

1.2. THE STRUCTURE FACTOR

$$\begin{aligned}
 f_j(S) &= \int_{\text{atom}} \rho_j(r) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) \, d\mathbf{r} \\
 &= \int_{\nu=0}^{\pi} \int_{\varphi=0}^{2\pi} \int_{r=0}^{\infty} \rho_j(r) \exp(2\pi i S r \cos \vartheta) r^2 \sin \vartheta \, dr \, d\vartheta \, d\varphi \\
 &= \int_0^{\infty} 4\pi r^2 \rho_j(r) \frac{\sin 2\pi S r}{2\pi S r} \, dr \equiv \int_0^{\infty} 4\pi r^2 \rho_j(r) j_0(2\pi S r) \, dr \\
 &\equiv \langle j_0 \rangle,
 \end{aligned} \tag{1.2.4.3}$$

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 (1.2.4.2b) 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 expressions 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 (1.2.4.2b).

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

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

where the unit vector $\hat{\lambda}$ describes the polarization vector for the neutron spin, $F_N(\mathbf{H})$ is given by (1.2.4.2b) 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}), (1.2.5.2a) 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 (1.2.5.1a) gives

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

and

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

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

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the screening of the nuclear charge by the electrons and therefore affects the radial dependence of the atomic electron distribution (Coulson, 1961). A change in radial dependence of the density may also occur in a purely covalent bond, as, for example, in the H₂ molecule (Ruedenberg, 1962). It can be expressed as

$$\rho'_{\text{valence}}(r) = \kappa^3 \rho_{\text{valence}}(\kappa r) \quad (1.2.6.1)$$

(Coppens *et al.*, 1979), where ρ' is the modified density and κ is an expansion/contraction parameter, which is > 1 for valence-shell contraction and < 1 for expansion. The κ^3 factor results from the normalization requirement.

The valence density is usually defined as the outer electron shell from which charge transfer occurs. The inner or core electrons are much less affected by the change in occupancy of the outer shell and, in a reasonable approximation, retain their radial dependence.

The corresponding structure-factor expression is

$$F(\mathbf{H}) = \sum_j [P_{j,\text{core}} f_{j,\text{core}}(H) + P_{j,\text{valence}} f_{j,\text{valence}}(H/\kappa)] \times \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j), \quad (1.2.6.2)$$

where $P_{j,\text{core}}$ and $P_{j,\text{valence}}$ are the number of electrons (not necessarily integral) in the core and valence shell, respectively, and the atomic scattering factors $f_{j,\text{core}}$ and $f_{j,\text{valence}}$ are normalized to one electron. Here and in the following sections, the resonant-scattering contributions are incorporated in the core scattering.

1.2.7. Beyond the spherical-atom description: the atom-centred spherical harmonic expansion

1.2.7.1. Direct-space description of apherical atoms

Even though the spherical-atom approximation is often adequate, atoms in a crystal are in a nonspherical environment; therefore, an accurate description of the atomic electron density requires nonspherical density functions. In general, such density functions can be written in terms of the three polar coordinates r , θ and φ . Under the assumption that the radial and angular parts can be separated, one obtains for the density function:

$$\Phi(r, \theta, \varphi) = R(r)\Theta(\theta, \varphi). \quad (1.2.7.1)$$

The angular functions Θ are based on the spherical harmonic functions Y_{lm} defined by

$$Y_{lm}(\theta, \varphi) = (-1)^m \left[\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} P_l^m(\cos \theta) \exp(im\varphi), \quad (1.2.7.2a)$$

with $-l \leq m \leq l$, where $P_l^m(\cos \theta)$ are the associated Legendre polynomials (see Arfken, 1970).

$$P_l^m(x) = (1-x^2)^{|m|/2} \frac{d^{|m|} P_l(x)}{dx^{|m|}},$$

$$P_l(x) = \frac{1}{l!} \frac{d^l}{dx^l} [(x^2-1)^l].$$

The real spherical harmonic functions y_{lm} , $0 \leq m \leq l$, $p = +$ or $-$ are obtained as a linear combination of Y_{lm} :

$$\begin{aligned} y_{lm+}(\theta, \psi) &= \left[\frac{(2l+1)(l-|m|)!}{2\pi(1+\delta_{m0})(l+|m|)!} \right]^{1/2} P_l^m(\cos \theta) \cos m\varphi \\ &= N_{lm} P_l^m(\cos \theta) \cos m\varphi \\ &= (-1)^m (Y_{lm} + Y_{l,-m}) \end{aligned} \quad (1.2.7.2b)$$

and

$$\begin{aligned} y_{lm-}(\theta, \psi) &= N_{lm} P_l^m(\cos \theta) \sin m\varphi \\ &= (-1)^m (Y_{lm} - Y_{l,-m}) / (2i). \end{aligned} \quad (1.2.7.2c)$$

The normalization constants N_{lm} are defined by the conditions

$$\int y_{lm}^2 d\Omega = 1, \quad (1.2.7.3a)$$

which are appropriate for normalization of wavefunctions. An alternative definition is used for charge-density basis functions:

$$\int |d_{lm}| d\Omega = 2 \text{ for } l > 0 \text{ and } \int |d_{lm}| d\Omega = 1 \text{ for } l = 0. \quad (1.2.7.3b)$$

The functions y_{lm} and d_{lm} differ only in the normalization constants. For the spherically symmetric function d_{00} , a population parameter equal to one corresponds to the function being populated by one electron. For the nonspherical functions with $l > 0$, a population parameter equal to one implies that one electron has shifted from the negative to the positive lobes of the function.

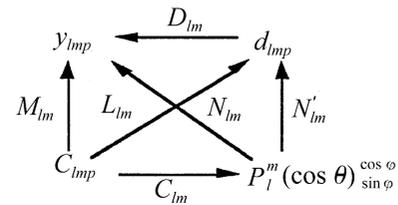
The functions y_{lm} and d_{lm} can be expressed in Cartesian coordinates, such that

$$y_{lm} = M_{lm} c_{lm} \quad (1.2.7.4a)$$

and

$$d_{lm} = L_{lm} c_{lm}, \quad (1.2.7.4b)$$

where the c_{lm} are Cartesian functions. The relations between the various definitions of the real spherical harmonic functions are summarized by



in which the direction of the arrows and the corresponding conversion factors X_{lm} define expressions of the type (1.2.7.4). The expressions for c_{lm} with $l \leq 4$ are listed in Table 1.2.7.1, together with the normalization factors M_{lm} and L_{lm} .

The spherical harmonic functions are mutually orthogonal and form a complete set, which, if taken to sufficiently high order, can be used to describe any arbitrary angular function.

The spherical harmonic functions are often referred to as multipoles since each represents the components of the charge distribution $\rho(\mathbf{r})$, which gives nonzero contribution to the integral $\Theta_{lm} = \int \rho(\mathbf{r}) c_{lm} r^l d\mathbf{r}$, where Θ_{lm} is an electrostatic multipole moment. Terms with increasing l are referred to as *monopolar* ($l = 0$), *dipolar* ($l = 1$), *quadrupolar* ($l = 2$), *octapolar* ($l = 3$), *hexadecapolar* ($l = 4$), *triacontadipolar* ($l = 5$) and *hexacontatetrapolar* ($l = 6$).

Site-symmetry restrictions for the real spherical harmonics as given by Kara & Kurki-Suonio (1981) are summarized in Table 1.2.7.2.

In cubic space groups, the spherical harmonic functions as defined by equations (1.2.7.2) are no longer linearly independent. The appropriate basis set for this symmetry consists of the 'Kubic harmonics' of Von der Lage & Bethe (1947). Some low-order terms are listed in Table 1.2.7.3. Both wavefunction and density-function normalization factors are specified in Table 1.2.7.3.

A related basis set of angular functions has been proposed by Hirshfeld (1977). They are of the form $\cos^n \theta_k$, where θ_k is the angle with a specified set of $(n+1)(n+2)/2$ polar axes. The Hirshfeld functions are identical to a sum of spherical harmonics