{array}{c} l_p & l'_p & l_{pp} \\ l_a & l'_a & l_{aa} \\ L_1 & L_2 & L_3 \end{array} \right\}$$

$$\left\{ Y_{l_{pp}}(\mathbf{k}_p) \otimes Y_{l_{aa}}(\mathbf{k}_a) \right\}_{L_3 M_3}$$

$$(3.85)$$

Then in the atomic case the coincidence cross section can be written as:

$$\frac{d^2\sigma}{d\mathbf{k}_a d\mathbf{k}_p} = 4\pi^2 \alpha \hbar \omega L_{\Gamma} \sum_{L_0 M_0 l_{pp} l_{aa}} \rho^*_{L_0 M_0} \left\{ Y_{l_{pp}}(\mathbf{k}_p) \otimes Y_{l_{aa}}(\mathbf{k}_a) \right\}_{L_0 M_0} A^{L_0}_{l_{pp} l_{aa}}$$
(3.86)

where $A_{l_{pp}l_{aa}}^{L_0}$ is different from the multiple scattering case, it contains combinations of Clebsch-Gordan, 6-j and 9-j coefficients, dipole and Coulomb matrix elements and the t_l which describe the strength of the scattering for each electron. The angular momentum l_{pp} , l_{aa} are given respectively by vector coupling of photoelectron's angular momentum l_p (l'_p) and Auger electron's orbital momentum l_a (l'_a) . l_{pp} , l_{aa} are restricted to even values due to parity conservation. The algebra of angular momentum allows to sum over all the projections quantum numbers, only the M_0 projections remains, caused by the introduction of a preference axis in photon impact. Generalizing this result to the case where the light polarization properties are expressed by Stokes parameters one recovers the result given by the statistical tensor approach for closed shell systems.

3.6 Light polarization dependence

For both cases, atomic emission and emission from a cluster, a general treatment of the dependence of the cross section on the light polarization properties and which unifies the case of circular and linear dichroism can be achieved. Writing the tensor for the radiation explicitly, we have, for the three possible values of the rank [182]:

- $\rho_{00} = -(1/\sqrt{3})(3/4\pi)\epsilon^* \cdot \epsilon$: this term is a scalar product between the two polarization, and thus it cannot give any kind of dichroism.
- $\rho_{1M_0} = (i/\sqrt{2})(3/4\pi)(\epsilon^* \times \epsilon)_{M_0}$: this tensor of rank one is present only in the case of circular polarization; in particular making the difference between the two cicularly polarized light this is the only one which contributes. This tensor is given by the vector product between two polar vector, i.e. it is an axial vector, and it is responsible for MCD. This tensor is sensitive to time reversal odd variables.
- finally, we have the irreducible rank-2 tensor: $\rho_{2\pm 2} = \frac{3}{4\pi} \epsilon_{\pm 1}^* \epsilon_{\pm 1}$ $\rho_{2\pm 1} = \frac{3}{4\pi} \frac{1}{\sqrt{2}} (\epsilon_{\pm 1}^* \epsilon_0 + \epsilon_0^* \epsilon_{\pm 1})$ $\rho_{20} = \frac{3}{4\pi} \frac{1}{\sqrt{6}} (\epsilon_1^* \epsilon_{-1} + 2\epsilon_0^* \epsilon_0 + \epsilon_{-1}^* \epsilon_1) = \frac{3}{4\pi} (3\epsilon_0^* \epsilon_0 - \hat{\boldsymbol{\epsilon}}^* \cdot \hat{\boldsymbol{\epsilon}})$

This 2 rank tensor is responsible for linear dichroism.

The analysis of the light polarization dependence can also be done on the amplitude, instead of directly on the intensity. For a solid target the z direction could also be taken perpendicular to the surface independently from the light polarization properties, in an atomic target the system is isotropic and no perpendicular direction can be defined. Generally, several choices can be done for the z axis both for the atomic and cluster emission cases: the z axis could coincide with the propagation direction of the light independently from the light polarization properties, it could be taken as the normal to the surface (this can be done only for the solid state case) or it could be parallel to the polarization vector for linearly polarized light and parallel to the propagation direction for circular polarization. In the following we will consider the case of emission from a cluster and we will refere to a coordinate system in which the z axis is perpendicular to the surface and the light propagation direction is in the xz plane ($\phi = 0^{\circ}$). The θ angle of the incidence direction is defined with respect to the z axis. It is possible to write a general light polarization as the superposition of light with two helicities. The helicity controvariant basis is expressed in terms of the cartesian basis as:

$$\epsilon'^{+1} = -\frac{\epsilon_x}{\sqrt{2}}\cos\theta + \frac{i}{\sqrt{2}}\epsilon_y + \frac{\epsilon_z}{\sqrt{2}}\sin\theta$$

$$\epsilon'^o = \epsilon_x \sin\theta + e_z \cos\theta \qquad (3.87)$$

$$\epsilon'^{-1} = \frac{\epsilon_x}{\sqrt{2}}\cos\theta + \frac{i}{\sqrt{2}}\epsilon_y - \frac{\epsilon_z}{\sqrt{2}}\sin\theta$$

$$(3.88)$$

thus a generic light polarization vector can be written as:

$$\vec{\epsilon} = q_a(\epsilon'^{+1}) + q_b(\epsilon'^{-1}) =$$

$$q_a(\epsilon^{+1}\frac{1-\cos\theta}{2} - i\epsilon^o\frac{\sin\theta}{\sqrt{2}} + \epsilon^{-1}\frac{1+\cos\theta}{2}) +$$

$$+q_b(\epsilon^{+1}\frac{1+\cos\theta}{2} + \epsilon^o\frac{\sin\theta}{\sqrt{2}} + \epsilon^{-1}\frac{1-\cos\theta}{2})$$
(3.89)

where we have written the helicity contravariant basis in terms of spherical controvariant basis.

For linearly polarized light the two helicities components have the same weight $q_a = 1/\sqrt{2}$, $q_b = -1/\sqrt{2}$. Then one has:

$$\vec{\epsilon}_L = -\frac{1}{\sqrt{2}} (\epsilon^{-1} - \epsilon^{+1}) \cos\theta + \epsilon^o \sin\theta = \epsilon_z \sin\theta - \epsilon_x \cos\theta$$
(3.90)

Then the cross section is given by:

$$\frac{d^2\sigma}{d\mathbf{k}_a d\mathbf{k}_p} = 4\pi^2 \alpha \hbar \omega \Gamma(\xi) \sum_{\sigma_p \sigma_a J_z} |(F_{+1} - F_{-1}) \frac{1}{\sqrt{2}} \cos\theta + \sin\theta F_0|^2$$
(3.91)

where F_{μ} is the amplitude corresponding to a particular spherical component μ of the light polarization vector and is given by

$$F_{\mu} = \frac{e^2}{\sqrt{2}} \sqrt{\frac{4\pi}{3}} \sqrt{\frac{3}{4\pi}} (\frac{1}{4\pi^2})^2 \sqrt{\frac{k_a}{\pi}} \sqrt{\frac{k_p}{\pi}} \hat{l}_1 \hat{l}_2 \hat{l}_c (-1)^{l_c+l_1+L} \sum_{l_p l_a \mu k} \frac{1}{\hat{l}_p} (\hat{\epsilon}) R(n_c l_c, E l_p)$$

$$[D_k (n_1 l_1 n_2 l_2, \epsilon l_a n_c l_c) d_{kl_a} + (-1)^{-L-S} E_k (n_2 l_2 n_1 l_1, \epsilon l_a n_c l_c) e_{kl_a}]$$

$$\sum_{m_a m_c \bar{m}_c s i \bar{g} m a_c m_p M S_z} C_{l_c 0 10}^{l_p m_p} C_{l_c m_c 1 \mu}^{JJ_z} C_{LM S S_z}^{JJ_z} C_{l_c \bar{m}_c \frac{1}{2} \sigma_c}^{l_c c_c} C_{l_a \bar{m}_a l_c \bar{m}_c}^{LM} C_{\frac{1}{2} \sigma_a \frac{1}{2} \bar{\sigma}_c}^{SS_z}$$

$$B_{l_a m_a} (\mathbf{k}_a) B_{l_p m_p} (\mathbf{k}_p)$$
(3.92)

An additional $\sqrt{\frac{3}{4\pi}}$ was needed to retransform the $Y_{1\mu}^*(\hat{\epsilon})$ in the notation ϵ_{μ} .

When the light propagation direction is along the x axis (polarization parallel to the z axis) then $\theta = \frac{\pi}{2}$ and only the ϵ^{o} component remains $|F_{0}|^{2}$. Thus only $\Delta_{m} = m_{c} - m_{p} = 0$ contributes to the cross section. If $\theta = 0^{o}$ then the light is impinging normally to the surface and the polarization is parallel to the x direction. In this case one has only the ϵ^{+1} , ϵ^{-1} components: $|\frac{1}{\sqrt{2}}(F_{+1} - F_{-1})|^{2}$.

For circular light polarization for positive helicity the one has $q_a = 0$ and $q_b = -1$ then the cross section is given by:

$$\frac{d^2\sigma}{d\mathbf{k}_a d\mathbf{k}_p} = 4\pi^2 \alpha \hbar \omega \Gamma(\xi) \sum_{\sigma_p \sigma_a J_z} |-\frac{1}{2} F_{+1}(\frac{1+\cos\theta}{2}) - F_0 \frac{\cos\theta}{\sqrt{2}} - F_{-1}(\frac{1-\cos\theta}{2})|^2 \quad (3.93)$$

while for negative elicity one has $q_a = 1$ and $q_b = 0$:

$$\frac{d^2\sigma}{d\mathbf{k}_a d\mathbf{k}_p} = 4\pi^2 \alpha \hbar \omega \Gamma(\xi) \sum_{\sigma_p \sigma_a J_z} \left| \frac{1}{2} F_{+1} \left(\frac{1 - \cos\theta}{2} \right) - F_0 \frac{\cos\theta}{\sqrt{2}} + F_{-1} \left(\frac{1 + \cos\theta}{2} \right) \right|^2 \tag{3.94}$$

The difference between the two circularly polarized lights is :

$$\frac{d^2\sigma}{d\mathbf{k}_a d\mathbf{k}_p}|_{CD} = 4\pi^2 \alpha \hbar \omega \Gamma(\xi) \sum_{\sigma_p \sigma_a J_z} |(|F_{+1}|^2 - |F_{-1}|^2) \cos\theta + \frac{2}{\sqrt{2}} (F_{+1}F_0^* + F_0F_{-1}^* + F_0F_{+1}^* + F_{-1}F_0^*) \sin\theta|^2$$
(3.95)

Thus when the light is impinging perpendicular to the surface (perpendicular geometry), $\theta = 0^{\circ}$ then only diagonal terms contribute to the cross section. when using grazing incidence one $(\theta = \frac{\pi}{2})$ only the interference terms contribute to the cross section. Let us suppose for example that we are ionizing a p shell, i.e. $l_c = 1$. Then, in perpendicular geometry, one has that the transitions which contribute to the cross section are those corresponding to $\Delta m = +1$ ($m_c = 0 \rightarrow m_p = 1, m_c = -1 \rightarrow m_p = 0$) and $\Delta m = -1$ ($m_c = 0 \rightarrow m_p = -1, m_c = 1 \rightarrow m_p = 0$). Subtracting the latter two cross sections to the first ones and looking at eqn 3.62 one notes that the transitions $\Delta m = +1$ ($m_c = 0 \rightarrow m_p = 1$) and $\Delta m = -1$ ($m_c = 0 \rightarrow m_p = -1$) have exactly the same coefficients ($C_{l_c m_c l \mu}^{l_p m_p} = C_{1011}^{211} = C_{101-1}^{221}$), the only things which change are the spherical harmonics or the scattering amplitudes $Y_{l_p m_p}$. For the atomic case the CD cross section thus is given by $|CY_{l_p 1}(\mathbf{k}_p)Y_{l_a m_a}(\mathbf{k}_a)|^2 - |CY_{l_p - 1}(\mathbf{k}_p)Y_{l_a m_a}(\mathbf{k}_a)|^2$ which results in $CC^*Y_{l_a m_a}(\mathbf{k}_a)(Y_{l_p 1}(\mathbf{k}_p)Y_{l_p 1}^*(\mathbf{k}_p) - Y_{l_p - 1}(\mathbf{k}_p)Y_{l_p - 1}(\mathbf{k}_p))$ which gives zero. Thus the only transitions contributing to the CD cross section are $\Delta m = +1$ ($m_c = -1 \rightarrow m_p = 0$).

3.6.1 Kinematic dependence of the atomic cross section for different light polarization

Now we can focus our attention on the geometrical part of the cross section. For the atomic cross section, it is possible to write the cross section as sums of scalar and vector products

between the three involved vectors (light polarization or incidence direction, direction of photoelectron, direction of Auger electron). In the multiple scattering case, this is not straightforward, but we think that a very simple atomic analysis can help in assessing the main effects and helps in gaining information on the ground state.

$$\frac{d^{2}\sigma}{d\mathbf{k}_{a}d\mathbf{k}_{p}} = 4\pi^{2}\alpha\hbar\omega\Gamma(\xi)\sum_{L_{0}M_{0}l_{pp}l_{aa}}(-1)^{M_{0}}\left\{Y_{1}(\epsilon)\otimes Y_{1}(\epsilon^{*})\right\}_{L_{0}-M_{0}}\left\{Y_{l_{pp}}(\mathbf{k}_{p})\otimes Y_{l_{aa}}(\mathbf{k}_{a})\right\}_{L_{0}M_{0}}A_{l_{pp}l_{aa}}^{L_{0}}$$

$$=\sum_{L_{0}M_{0}l_{pp}l_{aa}}(-1)^{M_{0}}\sum_{\mu\mu'}C_{1-\mu+1-\mu'}^{L_{0}-M_{0}}Y_{1-\mu}(\epsilon)Y_{1-\mu'}(\epsilon^{*})\cdot$$

$$\sum_{m_{pp}m_{aa}}C_{l_{pp}m_{pp}l_{aa}m_{aa}}^{L_{0}M_{0}}Y_{l_{pp}m_{pp}}(\mathbf{k}_{p})Y_{l_{aa}m_{aa}}(\mathbf{k}_{a})A_{l_{pp}l_{aa}}^{L_{0}}$$
(3.96)

3.6.2 Linearly polarized photon beam

With linearly polarized light, choosing the z axis parallel to the polarization vector, then one has that only the spherical components $Y_{10}(\epsilon)$ of the light polarization vector contribute; thus $M_0 = 0$ and $m_{aa} = -m_{pp}$. Thus the waves describing the photoelectrons and the Auger electrons have opposite azimuthal dependence. The polarization vector is real, thus $\epsilon^* = \epsilon$ and one can use the addition theorem for the spherical harmonics of the light [183] to obtain:

$$\frac{d^2\sigma}{d\mathbf{k}_a d\mathbf{k}_p} = 4\pi^2 \alpha \hbar \omega \Gamma(\xi) \cdot \sum_{L_0 l_{pp} l_{aa} m_{pp} m_{aa}} \sqrt{\frac{9}{4\pi}} \frac{1}{\hat{L}_0} C_{1010}^{L_0 0} Y_{L_0 0}(\epsilon) C_{l_{pp} m_{pp} l_{aa} - m_{pp}}^{L_0 0} Y_{l_{pp} m_{pp}}(\mathbf{k}_p) Y_{l_{aa} - m_{pp}}(\mathbf{k}_a) A_{l_{pp} l_{aa}}^{L_0}(3.97)$$

where $A_{l_{pp}l_{aa}}^{L_0}$ is similar to the corresponding factor in the multiple scattering case but some different angular momentum coefficients appear. The rank L_0 can only be even for linearly polarized case, thus $L_0 = 0, 2$ for linearly polarized light. The cross section will be the sum of a simple scalar product between the spherical harmonics of the two electrons and the zero component of the quadrupole tensor:

$$\frac{d^{2}\sigma}{d\mathbf{k}_{a}d\mathbf{k}_{p}} = 4\pi^{2}\alpha\hbar\omega\Gamma(\xi)\sum_{l_{pp}l_{aa}}\rho_{00}\left\{Y_{l_{pp}}(\mathbf{k}_{p})\otimes Y_{l_{aa}}(\mathbf{k}_{a})\right\}_{00}A_{l_{pp}l_{aa}}^{0} + \rho_{20}\left\{Y_{l_{pp}}(\mathbf{k}_{p})\otimes Y_{l_{aa}}(\mathbf{k}_{a})\right\}_{20}A_{l_{pp}l_{aa}}^{2} = 4\pi^{2}\hbar\omega\Gamma(\xi)\sum_{l_{pp}l_{aa}}\rho_{00}\frac{(-1)^{l_{pp}}}{\hat{l}_{pp}}(Y_{l_{pp}}(\mathbf{k}_{p})\cdot Y_{l_{aa}}(\mathbf{k}_{a}))\cdot A_{l_{pp}l_{aa}}^{0}\delta_{l_{pp}l_{aa}} + \rho_{20}\left\{Y_{l_{pp}}(\mathbf{k}_{p})\otimes Y_{l_{aa}}(\mathbf{k}_{a})\right\}_{20}A_{l_{pp}l_{aa}}^{2} \qquad (3.98)$$

Let's now concentrate on (3.97). We can define

$$\sum_{m_{pp}} C_{l_{pp}m_{pp}l_{aa}-m_{pp}}^{L_{00}} Y_{l_{pp}m_{pp}}(\mathbf{k}_{p}) Y_{l_{aa}-m_{pp}}(\mathbf{k}_{a}) Y_{L_{00}}(\epsilon) = U_{l_{pp}l_{aa}}^{L_{0}}(\mathbf{k}_{p}, \mathbf{k}_{a}, \epsilon)$$
(3.99)

Then the cross section 3.97 can be rewritten as:

$$\frac{d^2\sigma}{d\mathbf{k}_a d\mathbf{k}_p} = 4\pi^2 \alpha \hbar \omega \Gamma(\xi) \sum_{l_{pp} l_{aa} L_0} \sqrt{\frac{9}{4\pi} \frac{1}{\hat{L}_0}} C_{1010}^{L_0 0} U_{l_{pp} l_{aa}}^{L_0} (\mathbf{k}_p, \mathbf{k}_a, \epsilon) A_{l_{pp} l_{aa}}^{L_0}$$
(3.100)

Thus the cross section is given by the product of a kinematical part and a dynamical part. In different geometries the dynamical part can be weighted in different ways. The scalar product form of the cross section reflects its invariance with respect to rotations, indeed all sums over azimuthal quantum numbers have been eliminated. The values of l_{pp} , l_{aa} can only be even due to parity conservation. This happens both for linear and circular polarization. Moreover, for linear polarization also L_0 can only be even, thus it seems that there are no way in any geometries to measure odd magnetic properties of the system with linearly polarized light.

The angular function $U_{l_{pp}l_{aa}}^{L_0}$ for some values of L_0, l_{pp}, l_{aa} are listed below:

$$U_{00}^{0} = C_{0000}^{00} Y_{00}(\mathbf{k}_{p}) Y_{00}(\mathbf{k}_{a}) Y_{00}(\epsilon) = \frac{1}{4\pi\sqrt{4\pi}}$$
(3.101)

$$U_{22}^{0} = \frac{5}{16\pi^{\frac{3}{2}}} (3(\mathbf{k}_{p} \cdot \mathbf{k}_{a})^{2} - 1)$$
(3.102)

$$U_{02}^{2} = \frac{5}{16\pi^{\frac{3}{2}}} (3(\mathbf{k}_{a} \cdot \epsilon)^{2} - 1)$$
(3.103)

$$U_{20}^{2} = \frac{5}{16\pi^{\frac{3}{2}}} (3(\mathbf{k}_{p} \cdot \epsilon)^{2} - 1)$$
(3.104)

$$U_{22}^{2} = -\frac{15}{3} \sqrt{\frac{5}{14}} \frac{1}{16\pi^{\frac{3}{2}}} [2 - 3(\mathbf{k}_{a} \cdot \epsilon)^{2} - 3(\mathbf{k}_{p} \cdot \epsilon)^{2} - 3(\mathbf{k}_{p} \cdot \mathbf{k}_{a})^{2} + 9(\mathbf{k}_{a} \cdot \mathbf{k}_{p})(\mathbf{k}_{a} \cdot \epsilon)(\mathbf{k}_{p} \cdot \epsilon)]$$
(3.105)

$$U_{42}^{2} = \frac{30}{64\sqrt{14}\pi^{\frac{3}{2}}} [1 - 5(\mathbf{k}_{a} \cdot \epsilon)^{2} + 2(\mathbf{k}_{p} \cdot \epsilon)^{2} - 5(\mathbf{k}_{p} \cdot \mathbf{k}_{a})^{2} - 20(\mathbf{k}_{a} \cdot \mathbf{k}_{p})(\mathbf{k}_{a} \cdot \epsilon)(\mathbf{k}_{p} \cdot \epsilon) + 35(\mathbf{k}_{a} \cdot \mathbf{k}_{p})^{2}(\mathbf{k}_{p} \cdot \epsilon)^{2}]$$

$$(3.106)$$

where for $U_{22}^0, U_{02}^2, U_{20}^2$ we have used eqn 11 page 164 Varshalovich. Let's now consider for example the transition $L_{23}M_{23}M_{23}$ in a closed shell system like Argon. The angular momentum allowed by the selection rules are $l_p = 2, l_a = 1, l_{pp} = 0, 2, 4, l_{aa} = 0, 2, L_0 = 0, 2,$ where we have ignored the less dominant photoionization channel $l_p = 0$. We have:

If the photoelectron is revealed along the light polarization vector then the cross section is proportional to $\frac{d^2\sigma}{d\mathbf{k}_a d\mathbf{k}_p} \propto A + B(\cos\theta_a)^2$ like in a conventional single experiment. The same thing happens if the Auger electron is revealed along the light polarization vector, but with different weights A', B'. If one reveals the photoelectron perpendicular to the polarization vector, then some angular functions $U_{lpplaa}^{L_0}$ do not contribute anymore (for example the U_{20}^2 and some terms in U_{22}^2 and in U_{42}^2). It is clear that varying the detection angle of the first electron, the degree of anisotropy of the angular distribution of the second electron is different. Making the difference between cross section for \mathbf{k}_p parallel and perpendicular to ϵ then we could distinguish the contribution of dynamical and angular parts related to different waves describing the continuum electrons. If the photoelectron is revealed at the magic angle 54.7° which makes the $P_2(\cos\theta_p) = 0$) then the angular function U_{22}^0, U_{22}^2 and U_{20}^2 do not contribute anymore to the cross section.

A little note on linear dichroism: on an isotropic system (a free atom) changing the light polarization from a direction to the 90 degrees rotated direction cannot give any kind of dichroism. In non magnetic solids, to do such a change could give informations on the anisotropy of the bonds and charge densities in some particular directions.

3.6.3 Circularly polarized photon beam: circular natural dicroism

For circularly polarized radiation $\epsilon^* \neq \epsilon$ and we cannot use the addition theorem anymore. Remember that circular light polarization can be written as a superposition of two linearly polarization in the plane perpendicular to the propagation direction of the photon beam; we use the optical definition of circular polarization (M.Born and E.Wolf, Principles of Optics, 6th ed. (Pergamon, Oxford, 1980)) for positive elicity $(+\hbar)$ corresponds to left circularly polarized light $\epsilon_L = (\epsilon_{L_1} + i\epsilon_{L_2})/\sqrt{2}$ and $\epsilon_L^* = (\epsilon_{L_1} - i\epsilon_{L_2})/\sqrt{2}$. It is possible to write $Y(\epsilon^*) = Y(Re\epsilon^* + iIm\epsilon^*) = Y(Re\epsilon^*) + iY(Im\epsilon^*)$. Then one has:

$$\sum_{\mu\mu'} C_{1\mu1\mu'}^{L_0M_0} Y_{1\mu}^*(\epsilon_L) Y_{1\mu'}^*(\epsilon_L^*) = \sum_{\mu\mu'} C_{1\mu1\mu'}^{L_0M_0} \frac{1}{2} (Y_{1\mu}^*(\epsilon_{L_1}) + iY_{1\mu}^*(\epsilon_{L_2})) (Y_{1\mu'}^*(\epsilon_{L_1}) - iY_{1\mu'}^*(\epsilon_{L_2})) = \sum_{\mu\mu'} C_{1\mu1\mu'}^{L_0M_0} \frac{1}{2} (Y_{1\mu}^*(\epsilon_{L_1}) Y_{1\mu'}^*(\epsilon_{L_1}) + Y_{1\mu}^*(\epsilon_{L_2}) Y_{1\mu'}^*(\epsilon_{L_2}) + i(Y_{1\mu}^*(\epsilon_{L_2}) Y_{1\mu'}^*(\epsilon_{L_1}) - iY_{1\mu'}^*(\epsilon_{L_1})) = \sum_{\mu\mu'} C_{1\mu1\mu'}^{L_0M_0} \frac{1}{2} (Y_{1\mu}^*(\epsilon_{L_1}) Y_{1\mu'}^*(\epsilon_{L_1}) + Y_{1\mu}^*(\epsilon_{L_2}) Y_{1\mu'}^*(\epsilon_{L_2}) + i(Y_{1\mu}^*(\epsilon_{L_2}) Y_{1\mu'}^*(\epsilon_{L_1}) - iY_{1\mu'}^*(\epsilon_{L_1})) = \sum_{\mu\mu'} C_{1\mu1\mu'}^{L_0M_0} \frac{1}{2} (Y_{1\mu}^*(\epsilon_{L_1}) Y_{1\mu'}^*(\epsilon_{L_1}) + Y_{1\mu}^*(\epsilon_{L_2}) Y_{1\mu'}^*(\epsilon_{L_2}) + i(Y_{1\mu}^*(\epsilon_{L_2}) Y_{1\mu'}^*(\epsilon_{L_1}) - iY_{1\mu'}^*(\epsilon_{L_2})) = \sum_{\mu\mu'} C_{1\mu1\mu'}^{L_0M_0} \frac{1}{2} (Y_{1\mu}^*(\epsilon_{L_1}) Y_{1\mu'}^*(\epsilon_{L_1}) + Y_{1\mu}^*(\epsilon_{L_2}) Y_{1\mu'}^*(\epsilon_{L_2}) + i(Y_{1\mu}^*(\epsilon_{L_2}) Y_{1\mu'}^*(\epsilon_{L_1}) - iY_{1\mu'}^*(\epsilon_{L_2})) = \sum_{\mu\mu'} C_{1\mu1\mu'}^{L_0M_0} \frac{1}{2} (Y_{1\mu}^*(\epsilon_{L_1}) Y_{1\mu'}^*(\epsilon_{L_1}) + Y_{1\mu}^*(\epsilon_{L_2}) Y_{1\mu'}^*(\epsilon_{L_2}) + i(Y_{1\mu}^*(\epsilon_{L_2}) Y_{1\mu'}^*(\epsilon_{L_1}) - iY_{1\mu'}^*(\epsilon_{L_1}) + Y_{1\mu'}^*(\epsilon_{L_2}) + i(Y_{1\mu}^*(\epsilon_{L_2}) Y_{1\mu'}^*(\epsilon_{L_1}))$$

$$(3.107)$$

Using the addition theorem for the first two terms in the brackets we obtain:

$$\sum_{\mu\mu'} C_{1\mu1\mu'}^{L_0M_0} \frac{1}{2} \sum_{L_0M_0} \left(\sqrt{\frac{9}{4\pi (2L_0+1)}} C_{1010}^{L_00} C_{1\mu1\mu'}^{L_0M_0} (Y_{L_0M_0}^*(\epsilon_{L_1}) + Y_{L_0M_0}^*(\epsilon_{L_2})) + i(\epsilon_{L_2} \times \epsilon_{L_1})_{M_0} \right) = \sum_{\mu\mu'} C_{1\mu1\mu'}^{L_0M_0} \frac{1}{2} \left(\sum_{L_0M_0} \sqrt{\frac{9}{4\pi (2L_0+1)}} C_{1010}^{L_00} C_{1\mu1\mu'}^{L_0M_0} (Y_{L_0M_0}^*(\epsilon_{L_1}) + Y_{L_0M_0}^*(\epsilon_{L_2})) + i(\epsilon_{L_2} \times \epsilon_{L_1})_{M_0} \right) = \frac{1}{2} \left(\frac{1}{4\pi (2L_0+1)} \sqrt{\frac{9}{4\pi (2L_0+1)}} C_{1010}^{L_00} C_{1\mu1\mu'}^{L_0M_0} (Y_{L_0M_0}^*(\epsilon_{L_1}) + Y_{L_0M_0}^*(\epsilon_{L_2})) \right) + i(\epsilon_{L_2} \times \epsilon_{L_1})_{M_0} \right) = \frac{1}{4\pi (2L_0+1)} \left(\frac{1}{4\pi (2L_0+1)} \sqrt{\frac{9}{4\pi (2L_0+1)}} C_{1010}^{L_0M_0} C_{1\mu1\mu'}^{L_0M_0} (\epsilon_{L_1}) + Y_{L_0M_0}^*(\epsilon_{L_2}) \right) \right)$$

$$(3.108)$$

Then the cross section can be written as:

$$\frac{d^{2}\sigma}{d\mathbf{k}_{a}d\mathbf{k}_{p}} = 4\pi^{2}\alpha\hbar\omega\Gamma(\xi)\frac{1}{2}\sum_{M_{0}l_{pp}l_{aa}}\sum_{L_{0}}\left(\sqrt{\frac{9}{4\pi(2L_{0}+1)}}C_{1010}^{L_{0}0}(-1)^{M_{0}}(Y_{L_{0}-M_{0}}(\epsilon_{L_{1}}) + Y_{L_{0}-M_{0}}(\epsilon_{L_{2}})\right) \cdot \left\{Y_{l_{pp}}(\mathbf{k}_{p})\otimes Y_{l_{aa}}(\mathbf{k}_{a})\right\}_{L_{0}M_{0}}A_{l_{pp}l_{aa}}^{L_{0}} + \sqrt{\frac{8\pi}{3}}Y_{1M_{0}}^{*}(k_{\gamma})\left\{Y_{l_{pp}}(\mathbf{k}_{p})\otimes Y_{l_{aa}}(\mathbf{k}_{a})\right\}_{1M_{0}}A_{l_{pp}l_{aa}}^{1}\right)$$
(3.109)

For negative elicity (right circular polarization) one can write $\epsilon_R = (\epsilon_{L_1} - i\epsilon_{L_2})/\sqrt{2}$ and $\epsilon_R^* = (\epsilon_{L_1} + i\epsilon_{L_2})/\sqrt{2}$. Then one has:

$$\sum_{\mu\mu'} C_{1\mu1\mu'}^{L_0M_0} \frac{1}{2} \sum_{L_0M_0} \left(\sqrt{\frac{9}{4\pi (2L_0+1)}} C_{1010}^{L_00} C_{1\mu1\mu'}^{L_0M_0} (Y_{L_0M_0}^*(\epsilon_{L_1}) + Y_{L_0M_0}^*(\epsilon_{L_2})) - i(\epsilon_{L_2} \times \epsilon_{L_1})_{M_0} \right) = \\\sum_{\mu\mu'} C_{1\mu1\mu'}^{L_0M_0} \frac{1}{2} \sum_{L_0M_0} \left(\sqrt{\frac{9}{4\pi (2L_0+1)}} C_{1010}^{L_00} C_{1\mu1\mu'}^{L_0M_0} (Y_{L_0M_0}^*(\epsilon_{L_1}) + Y_{L_0M_0}^*(\epsilon_{L_2})) - i(\epsilon_{L_2} \times \epsilon_{L_1})_{M_0} \right) = \\-i\frac{\sqrt{2}}{i} C_{1\mu1\mu'}^{1M_0} \sqrt{\frac{8\pi}{3}} Y_{1M_0}^*(k_{\gamma}))$$

$$(3.110)$$

Then making the difference between left and right circular polarization we obtain:

$$\frac{d^2\sigma}{d\mathbf{k}_a d\mathbf{k}_p} = 4\pi^2 \alpha \hbar \omega \Gamma(\xi) \frac{2}{2} \sqrt{\frac{8\pi}{3}} \sum_{M_0 l_{pp} l_{aa}} Y^*_{1M_0}(k_\gamma) \left\{ Y_{l_{pp}}(\mathbf{k}_p) \otimes Y_{l_{aa}}(\mathbf{k}_a) \right\}_{1M_0} A^1_{l_{pp} l_{aa}} \quad (3.111)$$

Then one can define:

$$\sum_{n_{pp}m_{aa}} C_{l_{pp}m_{pp}l_{aa}m_{a}}^{L_{0}M_{0}} Y_{l_{pp}m_{pp}}(\mathbf{k}_{p}) Y_{l_{aa}m_{aa}}(\mathbf{k}_{a}) Y_{L_{0}M_{0}}(\mathbf{k}_{\gamma}) = U_{l_{pp}l_{aa}}^{L_{0}}(\mathbf{k}_{p}, \mathbf{k}_{a}, \mathbf{k}_{\gamma})$$
(3.112)

Choosing the photon beam propagation direction k_{γ} as the z axis, then for example the U_{22}^1 is given by:

$$U_{22}^{1} = \frac{3}{8\pi^{3/2}} \sqrt{\frac{15}{2}} i(\mathbf{k}_{a} \times \mathbf{k}_{p}) \cdot \mathbf{k}_{\gamma}(\mathbf{k}_{a} \cdot \mathbf{k}_{p})$$
(3.113)

Actually the angular function U with l_{pp} or l_{aa} with odd values are not possible since $Y_{l_{pp}}$ and $Y_{l_{aa}}$ are coupled together using eqn 7 page 161 (Varshalovich) in which the Clebsch-Gordan coefficients $C_{l_p0l'_p0}^{l_{pa}}$, $C_{l_a0l'_a0}^{l_{aa}0}$ (which are contained in the dynamical part of the cross section $A_{l_{pp}l_{aa}}^{L_0}$) imply that, since l_p and l'_p (and the same happens for l_a and l'_a) are of the same parity, l_{pp} and l_{aa} cannot assume odd values.

Choosing a determined coordinate system then one can see which components of the light and matter tensors contribute to the cross section for a particular circular polarization. Choosing the z axis parallel to the light propagation direction and analyzing eqn (3.107) then one has $M_0 \neq 0$ for the spherical harmonics depending on the linear components of the light polarization, and $M_0 = 0$ for the term which depends on the propagation direction. Thus with circular polarization one is sensitive also to the components $M_0 \neq 0$ of the quadrupole tensor while only to the zero component for the rank one tensor. Then considering for example the transition we considered before, $L_{23}M_{23}M_{23}$ of Ar, one has:

$$\frac{d^2\sigma}{d\mathbf{k}_a d\mathbf{k}_p} = 4\pi^2 \alpha \hbar \omega \Gamma(\xi) \left[\sqrt{\frac{9}{4\pi}} C_{1010}^{00} \frac{2}{\sqrt{4\pi}} \left[\frac{1}{4\pi} A_{00}^0 + \sum_{m_p p} C_{2m_{pp}2-m_{pp}}^{00} Y_{2m_{pp}}(\mathbf{k}_p) Y_{2-m_{pp}}(\mathbf{k}_a) A_{22}^0 \right] \right]$$

$$+\sum_{M_{0}} \sqrt{\frac{9}{20\pi}} C_{1010}^{20} (-1)^{M_{0}} (Y_{2-M_{0}}(\epsilon_{x}) + Y_{2-M_{0}}(\epsilon_{y})) [\sum_{m_{pp}m_{aa}l_{pp}l_{aa}} C_{l_{pp}m_{pp}l_{aa}m_{aa}}^{2M_{0}} Y_{2m_{pp}}(\mathbf{k}_{p}) \\Y_{2m_{aa}}(\mathbf{k}_{a}) A_{l_{pp}l_{aa}}^{2}] + \sqrt{\frac{8\pi}{3}} Y_{10}(\mathbf{k}_{\gamma}) \sum_{l_{pp}l_{aa}m_{pp}} C_{l_{pp}m_{pp}l_{aa}-m_{pp}}^{10} Y_{l_{pp}m_{pp}}(\mathbf{k}_{p}) Y_{l_{aa}-m_{pp}}(\mathbf{k}_{a}) A_{l_{pp}l_{aa}}^{1}] 114)$$

Thus for example the dynamical part $A_{l_{pp}l_{aa}}^2$ is weighted in a different way with respect to a linear polarization experiment. The chirality is an intrinsic property of the electron pair; performing the excitation using circular polarization one introduce also the chirality of the photon.

Chapter 4

Theory vs. Experiment

4.1 Introduction

The formulas for the cross section derived in the previous chapter have been tested versus three sets of experimental data. In the first two cases, the experimental data concern atomic physics experiments, the first one performed on the $L_3M_{23}M_{23}$ transition in Ar and the second one performed on $N_5O_{23}O_{23}$ transition in Xe. Then we moved to the solid state and we have performed a calculation for the transition $L_3M_{45}M_{45}$ in Ge, referring to the experiment we have presented in the first chapter. To be able to perform the calculation of the coincidence cross section for emission of two correlated electrons from a solid, we first modified a preliminary code (PHAGEN [184]), which calculates radial dipole matrix elements) in order to make it calculate also the Coulomb matrix elements and the related phase shifts (t_l) needed for the second step of the process (the Auger decay). Then we have tested the calculation of such integrals performing a calculation reducing the Coulomb matrix elements to Slater integrals and made a comparison between our results and results which are known in literature. Then, we have implemented the coincidence cross section in the multiple scattering code (the SPEC code [185]), both using the tensorial form of the cross section and the modulus square formulation. The implementation was done in order to make possible both a multiple scattering calculation and an atomic calculation, just turning on or switching off the multiple scattering of the electrons. Thus we can summarize our steps as follows:

- implementation of the Coulomb integrals and phase shifts related to the Auger electron in the PHAGEN code
- calculation of Slater integrals for different 4 particle states configurations: comparison with known results
- implementation of the Auger emission cross section; implementation of the coincidence cross section (both atomic and multiple scattering case) in the SPEC code
- comparison of the speed of an atomic calculation using the tensorial formulation and the modulus square formulation of the cross section

- calculation of the Auger coincidence angular distribution in transition $L_3M_{23}M_{23}$ in Ar; comparison with experimental data for different detection angles of the photoelectron and for different multiplet terms of the final state
- calculation of the Auger coincidence angular distribution in transition $N_5O_{23}O_{23}$ in Xe; comparison with experimental data
- calculation of the Auger diffraction patterns related to transition $L_3M_{45}M_{45}$ in Ge(100); comparison with experimental data
- calculation of the Auger coincidence angular distribution in transition $L_3M_{45}M_{45}$ in Ge(100); comparison with experimental data for different detection angles of the photoelectron.

Let us go into the details of the whole work.

4.2 Generation of phase shift and radial matrix elements (PHAGEN)

The program PHAGEN (phases generator) has been used in the past as a first step to perform calculations related to different spectroscopies using the photon beam as exciting source (XAS and photoelectron diffraction). It calculates the dipole radial matrix elements and atomic phase shifts in the muffin tin approximation. We do not want here to go into the details of the calculation but just to give an idea of how the code works. The input of the program is a set of atomic and geometrical information on one (or more) prototypical atomic environment present in the structure. For each atomic cluster the program computes the spherically averaged potential around each atomic site up to the respective muffin-tin radius and the corresponding interstitial potential level. Exchange and correlation potential can be included using various approximations. The phase shifts are calculated up to high angular momentum. Useful reference can be found in [186] (muffin-tin model), [157] (multiple scattering computation) and [163] (exchange correlation potentials). For the final state several approximations for the exchange correlation potential are possible: X-alpha exchange, real Dirac-Hara, exchange, real Hedin-Lundqvist exchange, complex Dirac-Hara exchange, complex Hedin-Lundqvist exchange. Both the initial state and the final state radial functions are calculated with the single configuration Dirac-Fock approximation [?].

The general idea behind the program phagen is that the phase-shifts have to be calculated, at least, for every atomic species present in the structure. The phase shifts will depend primarily on the atomic number Z, however, they will be also different for a neutral or for the photoabsorber atom since the core-hole and the resulting charge relaxation will modify sligtly the potential. Finally, there will be a small "chemical" difference according to the immediate environment of the atoms. This chemical effect is accounted for by the charge overlap from the neighboring atoms. The user will select the number of different phase shift to consider for photoabsorber and backscattering atoms. For each phase-shift the program will require information on the central atom (possible core-hole presence) and on the type and position of surrounding atoms. This set of atoms is referred to as "mini-cluster". For each inequivalent site in the molecule or crystal the environment will be in principle different, however, the phase-shift difference will be usually negligible, for the same Z, so that a single average structure for every Z is usually sufficient. The size of the mini-clusters should be wisely chosen. For a simple molecule it is possible to include always all of the atoms. This choice guarantees the phase shifts for the different atoms are exactly referred to the same interstitial potential level. In the case of complicated structures the limited size of the mini-cluster introduces approximations in the phase-shift calculation. In the majority of cases, however, the inclusion of the first shell environment is sufficient.

Muffin-tin (MT) radii should be regarded as empirical calculation parameters. The final calculated x-ray absorption fine structure signal will be weakly dependent on the actual radii provided that they are chosen in a resonable range. The covalent atomic radii can be used as a first guess MT radii. As an example in a Br_2 molecule (R = 2.29 angstrom) the optimal choice is about $R_{MT} = 1.14$ angstrom. For the Ge crystal where R = 2.45 angstrom, $R_{MT} = 1.22$ angstrom etc. The advantage of using short MT radii is in the smaller number of angular momenta required to describe the atomic scattering. The maximum angular momentum in fact of the order of $l_{max} = k_{max}R_{MT}$. A too small MT radius, however is likely to leave too much of the electronic charge in the interstitial region and should be avoided, especially for covalent bonds. Optimal size of the MT spheres should correspond to the integrated charge related to the electrons Z-b which are not delocalized by the chemical bonding (usually b=1-3 electrons per atom). For different Z the ratio among the relative MT radii can be taken equal to the ratio of the corresponding Norman radii. These are defined in such a way that the spherically integrated electronic charge, including the charge of the neighboring atoms up to a distance R_N equals Z. Norman radii are calculated by phagen and these radii scaled by a factor, are used as MT radii. Typical values of this scaling factor are in the range 0.7-0.8. Notice that R_N is calculated correctly only if all the neighbors of the atom are specified. For mini-clusters containing only the first shell of neighbors R_N and R_{MT} will be estimated correctly only for the first (central) atom in the list. As a consequence PHAGEN should run twice for these cases.

4.3 Calculation of the Coulomb integrals

Until the work of this thesis was done the code PHAGEN for calculation of radial matrix elements and phase shifts was used only for photoionization and absorption calculations, since this was its main original scope. Now also calculation of Coulomb matrix elements is possible, through a very simple implementation of this kind of integrals. Coulomb integrals are necessary for the calculation of the Auger photoelectron coincidence cross section, but also for a simple Auger calculation.

The Coulomb matrix elements are given by:

$$V_{1234} = \int d\mathbf{r} \int d\mathbf{r}' \phi_{nl_1m_1}(\mathbf{r}) \phi_{nl_2m_2}(\mathbf{r}') V(\mathbf{r}, \mathbf{r}') \phi_{nl_3m_3}(\mathbf{r}) \phi_{nl_4m_4}(\mathbf{r}')$$
(4.1)

where $d\mathbf{r} = d^3 r$. We transform to spherical polar coordinates, then $d\mathbf{r} = dr \sin\theta d\theta$. The wave functions $\phi_{nlm}(\mathbf{r})$ can be written in a central potential as $\phi_i(\mathbf{r}) = R_{nl}(r)Y_{lm}(\hat{\mathbf{r}})$ where

 $\hat{\mathbf{r}} = (\theta, \phi)$. For Coulomb interaction $V(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|}$. The integration over the angular variables give rise to the well known Gaunt coefficients, which express the selection rules for the process under consideration. They can be evaluated using a computer code. The integral over the radial coordinates is thus expressed only by:

$$C_{1234} = \int dr r^2 \int dr' r'^2 R_{nl_1}(r) R_{nl_2}(r') V(\mathbf{r}, \mathbf{r}') R_{nl_3}(r) R_{nl_4}(r') = \int dr \int dr' P_{nl_1}(r) P_{nl_2}(r') V(\mathbf{r}, \mathbf{r}') P_{nl_3}(r) P_{nl_4}(r')$$
(4.2)

where we have inserted the one electron radial wave functions $P_{nl} = R_{nl}r$ commonly used in atomic theory. For the Coulomb interaction we can use the following expression, which we used to simplify the Coulomb integral to allow integration over angular coordinates:

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = 4\pi \sum_{k=0}^{\infty} \frac{1}{2k+1} \frac{r_{<}^k}{r_{>}^{k+1}} Y_k(\hat{\mathbf{r}}) Y_k(\hat{\mathbf{r}'})$$
(4.3)

k is the multipole moment of the Coulomb interaction. Using expression (4.3) then the Coulomb radial integral becomes:

$$C_{1234} = \int_{0}^{R} \int dr dr' P_{nl_{1}}(r) P_{nl_{2}}(r') \frac{r_{<}^{k}}{r_{>}^{k+1}} P_{nl_{3}}(r) P_{nl_{4}}(r') = \\ = \int_{0}^{R} dr \frac{P_{nl_{1}}(r) P_{nl_{3}}(r)}{r_{>}^{k+1}} \int_{0}^{r} dr' P_{nl_{2}}(r') r_{<}^{k} P_{nl_{4}}(r') + \int_{0}^{R} dr' \frac{P_{nl_{2}}(r') P_{nl_{4}}(r')}{r_{>}^{'k+1}} \int_{0}^{r'} dr P_{nl_{1}}(r) r_{<}^{k} P_{nl_{4}}(t')$$

where the first part is the one related to r > r' and the secon term to r' > r.

These integrals have been implemented inside PHAGEN, in the subroutine for the calculation of radial matrix elements. In order to calculate them and the dipole matrix elements, the code must run two times, with an input parameter indicating which calculation is needed.

We tested the calculation of the Coulomb radial integrals, for the very special case in which all the states correspond to bound states. Such integrals are called Slater integrals and are used to calculate the energy position of multiplet terms in the energy spectra. Of course, the Coulomb matrix element that we need contain one continuum wave function corresponding to the Auger outgoing electron. The tests have been performed using Cu wavefunctions and choosing a configuration in which all the electrons involved are from the same shell (configuration 3d, 3d) and a configuration where two different shells are involved (configuration 2p, 3d). The wave functions are calculated using a cluster made of Cu atoms with dimensions of the shell with only first neighbours around the origin atom. The results are compared with atomic results taken from the widely used Mann tables [188]. Mann's results are obtained using the self consistent field method of Hartree-Fock, without any corrections due to correlations not taken into account by this method. Our results and Mann's results are:

MANN

$F^0(3d, 3d) = G^0(3d, 3d) = 1.99591$	$F^0(3d, 3d) = G^0(3d, 3d) = 1.930689$
$F^2(3d, 3d) = G^2(3d, 3d) = 0.90964$	$F^2(3d, 3d) = G^2(3d, 3d) = 0.8837736$
$F^4(3d, 3d) = G^4(3d, 3d) = 0.56277$	$F^4(3d, 3d) = G^4(3d, 3d) = 0.5480677$

for the first configuration in which, since the electrons are all equivalent, the direct integrals F^k are equal to the exchange integrals G^k . For the second configuration we have

PHAGEN	MANN
$F^0(2p, 3d) = 2.72964$	$F^0(2p, 3d) = 2.744767$
$F^2(2p, 3d) = 0.49660$	$F^2(2p, 3d) = 0.5049849$
$G^1(2p, 3d) = 0.36076$	$G^1(2p, 3d) = 0.3702332$
$G^3(2p, 3d) = 0.20474$	$G^{3}(2p, 3d) = 0.2102996$

As one can see the two results are in agreement at 3%, i.e. the first number which differs in the groups is the second decimal one. The agreement can be considered sufficient. The differences are mainly due to the difference in the two models adopted for the calculations (Dirac Fock model for our calculations and Hartree Fock method for Mann's results). However, since our aim is mainly concerned to the study of angular correlation at fixed kinetic energy of the outgoing electrons, we suppose that such disagreement will not have influence at all in the cross sections results.

For many simple atoms the F^k and G^k integrals are sufficient for the calculation of multiplet splittings of the configuration. For others, a spin-orbit parameter and a spin-spin parameter are needed. However, at least for simple cases, we can use Mann tables in order to predict the photoemission energy spectra of the systems under investigation, which can then be compared with observed spectra in order to assess the importance of spin-orbit and spin-spin interactions. Relativistic effects become important for heavier elements but are not included in the usual Hartree-Fock formulation. Hartree-Fock calculations results are higly used for many purposes, but it should be realized that the neglect of the above effects does reduce the accuracy of conclusions drawn for heavy elements such as actinides. In our case the wave functions include some relativistic corrections, thus they should be more accurate than those presented in Mann tables.

4.4 Implementation of the cross section in the multiple scattering code (SPEC)

To perform the numerical calculation of the cross section, we implemented the formula in a multiple scattering code for photoelectron diffraction [185]. This code is based on the path approach and the order to which the series expansion is cut can be chosen in the input file. It works only in the high energy regime (>50 eV) where the series converges. It is base on the Rehr-Albers approach which takes advantage of the separability of the matrix elements of the photoelectron propagator to reorganize the equations in a plane wave-like manner with scattering matrices replacing the scalar plane wave scattering factor. the main advantage of this method is to get rid of the nested and therefore tedious sums over the angular momenta

indices in the multiple scattering expansion. The cost (matrices instead of scalars) is minor in view of the gain in efficiency and speed, and especially as the size of the scattering matrices can be reduced to 6x6 or even 3x3 with no loss of accuracy at high energies. The input parameters for the SPEC code can be divided into structural parameters (regarding the cluster), experimental parameters (kinematic condizion of the experiment to which one is referring to), and calculation parameters which allows to indicate which approximations one wants to use to speed up the calculation. Among these last parameters, the most important allows to:

- to choose between a spherical wave calculation or a plane wave approximation for the emitted electron
- to choose the order of truncation of the multiple scattering series
- to consider paths which are contained in a specific cone. The angle can be set to different values depending on the energy of the electron. This allows to reduce the number of the paths which contribute to the cross section
- to put a cut off on the length of the paths
- to consider or not the backscattering contribution (the importance of this contribution again depends on the energy of the emitted electron)

Moreover, the code reads other input files, in which radial matrix elements and t_l values are specified. For coincidence calculation we implemented both the modulus square formula

$$\frac{d^{2}\sigma}{d\mathbf{k}_{a}d\mathbf{k}_{p}}(l_{c}, j_{c}, l_{1}, l_{2}, L, S, J) = 4\pi^{2}\alpha\hbar\omega\Gamma(\xi)\sum_{\sigma_{a}\sigma_{p}J_{z}}|A|^{2} = 4\pi^{2}\alpha\hbar\omega\Gamma(\xi)\sum_{\sigma_{a}\sigma_{p}J_{z}}|\frac{e^{2}}{\sqrt{2}}\sqrt{\frac{4\pi}{3}}(\frac{1}{4\pi})^{2}\sqrt{\frac{k_{a}}{\pi}}\sqrt{\frac{k_{p}}{\pi}}\hat{l}_{1}\hat{l}_{2}\hat{l}_{c}(-1)^{l_{c}+l_{1}+L}\sum_{l_{p}l_{a}\mu k}\frac{1}{\hat{l}_{p}}Y_{1\mu}^{*}(\hat{\epsilon})R(n_{c}l_{c}, El_{p})$$

$$[D_{k}(n_{1}l_{1}n_{2}l_{2}, \epsilon l_{a}n_{c}l_{c})d_{kl_{a}} + (-1)^{-L-S}E_{k}(n_{2}l_{2}n_{1}l_{1}, \epsilon l_{a}n_{c}l_{c})e_{kl_{a}}]\sum_{m_{a}m_{c}m_{p}MS_{z}\bar{m}_{c}\bar{\sigma}_{c}}C_{l_{c}010}^{l_{p}0}$$

$$C_{l_{c}m_{c}1\mu}^{l_{p}m_{p}}C_{LMSS_{z}}^{JJ_{z}}C_{l_{c}\bar{m}_{c}\frac{1}{2}\bar{\sigma}_{p}}C_{l_{c}\bar{m}_{c}\frac{1}{2}\bar{\sigma}_{c}}C_{l_{a}m_{a}l_{c}\bar{m}_{c}}C_{\frac{1}{2}\sigma_{a}\frac{1}{2}\bar{\sigma}_{c}}^{SS_{z}}B_{l_{a}m_{a}}(\mathbf{k}_{a})B_{l_{p}m_{p}}(\mathbf{k}_{p})|^{2}$$

$$(4.5)$$

and the tensorial formula

$$\frac{d^{2}\sigma}{d\mathbf{k}_{a}d\mathbf{k}_{p}} = 4\pi^{2}\alpha\hbar\omega\Gamma(\xi)\sum_{L_{0}M_{0}l_{a}l_{a}''}l_{p}l_{p}''L_{1}M_{1}L_{2}M_{2}}(-1)^{M_{2}}C_{L_{1}M_{1}L_{2}-M_{2}}^{L_{0}M_{0}}$$

$$\rho_{L_{0}M_{0}}^{*}\left\{B_{l_{p}m_{p}}^{i}(\mathbf{k}_{p})\otimes B_{l_{a}m_{a}}^{i}(\mathbf{k}_{a})\right\}_{L_{1}M_{1}}\left\{B_{l_{p}''m_{p}''}^{i*}(\mathbf{k}_{p})\otimes B_{l_{a}''m_{a}''}^{i*}(\mathbf{k}_{a})\right\}_{L_{2}M_{2}}A_{L_{1}L_{2}L_{0}}^{l_{p}l_{p}'}l_{a}''a_{a}''a_{a}''(4.6)$$

presented in the previous chapter. The tensorial formula (4.6) is surely more convenient from the point of view of the analysis of the cross section, since it separates the dynamical properties of the process, contained in the $A_{L_1L_2L_0}^{l_pl'_pl''_al'_al''_a}$ factor, from the kinematic properties and the beam polarization properties which are expressed by $\rho_{L_0M_0}^* \left\{ B_{l_pm_p}^i(\mathbf{k}_p) \otimes B_{l_am_a}^i(\mathbf{k}_a) \right\}_{L_1M_1} \left\{ B_{l_pm_p''}^{i*}(\mathbf{k}_p) \otimes B_{l_a'm_a''}^{i*}(\mathbf{k}_a) \right\}$. Looking at expression (3.80) for the $A_{L_1L_2L_0}^{l_pl_p''_pl_al_a'l_a''}$ factor, one can see that it contains several Wigner symbols, i.e. 6j and 9j symbols. The calculation of these angular momenta coupling coefficients strongly reduce the speed of the calculation. Thus, even if more convenient from the *physical* point of view, the tensorial formulation of the cross section is not convenient for numerical calculations, thus the modulus square has been used for all the following calculation.

4.5 Tests on atomic targets: the case of Ar and Xe

Calculations are performed for experimental data published by *P.Bolognesi et al.* [43] on the Ar $L_3M_{23}M_{23}$ transition with photon energy 253.6 eV (only 5 eV above threshold). No distortions of the cross section due to PCI between the photoelectron and the Auger electron (with 200 eV kinetic energy) are included in our simple model. Experimental data have been acquired using linearly polarized light at the Gas Phase beamline at ELETTRA synchrotron radiation facility in Trieste. The decay paths for the considered transition are:

$$h\nu + Ar \longrightarrow Ar^{+}2p_{\frac{3}{2}}^{5}({}^{2}P_{\frac{3}{2}}) + e_{p}^{-}(\epsilon_{s}, \epsilon_{d})$$

$$\hookrightarrow Ar^{2+}3p^{4}({}^{1}S_{0}) + e_{a}^{-}(\epsilon_{p})$$

$$\hookrightarrow Ar^{2+}3p^{4}({}^{3}P_{0,1,2}) + e_{a}^{-}(\epsilon_{p})$$

$$\hookrightarrow Ar^{2+}3p^{4}({}^{1}D_{2}) + e_{a}^{-}(\epsilon_{p}, \epsilon_{f})$$

$$(4.7)$$

For each multiplet term of the final ion state three coincidence angular distributions have been analyzed, corresponding to photoelectron detection at 0° , 30° , 60° from the light polarization direction in the plane of detection of the two electrons perpendicular to the photon beam. Normalization between theory and experimental data has been performed by comparing the integrated cross section and scaling the theoretical results using the ratio between the two integrals.

The comparison between experimental data and theoretical curves for ${}^{1}S_{0}$ final state is presented in fig. 4.1. The agreement is good for the experimental condition in which the photoelectron is revealed along the light polarization vector. In this case no additional quantization axis are introduced and the angular distribution of coincident Auger electrons retains its axial symmetry with respect to the light polarization direction. In this case also the anisotropy is reproduced well by the theoretical calculations. When the direction of detection of the first electron is moved to 30° from the polarization vector the calculations seems to reproduce still rather well the position of the lobes observed in the experiments, but the theoretical predictions appear to be more anisotropic than the measurements. This could be due to the fact that in our simple model without PCI the alignment in the intermediate state is the only link between photoionization and Auger decay. A more complete treatment of the intermediate state should improve the agreement between the theoretical results and the experimental data. The discrepancy concerning the anisotropy appears also in the case when the photoelectron is detected at 60° from the light polarization. In this latter condition also a disagreement in reproducing the lobe at $\approx 300^{\circ}$ can be noted. In contrast to the two previous cases (0° and 30°), the experimental results are dissymetrical. Agreement with upper experimental experimental lobe is good, while that with the lower one is not. This discrepancy has quite a strange character, since the calculations seems to reproduce quite well the position of the lobe but overestimates its intensity. A distorted angular distributions can be induced in cases in which PCI effects are important. In the experiment the photon energy was just 5 eV above the Ar L_3 threshold, thus the photoelectron has a much lower energy with respect to the Auger electron, and some interference effects could arise, i.e. the photoelectron with its lower energy acts as a post collision effect inducer for the process of Auger electron emission. This could lead to distortions of the coincidence cross section which are not included in our simple model. However, to test if such effects are present or not, one should improve the experiment with better statistics and measurements over a larger angular range.

Considering the reference system with the z axis along the beam polarization and the y axis along the beam propagation direction, the analytical expressions for the angular distributions presented in fig. 4.1 are given by (both $\phi_p = \phi_a = 0^{\circ}$):

$$\frac{d\sigma}{d\theta_a}|_{\theta_p=0^o} \propto 3.46\cos^2\theta_a + 0.87\sin^2\theta_a$$

$$\frac{d\sigma}{d\theta_a}|_{\theta_p=30^o} \propto 1.86 - 0.23\cos^2\theta_a + 1.09\sin^2\theta_a$$

$$\frac{d\sigma}{d\theta_a}|_{\theta_p=60^o} \propto 1.25 - 0.60\cos^2\theta_a - 0.46\sin^2\theta_a \qquad (4.8)$$

The weights of the sine and cosine functions are given by angular momentum coefficients and matrix elements which govern the transition. In principle, for more complex distributions, one could use the analysis provided by the $F_{l_ppl_{aa}}^{L_0}(\mathbf{k}_p, \mathbf{k}_a, \epsilon)$ functions to suppress some terms in the cross section. In our case, we did not consider the spin orbit interaction in the continuum, and thus a comparison between extracted and calculated photoionization matrix elements related to $l_p = 0$, $j_p = 1/2$ and $l_p = 2$, $j_p = 3/2$; 5/2 is not feasible and was beyond the scope of this work.

In fig. 4.2 the comparison between theoretical calculations and experimental data for the ${}^{3}P_{J}$ final state is reported. Since the different spin orbit component J of the final ion state are not resolved experimentally, we summed over the theoretical contributions from the different values of J with their statistical weights. It can be observed that for all the angular distributions (photoelectrons detected at 0° , 30° , 60° from the light polarization vector) the positions of the peaks are well reproduced while the anisotropy of the calculations is more pronounced than that of the experimental data. The discrepancy is larger at large angle between the light polarization and the direction of detection of the photoelectron. It can be noted that, especially in the case in which the photoelectron is detected at $\theta_{p} = 0^{\circ}$ and $\theta_{p} = 60^{\circ}$, the experimental data behave in a different way from what expected since in the position of the theoretical minimum the measurements seems to have a slight increase in intensity. These structures are far from being possible additional lobes, but the effect is clear and probably more evident in the condition $\theta_p = 0^{\circ}$ where at 180° a secondary local maximum appears in the experimental data. The theory only reproduces the two main structures in the cross section and completely misses such extra structures with lower intensity. The reason for this discrepancy between theory and experiments could again rely on the neglect of PCI effects in the model calculations. PCI effects are known to eventually predict a collapse of the angular pattern for small relative angle between the two electrons [51], but here no experimental data for the Auger electron are present near $\theta_p = 0^{\circ}$. The slight increase in the intensity appears exactly when the two electrons are measured in opposite directions. Moreover, these structures are not present in the case of 1S_0 and 1D_2 final state. This could suggest that the triplet character of the two electrons wavefunctions in the case of 3P_J could lead to differences with respect to a singlet emission case, apart from considering the whole rotation of the angular distribution. The unclear origin of this behaviour should be further investigated with measurements over a larger angular range.

The analytical expressions for the angular distributions for ${}^{3}P_{J}$ final state are obtained very quickly using the modulus square formulation of the cross section, whose calculation is much faster than the tensorial representation:

$$\frac{d\sigma}{d\theta_a}|_{\theta_p=0^o} \propto 2.48 + 0.91 cos 2\theta_a$$

$$\frac{d\sigma}{d\theta_a}|_{\theta_p=30^o} \propto 1.74 - 0.0007 cos 2\theta_a - 0.63 sin 2\theta_a$$

$$\frac{d\sigma}{d\theta_a}|_{\theta_p=60^o} \propto 1.04 + 0.25 cos 2\theta_a + 0.26 sin 2\theta_a \qquad (4.9)$$

In fig. 4.3 we present the comparison between the experimental data and the theoretical calculations for ${}^{1}D_{2}$ final state. As can be seen, also in this case the calculations reproduce well the shift of the coincidence angular distributions with respect to the light polarization vector. The position of the lobes agrees in all three kinematic conditions while the anisotropy is not well reproduced in all kinematic conditions. In the other cases the theoretical angular distributions are more anisotropic than the experimental patterns, especially when $\theta_{p} = 30^{\circ}$ from the light polarization. No other structures seem to be present in the experimental data, contrary to the case of ${}^{3}P$ final state. However, in the case $\theta_{p} = 0^{\circ}$ the experimental cross section seems to have not the simple form predicted by theory. Such disagreement goes beyond the anisotropic problem and should be investigated at different photon energy to assess its origin.

The analytical expressions for the angular distributions for ${}^{1}D_{2}$ state are given by:

$$\frac{d\sigma}{d\theta_a}|_{\theta_p=0^o} \propto 4.06 + 4.32\cos 2\theta_a + 0.81\cos 4\theta_a + 0.12\cos 6\theta_a$$
$$\frac{d\sigma}{d\theta_a}|_{\theta_p=30^o} \propto 2.83 + 1.82\cos 2\theta_a + 0.073\cos 4\theta_a$$
$$+ 0.046\cos 6\theta_a + 2.37\cos \theta_a \sin \theta_a + 0.046\cos 6\theta_a + 0.012\cos \theta_a \sin \theta_a \theta_a \sin$$

$$\begin{array}{l} +0.45sin4\theta_{a} + 0.043sin6\theta_{a} \\ \frac{d\sigma}{d\theta_{a}}|_{\theta_{p}=60^{o}} \propto 1.68 + 0.603cos2\theta_{a} - 0.155cos4\theta_{a} + \\ 0.114cos6\theta_{a} - 0.995cos\theta_{a}sin\theta_{a} - \\ 0.19sin4\theta_{a} - 0.18sin6\theta_{a} \end{array}$$

$$(4.10)$$

These expressions are more complex with respect to the case of ${}^{1}S_{0}$, ${}^{3}P_{J}$ final states, since for ${}^{1}D_{2}$ final state also the $l_{a} = 3$ is possible for the Auger electron.

Apart from Argon we have performed another calculation on the transition $Xe N_5O_{23}O_{23}$ (¹S₀). Experimental data [42] have acquired with linearly polarized light with a photon energy 94.5 eV. Both electrons have been detected in the plane perpendicular to the photon beam propagation direction. the decay path related to the (¹S₀) final state can be represented by the following scheme:

$$h\nu + Xe \longrightarrow Xe^{+}4d_{\frac{5}{2}}^{-1} + e_{p}^{-}(\epsilon_{p}, \epsilon_{f})$$
$$\hookrightarrow Xe^{2+}5p^{4}(^{1}S_{0}) + e_{a}^{-}(\epsilon_{d})$$
(4.11)

Thus only one angular momentum is allowed by the Coulomb selection rules for the Auger continuum electron. The Auger electrons have been acquired with a fixed detection angle of the photoelectron ($\phi = 150^{\circ}$ from the polarization vector). The comparison between experimental data and our calculation is represented in fig. 4.4.

As one can see, the agreement between theoretical calculations and experimental data is very good. Most of the experimental points lies, within their error bars, on the theoretical curve. In principle, we expected less agreement in this case with respect to the case of Argon, due to the fact that Xenon would require more complicated calculations with the inclusion of further relativistic and correlation corrections. However, also in the $({}^{1}S_{0})$ Argon case the agreement was good, even if it was reduced going far from the light polarization vector with the photoelectron's detection angle. Here we only have one set of measurements, thus we cannot say what happens for different photoelectron's detection angles. Nevertheless, we can say that when the two electrons (or the two final holes, it is equivalent to talk about the final holes or the continuum electrons since the Coulomb scalar interaction must conserves the quantum numbers) are coupled to a ${}^{1}S_{0}$ state then the angular correlation factor inside our simple model describe well the experimental data. This sentence is also strengthened by the fact that, since only one channel is present for the Auger continuum electron, and moreover the k = 0 Coulomb term is usually the dominant one while the others can be neglected, then the Auger matrix element can be factorized in front of the cross section and the angular distribution is completely described by the angular correlation part.

A 3D visualization of the coincidence angular correlation patterns is given in fig. 4.5. These representations have been obtained from calculations on $Xe N_5O_{23}O_{23}$ (1S_0), varying both the polar and azimuthal angle of the Auger electron at different fixed detection angles of the photoelectron. The first picture in fig. 4.5 represents the kinematical situation studied in the experiment to which we compared the previous polar scan [42]; the second one represents the case in which the photoelectron is detected along the light polarization and the third one when the photoelectron is detected outside the plane normal to the light propagation direction ($\theta = 150^{\circ}, \phi = 45^{\circ}$). It must be clear that the polar plots we have presented until now are cuts of the 3D angular distributions along a certain plane. Unfortunately, due to the difficulties and the low count rates in coincidence experiments, no full-hemispherical experimental data are available in the world, but several groups are employing new techniques to increase the speed of the measurements with high technology analyzers.

4.6 Multiple scattering calculation of Auger and coincidence diffraction pattern

We now start the discussion about the numerical calculations of conventional single Auger diffraction pattern and coincidence Auger diffraction patterns from Ge(100) $L_3M_{4,5}M_{4,5}$. The transition we considered can be schematized as :

$$h\nu + Ge \longrightarrow Ge^{+2}p_{\frac{3}{2}}^{-1} + e_p^{-}(\epsilon_s, \epsilon_p)$$
$$\hookrightarrow Ge^{2+3}d^8({}^1G_4) + e_a^{-}(\epsilon_f, \epsilon_h)$$
(4.12)

The experimental data are those showed in the first chapter in figure 1.4 [10]. The bottom curve is conventional AED pattern (i.e. non coincidence Auger diffraction), while the other curves are coincidence Auger diffraction patterns related to different detection angles of the photoelectron. Before starting the real calculation, it is often convenient to do some preliminary tests. It is indeed necessary to perform test calculations on a model cluster trying to optimize the parameters in order to reduce the CPU time. This is because multiple scattering calculations can become rapidly very lengthy and cumbersome. These tricks allow to decrease sensibly the CPU time while remaining within the bounds of the experimental error bars. Obviously, the results should be controlled against that of a full calculation. In the following we will describe the parameters to optimize the CPU time while remaining within the bounds only the final ones which are compared to the experimental data.

For the preliminary calculations a very small clusters have been used (a cluster with a radius which is a little bit bigger than the first neighbours distance). This cluster was a complete bulk cluster with no terminated surface. This is because in these first test calculations we need to consider also the backscattering effects to assess their importaance, which cannot be estimated from the beginning starting with a surface cluster since the atoms in the deepest row would not have the possibility to give rise to backscattering. The real calculations (the final ones which will be presented) have been performed using a cluster with reconstructed surface. This is because the Ge surface is known to reconstruct with a reconstruction denoted by 2x1 [189]. This means that the periodicity of the surface structure doubles, since to be reproduced it requires two unitary surface cell with the new position of the atoms. In particular, the atoms which are at opposite side of the unitary cell come closer to each other moving their position of about 0.8 angstrom-the surface cell side is 4 angstrom long- and they constitute what is called *dimers*. This happens only for atoms on two sides of the square of the surface cell, not for all the four sides. All calculations are performed moving the absorber from one plane to the next one and then summing incoherently the contributions given by the different planes in the cluster.

There are many parameters that can affect the CPU time. The most important whose decrease will speed up the calculation, provided they don't destroy the quality of the results, are given by:

- the number of l values used for the spherical wave expansions on the atomic centers. The number of the l values is $l_{max} - 1$ with l_{max} given by $(l_{max} * (l_{max} - 1))^{1/2} = kR_{MT}$. This value can often be decreased slightly. This can be done automatically using a little code which erases the contribution of a selected number of l. In this way we have reduced both the number of the l values related to the spherical wave expansion of the photoelectron (used for the coincidence spectra), and the number of the l values related to the spherical wave expansion of the Auger electron (used both for the conventional Auger and coincidence Auger diffraction patterns). The reduction (from 22 l values to 20 for the photoelectron and from 32 to 25 for the Auger electron) was checked step by step with the calculation performed with the maximum values. If the difference between the two curves was not bigger than the experimental error bars then the reduced l value calculation was considered to be good. The gain in CPU time was about one third of the total calculation both for the photoelectron and the Auger electron.
- The Rehr Albers parameter, which is the order of truncation in the expansion of the propagator, was reduced from the value 3 to 2, since the differences between these two calculations were visible only in an angular range outside the one which of interest. Indeed, the difference were only in the peak at 45° from the normal to the surface, which is not in the range of the available experimental data (see figure 1.4 in chapter 1).
- The parameter which describes the order of truncation of the multiple scattering series was reduced from 2 to 1. This means that we choose to use a single scattering approximation, both for the Auger electron (in conventional Auger diffraction pattern and in coincidence diffraction patterns) and the photoelectron (in coincidence diffraction pattern). In the case of Auger electron, the kinetic energy was 1362 eV. In this high energy regime the single scattering approximation was good and no remarkable differences were observed with the calculation performed with a scattering order equal to 2. For the photoelectron, the kinetic energy was 252 eV, and some differences appeared in the calculations with different scattering order. However, since the photoelectron was needed only in the coincidence calculations, we supposed that such differences would not influence strongly the coincidence Auger diffraction pattern, which are calculated for fixed direction of the photoelectron. Moreover, note that single scattering was treated exactly while for higher scattering orders we only took into account scattering in a cone of 20° centered on the forward direction as suggested by the shape of the scattering factoir. This allowed us to reduce the number of multiple scattering

pathways in the calculations, and therefore the CPU time required. We checked that this approximation was valid first by repeating the calculation with scattering order equal to 2 for a larger cone (35°) .

The last thing that must be notified about the time needed for performing the calculations does not really concern the calculation parameters but it allow us to gain much time in our numerical calculations. Both the single conventional Auger diffraction calculations and the coincidence Auger diffraction calculations were done only for the dominant final multiplet term (${}^{1}G_{4}$) which is present in the $L_{3}M_{45}M_{45}$ Ge energy spectra. This means that setting the Auger analyzers on the energy of such multiplet term with experimental resolution which is smaller that the separation between this and the other multiplet terms, then the diffraction patterns are essentially given by the angular distributions of Auger electrons giving rise to this dominant multiplet term. In the experiment to which we refer [10], with an energy resolution of 2 eV, the spin orbit splitting of the core level in photoemission, as well as the dominant ${}^{1}G$ multiplet of the Auger transition were resolved easily.

Moreover, we must spend a few words about the use of a closed shell model in describing an open shell system like Ge. The first important thing is the identification of the intermediate state with the quantum numbers of the core hole. As the 2p binding energies of Ge occur at 1217.0 eV ($2p_{3/2}$) and 1248.1 eV ($2p_{1/4}$) [190], the energy separation is sufficient to identify the intermediate ion with such quantum numbers, since the spin orbit interaction is much stronger than the Coulomb interaction between core and valence shells. Moreover, due to this large value of the spin orbit splitting, the Auger decays related to these spin orbit partner edges will not be overlapped and the Auger spectra related only to one of the two holes can be studied clearly without any complications.

The measurements of the single conventional Auger diffraction patterns and coincidence Auger diffraction patterns have been performed at the ALOISA beamline at the ELETTRA synchrotron radiation in Trieste, Italy. All details related to the experiment are reported in the related paper ([10]) and only a brief description is given here. A monochromatized beam ($\hbar \omega = 1450 \text{ eV}$) of linearly polarized photons is impinged at a grazing angle of 6° degree and nearly p polarized onto a Ge(100) syngle crystal surface that has been sputtered and annealed until it exhibited a sharp reflection high energy electron diffraction pattern indicating the 2x1 reconstruction. The measurement chamber of ALOISA beamline contains an array of seven electron analyzers arranged in two independent rotatable frames (two analyzers on the so called bimodal frame and five on the axial frame) that were used to detect electrons at preset energies and angles. A scheme of the arrangement of all analyzers is reported in fig. 4.6. The two analyzers on the bimodal (or scanning) frame were rotated as a unit to monitor the Ge $L_3M_{45}M_{45}$ (1G_4) Auger electron emission intensity as a function of the polar angle.

In figure 4.7 we present the comparison between the experimental and the calculated Auger electron diffraction pattern. The calculation is performed using the optimized parameters derived by preliminary calculations on a small but significative cluster and building a cluster with radius which is a little bit smaller than the one given by the mean free path of the Auger electrons at 1362 eV. At this energy, the mean free path is approximately 19 angstrom. In principle the cluster should be built with a radius twice the mean free path. Such quantity in this case would have been very large, giving a very big cluster, not

convenient for realiable calculations. Thus we built a cluster with a radius of 30 angstrom and a cluster with a radius of 19 angstrom, we calculated the signal coming from the first three planes and we verified that no remarkable differences were present. The cluster with radius equal to 19 angstrom was considered as sufficient, since the Auger electron have such high energy in the considered transition that mainly the atomic chains will contribute to the scattering process, and such atomic chains are also reproduced in such smaller cluster. Performing the calculation with this cluster, convergence was reached using 9 planes. We then proceeded with the calculation with 9 planes. The calculation presented in figure 4.7 is given by the sum over signals coming from 9 planes. As we can see from the comparison between theory and experiment, the theoretical curve reproduces the main structures. The first thing that can be noted is that the second peak, which starts to appear when considering the absorber in the sixth plane, is shifted by some degree but both right and left side shoulders are present in the calculations. The anisotropy is well reproduced and also the double peak structure at zero degree is present in the theoretical calculation. To underserstand the origin of this double peak structure we performed very simple calculations varying the value of the interstitial potential, the dimension of the cluster and switching off or turning on the reconstruction of the surface. Different trials calculations have been done in order to clearify the origin of such effect, if it was due to structural effects or to some electronic parameters used to describe the electronic structure of the sample. The result was that the double peak structure was given by signals originating from inequivalent absorbers in the same plane. These absorbers are surrounded by slightly different environment, due to reconstruction of the surface. The surface atoms reconstruct moving their position of a quantity which cannot be neglected and influence the scattering paths originating from the absorber and ending in a surface atom. However, we observed also a weak dependence of the presence of such double peak structure on the value of the interstitial potential, but this has no remarkable effect due to the very high kinetic energy of the Auger electrons.

We now move to the coincidence patterns. It is necessary to specify the geometrical conditions of the experiment. The five analyzers, placed at intervals of 18° on the axial frame (which is fixed in this experiment), were tuned to monitor the Ge $2p_{3/2}$ photoelectron in a plane that contained the photon beam axis and that was rotated 54° from the sample normal [10]. Thus the two bimodal analyzers measured an angular distribution in coincidence with five different values of the photoelectron momentum wave vector selected by the five axial analyzers. The conventional AED patterns and the coincidence pattern were recorded simultaneously.

The first coincidence calculation has been performed with the same cluster used for the conventional AED patterns (composed by 9 planes). The theoretical curves are given by the incoherent sum of the signals coming from 9 planes. As an example we show in figure 4.8 the comparison between the AED conventional pattern and the coincidence patterns related to photoelectron detected by analyzer 1 and analyzer 5, which are opposite with respect to the plane perpendicular to the beam propagation direction. In principle, the cluster that must be considered for a coincidence calculation is suggested by the theoretical model (see the next paragraphs for further details); however, at this step, our intention was just to see, with the same condition for the structure of the cluster (i.e. the same number of planes and

the same radius for the cluster), which are the differences between a single Auger diffraction calculation and a coincidence calculation. As it can be noted, the coincidence diffraction pattern are less anisotropic (we call anisotropy the ratio between the maximum of the intensity and the minimum) with respect to the AED noncoincidence pattern. This is due to the fact that the coincidence cross section has an intermediate state, in which the m_l sublevels related to the core hole interfere and this interference reduces the anisotropy of the angular distribution. In the single Auger cross section the core hole is the initial state and the sum over its magnetic quantum numbers is an external sum, i.e. the contributions from different sublevels are incoherent. A preliminary study we performed on the Ar coincidence angular distribution presented above has shown that without considering the spin orbit interaction for the core hole in the coincidence cross section then the m_l sublevels didn't interfere and the signal was much more anisotropic, even leading to some zeros in the cross section. The interference between magnetic sublevels revealed to be essential in order to reproduce the anisotropy of the Ar angular distribution presented above. The diminuishing anisotropy in coincidence distributions with respect to non coincidence distributions is also visible in the experimental data about Ge(100) in figure 4.9 [10]. It can be noted that also the experiment reveals a minor anisotropy in the coincidence patterns with respect to the non coincidence one. However, the anisotropy of the coincidence theoretical curves in fig. 4.8 is still very high with respect to coincidence experimental data, which suggests that not only the interference between magnetic sublevels is important for the anisotropy, but also the dimension of the cluster must be reduced (shortest chains of atoms give rise to peaks whose intensity is reduced). Moreover, both the theoretical curves in figure 4.8 and the coincidence experimental data (summed over all the analyzers) in figure 4.9 do not show the double peak structure at zero degree. For the experimental data this can be explained by the fact that many of the electrons pairs detected as coincidence pairs have no suffered scattering at all, thus there is no influence of the position of the other atoms or of the environment sourrounding the emitter, except for the calculation of the outer levels wave functions involved in the Coulomb integrals which can be more delocalized or not depending on the position and species of the other atoms. For the theoretical curves, the disappearence of the double peak structure has no clear origin, since all the signals are given considering single scattering, thus the position of the atoms in the cluster is important. However, the peak at zero degree seems to be larger then the one appearing in the noncoincidence AED calculation, thus we can argue that the coincidence calculation in someway spread out the peak and the double peak structure is not visible anymore. This effect has an unclear origin and must be investigated more deeply.

To roughly investigate the number of planes necessary to reproduce the anisotropy presented by the coincidence experimental data we calculated the intensity as the sum over the first 6 planes of the 9 planes which constituted the cluster. This can give just a first approximation about the sensitivity to the surface which is hown by the coincidence technique, but the right dimension of the cluster must be considered as a consequence of theoretical model, as it is discussed further. The comparison between the signal coming from just 6 planes of the original cluster with which we calculated the single Auger diffraction and the experimental data summed over all the electron analyzers is represented in figure 4.10. The anisotropy of the experimental data is still lower than the calculated curves but the agreement is acceptable. On the peak at 20 degree the theoretical curve do not show a well identified structure, and, where the experimental data have a local maximum, it has a local minimum. This effect cannot be caused by the different sensitivity of the experimental data and theoretical curves regarding the outgoing electron pairs, since the peak at 20 degree is only due to scattering along chains, thus it should be completely suppressed in the experimental data. However, of course not only the electron pairs which have not scattered at all are detected by the analyzers, but also a fraction of those which are scattered keeping their time correlation are revealed, thus this explains the presence of the 20 degree peak. Probably the electron pairs emitted along the light polarization vector (which coincides with the normal to the surface) are those that suffer to a less extent the scattering, while those emitted at larger angle are subjected to the scattering process in a more remarkable way.

To consider the right dimension for the cluster one has to make some preliminary considerations. In a coincidence event, the two electrons must originate from the same atoms, and, thus, the inverse of the effective escape depth λ_{eff} in solids is given by

$$\frac{1}{\lambda_{eff}} = \frac{1}{\lambda_p} + \frac{1}{\lambda_a} \tag{4.13}$$

Thus the mean free path in a coincidence experiment is reduced with respect to the corresponding photoemission experiment and to the corresponding Auger electron diffraction experiment, since the λ_{eff} has a lower value than the minor mean free path between the one related to the photoelectron and the one related to the Auger electron. In our case, the effective mean free path resulted to be about 7 angstrom. This means that in principle only a cluster with radius equal to this quantity is probed, which substantiates the increased surface sensitivity shown in the experiment we are considering and in some other coincidence experimental results. We then can perform calculations on a cluster whose radius is 7 angstrom. We used the same calculation parameters used in the previous calculations. This smaller cluster was also terminated with a reconstructed surface, following the 2x1 superstructure known to appear in Ge(100). The theoretical curves obtained for the coincidence Auger diffraction data corresponding to photoelectrons detected by analyzer 1,3,5 are shown in figure 4.11. We remember that analyzer 3 is the one which lies in the plane perpendicular to the photon beam propagation direction, while analyzers 1 and 5 are opposite with respect to this plane.

The first thing that must be noted is that the curve corresponding to Auger diffraction in coincidence with photoelectrons detected by analyzer 3 is symmetric with respect to the 0 degree direction, which corresponds to the normal to the surface and to the light polarization vector in our calculation. The other two curves related to Auger diffraction in coincidence with photoelectrons detected by analyzer 1 and 5 are not symmetric with respect to this direction. Moreover, the anisotropy in the results related to analyzer 3 is bigger then the anisotropy shown in the other cases. We have already said in chapters 1 and 3 that when one of the two electrons is detected along the light polarization vector then the coincidence angular distribution has the same behaviour of the single photoelectron (or

Auger) angular distribution (i.e. the well known formula $\frac{d\sigma}{d\Omega} \propto 1 + \beta P_2(\cos(\theta))$. The only thing that differs with respect to the non coincidence case is the anisotropy, which is reduced in the coincidence case. Out - of - polarization detection conditions even lead to a lower anisotropy. The anisotropy is reduced with respect to the non coincidence case due to the fact that the magnetic sublevels m_l of the core hole interfere. When the photoelectron is detected along the light polarization, then only $m_p = 0$ are detected. Moreover, taking the z axis along the light polarization vector, the excitation rule $\Delta m = 0$ holds, which means that only magnetic sublevels of the core hole $m_c = 0$ are contributing. In this case the projection of the spin of the core hole $\sigma_{cz} = \pm 1/2$ only couple to $m_c = 0$, which means that we have two terms in the cross section, corresponding to $j_{cz} = 1/2, -1/2$ (thus in the cross section one will have an amplitude related to each of these j_{cz} and an interference factor). In the second step j_{cz} is the same since the intermediate state characterized by j_c, j_{cz} is the same, but the core hole can migrate to different m_l without changing its energy. Thus in the second step the different m_l sublevels interfere. Thus, both the interference due to the different j_{cz} and the interference in the second step due to different possible m_l contribute to lower the anisotropy of the cross section. In the other cases, when the photoelectron is detected out of the light polarization direction, the different m_l sublevel interfere also in the first step of the process (photoemission case) since the $m_p = 0$ does not hold anymore but all m_p can contribute which are equal to the m_c sublevels (the rule $\Delta m = 0$ is still holding). This leads to an even lower anisotropy in such out - of - polarization condition. When the photoelectron (or the Auger electron) is detected along the light polarization, the alignment of the intermediate ion is maximum and can be represented by the figure 1.3.1 in the first chapter. Alignment is associated to the quadrupole moment. Then emission along the light polarization vector is preferred. When the electron is detected in another direction, then complex phases arise between the population in the different sublevels and they can interfere strongly giving rise to a less anisotropic coincidence distribution. In such geometrical conditions also other state multipoles of the system contribute to the cross section.

About the symmetry of the curves we can now explain why each of the coincidence patterns related to the photoelectron detected by analyzer 1 and 5 is not symmetric with respect to the light polarization vector. The contribution from the different multipoles of the system makes the preferred emission direction not to coincide anymore with the light polarization direction. The preferential emission direction is rotated since the whole system (intermediate ion with detection of the fixed electron outside the light polarization vector and angle scansion over the other electron) has no axial symmetry anymore. The coincidence diffraction patterns keeps memory of the fact that the preferential direction is now moved from the 0 degree direction, and the multiple scattering signal grows on a direct signal (the wave emitted by the absorber and directly reaching the detector) which is asymmetric. In particular for analyzer 1 and 5 the direct signal (which is similar to the atomic signal but slightly moved because of refraction effects) has a maximum in opposite direction with respect to the light polarization vector, and thus the diffraction patterns related to the two analyzers have opposite behaviour. In the curve related to analyzer 1, the shoulder of the main peak, which is due to the memory kept of the asymmetric direct signal, appears on the right side of the 0 degree peak, while for analyzer 5 it is on the opposite side. The

atomic coincidence signal related to all analyzers is shown in figure 4.12. These results are in contradiction with the experimental results shown in figure 1.4 shown in chapter 1. The experimental results suggest that the coincidence patterns related to opposite analyzers have the same shape, with the 0 degree peak moving slightly from the 0 degree position toward the same direction. It is important to note that, in the theoretical results the main peak does not rotate, but it is fixed at 0 degree, only little structures (the shoulder) appear indicating the memory kept about the initial atomic angular correlation between the two electrons. We also thought about the possibility of another multiplet term (i.e. the ${}^{3}F$ which is the second one in intensity in the Ge $L_3M_{45}M_{45}$ spectrum) contributing to the angular distribution. The hypothesis was that, similar to the case of Argon, in which multiplet terms with different spin character have an opposite behaviour of the angular distributions, the two curves in the bottom of figure 1.4 could be given by the angular distribution of the Auger electron coming from the ${}^{3}F$ term. The one related to the ${}^{1}G_{4}$ term would move towards negative polar angles in the figure 1.4. However, the experiment was performed with an energy resolution which allowed to discriminate the different multiplet terms in the Auger spectra. Nevertheless, to be sure that such contribution was not important, we performed the calculation also for the ${}^{3}F$ term, but, unlike the Argon case, the angular distribution followed the same behaviour of the one given by the ${}^{1}G_{4}$ term. Moreover, its contribution was about 2 order of magnitude smaller, and then we completely neglect its angular distribution. The atomic coincidence angular distributions of the ${}^{1}G_{4}$ and ${}^{3}F$ have been also calculated using equation (1.2), which is derived by a more detailed approach (based on the density matrix) in which all the angular momenta (of the whole atom and of the whole intermediate and final state) are considered. This means to consider a many body approach, while our simple model is based on the single particle approach. The angular distributions related to these two terms and derived by this model have nearly the same behaviour of the cross sections derived within our model, i.e. the angular distributions are shifted to opposite directions with respect to the light polarization when considering two analyzers which are opposite with respect to the plane perpendicular to the photon beam. This suggests that in general it is not true that different multiplet terms with different spin character (singlet and triplet states) have an opposite behaviour of the angular distribution for equal geometrical conditions (as it happened in the case of ${}^{1}S_{0}$ or ${}^{1}D_{2}$ against ${}^{3}F$ in the Argon case). The angular momenta of the outgoing electrons play a relevant role, and also the radial matrix elements which are related to them, which weight the angular distribution corresponding to each partial wave.

The disagreement with the observed behaviour is not good of course, but the theoretical results seem, at least at first sight, not so unreasonable. Indeed, at such high energy (Auger electron at 1362 eV), the Auger electrons are focused along the atomic chains and they do not care much about the initial angular *source wave*. The only thing which matters is the geometrical structure of the sample in this regime, thus it is reasonable that the peak at 0 degree is not shifted by the coincidence detection with the photoelectron, even if a little memory is kept by the angular pattern of emission from the solid sample. The forward focusing in the 0 degree direction gives rise to the main peak, whose anisotropy is much bigger than the one of the atomic angular correlation (which is the intrinsic anisotropy at
the atomic site). Then the atomic angular correlation is nearly completely oscured by the scattering effects since the diffraction signal grows on an asymmetric (with respect to the light polarization direction) direct signal, but characterized by a very small anysotropy with respect to the one induced by forward focusing. We have to note that is not meaningful to compare these theoretical curves with the experimental data, since the theoretical curves themselves would not be dinguishable one from each other in the description of the experimental results (because of large error bars shown by the measurements). Thus in order to see if the slight precession of the main peak is really present in the coincidence angular distribution, probably it would be better to repeat the experiment, with the new capability of ALOISA beamline, including higher resolution analyzers. The last thing which must be noted is that it does not seem that the approximations made within the theoretical model (single particle approximation, closed shell model) can be the reason for such disagreement. The model described well both the Argon and Xenon angular distribution, where we tested if the atomic angular correlation was predicted correctly. The high energy regime in the Ge transition suggests that the emission is strongly preferential along the chains of atoms, without regarding the intrinsic angular distribution at the atomic site, as it has been proved in the past for photoelectron and Auger diffraction.



Figure 4.1: Comparison between experimental data and theoretical results for Ar $L_3M_{2,3}M_{2,3}$ (¹S₀) Auger coincidence angular distributions for different detection angles of the photoelectron ($\theta_p = 0^\circ, \theta_p = 30^\circ, \theta_p = 60^\circ$). Both electrons are detected in the plane perpendicular to the photon beam



Figure 4.2: Comparison between experimental data and theoretical results for $Ar L_3 M_{2,3} M_{2,3}$ $({}^{3}P_{J})$ Auger coincidence angular distributions for different detection angles of the photoelectron $(\theta_p = 0^{\circ}, \theta_p = 30^{\circ}, \theta_p = 60^{\circ})$. Both electrons are detected in the plane perpendicular to the photon beam



Figure 4.3: Comparison between experimental data and theoretical results for Ar $L_3M_{2,3}M_{2,3}$ (¹D₂) Auger coincidence angular distributions for different detection angles of the photoelectron ($\theta_p = 0^{\circ}, \theta_p = 30^{\circ}, \theta_p = 60^{\circ}$). Both electrons are detected in the plane perpendicular to the photon beam



Figure 4.4: Comparison between experimental data and theoretical curves of the coincidence angular correlation in Xe $N_5O_{23}O_{23}$ (1S_0) when both electrons are detected in the plane perpendicular to the photon beam and the photoelectron is fixed at 150 degrees from the light polarization vector



Figure 4.5: 3D plots of the coincidence angular correlation in Xe $N_5O_{23}O_{23}$ (¹S₀). The polar and azimutal angle of the Auger electron are varied for fixed different detection angles of the photoelectron (see text for details)

experimental arrangement of the analyzers



Figure 4.6: A scheme of the arrangement of the analyzers at the ALOISA beamline



Figure 4.7: Comparison between AED experimental data and theoretical AED curve for $Ge(100) L_3M_{45}M_{45}$



Figure 4.8: Comparison between AED theoretical curve and coincidence theoretical curves (related to analyzer 1 and 5) for $Ge(100) L_3M_{45}M_{45}$



Figure 4.9: Comparison between experimental AED data and experimental coincidence diffraction data for $Ge(100) L_3M_{45}M_{45}$ (the latter given by the sum of the signals of all analyzers) [10]



Figure 4.10: Comparion between the coincidence signal obtained summing over all axial analyzers and the corresponding theoretical result obtained from a cluster with radius equal to 19 angstrom (in principle composed by 9 planes) considering only 6 planes



Figure 4.11: Coincidence Auger $L_3M_{45}M_{45}$ (¹G₄) diffraction pattern from Ge(100) detected with different direction of the photoelectron emission



Figure 4.12: Coincidence Auger $L_3M_{45}M_{45}$ (1G_4) atomic angular correlation for photoelectrons detected by the 5 axial analyzer of the beamline ALOISA in the experimental condition of the Ge(100) experiment.

Conclusions

In this work we have studied the correlations which arise in Auger-photoelectron emission, focusing our attention on the angular distribution of the electron pairs. The study of photon-induced Auger decay is among the most important goals in atomic and condensed matter physics, since it is only due to Coulomb interaction and thus it allows to study the many body dynamics of the system under investogation. In coincidence experiments the angular distribution (and hence also the energy lineshape) of the Auger electron cannot be treated as independent of the method of the hole production. Auger-photoelectron coincidence spectroscopy allows an insight into the interplay between symmetry reduction and interparticle correlation. We derived the Auger-photoelectron coincidence cross section within the multiple scattering theory (which is based on the single particle approach) and a closed shell model. The multiple scattering cross section cannot be coupled completely as the atomic one, due to breaking of the spherical symmetry of the problem. For the atomic cross section, our formula has the same structure of the one derived by other authors using the density matrix approach, which, however, is not suitable to be extended to diffraction problems. We have found a formulation which completely separates the dynamical and the geometrical part, giving rise to the possibility of predicting the expected anisotropy once the angular momentum components allowed for the outgoing electrons are known. We also analyzed the light polarization dependence. We showed that emission direction of one of the two electron influences the emission direction of the other one. This result was already known in atomic theory and it has been studied using the density matrix approach. Our aim was to extend such studies also the solid state case, and for this scope this approach was not suitable, due to complications coming from several angular momentum summations. We then developed a new approach, based on one particle multiple scattering theory, in which we consider the initial angular correlation of the two electrons at the atomic site and then they propagate independently one from each other. On the one hand, such model allows us to describe the scattering effects due to the environment of the absorber atom. However, on the other hand, using a single particle approach we loose some of the initial correlation since we consider only the angular momenta of the electrons strictly involved in the transition. Nevertheless, such correlation seems to be well described, as one can see from our results on atomic targets. About the calculations and comparison with experimental data, we now briefly summarize the main numerical results achieved and presented in this thesis.

• ATOMIC TARGETS: Ar and Xe. The agreement between theoretical calculations and experimental data for $Ar L_{23}M_{23}M_{23}$ Auger transition depends on the specific decay path and the photoelectron's direction. Regarding the geometry of the

experiment, for all possible ion final states the agreement in anisotropy decreases when the photoelectron is moved from the light polarization direction. For the position of the peaks some discrepancy appears, especially in the ${}^{1}S_{0}$ $\theta_{p} = 60^{\circ}$ case. However, the degree of agreement is of the same order than in the case of other calculations performed within statistical tensor approach used in angular correlations problems, where all possible angular momentum recoupling are considered and matrix elements are usually calculated using MCDF model. Disagreement in terms of anisotropy of the angular distributions can be noted in both approaches. This can be due to a a wrong description of the intermediate state. Without PCI effects, the only link between the two steps of the whole process is the alignment of the intermediate state. Regarding distortions which appear in the cross section which are not clearly explainable, one could argue that PCI effects could arise due to lower kinetic energy of the photoelectron. However, PCI effects generally induce some collapses of the correlation patterns at small relative angles due to repulsive interaction between the two electrons, and experimental data should be collected over a larger angular range in order to test the presence of such effects. Nevertheless, the inclusion of PCI effects should improve the agreement both in terms of anisotropy and in terms of possible distortions of the cross section.

For the case of Xe, we derived the full 3D angular pattern for three different geometrical conditions, and we compared a cut along a determined plane with experimental data. The agreement between theory and measurements is very good, and this result, together with the correct rotation of the Ar angular distributions, suggests that the angular correlation is well described by our simple model. It is important to note the decisive role played by spin orbit of the core electron, ionized in the first step of the process. Preliminary calculations which were not shown indicate that without such interaction, some nodes appeared in the cross section, which are however not detected by experimental measurements.

• THE CASE OF Ge(100). In the case of $Ge(100) L_3M_{45}M_{45}$ we first calculated the noncoincidence Auger diffraction pattern. The agreement was rather good, i.e. the two main structures (the peak at 0 degree and the peak at 20 degree) were reproduced and also the double-peak structure in the main peak at 0 degree appeared from the calculations, while some small discrepancies appeared in the second peak at 20 degree. About the coincidence Auger diffraction patterns, from theoretical calculations they resulted to be less anisotropic with respect to single Auger diffraction pattern. This is because in the coincidence cross section the magnetic sublevels interfere with each other, while in the usual Auger cross section they contribute incoherently. Among the coincidence pattern, the one related to photoelectron detection by analyzer 3 was the one more similar to the single Auger angular pattern, both in terms of symmetry and in terms of anisotropy. This is due to the fact that when one of the electron is detected along the light polarization vector the coincidence angular distribution has the same behaviour of the single photoelectron (or Auger electron) emission. In this case the alignment of the intermediate state is maximum and the preferential direction is along the only quantization axis introduced in the process, i.e. the polarization vector (for

linearly polarized light). When one of the electrons is detected out of the polarization the decay happens in a field without axial symmetry and the different state multipoles of the system interfere giving rise to a breaking of the axial symmetry in the other electron's distribution. In the case of high energy regime (such as in our case of Ge), the only memory kept about such symmetry breaking is the appearence of a small shoulder on different sides of the main peak, depending on the detection angle of the photoelectron. The electrons are mainly focused along atomic chains without regarding the features of their initial coincidence angular distribution at the atomic site. This is in contrast to what suggested by the experimental data, which seem to suggest a slight precession of the main peak in the coincidence diffraction patterns. Photoelectron detection by analyzers which are opposite with respect the plane perpendicular to the light polarization gives rise to similar coincidence pattern, rotated in the same direction. Calculations suggest that there is no rotation of the diffraction pattern, but the diffraction patterns grow on an asymmetric (with respect the 0 degree direction) direct signal, which is, however, opposite for photoelectron analyzers which are opposite with respect to the plane perpendicular to the beam direction. However, since the experiment was one of the pioneering experiment in the field, we are sure that the present high-quality capability of the beamline ALOISA could be fully exploited to shed a new light of these kind of experiments and to clearify the disagreement between theoretical and experimental results. For the theoretical point of view, the developing of a model in which also the whole set of intermediate state is considered is attracting a new interest, leading to a more detailed model whose applications can be exploited both in the angular correlation problems, and in the energy spectra calculations. In order to test the model and to see if the diffraction coincidence pattern keeps a more noticable memory of the intrinsic angular correlation, we suggest, in the future, to choose Auger decays which are more anisotropic and characterized by a lower energy with respect to the case analyzed here. If the anisotropy of the intrinsic angular correlation at the atomic site is higher, then there is a hope that the diffraction pattern is really altered by such initial correlation. But this can happen only if the emitted electrons have no very high energy, otherwise they essentially will be focused along atomic chains, loosing almost any memory about their original preferential emission directions.

Our model relies on a single particle approach and we considered a closed shell model. In case of open shell systems, our approach should be extended considering also the possible recoupling with open shells, which requires the usage of fractional parentage coefficients. In this case the statistical tensor approach is much more convenient. However, the statistical tensor approach is not suitable to extension to the solid state. Thus, to consider open shell systems one is forced to introduce fractional parentage coefficients. Summations related to all the possible recoupling bring further complications, which should be added to summations due to the scattering processes, caused by non spherical environment of the absorbing atom. About the single particle approximation, there are several situations in which it is not appropriate. For example, when the photoelectron has higher kinetic energy, it spends less time at the absorption site. The core hole potential in the final state will then be less effectively screened by the photoelectron and thus will also be screened by the valence electrons of the surrounding atoms. Such extra-atomic screening is a well known phenomenum in core-level photoemission, where it gives rise to asymmetric lineshapes or additional peaks in the spectrum, so-called "charge transfer satellites" (in 2p-level photoemission of 3d-transition-metal oxides, for instance). The latter can be reproduced with semi-empirical calculations based on the Anderson impurity model, in which both the valence electrons' interaction with the core hole and their delocalization is taken into account. Such model calculations lack, however, the accuracy of ab initio calculations (multiple scattering or band structure calculations on the one hand and atomic multiplet calculations on the other hand). Moreover, there are some cases in which the photoelectron is not only a spectator to the second step process, as we supposed, but it can give rise to different intermediate state configurations, not only the fully relaxed one which follows from the assumption of the sudden approximation. Even repeating the experiment on Ge, it should not come as a surprise the fact that no differences are observed between curves related to photoelectron detection at different angles, since, as suggested by calculations, the differences are very small and probably hardly visible in an experiment. A preliminary analysis on the transition one wants to consider must be performed, to see if it is suitable to observe any initial correlation effects.

C. R. Natoli et al. [119] have presented a generalized multiple scattering theory, which was discussed at the end of chapter 2, for photoabsorption and photoemission such that electron correlation can be incorporated from some underlying microscopic theory such as atomic multiplet theory. It is a multichannel scattering theory that naturally accounts for both elastic and inelastic scattering events (historically, multichannel scattering theory was developed for inelastic scattering). Our current research project consists of developing a new computational scheme for second order processes that combines multiple scattering and atomic multiplet theory by using Natoli's approach [191]. Roughly speaking, one first makes a photoemission calculation within atomic multiplet theory, calculates from that the onsite interchannel scattering potential and finally solves the multichannel multiple scattering equations. By joining the virtues of multiple scattering and atomic multiplet calculations, such a theory treats band structure and intra-atomic electron correlation features on an equal footing. In contrast to impurity model calculations it does not rely on empirical parameters, but has the accuracy of an ab initio method. Moreover, Natoli et al. [119] showed that it naturally accounts for dynamical effects of the photoabsorption process and goes beyond the commonly used sudden approximation. The derivation of the coincidence cross section within such approach is essential to describe correctly the correlation between the two electrons in an open shell system where more degree of freedom are available to be excited and can give rise to inelastic channels.

Acknowledgements

There are no words to thank my professor G.Stefani, who has always encouraged me and supported me in any occasion, who allowed me to travel (and to spend the money of the group !!) and to meet many interesting people, to thank Rino Natoli with his neverending sentences, his genius and our phylosophical conversations, to thank Sergio Di Matteo, who has teached me everything and he has always been very patient with me. Thank you to all my friends, Fabio, Meena, Claudia, Marianna, Cinzia, Linda, Francesco, Fabrizio, Eleonora, Cecilia, Paola, Giulia...they have never left me alone in sad situations...I also thank a very special professor: Nikolay Kabachnik, who is a real gentlemen and working with him is a real pleasure. The work done with him was not presented in this thesis, but only because it looks too fast to the future, and maybe still many things must be understood today in coincidence problems.

But above all, I want to thank my father, who has allowed me to study during all these years, and my family, I hope that we will never be separated. Ciao Papá !

Bibliography

- [1] L.H.Tjeng et al., Phys.Rev.Lett. 78, 1126 (1997)
- [2] P.G.Steeneken et al., Phys.Rev.Lett. 88, 047201 (2002)
- [3] C.Edere et al, Phy. Rev. B 68, 052402 (2003)
- [4] M.Tischer et al, Phys.Rev.Lett. 75, 1602 (1995)
- [5] G.van der Laan, B.T.Thole: J.Phys.Condens.Matter 7, 9947 (1995)
- [6] L.Braicovich et al, Phys.Rev.Lett. 82, 1566 (1999)
- [7] L.Braicovich et al, Phys.Rev.Lett. 90, 117401 (2003)
- [8] H.W.Haak et al, Phys.Rev.Lett. 41 (1978) 1825
- [9] E.Jensen et al, Phys.Rev.Lett. 62 (1989) 71
- [10] R.Gotter et al, Phy. Rev. B 67, 033303 (2003)
- [11] P.Carra et al., Phys.Rev.Lett. 70, 694 (1992)
- [12] B.T.Thole et al, Phys.Rev.Lett. 68, 1943 (1992)
- [13] G.van der Laan et al, Phy. Rev. B 34, 6529 (1986)
- [14] B.T.Thole et L, Phys.Rev.Lett. 55, 2086 (1985)
- [15] J.B.Goedkoop et al, Phy. Rev. B 37, 2086 (1988)
- [16] B.T.Thole and G.van der Laan, Phy. Rev. B 38, 3158 (1988)
- [17] G.van der Laan and B.T.Thole, Phys.Rev.Lett. 60, 1977 (1988)
- [18] Y.Teramura, A.Tanaka, B.T.Thole and T.Jo, J.Phys. Soc. Jpn 65, 3056 (1996)
- [19] M.Cini, Solid State Comm. 20, 605 (1976)
- [20] M.Cini, Solid State Comm. 24, 681 (1977)

- [21] W.Mehlhorn, in X-Ray and Atomic inner shell Physics-1982 (International conference, University of Oregon), Proceedings of the International Conference on X-Ray and Atomic -Inner Shell Physics, edited by B.Crasemann (AIP,NewYork,1982)
- [22] T.E.Gallon Jour. Phys. D: Appl.Phys. 5, 822 (1972)
- [23] B. Sinkovic et al, Phys. Rev. Lett. 79, 3510-3513 (1997)
- [24] L.H.Tjeng et al, Phys. Rev. Lett. 78, 1126-1129 (1997)
- [25] R.A.Bartynsky et al, Phys. Scripta T41 (1992) 168
- [26] S.M.Thurgate, JES 109 (1999) 161
- [27] M.Ohno, JES 124 (2002) 39-51
- [28] Heinzmann U 1980 J. Phys. E: At. Mol. Phys. 13 4353-66 and 4367-81
- [29] Kessler J 1981 Commem. Ar. Mol. Phys. 10 47-56
- [30] Klar H and Kleinpoppen H 1982 J. Phys. B: AI. Mol. Phys. 15 933
- [31] Cherepkov N A 1983 At. Ar. Mol. Phys. 19 395-447
- [32] Bohn J and Fano U 1990 Phys. Rev. A 41 5953
- [33] Kabachnik N M and Sazhina I P 1990 3. Phys. 8: Ai. Mol. Opt. Phys. 23 L353-7
- [34] Pan X C and Chakravorty A 1990 Phys. Rev. A 41 5962-7
- [35] Becker U and Cherepkov N A 1996 VUV and Soft X-Ray Photoionization ed U Becker and D A Shirley p 521
- [36] V Schmidt 1997 Electron Spectrometry of Atoms using Synchrotron Radiation (Cambridge: Cambridge University Phys.Rev.ess)
- [37] Beyer H-J, West J B, Ross K J, Ueda K, Kabachnik N M, Hamdy H and Kleinpoppen H 1995 J. Phys. B: At. Mol. Opt. Phys. 28 L47
- [38] Plotzke O, Prmper G, Zimmermann B, Becker U and Kleinpoppen H 1996 Phys. Rev. Lett. 77 2642
- [39] von dem Borne A, Dohrmann T, Verweyen A, Sonntag B, Godehusen K and Zimmermann P 1997 Phys. Rev. Lett. 78 4019
- [40] A.von dem Borne et al, J.Phys. B 31 (1998) L41-48
- [41] V.Schmidt, Nucl. Instr. Meth. B 87 (1994) 241-246
- [42] B.Kammerling and V.Schmidt, J.Phys. B 26 (1993) 1141-1161

- [43] P.Bolognesi et al, Phys. Rev. A 70, 022701 (2004)
- [44] Berezhko E G and Kabachnik N M 1979 J. Phys. 8: Ar. Mol. Phys. 12 2993-3004
- [45] Kabachnik N.M. 1992 J. Phys. 8: At. Mol. Opt. Phys. 25 L389-393
- [46] Vegh L and Becker R L 1992 Phys. Rev. A 46 2445-8
- [47] K.Blum et al, J.Phys. B 19, 3815 (1986)
- [48] K.Ueda et al, J.Phys. B 36 319 (2003)
- [49] V.V.Balashov, A.N.Grum-Grzhimailo and N.M.Kabachnik, Polarization and Correlation Phenomena in Atomic Collisions, edited by Kluwer Academic/Plenum Publishers, New York (2000)
- [50] N.M.Kabachnik, J.Phys. B **25**, L389 (1992)
- [51] N.Scherer, H.Lörch, T.Kerkau and V.Schmidt, J.Phys. B 37, L121 (2004)
- [52] F.Da Pieve et al, J. Phys. B 38, 3619 (2005)
- [53] S.Fritzsche Comput.Phys.Commun. 103, 51 S (1997)
- [54] Aberg T 1980 Phys. Scr. 21 495
- [55] Tulkki J, Armen G B, berg T, Crasemann B and Chen M H 1987 Z. Phys. D 5 241
- [56] L.Vegh and J.H.Macek, Phy. Rev. A 50, 4031 (1994)
- [57] Schaphorst S J et al, 1996 J. Phys. B. 29 1901
- [58] Schwarzkopf O and Schmidt V 1996 J. Phys. B 29 3023
- [59] M.Y.Kuchiev and S.A.Sheinerman, J.Phys. B 21, 2027 (1988)
- [60] S.A.Sheinerman and V.Schmidt, J.Phys. B 32, 5205 (1999)
- [61] S.A. Sheinerman and V.Schmidt, J.Phys. B 30, 1677 (1997)
- [62] O.Gunnarson and K.Schonhammer, Phy. Rev. B 22, 3710 (1980)
- [63] N.M.Kabachnik and V.Schmidt, J. Phys. B 28 (1995) 233-243
- [64] J.Berakdar, J.Phys. B 31,3167 (1998)
- [65] J.Berakdar and K.Hubert, Phys.Rep.340, 473 (2001)
- [66] V.V.Balashov et al, J.Phys. B 30 (1997) 1269-1291
- [67] J.Berakar and N.M.Kabachnik, J.Phys. B 38, 23 (2005)

- [68] Luke G. M et al, Nature 394 (1998) 558
- [69] F.Da Pieve et al, submitted to J.Phys. B
- [70] M.Ohno and G.Wendin, J.Phys. B 12, 1305 (1979)
- [71] N.V.Schmidt and F.J.Himpsel, in Handbook of synchrotron Radiation, ed. by E.E.Koch, North Holland, amsterdam, vol.1 (1983)
- [72] F.J.Himpsel, Adv.Phys. 32, 1 (1983)
- [73] E.Jensen et al, Phys.Rev.Lett. 62, 71 (1989)
- [74] S.M.Thurgate and Z.T.Jiang, Surf.Sci. 466 (2000) L807
- [75] S.M.Werner et al, Surf.Sci.Lett. 518, L569 (2002)
- [76] Werner W.S.M., Surf. Interface Anal., Volume: 23, (1995), pp. 737
- [77] H.W.Haak et al, Rev.Sci.Instrum. 55 (1984) 696
- [78] R.Gotter et al, Phy. Rev. B 61 (2000) 4373
- [79] Yu Kucherenko and P. Rennert, JP:Cond. Matt. 9 (1997) 5003-5013
- [80] R.Gotter et al, Phy. Rev. B 72, 235409 (2005)
- [81] L.-G. Peterson et al, Phy. Rev. B 14, 4177 (1976)
- [82] J.Hubbard, Phy. Rev. B 19, 2626 (1979)
- [83] You and Neine, J.Phys. F 12, 177 (1982)
- [84] Hasegawa, J.Phys.Soc.Jpn 49, 963 (1980)
- [85] W.A.Harrison, Solid State Theory (McGraw-Hill, New York (1970))
- [86] Z.-X.Shen et al, Phy. Rev. B 42, 1817 (1990)
- [87] D.Eastman et al, Phys.Rev.Lett. 40, 1514 (1978)
- [88] H.Hopster et al, Phys.Rev.Lett. 51, 829 (1983)
- [89] E.Eisker et al, Phys.Rev.Lett. 52, 2285 (1984)
- [90] M.D.Rechtin and B.L.Averbach, Phy. Rev. B 5, 2693 (1972)
- [91] M.R.Norman, Phys.Rev.Lett. 64, 1162 (1990)
- [92] K.Terakura et al, Phys.Rev.Lett. 52, (1984)
- [93] K.Terakura et al, Phy. Rev. B 30, 4734 (1984)

- [94] M.R.Norman, Phys.Rev.Lett. 64, 1162 (1990)
- [95] D.C.Khan and R.A.Erickson, Phy. Rev. B 1, 2243 (1970)
- [96] A.Svane and O.Gunnarsson, Phys.Rev.Lett. 65, 1148 (1990)
- [97] Z.Szotek et al., Phy. Rev. B 47, 4029 (1993)
- [98] M.Takahashi and J.-ichi Igarashi, Phy. Rev. B 54, 13566 (1996)
- [99] F.Aryasetiawan and O.Gunnarsson, Phys.Rev.Lett. 74, 3221 (1995)
- [100] L.Hedin, Phys.Rev. 139, A796 (1965)
- [101] L.Hedin and S.Lundqvist, in Solid State Physics, edited by H.Ehrenreich, F.Seitz and .Turnbull (Academic, New York, 1969) Vol. 23, p.1))
- [102] N.Andersen et al, Phys. Rep. 165 (1988) 1-188
- [103] H.Hilferink et al, Surf.Sci. 93 (1980) 398
- [104] R.N.Lindsay and C.G.Kinniburg, Surf.Sci. 63, 162 (1977)
- [105] S.P.Weeks and A.Liebsch, Surf.Sci. 62, 197 (1977)
- [106] D.Aberdam et al, Surf.Sci. 57, 306 (1976)
- [107] L.McDonnel et al, Surf.Sci. 51 249 (1975)
- [108] X.Chen et al, J.Vac.Sci.Technol. A 12 428 (1994)
- [109] A.Chass et al, Surf.Sci. 501, 244 (2002)
- [110] Y.U.Idzerda, Surf.Sci.Rev.Lett. 4, 161 (1994)
- [111] D.E.Ramaker et al, JES 68, 64 (1994)
- [112] T.Greber et al, Phys.Rev.Lett. 69 1947 (1992)
- [113] D.E.Ramaker et al, JES 72 169 (1995)
- [114] T.Greber et al, Phy. Rev. B 45 4540 (1992)
- [115] J.Korringa, Physica 13, 392 (1947)
- [116] W.Kohn and N.Rostoker, Phys.Rev. 94, 1111(1954)
- [117] A.L.Ankudinov et al, Phy. Rev. B 65, 104107 (2002)
- [118] C.R.Natoli Physica B 208-209 (1995) 5-10
- [119] C.R.Natoli et al, Phy. Rev. B 42, 1944 (1990)

- [120] J.J.Barton, Phys.Rev.Lett. 61, 1356 (1988)
- [121] C.S.Fadley et al, JES 75, 273 (1995)
- [122] J.Osterwalder et al, Surf.Sci. 331, 1002 (1995)
- [123] H.Wu et al, Phys.Rev.Lett. 71, 251 (1993)
- [124] P.M.Len et al, JES 85, 145 (1997)
- [125] J.J Rehr et al, Phys.Rev.Lett. 69, 3397 (1992)
- [126] Beeby, J.L., Phys. Rev. oc. R. Soc. London, Ser A 279, 82
- [127] W.L.Schaich, Phy. Rev. B 8, 4028 (1973)
- [128] C.A.Ashley and S.Doniach, Phy. Rev. B 11, 1279 (1975)
- [129] P.A.Lee and J.B.Pendry, Phy. Rev. B 11, 2795 (1975)
- [130] J.J.Rehr et al, Phy. Rev. B 34, 4350 (1986)
- [131] J.J.Rehr et al, Phy. Rev. B 41, 8139 (1990)
- [132] Cohen-Tannoudji C., Dupont-Roc J and Grynberg G 1988 Processus d'interaction entre photons et atomes (InterEditions/Editions du CNRS, Paris) p.36
- [133] G.Breit and H.Bethe Phy. Rev. A93, 888 (1954)
- [134] see chapter 2.7 of L.Fonda and G.Ghiradi in Symmetry Principles in Quantum Physics (New York: Dekker) 1970
- [135] W.H.Butler Phy. Rev. B 41 (1990) 2684
- [136] Handbook of Mathematical functions, edited by M.Abramowitz and I.A.Stegun (Dover, London, 1965)
- [137] C.R.Natoli and M.Benfatto, J.de Phys. C8, 11 (1986)
- [138] Natoli C. R. et al, Phys.Rev. A 34, 4682 (1986)
- [139] A.Messiah, Quantum Mechanics (wiley, New York) 1966
- [140] Brouder et al., Phy. Rev. B 39, 1488 (1989)
- [141] D.E.Sayers et al, Adavnces in X-ray Analysis (Plenum, New York) 1970, Vol. 13, p.248
- [142] J.J.Barton and D.A.Shirley, Phy. Rev. B 32, 1892 (1985)
- [143] J.J.Rehr and R.C.Albers, Phy. Rev. B 41, 8139 (1990)
- [144] J.J.Barton and D.A.Shirley, Phy. Rev. A 32, 1019 (1985)

- [145] L.J.Sham and W.Kohn, Phys.Rev. 145, 561 (1966)
- [146] L.Hedin and S.Lundqvist, in Solid State Physics, edited by F.Seitz, D.Turnbull and H.Ehrenreich (Academic, New York), p.1 (1969)
- [147] P.A.Lee and G.Beni, Phy. Rev. B 15, 2862 (1977)
- [148] T.Fujikawa and L.Hedin, Phy. Rev. B 40, 11507 (1989)
- [149] (W.Kohn and L.J.Sham, Phy. Rev. A 140, 1133 (1965)
- [150] L.F.Mattheiss, Phys.Rev. 133, A1399 (1964)
- [151] T.L. Loucks, Augmented Plane Wave Method (Benjamin, New York) (1967)
- [152] L.Hedin and B.I.Lundqvist, J. Phys. C 4, 2064 (1971)
- [153] J.J.Rehr et al, Phy. Rev. B 17, 560 (1978)
- [154] B.-K.Teo and P.A.Lee, J.Am.Chem.Soc. 101, 2815 (1979)
- [155] Muller et al., Solid. State Commun. 42, 365 (1982)
- [156] J.Mustre de Leon et al., Phy. Rev. B 44, 4146 (1991)
- [157] T.A.Tyson et al., Phy. Rev. B 46, 5997 (1992)
- [158] A.Ankudinov et al., Phy. Rev. B 58, 7565 (1998)
- [159] O.K.Andersen, Phy. Rev. B 12, 3060 (1975)
- [160] D.D.Koelling and B.N.Harmon, J.Phys. C 10, 3107 (1977)
- [161] A.Ankudinov and J.J.Rehr, Phy. Rev. B 56, R1712 (1997)
- [162] B.I.Lundqvist, Phys. Kondens. Mater. 6, 206 (1977)
- [163] S.-H.Chou et al., Phy. Rev. B 35, 2604 (1987)
- [164] R.Manne and T. Aberg, Chem. Phys. Lett. 7,282 (1970)
- [165] F.Beleznay and M.J.Lawrence, J.Phys. C 1, 1288 (1968)
- [166] N.F.Lane, Rev. Mod. Phys. 52, 29 (1980)
- [167] A.Zangwill and P.Soven, Phys. Rev. A 21, 1561 (1980)
- [168] U.Fano, Phys.Rev. 124, 1866 (1961)
- [169] L.C.Davis and L.A.Feldkamp, Phy. Rev. B 15, 2961 (1977)
- [170] L.C.Davis and L.A.Feldkamp, Phy. Rev. B 23, 6239 (1981)

- [171] L.Alagna et al, Phys. Rev. Lett. 80, 4799-4802 (1998)
- [172] Chandrasekhar, Astrophys.Journal 102, 223 (1945)
- [173] A.Starace, Phy. Rev. A 3, 1242
- [174] A.Starace, Phy. Rev. A 8, 1141
- [175] R.Gunnella et al., Phy. Rev. B 57, 14739 (1998)
- [176] see Varshalovich et al, Quantum Theory of Angular Momentum (World Scientific) 1996, equation 9 and equation 14 page 144
- [177] see Varshalovich et al, Quantum Theory of Angular Momentum (World Scientific) 1996, equation 21 page 165 and equation 9 page 161
- [178] see Varshalovich et al, Quantum Theory of Angular Momentum (World Scientific) 1996, equation 7 page 161
- [179] see Varshalovich et al, Quantum Theory of Angular Momentum (World Scientific) 1996, equation 34 page 261
- [180] see Varshalovich et al, Quantum Theory of Angular Momentum (World Scientific) 1996, equation 15 page 260
- [181] see Varshalovich et al, Quantum Theory of Angular Momentum (World Scientific) 1996, equation 39 page 262
- [182] see Varshalovich et al, Quantum Theory of Angular Momentum (World Scientific) 1996, page 66
- [183] see Varshalovich et al, Quantum Theory of Angular Momentum (World Scientific) 1996, equation 14 page 144
- [184] see gnxas.unicam.it/XASLABwww/paggnxas/doc/phagendoc.html
- [185] SPEC code by D.S.Sébilleau (multiple scattering code for photoelectron, Auger electron diffraction and APECS). Available upon request (didier.sebilleau@univrennes1.fr)
- [186] K.H Johnson, Adv.Quantum Chem. 7, 143 (1973)
- [187] for a review on Dirac-Fock method see "Relativistic and Qunatum electrodynamic Effects on Atomic Inner Shells" W.R.Johnson and K.T.Cheng in Atomic Inner Shell Physics,ed. Bernd Crasemann (Plenum, New YOrk, 1985), Chapter 1, pp.1-29
- [188] J.B.Mann, Atomic Structure Calculations Vol. 1, Los Alamos Research Laboratory, L.A.-3960
- [189] R.M.Tromp et al, Phys. Rev. Lett. 55, 1303 (1985)

- [190] Ley L and Cardona M (ed) 1979 Photoemission in solids II (Berlin:Springer)
- [191] P.Krüger and C.R.Natoli, Phys. Rev. B 70, 245120 (2004)