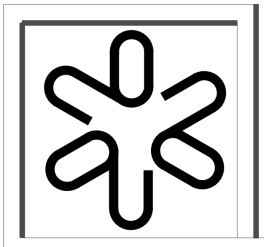

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X-Ray Scattering by Atoms: Basic Equations

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X-Ray Scattering by Atoms: Basic Equations.

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Abstract. In this paper we briefly show how to calculate the intensity of X-rays scattered by bound electrons in atoms. This paper was written to graduate and postgraduate students of physics.

Introduction.

In this article, written to graduate and postgraduate students of physics, we shown how to calculate the basic equations proposed to describe the X-ray scattered intensities by atoms. In Section I is studied the light scattering from free-electrons according to the quantum-relativistic Compton model, the classical electromagnetic Thomson formalism and the quantum-relativistic Klein-Nishina approach. In Section II we analyze the X-ray scattered by one-electron atom and by many-electron atoms.

I)Light Scattering by Free-Electrons.

1. Compton Scattering.

According to basic text books,[1,2] when a photon with initial frequency $\omega = 2\pi f$, wavelength $\lambda = cf = 2\pi c/\omega$, energy $E = \hbar\omega$ and linear momentum $\hbar\mathbf{k}$, where $k = 2\pi/\lambda$, collides with a free-electron at rest with mass m due to the relativistic energy and momentum conservations we have, respectively,

$$\hbar\omega + mc^2 = \hbar\omega' + E \qquad \text{and} \qquad \mathbf{p} = \hbar\mathbf{k} - \hbar\mathbf{k}' = \hbar\mathbf{q} \qquad (1.1).$$

This collision process is known simply as **"Compton scattering"** or **"free-electron Compton Scattering."** In (1.1) E and **p** are the electron kinetic energy and momentum after the collision and $hf' = \hbar\omega'$ and $\hbar\mathbf{k}'$ are the energy and momentum of the photon after the collision.

Indicating by θ the angle between **k** and **k´,** which is the scattering angle of the incident photon, one can show, using (1.1) that

$$\hbar\omega' = \hbar\omega/[1+\gamma(1-\cos\theta)] \qquad (1.2),$$

where $\gamma = \hbar\omega/mc^2$. It will be assumed in what follows that the incident energy is sufficiently large compared to the energy transfers. In these

conditions the momentum transfer $\hbar\mathbf{q}$ for a given scattering angle can be taken as independent of the out going energy. So, we can write

$$\hbar q = 2\hbar k \sin(\theta/2) \quad \text{or} \quad \chi = 2k \sin(\theta/2) \qquad (1.3).$$

Being λ the incident wavelength $\lambda = cf = 2\pi c/\omega$ the scattered one λ' will be given by

$$\lambda' = \lambda + \lambda_C (1-\cos\theta) \qquad (1.4),$$

where $\lambda_C = h/mc = 0.02426\ 10^{-8}$ cm is the Compton wavelength.

2. Thomson Scattering.

According to the non-relativistic Classical Electrodynamics[3] a free-electron submitted to an incident electromagnetic wave with frequency ω irradiates an average power by unit of solid angle $< dP/d\Omega >$ given by (A.6) shown in Appendix A,

$$< dP/d\Omega > = S_o\, r_e^2\, (1+\cos^2\theta)/2 \qquad (2.1),$$

where θ is the scattering angle defined by (1.2), S_o is the incident energy flux $S_o = (c/8\pi)\,|E_o|^2$ (which is the time-average Poynting vector for a plane wave), $r_e = e^2/mc^2$ and m are the classical radius and the mass of the electron, respectively. From (2.1) we obtain the differential scattering cross section per unit of solid angle,

$$d\sigma_T/d\Omega = < dP/d\Omega > / S_o = r_e^2\, (1+\cos^2\theta)/2 \qquad (2.2).$$

This is called **Thomson Formula** for scattering of radiation by a free charge. The total scattering cross section, called the **Thomson cross section**, is

$$\sigma_T = (8\pi/3)\, r_e^2 \qquad (2.3),$$

where $r_e = 2.82\ 10^{-13}$ cm and $\sigma_T = 0.665\ 10^{-24}$ cm^2.

Note that in the Thomson process the frequency of scattered light is equal to the frequency ω of the incident light. That is, frequency ω of the incident light is not modified by the scattering.

Using the Guinier[4] notation, the energy $I_e = I_T$ scattered by a free electron per unit of solid angle per second is given by

$$I_e = I_T = S_o\, (d\sigma_T d\Omega) = S_o\, r_e^2\, (1+\cos^2\theta)/2 \qquad (2.4).$$

Relativistic correction of the Thomson intensity I_e

During the scattering process the electron acquires a recoil velocity v relatively to the observation point P which is localized in an inertial frame.

It can be shown[10] that due to relativistic effects instead of (2.4) we have now

$$I'_e = R\, S_o\, r_e^2\, (1+\cos^2\theta)/2 \qquad (2.5),$$

where $R = (\omega'/\omega)^3$ and $\omega' = \omega/[1+\gamma(1-\cos\theta)]$ is given by (1.2).

3. Klein-Nishina Scattering.

Within the quantum mechanical relativistic context the differential collision cross section $d\sigma_{KN}(\theta)/d\Omega$ for the Compton scattering due to a free-electron is given by the **Klein-Nishina formula**[5–9]

$$d\sigma_{KN}(\theta)/d\Omega = (d\sigma_T(\theta)/d\Omega)$$

$$x\, [1+ (1-\gamma\cos(\theta))]^{-3}\{1+\gamma^2(1-\cos\theta)^2/[(1+\cos^2\theta)[1+\gamma(1-\cos\theta)]\} \quad (3.1),$$

where $d\sigma_T(\theta)/d\Omega$ is the **Thomson cross section** defined by (2.2) and $\gamma = h\omega/mc^2$. The Klein-Nishina formula (3.1) was deduced using the traditional relativistic quantum mechanical perturbation theory[5–8] or the Feynman diagrams formalism,[9] both up to the second order Born approximation.

According to (3.1) we verify that in the non relativistic limit, that is, when $\gamma \to 0$ we have $d\sigma_{KN}(\theta)/d\Omega = d\sigma_T(\theta)/d\Omega$. The differential cross sections $d\sigma_T(\theta)/d\Omega$ and $d\sigma_{KN}(\theta)/d\Omega$ as a function of θ and γ are shown in Fig. 14.13 of the reference 3 or Fig.10 of reference.[8] From these figure we verify that for $\gamma \neq 0$ $d\sigma_T(\theta)/d\Omega$ is larger than $d\sigma_{KN}(\theta)/d\Omega$ for $\theta > 0$ (for $\theta = 0$ they are equal). The total cross-section σ_{KN} for the Compton scattering is given by[8]

$$\sigma_{KN} = 2\pi\, r_e^2\, \{\, [(1+\gamma)/\gamma^2]\, [\, 2(1+\gamma)/(1+2\gamma) - (1/\gamma)\ln(1+2\gamma)] +$$

$$+ (1/2\gamma)\, \ln(1+2\gamma) - (1+3\gamma)/(1+2\gamma)^2\, \} \qquad (3.2).$$

From (3.2) we see that the ratio $\sigma_{KN}/\sigma_T \leq 1$ for $\gamma \geq 0$. This is expected since part of the incident energy flux is lost due to the inelastic collisions between photons and electrons. According to the Thomson formula the frequency of the diffracted light is equal to the incident one. No inelastic effects are predicted by the Thomson scattering. So, rigorously, according to the quantum theory, scattering from a free-electron occurs only through the Compton Effect.

From (3.1) we get the Klein-Nishina intensity

$$I_{KN} = I_e\, [1+ (1-\gamma\cos(\theta))]^{-3}\{1+\gamma^2(1-\cos\theta)^2/[(1+\cos^2\theta)[1+\gamma(1-\cos\theta)]\} \quad (3.3)$$

It will be assumed in what follows that in the X-ray diffraction the relativistic effects are very small, that is, $\gamma << 1$. Since $\gamma = \hbar\omega/mc^2 = h/mc\lambda = 0.0243/\lambda$ we verify that to have $\gamma = 0.0243/\lambda << 1$ the incident wavelengths λ must be $\lambda >> 0.0243$ Å. In these conditions the ratio I / I_e given by (3.3), in a first order γ approximation, becomes

$$I / I_e \approx [1 + \gamma (1-\cos\theta)]^{-3} \qquad (3.4).$$

Since, according to (1.2), $\omega'/\omega = 1+ \gamma(1-\cos\theta)$, we see that (3.4) is the same result given by (2.5).

II) Scattering from Atoms.

It is well known that light wavelengths change[1–4] when scattered by atoms and molecules. Typical plots of the scattered X-ray intensities $I(\lambda,\theta)$ from atoms are shown in all basic text books.[1–3] In Figure 1 is shown[2] the scattered intensities $I(\lambda,\theta)$ as a function of λ and $\theta = 0°,45°, 90°$ and $135°$ for carbon atoms for the incident $\lambda = 0.708\ 10^{-8}$ cm. When this wavelength change became known, about 1922, it became clear that the classical methods of applying classical electrodynamics to the scattering of light by bound or free electrons were inadequate.[10] In this way, many quantum mechanical approaches have been developed to calculate the radiation scattering from atoms.[10–17]

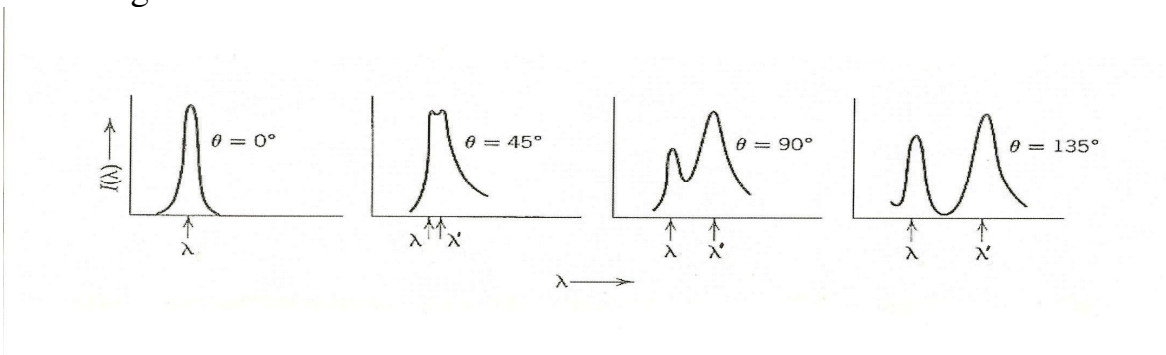

Figure 1. Scattered intensities $I(\lambda,\theta)$ as a function of λ and $\theta = 0°,45°, 90°$ and $135°$ for carbon atoms[2] for the incident $\lambda = 0.708\ 10^{-8}$ cm.

From Figure 1 we see that there are, essentially, two peaks: one centered around the incident wavelength λ ("Thomson peak") and another centered around the wavelength $\lambda' = \lambda + \lambda_C (1-\cos\theta)$, given by (1.4) ("Compton peak"). As will be shown in what follows the Thomson peak is due to elastic collisions (*coherent collisions*) between photons and bound electrons and the Compton peak due to inelastic collisions (*incoherent collisions*). Indeed, in inelastic collisions the diffracted photon frequencies are given by $\omega' = \omega - (E_n - E_m)/\hbar = \omega - \omega_{nm}$ where E_j are the stationary electronic energies in the atom. When $\omega >> \omega_{nm}$, that is, when the electrons can be considered as almost free-electrons, since $\lambda' = 2\pi/\omega' = 2\pi/(\omega - \omega_{nm})$

we get $\lambda' \approx \lambda\,(\,1 + \hbar\omega_{nm}/\hbar\omega\,)$. Taking into account that in the photon-electron collision the energy exchange $\hbar\omega_{nm} = \Delta E_{nm}$ is equal to $(\hbar q)^2/2m = [2\hbar k \sin(\theta/2)]^2/2m$, according to (1.3), and that $k = 2\pi/\lambda$ and $\omega = 2\pi c/\lambda$ we verify that $\lambda' = \lambda + \lambda_C\,(1-\cos\theta)$, in agreement with (1.4).

4. Scattering from One-Electron Atoms.

In a non-relativistic approximation the hamiltonian H for an electron of mass m in a field of a vector potential **A** and of a scalar potential Φ, is written as[8,17,18]

$$H = (\mathbf{p}-e\mathbf{A})^2/2m + e\Phi,$$

where $p = m\mathbf{v} + e\mathbf{A}/c$. Let us consider an hydrogen-like atom where Φ is the Coulomb electron-nucleus interaction potential and **A** is an applied external wave-field that can be treated as a small perturbation w(t) given by[8,17,18]

$$w(t) = -(e/mc)\mathbf{A}\cdot\mathbf{p} + (e^2/2mc^2)\mathbf{A}^2 \qquad (4.1).$$

Supposing that the **A** perturbation is so small that we can neglect $\mathbf{A}^2$ in (4.1), that is putting $w(t) \approx -(e/mc)\mathbf{A}\cdot\mathbf{p}$, the wave−equation for this electron is written as[8,17,18] as

$$\{-(\hbar^2/2m)\,\Delta^2 + e\Phi\}u + (i\hbar e/mc)\,(\mathbf{A}\cdot\mathrm{grad})u = i\hbar\partial u/\partial t \qquad (4.2),$$

where Δ^2 is the laplacian and $H_a = -(\hbar^2/2m)\,\Delta^2 + e\Phi$ is the hamiltonian of the unperturbed atom. The stationary electronic wavefunctions Ψ_n of H_a , that is,

$$H_a\,\Psi_n = i\hbar\,\partial\Psi_n/\partial t = E_n\,\Psi_n$$

will be indicated by $\Psi_n(\mathbf{r},t) = \psi_n(\mathbf{r})\exp(-iE_nt/\hbar)$. In this way, (4.2) can be written as

$$(H_a + H') = i\hbar\partial u/\partial t \qquad (4.3),$$

where $H' = (i\hbar e/mc)\,(\mathbf{A}\cdot\mathrm{grad})$ represents the perturbation due the incident external field $\mathbf{A} = (ic\mathbf{E}_o/2\omega)\,\{\exp(-i\mathbf{k}\cdot\mathbf{r} + i\omega t) + \text{complex conjugate}\}$.

Using the quantum perturbation theory [8,17,18] up to second order approximation in H´, including the lifetimes Γ_n of the n states,[18] it can be shown[17,18] that the functions u are given by

$$u = \Psi_n(\mathbf{r},t) + (eE_o/2m\omega)\Sigma'_k\{C_{nk}(t)/(\omega_{kn}+\omega + i\gamma_{kn}) + C^*_{nk}(t)/(\omega_{kn}-\omega + i\gamma_{kn})\} \quad (4.4),$$

where $\omega_{kn} = (E_k - E_n)/\hbar$, γ_{kn} is the linewidth[18] of the line $k \rightarrow n$, $C_{nk}(t)$ are functions defined[17] by $C_{nk}(t) = B_{nk} \exp[i(\hbar\omega - E_n t)/h]$ and Σ'_k is a sum over k with $k \neq n$. Eq.(4.4) shows that when the energy $\hbar\omega$ of the incident field is much larger than energy differences between the atomic levels E_n, that is, when $\hbar\omega >> E_k - E_n$ the perturbation on the atomic states can be neglected and we can put $u \approx \Psi_n(\mathbf{r},t)$. In these conditions the charge current matrix density $\mathbf{j}_{nm}$ becomes written as[17,18,19]

$$\mathbf{j}_{nm} = (ie\hbar/2m)\,[\Psi_n^* \mathrm{grad}(\Psi_m) - \Psi_m \,\mathrm{grad}\, \Psi_n^*] - (e^2/mc)\mathbf{A}\Psi_n^*\Psi_m \quad (4.5).$$

The first term of (4.5) does not depend on the time when n = m and when $n \neq m$ it is associated with the spontaneous emission by the atom.[17] So, to estimate scattered radiation by the atom only the term $(e^2/mc)\mathbf{A}\Psi_n^*\Psi_m$ will be relevant.

The scattered field $\mathbf{E}_a$, due to one electron, in the wave zone is given by (see Appendix A)

$$\mathbf{E}_a = (e/c)\,\mathbf{n} \times (\mathbf{n} \times d\mathbf{v}/dt) = (1/c)d[\mathbf{n} \times (\mathbf{n} \times \mathbf{j})]/dt \qquad (4.6),$$

where $\mathbf{j}$ is the current density $\mathbf{j} = e\mathbf{v}$. Since $\mathbf{A} = a\boldsymbol{\varepsilon} \exp[i(\mathbf{q}\cdot\mathbf{r} - \omega t)]$ we have in the quantum approach[17–20]

$$(\mathbf{E}_a)_{nm} = (1/c)d[\mathbf{n} \times (\mathbf{n} \times \mathbf{j}_{nm})]/dt =$$

$$= (a/c)d\left\{\exp(-i\omega t)\int \Psi_n^*\Psi_m \exp(i\mathbf{q}\cdot\mathbf{r})\, d^3\mathbf{r}\right\}/dt\ (\mathbf{n} \times (\mathbf{n} \times \boldsymbol{\varepsilon})) \quad (4.7)$$

$$= (-i\omega'_{nm}\, a/c) \exp(-i\omega' t)\ \{\int \psi_n^*\psi_m \exp(i\mathbf{q}\cdot\mathbf{r})\, d^3\mathbf{r}\}(\mathbf{n} \times (\mathbf{n} \times \boldsymbol{\varepsilon})),$$

where $\omega'_{nm} = \omega - (E_n - E_m)/\hbar$, remembering that $\Psi_j(\mathbf{r},t) = \psi_j(\mathbf{r}) \exp(-iE_j t/\hbar)$, is the frequency change of the light due to the $n \rightarrow m$ atomic transition. Taking into account that $\mathbf{E} = -(1/c)\,\partial\mathbf{A}/\partial t$ we get $a = icE_o/\omega$. From (4.7), following the procedure used in Appendix A we obtain

$$\langle dP_{nm}/d\Omega \rangle = (cE_o^2/8\pi)(e^2/mc^2)^2\, (\omega'_{nm}/\omega)^2\, |f_{nm}|^2 \sin^2\Theta \qquad (4.8),$$

where

$$f_{nm} = \int \psi_n^*(\mathbf{r})\psi_m(\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{r})\, \mathbf{d^3r} \qquad (4.9)$$

is the *electronic form factor*. When $n \neq m$ we have *incoherent scattering* and *coherent scattering* is when n = m. In the coherent case we have

$$f_{nn} = \int |\psi_n(\mathbf{r})|^2 \exp(i\mathbf{q}\cdot\mathbf{r})\, d^3\mathbf{r} = \int \rho_n(\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{r})\, d^3\mathbf{r}$$

where $\rho_n(\mathbf{r}) = |\psi_n(\mathbf{r})|^2$ is the electronic charge density at the state n in units of the electronic charge.

From (4.9) we get the cross section for the transition $n \rightarrow m$,

$$d\sigma_{nm}/d\Omega = < dP_{nm}/d\Omega >/ S_o = r_e^2 (\omega'_{nm}/\omega)^2 |f_{nm}|^2 (1+\cos^2\theta)/2 \quad (4.10),$$

and the intensity $I_{nm} = S_o\, d\sigma_{nm}/d\Omega$ given by

$$I_{nm} = S_o\, r_e^2 (\omega'_{nm}/\omega)^2 |f_{nm}|^2 (1+\cos^2\theta)/2 = I_e (\omega'_{nm}/\omega)^2 |f_{nm}|^2 \quad (4.11),$$

where $I_e = I_T = S_o\, r_e^2 (1+\cos^2\theta)/2$ is the scattering intensity due to one free electron or *Thomson intensity*.

Considering the relativistic effects as very small, according to Section 3, putting $\omega'_{nm} \approx \omega$, (4.11) becomes

$$I_{nm} \approx I_e\ |f_{nm}|^2 \quad (4.12).$$

The *total scattered intensity* I_{total} would be given by

$$I_{total} = I_e \sum_m |f_{nm}|^2 \quad (4.13).$$

Since, due to the orthonormal properties of the state functions $\psi_j(\mathbf{r})$ it can be easily shown that $\sum_m |f_{nm}|^2 = 1$, we verify that the total inelastic scattered intensity is given

$$I_{total} = I_e \quad (4.14).$$

The above result is exactly the same derived from the purely classical theory of scattering.[10,17] According to this theory an atom containing only a single loosely bound electron should scatter as a single free-electron.

In order to simplify the notation that in the case of many-electron atom we consider confuse,[10–17] we assume in what follows, as will usually be the case, that the initial $| n >$ is the *fundamental state* and will be indicated by $| 0 >$. In this context for a single electron atom, within the limits of frequency imposed, we have therefore the following results for the *coherent* (elastic) and *incoherent* (inelastic) scatterings:

$$I_{coh} = I_e |f_{oo}|^2 = I_e |f_1|^2$$

and (4.15),

$$I_{inc} = I_e (1 - |f_{oo}|^2) = I_e (1 - |f_1|^2)$$

where the suffix 1 means "electron 1" and f_1 is given by

$$f_1 = f_{oo}(1) = \int |\psi_o(\mathbf{r}_1)|^2 \exp[i(\mathbf{q}\cdot\mathbf{r}_1)]\, d^3\mathbf{r}_1 \qquad (4.16),$$

$\mathbf{r}_1$ the coordinate of the (single) electron 1.

Example: Hydrogen Atom.

The wavefunction $\psi_o(\mathbf{r})$ for the fundamental hydrogen state is $\psi_o(\mathbf{r}) = \exp(-r/a_o)/(\pi a_o^3)^{1/2}$, where $a_o = (\hbar^2/me^2) = 0.53\ 10^{-8}$ cm is the Bohr radius. Since the electron density $\rho(r) = |\psi_o(\mathbf{r})|^2 = \exp(-2r/a_o)/(\pi a_o^3)$ we verify that the form factor (4.16) becomes

$$f_1 = f_H = f(q,H) = \int \rho(r)\ \{\sin(qr)/qr)\}\ 4\pi r^2 dr \qquad (4.17),$$

where $q = 4\pi \sin(\theta/2)/\lambda$. Integrating r from 0 up ∞ we obtain

$$f_H = (1+ q^2a_o^2/4)^{-2} = (1+4\pi^2a_o^2x^2)^{-2} \qquad (4.18),$$

where $x = \sin(\theta/2)/\lambda$. The form factor $f_H(x) = f(x,Z=1) = f(x,H)$ can be seen plotted as a function of x in Figure 1 of reference 21. According to (4.15) the coherent I_{coh} and the incoherent $I_{inc}(x)$ intensities are given, respectively, by

$$I_{coh}(x) = I_e\ (1+4\pi^2a_o^2x^2)^{-4} \qquad (4.19)$$

and

$$I_{inc}(x) = I_e\ [1-(1+4\pi^2a_o^2x^2)^{-4}] \qquad (4.20).$$

5. Scattering from Many-Electron Atoms.

Let us show how the ideas developed in Section 4 may be extended to the case of an atom with Z electrons[17] that will be indicated by the suffix k =1,2,…, Z. So, instead of (4.1) the appropriate form for the first order perturbative term w(t) is given by

$$w(t) = -(e/mc)\sum_k \mathbf{A}_k\cdot\mathbf{p}_k \qquad (5.1),$$

and instead of (4.2) we have the wave-equation[17]

$$\sum_k \left\{\left[-(\hbar^2/2m)\ \Delta_k^2 + e\Phi\right]u\ + (i\hbar e/mc)\ (\mathbf{A}_k\cdot \mathrm{grad}_k)u\right\} = i\hbar\partial u/\partial t \qquad (5.2),$$

where the suffix k refers to the coordinates of the electron k and the potential $\Phi = \Phi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_Z)$. The wavefunctions corresponding to the stationary states u_n of the unperturbed atom, where the electrons are mutually interacting or not, are now given by

$$u_n = \Psi_n(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_Z)\ \exp(-iE_nt/\hbar) \qquad (5.3),$$

where E_n is the energy of the state n. The quantity $|u|^2\, dv$, where $dv = dv_1 dv_2 \ldots dv_Z$, gives the probability that the electron k lies within the element of volume dv_k, at the distance $\mathbf{r}_k$ and so on, with k =1,2,…,Z. The charge-density $\rho_k = \rho(\mathbf{r}_k)$ associated with the electron k is written as $\rho_k = e \int |u|^2\, dv'_k$ where dv'_k denotes that the integration is over all electrons coordinates except of k. The charge density ρ_k integrated over k coordinate, is, as should be, equal to the electronic charge, since $\int |u|^2\, dv = 1$, the function u as normalized to unit. The current-density of charge $\mathbf{j}_k = e\, \mathbf{v}_k$ obeys the equation $\mathrm{div}\, \mathbf{j}_k + \partial\rho_k/\partial t = 0$. The electronic charge density ρ_k of the electron k in the fundamental state $u_o(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_Z)$ is given by

$$\rho_k = \rho(\mathbf{r}_k) = \int |u_o|^2\, dv'_k = \int |\Psi_o|^2\, dv'_k$$

Coherent Scattering.

Thus, in analogy with Section 4, the new form factor F_{oo} due to a *coherent scattering* from the atom in the fundamental state, is given by

$$F_{oo} = \sum_k \int \rho(\mathbf{r}_k) \exp[i(\mathbf{q}\cdot\mathbf{r}_k)]\, dv_k = \int |\Psi_o|^2 \sum_k \exp[i(\mathbf{q}\cdot\mathbf{r}_k)] dv \qquad (5.4),$$

where the resultant radiated electric field $\mathbf{E}_a$ at the observation point P is given by coherent sum $\mathbf{E}_a = \sum_k (\mathbf{E}_a)_k$ of the emitted electric fields (that have the same frequency ω) due to the k electrons. Thus, the coherent radiated intensity $I_{coh} = I_e |F_{oo}|^2$ is

$$I_{coh} = I_e \left| \int |\Psi_o|^2 \sum_k \exp[i(\mathbf{q}\cdot\mathbf{r}_k)] dv \right|^2 \qquad (5.5).$$

Note that (5.5) gives the scattered intensity of the "Thomson peak" centered around the frequency λ.

If instead of the individual electronic densities $\rho_k = \rho(\mathbf{r}_k)$ we have an average electronic density $\rho(\mathbf{r})$ (see Thomas-Fermi model, Section 6) with spherical symmetry, that is, $\rho(\mathbf{r}) = \rho(r)$, (5.4) becomes

$$I_{coh}(\lambda,\theta) = I_e \left| \int \rho(r) \{\sin(qr)/qr\}\, 4\pi r^2 dr \right|^2 \qquad (5.6),$$

where $q = (4\pi a/\lambda) \sin(\theta/2)$ and $\rho(r)$ is the charge density of the atom in units of the electronic charge.

Limiting cases: ka << 1 and ka >>1.

(a) *ka << 1*. In this case (very large incident wavelengths λ) we have for all angles qa << 1. In this case, putting $\sin(qr)/qr \sim 1$, we get from (5.6)

$$I_{coh}(\lambda,\theta) \approx I_e \left| \int \rho(r)\, 4\pi r^2 dr \right|^2 = Z^2\, I_e \qquad (5.7),$$

where the factor Z^2 shows a collective effect of the Z electrons of the atom. (b) *ka >> 1*. To study this case it is more convenient to write F_{oo} (5.4) taking into account the electrons individually:

$$| F_{oo} |^2 = < | \sum_k \exp[i(\mathbf{q}\cdot\mathbf{r}_k)]|^2 > \qquad (5.8),$$

where the brackets <…> means an average over the electrons coordinates. In this limit (very small incident wavelengths λ) the arguments of the exponents are large and widely different in values. Consequently, the cross terms in the square of the sum will average to zero. Only the absolute square terms will survive. Then $| F_{oo} |^2 = Z$ and the I_{coh} will be given by

$$I_{coh}(\lambda,\theta) \approx I_e | F_{oo} |^2 = Z\, I_e \qquad (5.9),$$

where there are no collective effect between the electrons: the result corresponds to a simple superposition of scattering from individual electrons.

Incoherent Scattering.

For the *incoherent scattering* the form factor F_{om}, with $o \neq m$, is given by

$$F_{om} = \int \Psi^*_m \Psi_o \sum_k \exp[i(\mathbf{q}\cdot\mathbf{r}_k)]dv \qquad (5.6),$$

where the contributions of each intensity $(\mathbf{E}_a)_k$ are added incoherently at the observation point P since they have different frequencies $\omega' = \omega - \omega_{om}$ due to inelastic transitions $o \rightarrow m$. It is assumed that $\omega >> \omega_{om}$. The term m = o excluded from (5.6) gives, of course, the *coherent scattering*. So, the *total incoherent scattered intensity* is given by

$$I_{inc} = I_e \{ \sum_{m \neq o} |F_{om}|^2 \} \qquad (5.7).$$

Note that (5.7) gives the scattered intensity of the "Compton peak" centered around the frequency λ´.

Total Scattering Intensity.

So, from (5.7) we see that the *total scattered intensity* I_{total} is given by

$$I_{total} = I_e \{ \sum_m |F_{om}|^2 \} \qquad (5.8).$$

Using the orthonormality properties of the functions Ψ_n it can be shown that[17] (5.6) can be written as

$$|F_{om}|^2 = \int |\Psi_o|^2 \, |\sum_k \exp[i(\mathbf{q}\cdot\mathbf{r}_k)]|^2 \, dv \qquad (5.9).$$

Consequently, using (5.8) the total I_{total} scattered intensity given by (5.8) becomes written as

$$I_{total} = I_e \int |\Psi_o|^2 \, |\sum_k \exp[i(\mathbf{q}\cdot\mathbf{r}_k)]|^2 \, dv \qquad (5.10).$$

6. Approximate Forms for the Many−Electron Atom.

Since the exact solution of the wave equation for an atom containing many electrons is in general impossible we must look for approximate solutions.[17,18,20]

Non−Interacting Electrons and Neglecting Pauli´s Exclusion Principle.

In a first approximation, neglecting the interaction between the electrons and Pauli´s exclusion principle we can write[17,18,20]

$$\Psi_n(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_Z) = \psi_1(\mathbf{r}_1)\, \psi_2(\mathbf{r}_2) .. \psi_k(\mathbf{r}_k) ... \psi_Z(\mathbf{r}_Z) \qquad (6.1),$$

where $\psi_k(\mathbf{r}_k)$ is the state function of the electron k and $\mathbf{r}_k$ its coordinate. With this approximation F_{oo} defined by (5.4) becomes, taking into account that the electrons k are in the fundamental states $\psi_o(\mathbf{r}_k)$:

$$F_{oo} = \int |\Psi_o|^2 \left(\sum_k \exp[i(\mathbf{q}\cdot\mathbf{r}_k)]\right) dv_1 dv_2 \ldots dv_Z =$$

$$= \int \left(\prod_{k=1,\ldots,z} \psi_o^*(\mathbf{r}_k)\right)\left(\prod_{k=1,\ldots,z} \psi_o(\mathbf{r}_k)\right)\left(\sum_k \exp[i(\mathbf{q}\cdot\mathbf{r}_k)]\right) dv_1 dv_2 \ldots dv_Z$$

$$= \sum_{k-=1,2,\ldots,Z} \int |\psi_o(\mathbf{r}_k)|^2 \exp[i(\mathbf{q}\cdot\mathbf{r}_k)] dv_k \ , \qquad \text{that is,}$$

$$F_{oo} = \sum_k f_k \qquad (6.2),$$

where f_k is the form factor for the electron k

$$f_k = f_{oo}(k) = \int |\psi_o(\mathbf{r}_k)|^2 \exp[i(\mathbf{q}\cdot\mathbf{r}_k)] dv_k \ ,$$

similar to the form factor f_1 (4.13) obtained for one−electron atom.

So, the *total coherent intensity* I_{coh} for the non-interacting electrons is given by

$$I_{coh} = I_e \, | \sum_k f_k |^2 \qquad (6.3).$$

As, according to (4.12), the *incoherent intensity* due to each electron would be $I_e\ (1 - |f_k|^2\ )$, the *total incoherent intensity* I_{inc} due to the Z electrons is

$$I_{inc} = I_e \sum_k (1 - |f_k|^2) \qquad (6.4).$$

Consequently, the *total intensity* radiate $I_{total} = I_{coh} + I_{inc}$ is given by

$$I_{total} = I_e \left\{ Z + |\sum_k f_k|^2 - \sum_k |f_k|^2 \right\} \qquad (6.5).$$

Inclusion of Pauli´s Exclusion Principle and Relativistic Effects.

Taking into account the Pauli´s exclusion principle and relativistic effects it can be shown[15,16] that instead of (6.5) we have

$$I_{total} = I_e\, R \left\{ Z - \sum_k |f_k|^2 - \sum\nolimits'_{k,j} |f_{kj}|^2 + Z\, I_m \right\} \qquad (6.6),$$

where the double sum $\sum\nolimits'_{k,j} |f_{kj}|^2$ over k and j means that $k \neq j$ and

$$f_{kj} = \int \psi_o^{(k)}(\mathbf{r})^*\ \psi_o^{(j)}(\mathbf{r})\ \exp[i(\mathbf{q}\cdot\mathbf{r})] d^3\mathbf{r}\ ,$$

where $\mathbf{r} = \mathbf{r}_k$ or $\mathbf{r} = \mathbf{r}_j$. The function R according to (2.5) is

$$R = (\omega'/\omega)^3 \approx [1 + \gamma\ (1 - \cos\theta)]^{-3}$$

and I_m is the second term of Klein–Nishina formula (3.3) given by

$$I_m = 4\ \gamma^2\ \sin^2(\theta/2)/[(1+\cos^2\theta)\ (1 + 2\gamma\ \sin^2(\theta/2)],$$

which is negligible for ordinary X–ray wavelengths. Note that $I_e\ R$ is the first order γ term of the Klein–Nishina formula (3.1). However, taking into account the approximations used to calculate the forma factors (see Section 4) it can be verified that I_{total} (6.6) can be written as

$$I_{total} = I_{KN} \left\{ Z - \sum_k |f_k|^2 - \sum\nolimits'_{k,j} |f_{kj}|^2 + Z\, I_m \right\} \qquad (6.7),$$

where I_{KN} is given, in the general case, by (3.3).

Numerical Methods.

An electron in an atom is acted on by a central field due to the nucleus, together with the field due to all other electrons. So, to determine the wavefunction $\Psi_n(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_Z)$ is a "many body problem". There are many approximate methods to solve this problem like, for instance,[18,20–22]

"Thomas-Fermi Statistical Model", "Hartree and Hartree–Fock Self-Consistent Fields", Pauli and Sherman Method, Bethe-Levinger Method,… where relativistic and spin effects are also taken into account. We will analyze only the simplest methods of Thomas-Fermi and Hartree.

According to the Thomas-Fermi method [20–22] the Z electrons of an atom are considered as constituting a gas which is kept in equilibrium around the nucleus as a result, simultaneously, of the attraction between the nucleus and electrons, the repulsion among electrons and the kinetic energy of the electrons. The result of the calculations is a spherically symmetrical electronic cloud with the electrical density $\rho(x)$ given by

$$\rho(x) = (Z/4\pi a^3)\,[\Phi(x)/x]^{3/2} \qquad (6.8),$$

where $x = r/a$, a is the characteristic radius of the atom of atomic charge Z,

$a = (1/Z)^{1/3}(3/32\pi^2)^{2/3}\,(\hbar^2/me^2) = 0.47\,Z^{-1/3} \times 10^{-8}$ cm and r the distance to the atom centre; $\Phi(x)/x$ is the electrical potential in the system , measured in Ze/a units, calculated numerically.

The Thomas-Fermi approach does not reproduce exactly the details of the electron distribution in atoms since no account is taken of the different K,L,M,…, electron shells. However, it gives a good description for heavy atoms in which the individual peculiarities of the shells are to some extent averaged out in the dense electronic cloud.

Taking into account (6.8) the atomic coherent diffracted intensity I_{coh} is given by,

$$I_{coh}(\lambda,\theta) = I_{KN}\,|F_{oo}|^2 = I_{KN}\left|\int \rho(r)\{\sin(qr)/qr\}\,4\pi r^2 dr\,\right|^2 \qquad (6.9),$$

where $q = (4\pi a/\lambda)\sin(\theta/2)$ and $\rho(r)$ is the charge density of the atom in units of the electronic charge. The incoherent intensity $I_{inc}(\lambda,\theta)$ is given by

$$I_{inc}(\lambda,\theta) = I_{KN}\,(\,1 - |F_{oo}|^2\,) \qquad (6.10),$$

where $|F_{oo}|^2$ is shown in (6.9).

Hartree´s method[20–22] assumes that each electron moves in a central field that can be calculated from the nuclear potential and the wavefunctions of all other electrons, by assuming that the charge density associated with an electron is e times its position probability density. The Schrödinger equation is solved for each electron in its own central field, and the resulting wave functions made consistent with the fields from which they are calculated. Thus the k^{th} electron is described by a normalized wave function $u_k(\mathbf{r}_k)$ that is solution of a set of Z integro-differential equations for the functions $u_k(\mathbf{r}_k)$ [see Schiff, [20] Eq.(38.6)]. By

a method of successive approximations are calculated the wavefunctions $u_k(\mathbf{r}_k)$ and its energy eigenvalues ε_k given by

$$H_k\, u_k(\mathbf{r}_k) = \varepsilon_k\, u_k(\mathbf{r}_k) \qquad (6.11).$$

Hartree´s approach neglects correlations between the positions of the electron, since the entire wave function for all the electrons is assumed to be a simple product of one-eletron functions

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_Z) = u_1(\mathbf{r}_1)\, u_2(\mathbf{r}_2) .. u_k(\mathbf{r}_k) ... u_Z(\mathbf{r}_Z) \qquad (6.12).$$

Consequently, antisymmetrized wave functions are not employed. The antisymmetry is considered only in so far as the quantum numbers of the one-eletron states u_k are chosen in agreement with the exclusion principle.

Using the Hartree´s one-electron functions $u_k(\mathbf{r}_k)$ the form factor f_k (6.2) is now given by

$$f_k = \int |u_o(\mathbf{r}_k)|^2 \exp[i(\mathbf{q}\cdot\mathbf{r}_k)] dv_k \,,$$

and, consequently, the I_{coh} and I_{nc} are similar to (6.3) and (6.4):

$$I_{coh} = I_{KN} \mid \sum_k f_k \mid^2 \qquad (6.13),$$

and

$$I_{inc} = I_{KN} \sum_k (1 - |f_k|^2) \qquad (6.14).$$

7. Calculation of I_{coh} and I_{inc} Using Numerical Tables.

To calculate numerically the scattered intensities we will follow the paper of Hubbell et al.[21] where is defined the *scattering function* $F_m(\mathbf{q},Z)$ as

$$F_m(\mathbf{q},Z) = F_{mo}(\mathbf{q},Z) = \langle \Psi_m \mid \sum_k \exp(i\mathbf{q}\cdot\mathbf{r}_k) \mid \Psi_o \rangle \qquad (7.1).$$

In this way the *coherent scattering function* F_o defined by (5.4) is now written as

$$F_o(\mathbf{q},Z) = F_{oo} = \langle \Psi_o \mid \sum_k \exp(i\mathbf{q}\cdot\mathbf{r}_k) \mid \Psi_o \rangle \qquad (7.2),$$

and the *incoherent scattering function* F_{om} is now written as

$$S(\mathbf{q},Z) = F_{om} = \sum_{m>o} |F_m(\mathbf{q},Z)|^2 \qquad (7.3).$$

Using the closure property[18] $\sum_m \mid m \rangle\langle m \mid = 1$, (6.17) becomes

$$S(\mathbf{q},Z) = \sum_m < \Psi_o \mid \sum_k \exp(i\mathbf{q}\cdot\mathbf{r}_k) \mid \mathbf{\Psi}_m > < \mathbf{\Psi}_m \mid \sum_j \exp(i\mathbf{q}\cdot\mathbf{r}_j) \mid \mathbf{\Psi}_o >$$

$$- \mid < \Psi_o \mid \sum_j \exp(i\mathbf{q}\cdot\mathbf{r}_j) \mid \Psi_o > \mid^2 \quad ,$$

that is,

$$S(\mathbf{q},Z) = \sum_k \sum_j < \Psi_o \mid \exp[i\mathbf{q}\cdot(\mathbf{r}_k - \mathbf{r}_j)] \mid \Psi_o > - \mid F_o(\mathbf{q},Z) \mid^2 \qquad (7.4).$$

With these functions I_{coh} and I_{inc} are now written, respectively, as

$$I_{coh} = \quad I_{KN} \mid F_o(\mathbf{q},Z) \mid^2 \; = \; \mid < \Psi_o \mid \sum_k \exp(i\mathbf{q}\cdot\mathbf{r}_k) \mid \Psi_o > \mid^2 \qquad (7.5)$$

and

$$I_{inc} = I_{KN} \; S(\mathbf{q},Z) \qquad (7.6).$$

Hydrogen Atom.

Using the Hubbell et al.[22] notation we the wavefunction $\Psi_o(\mathbf{r})$ is $\Psi_o(\mathbf{r}) = \exp(-r/a_o)/(\pi a_o^3)^{1/2}$, where $a_o = (\hbar^2/me^2) = 0.53\ 10^{-8}$ cm is the Bohr radius. Since the electron density $\rho(r) = |\Psi_o(\mathbf{r})|^2 = \exp(-2r/a_o)/(\pi a_o^3)$ we verify that the form factor (4.16) becomes

$$F(q,H) = \int \rho(r) \; \{\sin(qr)/qr)\} \; 4\pi r^2 dr \qquad (7.7),$$

where $H = Z = 1$, $q = 4\pi \sin(\theta/2)/\lambda$. Integrating r from 0 up ∞ we obtain

$$F(x,H) \; = (1 + q^2 a_o^2/4)^{-2} = (1 + 4\pi^2 a_o^2 x^2)^{-2} \qquad (7.8),$$

where $x = \sin(\theta/2)/\lambda$. The form factor F(x,H) can be seen plotted in Figure 1.[22] Using (7.4) and (7.6) the incoherent function S(x,H) is written as $S(x,H) = 1 - [F(x,H)]^2$.

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APPENDIX A. Thomson Scattering.

Accelerated charges emit electromagnetic radiation.[1–3] Let us assume that a monochromatic electromagnetic plane wave with electric field $\mathbf{E}(\mathbf{r},t) = \boldsymbol{\varepsilon}\, E_o \exp(i\mathbf{k}\cdot\mathbf{r} - \omega t)$, $\boldsymbol{\varepsilon}$ the polarization vector, is incident on a free electron of charge e and mass m; $\mathbf{r}(t)$ is the electron coordinate in a given inertial

frame. Due to this field the electron will be accelerated and will emit radiation. The electric field $\mathbf{E}_a$ of the emitted radiation at a point P with coordinate **R** in the "wave zone" is given by[3]

$$\mathbf{E}_a = (E_o e^2/mc^2)\ \mathbf{n} \times (\mathbf{n} \times \boldsymbol{\varepsilon})\ \exp[i\mathbf{k}\cdot\mathbf{r} - i\omega(t - R/c + \mathbf{r}\cdot\mathbf{n}/c)]/\ R \qquad (A.1),$$

where $\mathbf{n}(t) = \mathbf{R}(t)/R$. Note that the amplitude and the phase of the emitted field are modified but not the frequency. Since the observation point P is assumed to be far away from the region of the space where the charge acceleration occurs, that is, $R >> r'$, the unit vector **n** is sensibly constant in time. In these condition (A.1) becomes, omitting the constant phase $\exp(i\omega R/c)$,

$$\mathbf{E}_a = (E_o e^2/mc^2)\ \mathbf{n} \times (\mathbf{n} \times \boldsymbol{\varepsilon})\ \exp[i(\mathbf{q}\cdot\mathbf{r} - \omega t)]/R \qquad (A.2),$$

where $\mathbf{q} = \mathbf{k} - (\omega/c)\ \mathbf{n}$ is the vectorial change in wave number in the scattering. Since $\mathbf{B}_a = \mathbf{n} \times \mathbf{E}_a$ the instantaneous energy flux is given by the Poynting vector $\mathbf{S}_a$ defined by

$$\mathbf{S}_a = (c/4\pi)\ (\mathbf{E}_a \times \mathbf{B}_a) = (c/4\pi)[\mathrm{Re}(\mathbf{E}_a)]^2\ \mathbf{n} \qquad (A.3),$$

where $\mathrm{Re}(\mathbf{E}_a)$ means the real part of $\mathbf{E}_a$. In this way, the average energy flux of radiated power at the point P that cross the area $dA = R^2\ d\Omega$ is given by $dP = \langle S_a \rangle\ dA$, where the brackets $\langle S_a \rangle$ indicates a time average of S. Consequently the average power radiated per unit of solid angle $\langle dP/d\Omega \rangle$ is written as

$$\langle dP/d\Omega \rangle = (cE_o^2/8\pi)(e^2/mc^2)^2\ [\mathbf{n} \times (\mathbf{n} \times \boldsymbol{\varepsilon})]^2 \qquad (A.4).$$

Defining by Θ the angle between **n** and $\boldsymbol{\varepsilon}$ we have

$$\langle dP/d\Omega \rangle = (cE_o^2/8\pi)(e^2/mc^2)^2\ \sin^2\Theta \qquad (A.5).$$

Defining a coordinate system (see Fig. 14.13 of reference 3) where **k** is along the z−axis the polarization vector $\boldsymbol{\varepsilon}$ would be in the (x,y), plane orthogonal to **k**, forming an angle ψ with the x−axis. The angle between **n** and **k** is θ and φ the angle of its projection on (x,y) plane with the x−axis. With this geometric construction we verify, using the addition theorem of spherical harmonics,[3] that $\sin^2\Theta = 1 - \sin^2\theta\ \cos^2(\varphi - \psi)$.

For unpolarized incident radiation $\langle dP/d\Omega \rangle$ defined by (A.5) gives, averaging over the angle ψ :

$$\langle dP/d\Omega \rangle = (cE_o^2/8\pi)(e^2/mc^2)^2\ (1+\cos^2\theta)/2 \qquad (A.6).$$

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