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