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Exact Random-Walk Models in Crystallographic Statistics. V. Non-Symmetrically Bounded Distributions of Structure-Factor Magnitudes

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Abstract

Derivations of exactly formulated Fourier-series representations of probability density functions (p.d.f.'s) of the magnitude of the structure factor are based on the fact that the structure factor and its real and imaginary parts are bounded. In some situations the bounds of the real and imaginary parts of the structure factor are different, and this gives rise to modified forms of the p.d.f.'s. Three physical examples that call for such modifications are investigated: (i) effect of dispersive scatterers on the p.d.f. of a centrosymmetric structure factor, (ii) effect of the presence of a centrosymmetric fragment in the asymmetric unit of a non-centrosymmetric space group, and (iii) effect of heavy scatterers in special positions of a non-centrosymmetric space group, where the imaginary part of the trigonometric structure factor for these special positions vanishes by symmetry. The general form of an exact Fourier p.d.f., taking account of such modifications, is derived, and expressions for Fourier coefficients are obtained for selected examples of the above three situations. It is seen that the effects of pseudocentrosymmetry may be most pronounced and those of dispersion are significant mainly in the range of small values of the structure factor.

Introduction

Properties of probability density functions (p.d.f.'s) of the magnitude of the structure factor have been investigated in a variety of ways. Approximations to the p.d.f.'s are generally derived using the central limit theorem (Wilson, 1949). Corrections to the central limit theorem are usually based on expansions in terms of orthogonal polynomials (*e.g.* the monograph by Srinivasan & Parthasarathy, 1976; Shmueli & Wilson, 1981). More recently we have considered exact representations of the p.d.f.'s in terms of Fourier or Fourier-Bessel series (*e.g.* Shmueli, Weiss, Kiefer & Wilson, 1984; Shmueli & Weiss, 1987). If we write $E = A + iB$ then the calculations of the p.d.f. of $|E|$ have been carried out in two classes of problems: (i) $B = 0$, in which case $|E| = |A|$, and (ii) $-A_{max} \le A$, $B < A_{max}$, in which case $|E| = (A^2 + B^2)^{1/2}$. However, there are cases in which the maximum values of $|A|$ and $|B|$ differ. Since the phases of the structure factors are then restricted to a certain subrange of $(0, 2\pi)$, calculation of the p.d.f.'s is somewhat more complicated than in the case when both A and B fall in the same range.

Three examples in which the problem of restricted phases appears are:

(i) The structure contains significantly dispersive scatterers so that the imaginary parts of some atomic scattering factors cannot be neglected. Even when the space group is centrosymmetric and the origin is chosen at a center of symmetry, the imaginary part, B, of the structure factor cannot be neglected. Since the maximum value of B is necessarily smaller than the maximum value of the real part, A (see tables of scattering factors in *International Tables for X-ray Crystallography*, 1974), the phase of the structure factor cannot assume every value in the $(0, 2\pi)$ range. This is true at least for X-rays, and not too close to an absorption edge. The problem of the effects of dispersion on intensity statistics was first considered by Wilson (1980), in the central limit theorem approximation, and was further studied by Shmueli & Wilson (1983) who derived further correction in terms of a Gram-Charlier expansion for the p.d.f. derived by Wilson (1980). In such approximate treatments the problem of unequal ranges never arises since A and B are inherently unrestricted in approximations based on the central limit theorem.

(ii) The structure belongs to a non-centrosymmetric space group but the asymmetric unit contains one or more centrosymmetric structural fragments. The presence of such centrosymmetric fragments ensures that the maximum values of the real and imaginary parts of the structure factor are unequal. This implies a phase restriction that must be accounted for in the exact analysis of the problem.

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This kind of non-crystallographic symmetry was studied by a number of investigators (*cf.* Srinivasan & Parthasarathy, 1976, and references quoted therein; Wilson, 1980) in the central limit theorem approximation, and was further investigated by Shmueli & Wilson (1983), who also termed the corresponding p.d.f. 'subcentric'. Wilson (1980) noted that p.d.f.'s accounting for dispersion and for the presence of centrosymmetric fragments in a non-centrosymmetric space group have, in the central limit theorem approximation, identical functional forms and different distribution parameters.

(iii) The problem of calculating the p.d.f. of $|E|$ allowing for the presence of scatterers in special positions has been investigated recently (Shmueli & Weiss, 1988). While most low-symmetry space groups can be treated on the assumption that the phase of the structure factor is unrestricted in the $(0, 2\pi)$ range, this is not possible in most space groups isomorphous with the point group 222 since the imaginary parts of the trigonometric structure factors corresponding to special positions vanish identically; in the space groups in which this happens, a phase restriction is clearly introduced.

The three problems mentioned above have in common the inequality of the maximum values of the real and the imaginary parts of the structure factor. It therefore appears of interest to derive the p.d.f. of $|E|$ on the assumption that the maximum values of A and B differ. We then apply the results to typical examples that illustrate the three cases enumerated above. The next section presents the derivation of the general functional form of the p.d.f., and the following sections deal with exactly formulated p.d.f.'s of $|E|$ accounting for the effects of dispersion, subcentrosymmetric arrangements, and the presence of heavy scatterers in the general as well as special position of the space group $P222$.

Derivation of the general functional form of the p.d.f.

The starting point of the derivation of the p.d.f. of $|E|$ is the representation of the joint p.d.f. of the (A, B) pair in terms of a Fourier series. We are entitled to do this since each of A and B is bounded (Barakat, 1974; Weiss & Kiefer, 1983; Shmueli *et al.*, 1984), but we must now assume that the upper bounds A_M and B_M of A and B respectively may be unequal; we assume for simplicity that $A_M > B_M$. The exact contour in the (A, B) complex plane, surrounding all (A, B) values for which $p(A, B)$ is non-zero, may assume different shapes in the various situations of interest, and any such contour must be contained within the rectangle of vertices: $(-A_M, -B_M)$, $(-A_M, B_M)$, $(A_M, -B_M)$ and (A_M, B_M). The joint p.d.f., $p(A, B)$, vanishes by definition at any point (A, B) lying outside the exact contour. The region of the (A, B) plane, bounded by this contour can thus be taken as a compact support of the p.d.f., which can therefore be expanded in the double Fourier series

$$p(A, B) = \frac{1}{4A_M B_M} \sum_u \sum_v C_{uv} \exp\left[-\pi i\left(\frac{uA}{A_M} + \frac{vB}{B_M}\right)\right], \tag{1}$$

where the Fourier coefficient C_{uv} is given by

$$C_{uv} = \int_{A_M}^{A_M} \int_{-B_M}^{B_M} p(A, B) \exp\left[\pi i\left(\frac{uA}{A_M} + \frac{vB}{B_M}\right)\right] \mathrm{d}A\, \mathrm{d}B$$

$$= \left\langle \exp\left[\pi i\left(\frac{uA}{A_M} + \frac{vB}{B_M}\right)\right]\right\rangle. \tag{1a}$$

In order that the expansion (1) correctly represent the joint p.d.f. $p(A, B)$, the integration limits in (1*a*) should include (or coincide with) the region of non-vanishing $p(A, B)$, *i.e.* the region enclosed within the exact contour mentioned above. The integration extends over the area of the above-defined rectangle but, obviously, only those values of $p(A, B)$ which correspond to the inside of the exact contour give rise to non-vanishing contributions to the Fourier coefficient C_{uv}. Hence, the value of the integral in (1*a*) is independent of the precise shape of the exact contour, provided the latter is contained within the rectangular boundary, on which the Fourier expansion (1) is based. The actual exact formulation of the Fourier coefficients is based on their representation as values of the characteristic function at the points $(\pi u/A_M, \pi v/B_M)$, *i.e.* on the evaluation of the average appearing in (1*a*) for the cases of interest. This average, in turn, is based mainly on the statistical properties of the trigonometrical structure factors for the problem examined, and can usually be evaluated in closed form. This is analogous to our approach to other (*e.g.* Shmueli & Weiss, 1987, 1988) distributions in crystallographic statistics.

In order to obtain the desired expression for the p.d.f. of $|E|$ from (1), we replace A and B in (1) by $|E|\cos\varphi$ and $|E|\sin\varphi$ respectively and then use the fact that $p(|E|, \varphi) = |E|\, p(|E|\cos\varphi, |E|\sin\varphi)$. We finally integrate out the phase, taking account of the proper limits of the integration. As shown in Fig. 1, three ranges of E have to be considered in order to cover conveniently the whole rectangle described above:

(*a*) $|E| \le B_M < A_M$

In this range the phase of E can have any value between 0 and 2π.

(*b*) $B_M < |E| \le A_M$

The phase is here restricted and its limits in the positive quadrant are $\varphi_1 = 0$ and $\varphi_2 = \sin^{-1}(B_M/|E|)$.

(*c*) $A_M < |E| \le (A_M^2 + B_M^2)^{1/2}$

The phase is here restricted and its limits in the positive quadrant are $\varphi_1 = \cos^{-1}(A_M/|E|)$ and $\varphi_2 = \sin^{-1}(B_M/|E|)$.

In range (*a*) the p.d.f. of $|E|$ is analogous to that given by Shmueli & Weiss (1987),

$$p(|E|) = \frac{\pi|E|}{2A_M B_M} \sum_u \sum_v C_{uv} J_0\left[\pi|E|\left(\frac{u^2}{A_M^2} + \frac{v^2}{B_M^2}\right)^{1/2}\right]. \tag{2}$$

The ranges (*b*) and (*c*) can be treated by first summing the exponential phase factor in (1) at the points φ, $-\varphi$, $\pi - \varphi$ and $\pi + \varphi$ and subsequently integrating over φ in the positive quadrant only. The p.d.f. of $|E|$ then takes the form

$$p(|E|) = \frac{|E|}{A_M B_M} \sum_u \sum_v C_{uv} \times \int_{\varphi_1}^{\varphi_2} \cos[G(u)\cos\varphi] \cos[H(v)\sin\varphi]\, d\varphi. \tag{3}$$

where $G(u) = \pi|E|u/A_M$ and $H(v) = \pi|E|v/B_M$. The integral in (3) can either be evaluated by numerical integration or in terms of an infinite series. If the former procedure is adopted we recommend use of the Romberg algorithm (*e.g.* Davis & Rabinowitz, 1967), available in user libraries for mainframes (*e.g.* in IMSL) as well as for personal computers (*e.g.* in Borland's Pascal 4.0 Numeric Toolbox). Alternatively, the integrand in (3) can be expressed as an infinite series of Bessel functions, the angular part of which is integrable in closed form. The result is a replacement of the integral by a rapidly converging series. This alternative representation of (3) is

$$p(|E|) = (|E|/A_M B_M)[(\varphi_2 - \varphi_1) + 2(S_1 + S_2 + S_{12})], \tag{4}$$

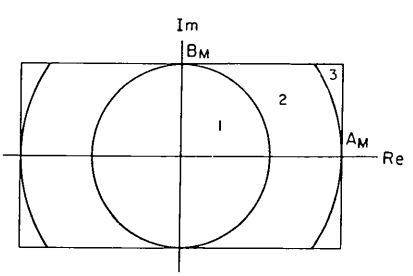

Fig. 1. Geometrical locus of $E = A + iB$ for unequally bounded A and B and its subdivision for the purpose of calculation of the p.d.f. of $|E|$. The numbers 1, 2 and 3 denote the three ranges of the rectangular region which were denoted in the text by (*a*), (*b*) and (*c*) respectively.

where

$$S_1 = \sum_{u=1}^{\infty} C_{u0}\left\{(\varphi_2 - \varphi_1) J_0[G(u)] + \sum_{p=1}^{\infty} (-1)^p J_{2p}[G(u)] \times [\sin(2p\varphi_2) - \sin(2p\varphi_1)]/p\right\}, \tag{5}$$

$$S_2 = \sum_{v=1}^{\infty} C_{0v}\left\{(\varphi_2 - \varphi_1) J_0[H(v)] + \sum_{p=1}^{\infty} J_{2p}[H(v)] \times [\sin(2p\varphi_2) - \sin(2p\varphi_1)]/p\right\}, \tag{6}$$

and

$$S_{12} = \sum_{u=-\infty}^{\infty} \sum_{v=1}^{\infty} C_{uv}\left\{(\varphi_2 - \varphi_1) J_0(\zeta) + \sum_{p=1}^{\infty} (-1)^p J_{2p}(\zeta) \times \{[\sin(2p\varphi_2) - \sin(2p\varphi_1)]/p\} \cos(2p\Delta)\right\}, \tag{7}$$

with

$$\zeta = \{[G(u)]^2 + [H(v)]^2\}^{1/2} \quad \text{and} \quad \Delta = \tan^{-1}(vA_M/uB_M). \tag{8}$$

Summations over the indices u and v in (2) and (3) extend over the range $(-\infty, \infty)$, and even with favorable convergence properties it is worthwhile to take advantage of the symmetry of these summations. It is easily seen that the summations can often be confined to positive indices only, and the multiplicities are best accounted for if the index combinations $u = 0$, $v \neq 0$; $u \neq 0$, $v = 0$; $u \neq 0$, $v \neq 0$ are considered separately. Furthermore, the double summation over non-zero indices need only be evaluated for $u \geq v$, provided suitable internal symmetrization is performed (Shmueli, Rabinovich & Weiss, 1989).

Derivation of Fourier coefficients and related examples

We shall now present the Fourier coefficients for (2) and (3), for the cases (i), (ii) and (iii) outlined in the *Introduction*, and illustrate the corresponding p.d.f.'s.

Anomalous dispersion in the space group $P\bar{1}$

The normalized structure factor can now be written as

$$E = 2 \sum_{j=1}^{N/2} (n_j' + in_j'') \cos\theta_j, \tag{9}$$

where $\theta_j = 2\pi \mathbf{h} \cdot \mathbf{r}_j$, and the real and imaginary parts

of the normalized scattering factor are defined by

$$n'_j = f'_j\left(\sum_{k=1}^{N}|f_k|^2\right)^{-1/2} \quad \text{and} \quad n''_j = f''_j\left(\sum_{k=1}^{N}|f_k|^2\right)^{-1/2}, \tag{10}$$

where $f_j = f'_j + if''_j$ is the conventional scattering factor of the jth atom. The maximum values of A and B are here

$$A_M = \sum_{j=1}^{N} n'_j \quad \text{and} \quad B_M = \sum_{j=1}^{N} n''_j \tag{11}$$

and the locus of E, corresponding to this case, is the rectangle shown in Fig. 1. The characteristic function corresponding to the p.d.f. of $|E|$ is given by

$$C(\omega_1, \omega_2) = \prod_{j=1}^{N/2} C_j(\omega_1, \omega_2),$$

where

$$\begin{aligned} C_j(\omega_1, \omega_2) &= (1/2\pi)\int_{-\pi}^{\pi} \exp\left[2i(\omega_1 n'_j \cos\theta + \omega_2 n''_j \cos\theta)\right] d\theta \\ &= J_0[2(n'_j\omega_1 + n''_j\omega_2)]. \end{aligned} \tag{12}$$

The Fourier coefficients appearing in (2) or (3) are therefore

$$C_{uv} = \prod_{j=1}^{N/2} J_0\left[2\pi\left(n'_j\frac{u}{A_M} + n''_j\frac{v}{B_M}\right)\right]. \tag{13}$$

This situation is illustrated in Fig. 2 by comparing the p.d.f. of $|E|$ for a heterogeneous asymmetric unit of $P\bar{1}$ with and without allowing for dispersion. This hypothetical asymmetric unit is taken as $C_{19}Pt$, all the atoms being assumed to reside in general positions of the space group. It is seen that the effects of dispersion (allowed for only for the heavy atom) are: (i) the p.d.f. equals zero at $|E| = 0$, in contrast to the dispersionless p.d.f. which starts off from some finite value, and (ii) the p.d.f. of $|E|$ shows a small but significant spike at a low value of $|E|$, while its shape is very close to that of the dispersionless one at larger values of $|E|$. Two points might be made about these results: (*a*) one might say that the p.d.f. of $|E|$ is affected by dispersion mainly for small (and usually not so accurately measured) values of $|E|$, so that ignoring dispersion should not affect greatly the resolution of $P1$ *vs* $P\bar{1}$ space-group ambiguity, and (*b*) methods of accurately processing the intensities of weak and 'unobserved' reflections could be gauged against p.d.f.'s of $|E|$ in which dispersion has been allowed for. It appears to be of interest to extend this result to other centrosymmetric space groups in order to confirm these conclusions more generally.

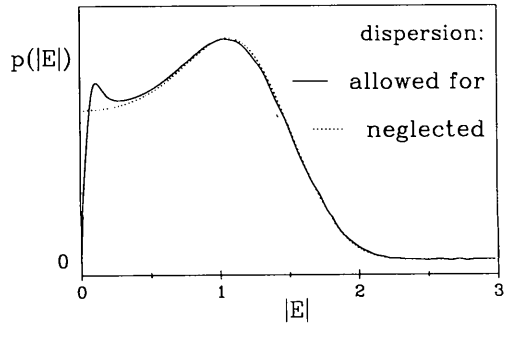

Fig. 2. P.d.f. of $|E|$ for $P\bar{1}$: a strongly dispersive scatterer. The figure presents the p.d.f. of $|E|$ for the space group $P\bar{1}$, for the assumed composition $C_{19}Pt$ of the asymmetric unit. The solid line denotes the p.d.f. computed from (2) and (3) with Fourier coefficients obtained from (13). The real and imaginary parts of the dispersion correction are taken from *International Tables for X-ray Crystallography* (1962). The dotted curve corresponds to the p.d.f. of $|E|$ for the above composition but with neglect of dispersion (as in Shmueli *et al.*, 1984).

A subcentric arrangement in the space group P1

An exact characteristic function for this example was briefly presented elsewhere (Weiss, Shmueli, Kiefer & Wilson, 1985) and is rederived here for completeness. Let the unit cell of $P1$ contain N atoms and let M of them constitute a centrosymmetric fragment, the remaining $N - M$ atoms not being related by any symmetry operation. It is also easy to account for anomalous dispersion in the centrosymmetric fragment of such an arrangement.

If we choose the origin at the (non-crystallographic) center of symmetry the normalized structure factor can be written as

$$\begin{aligned} E &= 2\sum_{j=1}^{M/2} n_j \cos\theta_j + \sum_{j=M+1}^{N} n_j(\cos\theta_j + i\sin\theta_j) \\ &\equiv A + iB, \end{aligned} \tag{14}$$

where n_j is the normalized scattering factor of the jth atom. The maximum values of the real and imaginary parts of E are, in the present case,

$$A_M = 2\sum_{j=1}^{M/2} n_j + \sum_{j=M+1}^{N} n_j$$

and

$$B_M = \sum_{j=M+1}^{N} n_j \tag{15}$$

and are used in the construction of the Fourier series for the p.d.f. of $|E|$ for this situation. The locus of E is also contained in the rectangle shown in Fig. 1. The Fourier coefficients are obtained by evaluating the average in (1*a*), with A and B defined in (14). These coefficients evaluate to

$$C_{uv} = \prod_{j=1}^{M/2} J_0\left(\frac{2\pi u n_j}{A_M}\right) \prod_{j=M+1}^{N} J_0\left[\pi n_j\left(\frac{u^2}{A_M^2} + \frac{u^2}{B_M^2}\right)^{1/2}\right], \tag{16}$$

where dispersion has been neglected. All one has to

do in order to account for anomalous dispersion of the centrosymmetric fragments is to replace un_j/A_M in the first product in (16) by $un'_j/A_M + vn''_j/B_M$, where $n_j = n'_j + in''_j$, for the dispersive scatterer. The p.d.f. of $|E|$ is then computed from (2) or (3) according to the value of $|E|$, as described above.

As pointed out above, the influence of the subcentric arrangement on the p.d.f. of the structure-factor magnitude was considered by several authors (Srinivasan & Parthasarathy, 1976; Wilson, 1980; Shmueli & Wilson, 1983), who used approximations based on the central limit theorem as well as higher-order corrections. The present result allows one to evaluate this effect from an exactly formulated p.d.f., for any atomic composition. Dispersion corrections as outlined in the previous section can also be taken into account. Curves of some typical p.d.f.'s for the present case are shown in Figs. 3 and 4. Fig. 3 shows the p.d.f. of $|E|$ for the space group $P1$, the unit cell of which contains a centrosymmetric fragment with

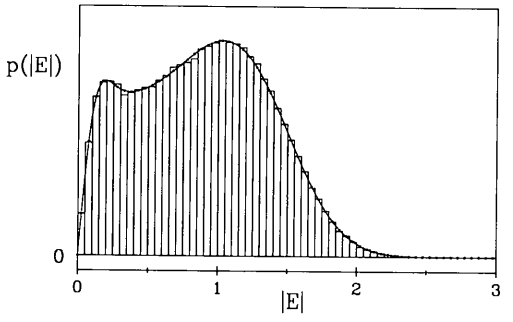

Fig. 3. P.d.f. of $|E|$ for $P1$: a heterogeneous subcentric arrangement. The assumed composition of the unit cell of $P1$ is $C_{43}Pt_2$, where $C_{38}Pt_2$ comprises a centrosymmetric fragment with the atoms in general positions and the dispersion of platinum is allowed for. Solid line: theoretical p.d.f. from (2) and (3) and a modified version of (17) that accounts also for dispersion. The histogram is constructed from magnitudes of simulated normalized structure factors, for the above composition and dispersive contribution of platinum.

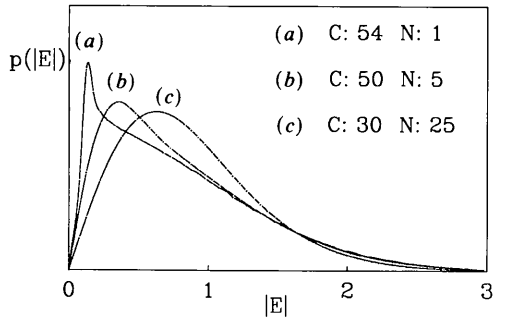

Fig. 4. P.d.f. of $|E|$ for $P1$: equal-atom subcentric arrangements. The assumed composition of the unit cell is C_{55} in each of the three cases here considered. In the label above, C: is followed by the number of atoms in the centrosymmetric fragment and N: by the number of atoms outside the centrosymmetric fragment.

composition $C_{38}Pt_2$ and five C atoms not related by a non-crystallographic center of symmetry. Moreover, the dispersion of the Pt atom is also taken into account. As expected, there is here only a slight departure from centrosymmetry which gives rise to a considerable similarity to the centrosymmetric p.d.f. (with dispersion) in Fig. 2. Fig. 4 shows the effect of subcentric arrangements for the equal-atom case; three situations are considered, all corresponding to 55 C atoms in the unit cell of $P1$. It is interesting to note that even the extreme pseudocentrosymmetry in Fig. 4(a) leads to a p.d.f. significantly different from the ideal centric one.

Special positions in the space group P222

Let the asymmetric unit of this space group contain M atoms, K of them occupying general positions and $L = M - K$ being located on twofold axes of the space group. Since the Fourier coefficients of the p.d.f. of $|E|$ are just the values of the characteristic function at points corresponding to summation indices, the general form of the Fourier coefficient must be a product of contributions of atoms lying in general positions and those located on twofold axes. The contributions from general positions can be taken from Shmueli & Weiss (1987), while those from the special ones are obtained by noting that the trigonometric structure factor for an atom located on a twofold axis of $P222$ has the form

$$\xi_s = 2\cos\theta \quad \text{and} \quad \eta_s = 0, \tag{17}$$

for any of the three independent axes of rotation. The structure factor for the above arrangement is therefore given by

$$E = \sum_{j=1}^{K} n_j\xi_{gj} + i\sum_{j=1}^{K} n_j\eta_{gj} + \sum_{j=1}^{L} n_j\xi_{sj}, \tag{18}$$

where $\xi_{gj} + i\eta_{gj}$ is the trigonometric structure factor for an atom located in a general position of this space group. The maximum values of the real and imaginary parts of $|E|$ are now given by

$$A'_M = \sum_{j=1}^{K} n_j, \qquad q = \sum_{j=K+1}^{M} n_j, \qquad A_M = A'_M + q,$$
$$B_M = \sum_{j=1}^{K} n_j \tag{19}$$

and are used in the calculation of the p.d.f. of $|E|$. As pointed out by Wilson (1989) the contour surrounding the locus of possible non-zero $p(A, B)$ values, corresponding to this case, is a rectangle of sides $2q$ and $2B_M$ terminated by two semicircles of radius B_M. This contour is obviously contained in the rectangular boundary shown in Fig. 1. The expressions for the p.d.f. of $|E|$ are analogous to those in the previous subsection. The required Fourier coefficient is a product of all the atomic contributions

and is therefore given by

$$C_{uv} = \prod_{j=1}^{K} \left[(2/\pi) \int_0^{\pi/2} J_0(|X_j + Y_j|) J_0(|X_j - Y_j|)\, \mathrm{d}\theta \right] \times \prod_{j=K+1}^{M} J_0(2\pi u n_j / A_M), \quad (20)$$

where

$$X_j = (2\pi u n_j / A_M) \cos\theta$$

and

$$Y_j = (2\pi v n_j / B_M) \sin\theta. \quad (21)$$

Results of numerical calculations based on the formulae just derived are illustrated by curves shown in Fig. 5, where we compare the case of a highly heterogeneous asymmetric unit with all the atoms in general positions (Fig. 5*a*) of the space group *P*222, the above plus two Pt atoms on one of the twofold axes (Fig. 5*b*) and the ideal acentric p.d.f. (Fig. 5*c*). The three p.d.f.'s are remarkably similar which indicates that intensity statistics for this space group are insensitive to both atomic heterogeneity and the presence of heavy scatterers in special positions. This insensitivity is exceptional among the space groups of low symmetry. This could be demonstrated only by recourse to the present general theory.

We have also carried out a number of test calculations that suggested themselves in view of the referee's remarks and the novel aspect of the study here reported. Thus, phase integrations using the exact contours were compared with those done on the rectangular boundary, and a complete agreement was observed. All the calculated p.d.f.'s have been compared with corresponding simulated histograms of $|E|$ as described by Shmueli *et al.* (1984). The sample size was kept at 200 000 and the resulting R factors range from 0·01 to 0·02. All these results are consistent with our arguments presented above which justify the use of the analytically more convenient rectangular boundary rather than the exact contour that might correspond to a given situation. It should be pointed out, however, that the larger the regions within the boundary for which $p(|E|) = 0$, the more terms in the Fourier summation are required for good convergence.

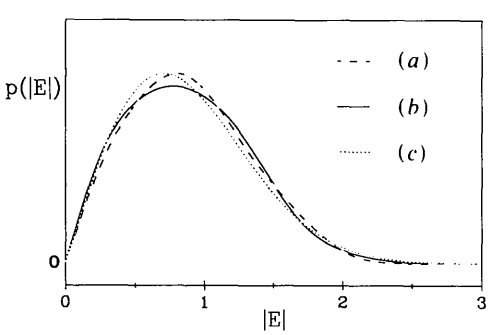

Fig. 5. P.d.f. of $|E|$ for *P*222: ideal and non-ideal distributions. (*a*) Asymmetric unit: $C_{19}Pt$, all atoms in general positions, (*b*) as (*a*), but with a Pt atom on a twofold axis, (*c*) ideal acentric p.d.f.

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