

## 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  $r$ ,  $\varphi$  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

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

$\theta$  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.