

## 6.1. Intensity of diffracted intensities

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### 6.1.1. X-ray scattering

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#### 6.1.1.1. Coherent (Rayleigh) scattering

An electromagnetic wave incident on a tightly bound electron is scattered coherently. For an incident wave of unit amplitude with the electric vector normal to the plane of the reflection  $xOy$  containing the incident and diffracted beams (Fig. 6.1.1.1), the amplitude of the scattered wave at a distance  $r$  is

$$r_e/r, \quad (6.1.1.1)$$

where  $r_e = (\mu_0/4\pi)(e^2/m)$  is the classical radius of the electron ( $2.818 \times 10^{-15}$  m).

For a wave with the electric vector parallel to the plane  $xOy$ , the amplitude of the scattered wave is

$$\frac{r_e}{r} \cos 2\theta. \quad (6.1.1.2)$$

For unpolarized incident radiation with unit mean amplitude, the amplitude of the scattered wave is given by the Thomson formula

$$\frac{r_e}{r} \left\{ \frac{1 + \cos^2 2\theta}{2} \right\}^{1/2}. \quad (6.1.1.3)$$

The corresponding intensity of scattering per unit solid angle is

$$I_e = I_o r_e^2 \left[ \frac{1 + \cos^2 2\theta}{2} \right] \quad (6.1.1.4)$$

for an unpolarized incident beam of intensity  $I_o$ .

#### 6.1.1.2. Incoherent (Compton) scattering

For scattering from a free electron, the quantum nature of the radiation must be considered. Under the impact of a photon with energy  $hc/\lambda$ , momentum  $h/\lambda$ , the recoil of an electron, initially at rest, results in a change in wavelength of

$$\Delta\lambda = \frac{2h}{mc} \sin^2 \theta, \quad (6.1.1.5)$$

a geometry similar to that in Fig. 6.1.1.1 being assumed. There is no fixed relationship between the phases of the incident and scattered beams – *i.e.* the scattering is incoherent. The intensity  $I_e$  predicted by the Thomson formula is modified by the correction factor  $[\lambda/(\lambda + \Delta\lambda)]^3$ .

#### 6.1.1.3. Atomic scattering factor

For scattering by atomic electrons there are both coherent and incoherent components, with total intensity given by the

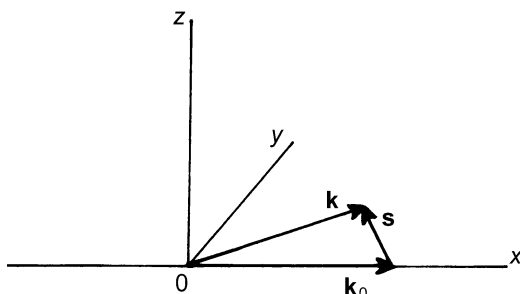


Fig. 6.1.1.1. Scattering by an electron.  $\mathbf{k}_0$  and  $\mathbf{k}$  are the incident and scattered wavevectors, respectively.

Thomson formula. The phase for coherent scattering is by convention related to that of a free electron at the nucleus. There is a phase shift of  $\pi$  for scattering from a free electron. The scattering from an element of electron density  $\rho(\mathbf{r}_j)$  has a phase difference of  $i\mathbf{S} \cdot \mathbf{r}_j$ , where

$$\mathbf{S} = 2\pi\mathbf{s}. \quad (6.1.1.6)$$

The total amplitude for coherent scattering from the  $j$ th electron is

$$f_j = \int \rho(\mathbf{r}_j) \exp(i\mathbf{S} \cdot \mathbf{r}_j) d\mathbf{r}_j. \quad (6.1.1.7)$$

The intensity of coherent scattering is

$$I_{\text{coh}} = I_e f_j^2. \quad (6.1.1.8)$$

The intensity of Compton scattering from that electron is

$$I_{\text{incoh}} = I_e - I_{\text{coh}} = I_e(1 - f_j^2). \quad (6.1.1.9)$$

For an atom with atomic number  $Z$ ,

$$I_{\text{coh}} = I_e \left( \sum_{j=1}^Z f_j \right)^2 \quad (6.1.1.10)$$

and

$$I_{\text{incoh}} = I_e \left( Z - f_j^2 - \sum_{j,k} f_{jk} \right), \quad (6.1.1.11)$$

where the correction term

$$f_{jk} = \int \psi_j^* \psi_k \exp(i\mathbf{S} \cdot \mathbf{r}) d\mathbf{r}, \quad (6.1.1.12)$$

owing to exchange, meets the requirements of the Pauli exclusion principle.

Atomic scattering factors for neutral atoms are listed in Table 6.1.1.1 for the range  $0 < (\sin \theta)/\lambda < 6.0 \text{ \AA}^{-1}$ . The values for hydrogen are calculated from the analytical solution to the Schrödinger equation and are effectively zero for  $(\sin \theta)/\lambda > 1.5 \text{ \AA}^{-1}$ . Those for heavier atoms are for relativistic wavefunctions, based on the calculations of Doyle & Turner (1968) using the wavefunctions of Coulthard (1967) (designated RHF in Table 6.1.1.1), or on those of Cromer & Waber (1968) using the wavefunctions of Mann (1968a) (designated \*RHF). The latter are based on a more exact treatment of potential that allows for the finite size of the nucleus, but the effect on the scattering factors is small. The calculations of Cromer & Waber (1968) were originally made for  $0 < (\sin \theta)/\lambda < 2.0 \text{ \AA}^{-1}$ , but these have been extended to  $6 \text{ \AA}^{-1}$  by Fox, O'Keefe & Tabernor (1989); this has been done because there are increasing numbers of applications for high-angle scattering factors.

For a detailed study of the effect of changes in the electron density due to chemical bonding and lattice formation, a more general procedure is necessary, as described in Subsection 6.1.1.4. The changes due to chemical bonding are small in absolute terms, and are relatively small except in the case of hydrogen.

A more approximate treatment is adequate for many purposes. An isotropic approximation to the scattering factor for bonded hydrogen, based on an analysis of the hydrogen molecule by Stewart, Davidson & Simpson (1965), is listed in Table 6.1.1.2.

Scattering for ionic models of solids may be related to the scattering factors for the corresponding free ions. Values for