Among the many papers relevant to the problem are Mack & Spielberg (1958), Pike & Wilson (1959), Thomsen & Yap (1968*a,b*), Wilson (1965*a,b,c*, 1967, 1971), Wilson, Thomsen & Yap (1965), and Zevin, Umanskij, Khejker & Pančenko (1961). The formulae are complicated, and depend on the measure of location that is adopted for the diffraction profile. In general, however, the variance of the angle is inversely proportional to the number of counts accumulated.

5.2.3. Geometrical and physical aberrations

5.2.3.1. *Aberrations*

The systematic errors are generally called aberrations; they differ from random errors in that in principle they can be calculated for any particular experimental arrangement and the observations corrected for them, leaving only the random error. In practice, of course, the calculation may be difficult. Aberrations can be divided broadly into two classes: (i) geometrical and (ii) physical. The geometrical aberrations are those that depend on the dimensions of the source, specimen, and detector (or of the slits that limit their effective dimensions). In angle-dispersive techniques, the physical aberrations depend on the intensity distribution in the range of wavelengths used, and in both angle- and energy-dispersive techniques they depend on the response characteristics of the detector and associated circuits.

The aberrations shift and distort the diffraction maxima. The study of their effects can be divided into four stages, corresponding to four levels of mathematical difficulty, and the stage to which it is necessary to carry the calculation depends on the purpose in view and the identifiable feature (Subsection 5.2.2.1) of the wavelength distribution that it is intended to adopt as a measure of the position of the line profile. The three usual features are:

(i) the centroid (centre of gravity, mean, average) of the wavelength distribution;

(ii) the peak (mode, maximum); and

(iii) the best overall fit between the observed and the synthesized line profile.

The first of these, the centroid, requires only the first stage of the calculation for the geometrical aberrations and the first and second for the physical; the second, the peak, logically requires all four stages, but approximations can be obtained at the second stage; and the third, the best overall fit, requires all four stages.

The first stage of the calculation is the determination of the effect of the aberration on the centroid of the diffraction maximum, and ordinarily this gives rise to no insurmountable difficulty (Spencer, 1931, 1935, 1937, 1939, 1941, 1949; Wilson, 1950; Ladell, Parrish & Taylor, 1959; Pike & Wilson, 1959). It is all that is required for the correction of centroid positions for geometrical aberrations, which should be strictly additive. There is some limitation for physical aberrations (Edwards & Toman, 1970; Wilson, 1970*b*).

The second stage is the calculation of the mean-square broadening (variance). This can be used to obtain a reasonable approximation to the correction of peak positions over a wide range of Bragg angle (Wilson, 1961; Gale, 1963, 1968). To this approximation, the position of the observed peak is given by

$$(2\theta)_{\rm obs} = (2\theta)_{\rm true} + \langle \Delta(2\theta) \rangle + WI'''/2I'', \qquad (5.2.3.1)$$

where $\langle \Delta(2\theta) \rangle$ is the centroid and W the variance of the geometrical aberrations and I'' and I''' are second and third derivatives of the observed line profile evaluated at its maximum. The physical aberrations of the centroid depend on the variance of the part of the wavelength distribution used in determining the centroid (Wilson, 1958, 1963; Wilson & Delf, 1961). Those of the peak depend on the ratio of the peak intensity I to its second derivative I'' (Wilson, 1961, 1963, 1965*c*).

Often an aberration can be expressed in the form

$$\Delta(2\theta) = KF(2\theta), \qquad (5.2.3.2)$$

where the function F gives the angular variation of the aberration and K depends only on dimensions *etc*. that are fixed for a particular experiment but whose actual measurement is too difficult or tedious. The constant K can then be treated along with the lattice parameters as an adjustable parameter in least-squares refinement (analytical extrapolation; see Subsection 5.2.3.2).

The third stage is the calculation of the line profile corresponding to each geometrical aberration. These aberration profiles can be combined by convolution (folding), either directly or by Fourier methods, and, in the fourth stage, the combined aberration profile can be convoluted with the emission profile of the X-ray source (or the emission profile as trimmed by a monochromator, pulse-height analyser, filter *etc*.) and with the diffraction profile corresponding to the state of strain, crystallite size, *etc*. of the specimen. This calculation of the composite line profile would be a necessary preliminary to an exact use of peak positions or of overall-profile fitting in lattice-parameter determination.

Such calculations were proposed many years ago (for example, by Alexander, 1948, 1950, 1953, 1954), and have been used by Beu and co-workers (see Section 5.2.9), and also by Boom and Smits (Boom & Smits, 1965; Boom, 1966). With the development of more powerful computer methods, such calculations can now be carried out routinely (*e.g*. Cheary & Coelho, 1992, 1994; Kogan & Kupriyanov, 1992; Timmers, Delhez, Tuinstra & Peerdeman, 1992). However, not all the relevant instrumental parameters can in general be determined with sufficient accuracy and overall instrumental line profiles are normally obtained by means of a suitable standard material, for which sample broadening is negligible (Section 5.2.12). There is, however, a related common approach, empirical rather than fundamental, based on the proposal of Rietveld (1967, 1969). Its use in structure determination is treated in detail in Chapter 8.6, and its use in lattice-parameter determination in Section 5.2.6. There seems to be no detailed published study of the accuracy attainable for lattice parameters, but the estimated standard deviations quoted (see, for example, Young, 1988) are comparable with those obtained for simpler structures giving resolved reflections.

5.2.3.2. *Extrapolation, graphical and analytical*

Equation (5.2.1.4) indicates that for a given error in θ the fractional error in the spacing d approaches zero as θ approaches 90°. The errors in θ – expressed as $\Delta(2\theta) = KF(2\theta)$ in (5.2.3.2) – arising from any specified aberration may increase as θ increases, but ordinarily this increase is insufficient to outweigh the effect of the $\cot\theta$ factor. In the simple cubic case, one can write

$$a_{\rm true} = [(h^2 + k^2 + l^2)^{1/2}\lambda/2\sin\theta] + KF(\theta), \qquad (5.2.3.3)$$

where K is a proportionality factor and $F(\theta)$ represents the angular variation of the systematic errors in the lattice parameter. The functions F in (5.2.3.2) and (5.2.3.3) are not exactly the same; they are transformed into one another by the use of (5.2.1.4). Functions suitable for different experimental arrangements are quoted in the following sections; see, for example, equation (5.2.8.1) for the Debye–Scherrer camera and Tables 5.2.4.1 and 5.2.7.1 for diffractometers. Simple graphical

Table 5.2.4.1. *Centroid displacement* $\langle \Delta\theta/\theta \rangle$ *and variance* W *of certain aberrations of an angle-dispersive diffractometer; for references see Wilson (1963, 1965c, 1974) and Gillham (1971)*

For the Seemann–Bohlin arrangement, S and R are given by equations (5.2.4.1) and (5.2.4.2); for the symmetrical arrangement, they are equal to R_0. Other notation is explained at the end of the table.

Aberration	$\langle \Delta(2\theta) \rangle$	W
Zero-angle calibration	Constant	0
Specimen displacement	$-s\{R^{-1}\cos(2\theta-\varphi)+S^{-1}\cos\varphi\}$	0
Specimen transparency Thick specimen	$-\sin 2\varphi/\mu(R+S)$	$\sin^2 2\varphi/\mu^2(R+S)^2$
Thin specimen	See Wilson (1974, p. 547)	
2:1 mis-setting	Zero if centroid of illuminated area is centred	$\beta^2A^2[R^{-1}\cos(2\theta-\varphi)+S^{-1}\cos\varphi]^2/3$
Inclination of plane of specimen to axis of rotation	Zero if centroid of illuminated area on equator of specimen	$\gamma^2h^2[R^{-1}\cos(2\theta-\varphi)+S^{-1}\cos\varphi]^2/3$ for uniform illumination
Flat specimen	$-A^2\sin 2\theta/3RS$	$4A^4\sin^2 2\theta/45R^2S^2$
Focal-line width	Small	$\sim f_1^2/12S^2$
Receiving-slit width	Small	$\sim r_1^2/12R^2$
Interaction terms	Small if adjustment reasonably good	See Wilson (1963, 1974)
Axial divergence No Soller slits, source, specimen and receiver equal	$-h^2[(S^{-2}+R^{-2})\cot 2\theta+(RS)^{-1}\operatorname{cosec}2\theta]/3$	$h^4[\{7S^{-4}+2(RS)^{-2}+7R^{-4}\}\cot^2 2\theta$ $+14(RS)^{-1}(S^{-2}+R^{-2})\cot 2\theta\operatorname{cosec}2\theta$ $+19(RS)^{-2}\operatorname{cosec}^2 2\theta]/45$
Narrow Soller slits One set in incident beam	$-[\Delta^2/12+h^2/3R^2]\cot 2\theta$	$7[\Delta^4/720+h^4/45R^2]\cot^2 2\theta$ $+h^2\operatorname{cosec}^2 2\theta/9R^2$
One set in diffracted beam	Replace R by S in the above	
Two sets	$-(\Delta^2\cot 2\theta)/6$	$\Delta^4(10+17\cot^2 2\theta)/360$
Wide Soller slits	Complex. See Pike (1957), Langford & Wilson (1962), Wilson (1963, 1974), and Gillham (1971)	
Refraction	$\sim -2\delta\tan\theta$	$\sim \delta^2[-6\ln(\Delta/2)+25]/4\mu p$
Physical aberrations	See Wilson (1963, 1965*c*, 1970*a*, 1974) and Gillham & King (1972)	

Notation: $2A$ = illuminated length of specimen; β = angle of equatorial mis-setting of specimen; γ = angle of inclination of plane of specimen to axis of rotation; Δ = angular aperture of Soller slits; μ = linear absorption coefficient of specimen; r_1 = width of receiving slit (varies with θ in some designs of diffractometer); s = specimen-surface displacement; f_1 = projected width of focal line; h = half height of focal line, specimen, and receiving slit, taken as equal; $1-\delta$ = index of refraction; p = effective particle size.

extrapolation is quick and easy for cubic substances, and by the use of successive approximations it can be applied to hexagonal (Wilson & Lipson, 1941), tetragonal, and even orthorhombic materials. It is, however, very cumbersome for non-cubic substances, and impracticable if the symmetry is less than orthorhombic.

Analytic extrapolation seems to have been first used by Cohen (1936*a*,*b*). It is now usual even in the cubic case: programs are often included in the software accompanying powder diffractometers, and many others are available separately. Some programs that are frequently referred to are described by Appleman & Evans (1973), Mighell, Hubbard & Stalick (1981), and Ferguson, Rogerson, Wolstenholme, Hughes & Huyton (1987); for a comparison, see Kelly (1988). If the precision warrants it, the single function $KF(\theta)$ may be replaced by a sum of functions $K_iF_i(\theta)$, one for each of the larger aberrations listed in Tables 5.2.4.1, 5.2.7.1, and 5.2.8.1. Two – the zero error and a function corresponding to specimen-surface displacement and transparency – must be used routinely; one or two more may be added if the precision warrants it.