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 (2.82×10^{-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, ψ 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

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

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

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

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 δ is the Dirac delta function.

Thus, according to the Fourier convolution theorem,

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

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)

$$f_j(S) = \int\limits_{\text{atom}} \rho_j(r) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) \, d\mathbf{r}$$

$$= \int\limits_{\vartheta=0}^{\pi} \int\limits_{\varphi=0}^{2\pi} \int\limits_{r=0}^{\infty} \rho_j(r) \exp(2\pi i S r \cos\vartheta) r^2 \sin\vartheta \, dr \, d\vartheta \, d\varphi$$

$$= \int\limits_0^{\infty} 4\pi r^2 \rho_j(r) \frac{\sin 2\pi S r}{2\pi S r} \, dr \equiv \int\limits_0^{\infty} 4\pi r^2 \rho_j(r) j_0(2\pi S r) \, dr$$

$$\equiv \langle j_0 \rangle, \tag{1.2.4.3}$$

where $j_0(2\pi S r)$ is the zero-order spherical Bessel function.

$\rho_j(r)$ represents either the static or the dynamic density of atom j. In the former case, the effect of thermal motion, treated in Section 1.2.9 and following, is not included in the expression.

When scattering is treated in the second-order Born approximation, additional terms occur which are in particular of importance for X-ray wavelengths with energies close to absorption edges of atoms, where the participation of free and bound excited states in the scattering process becomes very important, leading to *resonance scattering*. [Resonance scattering is referred to as anomalous scattering in the older literature, but this misnomer is avoided in the current chapter.] Inclusion of such contributions leads to two extra terms, which are both wavelength- and scattering-angle-dependent:

$$f_j(S, \lambda) = f_j^0(S) + f_j'(S, \lambda) + i f_j''(S, \lambda). \tag{1.2.4.4}$$

The treatment of resonance effects is beyond the scope of this chapter. We note however (*a*) that to a reasonable approximation the *S*-dependence of f_j' and f_j'' can be neglected, (*b*) that f_j' and f_j'' are not independent, but related through the Kramers–Kronig transformation, and (*c*) that in an anisotropic environment the atomic scattering factor becomes anisotropic, and accordingly is described as a tensor property. Detailed descriptions and appropriate references can be found in Materlick *et al.* (1994) and in Section 4.2.6 of *IT* C (2004).

The structure-factor expressions (1.2.4.2) can be simplified when the crystal class contains nontrivial symmetry elements. For example, when the origin of the unit cell coincides with a centre of symmetry ($x, y, z \rightarrow -x, -y, -z$) the sine term in (1.2.4.2*b*) cancels when the contributions from the symmetry-related atoms are added, leading to the expression

$$F(\mathbf{H}) = 2 \sum_{j=1}^{N/2} f_j \cos 2\pi(hx_j + ky_j + lz_j), \tag{1.2.4.2c}$$

where the summation is over the unique half of the unit cell only.

Further simplifications occur when other symmetry elements are present. They are treated in Chapter 1.4, which also contains a complete list of symmetry-specific structure-factor expresions valid in the spherical-atom isotropic-temperature-factor approximation.

1.2.5. Scattering of thermal neutrons

1.2.5.1. Nuclear scattering

The scattering of neutrons by atomic nuclei is described by the atomic scattering length b, related to the total cross section σ_{total} by the expression $\sigma_{\text{total}} = 4\pi b^2$. At present, there is no theory of nuclear forces which allows calculation of the scattering length, so that experimental values are to be used. Two types of nuclei can be distinguished (Squires, 1978). In the first type, the scattering is a resonance phenomenon and is associated with the formation of a compound nucleus (consisting of the original nucleus plus a neutron) with an energy close to that of an excited state. In the second type, the compound nucleus is not near an excited state and the scattering length is essentially real and independent of the energy of the incoming neutron. In either case, b is independent of the Bragg angle θ, unlike the X-ray form factor, since the nuclear dimensions are very small relative to the wavelength of thermal neutrons.

The scattering length is not the same for different isotopes of an element. A random distribution of isotopes over the sites occupied by that element leads to an incoherent contribution, such that effectively $\sigma_{\text{total}} = \sigma_{\text{coherent}} + \sigma_{\text{incoherent}}$. Similarly for nuclei with nonzero spin, a spin incoherent scattering occurs as the spin states are, in general, randomly distributed over the sites of the nuclei.

For free or loosely bound nuclei, the scattering length is modified by $b_{\text{free}} = [M/(m + M)]b$, where M is the mass of the nucleus and m is the mass of the neutron. This effect is of consequence only for the lightest elements. It can, in particular, be of significance for hydrogen atoms. With this in mind, the structure-factor expression for elastic scattering can be written as

$$F(\mathbf{H}) = \sum_j b_{j,\,\text{coherent}} \exp 2\pi i(hx_j + ky_j + lz_j) \tag{1.2.4.2d}$$

by analogy to (1.2.4.2*b*).

1.2.5.2. Magnetic scattering

The interaction between the magnetic moments of the neutron and the unpaired electrons in solids leads to magnetic scattering. The total elastic scattering including both the nuclear and magnetic contributions is given by

$$|F(\mathbf{H})|^2_{\text{total}} = |F_N(\mathbf{H}) + \mathbf{Q}(\mathbf{H}) \cdot \hat{\boldsymbol{\lambda}}|^2, \tag{1.2.5.1a}$$

where the unit vector $\hat{\boldsymbol{\lambda}}$ describes the polarization vector for the neutron spin, $F_N(\mathbf{H})$ is given by (1.2.4.2*b*) and $\mathbf{Q}$ is defined by

$$\mathbf{Q} = \frac{mc}{eh} \int \hat{\mathbf{H}} \times [\mathbf{M}(\mathbf{r}) \times \hat{\mathbf{H}}] \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) \, d\mathbf{r}. \tag{1.2.5.2a}$$

$\mathbf{M}(\mathbf{r})$ is the vector field describing the electron-magnetization distribution and $\hat{\mathbf{H}}$ is a unit vector parallel to $\mathbf{H}$.

$\mathbf{Q}$ is thus proportional to the projection of $\mathbf{M}$ onto a direction orthogonal to $\mathbf{H}$ in the plane containing $\mathbf{M}$ and $\mathbf{H}$. The magnitude of this projection depends on $\sin\alpha$, where α is the angle between $\mathbf{Q}$ and $\mathbf{H}$, which prevents magnetic scattering from being a truly three-dimensional probe. If all moments $\mathbf{M}(\mathbf{r})$ are collinear, as may be achieved in paramagnetic materials by applying an external field, and for the maximum signal ($\mathbf{H}$ orthogonal to $\mathbf{M}$), (1.2.5.2*a*) becomes

$$\mathbf{Q} = \mathbf{M}(\mathbf{H}) = \frac{mc}{eh} \int \mathbf{M}(\mathbf{r}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) \, d\mathbf{r} \tag{1.2.5.2b}$$

and (1.2.5.1*a*) gives

$$|F|^2_{\text{total}} = |F_N(\mathbf{H}) - M(\mathbf{H})|^2 \tag{1.2.5.1b}$$

and

$$|F|^2_{\text{total}} = |F_N(\mathbf{H}) + M(\mathbf{H})|^2$$

for neutrons parallel and antiparallel to $\mathbf{M}(\mathbf{H})$, respectively.

1.2.6. Effect of bonding on the atomic electron density within the spherical-atom approximation: the kappa formalism

A first improvement beyond the isolated-atom formalism is to allow for changes in the radial dependence of the atomic electron distribution.

Such changes may be due to electronegativity differences which lead to the transfer of electrons between the valence shells of different atoms. The electron transfer introduces a change in