

4. PRODUCTION AND PROPERTIES OF RADIATIONS

The rapid development in computing techniques, improvements in materials of construction and experimental equipment, and the use of synchrotron-radiation sources for X-ray scattering experiments have led to the production of a number of reviews of both the theoretical and the experimental aspects of the anomalous scattering of X-rays. Review articles by Gavrilá (1981), Kissel, Pratt, Kane & Roy (1985), and Creagh (1985) discuss both the theoretical and the experimental techniques for the determination of the X-ray dispersion corrections. Creagh (1986) has discussed the use of X-ray anomalous scattering for the characterization of materials, and a review by Helliwell (1984) has described the anomalous scattering by atoms contained in proteins and its use for the solution of the structure of proteins. In a number of papers, Karle (1980, 1984*a,b,c*, 1985) has recently shown how powerful dispersion techniques can be in the solution of crystal structures. Indeed, the high intensity afforded by synchrotron-radiation sources, together with improvements in specimen-handling techniques, has led to the general use of dispersion techniques for the solution of the phase problem in crystal structures. In particular, the MAD (multiple-wavelength anomalous-dispersion) technique is used extensively for the solution of such macromolecular crystal structures as proteins and the like. The origin of the technique lies in the Bijvoet relations, but the implementation and the development of the technique is due to Hendrickson (1994).

In this section, a brief discussion of the physical principles underlying the theoretical tabulations of X-ray scattering will be given. This will be followed by a discussion of experimental techniques for the determination of the dispersion corrections. In the next section, theoretical and experimentally determined values for the dispersion corrections will be compared for a number of elements.

Currently, there is some discussion about the nature of the dispersion corrections: are they to be considered to exhibit tensor characteristics? It is clear that in all the theoretical calculations the atoms are considered to be isolated, and, therefore, if there is a tensor associated with the X-ray scattering, it must be associated with the reaction of the atoms with the polarization state of the incident radiation. Since the property of polarization of the X-ray beam is described by a first-rank tensor, it follows that the form factor must be described by a second-rank tensor (Templeton, 1994). Either the detection system of the experimental equipment must be capable of resolving the change in the polarization states of the incident and scattered radiation, or the incident radiation must be plane polarized for this property to be observable. Except for certain diffractometers at synchrotron-radiation sources, or for specially designed conventional laboratory equipment, it is not possible to determine the polarization states before and after scattering.

To a very good approximation, therefore, one can describe the form factor as being made up of a number of separate components, the largest of which is a zeroth-rank tensor that corresponds to the conventionally accepted description of the form factor. The magnitudes of any of the higher-order tensor components are small compared with this term. Whether or not they are observable depends on the characteristics of the diffraction system used in the experiment. The form-factor formalism in its zeroth-order mode has been used extremely successfully for the solution of crystal structures, the description of wavefields in crystals, the determination of the distribution of electron density in crystal structures, *etc.* as has been shown by Creagh (1993).

It must be stressed that all of the crystal structures solved so far have been solved using the conventionally accepted, zeroth-order, form-factor description of X-ray scattering. As well, all the data concerning the distribution of electron density within crystals have used this description.

Further discussion of this issue will be given in §4.2.6.3.3.4.

4.2.6.1. Definitions

4.2.6.1.1. Rayleigh scattering

When photons interact with atoms, a number of different scattering processes can occur. The dominant scattering mechanisms are: elastic scattering from the bound electrons (Rayleigh scattering); elastic scattering from the nucleus (nuclear Thomson scattering); virtual pair production in the field of the screened nucleus (Delbrück scattering); and inelastic scattering from the bound electrons (Compton scattering).

Of the elastic scattering processes, only Rayleigh scattering has a significant amplitude in the range of photon energies used by crystallographers (< 100 keV). Compton scattering will be discussed elsewhere (Section 4.2.4).

The essential feature of Rayleigh scattering is that the internal energy of the atom remains unchanged in the interaction. The momentum $\hbar\mathbf{k}_i$ and polarization $\boldsymbol{\varepsilon}_i$ of the incident photon may be modified during the process to $\hbar\mathbf{k}_f$ and $\boldsymbol{\varepsilon}_f$

$$(\hbar\mathbf{k}_i, \boldsymbol{\varepsilon}_i) + A \rightarrow A + (\hbar\mathbf{k}_f, \boldsymbol{\varepsilon}_f).$$

4.2.6.1.2. Thomson scattering by a free electron

From classical electromagnetic theory, it can be shown that the fraction of incident intensity scattered by a free electron is, at a position r , φ from the scattering electron,

$$I/I_0 = (r_e/r)^2 \frac{1}{2}(1 + \cos^2 \varphi), \quad (4.2.6.1)$$

where r_e is the classical radius of the electron ($= 2.817938 \times 10^{-15}$ m). The factor $\frac{1}{2}(1 + \cos^2 \varphi)$ arises from the assumption that the electromagnetic wave is initially unpolarized. Should the wave be polarized, the factor is necessarily different from that given in equation (4.2.6.1).

Equation (4.2.6.1) is the basis on which the scattering power of ensembles of electrons is compared.

4.2.6.1.3. Elastic scattering from electrons bound to atoms: the atomic scattering factor, the atomic form factor, and the dispersion corrections

In considering the interaction of a photon with electrons bound in an atom, one assumes that each electron scatters independently of its fellows, and that the total scattering power of the atom is the sum of the contributions from all the electrons in the atom. Assuming that one can define an electron density $\rho(\mathbf{r})$ for an atom containing a single electron, one can show that the scattering power of that atom relative to the scattering power of a Thomson free electron is

$$f(\Delta) = \int \rho(\mathbf{r}) \exp[i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r}] dV, \quad (4.2.6.2)$$

where

$$\begin{aligned} \Delta &= \mathbf{k}_f - \mathbf{k}_i \equiv \text{change in photon momentum} \\ &= 2|k| \sin(\theta/2), \end{aligned}$$

θ being the total angle of scattering of the photon.

The scattering power for the atom relative to a free electron is referred to as the *atomic form factor* or the *atomic scattering factor* of the atom.

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 ω_n and a damping factor κ_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 ω_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

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