2.1 Photon interaction with matter

In general, there are twelve different processes through which photons can interact with matter. Fano et al (1953, 1959) have classified the processes involved in the interaction of photons with matter systematically as given in Table 2.1. In the energy region from a few keV to about few hundred keV, three major processes contribute to the interaction viz., incoherent scattering, atomic photo effect and coherent scattering.

**Atomic photoeffect**

The atomic photo effect is a process in which the incident photons are absorbed by the atom and this energy is transferred to the bound atomic electron which uses part of this energy to overcome its binding to the atom and carries the rest as kinetic energy. This process is dominant at low energies and in high Z elements. The Z-dependence increases from $Z^4$ to $Z^5$ approximately as the energy increases.

**Rayleigh scattering**

It is a scattering by bound atomic electrons where the atom as a whole is considered to absorb the transferred momentum. It follows that the energies of the incident and scattered photons are the same and there is a definite phase relationship between the scattering amplitudes for different electrons of the same atom. The total scattered intensity is accordingly a coherent sum of the individual contributions i.e., the amplitude of the radiation scattered by each electron must be added together and the sum squared to obtain the resultant intensity. It is significant at low energies and confined to very small angles because the recoil imparted to the atom must not produce atomic excitation or ionization. For low energy and high Z elements, Rayleigh scattering is significant but for high energy and small Z it is negligible. It varies as $Z^2$ at small angles and as $Z^3$ at larger angles.

**Thomson scattering with free electrons**

Thomson scattering is coherent scattering of photons due to interaction with free electrons. It is independent of energy and is proportional to Z, this is treated as a limiting case of Compton effect.

**Nuclear Thomson scattering**

Here, the incident photon interacts with the nucleus as a whole to suffer coherent scattering. Its cross section is too small to observe experimentally. It is independent of the photon energy as well as nuclear energy levels, and is having $(Z^4/A^2)$ dependence.
Table 2.1 Photon interaction with matter (Fano et al (1953, 1959))

<table>
<thead>
<tr>
<th>Process</th>
<th>Kind of Interaction and approximate energy range</th>
<th>Other name and Z- dependence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption with atomic electrons</td>
<td>Complete absorption by bound atomic electrons. Dominates at low energy (1keV to 500keV). Decreases as E increases.</td>
<td>Photoeffect proportional to $Z^4$ to $Z^2$</td>
</tr>
<tr>
<td>Scattering from electrons</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coherent</td>
<td>With bound atomic electrons. $&lt;1$MeV-greatest at small scattering angles.</td>
<td>Rayleigh scattering. Electron resonance scattering. Proportional to $Z^2$ (small angles) to $Z^3$ (large angles)</td>
</tr>
<tr>
<td></td>
<td>With free electrons. Independent of energy</td>
<td>Thomson scattering. Proportional to $Z$.</td>
</tr>
<tr>
<td>Incoherent</td>
<td>With bound atomic electrons. $&lt;1$MeV-least at small scattering angles.</td>
<td>Proportional to $Z$.</td>
</tr>
<tr>
<td></td>
<td>With free electrons. Dominates in the region of 1MeV. Decreases as E increases.</td>
<td>Compton effect. Proportional to $Z$.</td>
</tr>
<tr>
<td>Absorption by nucleus</td>
<td>Complete absorption by the nucleus. Emits photon or nucleons. Dominates in the energy range 10 to 30 MeV</td>
<td>Nuclear Photoeffect.</td>
</tr>
<tr>
<td>Scattering with nucleons</td>
<td></td>
<td>Nuclear Photodisintegration.</td>
</tr>
<tr>
<td>Coherent</td>
<td>With the material as a whole. Dependent on nuclear energy levels. Important only in very narrow resonance range.</td>
<td>M&quot;ossbauer effect. Nuclear resonance scattering.</td>
</tr>
<tr>
<td></td>
<td>With nucleus as a whole. Dependent on nuclear levels. Narrow resonance maxima at low energies. Broad maximum in the range of 10 to 30 MeV.</td>
<td>Nuclear resonance scattering. Proportional to $(Z^2/A^2)$.</td>
</tr>
<tr>
<td></td>
<td>With nucleus as a whole. Independent of nuclear energy levels.</td>
<td>Nuclear Thomson scattering. Proportional to $(Z^2/A^2)$.</td>
</tr>
<tr>
<td>Incoherent</td>
<td>With individual nucleons $&gt;100$MeV</td>
<td>Nuclear Compton scattering.</td>
</tr>
<tr>
<td>Interaction with Coulomb field</td>
<td>In Coulomb field of nucleus. Threshold about 1MeV. Dominates at high E. (i.e., E&gt;5 or 10MeV). Increases as E increases.</td>
<td>Elastic pair production. Proportional to $Z^2$</td>
</tr>
<tr>
<td>Pair production</td>
<td>In Coulomb field of electrons. Threshold at 2 MeV. Increases at 2 MeV. Increases with E.</td>
<td>Triplet production. Inelastic pair production. Proportional to $Z$.</td>
</tr>
<tr>
<td>Nuclear potential scattering</td>
<td>In Coulomb field of nucleus. Increases with E.</td>
<td>Delbrück scattering. Proportional to $Z^4$.</td>
</tr>
<tr>
<td>Interaction with mesons</td>
<td>With the meson field of the nucleus $E \geq 150$ MeV</td>
<td>Photo meson production.</td>
</tr>
</tbody>
</table>
Compton scattering

This process is the incoherent scattering of incident photons by quasi free electrons. At energies much greater than the binding energies of the atomic electrons, the photons are scattered as if from free electron since the binding effects are negligible. The Compton scattering cross section decreases as incident energy increases and varies linearly with the atomic number Z. Around 1 MeV, it is the dominant mode of interaction.

Nuclear Compton scattering

In this case the incident photon suffers incoherent scattering by the interaction with individual nucleons. It happens when incident photon energy is greater than 100 MeV.

Nuclear photo disintegration

This process, also called nuclear photoeffect is possible when the incident photon energy exceeds the binding energy of nucleons in the given nucleus. So it starts in the energy range 10 to 20 MeV, depending on the nucleus involved. The cross section varies from a few millibarns, for light elements to hundreds of millibarns for heavy elements.

Nuclear resonance scattering

In nuclear resonance scattering, a nuclear level is excited by an incident photon. The nucleus in turn re-emits the excitation energy. If the energy of the incident photon is very close to the excitation energy of a nuclear level, a large resonance scattering is expected. Due to narrow width of nuclear levels at low energies, the chance of overlap of the incident photon energy with the excitation energy of a target nuclear level is very rare. Muckenheim et al (1981) have succeeded in observing the nuclear resonance scattering contribution of photons from a $^{56}$Co source. Nuclear resonance scattering is proportional to $(Z/A)^2$ and depends on nuclear energy levels.

Mössbauer effect

The recoilless emission and absorption of radiation by nuclei embedded in crystal lattice is referred to as Mössbauer effect. The energy that can be transferred to the lattice during nuclear transition is very small compared to the photon energy. The probability of recoilless transition in most cases is small and governed by the Debye-Waller factor familiar in the theory of X-ray and neutron scattering. The cross
sections for these processes show energy dependence and vary as the full width of the
absorption line.

**Pair production**

Pair production is an example of materialization of energy. It happens when a
photon with energy greater than or equal to 1.02 MeV interacts with the Coulomb
field of charged particles, mainly of atomic nucleus. The incident photon is
completely absorbed and in its place a positron-negatron pair appears. The total
energy of the pair is equal to that of the absorbed photon. Pair production dominates
at high energies and is proportional to $Z^2$.

**Delbrück scattering**

Delbrück scattering or Elastic Nuclear Potential scattering is the result of
interaction between the incident photon and strong Coulomb potential of the nucleus.
The actual mechanism involves the absorption of the incident photon by an electron in
the negative energy state and the subsequent production of a positron-negatron pair.
Here proximity of the nucleus is essential to conserve momentum. Annihilation of the
above positron-negatron pair produces a photon with energy just equal to that of the
incident photon. So, Delbrück scattering is referred as coherent scattering from
negative energy electrons.

The creation of positron-negatron pair takes place in the intermediate states
and gives rise to complex amplitudes. The real part is related to virtual pair
production and imaginary part to real pair production. If incident photon energy is
above 1.02 MeV real pair may result. When the incident photon energy is very high
($E>20$ MeV) creation of real pair dominates. Delbrück scattering has a $Z^4$
dependence.

**Inelastic pair production**

Inelastic pair production or triplet production is basically pair production in
the neighbourhood of an atomic nucleus, with a difference that here one portion of the
absorbed energy of the incident photon is transferred to an orbital electron. It may
result in either excitation or ionisation of the atom in question. It is possible when
incident photon energy is greater than 2 MeV. The process increases with energy.

We shall discuss in detail the three major processes of photon interaction in
the energy region of present investigation.
2.2 Incoherent scattering

In this process the incident photon interacts with an atomic electron and transmits part of its energy to the struck electron. The interacting electron may be treated as free or bound, depending on the relative energy of the incident photon. So there are two separate cases of incoherent scattering.

2.2(a) Incoherent scattering by free electron or Compton scattering

The energy at which incoherent scattering is more probable than the photoelectric effect is much greater than the binding energy of atomic electrons. At these energies the momentum of the photon can not be neglected, since the photon energy becomes comparable to the electron rest mass energy. Since the scattering invariably obeys the law of conservation of momentum, the scattered photon will have less momentum and hence lesser energy than that of the incident photon. The difference in momentum and energy is imparted to the struck electron. This phenomenon is called Compton effect. It is maximum at about 1 MeV and pronounced at large scattering angles. Binding energy of the struck electron, which is very small in comparison with the incident photon energy, may be neglected and the electron may be treated as free and at rest. This approximation is true in most cases of Compton scattering, because, when incident photon energy is comparable with the electron binding energy, photoeffect supersedes Compton scattering, so that the latter becomes insignificant. With the above assumption we may obtain the relation between the angle of scattering and the energies of the photon before and after scattering, from the laws of conservation of energy and momentum. The plane containing the paths of the incident and scattered photons is the scattering plane. Component of momentum in a direction perpendicular to this plane is zero. Hence the path of the struck Compton electron also should lie in the same scattering plane. Polarization does not have any influence on these momentum relationships.

2.2(b) Incoherent scattering by bound electrons

When the energy of the incident photon is comparable with the binding energy of the atomic electron, the electron can no longer be considered as free. Hence the electron should be treated as stationary. So the Klein-Nishina cross section will not hold good at low energies.

Incoherent scattering by bound electron involves the initial, intermediate and final states of the electron. Bound state wave functions should be used to describe all these states. The binding of the struck electron produces two effects in the energy
spectrum of scattered photons, (1) broadening of the width of the scattered lines (2) a slight defect in the Compton shift for bound electrons.

Jauncey (1924, 1925) arrived at two important conclusions. The first one is that the photon-electron interaction takes place impulsively, such that the electron has had no chance to move in the potential well to change its potential energy. This means that the bound electron may be treated as a free electron with the same momentum distribution. This impulse approximation has become the starting point for all subsequent Compton profile analysis. Secondly he recognized that Compton scattering occurs only when the energy transfer to the electron is greater than its binding energy. If this condition is not satisfied the scattering will be coherent.

The binding of atomic electron to the nucleus produces an experimentally observable defect in the magnitude of the most probable Compton shift. So for bound electrons the Compton shift is less by a term $\delta \lambda = \lambda^2 D$, $D = bB/\hbar c$ in which ‘b’ is a numerical constant of the order of unity (Bloch, 1934; Wentzel, 1929; Burkhardt, 1936) and B the binding energy of the electron. The Coulomb binding between the electron and the nucleus compels the electron to drag the nucleus along with it (Ross and Kirkpatrick, 1934). Hence not only the nucleus but the entire atom acquires some of the recoil momentum. So the wavelength shift and the energy shift, for a given energy and angles are slightly reduced.

In the bound electron incoherent scattering the final state of the electron can be any of the discrete states or the continuum. Thus most theories are based on approximate models of the charge distribution within the atom. These theories give valuable information regarding the angular distribution of scattering and the variation with atomic number and energy.

2.2(c) Incoherent scattering function $S(X,Z)$

The currently available theories, which are based on non-relativistic calculations, gave a correction factor for the Klein-Nishina formula evaluated for all the electrons in an atom of a given element. This is expressed as the incoherent scattering function. It gives the probability that an atom will absorb energy and be raised to an excited or ionized state when an incident photon transfers momentum to any of its electrons. It has been evaluated using different non-relativistic atom models. If the momentum transferred by the photon in comparison with the initial electron momentum is small, the incoherent scattering function $S(X,Z)$ approaches zero and if
it is large $S(X,Z)$ approaches the atomic number $Z$. The formula obtained from these calculations, for the cross section is a function of the photon scattering angle and is integrated over all photon energies, at a given angle. Photon scattering from all the atomic electrons, which are having different binding energies, is considered in this equation. The total incoherent bound electron scattering cross section per atom is given by

$$\sigma_{\text{incoh}} = \int_0^\infty d(\sigma_{\text{KN}})S(x,Z)$$

(2.1)

The generalized form factor of an atom with atomic number $Z$ can be expressed as a matrix element

$$f(q,Z) = \sum_{n=1}^{\infty} \langle \psi_0 \mid \exp(i \mathbf{q} \cdot \mathbf{r}_n) \mid \psi_0 \rangle$$

(2.2)

where $\psi_0$ is the ground state wave function of the atom, $\mathbf{q}$ is the momentum transfer vector with magnitude $q = \frac{2k}{\hbar} \sin(\theta / 2)$ and $\mathbf{r}_n$ is the radius vector from the nucleus to the $n$th electron. Since

$$S(q,Z) = \sum_{\varepsilon \neq 0} |f_\varepsilon(q,Z)|^2$$

(2.3)

where $\varepsilon$ is the energy of an excited or ionized stationary state as measured from the ground state. The sum in the above equation is taken to mean a sum over the discrete states and an integral over the continuum states, excluding the ground state $\varepsilon_0$.

In the case of atomic hydrogen the equation for $S(x,Z)$ may be written as

$$S(x,Z) = 1 - |f(x,Z)|^2$$

(2.4)

For molecular or terminally bonded hydrogen the situation is more complicated (Hubbell et al (1975).)

To calculate the ground state wave functions, approximate atomic model or technique should be used except that in the case of hydrogen. Grodstein (1957) describes some of these models in detail. Two of these model viz. Thomas-Fermi and Hartree-Fock-Slater models are practically important.

2.2(d) Thomas - Fermi model

Thomas (1927) and Fermi (1928) treated the atomic electrons as a degenerate gas obeying Fermi-Dirac statistics and Pauli exclusion principle, with the ground state energy of the atom equal to the zero-point energy of this gas.

The limitations of using TF model in calculating incoherent scattering functions are:
i) The effects of the atomic shell structure are smoothed out.

ii) Near the edge of the atom, the TF theory predicts an electron distribution that is excessively smeared out, with the result that the incoherent scattering is overestimated for low values of $V$.

iii) Near the nucleus, the TF model predicts an incorrectly high density of electrons with the result that the incoherent scattering is underestimated for high values of the momentum transfer. TF model being statistical in nature gives better results as $Z$ increases.

Brown (1966) has tabulated total and differential cross sections of coherent and incoherent scattering, using the TF model. Donaldson et al (1965) calculated incoherent scattering differential cross sections for different energies and elements, on the basis of TF model.

2.2(e) Hartree-Fock model

The self-consistent field (SCF) method of Hartree (1928) is an independent particle model in which each electron is assumed to be in a composite field, comprising the field of nucleus and an average field due to the other electrons. Fock (1930, 1934) to include the effects of exchange has generalized Hartree scheme. Slater (1951) has shown that the Hartree and Hartree-Fock wave functions arise out of variational treatment in which the wave functions of the many electron atom are assumed to be a product of individual electron wave functions.

In calculating $S(X,Z)$ it is assumed in Hartree method that the excitation of other electrons is undisturbed. Hence $S(X,Z)$ for an element of atomic number $Z$ represents an average of the incoherent scattering functions for its individual electrons.

Tseng et al (1973) have examined the validity of the incoherent scattering function approximation and the impulse approximation for the inelastic scattering, using the non-relativistic $A^2$ (form-factor approximation) of Schnaidt (1934) and the non-relativistic dipole formula of Gavrilova (1967, 1972) for a hydrogen-like atom and using the relativistic result of Wittingham (1971) for the pure Coulomb potential. They found that the correction to the incoherent scattering function approximation is less than about 10% for $Z \leq 13$.

Cromer et al (1974) have used Hartree-Fock SCF wave functions by Mann (1967) and the complete Waller-Hartree theory with exchange terms to calculate non-
relativistic values of $S(X,Z)$ for all elements $Z=2$ to 102 for $x$ from 0.005 to 80 Å$^{-1}$ to enable Veigele (1971, 1973) to calculate photon incoherent scattering cross sections up to 1 MeV, without extrapolation. Hubbell et al (1975) tabulated incoherent scattering functions $S(X,Z)$ for $x$ from 0.005 to $10^9$ Å$^{-1}$ for $Z=1$ to 100 based on non-relativistic SCF Hartree-Fock & values of Cromer et al (1969) and Cromer-Mann (1967). Hubbell et al (1975) have reviewed the status of atomic form factors, incoherent scattering functions and photon scattering cross sections together with available measurements. The compiled data of Hubbell et al (1975) have been interpolated to the energies of interest and used in the present work.

2.2(f) S-Matrix approach

Bergstorm et al (1993) studied Compton scattering from bound electrons within external field quantum electrodynamics and the Independent-Particle Approximation (IPA), without using any additional approximations such as the impulse or incoherent scattering factor approximations. They have done calculations of the doubly differential cross section for scattering of unpolarized and polarized photons from bound atomic electrons as a function of scattered photon energy and angle, based on numerical evaluation of the second-order S-matrix in self-consistent screened atomic potentials which permit the simultaneous discussion of all regions of the Compton spectrum for scattering from any atomic sub-shell. They have presented a systematic theoretical investigation of this process for atomic inner sub-shells at energies where binding effects in these shells are important. They have discussed,

a) the evaluation of the total atom scattering cross section in these cases
b) the applicability of widely used approximate methods with regard to the spectral features they describe in the case of individual sub-shells
c) the cross section singly differential in scattered photon angle, emphasizing the contribution of terms neglected when making the incoherent scattering factor approximation, as well as implications for total cross sections and for attenuation coefficients
d) several recent experiments, including the efforts to find the infrared rise for soft photons.
e) The calculations are compared with, earlier works within the relativistic S-matrix framework.
The incoherent scattering function $S$ for photon was calculated in the relativistic treatment of Ribberfors and Berggren, using Dirac-Hartree-Fock relativistic wave functions. Table of $S$, for $Z=1$-110, are presented on momentum transfer mesh identical to previous nonrelativistic calculation. $S$ has been calculated at a representative scattering angle of $\theta=60^\circ$ and energies compatible with the presentation mesh. For other scattering angles, the values presented in the tables are accurate to within 1-2% for momentum transfers large than $0.1A^{0.1}$. In the region below $0.1A^{0.1}$ the accuracy worsens with decreasing momentum transfer, reaching 6% at $0.01A^{0.1}$ and 10% at $0.005A^{0.1}$.

Kissel and Pratt (1990) have suggested a $Z$ dependent, energy independent correction term to the high-energy limit based on the $S$-matrix calculations. They have also given a correction term that is to be added to Cromer-Liberman's values to get the appropriate value of $f'$. The predicted values of dispersion corrections are commensurate with those of Creagh and McAuley's relativistic multipole correction term for very low $Z$ elements and are different by about 6% to 7% for $Z>20$.

### 2.3 Photoeffect

The emission of an atomic electron as a result of absorption of an incident photon is called the photoeffect. The ejected electron uses part of the incident photon energy to overcome its binding to the atom and the ejected electron and the residual atom according to the law of conservation of energy share the remaining energy. The photoelectrons emitted from free atoms have energies, which can be written as

$$T_e + T_r = h\nu - B$$  \hspace{1cm} (2.5)

where $T_e$ and $T_r$ are the kinetic energies of the photo electron and the residual atom and $B$ is the binding energy of the emitted electron. By conservation of linear momentum it follows that,

$$T_r = \frac{m_0(T_e + T_r)}{m_e + m_0}$$  \hspace{1cm} (2.6)

Since the mass of the electron is very small, the kinetic energy of the residual atom can be neglected and equation (2.5) simplifies to

$$T_0 = h\nu - B$$  \hspace{1cm} (2.7)

The theoretical calculations of the photoeffect cross sections can be divided into two groups, 1) Analytical calculations and 2) Exact numerical calculations using different atomic models.
2.3(a) Analytical calculations

The theoretical analysis of photoeffect depends upon the choice of the wave functions of the initial and the final ejected photoelectron and the evaluation of the matrix element. Since a free electron cannot absorb an incident photon, the probability of photoeffect absorption is greater if the electron is more tightly bound. Therefore the calculations are confined to the absorption by K-shell electrons only. These calculations are tedious and difficult to make because exact relativistic wave functions must be used. The theoretical knowledge of the process is discussed by Bethe and Salpeter (1957) and can be classified into four groups:

a) non-relativistic case  

b) relativistic Born Approximation formula  

c) high energy limit and  

d) exact relativistic case.

2.3 (a) Non-relativistic case

The non-relativistic formula is obtained by using non-relativistic quantum mechanics and representing the K-shell electrons by hydrogen like wave functions and the liberated electrons by Plane Waves (Born approximation). The corresponding matrix element for the absorption of a single quantum is given by (Heitler 1954)

\[ H = -\left(\frac{e}{mc^2}\right)\left(\frac{2\pi \hbar^2 c^2}{\hbar \nu}\right)^{\frac{1}{2}} \int \psi_b p_\nu e^{i\mathbf{r} \cdot \mathbf{p}} \psi_a \]  

(2.8)

where \( p_\nu \) is the component of the momentum in the direction of polarization of the primary photon, \( \psi_a \) the wave function of the electron in the K-shell and \( \psi_b \) the wave function of the electron in the continuum with the momentum \( \mathbf{p} \). Here

\[ \psi_a = \left(\frac{1}{na^3}\right)^{\frac{1}{2}} \exp\left(-\frac{r}{a}\right) \]

\[ \psi_b = \exp\left(\frac{ipr}{\hbar c}\right) \]  

(2.9)

and momentum transferred to the atom is \( \mathbf{q} = \mathbf{k} - \mathbf{p} \)  

(2.10)

On integration of equation (2.8), we get

\[ H = \frac{e}{mc^2} P_\nu \left(\frac{\alpha_1}{\alpha_0}\right)^2 \left(\frac{2\pi \hbar^2 c^2}{\hbar \nu}\right)^{\frac{1}{2}} \left(\frac{8\pi \hbar^3 c^3}{(\alpha_1^2 + q^2)}\right) \]  

(2.11)

where \( \alpha_1 = \frac{Ze}{a_0} = \frac{1}{137}mc \)  

(2.12)

Therefore the transition probability for the photoeffect absorption is given by the expression
\[ W = \left( \frac{2\pi}{\hbar} \right) |H|^2 \rho_k \]  

(2.13)

where \( \rho_k \) is the number of quantum states per unit energy of the electron. Dividing the transition probability per time by the velocity of the primary beam, one can obtain the differential cross section. Therefore using equation (2.11), one can get the differential cross section as

\[
\frac{d\sigma_{r,k}}{d\Omega} = \left( \frac{r_0^2 Z^4 \alpha^4}{k^{3/2}} \right) \left( 4 \sqrt{2} \sin^2 \theta \cos^2 \theta \right) \left( 1 - \beta \cos \theta \right)^4
\]  

(2.14)

where \( r_0 = \frac{e^2}{mc^2} \) is the classical radius of the electron, \( \beta = v/c \), \( \alpha = 1/137 \), the fine structure constant and \( \theta \) is the angle between the emitted electron and the incident photon and \( \phi \) the angle between the \((p,k)\) plane and the plane formed by \( k \) and the direction of polarization. After integrating over all angles and neglecting the term \( \beta \cos \theta \) in the denominator, the equation (2.14) yields for the total K-shell photoeffect cross section

\[
\sigma_{r,k} = 4 \sqrt{2} \alpha^4 Z^5 \frac{\sigma_0}{k^{3/2}}
\]  

(2.15)

where \( \sigma_0 = \frac{8}{3} (\sigma_0^2) \) is the cross section for the Thomson scattering.

The equation (2.14) is invalid when the photon energy is near the ionisation energy and the Born approximation no longer holds good. In such cases exact wave functions must be used.

The matrix element (2.8) with the correct wave functions of the continuous spectrum has been used by Stobbe (1930) and Hall (1936) and they have obtained an expression similar to equation multiplied by a factor \( F(x_1) \) which is

\[
F(x_1) = 2\pi \left( \frac{\nu_1}{\nu} \right)^{1/2} \frac{\exp(-4x_1 \cot^{-1} x_1)}{1-\exp(-2\pi x_1)}
\]  

(2.16)

where \( x_1 = \left( \frac{\nu_1}{\nu - \nu_1} \right)^{1/2} \) is the ratio of the initial orbital velocity of the electron to the velocity of the photo electron and \( h\nu_1 \) is the ionisation energy of the K-shell electron. This correction factor obtained by Stobbe is discussed in great detail by Heitler (1954), Bethe and Ashkin (1953) and Hall (1936).

Hall (1936) and Stobbe (1930) using the equations (2.15) and, (2.16) have calculated the cross sections for L1-, L2-, L3- and the M-shells. The non-relativistic formula is expected to be valid apart from screening corrections, for light atoms and
low energies but far from the ionisation energy of the K-shell electrons. A comparison of experimental results at low energies by McGinnies (1959) indicates that the values calculated from the above equations are too low.

2.3(aii) Relativistic Born approximation formula

The first order relativistic Born approximation result was obtained by Sauter (1931a, 1931b). When the energy of the incident photon is of the order of \( mc \) or higher, he used the relativistic wave functions to calculate the transition matrix and obtained an expression for the total K-shell photoeffect cross section

\[
\sigma_{\text{r,k}} = \frac{3\alpha^4 Z^5}{2k^5} (u^2 - 1)^2 \left( \frac{4}{3} + \frac{u(u-2)}{u+1} \left[ 1 - \frac{1}{2u(u^2-1)^{1/2}} \ln \frac{u+(u^2-1)^{1/2}}{u-(u^2-1)} \right] \right) \tag{2.17}
\]

where \( u = \frac{1}{(1 - \frac{v^2}{c^2})^{1/2}} = (\frac{hv+mc^2}{mc^2}) \). Grodstein (1957) has modified Sauter's result with the correction factor of Stobbe (1930) to yield \( \sigma_{\text{r,k}} \) with \( F(\alpha_f) \). In the non-relativistic limit the equation (2.17) reduces to equation (2.15). In the extreme relativistic limit it becomes,

\[
\sigma_{\text{r,k}} = \frac{3}{2} \left( \frac{\alpha^4 Z^5}{k} \right) \sigma_0 \tag{2.18}
\]

It can be seen that for high energies the decrease of the cross section with energy becomes slower.

Sauter's approximate theory of the photoeffect is of very low accuracy in its predictions for heavy elements. Fano et al (1959), have re-examined Sauter's theory from the transition matrix point of view and have interpreted some of the shortcomings of the theory as being due to cancellation between certain Feynman diagrams and have carried out a Born expansion of the wave functions.

Gavrila (1959) performed the next order Born approximation calculation, correct to one higher order in \( \alpha Z = \alpha, \) valid for small \( Z \). With this, we have,

\[
\sigma_{\text{r,k}} = \frac{3}{2} Z^5 \alpha^4 \sigma_0 \left( \frac{\beta^3 u^3}{(u-1)^2} \right) \{ M(\beta) (1 - \frac{\pi \alpha}{\beta}) + \pi \alpha N(\beta) \} \tag{2.19}
\]

where

\[
M(\beta) = \frac{4}{3} + \frac{u(u-2)}{(u+2)} \left( 1 - \frac{1}{2u^3(u-1)^{1/2}} \ln \frac{u+(u^2-1)^{1/2}}{u-(u^2-1)^{1/2}} \right)
\]

\[
N(\beta) = \frac{1}{\beta^3} \left( \frac{4u}{15} + \frac{34}{15u} + \frac{63}{15u^2} + \frac{25}{15u^3} + \frac{8}{2\beta u^3} \ln \left( \frac{(1-\beta)}{(1+\beta)} \right) \right)
\]

\[
\frac{\sigma_{\text{r,k}}}{e^2} = 2.34 \times 10^{-27} \text{ m}^2 \text{ atm}^{-1} \text{ cm}^{-2} \text{ sr}^{-1}
\]
This result is useful when $\pi aZ/\beta << 1$.

2.3 (aIII) The high energy limit formula

The Born series technique described earlier gives the energy dependence in the limit of small $Z$. Pratt (1960a) used a distorted plane wave (Furry-Sommerfield-Maue wave) to obtain an expression for the cross section in the limit of high energies. All the relativistic calculations valid to varying orders of $\alpha Z$ are discussed by Gavrila (1960) and Gorskhov and Mikhailov (1963). The most comprehensive studies have been made by Gavrila (1959), Pratt (1960) and Nagel (1960). Using a numerical method and a modified plane wave approximation, Pratt obtains values of the high energy limit of the K-shell cross section for all values of $\alpha Z$.

Pratt combining his high-energy $Z$ dependent formula with Gavrila's energy dependent equation (2.19) obtains the following composite formula which has been the basis for high energy cross section predictions,

$$\sigma_{r,x} = \frac{3}{2} \left( \frac{\alpha^4 Z^2 \sigma_0}{k^3} \right) \frac{\beta^3 a^2 \xi M(\beta)}{\cos^{-1} \alpha} \exp(-2 \frac{a}{\beta} \cos^{-1} \alpha) \{1 + \pi a \frac{N(\beta)}{M(\beta)} + R(a)\}$$

where $\xi = \{(1-a^2)^2 - 1\} - \frac{1}{2a^2} = -\frac{1}{2} \alpha^2 Z^2$, the binding energy of K-electron in $mc$ units, $N(\beta)$ and $M(\beta)$ are same as in equation (2.19) and $R(aZ)$ is the difference between Pratt's exact numerical values and his approximate analytical equation, which is small for the values of $\alpha Z$ and as

$$\lim_{\beta \to 0} \frac{N(\beta)}{M(\beta)} = -\frac{4}{15}$$

The first high energy formula was derived by Hall (1934, 1936) who obtained a closed expression by writing an approximation to a double integral equivalent to, though more complicated than Pratt (1960). In his formula the term $(-4/15)\pi aZ$ is missing, which is not small.

2.3 (aIV) Exact relativistic case

Before about 1954 the most accurate theoretical calculations were the numerical calculations of Hulme et al (1931) who assumed that each K-electron is independent of the other and the results being doubled to give the total K-shell cross sections. They have numerically calculated the values for the two energies 0.354 and 1.13 MeV and the three atomic numbers Z=26, 50 and 84. Atomic electron screening was taken into account by considering cross sections as a function of atomic number and replacing $Z$ by $Z_{\text{effective}}$. It was customary to multiply the K-shell cross sections to
get the total atomic photoeffect cross sections by $5/4$. The $5/4$ rule has been found to be fairly good for high Z but not for low Z elements.

2.3 (b) Exact numerical calculations using different atomic models

Nagel (1960) for the first time deduced an expression for the calculation of photoeffect cross sections applicable to all elements at all energies. Using improved Sommerfield-Maue wave functions, he analyzed the K-shell photoeffect including all polarization effects in a way which can serve as a convenient starting point both for appropriate analytical treatment and exact numerical calculations. The total K-shell cross section can be written as

$$
\sigma_{t,k} = \sigma_{r,k}(a) T \{1 + a + (u) + \ldots\} \tag{2.22}
$$

where

$$
T = \frac{2\pi R(1 + R^2)}{1 - \exp(-2\pi R)} \exp\{-2R \arctg \frac{R(u+1)}{R^2 - 1}\} \tag{2.23}
$$

$$
R = a/\beta, \quad a = \alpha Z, \quad u = (h\nu + m c^2)/m c^2 \quad \text{and} \quad \sigma_{r,k}(s)
$$

is the Sauter equation (2.16). The behavior of $f(u)$ for small $\beta$ and for large $u$ are is the Sauter equation (2.16). The behaviour of $f(u)$ for small $\beta$ and for large $u$ are

$$
f(u) = \frac{1}{8} \pi \beta \left(1 + \frac{\beta^2}{2} + \ldots\right) \tag{2.24}
$$

$$
f'(u) = \frac{4}{15} (1 - \frac{41}{6u} + \ldots) \tag{2.25}
$$

Using the detailed equation for $f(u)$ and expanding " $r$ " to the first order in $R$, Hultberg et al (1961) carried out numerical calculations. They obtained an exhaustive data on differential and total K-shell photoeffect cross sections for different polarizations, correct to the first order in $\alpha Z$ without any screening corrections.

Pratt et al (1964a) have developed rigorous numerical method for the calculation of differential and total K-shell cross sections utilizing relativistic Coulomb wave function in a screened central potential including all polarization effects. In a central field approximation, they assume that any electron, whether bound or in continuum, interacts only with a scalar spherical symmetric potential and neglect the effect of finite nuclear size. So for sufficiently small distances, this potential reduces to the pure Coulomb potential ($Ze^2/r$). The relativistic effects are significant even at low energies for high elements. The differential cross section for photoeffect is,
\[ \frac{d\sigma}{d\Omega} = (2\pi)^2 |p_e|^2 |H|^2 \]  (2.26)

\[ H = -ie\left( \frac{2\pi}{k} \right)^{\frac{1}{2}} \int d^3 r \psi_f^* \alpha \cdot e \exp(ik \cdot r) \psi_i \]  (2.27)

Here \( k \) is the momentum of the absorbed radiation and \( e \) is the polarization vector. \( \psi_i \) is a solution of the Dirac equation in a central potential corresponding to an initial bound state and \( \psi_f \) is a solution corresponding to an outgoing electron of definite momentum and energy \( \epsilon \).

Pratt et al (1964b) developed a mathematical formalism for the given central potential to solve the Dirac equation for the desired wave functions and integrated to obtain the matrix element \( H \). They also developed a computer code for the IBM-7090 and obtained the K-shell photoeffect cross sections of elements from \( Z = 13 \) to 92 for photon energies from 200 keV to 2 MeV. They have discussed the seven possible correlations between incident photon and ejected electron in K-shell photoeffect, for the same \( Z \) and photon energies.

Alling and Johnson (1965) have reported an exact calculation of differential and total cross sections for the K-shell and L-shell photoeffect under the assumption of pure Coulomb potential in relativistic case. They assume that both the initial and final electrons are moving in a pure Coulomb field. This implies that the higher order radiation corrections may be neglected and the interaction with radiation field may be treated in lowest order perturbation theory. The relativistic effects become important even for low energies, since the momentum associated with the bound state is appreciable for intermediate and high \( Z \) elements. The differential cross section can be written in the form,

\[ \frac{d\sigma}{d\Omega} = \frac{\alpha}{2\pi} \left( \frac{pW}{k} \right) \frac{1}{2} \sum |M|^2 \]  (2.28)

where \( (p, iw) \) and \( (k, ik) \) are the four momenta of the final electron and the incident photon respectively and \( M \) is the matrix element given by

\[ M = \int dr \psi_f^* \alpha e \exp(ik \cdot r) \psi_i \]  (2.29)

where \( \alpha = \begin{pmatrix} 0 & \sigma \\ 0 & 0 \end{pmatrix} \), the \( \sigma_i \) being \((2 \times 2)\) Pauli matrices, \( \epsilon \) = unit vector which specifies the direction of polarization of the incident photon. In equation (2.28), \( \frac{1}{2} \sum |M|^2 \) represents the average over photon polarizations and the sum over the initial and final
electrons. $\psi_i$ is the wave function for the initial bound electron and $\psi_f$ is the Hermitian adjoint of the final state. $\psi_f$ is a continuum solution of Dirac's equation for energy $W>M$ which occurs as an infinite sum of partial waves. The nucleus is considered to be infinitely heavy, so that it can absorb an arbitrary amount of momentum. However energy is conserved among the photon and the initial and final electrons. Under these assumptions the solutions are obtained and a computer program was carried out to evaluate $\partial \sigma/\partial \Omega$ for an arbitrary target and photon energy, for the K-shell and L-shells. Explicit numerical evaluation was done for uranium and lead and for incident energies 81, 103, 279, 354, 412, 662 and 1332 keV. At the first two energies, only the sub shell cross sections were evaluated. The K-shell total cross sections agreed with values reported by Pratt et al. (1964a), within 1%. The discrepancies found in these cross sections were attributed to the neglect of atomic screening. Matese and Johnson (1965) extended the previous work of Alling and Johnson (1965) to include the effects of screening through the introduction of a screening parameter $\lambda$, in a central field potential of the form,

$$V(r) = -\frac{a}{r} \exp(-\lambda r)$$  \hspace{1cm} (2.30)

Numerical calculations were presented for $Z=50$, 82 and 92 with incident energies 81 and 1332 keV. Results for the L-shell total cross sections for $Z=92$ with $\lambda=0$ showed discrepancies with the earlier values of Alling and Johnson (1965) at low photon energies. The effect of screening in their calculations was to decrease uniformly the total, K-shell and L-shell cross sections.

Hall and Sullivan (1966) have calculated the relativistic K-shell photoeffect cross sections for $Z=26$, 50, 84 and 92 in the energy range from 300 keV to 1.23 MeV using the Fermi-Thomas central field approximation. Here each electron in the K-shell is assumed to move under the influence of a potential,

$$V(r) = \frac{e^2}{r} \{\phi(x)(Z-1) + 1\}$$  \hspace{1cm} (2.31)

where "$e" is the electron charge and $Z$ is the atomic number. The function $\phi(x)$ is defined by the differential equation,

$$\frac{d^2 \phi}{dx^2} = \frac{3\phi}{x^{3/2}}$$  \hspace{1cm} (2.32)

where $x = r/\mu$, $\mu_0 = a_0 (9\pi^2/128Z)$ with the limiting values $\phi(0)=1$, $\phi(\infty)=0$ and here $a_0$ is first Bohr radius for hydrogen. Computation of the cross sections involves the
numerical solution of the radial differential equations obtained from the Dirac relativistic equation for hydrogen-like atoms. The results are lower than for the unscreened Coulomb potential by an amount from 7% at 354 keV for Z=26 to 2.2% at 1.23 MeV for Z=92.

Rakavy and Ron (1967) are the first to calculate the cross sections for higher (L, M, N..etc.,) shells for photon energies in the range 1-2000 keV. The atomic wave functions have been evaluated using Shalitin's modified Fermi-Amaldi potential, except for uranium for which the Thomas-Fermi potential is used. In the low energy limit and for high Z elements the effect of atomic screening is expected to be important and for the heaviest atoms relativistic effects are not negligible. So by inserting the matrix element, for \( q = \pm 1 \),

\[
T_p = \left( \frac{2\mu e^2 c^2 \hbar}{\alpha V_{\text{norm}}} \right)^{1/2} \int \psi_f^* \exp(ikz) \sigma_q \psi_i d^3r 
\]  

(2.33)

Into the general formula,

\[
\frac{d\sigma_i}{d\Omega} = \frac{2p_i}{(2\pi\hbar c)^3} \sqrt{\sigma_i^2} |T_p|^2 
\]  

(2.34)

where \( \psi_i \) and \( \psi_f \) are the initial and final state wave functions. They expanded the interaction in spherical harmonics and performed all the summations over magnetic quantum numbers and developed a computer code for calculating the cross sections in K, L, M and N-shells. In the intermediate region (Z=50 to 80) it was found that the difference in cross sections obtained by using Fermi-Amaldi and Thomas-Fermi potentials is less than 1.5%. The numerical accuracy of the calculations is found to be better than 0.5%.

The work of Schmickley and Pratt (1967) is a report of further numerical calculations of Photoeffect cross sections for K-through M-sub shells from 412 to 1332 keV photons using a relativistic multipole expansion of the matrix element following the previous work of Pratt et al (1964). In this work the effects of atomic screening and the properties of higher shells are worked out. The only significant effect of electron screening comes from the change in normalization of the bound state wave function. For energies above the threshold, screening is simply a normalization effect. The reason is as follows: (1) The main region of importance for the matrix element is the region of space where \( r = O(1/\Delta) \), \( \Delta \) being the minimum momentum transfer to the nucleus. For photons well above the threshold \( \Delta = O(1) \).
(2) The bound state wave functions in the region $r=0$ (1) are in the field of the bare nuclear Coulomb wave functions in normalization only. (3) Except at very low energies the continuum electron is not much affected by screening at distances $r=0(1)$, so the final state can be approximated by an exact Coulomb wave function. Similarly the shift in energy of ejected electrons due to the shift in binding energy for a screened bound state is negligible $(\Delta -1) >> a^2$. Thus the screened cross section should be proportional to the Coulomb cross section for the same photon energy, the constant of proportionality being the square of the ratio of screened $(s)$ to Coulomb $(c)$ bound-state normalization, independent of energy. The normalization effect error $NE(s)$ is given by

$$NE(s) = \sum \frac{\sigma(c)}{\sigma(s)} - 1$$  \hspace{1cm} (2.35)$$

where $\sum = \lim_{r \to 0} \frac{G_i^s(r)}{G_i^c(r)}$ \hspace{1cm} (2.36)

is the ratio of screened to Coulomb bound-state normalizations for a given state $K$.

Schmickley and Pratt (1967) calculated a set of cross sections for a "realistic" screened potential. They calculated the values of $\sum^2$ for various sub shells of several atoms using relativistic Hartree-Fock-Slater potential computed by Liberman, Weber and Cromer (1965). These ratios were multiplied by Coulomb cross sections and they presented the results for K-shell and total atomic photoeffect cross sections for energies 10 to 3000 keV and elements $Z=13$ through 92. The accuracy is believed to be better than 0.1% for $Z=20$ and 0.5% for $Z=13$.

Brysk and Zerby (1968) made more accurate and exact calculations in aluminium in the energy range 1-150 keV and for uranium in the range 50-150 keV using bound state wave functions and potential from a relativistic Dirac-Slater self consistent- field program and numerical integration for the continuum wave functions and the matrix elements. The derived cross sections agree substantially with that given by Rakavy and Ron (1967), differing only in the exploitation of some specialized results of Racah algebra for computational advantage.

Scofield (1973) treated the electrons relativistically and assumed to be moving in the Hartree-Slater central potential both before and after the absorption of photon. The bound state energy eigen values and wave functions are obtained for a given potential. All contributing multipoles and retardation effects are included in the
treatment of the radiation field. The cross sections are tabulated for elements \( Z = 1 \) to 101 and for photon energies from 1 to 1500 keV. The individual sub shell cross sections are also given. During the computation an accuracy of 0.1% was maintained in calculating the total absorption cross section. Tabulations of theoretical photoeffect cross sections for the energies and elements of interest, obtained by interpolation of Scofield (1973), with and without renormalization are used for comparison in this investigation.

2.4 Theoretical calculations of coherent scattering

Photons may be scattered coherently, in which case the energy of the incident and scattered photon is the same. The electron returns to its initial state after the interaction. Alternatively, the photon may be scattered incoherently, in which case the energy of the scattered photon is less than that of the incident photon. Some of the momentum of the incident photon is transferred to the bound electron, which is then raised to an excited state or may even be ejected from the atom altogether. Since an isolated atom itself is a composite system of nucleus and a bound electrons, the total elastic scattering amplitude \( A \) can be written as the coherent sum of each of the elastic scattering amplitudes,

\[
A = A_R + A_{NT} + A_{NR} + A_D
\]  

where \( A_R, A_{NT}, A_{NR} \) and \( A_D \) represent respectively the Rayleigh, nuclear Thomson, nuclear resonance and Delbrück scattering amplitudes. Each of the scattering processes may be described in terms of linearly or circularly polarized photons. The corresponding amplitudes are represented by \( A_{||} \) and \( A_{\perp} \) for the case of linear polarization parallel and perpendicular respectively to the scattering plane, and \( A^{NSF} \) (no spin flip) and \( A^{SF} \) (spin flip) for the case of no change, and change respectively in the state of circular polarization. The differential scattering cross section for the elastic scattering of initially unpolarized photons in the linear polarization description is given by

\[
\frac{d\sigma}{d\Omega} = \frac{1}{2} \left| A_R + A_{NT} + A_{NR} + A_D \right|^2 + \frac{1}{2} \left| A_{||} + A_{\perp} + A_{NR} + A_D \right|^2
\]

The expression for the elastic differential cross section in the circular polarization description is

\[
\frac{d\sigma}{d\Omega} = \frac{1}{2} \left| A_{||} + A_{\perp} + A_{NR} + A_D \right|^2
\]
The theory of scattering of photons by electrons is most complete and satisfactory for energies large compared with the electron binding energies. In the more general case, the effects of the binding of electrons to the atom and their motions and distributions within the atom must be considered. Theoretically, the scattering of photons by bound electrons is described as a second order process where one photon is absorbed and another one is emitted, the process involving initial intermediate and final states of the electron. An accurate theory must include all possible intermediate states and must take into account the two cases of the absorption of the incident photon first, emission of the scattered photon second, and vice-versa.

It should also take into account the two possible spin orientations of the scattering electron and the two possible polarizations of the incident photon as well as the two of the outgoing photon. These accurate calculations would have to be carried out separately for each electron shell of the atom. This is difficult enough for coherent scattering where the final state is the same as the initial one, but is much more difficult for incoherent scattering where the final state can be any one of the discrete states or the continuum. Thus, most of the presently available theories for coherent and incoherent scattering are based on approximate models of the charge distribution within the atom (Davisson (1968)).

2.5 Calculations of Rayleigh scattering cross section

Rayleigh scattering is an atomic process in which the incident photon is absorbed by a bound atomic electron. This electron is raised to a higher energy state, and a second photon of the same energy as the incident photon is then emitted, and the excited electron returns to its original state. It is also called elastic (coherent) scattering, or electron resonance scattering. This process predominates at energies below 1 MeV and at small scattering angles. Then the recoil momentum imparted to the atom does not produce any excitation or ionisation.

In the lowest non-vanishing order of perturbation theory, Rayleigh scattering is a two-vertex process described by the two Feynman diagrams displayed in Figures 2.2a and 2.2b. The double lines indicate that the electron in the initial, intermediate, and final states is within the influence of the atomic field. Therefore bound state wave
functions must be used to describe the electron in the initial and final states, whereas in the intermediate states, bound state and Coulomb continuum state wave functions must be used. As a result the treatment of Rayleigh scattering is difficult.

Rayleigh scattering can also be formulated in terms of conventional second order, three dimensional perturbation theory, which predicts a transition amplitude given by the expression

$$A_n = \sum_{n} \frac{\langle f | \delta H | n \rangle \langle n | \delta H | i \rangle}{E_1 - E_n \pm h\nu}$$

(2.40)

Because the scattering is elastic, the final state $|f\rangle$ is equal to the initial state $|i\rangle$. The summation is over all intermediate states $|n\rangle$ and integration over intermediate states in the continuum. The (+ ve) sign refers to absorption of the incoming photon first and the (-ve) sign refers to emission of the outgoing photon first. They are represented in Figures (2.2a) and (2.2b) respectively. The perturbation Hamiltonian is given by

$$\delta H = e\alpha \cdot A(x),$$

(2.41)

where $A$ is the vector potential, $\alpha$ is the Dirac matrix, which is expressed in terms of the $2 \times 2$ Pauli matrices as

$$\alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}$$

(2.42)

Fig. 2.2. Feynman diagram:

(a) "absorption-first"  
(b) "emission-first"
In the non-relativistic limit,

\[ \delta H = \frac{e}{mc}(p \cdot A) \quad (2.43) \]

\[ \delta H = -i \frac{e\hbar}{mc}(\nabla \cdot A). \quad (2.44) \]

In addition to the difficulties of using bound state wave functions and of summing over an infinite number of intermediate states, an accurate treatment of Rayleigh scattering must take into account: (i) The two cases of absorption first or emission first represented by the two diagrams in Figures 2.2a and 2.2b. (ii) Two possible spin orientations of the scattering electron. (iii) The two possible polarizations of the incident photon and the two polarization of the outgoing photon, leading to four possible cases. It is usually assumed that the incident radiation is unpolarized and ignoring the polarization of the outgoing photon the transition probability is averaged over incident polarizations and summed over final polarizations. (iv) The scattering from each atomic sub-shell takes place separately. Because, the bound state wave functions describing electrons in different sub-shells are not the same, a separate calculation must be performed for each sub-shell.

J.J. Thomson (1906) made the first calculation of the photon elastic scattering cross sections by a free electron. These cross sections are called the "Thomson scattering cross sections". The photon scattering by bound electrons is called "coherent scattering" or "Rayleigh scattering".

2.5 (a) Scattering by a bound electron (Form factor approximation)

The form factor approximation, which was originally derived classically to correct the Thomson formula for scattering by a distribution rather than a point charge, is still used extensively today to predict Rayleigh scattering amplitudes in the x-ray and y-ray region (Kissel et al 1980). In fact, all the present tabulations of elastic scattering cross sections (Hubbell et al 1975, Hubbell and Øverbo 1979) use this approximation to estimate the contribution made by Rayleigh scattering. It is particularly attractive due to its relative ease of calculation, requiring simply the evaluation of a radial integral over the atomic charge density.
The form factor was also derived using non-relativistic quantum mechanics (Sommerfeld 1939) followed by relativistic derivations due to Franz (1935,1936) and Bethe (1952). The form factor for an atom of atomic number Z, \( f(q,Z) \) is defined [Nelms and Oppenheimer (1955)] as the matrix element

\[
f(q, Z) = \sum_{j=1}^{Z} \langle \psi_0 | \exp(iq \cdot r_j) | \psi_0 \rangle
\]

(2.45)

Where \( \psi_0 \) is the ground state wave function of the atom, \( \vec{q} \) is the momentum transfer vector with magnitude \( q = \frac{2K}{\hbar} \sin(\theta / 2) \), \( K \) is the photon energy in units of electron rest energy and is the radius vector from the nucleus to the \( j^{th} \) electron. The matrix element in equation (2.45) can be evaluated in the position representation

\[
\sum_{j=1}^{Z} \langle \psi_0 | \exp(iq \cdot r_j) | \psi_0 \rangle = \sum_{j=1}^{Z} \int \exp(iq \cdot r_j) \left( \int \psi_0^* \prod_{i=1}^{j} d^3 r_i \right) d^3 r_j
\]

(2.46)

the quantity in the curly brackets is the probability density of the \( j^{th} \) electron. Defining

\[
\rho(r_j) = Z \int \psi_0^* \prod_{i=1}^{j} d^3 r_i
\]

(2.47)

\( f(q, Z) \) then becomes

\[
f(q, Z) = \frac{1}{Z} \sum_{j=1}^{Z} \int \rho(r_j) \exp(iq \cdot r_j) d^3 r_j
\]

\[
= \int \rho(r) \exp(iq \cdot r) d^3 r
\]

(2.48)

Where \( \rho(r) \) is the total electron-density at \( r \). It may be noticed that the form factor is essentially the Fourier transform of the electron-density. Hence, by performing the inverse Fourier transformation, the electron-density can be expressed in terms of the integral over the form factor. i.e.,

\[
\rho(r) = 2\pi^{-3} \int f(q, Z) \exp(iq \cdot r) d^3 q
\]

(2.49)

For a spherically symmetric atom the angular integration in equation (2.48) can be performed resulting in (Debye 1930, and Pirenne 1946),

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

(2.50)
The variable $x$, which is proportional to the momentum transfer $q$, is often used in place of $q$ in recent tabulations (Hubbell et al 1975; Hubbell and Øverbø 1979) and is defined by

$$x = \frac{\sin(\theta/2)}{\lambda (\text{Å})}$$  \hspace{1cm} (2.51)

The momentum transfer variable $x$ may be converted from the $q$-argument in mc units by multiplying by the factor 20.60744. In terms of the $x$-argument, the form factors $f(x, Z)$ with the assumption that the atom is spherically symmetric is

$$f(x, Z) = 4\pi \int_0^\infty \rho(r) \frac{\sin(4\pi r)}{4\pi r} r^2 dr$$  \hspace{1cm} (2.52)

The form factor so defined may be understood either to describe coherent scattering from all the bound electrons, as characterized by a charge distribution $\rho(r)$, or the contribution to scattering due to a given sub-shell characterized by its charge distribution.

In the form factor approximation, the Rayleigh scattering amplitudes in the circular polarization description are given by

$$A_{RF}^{NSF} = \frac{r_0}{2} (1 + \cos\theta) f(q, Z)$$  \hspace{1cm} (2.53)

and

$$A_{RF}^{SF} = \frac{r_0}{2} (1 - \cos\theta) f(q, Z)$$  \hspace{1cm} (2.54)

Where $r_0 = e^2 / m c^2$ is the classical electron-radius. Hence, the differential cross section for the Rayleigh scattering of unpolarized photons through an angle $\theta$ and averaged over final polarizations may be written a

$$\frac{d\sigma_R}{d\Omega} = \frac{r_0^2}{2} (1 - \cos^2\theta) |f(q, Z)|^2$$

$$\frac{d\sigma_R}{d\Omega} = \frac{d\sigma_0}{d\Omega} |f(q, Z)|^2$$  \hspace{1cm} (2.55)

Thus, the differential Rayleigh scattering cross section in the form factor approximation can be expressed as the product of two factors. The first factor is the
expression for the Thomson scattering cross section \( \frac{d\sigma}{d\Omega} \) which concerns the probability that the photon is deflected by a certain angle and transfer to the electron a corresponding amount of momentum as though the electron were free. The second factor is the square of the atomic form factor, which takes into account the electron-charge distribution and expresses the probability that the Z electrons of an atom take up a recoil momentum without absorbing any energy.

(i) Calculation of form factor

To calculate the form factor, the ground state wave function \( \psi_0(\eta \ldots n_z) \) for the atom must be known. hydrogen is the only atom for which it is known exactly. If the Coulomb wave function describing the ground state of hydrogen is inserted into equation (2.50), the integration can be performed analytically, resulting in (Pirenne 1946),

\[
f(x, Z = 1) = \left[ 1 + \left( \frac{a_0 q}{2} \right)^2 \right]^2
\]

in which \( a_0 = \hbar^2 / me^2 = 0.529177 \, \text{Å} \) is the first Bohr radius.

From equation (2.52), we get

\[
f(x, 1) = \left[ 1 + 4\pi^2 a_0^2 x^2 \right]^{-2}
\]

For all other atoms, we have to take recourse to different approximate models of charge distribution within the atom, such as Thomas-Fermi, Hartree-Fock, and others to determine the atomic form factor (Thomas 1927; Fermi 1928; Hartree 1928; Fock 1930, 1934; Slater 1951). Grodstein (1957) has discussed several of these approximate models in detail of these various models, only the Thomas-Fermi and Hartree-Fock-Slater models are important from the standpoint of applicability and accuracy.

(ii) Thomas-Fermi statistical model

The distribution proposed by Thomas (1927) and Fermi (1928) considers the electrons as a gas surrounding the nucleus, with a charge density which is a function only of the distance from the nucleus. The average charge density \( \rho(r) \) is a radial function of the potential \( V(r) \) given by
\( \rho(r) = \frac{8\pi e}{3h^3} [2meV(r)]^{\frac{3}{2}} \)  

(2.58)

which in turn can be substituted in the Poisson's equation

\[
\nabla^2 V(r) = 4\pi \rho(r)
\]

to get,

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dV(r)}{dr} \right) = \frac{32\pi^2 e}{3h^3} [2meV(r)]^{\frac{3}{2}}
\]

(2.59)

The above equation is to be solved for \( V(r) \) under the condition that \( \lim_{r \to \infty} V(r) = 0 \) and that \( \lim_{r \to 0} V(r) = Ze \). Thomas (1927) solved this equation numerically for the case of Cesium (\( Z=55 \)) and obtained \( V(r) \). The average charge density \( \rho(r) \) is in turn obtained by using equation (2.58) and thence \( f(X,Z) \) by using equation (2.31), again with assumed spherical symmetry. The Thomas-Fermi charge distributions for different atoms are related to each other such that once \( f(X',Z) \) has been calculated for a "standard" atom \( Z_0 \) (e.g. Cs, \( Z_0=55 \)), \( f(X, Z) \) for any other atom \( Z \) is given by

\[
f(x, Z) = \frac{Z}{Z_0} f(x', Z_0)
\]

where \( x \) is the desired argument and if \( x \) is the tabulated argument for \( Z_0 \) then

\[
x' = x(Z / Z_0)^{\frac{1}{4}}
\]

(2.60)

Also, exchange effects have been incorporated into the Thomas-Fermi model by Dirac(1930), taking into account the fact that electrons are identical particles which must be described by a totally anti symmetric wave function.

(iii) Hartree-Fock model

The most accurate computations of wave functions of many-electron atoms are based on the self-consistent field (SCF) method of Hartree (1928). This is an independent particle model in which each electron is assumed to be in the field of the nucleus and in an average field due to the other electrons. Thus, the charge distribution \( \rho(r) \) can be written
\[ \rho(r) = \sum_{j=1}^{Z} \rho_j(r) = \sum_{j=1}^{Z} \psi_j^*(r) \psi_j(r) \]  

(2.61)

where \( \rho_j(r) \) is the charge density distribution of the \( j \)th electron and \( \psi_j(r) \) is its wave function. The Hartree scheme has been generalized by Fock (1930, 1934) to include the effects of exchange, and Slater (1951) has shown that the Hartree and Hartree-Fock wave functions arise out of variational treatments in which the wave functions of the many electron atom is assumed to be a product of individual electron wave functions. Recently, Hubbell et al (1975) and Hubbell and Øverbø (1979) have published respectively the tables of non-relativistic and relativistic atomic form factors for all elements \( Z=1 \) to 100 over wide range of momentum transfer values \( (X=0.01-10^9 \text{Å}^{-1}) \).

2.5(b) Qualitative features predicted by form factor approximation

Although form factor predictions are often wrong in quantitative detail, their qualitative features give considerable insight into the behaviour of the Rayleigh amplitudes (Kissel et al 1980). The behaviour of the total atom Form-factor \( f(q) = \sum f_i(q) \) can be better understood by considering the behaviour of its components \( f_i(q) \) contributed by each particular electron, sub-shell or shell, as a function of momentum transfer. For zero momentum transfer, the integral for a sub-shell form factor reduces to an integral over the corresponding sub-shell charge density and is equal to the number of electrons in that sub-shell. As the momentum transfer increases, the value of \( f_i(q) \) remains approximately constant until the typical momentum \( q_{typ} \) of electrons in that sub-shell is reached. This \( q_{typ} \), for inner shells such as K-shell, is inversely proportional to the radius of that shell. Beyond this, \( q_{typ} \), the magnitude of the form factor becomes small. For nodeless sub-shell (such as the K-shell), the value of the form factor for \( q > q_{typ} \) decreases monotonically. For sub-shells with nodes (such as the L\(_1\) sub-shell), there is a region of more rapid variation or oscillation for \( q > q_{typ} \) before reaching the asymptotic region, where \( f_i(q) \) decreases monotonically. For large \( q \), \( f_i(q) \) decreases rapidly with \( q \) (but most slowly for \( l=0 \)) and is larger for heavy atoms. Thus, for small momentum transfers, each sub-shell contributes to the total-atom form factor proportional to the number of electrons in that sub-shell. As the momentum transfer increases, the contributions to the total
atom form factor becomes more and more of the outer electrons it becomes small. This process continues until the K-shell’s typical momentum (Zα) is exceeded. Beyond this point contributions to the total atom form factor due to all sub-shells are monotonically decreasing. In this asymptotic region the S states (l=0) dominate, with the shells yielding the largest contribution. Therefore, for a heavy element such as lead, the form factor approximation predicts that the K-shell dominates at large momentum transfer, with the next largest contribution coming from the L₁ sub-shell and so on.

The differential Rayleigh scattering cross sections are obtained from the atomic form factors using equation (2.55). The range of momentum transfers possible for a fixed photon energy ω are 0 ≤ q ≤ 2 ω. Thus, for low photon energies, the form factor predicts little variation in the differential scattering cross sections. For high photon energies, the form factor is equal to the number of electrons in the forward direction but becomes very small at the backward angles, giving a highly forward peaked angular distribution. For small q, the cross section varies as Z², while for large “q” it will vary as Z⁶.

The form factor approximation also predicts the importance of screening of the nuclear charge by the atomic electrons. For small q, the form factor reduces to the number of electrons, which is independent of the potential used and suggests that screening effects are small. For large q, small radial distances are most important. For small radial distances, screening corrections to the Coulomb wave functions appear only in their normalization (Pratt and Tseng 1972). Thus, the form factor approximation predicts that, for large q, screening effects in the matrix elements can be expressed as the squared ratio of screened to unscreened bound state wave function normalizations.

(i) Limitations of form factor approximation

The range of validity of the form factor approximation for the description of the elastic photon scattering by bound electrons is limited (Kissel et al 1980). The effects of binding, although crucial in the low energy scattering of photons, are neglected by the form factor approximation. At high energies one might expect that binding effects would become less important and that scattering would approach that
for free electrons. In fact, corrections of the order of $(Z\alpha)^2$ remain at all energies and angles, because of the use of zero-order Born approximation for intermediate states. For a given atomic electrons, the form factor approximation is not valid for larger angles (high momentum transfers) or lower energies (compared with electron binding energy). With decreasing energy, the approximation first fails for inner electrons (or larger binding energies) which, however, give a dominant contribution at large momentum transfers (larger angles at higher energies). In addition, corrections due to relativity have been neglected, again implying deviations of the form factor for the inner shells of heavy atoms or for high photon energies.

(ii) Modified form factor

Within the relativistic framework, an electron binding correction to the form factor approximation was originally suggested by Franz (1935, 1936) and the resulting approximation later developed is known as the modified form factor (MFF) approximation. Brown and Mayers (1957) compared this modified form factor with their numerical scattering amplitudes and found that it gave improved results. The modified form factor is defined by

$$g(q,Z) = \sum_{j=1}^{Z} g_j(q,Z)$$

$$= \sum_{j=1}^{Z} \rho(r_j) \exp(iq r_j) \frac{1}{1 - \varepsilon_j - V(r_j)} d^3 r_j$$

(2.62)

Where $\varepsilon_j$ is the binding energy of the $j$th electron and $V(r_j)$ is the electrostatic potential at $r_j$, both in units of $mc^2$. For the spherically symmetric charge distribution, $g(q,Z)$ is

$$g(q,Z) = \sum_{j=1}^{Z} 4\pi \int_0^\infty \rho(r) \frac{\sin qr}{qr} \frac{1}{1 - \varepsilon_j - V(r)} r^2 dr$$

(2.63)

The additional denominator factor has its origin in the Green's function propagator of the intermediate states and represents a binding correction. In the modified form factor approximation, the differential cross section for the Rayleigh scattering of unpolarized photons is obtained by replacing $f(q,Z)$ by $g(q,Z)$ in equation (2.55).
A general investigation of the validity of the modified form factor has been carried out by Kissel et al (1978, 1980, 1983) and has resulted in the conclusion that the modified form factor is superior to the form factor in a wide range of momentum transfers. For the K-shell of light atoms, the modified form factor continues to provide good predictions for momentum transfers up to 0.5 mc (10 Å^−1). Errors in the K-shell amplitudes of light Z atoms predicted by the modified form factor are at the 10% level by about 5\(\varepsilon_K\), the 5% level by about 10\(\varepsilon_K\), and 1% level by about 25\(\varepsilon_K\). For the K-shell of medium and heavy atoms, the predictions of the modified form factor at finite energies is a major improvement over the ordinary form factor, and this improved agreement also extends to the higher momentum transfer of 0.5 mc. Errors in the K-shell amplitudes of heavy Z elements predicted by the modified form factor are at the 10% level by about 3\(\varepsilon_K\) the 5% level by about 5\(\varepsilon_K\) and the 1% level by about 10\(\varepsilon_K\). Improved agreement over the form factor is also found in the predictions of the modified form factor for higher shells for \(\omega \geq \varepsilon_K\). Thus, accurate total-atom differential scattering amplitudes may be calculated using the modified form factor approximation for all shells of all atoms for forward angles and photon energies greater than K-shell binding.

Hubbell et al (1975) reported the coherent and incoherent scattering cross section of elements, obtained using Non-relativistic Hartree-Fock wave functions. Also, using relativistic Hartree-Fock wave functions of Hubbell and Øverbø (1979) have tabulated coherent as well as incoherent scattering cross section of elements from Z=1 to 100. The modified form factor data are tabulated in Schaupp et al (1988). The compiled data of Hubbell et al (1975) interpolated to the energies of interest have been used in the present study.

2.6 Theories concerning the anomalous scattering of photons by isolated atoms

Electrons occupy definite energy levels within the atom and are characterised by natural angular frequency. When a photon interacts with an electron of the atom, natural amplitude of the electron is modified by a dispersive term (a real number) dependent on the proximity of the impressed frequency to the natural resonant frequency of the system and a absorptive term (an imaginary number) dependent on the damping factor for the resonant system. This results in the anomalous scattering of
photons. There are different models/theories to explain anomalous scattering of photons by isolated atoms.

2.6(a) Classical model

The concept of an atomic scattering factor has its origin in the classical electromagnetic theory. This aspect has been discussed thoroughly in a number of texts James (1962) and the review articles by Gavrila (1981) and Kissel and Pratt (1983).

Consider the scattering of an unpolarized electromagnetic wave by a free electron. For a free electron situated at the origin the fraction of the intensity of the wave scattered through an angle $\phi$ is (Creagh and McAuley (1992)),

$$\frac{I}{I_0} = \left(\frac{r_0}{r}\right)^2 \frac{1}{2} \left(1 + \cos^2 \phi \right)$$

(2.64)

where " $r_0$" is the classical radius of the electron and " $r$" is the distance measured along the scattering direction at which the intensity is measured. Implicit in the derivation of this equation is the assumption that the wavelength of the scattered radiation has been unmodified in the scattering process: elastic or Rayleigh scattering has occurred.

To consider the scattering of electromagnetic waves by the electrons bound to an atom one must assume that each electron scatters as an individual electron and the atomic scattering is the sum of each of these individual contributions. Because the electrons are not localized in space but are in rapid motion about the nucleus the atomic scattering factor can be written in terms of the electron density $\rho$ which exists at a distance 'r' from the nucleus. Also, because the size of the atom is comparable with the wavelength of the incident electromagnetic wave, an electron within the atom will scatter as though its scattering factor is

$$f = \int \left\{ \exp\left(\frac{2mi}{\lambda}(\vec{k}_f - \vec{k}_i).r \right) \right\} \rho dV$$

(2.65)

Here $\vec{k}_f - \vec{k}_i$ is the change in direction of the wave vector of the electromagnetic wave.

The scattering factor $f$ is the Fourier transform of the electronic charge distribution ' $\rho$' and is alternatively referred to as the atomic scattering factor. If the
atom is assumed to have a charge distribution with spherical symmetry equation (2.65) can be simplified, and

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

(2.66)

where \( \rho = \rho(r) \), \( q = 4\pi \frac{\sin \theta}{\lambda} \) and \( \theta = \frac{\phi}{2} \). The assumption of spherical symmetry for electron charge distribution is not unreasonable since the orbital involved directly in the scattering processes are often closed shells and therefore have spherical symmetry. For an atom containing several electrons the atomic scattering factor becomes

\[ f = \sum_n \int_0^\infty 4\pi r^2 \rho_n(r) \frac{\sin qr}{qr} dr \]  

(2.67)

For forward scattering \((\theta=0)\) the value of \( \sin(qr)/qr \) becomes unity and the scattering factor \( f \) becomes equal to \( Z \), the total number of electrons in the atom. Hence, we have

\[ Z = \sum_n \int_0^\infty 4\pi r^2 \rho_n(r) dr \]  

(2.68)

In general the radial distribution of electron density \( \rho(r) \) must be known before \( f \) can be determined.

In the model most frequently used to explain the scattering of electromagnetic radiation by an electron bound to an atom is scattering by a classical dipole oscillator.

The classical theory of dispersion supposes the atoms to scatter as if they contained electric dipole oscillators having certain definite natural frequencies, which are identified with the absorption frequencies of the atoms. Such oscillators may be considered as produced by the simple harmonic vibration of \(+e\) and \(-e\) charges with a relative displacement \( x \) at time \( t \). For definiteness, suppose the oscillator to consist of an electron of mass \( m \) vibrating about a massive positive charge, which we may consider to be at rest. Actually, the electrons are bound to the nucleus by forces that vary with the atomic field strength and the quantum state of the electron. When the external frequency approaches in magnitude the natural frequencies in the atom, we can not treat the electrons in an atom are free as considered by Thomson. The classical differential equation describing the motion of an electron of mass \( m \) and charge \( e \) under the action of an external field of intensity \( E = E_0 e^{iat} \) is given by

\[ \frac{d^2 x}{dt^2} + K \frac{dx}{dt} + \omega_n^2 x = \frac{e}{m} E_0 e^{iat} \]  

(2.69)
where $\omega_n$ is the natural angular frequency of the dipole if the charge is displaced and allowed to oscillate without either applied field or damping. The action of the magnetic field of the incident wave on the motion of the dipole which is small, has been neglected. $K(dx/dt)$ expresses a damping term resulting from the emission of radiation by a vibrating electron according to classical mechanics. 2.69 is nothing but a harmonic oscillator equation, whose solution has the form

$$\chi(t) = \frac{(e/m)}{\omega_n^2 - \omega^2 + iK\omega} E_0 e^{i\omega t}$$

(2.70)

The axis of the resultant dipole oscillator is parallel to the direction of the incident electric vector $E$. The oscillating dipole is the source of an electromagnetic wave of the same frequency. The amplitude $A$ of the scattered wave at unit distances in the equatorial plane of the dipole is

$$A = \frac{e^2}{mc^2} \frac{\omega^2 E_0}{\omega_n^2 - \omega^2 + iK\omega}$$

(2.71)

Suppose a free electron had occupied the same point in space and had been acted upon by the same incident electric field. Since $K=0$ and $\omega_n=0$ for a free electron, the scattered amplitude for this electron at the same point is given by

$$A' = \frac{e^2}{mc^2} \left(\frac{\omega^2 E_0}{-\omega^2}\right)$$

(2.72)

Now we can define a scattering factor for an electron as

$$f = \frac{\text{Amplitude scattered by the oscillator (atom)}}{\text{Amplitude scattered by a free classical electron under the same condition}}$$

$$f = \frac{A}{A'} = \frac{\omega^2}{\omega^2 - \omega_n^2 - iK\omega}$$

(2.73)

The negative sign means that the wave scattered by the free electron in the forward direction has a phase opposite to that of the primary wave.

If $\omega >> \omega_n$, $f$ is positive and the scattered wave is opposite in phase with the incident wave. If $\omega << \omega_n$, $f$ is negative and the dipole then scatters a wave in phase with the primary wave. When $\omega \approx \omega_n$, the scattering factor becomes complex, which means that both the amplitude and the phase of the scattered radiation depend on the incident frequency. Therefore one can express

$$f = f_1 + if_2$$
where $f_i$ is called dispersive term and $f_2$ is called absorptive term. Imaginary part can be neglected except $\omega = \omega_n$. It turns out that, physically the imaginary term corresponds to the ejection of an inner electron, so that it is equal to zero for energies too small to knock out a bound electron.

If the probability that the electron is to be found in the $n^{th}$ orbit is $g_n$, considering damping is small, the real part of the atomic scattering factor may be written as

$$f_i = \sum_n g_n - \sum_n \frac{g_n}{\omega_n^2 - \omega^2}$$  \hspace{1cm} (2.74)

The probability $g_n$ is referred to as the oscillator strength corresponding to the virtual oscillator having natural frequency $\omega_n$. Equation (2.74) can be written as

$$f_i = f_0 + f'$$  \hspace{1cm} (2.75)

where $f_0$, called form factor, represents the sum of all the elements of the set of oscillator strengths and is unity for a single-electron atom. Because a large, effectively infinite number of oscillator states exist in an atom it is possible to rewrite the second term for an incident wave of frequency $\omega_i$ as

$$f' = \int_{\omega_i}^{\omega_c} \frac{\omega^2 (dg / d\omega)}{\omega^2 - \omega_i^2} d\omega$$  \hspace{1cm} (2.76)

if the atom is assumed to have an infinite number of energy states. For an atom containing $k$ electrons it is assumed that the overall of $f_i$ is the coherent sum of the contribution of each individual electron, so that we can write,

$$f' = \sum_k \int_{\omega_i}^{\omega_c} \frac{\omega^2 (dg / d\omega)_k}{\omega^2 - \omega_i^2} d\omega$$  \hspace{1cm} (2.77)

and the oscillator strength of the $k^{th}$ electron

$$g_k = \int_{\omega_i}^{\omega_c} \frac{dg}{d\omega}_k d\omega$$  \hspace{1cm} (2.78)

is not unity but the total oscillator strength for the atom must be equal to the total number of electrons in the atom. This is nothing but Thomas-Reiche-Kuhn sum-rule result.

The imaginary part of the dispersion correction $f'$ is associated with the damping of the incident wave by the bound electrons. It is therefore functionally related to the linear absorption coefficient "$\mu$" which can be determined from experimental measurement of the decrease in intensity of the photon beam as it passes
through a medium containing the atoms under investigation. It can be shown that the attenuation coefficient per atom \( \mu_a \) is related to the density of the oscillator states by

\[
\mu_a = \frac{\pi^2}{2\varepsilon_0 mc} \left( \frac{dg}{d\omega} \right)
\]  

whence

\[
f^* = \frac{\pi}{2} \omega \left( \frac{dg}{d\omega} \right)_{k_i}
\]  

(2.80)

dispersion corrections can now be written

\[
f' = \frac{2}{\pi} \sum_k P \int \frac{\omega f^*(\omega)}{\omega_i^2 - \omega^2} d\omega
\]

(2.81)

This is referred to as the Kramers-Kronig transform. Equation (2.77), (2.80) and (2.81) are the fundamental equations of the classical theory of photon scattering and it is to these equations that the predictions of other theories are compared.

2.6 (b) Non-relativistic quantum mechanical model

The non-relativistic quantum mechanical theories are based on the assumption that the photon interacts with a spherical free atom and in elastic scattering only those interactions for which the internal energy of the atom remains invariant will be considered. It will also be assumed that the photon energy will be in the X-ray range so that only the electrons interact with photons. The nuclear Thomson, nuclear resonance scattering and Delbrück scattering processes are neglected.

In the elastic scattering processes we have \( \mathbf{k}_f = \mathbf{k}_i \), where, \( \mathbf{k}_i \) and \( \mathbf{k}_f \), are the wave vectors of the incident and the scattered photons respectively. The scattering vector \( \Delta = \mathbf{k}_f - \mathbf{k}_i \) and the scattering angle is denoted by \( \phi \). If it can be assumed that the atom has a rotationally symmetric electron cloud the Rayleigh scattering matrix element can be written as

\[
M = M_1(e_i \cdot e_f') + M_2(e_i \cdot \mathbf{K}_f)(e_f' \cdot \mathbf{K}_i)
\]

(2.82)

where \( k_i \) and \( k_f \) are unit vectors in the directions of the wave vectors \( k_i \) and \( k_f \) respectively, and \( e_i \) and \( e_f \) represent the polarization of the photon. The amplitudes \( M_1 \) and \( M_2 \) depend now on \( \omega \) and \( \Delta \). This matrix element depends on the state of polarization of the photons. The matrix element \( M_1 \) corresponds to a linear polarization state for which \( e_i \) and \( e_f \) lie perpendicular to the scattering plane and \( M_2 \) represents scattering for polarization states lying in the plane of scattering. When
average is taken over all polarization states, the differential cross section takes the form

$$\frac{d\sigma}{d\Omega} = \frac{1}{2} r_0^2 \left( |M_1|^2 + |M_2|^2 \right)$$  \hspace{1cm} (2.83)

The perturbed Hamiltonian for an atom containing one electron coupled to a radiation field having vector potential $A$ is given by

$$\hat{H} = \hat{H}_0 - \frac{e}{mc} A \cdot p + \frac{e^2}{2mc^2} A^2$$  \hspace{1cm} (2.84)

where $\hat{H}_0$ is the Hamiltonian for the unperturbed atom and $p = i\hbar \nabla$

Applying second order perturbation theory one can obtain the matrix element for Rayleigh scattering of photons by an atom whose initial state is designated by $1$. Following Akhiezer and Berestetskii (1957) one can write for the matrix element

$$M = (e_1 \cdot e_2') f_0(\Delta)$$

$$+ \frac{1}{m} \langle 1 | e_2' p \exp(-ik_2 \cdot r) \frac{1}{\Omega_1 - \hat{H}_0} e_1 p \exp(ik_1 \cdot r) | 1 \rangle$$

$$+ \frac{1}{m} \langle 1 | e_1 p \exp(ik_1 \cdot r) \frac{1}{\Omega_2 - \hat{H}_0} e_2' p \exp(-ik_2 \cdot r) | 1 \rangle$$  \hspace{1cm} (2.85)

where $e_1$ and $e_2'$ are the initial and final polarization of the photon $\Delta = \vec{k}_f - \vec{k}_i$; $\hat{H}_0 | 1 \rangle = E_1$ and $\Omega - \hat{H}_0$ is Green’s operator associated to the Hamiltonian $\hat{H}_0$. Further we have

$$\Omega_1 = E_1 + \hbar \omega + i\xi \quad \text{and} \quad \Omega_2 = E_2 - \hbar \omega - i\xi$$

where $\xi$ is an infinitesimal positive quantity. The first term in (2.85) corresponds to the atomic form factor and for spherically symmetric states, has the form

$$f_0(\Delta) = \int_0^\infty \rho(r) \frac{\sin \Delta r}{\Delta r} r^2 dr$$  \hspace{1cm} (2.86)

For photon energies close to the resonance energy of an orbital the matrix element has a resonant behaviour due to the second and third terms of equation (2.85). These comprise the dispersion corrections. Note that the derivation of (2.85) does not contain any contribution to the scattering from radiation damping. This can be extended to an atom containing $Z$ electrons. For the scattering of a photon with respect to change in momentum, it is proper to write the atomic scattering factor as

$$f(\omega, \Delta) = f_0(\Delta) + f'(\omega, \Delta) + if'^*(\omega, \Delta)$$  \hspace{1cm} (2.87)
where \( f_0(\Delta) \) is the atomic form factor and \( f'(\omega, \Delta) \) and \( f''(\omega, \Delta) \) are respectively the real and the imaginary parts of the dispersion corrections. In the dipole approximation [Goldberger and Watson (1965)], for forward scattering

\[
f'(\omega, 0) = \frac{2}{\pi} \omega \int_0^{\omega} \frac{f''(\omega)}{\omega^2 - \omega_i^2} d\omega
\]

(2.88)

From Optical theorem it follows that

\[
f''(\omega, 0) = \frac{\omega}{4\pi e'} \sigma_{\text{tot}}(\omega)
\]

(2.89)

Hydrogen-like wave functions were assumed for the electrons comprising the atom and appropriate shielding constants were introduced to account for inner-electron interactions. The technique was applied initially by Hönl (1933a, 1933b) to K-shell electrons and was later extended to the case of L-shell electrons by Wagenfeld's (1975) use of the Bethe and Salpeter (1957) expression for the atomic photoeffect cross section and his use of hydrogen-like eigen functions enabled a description of the scattering of a photon incident in the +x direction, polarization in the y-direction, by

\[
\frac{2}{\pi} \omega \int_0^{\omega} \frac{f''(\omega)}{\omega^2 - \omega_i^2} d\omega
\]

(2.90)

The bra-ket notation is used to represent the matrix element for the transition of an electron from a hydrogen-like eigen state characterized by \( \rho \), for which the quantum numbers are \( n, l, m \) to an unbound state \( \rho' \) characterized by the quantum numbers of the ejected free electron. Each shell contributes to the total cross section. The retardation factor within the matrix elements was expanded as a power series:

\[
\exp(ikr) = 1 + ikr - \frac{1}{2}(kr)^2 + \ldots
\]

The first term in this equation corresponds to the dipole approximation (the forced vibration of the electron was assumed to give rise to an electric dipole radiation field). The second and third terms correspond respectively to the electric quadruple and mixed quadruple and mixed electric-dipole-octupole transitions. As Wagenfeld (1966) has shown these terms form part of a rapidly converging series for which analytic expressions can be obtained. From these values of the cross section the imaginary part \( f''(\omega, 0) \) and the real part \( f'(\omega, 0) \) can be calculated. The attractive feature of this technique is that the wave functions have an analytical form. Other
techniques, using self-consistent fields, require numerical solutions. These are also able to predict values of $f' (\omega, \Delta)$ and $f^* (\omega, \Delta)$, scattering in other than the forward direction can be considered.

There are inadequacies in this approach, the most serious being the assumption that each electron acts as though it is part of a hydrogen-like atom. The sole concession to electron-electron interaction is the inclusion of Grodstein's (1957) screening constant.

2.6 (c) Relativistic quantum mechanical model:

**Cromer and Liberman's relativistic dipole approach**

According to relativistic quantum theory, the scattering amplitude for photons by bound electrons is given by [Cromer and Liberman (1970)]

$$S_{1\rightarrow 2} = -2\pi i \delta (\varepsilon_1 + \hbar \omega_1 - \varepsilon_2 - \hbar \omega_2) \frac{2m^2 c^2}{(\omega_1 \omega_2)^{1/2}} f$$

where

$$f = mc^2 \sum_{s} \left( \frac{\langle 2| \varepsilon_2 \cdot \hat{\alpha} \exp(-ik_2 \cdot r)|n^+ \rangle \langle n^+ | \varepsilon_1 \cdot \hat{\alpha} \exp(ik_1 \cdot r)|1 \rangle}{(\varepsilon_1 - \varepsilon_{s^+} - \hbar \omega_2)} + \frac{\langle 2| \varepsilon_1 \cdot \hat{\alpha} \exp(ik_1 \cdot r)|n^+ \rangle \langle n^+ | \varepsilon_2 \cdot \hat{\alpha} \exp(-ik_2 \cdot r)|1 \rangle}{(\varepsilon_1 - \varepsilon_{s^+} - \hbar \omega_2)} \right)$$

$$+ mc^2 \sum_{s^*} \left( \frac{\langle 2| \varepsilon_2 \cdot \hat{\alpha} \exp(-ik_2 \cdot r)|n^- \rangle \langle n^- | \varepsilon_1 \cdot \hat{\alpha} \exp(ik_1 \cdot r)|1 \rangle}{(\varepsilon_1 + \varepsilon_{s^-} + \hbar \omega_2)} + \frac{\langle 2| \varepsilon_1 \cdot \hat{\alpha} \exp(ik_1 \cdot r)|n^- \rangle \langle n^- | \varepsilon_2 \cdot \hat{\alpha} \exp(-ik_2 \cdot r)|1 \rangle}{(\varepsilon_1 + \varepsilon_{s^-} + \hbar \omega_2)} \right)$$

$$= \frac{mc^2 \langle 2| \varepsilon_2 \cdot \hat{\alpha} \cdot \hat{\alpha} + \varepsilon_1 \cdot \hat{\alpha} \cdot \hat{\alpha} \rangle \exp \{i(k_2 - k_1) \cdot r \}|1 \rangle}{2mc^2}$$

$$f_0 = \varepsilon_1 \cdot \varepsilon_2 \langle 2| \exp(i\Delta \cdot r)|1 \rangle$$

which is identical in form to the non-relativistic equation (2.86) for the atomic form factor. The relativistic atomic scattering factor $f$ may then be written as

$$f = f_0 + (f - f_0)$$

1 and 2 represents the initial and final states of the system, $n^+$ and $n^-$ represents the intermediate energy states of positive and negative energy respectively. The Dirac velocity operator $c\hat{\alpha}$ operates on the retardation factors within the bra-ket. The summations are over all states of positive and negative energy not already occupied by electrons.

We can define an atomic scattering factor $f_0$ similar to $f$ in equation (2.92), except that all the energy denominators are written as $2mc^2$ and the sums $n^+$ and $n^-$ occur for all states without exception, then

$$f_0 = \frac{mc^2 \langle 2| \varepsilon_2 \cdot \hat{\alpha} \cdot \hat{\alpha} + \varepsilon_1 \cdot \hat{\alpha} \cdot \hat{\alpha} \rangle \exp \{i(k_2 - k_1) \cdot r \}|1 \rangle}{2mc^2}$$

$$f_0 = \varepsilon_1 \cdot \varepsilon_2 \langle 2| \exp(i\Delta \cdot r)|1 \rangle$$

101
where \((f - f_0)\) is analogous to the anomalous scattering terms. There will be contributions to \((f - f_0)\) from both positive and negative energy states and it is convenient to write

\[
(f - f_0) = f^* - f_0^* + f^- - f_0^-
\]  

(2.96)

The term's \(f_0^*\) corresponds to transition similar to those in equation (2.94) but involving only transitions from the initial state to unbound positive energy states.

Using the dipole approximation and averaging over polarization, Cromer and Liberman (1970) showed that

\[
f_0^* = \frac{2}{3} \frac{1}{mc^2} \langle |\frac{\hat{p}}{2m}|1\rangle
\]  

(2.97)

which, when summed over all the electrons, is equal to the total electronic kinetic energy \(E_{\text{tot}}\), which can be estimated using self-consistent field techniques. The two terms involving the negative energy states can also be evaluated in a similar fashion, using the dipole approximation, and the three final terms of (2.96) can be written as

\[
(-f_0^* + f^- - f_0^-) = \frac{5}{3} \left(\frac{E_{\text{tot}}}{mc^2}\right)
\]  

(2.98)

which is a constant for a particular atom.

The principal anomalous scattering factor \(f^*\) is given by

\[
f^* = mc^2 \sum_n |\langle n^+| e \cdot \hat{A} \exp(ik \cdot r)|1\rangle|^2 \left[ (\epsilon_n - \epsilon_n^+ + \hbar \omega)^{-1} + (\epsilon_n - \epsilon_n^+ - \hbar \omega)^{-1} \right]
\]  

(2.99)

contributions from both occupied and continuum states are included in \(f^*\). However, contribution due to unoccupied bound states is neglected because it is small compared with the value of \(f^*\). A similar assumption was made for the non-relativistic treatment of photon scattering. The assumption over the continuum energy states \(\epsilon^+\) may be considered adequately represented by an integration over the continuum energy states.

A singularity exists in the first term in the denominator of equation (2.99) when \(\epsilon^+\) equals \(\epsilon + \hbar \omega\). Using the Cauchy’s principal value theorem, \(f^*\) can be evaluated as

\[
f^* = mc^2 \left( \int \frac{2(\epsilon^+ - \epsilon^1)|\langle n^+| e \cdot \hat{A} \exp(ik \cdot r)|1\rangle|^2}{(\hbar \omega)^2 - (\epsilon^+ - \epsilon^1)^2} + i \pi \left| \langle n^+ + \hbar \omega | e \cdot \hat{A} \exp(ik \cdot r)|1\rangle \right|^2 \right)
\]  

(2.100)

\(f^*\) contains a real part which can be equal to \(f^*(\omega, 0)\) and an imaginary part which can be equal to \(f^\prime(\omega, 0)\).
Akhiezer and Berestetskii (1957) have shown that the photoelectric cross section at photon energy $\hbar \omega$ is given by

$$
\sigma(\hbar \omega) = \left( \frac{4 \pi^2 e^2 m}{c \omega} \right) mc^2 \left| \langle \epsilon_1 + \hbar \omega | e \cdot \alpha \exp(ik \cdot r) \rangle \right|^2
$$

whence, we have

$$
f^*(\omega, 0) = \frac{mc}{4 \pi \hbar c^2} \left( \hbar \omega \sigma(\hbar \omega) \right)
$$

Evidently a one-to-one correspondence exists between the classical, the non-relativistic and the relativistic formulae for the imaginary part of the dispersion correction at the level of approximation used, namely for forward scattering by isolated atoms and neglecting bound state contributions.

The real part of $f^*$ may be rewritten using the cross section $\sigma(\hbar \omega) = \sigma(\epsilon^+ - \epsilon^-)$:

$$
\text{Re} f^* = \left( \frac{mc}{2 \pi^2 \hbar c^2} \right) P \int_{m_c^2}^\infty \frac{(\epsilon^+ - \epsilon^-)^2 \sigma(\epsilon^+ - \epsilon^-)}{(\hbar \omega)^2 - (\epsilon^+ - \epsilon^-)^2} d\epsilon^+
$$

This is identical in form to equation (2.81). It is not, however, equal to the real part of the dispersion correction $f^*(\omega, 0)$, and in this respect the relativistic approach differs from the other two.

The term $-f_0^* + f^* - f_0^*$ must be included so that

$$
f^*(\omega, 0) = \text{Re} f^* + \frac{5 E_{\text{tot}}}{3 mc^2}
$$

In addition, the matrix element in the high energy limit for forward scattering without change in polarization is

$$
f^*(\infty, 0) = \frac{5 E_{\text{tot}}}{3mc^2} + \frac{mc}{2 \pi^2 \hbar c^2} \int_0^\infty \sigma(\epsilon^+ - \epsilon^-) d\epsilon^+
$$

Rewritten in terms of oscillator strengths equation (2.105) is the relativistic form of the Thomas-Reiche-Kuhn sum rule which in the non-relativistic case becomes $Z$, the total number of electrons in the atom. In the non-relativistic case the rule represents only the matrix element, which characterises the selection rules and thus the allowed transitions, for forward scattering at infinite energy. This implies that the quantum mechanical results are fundamentally different from the classical results. From quantum theory it follows that anomalous dispersion occurs in the neighbourhood of frequencies corresponding to allowed transitions, and not, as in classical theory, in the neighbourhood of the eigen frequencies of oscillator of the electrons. The quantum theory results also leads to negative dispersion—a phenomena
which has no classical analog. This can be attributed to the scattering of photons from excited atoms.

Stibius-Jensen (1979) pointed out that in addition to Cromer and Liberman's (1970) correction term $5/3(E_{tot}/mc^2)$, a magnetic correction term $(1/2)Z(\hbar\alpha/mc^2)$ must be added to get appropriate value of $f'(0, 0)$. Later Sasaki (1989), Smith (1987) and Creagh and McAuley (1992) have pointed out that when higher order multipolar terms are considered Jensen term becomes negligible.

Smith (1987) pointed out that Cromer and Liberman's (1970) non-retarded dipole correction term $5/3(E_{tot}/mc^2)$ overestimates the magnitude of relativistic effects in the deeper core states. Levinger et al (1957) have shown that, the high frequency or Thomson limit, the electric field scattered by an electron is proportional to the classical radius $r_0 = e^2/mc^2$ times $f'(\infty)$. To first order in $(v/c)^2$ the one can obtain an approximation

$$E_{scat} \approx e^2/(mc^2 + <0/T/0>)$$

Hence one can have

$$f'(\infty) = -<0/T/0>/mc^2 + \ldots$$

$$f'(\infty) \approx E_{tot}/mc^2$$

where $<0/T/0>$ is the total ground-state kinetic and $E_{tot}$ the total ground-state binding energy. The second form follows in a first approximation using the virial theorem in zeroth order. This result is obtained using the relativistic multipole approximation including retardation effects. Creagh and McAuley (1992) have listed the values of $E_{tot}/mc^2$ as a function of atomic number $Z$. When relativistic multipole correction term including retardation effects is added to the attenuation values there is an excellent agreement with the direct interferometric values for the real part of the anomalous scattering factor.

Kissel and Pratt (1990) have pointed out that the relativistic multipole approximation including retardation effects is very good for low $Z$-elements but the difference increases with $Z$, becoming 2% for $Z=20$, 6% for $Z=40$, 9% for $Z=60$, 13% for $Z=80$ and 15% for $Z=100$. They have illustrated numerical S-matrix calculations appear at forward angles approach the relativistic modified form factor at high energy. They have provided the $Z$-dependent energy-independent correction term which is to be added to Cromer and Liberman’s (1970) high-energy limit to get appropriate value for high-energy limit. Kissel and Pratt (1990) also provided more accurate high energy limit of the S-matrix anomalous scattering factor for neutral atoms as $f'(\infty) =$
\[ g(0) - Z, \] where \( Z \) is the atomic number and \( g(0) \) is the value of the relativistic modified form factor at zero momentum transfer as computed by Schaupp et al (1983). S-matrix calculation of high energy limit is very close to that obtained in the relativistic multipole approximation including retardation effects.

Both the Cromer and Liberman (1970) and Storm and Israel (1970) have used Brysk and Zerby's (1968) program designed to use relativistic Dirac-Slater wave functions to compute photoelectric cross sections. Cromer and Liberman differ from Storm and Israel is in the use of the Kohn and Sham (1965) rather than the Slater (1951) exchange potential of \( 0.667 \rho(r)^{1/3} \). In addition they used experimental rather than computed eigen values. Scofield (1973) on the other hand employed a relativistic Hartree-Fock approach. Comparisons by Kissel et al (1980) of the results of the several Dirac-Hartree-Fock-Slater calculations show that they predict cross sections in excellent agreement with one another despite their different origin and simplifying assumptions. Creagh and Hubbell (1987) suggested based on the experimental data that there exists no rational basis for preferring one data set to another.

However, it must be stressed that both \( f'(\omega, 0) \) and \( f^*(\omega, 0) \) have been calculated for the forward scattering case with no change in polarization. The extension to the more general case of a nonzero scattering vector \( \Delta \) is usually made using the assumption that the dispersion corrections have the same angular dependence as the form factor. However, Parker and Pratt (1982) have shown that \( f'(\omega, \Delta) \) and \( f^*(\omega, \Delta) \) are independent of angle. This conclusion must be compared with the predictions of Wagenfeld (1975) using the hydrogen-like model, which predicts a simple dependence on scattering angle. It must be further stressed that polarization changes in the scattering process have not been considered and that the state of polarization of the incident beam has a significant effect on the scattering cross section in the region of the absorption edge (Templeton and Templeton (1985)).

There is a direct correspondence between the predictions of the classical theory and the theory using second-order perturbation theory and non-relativistic quantum mechanics. The extension of Hönl's (1933a, b) study of the scattering of X-rays by the K-shell of atoms to other electrons shell has been presented by Wagenfeld (1975).

In these calculations the energy of the photon was assumed to be such that relativistic effects do not occur, nor do transitions within the discrete states of the
atom occur. Transitions to continuum states do occur and, using the analytical expressions for the wave functions of the hydrogen-like atom, analytical expressions may be developed for the photoelectric scattering cross sections. By expanding the retardation factor

\[ \exp(-ik.r) \]

as the power series \( 1 + ik.r - \frac{1}{2}(ik.r)^2 + \ldots \ldots \) it is possible to determine dipole, quadrupolar and higher order terms in the analytical expression for the photoelectric scattering cross section.

Kissel et al (1995) have discussed partition of the elastic scattering amplitude into Rayleigh and Delbrück scattering components. This partition of the optical theorem reveals contributions from bound-bound atomic transitions, bound pair annihilation and bound pair production that are not usually associated with elastic scattering. These terms are needed, in addition to the familiar terms for photoionization, to relate the real and imaginary parts of the scattering amplitude.

2.6 (d) The scattering matrix formalism

Kissel, Pratt and Roy (1980) have developed a computer programme based on the second-order S-matrix formalism suggested by Brown, Peierls and Woodward (1955). Their aim was to provide a prescription for the accurate (~1%) prediction of the total atom Rayleigh scattering amplitude.

The starting point is Furry's extension of the Feynman-Dyson formalism of quantum electrodynamics, in which the interaction of electrons and positrons with the atomic field is included in the unperturbed Hamiltonian, while the interaction with the radiation field is treated as a perturbation. Their model treats the elastic scattering as the sum of bound electron, nuclear and Delbrück scattering cross sections, and treats the Rayleigh scattering by considering second order single-electron transitions from electrons bound in a relativistic self-consistent central potential. This potential was a Dirac-Hartree-Fock-Slater potential and exchange was included by use of the Kohn and Sham (1965) exchange model. They have omitted radioactive corrections.

In principle the observable in an elastic scattering process are momentum \( (hk) \) and polarisation \( \varepsilon \). The complex polarization vectors \( \varepsilon \) satisfy the conditions:

\[
\varepsilon^* \cdot \varepsilon = 1; \quad \varepsilon \cdot k = 0
\]

In quantum mechanics elastic scattering is described in terms of differential scattering amplitude \( M \) which is related to the elastic cross section by equation (2.82).
If polarization is not an observable then the expression for the differential scattering cross section takes the form of equation (2.83). If polarization is taken into account, as may be the case when a polarizer is used on a beam scattered from a sample irradiated by the linearly polarized beam from a synchrotron-radiation source, the full equation, and not equation (2.84), must be used to compute the differential scattering cross section.

The principle of causality implies that the forward scattering amplitude \( A(\omega, 0) \) should be analytic in the upper half of the \( \omega \) plane and that the dispersion relation should hold,

\[
\text{Re} A(\omega, 0) = \frac{2\omega^2}{\pi} \int_0^\infty \frac{\text{Im} A(\omega', 0)}{\omega'(\omega^2 - \omega'^2)} \, d\omega'
\]  

(2.106)

with the consequence that

\[
\text{Re} A(\infty, 0) = -\frac{2\omega}{\pi} \int_0^\infty \frac{\text{Im} A(\omega', 0)}{\omega'} \, d\omega'
\]  

(2.107)

This may be rewritten as,

\[
A(\omega, 0) - A(\infty, 0) = f'(\omega, 0) + if''(\omega, 0)
\]  

(2.108)

with the value of \( f'(\omega, 0) \) defined by Kramers-Kronig transform. Using the conservation of probability we can write

\[
\text{Im} A(\omega, 0) = \frac{\omega}{4\pi^2} \frac{\sigma_{\text{tot}}}{c}
\]  

(2.109)

which is to be compared with equation (2.89).

The total Rayleigh amplitude may be written as

\[
A_n = \sum_p \left( \frac{\langle n|T_1^*|p\rangle \langle p|T_2|n\rangle}{(E_n - E_p + \hbar\omega)} + \frac{\langle n|T_1|p\rangle \langle p|T_2^*|n\rangle}{(E_n - E_p - \hbar\omega)} \right)
\]  

(2.110)

where \( T_1 = \hat{\alpha} \cdot \epsilon_i \cdot \exp(ik_i \cdot r) \) and \( T_2 = \hat{\alpha} \cdot \epsilon_j \cdot \exp(-ik_f \cdot r) \)

The \( |p\rangle \) are the complete set of bound and continuum states in the external field of the atomic potential. Singularities occur at all photon energies which correspond to transitions between bound \( |n\rangle \) and bound \( |p\rangle \) state. These singularities are removed if the finite widths of these states are considered and the energies \( E \) are replaced by \( \left( \frac{i\hbar\Gamma}{2} \right) \) where \( \Gamma \) is the total (radioactive plus non-radioactive) width of the state.

Gavrila, (1981). By using the formalism suggested by Brown et al (1955), it is possible to reduce the numerical problems to one-dimensional radial integrals and
differential equations. The required multipole expansions of \( T_i \) and the specification of the radial perturbed orbitals which are characterized by angular momentum quantum numbers have been discussed by Kissel (1977). Ultimately, all the angular dependence on the photon scattering angle is written in terms of the associated Legendre functions and all the energy dependence is in terms of multipole amplitudes. Solutions are not found for the inhomogeneous radial wave equations, and Kissel has expressed the solution as the linear sum of two solutions of the homogeneous equation, one of which was regular at the origin and the other regular at infinity.

Because excessive amounts of computer time are required to use these direct techniques for calculating the amplitudes from all the sub shells simpler methods are usually used for calculating outer-shell amplitudes. Kissel and Pratt (1985) used estimates for outer-shell amplitudes based on the predictions of the modified form-factor approach. A tabulation of the modified form-factors has been given by Schaupp et al (1983).

2.7 Anomalous scattering factors (ASF)

While the S-matrix method is, in many cases, accurate in predicting Rayleigh scattering for X-ray and higher photon energies, it is too expensive in terms of computer time for extensive systematic photon tabulation. On the other hand, the form factor or modified form factor approximations, though very simple and easy to compute, only work in limited situations and totally fail near and below the K-shell photoeffect threshold. A simple but more accurate method is needed. The use of anomalous scattering factors appear to provide such a method.

An important approach to the calculation of the amplitude \( A(\omega_0, \Theta) \) for elastic scattering, not requiring the assumption of independent particle approximation (IPA) but in practice restricted to the case of forward scattering, utilises the analytic nature of the forward scattering amplitude that follows from causality, leading to the dispersion relation

\[
\text{Re} \ A(\omega,0) = \frac{2\omega^2}{\pi} \int_0^\pi \frac{\text{Im} \ A(\omega',0)}{\omega' (\omega'^2 - \omega^2)} d\omega' \\
\text{Im} A(\omega,0) = \left( -\frac{2\omega}{\pi} \right) \int_0^\pi \frac{\text{Re} \ A(\omega',0)}{\omega'^2 - \omega^2} d\omega' \quad (2.111)
\]

\[
\text{Re} \ A(\omega,0) = \frac{2\omega^2}{\pi} \int_0^\pi \frac{\text{Im} A(\omega',0)}{\omega' (\omega'^2 - \omega^2)} d\omega' \\
\text{Im} A(\omega,0) = \left( -\frac{2\omega}{\pi} \right) \int_0^\pi \frac{\text{Re} A(\omega',0)}{(\omega'^2 - \omega^2)} d\omega' \quad (2.112)
\]
so that
\[ \text{Re} A(\infty,0) = (-\frac{2}{\pi}) \int_0^\infty \frac{\text{Im} A(\omega',0)}{\omega'} d\omega' \] (2.113)

\[ \text{Im} A(\infty,0) = 0 \] (2.114)

On the basis of partitioning of the many body particle scattering problem in Rayleigh and Delbrück amplitudes, we can write down dispersion relations separately for these two scattering amplitudes. In non-relativistic dipole approximation,
\[ \text{Re} A^R(\omega,0) = -N \] (2.113)

with \( N \) the number of bound electrons. This is precisely the Thomas-Reiche-Kuhn sum rule. There are, however, small relativistic corrections to \( \text{Re} A^R(\omega,0) \), now understood as the amplitude for scattering off the bound electrons partitioned from the amplitude for Delbrück scattering.

Another form of the dispersion relation may be written in terms of the real and imaginary parts \( f' \) and \( f'' \) of the anomalous amplitude with reference to the relativistic high-energy limit. The real quantities are defined by
\[ A^R(\omega,0) - A^R(\infty,0) = -r_0 (g' + ig'') \] (2.115)

These anomalous scattering factors are closely related to the anomalous scattering factor \( f' \) and \( f'' \) conventionally defined in reference to the non-relativistic high-energy limit, \(-N\), as
\[ g' = f'\{N + [\text{Re} A^R(\infty,0)]/r_0 \} \quad \text{and} \quad g'' = f'' \] (2.116)

The anomalous scattering factors satisfy
\[ g'(\omega) = \frac{2}{\pi} \int_0^\infty \frac{\omega' g''(\omega')}{(\omega'^2 - \omega^2)} d\omega' \] (2.117)
In the non-relativistic case, $g'$ reduces to the corresponding $f'$; the difference between $g'$ and $f'$ at all energies from non-relativistic predictions. One now utilises the Optical theorem (Nussenzveig, 1972)

$$\text{Im} A_t^K (\omega, 0) = -r_0 g^* (\omega) = -r_0 f^*(\omega) = \left(\frac{\omega}{4\pi c}\right)\gamma_{\text{TOT}}$$

(2.118)

which follows from the unitarity of the S-matrix, relating the total cross section for photon-atom scattering (elastic and inelastic, including absorption) to the imaginary forward elastic scattering amplitude.

To the lowest order in fine structure constant, the Optical theorem for Rayleigh scattering states that

$$\text{Im} A_t^K (\omega, 0) = \left(\frac{\omega}{4\pi c}\right)(\tau + \sigma^{BBT+} - \sigma^{BBT-} - \sigma^{BPA})$$

(2.119)

where $\tau$ is the Photoeffect cross section, $\sigma^{BBT+}$ is the cross section for a transition from the initial state to an excited bound state of the system, $\sigma^{BBT-}$ is the cross section for a transition from the initial state to a bound state of lowest energy and $\sigma^{BPA}$ is the cross section for bound- electron pair annihilation, wherein an initial hole in the negative-energy sea is filled by one of the initial bound electrons. A similar discussion applies to the Delbrück amplitude, in which, in addition to transitions from negative-energy electrons to the continuum (the ordinary pair production), one has to add cross sections for transitions to the filled and unfilled bound states (bound pair production).

To lowest order in $\epsilon^2$, the total photoabsorption cross section for bound electrons is obtained from equation (2.119), where the bound-bound contributions are computed as

$$\sigma^{BBT+} (\omega) = \left(\frac{2\pi^2 c r_0}{\omega}\right) \sum_{n,m} \omega_{nm} f_{nm} \delta (\omega - \omega_{nm})$$

(2.120)

and

$$\sigma^{BBT-} (\omega) = \left(\frac{2\pi^2 c r_0}{\omega}\right) \sum_{n,m<n} \omega_{nm} f_{nm} \delta (\omega - \omega_{nm})$$

(2.121)
where $f_{nm}$ is the oscillator strength for the transition of energy $h\omega_{nm}$ of an electron from occupied state $n$ to unoccupied state $m$. [The notation $m > n$ or $m < n$ indicates the sum over unoccupied states $m$ with energies less than or greater than the occupied state $n$. For ground-state atoms, the contribution from (2.121) is zero]. Although the total cross section at X-ray energies is dominated by absorption, primarily the atomic photoeffect, contributions from bound-bound transitions (Wang and Pratt (1983)) must be included if accurate results are to be obtained from the dispersion relation for low-energy scattering. Subject to these qualifications, it should be possible to use better calculations of absorption (i.e. beyond IPA) or experimental data, and thereby obtain better predictions for forward elastic scattering.

The Rayleigh scattering amplitude $A^R(\omega, \theta)$ in the forward direction can be expressed as

$$A^R(\omega,0) = (\epsilon_f \cdot \epsilon_s^*) M(\omega,0)$$  \hspace{1cm} (2.122)

which can be written in terms of the anomalous scattering factors as

$$M(\omega,0) = -r_0 [f(0) + f'(\omega) + if''(\omega)]$$  \hspace{1cm} (2.123)

or

$$M(\omega,0) = -r_0 [g(0) + g'(\omega) + ig''(\omega)]$$  \hspace{1cm} (2.124)

The real quantities $f'$, $f''$ and $g'$, $g''$ are called anomalous scattering factors. They give the deviation of the forward-scattering amplitude from the form factor and from the modified form factor, respectively.

Even though $\sigma^{BPA}$ is zero until the photon energy reaches nearly $2mc^2$ and does not affect the energy dependence of the anomalous scattering factors at lower energies, the subtraction is required in order to have the integrals of (2.111), (2.112) and (2.117) converge at high energies as was first noted by Brown. However, their interpretation of the cross section to be subtracted differs somewhat from that of Brown. Their Rayleigh scattering amplitude requires the subtraction of the bound-electron pair-annihilation cross section, related to, but not the same as, the bound-
electron pair production (BPP) cross section noted by Brown. In their partition of the optical theorem, the BPP cross section is identified with the Delbrück amplitude.

With equations (2.117) and (2.118), we can use experimental or theoretical information regarding photoionization, photo-annihilation/photo-excitation and bound-electron pair annihilation to obtain the Rayleigh scattering amplitude in the forward direction. As a consequence, the ASF formalism provides us with an approach for going beyond IPA (Zhou et al., 1992b). Zhou et al., (1992a) have also used these expressions to investigate the connection between Cooper minima and shape resonances in the anomalous scattering factors. Zhou et al., (1992c) also used these expressions to devise scattering factors from ions using neutral atom photoeffect data.

2.8 Inter comparison of theories

A discussion of the validity of the non-relativistic dipole approximation for the calculation of forward Rayleigh scattering amplitudes has been given by Roy and Pratt (1982). They compared their relativistic multipole calculation with the relativistic dipole approximation for two elements, silver and lead. They concluded that a relativistic correction to the form factor of order \((Z\alpha)^2\) persists in the high-energy limit and that this constant correction accounts for much of the deviation from the non-relativistic dipole approximation at all energies above threshold. In addition, their results illustrate that cancelling occurs amongst the relativistic, retardation and higher multipole contributions to the scattering amplitude. This implies that care must be taken in assessing where to terminate the series which describes the multipolarity of the scattering process.

Kissel and Pratt (1983) discussed the elastic photon scattering for small momentum transfer and the validity of the form-factor theories. In this paper, which compares the relativistic modified form factor with experimental results for lead and a relativistic form factor and the tabulation by Hubbell et al (1975), it is shown that the modified relativistic form-factor approach gives better agreement with experiment for high momentum transfer (< 104 Å) than the non-relativistic form-factor theories.

Kissel et al (1980) used the S-matrix technique to calculate the real part of the forward scattering amplitude \(f'(\omega, 0)\) for the inert gases at the wavelength of MoK. These values are compared with the predictions of the relativistic dipole theory and
the relativistic multipole theory. In most cases the agreement between the S-matrix and the relativistic multipole theory including retardation effects is excellent, considering the differences in the methodology of the two sets of calculations. Although reasonably satisfactory agreement exists between the relativistic values large differences exist between the non-relativistic value (Wagenfeld 1975) and the relativistic values. The major difference between the relativistic values occurs because of differences in estimation of the self-consistent-field term, which is proportional to \((E_{101}/mc^2)\). The Cromer and Liberman (1970) relativistic dipole value is \(5/3(E_{101}/mc^2)\) whereas the tabulation uses the relativistic multipole value of \((E_{101}/mc^2)\). This causes a vertical shift of the curve but does not alter its shape. There is a significant discrepancy between the Kissel et al (1980) result for \(^{62}\text{Sm}\) and the other theoretical values. This is the only major point of difference, however, and the results are better in accord with the relativistic multipole approach than with the relativistic dipole approach. Note that the relativistic multipole approach does not include the Jensen correction, which alters the shape of the curve. There is little to choose between the different theoretical approaches when the calculation of \(f^*(\omega, 0)\) is concerned. In most cases the agreement between the scattering matrix, relativistic dipole and relativistic multipole values is within 1%. In contrast there are some significant differences between the relativistic and the non-relativistic values of \(f^*(\omega, 0)\). The extent of the discrepancies is greater the higher the atomic number, as one might expect from the assumptions made in the formulation of the non-relativistic model.

Some detailed comparisons of theoretical and experimental data for linear attenuation coefficients (proportional to \(f^*(\omega, 0)\)) have been given by Creagh and Hubbell (1987) for silicon, copper and carbon by Gerward (1982, 1983). These tend to confirm the assertion that, at the 1% level of accuracy, there is little to choose between the various relativistic models for computing scattering cross sections. The description of the experimental set up and procedure is provided in the next chapter.
REFERENCES


Brysk and Zerby (1968), Phys. Rev. 171, 292.


Fano U. (1953), Nuclonix, 11(8), 8 and 11(9), 55.


Fermi E. (1928), Z. Physik. 48, 73.

Fock V. (1930), Z. Physik 61, 126.

Fock V. and Petraschen M.J. (1934), Phys. Z. Sowjetunion, 6, 338.

Gavrila M. (1960), Soviet Phys. 11, 224.
Hönl H. (1933a), Z. Phys. 84, 1.
Hall H. (1936), Rev. Mod. Phys. 8, 358.
Kahane (1998), Atomic Data and Nuclear Data Table. 68, 323.
Nagel B. (1960), Arkiv for Fysik 18, 1.
Pirenne M.H. (1946), "The diffraction of X-rays and Electrons by Free Molecules" (Camb. Univ. Press).


Veigele Wm. J. (1973), Atomic Data Tables 5, 51.


