Chapter 1

Photon-atom interaction and subsequent processes

1.1 Introduction

Wilhelm C. Röntgen received the very first Nobel Prize in Physics in 1901 for discovery of X-rays. Röntgen believed that such discoveries are the property of all mankind. He did not file the patent and donated his prize money for further scientific studies at the University of Würzburg.

Since discovery of X-rays in Nov. 1895, interaction of X-ray photons with the matter has been widely studied. The X-rays are basically electromagnetic radiations (range of energies ~1-100 keV) which interact mainly with the electrons in atoms constituting the material. The interaction of X-rays with matter represents one of the most varied classes of phenomena in Physics.

If the hand be held between the discharge-tube and the screen, the darker shadow of the bones is seen within the slightly dark shadow-image of the hand itself. I shall use the expression 'rays'; and to distinguish them from others of this name I shall call them 'X-rays'.

Wilhelm Conrad Röntgen (1845-1923)

Fig.1.1: The first Medical X-ray recorded by Wilhelm Röntgen of his wife Anna Bertha Ludwig's hand with a clear image of the bones and wedding ring. Donated to University of Würzburg.
The interaction can primarily be a scattering event, in which a part of energy is imparted any of the electrons associated with it; or it may be essentially an absorption process, in which the energy of the photon will be transferred to one of its electrons. Interactions between X-ray photons and matter are single, identifiable, processes, each associated with an individual atom, and is characterised by a cross-section. When interaction of the X-ray photons involves material in the form of a periodic array of a large number of atoms bound by chemical bonds or other interatomic forces (crystal lattice), the planes in the periodic structure scatters the incident X-rays. The parallel scattered X-rays result in the interference pattern and the process is called Bragg’s diffraction. The phenomena was discovered in 1912 and provided a new method for investigating the fine lattice structure of material. The crystal lattice has planes in various orientations, which result in giving a variety of intensity patterns providing information about the structure of lattice. The absorption and scattering processes in crystals forms the basis of X-ray Crystallography. Interaction of photons with individual atoms and periodic array of a large number of atoms play role in development of various analytical and diagnostic techniques used for the scientific, industrial and medical purposes.

1.2 Photoelectric absorption

If an incident X-ray photon has slightly greater energy than the binding energy of a bound atomic electron participating in the interaction, the photon transfers its energy to knock out the participating electron. The ejected electron is known as photoelectron. From the energy-momentum conservation law it may be noted that a free electron cannot absorb a photon. It means that, the electron should be bound within an atom for photon absorption. So, the probability of photoelectric effect is always higher for electrons located at lower electronic shells, which are closer to the atomic nucleus and hence are bound more strongly. The total energy of the ejected electron is

\[ E_e = E_{inc} - E_B - T_N + m_o \]  

(1.1)

where \( E_{inc} \), \( E_B \), \( T_N \) and \( m_o \) are the incident photon energy, binding energy of electron, kinetic energy possessed by recoil nucleus and mass of electron, respectively. Therefore, the kinematic conditions for the minimum photon energy required for the photoelectric absorption to occur is

\[ E_{inc} > E_B + T_N \]
In case the energy of the incident photon is not able to eject photoelectron, it may be partly absorbed by the atomic electron participating in the interaction and scattered out. The process is termed as Compton scattering. The scattering with no net absorption of photon by the atomic electrons termed as Rayleigh scattering. The cross sections for various photon-atom interaction processes in $^{59}$Pr, one of the elements of present concern, are plotted as function of energy in Fig. 1.2.

![Graph showing cross section for various photon-atom interaction processes as a function of energy in case of $^{59}$Pr element.](image)

**Fig. 1.2:** The variation of cross section for various photon-atom interaction processes as a function of energy in case of $^{59}$Pr element.

During absorption Photoionization is prominent process if the energy of the incident photon matches with the ionization threshold of the atoms in the material. The probability of the photoelectric effect is characterized by the cross section $\sigma_{ph}$, which rapidly increases with the atomic number $Z$. If the X-ray energy is much higher than the ionization potential $I_j$ of a certain electronic shell $j$, the probability of X-ray absorption by electrons in this shell is $\sigma_{ph} \sim Z^5$ [1]. However, a quantitative comparison between different chemical elements is barely possible because of the great differences in the ionization potentials. Heavier elements such as, Pb absorb X-rays much more strongly than lighter elements. Photoelectric effect is a resonant process. The photoelectric cross section $\sigma_{ph}$, as a function of X-ray energy $E_x$, has sharp maxima at $E_x \approx I_j$ (Fig. 1.2). This forms the basis of selective used for X-ray filtering. The desired spectral lines from the polychromatic X-ray source can be obtained. Rayleigh scattering cross sections exceeds Compton scattering cross...
sections up to well above $K$-edge for all atomic numbers whereas the total cross section is photoelectric dominated. The total cross section curve attains a characteristic saw-tooth shape with the sharp discontinuity at the points where the incident energy matches with the ionization energy of electron in $K$, and $L_i$ shells/subshells. At the first matching point the total cross section decreases suddenly because of the reason here the incident energy photons with low energy can no longer eject from $K$ shell. Here photons continue to interact with more weakly attached electrons in lower energy $L$ and $M$ shells. These saw toothed discontinuities of the curve signifying the probability of photo electric absorption occurring energetically, are called as absorption edges. Therefore the photo electric absorption cross section falls off sharply as the photon energy decreases through this critical threshold value. The photoelectric absorption probability increases as the photon energy is decreased up to the limiting value of the absorption edge. Fewer electrons are available for absorption after crossing over the absorption edge and thus the probability of the process sharply decreased. In the high $Z$ elements Rayleigh scattering provides a significant contribution just below the $K$ shell ionization threshold. The Rayleigh scattering dominates Compton scattering till well above the $K$-shell ionization threshold afterwards the Compton scattering takes over. This is in general true for all elements. The total cross section is photo electric dominated up to photon energies increasing with atomic number, from 6 keV for $^3\text{He}$, to 25 keV for $^6\text{C}$ and 700 keV for $^{92}\text{U}$. The Compton scattering becomes the domination process at ~100 keV for low $Z$ elements and ~500 keV in case of high $Z$ elements.

1.3 Scattering by atomic electrons

The incident photons generally scatter while interacting with the atomic electrons, In case the energy is less the photon interacts with the electron and emitted out with the same energy process is called elastic scattering. When interaction takes place with the atomic bound electrons it is referred to as Rayleigh scattering. In case some part of energy is consumed by the electron from incident photon, the process is termed as inelastic scattering. For atomic bound electrons, it is referred to as Compton scattering. The theoretical approach to understand these processes is given in the following sections.

1.3.1 Rayleigh scattering

In Rayleigh scattering process, the incident photon imparts to the interacting electron some energy in the form of acceleration by the electromagnetic field associated with it. After
interaction the photon emits photon having the same energy as the incident photon, means there is no net energy transfer from the photon to electron, resulting a phase relationship between the incident and scattered photons. Due to this coherence, the Rayleigh scattering process is called coherent scattering. Theoretically, two major approaches are developed to characterise the scattering: (i) Form-factor formalism, (ii) S-Matrix approach. These approaches are given as follows.

(a) Form Factor formalism

J.J. Thomson gave a general formula for the scattering of unpolarised photons from the free electrons giving differential scattering cross section as

$$\frac{d\sigma_T}{d\Omega} = \frac{1}{2} r_o^2 \left(1 + \cos^2 \theta\right)$$

(1.2)

where, $\theta$ is the scattering angle through which the propagation direction of the incident photons changes and $r_o$ is the classical radius of the free electron. For extended charge distributions, it is modified by including atomic form factor for a spherical charge distribution as given by

$$f(q) = 4\pi \int_0^\infty \rho(r) \frac{\sin(qr)}{qr} r^2 dr$$

(1.3)

where, $f(q)$ is the form factor, $\rho(r)$ is electron density at distance $r$ from centre of the atom and $hq$ is momentum transferred to the atom during scattering. The $\rho(r)$ can be derived from the atomic ground state function given by

$$\rho(r) = \sum_{n=1}^{Z} |\psi_n(r)|^2$$

(1.4)

For an atom containing $Z$ electrons, the contributions of the individual electrons are added as,

$$4\pi \int_0^\infty \rho(r) r^2 dr = Z$$

(1.5)

The scattering cross section in the form factor formulation is obtained from the Thomson formula as

$$\left(\frac{d\sigma}{d\Omega}\right)_e = \left(\frac{d\sigma}{d\Omega}\right)_T |f(q)|^2$$

(1.6)
The better results of the scattering cross section are found using form factor approximation for the incident photon having energy well above the $K$-shell threshold of the target atom. Inner-shell electrons have the most compact spatial distribution which results in a form factor contribution that is more extended and persists to higher momentum transfer ($q$). For small $q$, all the electrons contribute equally to the form factor but for large $q$, only the innermost electrons contribute. When the relativistic and non-relativistic individual electrons, and total atom wave functions are used to derive the charge density, the resulting form factors are termed as relativistic (RF) and non-relativistic (NF) form factors, respectively. These form factors are tabulated by Hubbell et al. [2,3].

Franz [4] considered the effect of electron binding energy and incorporated the correction for the same, the resulting form factor is called modified form factor (MF) given as

$$g(q) = 4\pi \int_0^\infty \rho(r) \frac{\sin(qr)}{qr} \frac{mc^2}{E_i - V(r)} r^2 dr$$  \hspace{1cm} (1.7)$$

where, $\rho(r)$ is the charge distribution associated with the $i$th electron, $V(r)$ is the atomic potential and $E_i$ is the binding energy of the $i$th electron. The contributions from the electrons of the individual subshells are calculated and added to deduce $g(q)$. The resulting differential scattering cross section for the unpolarized photons is given by

$$\left( \frac{d\sigma}{d\Omega} \right)_{MF} = \left( \frac{d\sigma}{d\Omega} \right)|g(q)|^2$$  \hspace{1cm} (1.8)$$

A complete tabulation of the MF values for the elements with $1 \leq Z \leq 100$ and momentum transfer $0 \leq q \leq 100$ Å$^{-1}$ is available [5]. This approximation provides cross section values for the incident energies well above the ionisation threshold and failed to obtain cross section values for the incident energies approaching the ionisation threshold from below and above or at large momentum transfers (high photon energy and large scattering angles).

To overcome the problem, an anomalous scattering factor defined as the exact deviation of the scattering amplitude at forward angles from the form factor or modified form factor, is incorporated. The ASF’s were obtained using the dispersion relation between the real and imaginary parts of the scattering amplitude at forward angles and the imaginary part is related to the photo absorption cross section by the optical theorem. The real part represents the intimacy of the incident photon energy to the binding energy of participating electron and imaginary part arise from the enhanced absorption of the incident photon in vicinity of the resonance level. The resulting atomic form factor can be written as
\[ f(q) = f(q) + f'(0) + if''(0) \] (1.9)

where \( f(q) \) is the MF and is given by Eq. (1.9), \( f' \) is real part representing the dispersion effects in the elastic scattering near the resonance level and \( if'' \) is an imaginary number representing the absorptive part of the dispersion effects in the elastic scattering near a resonant state of the bound electron. The imaginary part can be calculated directly from the photoelectric absorption (\( \sigma_{\text{PE}} \)) at incident photon energy (\( E_{\text{inc}} \)) using the relation

\[ f^- = \frac{E_{\text{inc}} \sigma_{\text{PE}}(E_{\text{inc}})}{2\hbar c r_o} \] (1.10)

The real part \( f' \) of the resonant term is calculated using \( f'' \) with Kramer-Kronig relationship

\[ f' = \frac{2}{\pi} \int_{E_{\text{inc}}}^{\infty} \frac{E f''(E)}{E^2 - E'^2} dE \] (1.11)

where, \( E' \) is the scattered photon energy. A complete tabulation of the anomalous correction terms \( f' \) and \( f'' \) for the elements with \( 3 \leq Z \leq 98 \) is available in the literature [6-8]. Henke et al. [8-10] tabulated the values of the anomalous correction terms for elements with \( 1 \leq Z \leq 94 \). Both Cromer and Liberman [6-8] and Henke et al. [9-11] have tabulated the values using dipole approximations in estimation of relativistic correction to the high-energy limit of the forward scattering. Later, it was realized that the higher multipoles are also important [2-9]. The correct high-energy limit of \( f' \) has been obtained using the S-matrix calculations and the correction terms are defined as

\[ \delta f' = f'_{(\infty)} - f'_{\text{CL}} \] (1.12)

where, \( f'_{(\infty)} \) is the correct high-energy limit of \( f' \). The tabulation of the correction terms is available in the literature [12-13]. It has been demonstrated [12] that the use of the correct high-energy limit removes the discrepancy between the experimental values [14-16]. Using the MF values in place of FF values, the corresponding value of the atomic form factor becomes

\[ f(q) = g(q) + g' + ig'' \] (1.13)

Since MF values give the correct high energy predictions, the \( g' \) vanishes in the high-energy limit. The anomalous terms, \( g' \) and \( g'' \), are related to the Cromer and Liberman anomalous terms \( f'_{\text{CL}} \) and \( f''_{\text{CL}} \) as
\[ g' = f'_{CL} - f'_{CL}(\infty) \]  
\[ g'' = f''_{CL} \]  

This factor is called angle-independent anomalous factor (MFASF) approximation.

(b) S-Matrix approach

The scattering matrix (S-matrix) is an operator, which connects the final state of a time dependent system to its initial state. For Rayleigh scattering, the matrix element \( S = \langle N | S | P \rangle \) represents the amplitude of a specific stationary state \(|P\rangle\) that evolved through scattering from the initial state. The calculations begin with illustration of scattering in second order in terms of the Feynman-Dyson representations. In these calculations, interaction with the radiation field is treated as a perturbation, while the interaction of electrons and positrons with the atomic field is included in the unperturbed Hamiltonian. For these calculations, the independent particle approximation was used which is based upon the fact that independent electrons interact electrostatically. In the absorption, \( i.e., \) the first process as shown in Fig. 1.3 (a), the incident photon energy \( h\nu_i \) is absorbed by the initial state electron of energy \( E_i \) at time \( t_1 \). In the intermediate state (time \( t_1 \rightarrow t_2 \)), only an electron of energy \( (E_i + h\nu_i) \) is present and the photon does not exist at all. At the end of intermediate state (at time \( t_2 \)), the final (scattered) photon is emitted. In the emission first process (Fig 1.3 (b)), the final photon of energy \( h\nu_i \) is emitted at time \( t_1 \). In the intermediate state, an electron of energy \( (E_i - h\nu_i) \) and the incident and scattered photon is present. At time \( t_2 \), the incident photon is absorbed and the electron returns to the stationary bound state.

Fig. 1.3: Feynman diagram for the Rayleigh scattering amplitude (a) absorption first  
(b) emission first contribution.
The scattering of photons to the lowest non-vanishing order in the perturbation theory, is described by the second order $S$-matrix amplitude as

$$A = -\sum_{\nu} \left[ \frac{\langle N|O_\nu^*|P\rangle\langle P|O_\nu|N\rangle}{(E_\nu - E_P + h\nu_i + i\delta)} \right] + \left[ \frac{\langle N|O_\nu^*|P\rangle\langle P|O_\nu|N\rangle}{(E_\nu - E_P - h\nu_i - i\delta)} \right] \quad (1.16)$$

where, operator $O_\nu (O_\nu^*)$ describes the absorption (emission) of the incident (scattered) photon, $i = \sqrt{-1}$, $\delta$ is a small positive value and the states $|N\rangle$ and $|P\rangle$ are properly symmetrised solutions of many particle Dirac equation for non-interacting particles. The Rayleigh scattering cross section is described by

$$\frac{d\sigma}{d\Omega} = \frac{1}{2} \left( \sum_e |A_\parallel|^2 + \sum_e |A_\perp|^2 \right) r_e^2 \quad (1.17)$$

The summation represents the sum over all bound electrons. The $A_\parallel$ and $A_\perp$ are invariant amplitudes depending on the photon energy and the scattering angle.

All considerable partial waves and multipoles are incorporated in Rayleigh scattering of a photon by the electron in the atomic potential. The $S$-matrix calculations provide better results for the low momentum transfer as well as for large momentum transfers. The $S$-matrix approach correctly estimates the angular distribution of Rayleigh scattering at low as well as high incident photon energy. The calculations of scattering cross section values using $S$-matrix approach are computer intensive for high incident photon energies and high $Z$ elements. This is because more atomic shells are involved in high $Z$ elements and more partial wave and higher multipoles are required for high incident photon energies. The published elastic scattering cross section using $S$-matrix are available only for ten selected elements in the range $13 \leq Z \leq 104$ and for seven photon energies in the range $59.5$-$1332$ keV [17]. Tabulated values of Rayleigh scattering cross-section [18] are available for almost all the elements at seven selected photon energies of experimentalist’s choice in 65 angular steps in the range $0 \leq \theta \leq 180^o$. Therefore, the best possible method for the theoretical evaluation of scattering cross section is based on $S$-matrix calculations.

1.3.2 Compton scattering

Compton scattering is the process in which the participating electron absorbs a part of energy from the incident photon. The scattered photon has less energy than the incident one
this is also called inelastic or incoherent scattering. In case, the excited electron jumps to a higher unoccupied energy level, the process is known as Raman scattering.

(a) **Scattering from free electrons**

Compton scattering is a quantum electrodynamic interaction involving energy transfer between the interacting photon and electron. The process cannot be explained using classical electrodynamics theory but using quantum electrodynamics (QED) [19]. The incident photon interacts with a free electron and scattered with a loss of energy. The scattered photon energy ($E_{sc}$) is related to the incident energy ($E_{in}$) as

$$E_{sc} = \frac{E_{in}}{1 + (1 - \cos \theta)E_{in}/m_o c^2}$$

(1.18)

where, $m_0 c^2$ is the rest mass energy of the electron (0.511 MeV) and $\theta$ is the scattering angle for the incident photon. The assumption for calculating the energy of the scattered photon is not precisely accurate because in reality the interaction of the incident photon takes place with moving bound electrons. The equation written for non-zero pre-collision energy and momentum of the electron is

$$p_z = -m_o c \frac{E_{in} - E_{sc} - E_{in} E_{sc} (1 - \cos \theta)/m_o c^2}{\sqrt{E_{in}^2 + E_{sc}^2 - 2E_{in} E_{sc} \cos \theta}}$$

(1.19)

where $p_z$ is simply referred as the projection of the electron momentum. It is interesting to notice that Eq. (1.19) reduces to (1.18) when $p_z = 0$. The electron momentum values are deduced from consistently symmetric distributions. These symmetric distributions are also known as Compton profiles that depend on the atomic subshell and target atom [20].

Klein and Nishina successfully applied Dirac’s relativistic theory of electron for the scattering of photons by a free electron at rest to obtain a differential scattering cross section given as

$$\left( \frac{d\sigma}{d\Omega} \right)_{KN} = r_0^2 \left( \frac{1}{1 + \alpha(1 - \cos \theta)} \right)^3 \left( \frac{1 + \cos^2 \theta}{2} \right) \left( 1 + \frac{\alpha^2 (1 - \cos \theta)^2}{(1 + \cos^2 \theta)(1 + \alpha(1 - \cos \theta))} \right)$$

(1.20)

where $\alpha = E_{in}/m_0 c^2$. The above equation is well known Klein-Nishina formula for the calculation of differential inelastic scattering cross section. At low energy ($\alpha \rightarrow 0$), the entire general expression is reduced to classical Thomson scattering value. The Klein-
Nishina cross section represents the probability that a photon transfers some momentum to the free electron and gets scattered through some angle.

(b) Scattering from bound electrons

The energy distribution profile of the Compton scattered photons is much broader than that of the incident photons. The momentum distribution of the bound electrons is a cause of this broadening [21]. The exact deviations of the inelastic scattering cross section due to electron binding energy effects are removed using the incoherent scattering function (ISF) approximation. The incoherent scattering of the incident photon from a bound electron modify the Klein-Nishina differential cross section

\[
\left( \frac{d\sigma}{d\Omega} \right)_{\text{inc}} = \left( \frac{d\sigma}{d\Omega} \right)_{KN} S(q, Z) \tag{1.21}
\]

where, \( S(q, Z) \) is incoherent scattering function. The expression for the ISF in terms of atomic form factor can be expressed as

\[
S(q, Z) = \sum_{m=1}^{Z} \sum_{n=1}^{Z} \langle \psi_{gs} | \exp[iq(r_m - r_n) / \hbar c] | \psi_{gs} \rangle - |f(q, Z)|^2 \tag{1.22}
\]

where, the summations are over the number of electrons. The non-relativistic values of \( S(q, Z) \) has been tabulated by Hubbell et al. [2] for the values of \( q \) from .005 to \( 10^9 \) Å\(^{-1}\) for all elements with \( 1 \leq Z \leq 100 \).

S-matrix calculations

The relativistic second order S-matrix calculations in case of Compton scattering are much more complicated as compared to the Rayleigh scattering. These calculations for the Compton scattering are performed in the same framework as Rayleigh scattering. However, in Compton scattering the final electrons are in continuum states of different energies rather than in a bound state of definite energy and angular momentum. The additional simplification has been adopted from the work of Whittingham [22]. Relativistic second-order S-matrix calculations were published at 279.1 keV and 661.6 keV for \(^{62}\)Sm, \(^{73}\)Ta, \(^{82}\)Pb and \(^{92}\)U [22,23]. The calculations incorporating the effect of screening through the use of Dirac-Hartree-Slater potentials have become available [24] for the 100 keV photon energy in case of \(^{12}\)C, \(^{13}\)Al and \(^{30}\)Cu elements and for 145 keV, 279 keV and 320 keV energies in the case of \(^{50}\)Sn, \(^{67}\)Ho, \(^{79}\)Au and \(^{82}\)Pb elements.
1.4 Scattering processes at near edge energies

The processes involving incident photon energies near the binding energy of the participating electron received major impetus in recent years, because these are emerging as important probes of condensed matter systems. When the energy of the incident photon is slightly less than the ionization threshold of the target atom, then participating electron takes energy and leaves the state vacant by going to the unoccupied energy levels. An electron from the upper shell fills the created hole, simultaneously. If the excited atom returns to the ground state via radiative transition then it is termed as resonant Raman scattering (RRS). If it comes to ground state via non-radiative transition, it is termed as the Auger resonant Raman effect [25].

**Resonant Raman scattering**

The resonant Raman scattering (RRS) is an inelastic scattering process and becomes significant as the incident photon energy is slightly less than the ionization threshold of the target atom [26]. The Raman scattering in the X-ray energy region are of two types, resonant Raman scattering (RRS) and resonant Raman Compton scattering (RRC). The resonant Raman scattering process results in a symmetric and sharp peak as the excited electron in a bound state whereas the resonant Raman Compton scattering results in asymmetric and broad peak as the excited electron is in a continuum state. The angular independence and frequency dependence of inelastic scattering explained with the X-ray scattering theory of anomalous dispersion is known as resonant Raman scattering. The RRS effect was observed for the first time by Sparks [27] and explained later by Bannet and Freund [28].

The Hamiltonian for the interaction of incident photon having potential vector \(A\) with electron having momentum \(p\) in the non-relativistic approximation is given as

\[
H_{\text{int}} = -\frac{e}{mc} p.A + \frac{e^2}{2mc^2} A.A
\]  

(1.23)

The non-resonant scattering processes such as Rayleigh, Compton and normal Raman can be expressed in term of \(A.A\), in the first-order approximation [17] and the resonant inelastic scattering is expressed by the \(p.A\) term at the second-order expansion of the time-dependent perturbation theory. The double differential scattering cross section of resonant Raman scattering (RRS) can be given by Kramers-Hisenberg equation [29]
\[
\frac{d^2 \sigma_{\text{RRS}}}{dE d\Omega} = r_o^2 \left( \frac{E}{E_o} \right) \frac{1}{m^2} \sum_i \left[ \frac{\langle b | p_e, e_2 \rangle \langle e_1 | p_e, e_2 | a \rangle}{E_a - E_i + E_o + i \Gamma/2} \right]^2
\]

(1.24)

where \( e_1 \) and \( e_2 \) are the unit polarization vectors for the incident photon with energy \( E_o \) and scattered photon with energy \( E \) respectively. The terms, \( E_a, E_i \) and \( E_b \) are the energies corresponding to the atomic states denoted as \( | a \rangle \) (initial state), \( | i \rangle \) (intermediate state) and \( | b \rangle \) (final state) respectively, \( \Gamma \) is the lifetime of the excited atomic state. In KL-RRS process, the virtual hole is created by the incident photon having energy just below the ionization threshold of the \( K \) shell and the created hole is subsequently filled either by an \( L \)-shell electron (KL-RRS) or an \( M \)-shell electron (KM-RRS) and so on. The KL-RRS process is shown schematically in Fig 1.4. Applying the dipole approximation and neglecting the weak non-resonant terms in Kramers-Hisenberg equation, the double differential scattering cross section for KL-RRS process can be written as

\[
\left( \frac{d^2 \sigma_{\text{RRS}}}{d\Omega dE} \right) = \frac{r_o^2}{2} \frac{E}{E_0} \frac{(U_K + T_e)(U_K - U_L)}{(U_K - U_L - E)^2 + (\Gamma/2)^2} g_{1s,2p} \left( \frac{dg_K}{d\epsilon} \right)_{U_L+T_e}
\]

(1.25)

where \( E \) is energy of the RRS scattered photon corresponding to the incident photon having energy \( E_o \). According to the law of energy conservation, the average binding energy (\( U_L \)), the average kinetic energy of the ejected electron (\( T_e \)), the energy of Fermi level (\( E_F \)), \( E \) and \( E_o \) are related as \( E_o - U_L - E_F = E + T_e \). The oscillator strength, \( g_{1s,2p} \), is the oscillator

Fig. 1.4: Schematic representation of the \( KL_2 \) radiative RRS process.
strength between the \((1s)^{-1}\) and \((2p)^{-1}\) hole states and the oscillator density can be described as [30,31]

\[
\left( \frac{dg_k}{dT_e} \right)_{\nu=1} = \frac{\tau_k (U_K + T_e)}{2\pi^2 \hbar c r_0}
\]  

(1.26)

\[
g_{1s,2p} = \frac{1}{2} \frac{\hbar c \Gamma_K}{r_0 (U_K - U_L)^2}
\]  

(1.27)

where \(\Gamma_K\), \(\tau_k (U_K + T_e)\) and \(\Gamma_K\) are the total \(K\)-shell width, the photoionization cross section of the \(K\) shell at the energy \(U_K + T_e\) and width of the \(K\alpha\) fluorescence line respectively. As the oscillator density depends upon the density of empty states in the continuum, so it may be assumed constant if the contribution of the final state is ignored and thus an average kinetic energy \((T_e)\) for the ejected electron may be considered. From Eq. (1.26) and assuming a constant oscillator density, the double differential cross section can be written as

\[
\left( \frac{d^2\sigma_{RRS}}{d\Omega dE} \right) = \Gamma_K \frac{\tau_k (U_K + T_e)}{8\pi^2 (U_K - U_L)} \frac{E}{E_0} \frac{U_K - U_L + E_0 - E}{(U_K - U_L - E)^2 + (\Gamma/2)^2}
\]  

(1.28)

It is clear from Eq. (1.28), the RRS emission spectrum exhibits Lorentzian distribution which is centered at \(U_K - U_L\). However, the energy conservation imposes a limit on the RRS peak profile distribution and the maximum value of RRS peak is called cutoff energy \(E^\text{max}_s\) given by following expression

\[
E^\text{max}_s = E_0 - U_L
\]  

(1.29)

Due to this cutoff energy value, the RRS peak shows a left-wing of the Lorentzian distribution. The total RRS cross section per unit sold angle is obtained on integrating the Eq. (1.28) for all possible photon energies of the scattered radiation given as

\[
\frac{d\sigma_{RRS}}{d\Omega} = \int_0^{E^\text{max}_s} \frac{d^2\sigma_{RRS}}{d\Omega dE} \frac{dE_s}{U_K - E_o} \sim \frac{1}{U_K - E_o}
\]  

(1.30)

Recent review of the theoretical approach infers that RRS exhibits an isotropic emission independent from the incident photon polarization state. Aberg and Tulkki [32-34] have predicted that polarized radiations should exhibit an anisotropic RRS emission due to the interference between the non-resonant and the resonant terms of the KH formula and is not
incorporated in the earlier approach. The modified form of the RRS differential cross section can be rewritten as

\[
\left( \frac{d^2\sigma_{RRS}}{d\Omega dE_s} \right)_{pol} = \frac{d^2\sigma_{RRS}}{d\Omega dE_s} \left[ B(f - 1) + (1 + B)^2 \right]
\]  

(1.31)

where \( B \) denotes the influence of the non-resonant terms of the KH formula and can be obtained as

\[
B = \frac{U_K - U_L - E_s}{U_K - U_L + E}
\]  

(1.32)

The angular dependence effect on the RRS in conjunction with polarization influence is introduced by the parameter \( f \) and the formula is further modified according to the orientation of the scattering plane with respect to the polarization plane of the incident photon beam as follows [35]

\[
f_{\parallel/\perp} = \cos^2 \theta \ (\mp) \ P \sin^2 \theta
\]  

(1.33)

where symbols, \( \parallel \) and \( \perp \) indicate the parallel and perpendicular orientation of the scattering plane, \( P \) is the effective linear polarization for the incident beam. It is well known that the unpolarized beam can be expressed as a superposition of two perpendicular polarized constituents, \( i.e., \ I_{unpol} = \frac{1}{2} I_{\parallel} + \frac{1}{2} I_{\perp} \). Therefore, the RRS cross section in differential form for the unpolarized incident beam can be written as

\[
\left( \frac{d^2\sigma_{RRS}}{d\Omega dE_s} \right)_{pol} = \frac{d^2\sigma_{RRS}}{d\Omega dE_s} \left[ 1 + B(1 + B) \right]
\]  

(1.34)

Just above the absorption edge \( (E_s \geq I_j) \), there are small systematic oscillations in absorption cross section (Fig 1.5), which are called extended X-ray absorption fine structure (EXAFS). This phenomenon is related to the interference between the secondary electrons ejected at the first stage of the photoelectric effect. Some of these electrons experience scattering by neighbor atoms. EXAFS originates in the interference between the scattered and nonscattered electrons. Therefore, EXAFS oscillations in the cross section \( \sigma_{ph} \) are sensitive to the distances between neighboring atoms, \( i.e., \) to short-range atomic order. EXAFS has become a leading method for studying the short-range atomic structure in different materials (crystalline, amorphous, and liquids [35]).
Fig. 1.5: The contribution of various processes to the absorption in the vicinity of the $K$ shell ionization threshold of an element. EXAFS region involving oscillations in X-ray absorption is marked by a dashed arrow on the right-hand side of the absorption edge.

1.5 Scattering from an aggregate of atoms

Material is meant to be an aggregate of atoms, which may be crystalline or amorphous in nature. When scattering occurs from a solid or liquid consisting of an aggregation of atoms, other scattering effects may be noted. In case of crystalline materials, the atoms have periodically spaced structure called lattice. When the wavefront of X-rays impinges on this set of atoms, each atom scatters X-rays. If the atoms are centred on points in a plane, for example, a plane in a lattice array corresponding to a crystallographic plane $(hkl)$, two directions of scattering have special properties, as shown in Fig. 1.6. In both these directions, the distance from the original wave front, to an atom, and on to a new wave front is the same for all atom locations in the plane. These directions correspond, respectively, to a continuation of the beam in the original direction, and to a reflection of the beam by the plane on which the atoms lie. The scattering by atoms in a plane is, therefore, equivalent to reflection by the plane. A lattice array of atoms have equally spaced parallel planes. The waves associated with photons scattering from each of the regularly spaced atoms in crystal show coherence and result in the constructive interference (diffraction) in few directions. This results in the sharp peak maxima in the pattern, giving the characteristics of the structure for the material according to Bragg’s Diffraction law given by
Fig. 1.6: Two directions of wavefronts after interacting with a plane of atoms.

\[ 2dsin\theta = n\lambda \]  

(1.35)

where, \( d \) is the spacing between diffracting planes, \( \theta \) is the incident angle, \( n \) is the integer characterising the order of the diffraction, \( \lambda \) is the wavelength of the incident beam. This process is called Bragg’s diffraction. The coherent/incoherent intensity ratio will vary widely with scattering angle and will also depend upon the crystallinity and average atomic number of the specimen, as well as the energy of the scattering radiation. In specimens of finite thickness, absorption of the incident and scattered radiation in the specimen must also be considered. The X-ray diffraction effect is used in the wavelength-dispersive spectrometer as a basis for spectral separation. A single crystal is cleaved such that a selected set of atomic planes \((hkl)\) of interplanar spacing parallel with the surface. This crystal is used to diffract the polychromatic beam of fluorescence emission from the specimen, and rotating the crystal to an appropriate angle \( \theta \) will cause a given wavelength \( \lambda \) to be diffracted at angle \( 2\theta \), provided that the Bragg relation (eq. 1.35) is satisfied.

1.5.1 X-ray diffraction in polycrystalline materials

It is clear that the X-ray diffraction results from an electromagnetic wave (the X-ray) impinging on a regular array of scatterers (the repeating arrangement of atoms within the crystal). For polycrystalline materials, analytic solutions for diffraction intensity can be obtained in two extreme cases: ideal mosaic crystals, and random distribution of small crystallites which produces the so-called powder diffraction pattern. While explaining the
models in case of macroscopic samples, X-ray absorption within a material should be taken into account due to larger thickness of polycrystalline sample than the X-ray absorption length in the material. [37]

(a) Ideal Mosaic crystal

Consider small crystallites, each having volume $V$, that are slightly misoriented with respect to each other (Fig.1.7). The characteristic misorientation angle $\Omega_m$ defines the so-called crystal mosaicity. The geometry permits individual crystallites to scatter independently. The angle the angle $\Omega_m$ is less than the divergence $\Delta \alpha$ of the incident beam, so that all crystallites diffract simultaneously. So, in this model, the contributions of all small crystallites within the sample of thickness $T$ are added, taking into account the exponential attenuation of the incident and diffracted beams with depth $z$ due to X-ray absorption.

If the incident beam has the cross-sectional area $S_0$ (Fig.1.8) then the number $dN$ of crystallites within infinitesimally thin layer $dz$ which scatters X-rays by the angle $2\Theta$ is

$$dN = \frac{S_0}{V \sin \Theta} dz$$

(1.36)
If this layer is located at depth z, then its contribution \( dI \) to diffraction intensity is

\[
dI = E_{sc} \exp \left( -\frac{2\mu z}{\sin \theta} \right) dN
\]  

(1.37)

where \( E_{sc} \) is the scattering power of a small crystal and is given by the equation

\[
E_{sc} = \frac{|F|^2 r_0^2 \lambda^3 V}{\sin(2\theta_B) V^2} \left( 1 + \frac{\cos^2 2\theta_B}{2} \right) \exp \left( -2W \right) I_0
\]  

(1.38)

Substituting the value of \( dN \) and \( E_{sc} \) and integrating over sample thickness \( T \), the diffraction power \( E_{mc} \) for an ideal mosaic crystal \( 2\Theta \approx 2\Theta_B \) is given by

\[
E_{mc} = \int E_{sc} \exp \left( -\frac{2\mu z}{\sin \theta_B} \right) dN = \frac{|F|^2 r_0^2 \lambda^3}{\sin(2\theta_B) V^2} P_p \left( 1 - \exp \left( -\frac{2\mu z}{\sin \theta_B} \right) \right) \exp \left( -2W \right) S_o I_0
\]  

(1.39)

where \( P_p \) is the polarization factor for a non-polarized incident beam.

\[
P_p = \frac{1}{2} \left[ 1 + \cos^2 (2\theta_B) \right]
\]  

(1.40)

The diffraction does not depend on the sample thickness \( T \); its role is played by the parameter \( 1/2\mu \).

(b) Powder Diffraction

For powder diffraction, three additional issues have to take into account:

i) Random distribution of crystallite orientation within a sample;

ii) X-ray scattering within a diffraction cone;

iii) Multiplicity factor.

Item (i) means that only those crystallites will participate in the diffraction process in which the chosen \((hkl)\) planes meet incident X-rays at the correct entrance angle \( \theta_B \). In order to take account of this point, let us designate the angle between the normal to parallel planes \((hkl)\) and the wave vector of the incident X-rays as \( \Psi \) (Fig.1.9 (a)). The probability to find this normal at an angle between \( \Psi \) and \( \Psi + d\Psi \) is defined by the element of solid angle \( d\Omega \), given by

\[
d\Omega = 2\pi \sin \Psi d\Psi = 2\pi \sin \left( 90^\circ - \theta_B \right) d\Psi = 2\pi \cos \theta_B d\Psi
\]  

(1.41)

Item (ii) is related to the fact that the diffraction pattern from a random powder has axial symmetry with respect to the wave vector \( k_i \) of the incident X-ray beam. This means that
the diffraction intensity from a certain crystallographic plane \((hkl)\) is distributed along a conical surface (Fig. 1.9 (b)). The cone tip is at the center of the sample. In plane projection, the diffraction intensity forms the so-called Debye-Scherrer rings. This distribution should be taken into account in diffraction measurements utilizing point detector scans, since in the latter only a small part \(\zeta\) of the diffraction intensity is entering detector after passing through the receiving slit \(S_d\) in front of it

\[
\zeta = \frac{S_d}{2\pi R_d \sin 2\theta_B} \tag{1.42}
\]

where \(R_d\) is the length of the detector arm.

Fig. 1.9: Illustration for (a) Random distribution of crystallite orientation within a sample (b) X-ray scattering within a diffraction cone. Wave vector of the incident X-ray beam in denoted as \(k_i\).

Item (iii) reflects the fact that powder diffraction deals with Debye–Scherrer rings whose radii are defined by crystal \(d\)-spacings. If different combinations of Miller indices \((hkl)\) produce identical \(d\)-spacings, these planes will contribute to the same Debye–Scherrer ring, thus increasing its intensity. To take this effect into account, the multiplicity factor \(P_m\) is equal to the number of equivalent planes that are produced from the initial plane by all symmetry operations included in the crystal point group. The multiplicity factor differs for different types of crystallographic planes and depends also on the symmetry system to which investigated crystal belongs. Considering all the above factors, the powder diffraction intensity \(E_p\) is expressed as

\[
E_p = K_c \left( \frac{P}{V_c} \right)^{1/2} \frac{2}{\sin \theta_B \sin 2\theta_B} P_m \exp(-2W) \left( 1 - \exp\left(-\frac{2\mu}{\sin \theta_B}\right) \right) \left( 1 + \cos^2 2\theta_B \right) \tag{1.43}
\]
Where the coefficient $K_e$ unifies a number of experimental parameters, such as incident X-ray intensity ($I_o$), cross-sectional area ($S_o$) of the beam irradiating whole crystal $R_d$, and $S_d$, which are not varied in a particular measurement.

Kinematic diffraction theory is provided with diffraction peak positions (via Bragg law) and diffraction intensity. Three main parameters describing each diffraction line are intensity (peak or integrated) $I$, peak width $\Gamma$, and angular peak position $\Theta$. The latter, $\Theta=\Theta_B+\delta\Theta$, is composed of the expected Bragg position $\Theta_B$ and its deviation $\delta\Theta$. Measurement of all these parameters is the basis of important applications of X-ray diffraction to materials science. Specifically, the peak intensities $I$ and the peak positions $\Theta_B$ are used for structure determination and phase analysis of polycrystalline samples. Deviations of peak intensities from those predicted by powder diffraction theory are treated within texture analysis. The widths $\Gamma$ of the diffraction profiles are used for line-broadening analysis aimed at extracting crystallite size and averaged microstrain fluctuations. The angular deviations $\delta\Theta$ are the basis of the residual strain/stress analysis.

### 1.6 Photon absorption

For a material comprising only one type of atoms with atomic concentration considering as $c_a$ per unit volume. X-rays with intensity $I$ (per unit area) entering the material normal to the entrance surface (Fig. 1.10) will be attenuated by an amount $dI$ when passing through a material layer with thickness $dz$. For an infinitesimally thin layer, the attenuations caused by the individual atoms can be summed

$$dI = -I\sigma_{ph} c_a dz \quad (1.44)$$

Fig. 1.10: X-ray attenuation when passing through material at normal incidence.
The negative sign in eq. (1.44) reflects the decrease in the beam intensity after passing through the layer \(dz\). Integrating eq. (1.44) yields the exponential attenuation of X-ray intensity with depth \(z\) as

\[
I = I_0 \exp\left(-\sigma_{ph} c_a z\right) = I_0 \exp\left(-\mu z\right)
\]

where \(I_0\) is the incident X-ray intensity at \(z=0\). The product of the cross section \(\sigma_{ph}\) and atomic concentration \(c_a\)

\[
\mu = \sigma_{ph} c_a
\]

has the dimension of inverse length and is called the linear absorption coefficient \(\mu (\text{cm}^{-1})\). The parameter \(1/\mu\) defines the characteristic thickness of a material layer that causes attenuation of X-ray intensity \(e (=2.718)\) times that at normal incidence. For example, in Si, \(1/\mu \approx 70\ \mu\text{m}\) for Cu-K\(\alpha\) radiation \((\lambda=1.54\ \text{Å})\), while \(1/\mu \approx 700\ \mu\text{m}\) for Mo-K\(\alpha\) radiation \((\lambda=0.71\ \text{Å})\). The absorption in a material is also taken as a measure of mass attenuation coefficient defined as \(\mu_m = \mu / \rho\), with units \((\text{cm}^2/\text{g})\). In these units, the value of mass attenuation coefficient, \(\mu_m\) is independent of the physical state of the absorber. The value of the \(\mu_m\) in case of multielemental absorber can be written in terms of the values of \(\mu_m\) for the constituent elements, viz.,

\[
\mu_{\text{compd}} = \sum w_i \mu_i / \sum w_i ,\text{ where } w_i \text{ is the weight of } i\text{th element in the target.}
\]

**Absorption in Bragg scattering geometry**

For analysis of the diffraction intensity, another characteristic depth \(\Lambda_a\) is introduced, which also causes 2.718 \((e)\) times attenuation of X-ray intensity but takes into account actual trajectories of the incoming and diffracted X-rays in the symmetric Bragg scattering geometry (Fig. 1.11)

\[
\Lambda_a = \frac{\sin \Theta}{2 \mu}
\]

![Fig. 1.11: X-ray penetration depth in a symmetric Bragg scattering geometry](image-url)
where Θ is the diffraction angle defined at a fixed wavelength λ by the d-spacing. So, in this geometry, the exponential attenuation of the diffraction intensity $I_d$ with depth $z$ due to absorption is expressed as

$$I_d = I_{d0} \exp\left(-\frac{z}{\Lambda_a}\right)$$  \hspace{1cm} (1.48)$$

In asymmetric Bragg scattering geometry, that is, when the atomic planes used for X-ray diffraction meet the surface of the sample at some angle $\alpha \neq 0$ (Fig.1.12), the characteristic absorption depth $\Lambda_a$ is

$$\Lambda_a = \left\{ \mu \left( \frac{1}{\sin(\theta - \alpha)} \right) + \left( \frac{1}{\sin(\theta + \alpha)} \right) \right\}^{-1}$$  \hspace{1cm} (1.49)$$

If the glancing angle, $\omega = \theta - \alpha$, is very small (about 1° or less), the penetration depth, $\Lambda_a$, is considerably reduced down to the sub micrometer level

$$\Lambda_a \approx \frac{\omega}{\mu}$$  \hspace{1cm} (1.50)$$

Fig. 1.12: X-ray penetration depth in an asymmetric Bragg scattering geometry.

and hence the sensitivity of X-ray diffraction to thin layers of materials may be significantly enhanced. This is the basis of the glancing-incidence diffraction method for studying thin polycrystalline films. The glancing-incidence condition for single crystals, $\omega = \Theta - \alpha \approx 0$, that is,

$$\alpha = \Theta = \Theta_B = \sin^{-1}\left(\frac{\lambda}{2d}\right)$$  \hspace{1cm} (1.51)$$

can easily be achieved when working at synchrotron beam lines by changing the X-ray wavelength $\lambda$.  

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1.7 Inner shell vacancy decay processes

When the incident photon energy is well above the ionization threshold, it leads to creation of real vacancy in the corresponding shell/subshell due to photoionization. The real atomic inner-shell/subshell vacancy is also produced by electron-capture radioactive decay, direct ionization of charged particles and internal-conversion decay processes. In case the incident photon energy lies just below the ionization threshold, it leads to the creation of virtual hole in respective shell/subshell. The excited atomic energy levels have finite lifetime and there exist uncertainty in the orbital energy. Due to natural line width, Doppler and collision broadening, an excited atomic state has Lorentzian distribution profile. The excited ionized atom having both real and virtual vacancy relaxes by radiative (photon emission) and non-radiative (electron emission) decay within $10^{-16}$-$10^{-15}$ s.

1.7.1 Radiative transitions

In radiative transition, an inner-shell/subshell vacancy is filled by an electron from outer shell/subshell thereby shifting the inner-shell/subshell vacancy to the outer shell/subshell and the difference between energies of these two shell/subshell is emitted as characteristic X-ray. All the transitions from one shell to another shell do not result in characteristic X-ray emission, since there are certain selection rules which must be satisfied. These selection rules are $\Delta n \geq 1$, $\Delta l = \pm 1$ and $\Delta j = \pm 1$, 0 where $\Delta j$, $\Delta l$ and $\Delta n$ correspond to the change in the total angular momentum quantum number, the orbital angular momentum quantum number and the principle quantum number respectively. According to ligand field theory, if the metal orbitals are impure due to mixing with ligand orbitals, they lose their symmetrical purity and transition between them becomes possible leading to forbidden transition. It is important ot state that transition with $j$ varying as $0 \rightarrow 0$ is forbidden. The $\Delta l = \pm 1$ (electric dipole) corresponds to the most likely class of transitions. The allowed transitions involved in some of the typical $K$, $L$ and $M$ X-ray groups are shown in Fig. 1.13. According to the Dirac’s theory of radiation [38], transitions that are forbidden as electric dipole radiation can appear as electric quadrupole and magnetic dipole radiations. The selection rules for the electric quadrupole radiations are $\Delta l = 0 \text{ or } \pm 2$, $\Delta j = 0$, $\pm 1 \text{ or } \pm 2$. The transitions with $j$ varying as $0 \rightarrow 0$, $1/2 \rightarrow 1/2$ and $0 \leftrightarrow 1$ are forbidden. Here, $\Delta l = 0$ and $\Delta j = 0 \text{ or } \pm 1$ are the selection rules for the magnetic dipole radiations.
1.7.2 Non-radiative transitions

In the non-radiative transitions, an electron from the outer-shell fills the initial vacancy and the available energy is used to eject another electron from the outer-shell. The Auger transitions are denoted by the shells and subshells involved in the process, e.g., the \( L_1 \)-subshell vacancy is filled by an electron from the \( M_{11} \)-subshell followed by the emission of another electron from the \( M_3 \)-subshell of the same shell, and it is denoted by \( L_1M_{11}M_3 \) Auger transition. Auger process is used to describe those transitions in which an atomic shell/subshell leads to two vacancies in one or two different principal shells. The transitions where one of the two vacancies produced in radiationless decay is in a different subshell of the same principal shell that contained the initial vacancy are called the Coster-Kronig (CK) transitions. The transitions where initial vacancy decay results in two vacancies in the subshells of the same principal shell that contained the initial vacancy, are called Super Coster-Kronig (SCK) transitions. The various transitions are schematically shown in Fig. 1.14.
1.7.3 Physical parameters related to inner-shell vacancy decay processes

The various physical parameters such as fluorescence and CK yields, Auger and Coster-Kronig (CK) transition and X-ray emission rates and vacancy transfer probabilities are required to study the atomic inner-shell/subshell vacancy decay processes via radiative and non-radiative transitions. The calculations of relative X-ray line intensities and X-ray production (XRP) cross section require the accurate data of these various physical parameters. The calculated data further have variety of applications, namely, radiation transport, dosimetric computations, mass attenuation calculations, radiation shielding, emission techniques, industrial irradiation processes, surface chemical analysis and quantitative elemental analysis using X-ray fluorescence techniques. These parameters are briefly presented in the following sections.

(a) Fluorescence, Auger and Coster-Kronig yields

The lifetime ($\tau$) of this state is related to the total width $\Gamma_T$ of the level involved by Heisenberg’s uncertainty principle: $\Gamma_T \tau = \hbar$. The decay probability per unit time of a state is, therefore, $1/\tau = \Gamma_T / \hbar$. Assuming that the different modes of the decay are independent of each other, the total width $\Gamma_T$ can be expressed as the sum of the partial widths of all the processes by which the level can decay. Therefore the total width for the atomic excited state is given by
\[ \Gamma_T = \Gamma_R + \Gamma_A + \Gamma_{CK} \]  

(1.52)

where the subscript \( R \), \( A \) and \( CK \) denote the radiative, Auger and Coster-Kronig transitions respectively. The various physical parameters used in the X-ray production cross section calculations are the fluorescence, Auger, \( CK \) yields and X-ray emission rates. These parameters are briefly presented in the following sections.

The fluorescence yield \( (\omega) \) may be defined as the probability that a vacancy in a shell/subshell is filled through a radiative transition. In terms of radiative partial width \( (\Gamma_R) \) and total width \( (\Gamma_T) \), the fluorescence yield can be defined as, \( \omega_i = \Gamma_R/\Gamma_T \). The Auger yield \( (a_i) \) is the probability that a vacancy in the \( i \)th subshell is filled through a radiationless transition by an electron from the higher shell. The Coster-Kronig yield \( (f_{ij}) \) may be defined as the probability that a vacancy in the \( i \)th subshell of a major shell is filled by an electron making a transition from higher subshell of the same major shell. McGuire has published the theoretical \( L \)- and \( M \)-shell radiative, Auger and \( CK \) transition rates and fluorescence yield calculations for the elements with \( Z = 20-90 \) \([39,40]\). These calculations are based on the non-relativistic approximate Herman-Skillman (AHS) central potential. The calculations of the fluorescence yields \( (\omega_i) \) of \( L_i \) subshell and Coster-Kronig transition probabilities \( (f_{ij}) \) using radiative and non-radiative transition rates based upon the RDHS model for the elements with \( 25 \leq Z \leq 96 \) by considering the cutoffs and onsets of Coster-Kronig transitions are performed by Puri et al. \([41]\). Recently, Campbell \([42]\) has compiled the \( \omega_i \) and \( f_{ij} \) values for the elements with \( 25 \leq Z \leq 96 \) and provide a set of recommended values.

(b) Fractional X-ray emission rate

Transitions from the higher energy state give rise to emission of more than one X-rays. The fractional emission rate, \( F_{ij} \), is defined as the ratio of radiative rate \( S_{ij} \) for the \( ij \)th X-ray to the total radiative rate, \( S_{iR} \), for a vacancy in the \( i \)th subshell and is given by

\[ F_{ij} = \frac{S_{ij}}{S_{iR}} \]  

(1.53)

Two sets of values for fractional emission rates of the \( L_i \) subshell are available in the literature \([43,44]\). First set is based on the Dirac-Hartree-Slater (DHS) model \([43]\) and the second set is based on the Dirac-Fock model \([44]\). In the DHS model calculations, the potential was assumed to be equal for the initial and final states of the atom undergoing the transition, whereas in DF model calculations, the potential was assumed to be different in the
initial and the final states, and hence the exchange and overlap effects were included in these calculations. Campbell and Wang [45] reported a complete set of interpolated values based upon the DF model [44] for all the elements with \( 18 \leq Z \leq 94 \).

(c) X-ray production cross section

If \( \sigma_i \) is the photoionization cross section of the \( i \)th subshell, the probability of emission of \( ij \)th X-ray line of a given element at an excitation energy \( E \), is termed as X-ray production cross section \( (\sigma_{ij}) \) and is given by

\[
\sigma_{ij} = \sigma_i^p \omega_i \, F_{ij} \, f_{ij}
\]

where \( \sigma_i^p \) denotes the \( i \)th shell/subshell photoionization cross section, \( \omega_i \) is the corresponding fluorescence yield, \( F_{ij} \) is the fractional emission rate, \( f_{ij} \) is the factor pertaining to the hole transfer from \( i \) to \( j \) subshell of the same principle shell, if energetically allowed. The probability of production of fluorescent X-rays is measured in the form of X-ray production (XRP) cross section. Measurements of the X-ray production (or fluorescence) cross section are made by measuring the intensity of the emitted inner-shell fluorescent X-rays (total shell, subshell, individual line or group of lines depending upon different measurements) when a target is bombarded with known flux of photons. The value of the \( K \) XRP cross section can be calculated as

\[
\sigma_K = \sigma_K^p \omega_K F_K
\]

where \( \sigma_K^p \) is the \( K \)-shell XRP cross section, \( \sigma_K^p \) is \( K \) shell photoionization cross section, \( \omega_K \) is the \( K \) shell fluorescence yield and \( F_K \) is the \( K \) shell fractional emission rates. Theoretically the \( L \) XRP cross section for the \( L_p \) X-rays originating from the decay of \( L_i \) subshell vacancies can be expressed by the equations,

\[
\sigma_{L_p} = \sigma_{L_p}^p \omega_l F_{L_p}, \quad p = \beta_3, 4, 9, 10, \gamma 2, 3, 4
\]

\[
\sigma_{L_p} = (\sigma_{L_p}^p + \sigma_{L_p}^p f_{12}) \omega_{L_p} F_{L_p}, \quad p = \eta, \beta_1, \gamma 1, 5, 6
\]

\[
\sigma_{L_p} = (\sigma_{L_p}^p f_{13} + \sigma_{L_p}^p f_{1L} f_{23} + \sigma_{L_p}^p f_{23} + \sigma_{L_p}^p \omega_{L_p} F_{L_p}), \quad p = l, \alpha, \beta_2, 5, 6, 7, 15
\]

where \( \sigma_{L_p}^p \) is the photoionization cross section [46] for the \( L_p \) X-rays. Puri et al. [47] have calculated the \( K \) and \( L \) shell XRP cross section for elements in the atomic range \( 35 \leq Z \leq 94 \).
92 for incident photon energy range 1-200 keV. These calculations are based on the most reliable parameters, namely, partial photoionization cross section and emission rates of Scofield [46,48], $K$ and $L_i$ shell fluorescence yields [49] and CK transition probabilities based on DHS model [41].
References