Table 2.1.7.2. *Closed expressions for γ_{2k} [equation (2.1.7.11)] for space groups of low symmetry*

The normalized moments γ_{2k} are expressed in terms of M_k, where

$$M_k = \frac{(2k)!}{2^k(k!)^2} = \frac{(2k-1)!!}{k!},$$

and l', which takes on the values 1, 2 or 4 according as the Bravais lattice is of type P, one of the types A, B, C or I, or type F, respectively. The expressions for γ_{2k} are identical for all the space groups based on a given point group, except $Fdd2$ and $Fddd$. The expressions are valid for general reflections and under the restrictions given in the text.

Point group(s)	Expression for γ_{2k}
1	1
$\bar{1}, 2, m$	$l'^{k-1}M_k$
$2/m, mm2$	$l'^{k-1}M_k^2$
mmm	$l'^{k-1}M_k^3$
222	$\dfrac{l'^{k-1}}{2^k(k!)^2}\sum_{p=0}^{k}(M_pM_{k-p})^3[p!(k-p)!]^2$

of equation (2.1.7.13) and the first two terms on the right-hand side of equation (2.1.7.14) are just the cumulative distributions derived from the ideal centric and acentric p.d.f.'s in Section 2.1.5.6.

The moments $\langle|T|^{2k}\rangle$ were compiled for all the space groups by Wilson (1978*b*) for $k = 1$ and 2, and by Shmueli & Kaldor (1981, 1983) for $k = 1$, 2, 3 and 4. These results are presented in Table 2.1.7.1. Closed expressions for the normalized moments γ_{2p} were obtained by Shmueli (1982) for the triclinic, monoclinic and orthorhombic space groups except $Fdd2$ and $Fddd$ (see Table 2.1.7.2). The composition-dependent terms, Q_{2k}, are most conveniently computed as weighted averages over the ranges of $(\sin\theta)/\lambda$ which were used in the construction of the Wilson plot for the computation of the $|E|$ values.

2.1.7.4. *Fourier versus Hermite approximations*

As noted in Section 2.1.8.7 below, the Fourier representation of the probability distribution of $|F|$ is usually much better than the particular orthogonal-function representation discussed in Section 2.1.7.3. Many, perhaps most, non-ideal centric distributions look like slight distortions of the ideal (Gaussian) distribution and have no resemblance to a cosine function. The empirical observation thus seems paradoxical. The probable explanation has been pointed out by Wilson (1986*b*). A truncated Fourier series is a best approximation, in the least-squares sense, to the function represented. The particular orthogonal-function approach used in equation (2.1.7.5), on the other hand, is not a least-squares approximation to $p_c(|E|)$, but is a least-squares approximation to

$$p_c(|E|)\exp(|E|^2/4). \qquad (2.1.7.15)$$

The usual expansions (often known as Gram–Charlier or Edgeworth) thus give great weight to fitting the distribution of the (compararively few) strong reflections, at the expense of a poor fit for the (much more numerous) weak-to-medium ones. Presumably, a similar situation exists for the representation of acentric distributions, but this has not been investigated in detail. Since the centric distributions $p_c(|E|)$ often look nearly Gaussian, one is led to ask if there is an expansion in orthogonal functions that (i) has the leading term $p_c(|E|)$ and (ii) is a least-squares (as well as an orthogonal-function)* fit to $p_c(|E|)$. One does exist, based on the orthogonal functions

$$f_k = n(x)He_k(2^{1/2}x), \qquad (2.1.7.16)$$

where $n(x)$ is the Gaussian distribution (Myller-Lebedeff, 1907). Unfortunately, no reasonably simple relationship between the coefficients d_k and readily evaluated properties of $p_c(|E|)$ has been found, and the Myller-Lebedeff expansion has not, as yet, been applied in crystallography. Although Stuart & Ord (1994, p. 112) dismiss it in a three-line footnote, it does have important applications in astronomy (van der Marel & Franx, 1993; Gerhard, 1993).

2.1.8. Non-ideal distributions: the Fourier method

The starting point of the method described in the previous section is the central-limit theorem approximation, and the method consists of finding correction factors which result in better approximations to the actual p.d.f. Conceptually, this is equivalent to improving the approximation of the characteristic function [*cf.* equation (2.1.4.10)] over that which led to the central-limit theorem result.

The method to be described in this section does not depend on any initial approximation and will be shown to utilize the dependence of the exact value of the characteristic function on the space-group symmetry, atomic composition and other factors. This approach has its origin in a simple but ingenious observation by Barakat (1974), who noted that if a random variable has lower and upper bounds then the corresponding p.d.f. can be non-zero only within these bounds and can therefore be expanded in an ordinary Fourier series and set to zero (identically) outside the bounded interval. Barakat's (1974) work dealt with intensity statistics of laser speckle, where sinusoidal waves are involved, as in the present problem. This method was applied by Weiss & Kiefer (1983) to testing the accuracy of a steepest-descents approximation to the exact solution of the problem of random walk, and its first application to crystallographic intensity statistics soon followed (Shmueli *et al.*, 1984). Crystallographic (*e.g.* Shmueli & Weiss, 1987; Rabinovich *et al.*, 1991*a*,*b*) and noncrystallographic (Shmueli *et al.*, 1985; Shmueli & Weiss, 1985*a*; Shmueli, Weiss & Wilson, 1989; Shmueli *et al.*, 1990) symmetry was found to be tractable by this approach, as well as joint conditional p.d.f.'s of several structure factors (Shmueli & Weiss, 1985*b*, 1986; Shmueli, Rabinovich & Weiss, 1989). The Fourier method is illustrated below by deriving the exact counterparts of equations (2.1.7.5) and (2.1.7.6) and specifying them for some simple symmetries. We shall then indicate a method of treating higher symmetries and present results which will suffice for evaluation of Fourier p.d.f.'s of $|E|$ for a wide range of space groups.

2.1.8.1. *General representations of p.d.f.'s of $|E|$ by Fourier series*

We assume, as before, that (i) the atomic phase factors $\vartheta_j = 2\pi\mathbf{h}^T\mathbf{r}_j$ [*cf.* equation (2.1.1.2)] are uniformly distributed on (0–2π) and (ii) the atomic contributions to the structure factor are independent. For a centrosymmetric space group, with the origin chosen at a centre of symmetry, the random variable is the (real) normalized structure factor E and its bounds are $-E_M$ and E_M, where

* The condition for this desirable property seems to be that the weight function in equation (2.1.7.2) should be unity.

$$E_M = \sum_{j=1}^{N} n_j, \text{ with } n_j = \frac{f_j}{\left(\sum_{k=1}^{N} f_k^2\right)^{1/2}}. \quad (2.1.8.1)$$

Here, E_M is the maximum possible value of E and f_j is the conventional scattering factor of the jth atom, including its temperature factor. The p.d.f., $p(E)$, can be non-zero in the range $(-E_M, E_M)$ only and can thus be expanded in the Fourier series

$$p(E) = (\alpha/2) \sum_{k=-\infty}^{\infty} C_k \exp(-\pi i k \alpha E), \quad (2.1.8.2)$$

where $\alpha = 1/E_M$. Only the real part of $p(E)$ is relevant. The Fourier coefficients can be obtained in the conventional manner by integrating over the range $(-E_M, E_M)$,

$$C_k = \int_{-E_M}^{E_M} p(E) \exp(\pi i k \alpha E)\, \mathrm{d}E. \quad (2.1.8.3)$$

Since, however, $p(E) = 0$ for $E < -E_M$ and $E > E_M$, it is possible and convenient to replace the limits of integration in equation (2.1.8.3) by infinity. Thus

$$C_k = \int_{-\infty}^{\infty} p(E) \exp(\pi i k \alpha E)\, \mathrm{d}E = \langle \exp(\pi i k \alpha E) \rangle. \quad (2.1.8.4)$$

Equation (2.1.8.4) shows that C_k is a Fourier transform of the p.d.f. $p(E)$ and, as such, it is the value of the corresponding characteristic function at the point $t_k = \pi \alpha k$ [*i.e.*, $C_k = C(\pi \alpha k)$, where the characteristic function $C(t)$ is defined by equation (2.1.4.1)]. It is also seen that C_k is the expected value of the exponential $\exp(\pi i k \alpha E)$. It follows that the feasibility of the present approach depends on one's ability to evaluate the characteristic function in closed form *without* the knowledge of the p.d.f.; this is analogous to the problem of evaluating absolute moments of the structure factor for the correction-factor approach, discussed in Section 2.1.7. Fortunately, in crystallographic applications these calculations are feasible, provided individual isotropic motion is assumed. The formal expression for the p.d.f. of $|E|$, for any centrosymmetric space group, is therefore

$$p(|E|) = \alpha \left[1 + 2 \sum_{k=1}^{\infty} C_k \cos(\pi k \alpha |E|) \right], \quad (2.1.8.5)$$

where use is made of the assumption that $p(E) = p(-E)$, and the Fourier coefficients are evaluated from equation (2.1.8.4).

The p.d.f. of $|E|$ for a noncentrosymmetric space group is obtained by first deriving the joint p.d.f. of the real and imaginary parts of E and then integrating out its phase. The general expression for E is

$$E = A + iB = |E| \cos\varphi + i|E| \sin\varphi, \quad (2.1.8.6)$$

where φ is the phase of E. The required joint p.d.f. is

$$p(A, B) = (\alpha^2/4) \sum_m \sum_n C_{mn} \exp[-\pi i \alpha (mA + nB)], \quad (2.1.8.7)$$

and introducing polar coordinates $m = r \sin\Delta$ and $n = r \cos\Delta$, where $r = \sqrt{m^2 + n^2}$ and $\Delta = \tan^{-1}(m/n)$, we have

$$p(|E|, \varphi) = (\alpha^2/4)|E| \sum_m \sum_n C_{mn} \exp[-\pi i \alpha |E| \times \sqrt{m^2 + n^2} \sin(\varphi + \Delta)]. \quad (2.1.8.8)$$

Integrating out the phase φ, we obtain

$$p(|E|) = (\pi \alpha^2 |E|/2) \sum_m \sum_n C_{mn} J_0(\pi \alpha |E| \sqrt{m^2 + n^2}), \quad (2.1.8.9)$$

where $J_0(x)$ is the Bessel function of the first kind (*e.g.* Abramowitz & Stegun, 1972). This is a general form of the p.d.f. of $|E|$ for a noncentrosymmetric space group. The Fourier coefficients are obtained, similarly to the above, as

$$C_{mn} = \langle \exp[\pi i \alpha (mA + nB)] \rangle \quad (2.1.8.10)$$

and the average in equation (2.1.8.10), just as that in equation (2.1.8.4), is evaluated in terms of integrals over the appropriate trigonometric structure factors. In terms of the characteristic function for a joint p.d.f. of A and B, the Fourier coefficient in equation (2.1.8.10) is given by $C_{mn} = C(\pi \alpha m, \pi \alpha n)$.

We shall denote the characteristic function by $C(t_1)$ if it corresponds to a Fourier coefficient of a Fourier series for a centrosymmetric space group and by $C(t_1, t_2)$ or by $C(t, \Delta)$, where $t = (t_1^2 + t_2^2)^{1/2}$ and $\Delta = \tan^{-1}(t_1/t_2)$, if it corresponds to a Fourier series for a noncentrosymmetric space group.

2.1.8.2. *Fourier–Bessel series*

Equations (2.1.8.5) and (2.1.8.9) are the exact counterparts of equations (2.1.7.5) and (2.1.7.6), respectively. The computational effort required to evaluate equation (2.1.8.9) is somewhat greater than that for (2.1.8.5), because a double Fourier series has to be summed. The p.d.f. for *any* noncentrosymmetric space group can be expressed by a double Fourier series, but this can be simplified if the characteristic function depends on $t = (t_1^2 + t_2^2)^{1/2}$ alone, rather than on t_1 and t_2 separately. In such cases the p.d.f. of $|E|$ for a noncentrosymmetric space group can be expanded in a *single* Fourier–Bessel series (Barakat, 1974; Weiss & Kiefer, 1983; Shmueli *et al.*, 1984). The general form of this expansion is

$$p(|E|) = 2\alpha^2 |E| \sum_{u=1}^{\infty} D_u J_0(\alpha \lambda_u |E|), \quad (2.1.8.11)$$

where

$$D_u = \frac{C(\alpha \lambda_u)}{J_1^2(\lambda_u)} \quad (2.1.8.12)$$

and

$$C(\alpha \lambda_u) = \prod_{j=1}^{N/g} C_{ju}, \quad (2.1.8.13)$$

where $J_1(x)$ is the Bessel function of the first kind, and λ_u is the uth root of the equation $J_0(x) = 0$; the atomic contribution C_{ju} to equation (2.1.8.13) is computed as

$$C_{ju} = C(\alpha n_j \lambda_u). \quad (2.1.8.14)$$

The roots λ_u are tabulated in the literature (*e.g.* Abramowitz & Stegun, 1972), but can be most conveniently computed as follows. The first five roots are given by

$$\lambda_1 = 2.4048255577$$
$$\lambda_2 = 5.5200781103$$
$$\lambda_3 = 8.6537279129$$
$$\lambda_4 = 11.7915344390$$
$$\lambda_5 = 14.9309177085$$

and the higher ones can be obtained from McMahon's approximation (*cf.* Abramowitz & Stegun, 1972)

$$\lambda_u = \beta + \frac{1}{8\beta} - \frac{124}{3(8\beta)^3} + \frac{120928}{15(8\lambda)^5} - \frac{401743168}{105(8\lambda)^7} + \ldots, \tag{2.1.8.15}$$

where $\beta = (u - \frac{1}{4})\pi$. For $u > 5$ the values given by equation (2.1.8.15) have a relative error less than 10^{-11} so that no refinement of roots of higher orders is needed (Shmueli *et al.*, 1984). Numerical computations of single Fourier–Bessel series are of course faster than those of the double Fourier series, but both representations converge fairly rapidly.

2.1.8.3. *Simple examples*

Consider the Fourier coefficient of the p.d.f. of $|E|$ for the centrosymmetric space group $P\bar{1}$. The normalized structure factor is given by

$$E = 2\sum_{j=1}^{N/2} n_j \cos\vartheta_j, \quad \text{with} \quad \vartheta_j = 2\pi \mathbf{h}^T \cdot \mathbf{r}_j, \tag{2.1.8.16}$$

and the Fourier coefficient is

$$\begin{aligned} C_k &= \langle \exp(\pi i k \alpha E) \rangle & (2.1.8.17)\\ &= \left\langle \exp\left[2\pi i k\alpha \sum_{j=1}^{N/2} n_j \cos\vartheta_j\right] \right\rangle & (2.1.8.18)\\ &= \left\langle \prod_{j=1}^{N/2} \exp(2\pi i k\alpha n_j \cos\vartheta_j) \right\rangle & (2.1.8.19)\\ &= \prod_{j=1}^{N/2} \langle \exp(2\pi i k\alpha n_j \cos\vartheta_j) \rangle & (2.1.8.20)\\ &= \prod_{j=1}^{N/2} \left\{ (1/2\pi) \int_{-\pi}^{\pi} \exp(2\pi i k\alpha n_j \cos\vartheta)\, \mathrm{d}\vartheta \right\} & (2.1.8.21)\\ &= \prod_{j=1}^{N/2} J_0(2\pi k\alpha n_j). & (2.1.8.22) \end{aligned}$$

Equation (2.1.8.20) is obtained from equation (2.1.8.19) if we make use of the assumption of independence, the assumption of uniformity allows us to rewrite equation (2.1.8.20) as (2.1.8.21), and the expression in the braces in the latter equation is just a definition of the Bessel function $J_0(2\pi k\alpha n_j)$ (*e.g.* Abramowitz & Stegun, 1972).

Let us now consider the Fourier coefficient of the p.d.f. of $|E|$ for the noncentrosymmetric space group $P1$. We have

$$A = \sum_{j=1}^{N} n_j \cos\vartheta_j \quad \text{and} \quad B = \sum_{j=1}^{N} n_j \sin\vartheta_j. \tag{2.1.8.23}$$

These expressions for A and B are substituted in equation (2.1.8.10), resulting in

$$\begin{aligned} C_{mn} &= \left\langle \prod_{j=1}^{N} \exp[\pi i \alpha n_j (m\cos\vartheta_j + n\sin\vartheta_j)] \right\rangle & (2.1.8.24)\\ &= \left\langle \prod_{j=1}^{N} \exp[\pi i \alpha n_j \sqrt{m^2+n^2}\sin(\vartheta_j + \Delta)] \right\rangle & (2.1.8.25)\\ &= \prod_{j=1}^{N} J_0(\pi\alpha n_j \sqrt{m^2+n^2}). & (2.1.8.26) \end{aligned}$$

Equation (2.1.8.24) leads to (2.1.8.25) by introducing polar coordinates analogous to those leading to equation (2.1.8.8), and equation (2.1.8.26) is then obtained by making use of the assumptions of independence and uniformity in an analogous manner to that detailed in equations (2.1.8.12)–(2.1.8.22) above.

The right-hand side of equation (2.1.8.26) is to be used as a Fourier coefficient of the double Fourier series given by (2.1.8.9). Since, however, this coefficient depends on $(m^2+n^2)^{1/2}$ alone rather than on m and n separately, the p.d.f. of $|E|$ for $P1$ can also be represented by a Fourier–Bessel series [*cf.* equation (2.1.8.11)] with coefficient

$$D_u = \frac{1}{J_1^2(\lambda_u)} \prod_{j=1}^{N} J_0(\alpha n_j \lambda_u), \tag{2.1.8.27}$$

where λ_u is the uth root of the equation $J_0(x) = 0$.

2.1.8.4. *A more complicated example*

We now illustrate the methodology of deriving characteristic functions for space groups of higher symmetries, following the method of Rabinovich *et al.* (1991*a*,*b*). The derivation is performed for the space group $P\bar{6}$ [No. 174]. According to Table A1.4.3.6, the real and imaginary parts of the normalized structure factor are given by

$$\begin{aligned} A &= 2\sum_{j=1}^{N/6} n_j [C(hki)c(lz)]_j \\ &= 2\sum_{j=1}^{N/6} n_j \cos\tau_j \sum_{k=1}^{3} \cos\alpha_{jk} & (2.1.8.28) \end{aligned}$$

and

$$\begin{aligned} B &= 2\sum_{j=1}^{N/6} n_j [S(hki)c(lz)]_j \\ &= 2\sum_{j=1}^{N/6} n_j \cos\tau_j \sum_{k=1}^{3} \sin\alpha_{jk}, & (2.1.8.29) \end{aligned}$$

where

$$\begin{aligned} \alpha_{j1} &= 2\pi(hx_j + ky_j),\\ \alpha_{j2} &= 2\pi(kx_j + iy_j),\\ \alpha_{j3} &= 2\pi(ix_j + hy_j),\\ \tau_j &= 2\pi l z_j. \end{aligned}$$

Note that $\alpha_{j1} + \alpha_{j2} + \alpha_{j3} = 0$, *i.e.*, one of these contributions depends on the other two; this is a recurring problem in calculations pertaining to trigonal and hexagonal systems. For brevity, we write directly the general form of the characteristic function from which the functional form of the Fourier coefficient can be readily obtained. The characteristic function is given by

$$C(t_1,t_2) = \langle \exp[i(t_1A + t_2B)]\rangle \tag{2.1.8.30}$$

$$= \prod_{j=1}^{N/6}\left\langle \exp\left[2in_j\cos\tau_j\sum_{k=1}^{3}(t_1\cos\alpha_{jk} + t_2\sin\alpha_{jk})\right]\right\rangle \tag{2.1.8.31}$$

$$= \prod_{j=1}^{N/6}\left\langle \exp\left[2in_jt\cos\tau_j\sum_{k=1}^{3}(\sin\Delta\cos\alpha_{jk} + \cos\Delta\sin\alpha_{jk})\right]\right\rangle \tag{2.1.8.32}$$

$$= \prod_{j=1}^{N/6}\left\langle \exp\left[2in_jt\cos\tau_j\sum_{k=1}^{3}\sin(\alpha_{jk}+\Delta)\right]\right\rangle, \tag{2.1.8.33}$$

where $\Delta = \tan^{-1}(t_1/t_2)$, $t = (t_1^2 + t_2^2)^{1/2}$ and the assumption of independence was used. If we further employ the assumption of uniformity, while remembering that the angular variables α_{jk} are not independent, the characteristic function can be written as

$$C(t_1,t_2) = \prod_{j=1}^{N/6}\left\{(1/2\pi)\int_{-\pi}^{\pi}\mathrm{d}\tau\left([1/(2\pi)^2]\right.\right.$$
$$\times\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\mathrm{d}\alpha_1\,\mathrm{d}\alpha_2\,\mathrm{d}\alpha_3\delta_{2\pi}(\alpha_1+\alpha_2+\alpha_3)$$
$$\left.\left.\times\exp\left[2in_jt\cos\tau\sum_{k=1}^{3}\sin(\alpha_k+\Delta)\right]\right)\right\}, \tag{2.1.8.34}$$

where

$$\delta_{2\pi}(\alpha) = \frac{1}{2\pi}\sum_{k=-\infty}^{\infty}\exp(-ik\alpha) \tag{2.1.8.35}$$

is the Fourier representation of the periodic delta function. Equation (2.1.8.34) then becomes

$$C(t_1,t_2) = \prod_{j=1}^{N/6}\left\{(1/2\pi)\int_{-\pi}^{\pi}\mathrm{d}\tau\sum_{k=-\infty}^{\infty}\left[(1/2\pi)\right.\right.$$
$$\left.\left.\times\int_{-\pi}^{\pi}\exp\big(-ik\alpha + 2in_jt\cos\tau\sin(\alpha+\Delta)\big)\,\mathrm{d}\alpha\right]^3\right\}. \tag{2.1.8.36}$$

If we change the variable α to $\alpha' - \Delta$, $\sin(\alpha+\Delta)$ becomes $\sin\alpha'$ and $-ik\alpha = -ik\alpha' + ik\Delta$. Hence

$$C(t_1,t_2) = \prod_{j=1}^{N/6}\left\{(1/2\pi)\int_{-\pi}^{\pi}\mathrm{d}\tau\sum_{k=-\infty}^{\infty}\exp(3ik\Delta)J_k^3(2n_jt\cos\tau)\right\}. \tag{2.1.8.37}$$

The imaginary part of the summation, involving Bessel functions of odd orders, vanishes upon integration and the latter is restricted to the positive quadrant in τ. Thus, upon replacing cosines by sines (this is permissible at this stage) the atomic contribution to the characteristic function becomes

$$C_j(t,\Delta) = (2/\pi)\int_0^{\pi/2}\left[J_0^3(2n_jt\sin\tau) + 2\sum_{k=1}^{\infty}\cos(6k\Delta)J_k^3(2n_jt\sin\tau)\right]\mathrm{d}\tau \tag{2.1.8.38}$$

and a double Fourier series must be used for the p.d.f.

2.1.8.5. *Atomic characteristic functions*

Expressions for the atomic contributions to the characteristic functions were obtained by Rabinovich *et al.* (1991*a*) for a wide range of space groups, by methods similar to those described above. These expressions are collected in Table 2.1.8.1 in terms of symbols which are defined below. The following abbreviations are used in the subsequent definitions of the symbols:

$$s_\pm = 2an_j\sin(\tau\pm\rho),$$
$$c_\pm = 2an_j\cos(\tau\pm\rho) \quad \text{and}$$
$$\sigma_\pm = 2an_j\sin(\tau\pm 2\pi/3+\rho),$$

and the symbols appearing in Table 2.1.8.1 are given below:

$${}^{(a)}L_j(a,\rho) = \langle J_0(s_+)J_0(s_-)\rangle_\tau$$
$$= \sum_{k=-\infty}^{\infty}\cos(4k\rho)J_k^4$$
$$= J_0^4(an_j) + 2\sum_{k=1}^{\infty}\cos(4k\rho)J_k^4(an_j),$$
$${}^{(b)}Q_j^{(1)}(a,\rho) = \langle J_0^2(s_+)J_0^2(s_-)\rangle_\tau,$$
$${}^{(c)}Q_j^{(2)}(a,\rho) = \langle J_0(s_+)J_0(s_-)J_0(c_+)J_0(c_-)\rangle_\tau,$$
$${}^{(d)}T_j(a,\rho) = \sum_{k=-\infty}^{\infty}\exp(6ik\rho)J_k^6(an_j)$$
$$= J_0^6(an_j) + 2\sum_{k=1}^{\infty}\cos(6k\rho)J_k^6(an_j),$$
$${}^{(e)}H_j^{(1)}(a,\mu) = \left\langle\mathcal{R}\left[S_j^{(1)}(\tau;\,a,\mu,0)\right]\right\rangle_\tau,$$
$${}^{(f)}H_j^{(2)}(a,\mu) = \left\langle\mathcal{R}\left[S_j^{(2)}(\tau;\,a,\mu,0)\right]\right\rangle_\tau,$$
$${}^{(g)}\tilde{H}_j^{(1)}(a,\mu_1,\mu_2,\rho) = \left\langle\mathcal{R}\left[S_j^{(1)}(\tau;\,a,\mu_1,\rho)\times S_j^{(1)}(\tau;\,a,\mu_2,-\rho)\right]\right\rangle_\tau,$$
$${}^{(h)}\tilde{H}_j^{(2)}(a,\mu_1,\mu_2,\rho) = \left\langle\mathcal{R}\left[S_j^{(2)}(\tau;\,a,\mu_1,\rho)\times S_j^{(2)}(\tau;\,a,\mu_2,-\rho)\right]\right\rangle_\tau,$$

where

$$S_j^{(1)}(\tau;\,a,\mu,\rho) = \sum_{k=-\infty}^{\infty}e^{3ik\mu}J_k^3(s_+)$$

and

$$S_j^{(2)}(\tau;\,a,\mu,\rho) = \sum_{k=-\infty}^{\infty}e^{3ik\mu}J_k(s_+)J_k(\sigma_+)J_k(\sigma_-).$$

The averages appearing in the above summary are, in general, computed as

Table 2.1.8.1. *Atomic contributions to characteristic functions for $p(|E|)$*

The table lists symbolic expressions for the atomic contributions to exact characteristic functions (abbreviated as c.f.) for $p(|E|)$, to be computed as single Fourier series (centric), double Fourier series (acentric) and single Fourier–Bessel series (acentric), as defined in Sections 2.1.8.1 and 2.1.8.2. The symbolic expressions are defined in Section 2.1.8.5. The table is arranged by point groups, space groups and parities of the reflection indices analogously to the table of moments, Table 2.1.7.1, and covers all the space groups and statistically different parities of *hkl* up to and including space group $Fd\bar{3}$. The expressions are valid for atoms in general positions, for general reflections and presume the absence of noncrystallographic symmetry and of dispersive scatterers.

Space group(s)	g	Atomic c.f.	Remarks
Point group: 1			
$P1$	1	$J_0(tn_j)$	
Point group: $\bar{1}$			
$P\bar{1}$	2	$J_0(2t_1n_j)$	
Point groups: 2, *m*			
All P	2	$J_0^2(tn_j)$	
All C	4	$J_0^2(2tn_j)$	
Point group: 2/*m*			
All P	4	$J_0^2(2t_1n_j)$	
All C	8	$J_0^2(4t_1n_j)$	
Point group: 222			
All P	4	$L_j(t,\Delta)^{(a)}$	
All C and I	8	$L_j(2t,\Delta)$	
$F222$	16	$L_j(4t,\Delta)$	
Point group: *mm*2			
All P	4	$L_j(t,0)$	
All C and I	8	$L_j(2t,0)$	
$Fmm2$	16	$L_j(4t,0)$	
$Fdd2$	16	$L_j(4t,0)$	$h+k+l=2n$
	16	$L_j(4t,\pi/4)$	$h+k+l=2n+1$
Point group: *mmm*			
All P	8	$L_j(2t_1,0)$	
All C and I	16	$L_j(4t_1,0)$	
$Fmmm$	32	$L_j(8t_1,0)$	
$Fddd$	32	$L_j(8t_1,0)$	$h+k+l=2n$
	32	$L_j(8t_1,\pi/4)$	$h+k+l=2n+1$
Point group: 4			
$P4$, $P4_2$	4	$L_j(t,0)$	
$P4_1$*	4	$L_j(t,0)$	$l=2n$
	4	$L_j(t,\pi/4)$	$l=2n+1$
$I4$	8	$L_j(2t,0)$	
$I4_1$	8	$L_j(2t,0)$	$2h+l=2n$
	8	$L_j(2t,\pi/4)$	$2h+l=2n+1$
Point group: $\bar{4}$			
$P\bar{4}$	4	$L_j(t,\Delta)$	
$I\bar{4}$	8	$L_j(2t,\Delta)$	
Point group: 4/*m*			
All P	8	$L_j(2t_1,0)$	
$I4/m$	16	$L_j(4t_1,0)$	
$I4_1/a$	16	$L_j(4t_1,0)$	$l=2n$
	16	$L_j(4t_1,\pi/4)$	$l=2n+1$
Point group: 422			
$P422$, $P42_12$, $P4_222$, $P4_22_12$	8	$Q_j^{(1)}(t,\Delta)^{(b)}$	
$P4_122$,* $P4_12_12$*	8	$Q_j^{(1)}(t,\Delta)$	$l=2n$
	8	$Q_j^{(2)}(t,\Delta)^{(c)}$	$l=2n+1$
$I422$	16	$Q_j^{(1)}(2t,\Delta)$	
$I4_122$	16	$Q_j^{(1)}(2t,\Delta)$	$2k+l=2n$
	16	$Q_j^{(2)}(2t,\Delta)$	$2k+l=2n+1$
Point group: 4*mm*			
All P	8	$Q_j^{(1)}(t,0)$	
$I4mm$, $I4cm$	16	$Q_j^{(1)}(2t,0)$	
$I4_1md$, $I4_1cd$	16	$Q_j^{(1)}(2t,0)$	$2k+l=2n$
	16	$Q_j^{(1)}(2t,\pi/4)$	$2k+l=2n+1$
Point groups: $\bar{4}$2*m*, $\bar{4}$*m*2			
All P	8	$Q_j^{(1)}(t,\Delta)$	
$I\bar{4}2m$, $I\bar{4}m2$, $I\bar{4}c2$	16	$Q_j^{(1)}(2t,\Delta)$	
$I\bar{4}2d$	16	$Q_j^{(1)}(2t,\Delta)$	$2h+l=2n$
	16	$Q_j^{(2)}(2t,\Delta)$	$2h+l=2n+1$
Point group: 4/*mmm*			
All P	16	$Q_j^{(1)}(2t_1,0)$	
$I4/mmm$, $I4/mcm$	32	$Q_j^{(1)}(4t_1,0)$	
$I4_1/amd$, $I4_1/acd$	32	$Q_j^{(1)}(4t_1,0)$	$l=2n$
	32	$Q_j^{(1)}(4t_1,\pi/4)$	$l=2n+1$
Point group: 3			
All P and R	3	$J_0^3(tn_j)$	
Point group: $\bar{3}$			
All P and R	6	$J_0^3(2t_1n_j)$	
Point group: 32			
All P and R	6	$T_j(t,\Delta)^{(d)}$	
Point group: 3*m*			
$P3m1$, $P31m$, $R3m$	6	$T_j(t,\pi/2)$	
$P3c1$, $P31c$, $R3c$	6	$T_j(t,\pi/2)$	$l=2n$ (P), $h+k+l=2n$ (R)
	6	$T_j(t,0)$	$l=2n+1$ (P), $h+k+l=2n+1$ (R)
Point group: $\bar{3}$*m*			
$P\bar{3}m1$, $P\bar{3}1m$, $R\bar{3}m$	12	$T_j(2t_1,\pi/2)$	
$P\bar{3}c1$, $P\bar{3}1c$, $R\bar{3}c$	12	$T_j(2t_1,\pi/2)$	$l=2n$ (P), $h+k+l=2n$ (R)
	12	$T_j(2t_1,0)$	$l=2n+1$ (P), $h+k+l=2n+1$ (R)
Point group: 6			
$P6$	6	$H_j^{(1)}(t,\pi/2)^{(e)}$	
$P6_1$*	6	$H_j^{(1)}(t,\pi/2)$	$l=6n$
	6	$H_j^{(2)}(t,0)^{(f)}$	$l=6n+1,\ 6n+5$
	6	$H_j^{(2)}(t,\pi/2)$	$l=6n+2,\ 6n+4$
	6	$H_j^{(1)}(t,0)$	$l=6n+3$
$P6_2$*	6	$H_j^{(1)}(t,\pi/2)$	$l=3n$
	6	$H_j^{(2)}(t,\pi/2)$	$l=3n\pm1$
$P6_3$	6	$H_j^{(1)}(t,\pi/2)$	$l=2n$
	6	$H_j^{(1)}(t,0)$	$l=2n+1$
Point group: $\bar{6}$			
$P\bar{6}$	6	$H_j^{(1)}(t,\Delta)$	
Point group: 6/*m*			
$P6/m$	12	$H_j^{(1)}(2t_1,\pi/2)$	
$P6_3/m$	12	$H_j^{(1)}(2t_1,\pi/2)$	$l=2n$
	12	$H_j^{(1)}(2t_1,0)$	$l=2n+1$
Point group: 622			
$P622$	12	$\tilde{H}_j^{(1)}(t,\pi/2,-\pi/2,\Delta)^{(g)}$	

Table 2.1.8.1. *Atomic contributions to characteristic functions for $p(|E|)$ (cont.)*

Space group(s)	g	Atomic c.f.	Remarks
$P6_122$*	12	$\tilde{H}_j^{(1)}(t, \pi/2, -\pi/2, \Delta)$	$l = 6n$
	12	$\tilde{H}_j^{(2)}(t, 0, 0, \Delta)^{(h)}$	$l = 6n+1,\ 6n+5$
	12	$\tilde{H}_j^{(2)}(t, \pi/2, \pi/2, \Delta)$	$l = 6n+2,\ 6n+4$
	12	$\tilde{H}_j^{(1)}(t, 0, 0, \Delta)$	$l = 6n+3$
$P6_222$*	12	$\tilde{H}_j^{(1)}(t, \pi/2, -\pi/2, \Delta)$	$l = 3n$
	12	$\tilde{H}_j^{(2)}(t, \pi/2, \pi/2, \Delta)$	$l = 3n \pm 1$
$P6_322$	12	$\tilde{H}_j^{(1)}(t, \pi/2, -\pi/2, \Delta)$	$l = 2n$
	12	$\tilde{H}_j^{(1)}(t, 0, 0, \Delta)$	$l = 2n+1$
Point group: 6*mm*			
$P6mm$	12	$\tilde{H}_j^{(1)}(t, \pi/2, \pi/2, 0)$	
$P6cc$	12	$\tilde{H}_j^{(1)}(t, \pi/2, \pi/2, 0)$	$l = 2n$
	12	$\tilde{H}_j^{(1)}(t, \pi/2, -\pi/2, 0)$	$l = 2n+1$
$P6_3cm$, $P6_3mc$	12	$\tilde{H}_j^{(1)}(t, \pi/2, \pi/2, 0)$	$l = 2n$
	12	$\tilde{H}_j^{(1)}(t, 0, 0, 0)$	$l = 2n+1$
Point groups: $\bar{6}2m$, $\bar{6}m2$			
$P\bar{6}2m$, $P\bar{6}m2$	12	$\tilde{H}_j^{(1)}(t, \Delta, \Delta, 0)$	
$P\bar{6}2c$, $P\bar{6}c2$	12	$\tilde{H}_j^{(1)}(t, \Delta, \Delta, 0)$	$l = 2n$
	12	$\tilde{H}_j^{(1)}(t, \Delta+\pi/2, -\Delta-\pi/2, 0)$	$l = 2n+1$
Point group: 6*/mmm*			
$P6/mmm$	24	$\tilde{H}_j^{(1)}(2t_1, \pi/2, \pi/2, 0)$	
$P6/mcc$	24	$\tilde{H}_j^{(1)}(2t_1, \pi/2, \pi/2, 0)$	$l = 2n$
	24	$\tilde{H}_j^{(1)}(2t_1, \pi/2, -\pi/2, 0)$	$l = 2n+1$
$P6_3/mcm$, $P6_3/mmc$	24	$\tilde{H}_j^{(1)}(2t_1, \pi/2, \pi/2, 0)$	$l = 2n$
	24	$\tilde{H}_j^{(1)}(2t_1, 0, 0, 0)$	$l = 2n+1$
Point group: 23			
$P23$, $P2_13$	12	$L_j^3(t, \Delta)$	
$I23$, $I2_13$	24	$L_j^3(2t, \Delta)$	
$F23$	48	$L_j^3(4t, \Delta)$	
Point group: $m\bar{3}$			
$Pm\bar{3}$, $Pn\bar{3}$, $Pa\bar{3}$	24	$L_j^3(2t_1, 0)$	
$Im\bar{3}$, $Ia\bar{3}$	48	$L_j^3(4t_1, 0)$	
$Fm\bar{3}$	96	$L_j^3(8t_1, 0)$	
$Fd\bar{3}$	96	$L_j^3(8t_1, 0)$	$h+k+l = 2n$
	96	$L_j^3(8t_1, \pi/4)$	$h+k+l = 2n+1$

* And the enantiomorphous space group.

$$\langle f(\tau)\rangle = (2/\pi)\int_0^{\pi/2} f(\tau)\,\mathrm{d}\tau, \tag{2.1.8.39}$$

except $H_j^{(2)}$ and $\tilde{H}_j^{(2)}$ which are computed as

$$\langle f(\tau)\rangle = (3/\pi)\int_0^{\pi/3} f(\tau)\,\mathrm{d}\tau, \tag{2.1.8.40}$$

where $f(\tau)$ is any of the atomic characteristic functions indicated above. The superscripts preceding the symbols in the above summary are appended to the corresponding symbols in Table 2.1.8.1 on their first occurrence.

2.1.8.6. *Other non-ideal Fourier p.d.f.'s*

As pointed out above, the representation of the p.d.f.'s by Fourier series is also applicable to effects of noncrystallographic symmetry. Thus, Shmueli *et al.* (1985) obtained the following Fourier coefficient for the bicentric distribution in the space group $P\bar{1}$

$$C_k = (2/\pi)\int_0^{\pi/2}\left[\prod_{j=1}^{N/4} J_0(4\pi k\alpha n_j\cos\vartheta)\right]\mathrm{d}\vartheta \tag{2.1.8.41}$$

to be used with equation (2.1.8.5). Furthermore, if we use the important property of the characteristic function as outlined in Section 2.1.4.1, it is easy to write down the Fourier coefficient for a $P\bar{1}$ asymmetric unit containing a centrosymmetric fragment centred at a noncrystallographic centre and a number of atoms not related by symmetry. This Fourier for the above partially bicentric arrangement is a product of expressions (2.1.8.17) and (2.1.8.41), with the appropriate number of atoms in each factor (Shmueli & Weiss, 1985*a*). While the purely bicentric p.d.f. obtained by using (2.1.8.41) with (2.1.8.5) is significantly different from the ideal bicentric p.d.f. given by equation (2.1.5.13) only when the atomic composition is sufficiently heterogeneous, the above partially bicentric p.d.f. appears to be a useful development even for an equal-atom structure.

The problem of the coexistence of several noncrystallographic centres of symmetry within the asymmetric unit of $P\bar{1}$, and its effect on the p.d.f. of $|E|$, was examined by Shmueli, Weiss & Wilson (1989) by the Fourier method. The latter study indicates that the strongest effect is produced by the presence of a single noncrystallographic centre.

Another kind of noncrystallographic symmetry is that arising from the presence of centrosymmetric fragments in a noncentrosymmetric structure – the subcentric arrangement already discussed in Section 2.1.5.4. A Fourier-series representation of a non-ideal p.d.f. corresponding to this case was developed by Shmueli, Rabinovich & Weiss (1989), and was also applied to the mathematically equivalent effects of dispersion and presence of heavy scatterers in centrosymmetric special positions in a noncentrosymmetric space group.

A variety of other non-ideal p.d.f.'s occur when heavy atoms are present in special positions (Shmueli & Weiss, 1988). Without going into the details of this development, it can be noted that if the atoms are distributed among k types of Wyckoff positions, the characteristic function corresponding to the p.d.f. of $|E|$ is a product of the k characteristic functions, each of which is related to one of these special positions; the same property of the characteristic function as that in Section 2.1.4.1 is here utilized.

2.1.8.7. *Comparison of the correction-factor and Fourier approaches*

The need for theoretical non-ideal distributions was exemplified by Fig. 2.1.7.1(*a*), referred to above, and the performance of the two approaches described above, for this particular example, is shown in

Fig. 2.1.7.1(*b*). Briefly, the Fourier p.d.f. shows an excellent agreement with the histogram of recalculated $|E|$ values, while the agreement attained by the Hermite correction factor is much less satisfactory, even for the (longest available to us) five-term expansion. It must be pointed out that (i) the inadequacy of 'short' correction factors, in the example shown, is due to the large deviation from the ideal behaviour and (ii) the number of terms used there in the Fourier summation is twenty, whereafter the summation is terminated. Obviously, the computation of twenty (or more) Fourier coefficients is easier than that of five terms in the correction factor. The convergence of the Fourier series is very satisfactory. It appears that the (analytically) exact Fourier approach is the preferred one in cases of large or intermediate deviations, while the correction-factor approach may cope well with small ones. As far as the availability of symmetry-dependent centric and acentric p.d.f.'s is concerned, correction factors are available for all the space groups (see Table 2.1.7.1), while Fourier coefficients of p.d.f.'s are available for the first 206 space groups (see Table 2.1.8.1). It should be pointed out that p.d.f.'s based on the correction-factor method cope very well with cubic symmetries higher than $Fd\bar{3}$, even if the asymmetric unit of the space group is strongly heterogeneous (Rabinovich *et al.*, 1991*b*).

Both approaches described in this section are related to the characteristic function of the required p.d.f. The correction-factor p.d.f.'s (2.1.7.5) and (2.1.7.6) can be obtained by expanding the logarithm of the appropriate characteristic function in a series of cumulants [*e.g.* equation (2.1.4.13); see also Shmueli & Wilson (1982)], truncating the series and performing its term-by-term Fourier inversion. The Fourier p.d.f., on the other hand, is computed by forming a Fourier series whose coefficients are *exact* analytical forms of the characteristic function at points related to the summation indices [*e.g.* equations (2.1.8.5), (2.1.8.9) and (2.1.8.11), and Table 2.1.8.1] and truncating the series when the terms become small enough.

references