

## 4.2. X-RAYS

The result (4.2.6.2), which was derived using purely classical arguments, has been shown by Nelms & Oppenheimer (1955) to be identical to the result gained by quantum mechanics. If it is assumed that the atom has spherical symmetry,

$$f(\Delta) = 4\pi \int_0^{\infty} \rho(r) \frac{\sin \Delta r}{\Delta r} r^2 dr. \quad (4.2.6.3)$$

For an atom containing  $Z$  electrons, the atomic form factor becomes

$$f(\Delta) = 4\pi \sum_{n=1}^{n=Z} \int_0^{\infty} \rho_n(r) \frac{\sin \Delta r}{\Delta r} r^2 dr. \quad (4.2.6.4)$$

Exact solutions for the form factor are difficult to obtain, and therefore approximations have to be made to enable equation (4.2.6.4) to be evaluated. The two most commonly used approximations are the Thomas–Fermi (Thomas, 1927; Fermi, 1928) and the Hartree–Fock (Hartree, 1928; Fock, 1930) techniques.

In the Thomas–Fermi model, the atomic electrons are considered to be a degenerate gas obeying Fermi–Dirac statistics and the Pauli exclusion principle, the ground-state energy of the atom being equal to the zero-point energy of this gas. The average charge density can be written in terms of the radial potential function,  $V(r)$ , which may then be substituted into Poisson’s equation,  $\nabla^2 V(r) = \rho(r)/\epsilon_0$ , which can then be solved for  $V(r)$  using the boundary conditions that  $\lim_{r \rightarrow \infty} V(r) = 0$  and that  $\lim_{r \rightarrow 0} rV(r) = Ze$ .

The Thomas–Fermi charge distributions for different atoms are related to each other. If the form factor is known for a ‘standard’ atom for which the atomic number is  $Z_0$  then, for an atom with atomic number  $Z$ ,

$$f_Z(\Delta) = (Z/Z_0) f_0(\Delta'). \quad (4.2.6.5)$$

Here,

$$\Delta' = \Delta(Z/Z_0)^{1/3}.$$

The most accurate calculations of wavefunctions of many-electron atoms have been made using the self-consistent-field (Hartree–Fock) method. In this independent-particle model, each electron is assumed to move in the field of the nucleus and in an average field due to the other electrons. With this approach, the charge distribution can be written as

$$\rho(r) = \sum_{n=1}^{n=Z} \rho_n(r) = \sum_{n=1}^{n=Z} \Psi_n^*(r) \Psi_n(r), \quad (4.2.6.6)$$

where  $\rho_n(r)$  is the charge-density distribution of the  $n$ th electron and  $\Psi_n(r)$  is its wavefunction. The technique has been extended to include the effects of both exchange and correlation. Tables of relativistic Hartree–Fock values have been given by Cromer & Waber (1974). Their notation  $F(x, Z)$  is related to the notation used earlier as follows:

$$f_Z(\Delta) \equiv F(x, Z),$$

where

$$x = \frac{|k|}{2\pi} \sin(\varphi/2) = \frac{\Delta}{4\pi}.$$

In the foregoing discussion, the fact that the electrons occupy definite energy levels within the atoms has been ignored: it has been assumed that the energy of the photon is very different from any of these energy levels. The theory for calculating the scattering power of an atom near a resonant energy level was

supposed to be effectively the same as the well understood problem of the driven damped pendulum system. In this type of problem, the natural amplitude of the system was modified by a correction term (a real number) dependent on the proximity of the impressed frequency to the natural resonant frequency of the system and a loss term (an imaginary number) that was related to the damping factor for the resonant system. Thus the scattering power came to be written in the form

$$f = f_0 + \Delta f' + i \Delta f'', \quad (4.2.6.7)$$

where  $f_0$  is the atomic scattering factor remote from the resonant energy levels,  $\Delta f'$  is the real part of the anomalous-scattering factor, and  $\Delta f''$  is the imaginary part of the anomalous-scattering factor. The nomenclature of (4.2.6.7) has been superseded, but one still encounters it occasionally in modern papers.

In what follows, a brief exposition of the various theories for the anomalous scattering of X-rays and descriptions of modern experimental techniques for their determination will be given. Comparisons will be made between the several theoretical and experimental results for a number of atomic species. From these comparisons, conclusions will be drawn as to the validity of the various theories and the relevance of certain experiments.

## 4.2.6.2. Theoretical approaches for the calculation of the dispersion corrections

All the theories that will be discussed here have the following assumptions in common: the elastic scattering is from an isolated neutral atom and that atom is spherically symmetrical. All but the most recent of the theoretical approaches neglect changes in polarization of the incident photon caused by the interaction of the photon with the atom. In the event, few experimental configurations are able to detect such changes in polarization, and the only observable for most experiments is the momentum change of the photon.

## 4.2.6.2.1. The classical approach

In the classical approach, electrons are thought of as occupying energy levels within the atom characterized by an angular frequency  $\omega_n$  and a damping factor  $\kappa_n$ . The forced vibration of an electron gives rise to a dipolar radiation field, when the atomic scattering factor can be shown to be

$$f = \frac{\omega^2}{\omega^2 - \omega_n^2 - i\kappa_n \omega}. \quad (4.2.6.8)$$

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

$$\text{Re}(f) = \sum_n g_n + \sum_n \frac{g_n \omega_n^2}{\omega^2 - \omega_n^2}. \quad (4.2.6.9)$$

The probability  $g_n$  is referred to as the oscillator strength corresponding to the virtual oscillator having natural frequency  $\omega_n$ . Equation (4.2.6.9) may be written as

$$\text{Re}(f) = f_0 + f', \quad (4.2.6.10)$$

where  $f_0$  represents the sum of all the elements of the set of oscillator strengths and is unity for a single-electron atom. The second term may be written as

$$f' = \int_{\omega_{\kappa_i}}^{\infty} \frac{\omega'^2 (dg_{\kappa}/d\omega')}{\omega^2 - \omega'^2} d\omega' \quad (4.2.6.11)$$

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if the atom is assumed to have an infinite number of energy states. For an atom containing  $\kappa$  electrons, it is assumed that the overall value of  $f'$  is the coherent sum of the contribution of each individual electron, whence

$$f' = \sum_{\kappa} \int_{\omega_{\kappa}}^{\infty} \frac{\omega'^2 (dg_{\kappa}/d\omega')}{\omega^2 - \omega'^2} d\omega' \quad (4.2.6.12)$$

and the oscillator strength of the  $\kappa$ th electron

$$g_{\kappa} = \int_{\omega_{\kappa}}^{\infty} \left[ \frac{dg}{d\omega} \right]_{\kappa} d\omega$$

is not unity, but the total oscillator strength for the atom must be equal to the total number of electrons in the atom.

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,  $\mu_l$ , 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

$$\mu_a = \frac{2\pi^2 e^2}{\epsilon_0 mc} \left[ \frac{dg}{d\omega} \right], \quad (4.2.6.13)$$

whence

$$f'' = \frac{\pi}{2} \omega \left[ \frac{dg_{\kappa}}{d\omega} \right]. \quad (4.2.6.14)$$

An expression linking the real and imaginary parts of the dispersion corrections can now be written:

$$f' = \frac{2}{\pi} \sum_{\kappa} P \int_{\omega_{\kappa}}^{\infty} \frac{\omega' f''(\omega', 0)}{\omega^2 - \omega'^2} d\omega'. \quad (4.2.6.15)$$

This is referred to as the Kramers–Kronig transform. Note that the term involving the restoring force has been omitted from this equation.

Equations (4.2.6.12), (4.2.6.14), and (4.2.6.15) 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.

##### 4.2.6.2.2. Non-relativistic theories

The matrix element for Rayleigh scattering from an atom having a radially symmetric charge distribution may be written as

$$M = M_1(\epsilon_i \cdot \epsilon_f^*) + M_2(\epsilon_i \cdot \kappa_f)(\epsilon_f^* \cdot \kappa_i), \quad (4.2.6.16)$$

where  $\epsilon_i$  and  $\epsilon_f$  represent the initial and final states of the photon. The matrix element  $M_1$  represents scattering for polarizations  $\epsilon_i$  and  $\epsilon_f$  perpendicular to the plane of scattering and  $M_2$  represents scattering for polarization states lying in the plane of scattering.

Averaged over polarization states, the differential scattering cross section takes the form

$$\frac{d\sigma}{d\Omega} = \frac{r_e^2}{2} (|M_1|^2 + |M_2|^2). \quad (4.2.6.17)$$

Here  $\sigma$  is the photoelectric scattering cross section, which is related to the mass attenuation coefficient  $\mu_m$  by

$$\sigma = (M/N_A)\mu_m \times 10^{-24}, \quad (4.2.6.18)$$

where  $M$  is the molecular weight and  $N_A$  is Avogadro's number.

Using the vector potential of the wavefield  $\mathbf{A}$ , an expression for the perturbed Hamiltonian of a hydrogen-like atom coupled to the radiation field may be written as

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 - r_e c \mathbf{A} \cdot \mathbf{P} + \frac{r_e^2}{2} \mathbf{A}^2, \quad (4.2.6.19)$$

where  $\hat{\mathcal{H}}_0$  is the Hamiltonian for the unperturbed atom and  $\mathbf{P} = i\hbar \nabla$ .

After application of the second-order perturbation theory, the matrix element may be deduced to be

$$M = (\epsilon_i \cdot \epsilon_f^*) f_0(\Delta) + \frac{1}{m} \langle 1|T_1|1 \rangle + \frac{1}{m} \langle 1|T_2|1 \rangle. \quad (4.2.6.20)$$

In this equation, the initial and final wavefunctions are designated as  $\langle 1|$  and  $|1 \rangle$ , respectively, and the terms  $T_1$  and  $T_2$  are given by

$$T_1 = \epsilon_f \cdot \mathbf{P} \exp(-i\mathbf{k}_f \cdot \mathbf{r}) \frac{1}{E_1 - \mathcal{H}_0 + \hbar\omega + i\xi} \epsilon_i \cdot \mathbf{P} \exp(-i\mathbf{k}_i \cdot \mathbf{r})$$

and

$$T_2 = \epsilon_i \cdot \mathbf{P} \exp(-i\mathbf{k}_i \cdot \mathbf{r}) \frac{1}{E_1 - \mathcal{H}_0 + \hbar\omega + i\xi} \epsilon_f \cdot \mathbf{P} \exp(-i\mathbf{k}_f \cdot \mathbf{r})$$

where  $\xi$  is an infinitesimal positive quantity.

The first term of equation (4.2.6.20) corresponds to the atomic scattering factor and is identical to the value given by classical theory. The terms involving  $T_1$  and  $T_2$  correspond to the dispersion corrections. Equation (4.2.6.20) contains no terms to account for radiation damping. More complete theories take the effect of the finite width of the radiating level into account.

It is necessary to realize that the atomic scattering factor depends on both the photon's frequency  $\omega$  and the momentum vector  $\Delta$ . To emphasize this dependence, equation (4.2.6.7) is rewritten as

$$f(\omega, \Delta) = f_0(\Delta) + f'(\omega, \Delta) + if''(\omega, \Delta). \quad (4.2.6.21)$$

In the dipole approximation, it can be shown that

$$f'(\omega, 0) = \frac{2}{\pi} P \int_0^{\infty} \frac{\omega' f''(\omega', 0)}{\omega^2 - \omega'^2} d\omega', \quad (4.2.6.22)$$

which may be compared with equation (4.2.6.15) and

$$f''(\omega, 0) = \frac{\omega}{4\pi r_e c} \sigma(\omega), \quad (4.2.6.23)$$

which may be compared with equation (4.2.6.14).

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 electron shells 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 wavefunctions of the hydrogen-like atom, analytical expressions may be developed for the photoelectric scattering cross sections. By expansion of the retardation factor  $\exp(-i\mathbf{k} \cdot \mathbf{r})$  as the power series  $1 - i\mathbf{k} \cdot \mathbf{r} - \frac{1}{2}(\mathbf{k} \cdot \mathbf{r})^2 + \dots$ , it is possible to determine dipolar, quadrupolar, and higher-order