2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

so that

$$p(|E|)\, \mathrm{d}|E| = 2|E| \exp(-|E|^2)\, \mathrm{d}|E| \qquad (2.1.5.8)$$

is the normalized-structure-factor version of (2.1.5.6).

Distributions resulting from noncentrosymmetric crystals are known as *acentric* distributions; those arising from centrosymmetric crystals are known as *centric*. These adjectives are used to describe *distributions*, not crystal symmetry.

2.1.5.2. *Ideal centric distributions*

When a non-dispersive crystal is centrosymmetric, and the space-group origin is chosen at a crystallographic centre of symmetry, the imaginary part B of its structure amplitude is zero. In the simplest case, space group $P\bar{1}$, the contribution of the jth atom plus its centrosymmetric counterpart is $2f_j \cos \vartheta_j$. The calculation of $p(A)$ goes through as before, with allowance for the fact that there are $N/2$ pairs instead of N independent atoms, giving

$$p(A)\, \mathrm{d}A = (2\pi\Sigma)^{-1/2} \exp[-A^2/(2\Sigma)]\, \mathrm{d}A \qquad (2.1.5.9)$$

or equivalently

$$p(|F|)\, \mathrm{d}|F| = [2/(\pi\Sigma)]^{1/2} \exp[-|F|^2/(2\Sigma)]\, \mathrm{d}|F| \qquad (2.1.5.10)$$

or

$$p(|E|)\, \mathrm{d}|E| = (2/\pi)^{1/2} \exp(-|E|^2/2)\, \mathrm{d}|E|. \qquad (2.1.5.11)$$

2.1.5.3. *Effect of other symmetry elements on the ideal acentric and centric distributions*

Additional crystallographic symmetry elements do not produce any essential alterations in the ideal centric or acentric distribution; their main effect is to replace the parameter Σ by a 'distribution parameter', called S by Wilson (1950) and Rogers (1950), in certain groups of reflections. In addition, in noncentrosymmetric space groups, the distribution of certain groups of reflections becomes centric, though the general reflections remain acentric. The changes are summarized in Tables 2.1.3.1 and 2.1.3.2. The values of S are integers for lattice centring, glide planes and those screw axes that produce absences, and approximate integers for rotation axes and mirror planes; the modulations of the average intensity in reciprocal space outlined in Section 2.1.3.2 apply.

It should be noted that if intensities are normalized to the average of the group to which they belong, rather than to the general average, the distributions given in equations (2.1.5.8) and (2.1.5.11) are not affected.

2.1.5.4. *Other ideal distributions*

The distributions just derived are asymptotic, as they are limiting values for large N. They are the only ideal distributions, in this sense, when there is only strict crystallographic symmetry and no dispersion. However, other ideal (asymptotic) distributions arise when there is noncrystallographic symmetry, or if there is dispersion. The *subcentric* distribution,

$$p(|E|)\, \mathrm{d}|E| = \frac{2|E|}{(1-k^2)^{1/2}} \exp[-|E|^2/(1-k^2)]$$
$$\times I_0\left(\frac{k|E|^2}{1-k^2}\right) \mathrm{d}|E|, \qquad (2.1.5.12)$$

where $I_0(x)$ is a modified Bessel function of the first kind and k is the ratio of the scattering from the centrosymmetric part to the total scattering, arises when a noncentrosymmetric crystal contains centrosymmetric parts or when dispersion introduces effective

noncentrosymmetry into the scattering from a centrosymmetric crystal (Srinivasan & Parthasarathy, 1976, ch. III; Wilson, 1980a,b; Shmueli & Wilson, 1983). The *bicentric* distribution

$$p(|E|)\, \mathrm{d}|E| = \pi^{-3/2} \exp(-|E|^2/8) K_0(|E|^2/8)\, \mathrm{d}|E| \qquad (2.1.5.13)$$

arises, for example, when the 'asymmetric unit in a centrosymmetric crystal is a centrosymmetric molecule' (Lipson & Woolfson, 1952); $K_0(x)$ is a modified Bessel function of the second kind. There are higher hypercentric, hyperparallel and sesquicentric analogues (Wilson, 1952; Rogers & Wilson, 1953; Wilson, 1956). The ideal subcentric and bicentric distributions are expressed in terms of known functions, but the higher hypercentric and the sesquicentric distributions have so far been studied only through their moments and integral representations. Certain hypersymmetric distributions can be expressed in terms of Meijer's G functions (Wilson, 1987b).

2.1.5.5. *Relation to distributions of I*

When only the intrinsic probability distributions are being considered, it does not greatly matter whether the variable chosen is the intensity of reflection (I), or its positive square root, the modulus of the structure factor ($|F|$), since both are necessarily real and non-negative. In an obvious notation, the relation between the intensity distribution and the structure-factor distribution is

$$p_I(I) = (1/2)I^{-1/2} p_{|F|}(I^{1/2}) \qquad (2.1.5.14)$$

or

$$p_{|F|}(|F|) = 2|F| p_I(|F|^2). \qquad (2.1.5.15)$$

Statistical fluctuations in counting rates, however, introduce a small but finite probability of negative observed intensities (Wilson, 1978a, 1980a) and thus of imaginary structure factors. This practical complication is treated in *IT* C (1999, Parts 7 and 8).

Both the ideal centric and acentric distributions are simple members of the family of gamma distributions, defined by

$$\gamma_n(x)\, \mathrm{d}x = [\Gamma(n)]^{-1} x^{n-1} \exp(-x)\, \mathrm{d}x, \qquad (2.1.5.16)$$

where n is a parameter, not necessarily integral, and $\Gamma(n)$ is the gamma function. Thus the ideal acentric intensity distribution is

$$p(I)\, \mathrm{d}I = \exp(-I/\Sigma)\, \mathrm{d}(I/\Sigma) \qquad (2.1.5.17)$$
$$= \gamma_1(I/\Sigma)\, \mathrm{d}(I/\Sigma) \qquad (2.1.5.18)$$

and the ideal centric intensity distribution is

$$p(I)\, \mathrm{d}I = (2\Sigma/\pi)^{1/2} \exp[-I/(2\Sigma)]\, \mathrm{d}[I/(2\Sigma)] \qquad (2.1.5.19)$$
$$= \gamma_{1/2}[I/(2\Sigma)]\, \mathrm{d}[I/(2\Sigma)]. \qquad (2.1.5.20)$$

The properties of gamma distributions and of the related beta distributions, summarized in Table 2.1.5.1, are used in Section 2.1.6 to derive the probability density functions of sums and of ratios of intensities drawn from one of the ideal distributions.

2.1.5.6. *Cumulative distribution functions*

The integral of the probability density function $f(x)$ from the lower end of its range up to an arbitrary value x is called the cumulative probability distribution, or simply the distribution function, $F(x)$, of x. It can always be written

$$F(x) = \int_{-\infty}^{x} f(u)\, \mathrm{d}u; \qquad (2.1.5.21)$$

if the lower end of its range is not actually $-\infty$ one takes $f(x)$ as identically zero between $-\infty$ and the lower end of its range. For the distribution of A [equation (2.1.5.4) or (2.1.5.9)] the lower limit is in

196