

6.1. INTENSITY OF DIFFRACTED INTENSITIES

Table 6.1.1.2. Spherical bonded hydrogen-atom scattering factors from Stewart, Davidson & Simpson (1965)

$(\sin \theta)/\lambda$ (\AA^{-1})	f	$(\sin \theta)/\lambda$ (\AA^{-1})	f
0.0000	1.0000	0.7729	0.0254
0.0215	0.9924	0.8158	0.0208
0.0429	0.9704	0.8588	0.0171
0.0644	0.9352	0.9017	0.0140
0.0859	0.8892	0.9447	0.0116
0.1073	0.8350	0.9876	0.0096
0.1288	0.7752	1.0305	0.0080
0.1503	0.7125	1.0735	0.0066
0.1718	0.6492	1.1164	0.0056
0.1932	0.5871	1.1593	0.0047
0.2147	0.5277	1.2023	0.0040
0.2576	0.4201	1.2452	0.0035
0.3006	0.3301	1.2882	0.0031
0.3435	0.2573	1.3311	0.0027
0.3864	0.1998	1.3740	0.0025
0.4294	0.1552	1.4170	0.0022
0.4723	0.1208	1.4599	0.0020
0.5153	0.0945	1.5029	0.0018
0.5582	0.0744	1.5458	0.0016
0.6011	0.0592	1.5887	0.0015
0.6441	0.0474	1.6317	0.0013
0.6870	0.0383	1.6746	0.0011
0.7300	0.0311	1.7176	0.0010

some of the more chemically significant ions are listed in Table 6.1.1.3. For H^- , Li^+ and Be^{2+} these are based on the correlated electron calculations of Thakkar & Smith (1992). For other ions lighter than rubidium, values are based on the Hartree–Fock calculations of Cromer & Mann (1968), using the wavefunctions of Mann (1968*b*). For the heavier ions, the calculations are by Cromer & Waber (1968), based on relativistic Dirac–Slater wavefunctions, which are a good approximation to the corresponding relativistic Hartree–Fock wavefunctions. If ionic scattering factors are required for values of $(\sin \theta)/\lambda$ greater than those shown in Table 6.1.1.3, the free-atom scattering factors of Table 6.1.1.1 can be used because high-angle scattering is dominated by core electrons and is therefore very little affected by ionicity.

6.1.1.3.1. Scattering-factor interpolation

A general treatment of interpolation is complicated by possible difficulties resulting from singularities in tabulated functions. The interpolation of scattering factors does not involve such problems, however, and a more restricted treatment suffices.

An iterative method, applicable to a function $f(x)$ tabulated at arbitrary values x_0, x_1, \dots, x_n is due to Aitken. $f(x|x_0, x_1, \dots, x_k)$ is the polynomial that coincides with the tabulated values at x_0, x_1, \dots, x_k .

$$\begin{aligned}
 f(x|x_0, x_1) &= \frac{1}{x_1 - x_0} \begin{vmatrix} f_0 x_0 - x \\ f_1 x_1 - x \end{vmatrix} \\
 f(x|x_0, x_1, x_2) &= \frac{1}{x_2 - x_1} \begin{vmatrix} f(x|x_0, x_1) & x_1 - x \\ f(x|x_0, x_2) & x_2 - x \end{vmatrix} \\
 f(x|x_0, x_1, x_2, x_3) &= \frac{1}{x_3 - x_2} \begin{vmatrix} f(x|x_0, x_1, x_2) & x_2 - x \\ f(x|x_0, x_1, x_3) & x_3 - x \end{vmatrix}.
 \end{aligned}
 \tag{6.1.1.13}$$

Iteration is continued until increasing k does not change the interpolated value significantly.

Another interpolation formula, due to Lagrange, is

$$f(x) = \sum_{i=0}^n l_i(x) f_i + R_n(x),$$

where

$$l_i(x) = \frac{\pi_n(x)}{(x - x_i)\pi'_n(x_i)}$$

and

$$R_n(x) = \pi_n(x)[x_0, x_1, \dots, x_n, x]. \tag{6.1.1.14}$$

$\pi_n(x)$ is $(x - x_0)(x - x_1)\dots(x - x_n)$ and $\pi'_n(x)$ is its derivative, so that

$$\begin{aligned} \pi'_n(x_k) &= (x_k - x_0)(x_k - x_1)\dots(x_k - x_{k-1}) \\ &\quad \times (x_k - x_{k+1})\dots(x_k - x_n) \end{aligned}$$

while

$$\begin{aligned} [x_0, x_1] &= \frac{f_0 - f_1}{x_0 - x_1} \\ [x_0, x_1, x_2] &= \frac{[x_0, x_1] - [x_1, x_2]}{x_0 - x_2} \\ [x_0, x_1, \dots, x_n] &= \sum_{k=0}^n \frac{f_k}{\pi'_n(x_k)}. \end{aligned}$$

For the scattering factors of Tables 6.1.1.1 and 6.1.1.3, the expansion

$$f(\sin \theta/\lambda) = \sum_{i=1}^4 a_i \exp(-b_i \sin^2 \theta/\lambda^2) + c \tag{6.1.1.15}$$

has been found to be particularly effective. The coefficients listed in Table 6.1.1.4 give a close fit to the atomic scattering curves over the range $0 < (\sin \theta)/\lambda < 2.0 \text{\AA}^{-1}$. Table 6.1.1.4 also contains the maximum and minimum deviations from the true curve, and the mean of the magnitude of the deviation. For $2.0 \text{\AA}^{-1} < (\sin \theta)/\lambda < 6.0 \text{\AA}^{-1}$, Fox *et al.* (1989) have shown that (6.1.1.15) is highly inaccurate, and they produced a ‘logarithmic polynomial’ curve-fitting routine based on the equation

$$\ln\{f[(\sin \theta)/\lambda]\} = \sum_{i=0}^3 a_i s^i \tag{6.1.1.16}$$

for these high angles. The a_i values listed in Table 6.1.1.5 give a close fit to the atomic scattering factor curves over the range $2.0 < (\sin \theta)/\lambda < 6.0 \text{\AA}^{-1}$. Because f varies slowly with $(\sin \theta)/\lambda$ at these high angles, four parameters are all that is necessary for accurate fitting. Confirmation of this is given in Table 6.1.1.5 where the correlation coefficients, C , associated with each fit are also shown, and it can be seen that these are close to 1.0 in every case.

6.1.1.4. Generalized scattering factors

For bound atoms, it may be necessary to account for the perturbation of the electron density by interaction with other atoms, and to analyse its effect on the scattering.

The generalized scattering factor is obtained from the Fourier transform of a perturbed atomic electron-density function. The exponential factor in the transform may be written as an expansion in terms of Legendre polynomials $P_l(\cos \theta)$.†

† Special functions are as given in Abramowitz & Stegun (1964), unless defined otherwise in the text.