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

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

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

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

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

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

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.

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

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

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

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 $P\bar{1}$

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

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

references