

## 1.2. The structure factor

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### 1.2.1. Introduction

The *structure factor* is the central concept in structure analysis by diffraction methods. Its modulus is called the *structure amplitude*. The structure amplitude is a function of the indices of the set of scattering planes  $h$ ,  $k$  and  $l$ , and is defined as the amplitude of scattering by the contents of the crystallographic unit cell, expressed in units of scattering. For X-ray scattering, that unit is the scattering by a single electron ( $2.82 \times 10^{-15}$  m), while for neutron scattering by atomic nuclei, the unit of scattering length of  $10^{-14}$  m is commonly used. The complex form of the structure factor means that the phase of the scattered wave is not simply related to that of the incident wave. However, the observable, which is the scattered intensity, must be real. It is proportional to the square of the scattering amplitude (see, *e.g.*, Lipson & Cochran, 1966).

The structure factor is directly related to the distribution of scattering matter in the unit cell which, in the X-ray case, is the electron distribution, time-averaged over the vibrational modes of the solid.

In this chapter we will discuss structure-factor expressions for X-ray and neutron scattering, and, in particular, the modelling that is required to obtain an analytical description in terms of the features of the electron distribution and the vibrational displacement parameters of individual atoms. We concentrate on the most basic developments; for further details the reader is referred to the cited literature.

### 1.2.2. General scattering expression for X-rays

The total scattering of X-rays contains both elastic and inelastic components. Within the first-order Born approximation (Born, 1926) it has been treated by several authors (*e.g.* Waller & Hartree, 1929; Feil, 1977) and is given by the expression

$$I_{\text{total}}(\mathbf{S}) = I_{\text{classical}} \sum_n \left| \int \psi_n^* \exp(2\pi i \mathbf{S} \cdot \mathbf{r}_j) \psi_0 \, d\mathbf{r} \right|^2, \quad (1.2.2.1)$$

where  $I_{\text{classical}}$  is the classical Thomson scattering of an X-ray beam by a free electron, which is equal to  $(e^2/mc^2)^2(1 + \cos^2 2\theta)/2$  for an unpolarized beam of unit intensity,  $\psi$  is the  $n$ -electron space-wavefunction expressed in the  $3n$  coordinates of the electrons located at  $\mathbf{r}_j$  and the integration is over the coordinates of all electrons.  $\mathbf{S}$  is the scattering vector of length  $2 \sin \theta/\lambda$ .

The coherent elastic component of the scattering, in units of the scattering of a free electron, is given by

$$I_{\text{coherent, elastic}}(\mathbf{S}) = \left| \int \psi_0^* \sum_j \exp(2\pi i \mathbf{S} \cdot \mathbf{r}_j) \psi_0 \, d\mathbf{r} \right|^2. \quad (1.2.2.2)$$

If integration is performed over all coordinates but those of the  $j$ th electron, one obtains after summation over all electrons

$$I_{\text{coherent, elastic}}(\mathbf{S}) = \left| \int \rho(\mathbf{r}) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) \, d\mathbf{r} \right|^2, \quad (1.2.2.3)$$

where  $\rho(\mathbf{r})$  is the electron distribution. The scattering amplitude  $A(\mathbf{S})$  is then given by

$$A(\mathbf{S}) = \int \rho(\mathbf{r}) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) \, d\mathbf{r} \quad (1.2.2.4a)$$

or

$$A(\mathbf{S}) = \hat{F}\{\rho(\mathbf{r})\}, \quad (1.2.2.4b)$$

where  $\hat{F}$  is the Fourier transform operator.

### 1.2.3. Scattering by a crystal: definition of a structure factor

In a crystal of infinite size,  $\rho(\mathbf{r})$  is a three-dimensional periodic function, as expressed by the convolution

$$\rho_{\text{crystal}}(\mathbf{r}) = \sum_n \sum_m \sum_p \rho_{\text{unit cell}}(\mathbf{r}) * \delta(\mathbf{r} - n\mathbf{a} - m\mathbf{b} - p\mathbf{c}), \quad (1.2.3.1)$$

where  $n$ ,  $m$  and  $p$  are integers, and  $\delta$  is the Dirac delta function.

Thus, according to the Fourier convolution theorem,

$$\begin{aligned} A(\mathbf{S}) &= \hat{F}\{\rho(\mathbf{r})\} \\ &= \sum_n \sum_m \sum_p \hat{F}\{\rho_{\text{unit cell}}(\mathbf{r})\} \hat{F}\{\delta(\mathbf{r} - n\mathbf{a} - m\mathbf{b} - p\mathbf{c})\}, \end{aligned} \quad (1.2.3.2)$$

which gives

$$A(\mathbf{S}) = \hat{F}\{\rho_{\text{unit cell}}(\mathbf{r})\} \sum_h \sum_k \sum_l \delta(\mathbf{S} - h\mathbf{a}^* - k\mathbf{b}^* - l\mathbf{c}^*). \quad (1.2.3.3)$$

Expression (1.2.3.3) is valid for a crystal with a very large number of unit cells, in which particle-size broadening is negligible. Furthermore, it does not account for multiple scattering of the beam within the crystal. Because of the appearance of the delta function, (1.2.3.3) implies that  $\mathbf{S} = \mathbf{H}$  with  $\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ .

The first factor in (1.2.3.3), the scattering amplitude of one unit cell, is defined as the structure factor  $F$ :

$$F(\mathbf{H}) = \hat{F}\{\rho_{\text{unit cell}}(\mathbf{r})\} = \int_{\text{unit cell}} \rho(\mathbf{r}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) \, d\mathbf{r}. \quad (1.2.3.4)$$

### 1.2.4. The isolated-atom approximation in X-ray diffraction

To a reasonable approximation, the unit-cell density can be described as a superposition of isolated, spherical atoms located at  $\mathbf{r}_j$ .

$$\rho_{\text{unit cell}}(\mathbf{r}) = \sum_j \rho_{\text{atom},j}(\mathbf{r}) * \delta(\mathbf{r} - \mathbf{r}_j). \quad (1.2.4.1)$$

Substitution in (1.2.3.4) gives

$$F(\mathbf{H}) = \sum_j \hat{F}\{\rho_{\text{atom},j}\} \hat{F}\{\delta(\mathbf{r} - \mathbf{r}_j)\} = \sum_j f_j \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j) \quad (1.2.4.2a)$$

or

$$\begin{aligned} F(h, k, l) &= \sum_j f_j \exp 2\pi i (hx_j + ky_j + lz_j) \\ &= \sum_j f_j \{ \cos 2\pi (hx_j + ky_j + lz_j) \\ &\quad + i \sin 2\pi (hx_j + ky_j + lz_j) \}. \end{aligned} \quad (1.2.4.2b)$$

$f_j(S)$ , the spherical atomic scattering factor, or form factor, is the Fourier transform of the spherically averaged atomic density  $\rho_j(r)$ , in which the polar coordinate  $r$  is relative to the nuclear position.  $f_j(S)$  can be written as (James, 1982)