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Moments of the Trigonometric Structure Factor

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Abstract

The eighth moment of the magnitude of the trigonometric structure factor has been computed for all the space groups and all the reflection subsets giving rise to different functional forms of this quantity. This extension of previously published computations of lower moments permits the construction of four-term generalized distributions of normalized intensity, which are necessary in treating problems arising from highly heterogeneous atomic compositions in various space-group symmetries. The related problem of odd–even mixed partial moments of the trigonometric structure factor has also been investigated, and these mixed moments were found to vanish for all the three-dimensional space groups, confirming the correctness of the hitherto published theoretical statistics. Similar computations for the plane groups showed that non-zero values of the mixed partial odd–even moments are obtained for *p*3, *p*31*m*, *p*3*m*1, *p*6 and *p*6*m*. This result calls for some modifications of the statistical formalism to be applied to two-dimensional sets of intensity data. The modifications required for the centrosymmetric case are indicated in some detail.

Introduction

Statistical treatments of distributions of the diffracted intensity range from the use of asymptotic distributions based on the central-limit theorem (*e.g.* Cramér, 1951, p. 214) to applications of generalized expansions, associated with such asymptotic probability functions. The latter include the well known centric and acentric Wilson (1949) distributions, as well as a few others which allow for hypersymmetry (Rogers & Wilson, 1953), partial centrosymmetry (Srinivasan & Parthasarathy, 1976) and dispersion (Wilson, 1980). Generalizations of the above consist of expansions in terms of orthogonal polynomials with coefficients depending explicitly on the space-group symmetry, number of atoms in the unit cell and their scattering powers (*e.g.* Hauptman & Karle, 1953; Bertaut, 1955; Klug, 1958; Shmueli, 1979; Shmueli & Wilson, 1981, 1983; Shmueli, 1982*a*). The dependence on symmetry enters the formalisms *via* mean values of powers of trigonometric structure-factor moduli and the computation of these mean values, or moments, is a prerequisite for any practical application of these generalized statistics. The first extensive calculation of this kind was carried out by Wilson (1978) who found the fourth moment of the trigonometric structure factor for all the space groups but two (*Fd*3*m* and *Fd*3*c*). Similar straightforward calculations of moments higher than the fourth proved impracticably cumbersome and error-prone, and two computer programs were developed whereby the fourth and sixth moments have been obtained for all the space groups and all the reflection subsets that give rise to different functional forms of the structure factor (Shmueli & Kaldor, 1981). Since moments up to and including the 2*n*th are required for *n*-term expansions (*cf.* Shmueli & Wilson, 1981) the above computations led to generally usable three-term distributions. However, simulated distributions (Shmueli, 1982*b*), as well as those recalculated from published structures of several organometallic compounds (Shmueli, 1982*a*), show clearly that for extreme atomic heterogeneities (*e.g.* a platinum among fifteen light non-H atoms), still encountered in practical work, at least four-term generalized expansions are

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required and hence the numerical values of the eighth moment of the trigonometric structure factor are of importance. The computation of this moment is described in the present paper.

While this work was being planned, we have also decided to investigate the problem of mixed odd–even partial moments of the trigonometric structure factor, which were stated to be non-zero for some (unspecified) space groups (Foster & Hargreaves, 1963; Srinivasan & Parthasarathy, 1976). These partial moments were ignored in previous investigations, which dealt only with three-dimensional groups. In fact, a computation of the third moment of the trigonometric structure factor, for a large variety of space groups (Shmueli & Wilson, 1982), did not reveal any non-vanishing moments, in the three-dimensional case. Since, however, these partial moments form part of the even cumulant of the structure factor (*e.g.* Shmueli & Wilson, 1982) it was deemed worth while, in this study, to supplement previous preliminary considerations by a proper all-space-group computation of these quantities. As will be seen, such odd–even partial moments indeed exist in some *plane* groups only, and can be readily incorporated into generalized intensity statistics of two-dimensional sets of intensity data. The problem of odd moments has been briefly mentioned elsewhere (Foster, Hargreaves, Shmueli & Wilson, 1982).

Computation of the eighth moment

The trigonometric structure factor is given by

$$J_j(\mathbf{h}) = \sum_{s=1}^{g} \exp[2\pi i \mathbf{h}^T(\mathbf{P}_s \mathbf{r}_j + \mathbf{t}_s)], \qquad (1)$$

where g is the order of the point group of the crystal times the multiplicity of its Bravais lattice, $\mathbf{h}^T$ is the diffraction vector (hkl), $(\mathbf{P}_s|\mathbf{t}_s)$ is the sth space-group operation and $\mathbf{r}_j$ is the position vector of the jth atom in the asymmetric unit of the crystal.

Even absolute moments of J can be computed either by making direct use of (1) (Shmueli & Kaldor, 1981) or by using simplified trigonometric expressions for the real and imaginary parts of J, in the process of averaging (Wilson, 1978; Shmueli & Kaldor, 1981).

In the direct approach, the absolute even moment of J is written as

$$\begin{aligned}\langle |J|^{2n}\rangle &= \langle (JJ^*)^n\rangle \\ &= \sum_{k_1}\ldots\sum_{k_{2n}} \left\langle \exp\left[2\pi i \mathbf{h}^T \sum_{k_m=k_1}^{k_{2n}} (-1)^{m-1} \right.\right. \\ &\qquad \left.\left. \times (\mathbf{P}_{k_m}\mathbf{r} + \mathbf{t}_{k_m})\right]\right\rangle. \qquad (2)\end{aligned}$$

As shown by Shmueli & Kaldor (1981), a term in (2) may give a non-zero contribution provided the sum

$$\sum_{k_m=k_1}^{k_{2n}} (-1)^{m-1} \mathbf{P}_{k_m} \qquad (3)$$

reduces to a zero matrix. When this condition is satisfied and $\mathbf{r}$ is not a special position with respect to the set of symmetry operations in (1), the value of such a contribution is given by

$$\exp\left[2\pi i \mathbf{h}^T \sum_{k_m=k_1}^{k_{2n}} (-1)^{m-1} \mathbf{t}_{k_m}\right]. \qquad (4)$$

Of course, only the representative parities of h, k and l need be considered in evaluating (4).

For $n = 2$, the (fourth) moments of $|J|$ can be readily computed for all the space groups by a rather straightforward search for zero matrices, employing (3) and (4). For $n = 3$, computations for space groups with g exceeding 24 become time-consuming (Shmueli & Kaldor, 1981), while for $n = 4$, *i.e.* for the present application to the eighth moment of $|J|$, $g = 12$ appears to be a convenient practical upper limit. Of course, in all such computations the inherent symmetry of the multiple summation (2) is allowed for, some programming shortcuts that suggest themselves are employed and the above feasibility estimates refer to the computational facilities at our disposal (a CDC 6600 computer).

For space groups of higher orders the trigonometric approach was found to be much more suitable (Shmueli & Kaldor, 1981). The algorithm for such computations is based on encoding the standard sine/cosine products (*e.g.* $\cos 2\pi kx \cos 2\pi hy \sin 2\pi lz$, *International Tables for X-ray Crystallography*, 1952) in a form which permits us to keep track of the exponents of their powers, deleting terms which contain odd powers and substituting the appropriate integrals for the averages of even-powered terms. This algorithm was modified for the present application in two respects: (i) standard sine/cosine products containing two factors (for plane groups) or four factors (for hexagonal space groups) were allowed for and (ii) the computation was made to include mixed partial moments $\langle A^k B^l\rangle$, where A and B are the real and imaginary parts of J.

A practical difficulty was posed here by the elegantly simplified forms of A and B for the trigonal and hexagonal space groups (*International Tables for X-ray Crystallography*, 1952), the expansion of which to the standard triple and quadruple sine/cosine products proved to be rather tedious. This was overcome by making use of the Lisp-based Reduce system (*cf. Computers in the New Laboratory – A Nature Survey*, 1981), which accepts as input arguments of the form: $hx_s + ky_s + lz_s$, where x_s, y_s and z_s are symbolic coordinates of a point generated by the sth space-group operation, and expands the sums of their cosines and sines to the required form and format (see Appendix *B*).

The modification of the second algorithm was checked in several ways, among them a comparison with results produced by the first algorithm described above and a computation of $\langle|J|^4\rangle$ as $\langle A^4\rangle$ + $2\langle A^2B^2\rangle + \langle B^4\rangle$, as well as by the usual method.

The results of this computation are presented in Table 1 as $s = \langle|J|^8\rangle$ and $p = \langle|J|^2\rangle$, for all the space groups and all reflection subsets for which different numerical values of the eighth moment were obtained. These moments are strictly valid for statistics involving sets of general *hkl* reflections and structures with all the atoms distributed among the general Wyckoff positions.

The results obtained for triclinic, monoclinic and orthorhombic space groups (except *Fdd*2 and *Fddd*) are in agreement with those obtainable from the works of Foster & Hargreaves (1963) and Srinivasan & Parthasarathy (1976) and with the closed exact expressions for

$$\gamma_{2n} = \langle|J|^{2n}\rangle/\langle|J|^2\rangle^n,$$

given by Shmueli (1982*a*) for these simple but important cases.

It may also be pointed out that approximate moments of *J*, as well as the partial moments $\langle A^kB^l\rangle$, can be evaluated by replacing *hx*, *ky*, *lz*, *etc.* with pseudo-random numbers which are uniform in the [0,1] range. This approach is more rapid for higher moments since the computing time is independent of the order of the moment required. It is also much easier to program. However, in order to obtain accurate values of such simulated moments, it is important to use random 'seeds' with the computer-generated pseudo-random numbers. Exact moments, such as those published elsewhere (Wilson, 1978; Shmueli & Kaldor, 1981) and given in Table 1, are of course preferable but the approximate ones may be sufficient for some applications.

The first four even moments of $|J|$ have also been computed for the 17 plane groups and general reflections. The results for the fourth moment, $q = \langle|J|^4\rangle$, are in agreement with those given by Wilson (1978) and the same correspondence between the q values for the plane and related space groups (*cf.* Tables 1 and 2, Wilson, 1978) also exists for the sixth and eighth moments of *J*. For example, the moments obtained for the plane groups *p*4*m* and *p*4*g* are the same as those for *P*4*mm*, and the moments for *p*6*m* coincide with those for *P*6*mm*.

The partial odd–even moments of the trigonometric structure factor are treated in the next section.

The mixed partial moments of $|J|$

In order to state the problem of non-vanishing odd–even moments and indicate how the results obtained in the previous section fit into generalized intensity statistics it is recalled that the probability density function for the normalized structure amplitude $|E|$ is given by

$$P(|E|) = \left(\frac{2}{\pi}\right)^{1/2} \exp\left(-\frac{|E|^2}{2}\right) \times \left[1 + \sum_{k=2}^{N} \frac{A_{2k}}{2^k(2k)!} H_{2k}\left(\frac{|E|}{\sqrt{2}}\right)\right] \quad (5)$$

for centrosymmetric space groups (Shmueli & Wilson, 1981; Shmueli, 1982*a*), where H_{2k} are Hermite polynomials as defined, for example, by Abramowitz & Stegun (1972) and A_{2k} are coefficients depending on space-group symmetry and atomic composition. It has recently been shown that these expansion coefficients are simply related to the cumulants of the centrosymmetric structure factor F (Shmueli & Wilson, 1982). We have

$$\Sigma^2 A_4 = K_4(F) \quad (6)$$

$$\Sigma^3 A_6 = K_6(F), \quad (7)$$

$$\Sigma^4 A_8 = K_8(F) + 35[K_4(F)]^2, \textit{etc.} \quad (8)$$

with

$$K_{2r}(F) = \sum_{j=1}^{m} f_j^{2r} K_{2r}(J_j), \quad (9)$$

where $K_{2r}(y)$ is the 2*r*th cumulant of the real random variable y (*e.g.* Kendall & Stuart, 1969), Σ is the sum of squared moduli of the atomic scattering factors f (Wilson, 1942, 1978) and m is the number of atoms in the asymmetric unit.

Standard cumulant–moment relationships are available in the statistical literature and those relevant to (6)–(8) are given by

$$K_4 = \mu_4 - 3\mu_2^2 \quad (10)$$

$$K_6 = \mu_6 - 15\mu_4\mu_2 - 10\mu_3^2 + 30\mu_2^3 \quad (11)$$

and

$$K_8 = \mu_8 - 28\mu_6\mu_2 - 56\mu_5\mu_3 - 35\mu_4^2 + 420\mu_4\mu_2^2 + 560\mu_3^2\mu_2 - 630\mu_2^4, \quad (12)$$

where K_r are the cumulants and μ_r the moments of the distribution in question (Kendall & Stuart, 1969). In our case, μ_r should be replaced with $\langle J^r\rangle$ in order to compute (9) and use it with the distribution given by (5). A corresponding formalism can also be given for the non-centrosymmetric case but the complexity increases, since, with possibly non-vanishing odd moments, the moments of $|J|$ must be replaced with combinations of mixed moments of the form $\langle A^kB^l\rangle$ (see moments and cumulants of bivariate distributions; Kendall & Stuart, 1969). If, however, the odd moments vanish, the absolute moments $\langle|J|^{2n}\rangle$ can be

Table 1. *The eighth absolute moment of the trigonometric structure factor*

The symbols *p* and *s* denote the second and eighth moments of $|J|$ respectively. The numbers in parentheses, appearing beside some space-group entries, refer to *hkl* subsets which are defined in the footnotes† to the table. These subset references are identical with those in Table 1 of Shmueli & Kaldor (1981).

Symmetry	*p*	*s*
Point group: 1		
P1	1	1
Point group: $\bar{1}$		
P$\bar{1}$	2	70
Point groups: 2, m		
All P	2	70
All C	4	8960
Point group: 222		
All P	4	2716
All C and I	8	347648
F222	16	44498944
Point groups: 2/m, mm2		
All P	4	4900
All C and I	8	627200
Fmm2	16	80281600
Fdd2 (1)	16	80281600
Fdd2 (2)	16	11075584
Point group: mmm		
All P	8	343000
All C and I	16	43904000
Fmmm	32	5619712000
Fddd (1)	32	5619712000
Fddd (2)	32	775290880
Point group: 4		
P4, P4_2	4	4900
P4_1* (3)	4	4900
P4_1* (4)	4	676
I4	8	627200
I4_1 (5)	8	627200
I4_1 (6)	8	86528
Point group: $\bar{4}$		
P$\bar{4}$	4	2716
I$\bar{4}$	8	347648
Point group: 4/m		
All P	8	343000
I4/m	16	43904000
I4_1/a (7)	16	43904000
I4_1/a (8)	16	6056960
Point group: 422		
P422, P42_12, P4_222 and P4_22_12	8	107656
P4_122, P4_12_12* (3)	8	107656
P4_122, P4_12_12* (4)	8	30088
I422	16	13779968
I4_122 (7)	16	13779968
I4_122 (8)	16	3851264
Point group: 4mm		
All P		190120
I4mm, I4cm	16	24335360
I4_1md, I4_1cd (7)	16	24335360
I4_1md, I4_1cd (8)	16	3888128
Point groups: $\bar{4}$2m, $\bar{4}$m2		
All P	8	107656
I$\bar{4}$m2, I$\bar{4}$2m, I$\bar{4}$c2	16	13779968
I$\bar{4}$2d (5)	16	13779968
I$\bar{4}$2d (6)	16	3851264

Symmetry	*p*	*s*
Point group: 4/mmm		
All P	16	13308400
I4/mmm, I4/mcm	32	1703475200
I4_1/amd, I4_1/acd (5)	32	1703475200
I4_1/amd, I4_1/acd (6)	32	272168960
Point group: 3		
All P and R	3	639
Point group: $\bar{3}$		
All P and R	6	44730
Point group: 32		
All P and R	6	18306
Point group: 3m		
P3m1, P31m, R3m	6	21762
P3c1, P31c (3); R3c (1)	6	21762
P3c1, P31c (4); R3c (2)	6	14850
Point group: $\bar{3}$m		
P$\bar{3}$m1, P$\bar{3}$1m, R$\bar{3}$m	12	1523340
P$\bar{3}$c1, P$\bar{3}$1c (3); R$\bar{3}$c (1)	12	1523340
P$\bar{3}$c1, P$\bar{3}$1c (4); R$\bar{3}$c (2)	12	1039500
Point group: 6		
P6	6	54810
P6_1* (9)	6	54810
P6_1* (10)	6	5814
P6_1* (11)	6	6966
P6_1* (12)	6	34650
P6_2* (13)	6	54810
P6_2* (14)	6	6966
P6_3 (3)	6	54810
P6_3 (4)	6	34650
Point group: $\bar{6}$		
P$\bar{6}$	6	44730
Point group: 6/m		
P6/m	12	3836700
P6_3/m (3)	12	3836700
P6_3/m (4)	12	2425500
Point group: 622		
P622	12	792900
P6_122* (9)	12	792900
P6_122* (10)	12	221436
P6_122* (11)	12	230652
P6_122* (12)	12	683460
P6_222* (13)	12	792900
P6_222* (14)	12	230652
P6_322 (3)	12	792900
P6_322 (4)	12	683460
Point group: 6mm		
P6mm	12	1845900
P6cc (3)	12	1845900
P6cc (4)	12	878220
P6_3cm, P6_3mc (3)	12	1845900
P6_3cm, P6_3mc (4)	12	1200780
Point groups: $\bar{6}$m2, $\bar{6}$2m		
P$\bar{6}$m2, P$\bar{6}$2m	12	1523340
P$\bar{6}$c2, P$\bar{6}$2c (3)	12	1523340
P$\bar{6}$c2, P$\bar{6}$2c (4)	12	1039500

Table 1 (*cont.*)

Symmetry	p	s
Point group: 6/mmm		
P6/mmm	24	129213000
P6/mcc (3)	24	129213000
P6/mcc (4)	24	61475400
P6_3/mcm, P6_3/mmc (3)	24	129213000
P6_3/mcm, P6_3/mmc (4)	24	84054600
Point group: 23		
P23 , P$2_1$3	12	388116
I23 , I$2_1$3	24	49678848
F23	48	6358892544
Point group: m3		
Pm3 , Pn3 , Pa3	24	38997000
Im3 , Ia3	48	4991616000
Fm3	96	638926848000
Fd3 (1)	96	638926848000
Fd3 (2)	96	259740794880
Point group: 432		
P432 , P$4_2$32	24	14524920
P$4_1$32* (15)	24	14524920
P$4_1$32* (16)	24	8016120
P$4_1$32* (17)	24	4990968
P$4_1$32* (18)	24	3790584
I432	48	1859189760
I$4_1$32 (15)	48	1859189760
I$4_1$32 (17)	48	638843904
F432	96	237976289280
F$4_1$32 (15)	96	237976289280
F$4_1$32 (18)	96	62104928256
Point group: $\bar{4}$3m		
P$\bar{4}$3m	24	18948600
P$\bar{4}$3n (1)	24	18948600
P$\bar{4}$3n (2)	24	10101240
I$\bar{4}$3m	48	2425420800
I$\bar{4}$3d (15);(20)	48	2425420800
I$\bar{4}$3d (15);(21)	48	1292958720
I$\bar{4}$3d (17)	48	638843904
F$\bar{4}$3m	96	310453862400
F$\bar{4}$3c (15)	96	310453862400
F$\bar{4}$3c (18)	96	165498716160
Point group: m3m		
Pm3m , Pn3m	48	2241141840
Pn3n, Pm3n (1)	48	2241141840
Pn3n, Pm3n (2)	48	1126374480
Im3m	96	286866155520
Ia3d (15);(20)	96	286866155520
Ia3d (15);(21)	96	144175933440
Ia3d (17)	96	41452185600
Fm3m	192	36718867906560
Fm3c (1)	192	36718867906560
Fm3c (2)	192	18454519480320
Fd3m (1)	192	36718867906560
Fd3m (2)	192	7573068840960
Fd3c (1)	192	36718867906560
Fd3c (2)	192	5036353781760

* And the enantiomorphous space group.

† Remarks: (1) $h + k + l = 2n$; (2) $h + k + l = 2n + 1$; (3) $l = 2n$; (4) $l = 2n + 1$; (5) $2h + l = 2n$; (6) $2h + l = 2n + 1$; (7) $2k + l = 2n$; (8) $2k + l = 2n + 1$; (9) $l = 6n$; (10) $l = 6n + 1, 6n + 5$; (11) $l = 6n + 2, 6n + 4$; (12) $l = 6n + 3$; (13) $l = 3n$; (14) $l = 3n + 1, 3n + 2$; (15) *hkl* all even; (16) only one index odd; (17) only one index even; (18) *hkl* all odd; (19) two indices odd; (20) $h + k + l = 4n$; (21) $h + k + l = 4n + 2$.

used as they stand and the acentric analogs of (6)–(8) have the same functional form but different numerical coefficients (Shmueli & Wilson, 1981, 1981) for non-centrosymmetric space groups.

It was pointed out by Foster & Hargreaves (1963) that the mixed partial moments

$$m_{kl} = \langle A^k B^l \rangle,$$

where $J = A + iB$, vanish for triclinic, monoclinic and orthorhombic space groups if either k or l are odd, that m_{kl} with l odd vanish always but m_{kl} with k odd and l even may be non-zero for some space groups of higher symmetry.

We have examined the latter possibility by computing m_{kl}, for all combinations of k and l with $k + l = 3$ and 5, for all the three-dimensional and two-dimensional (plane) groups. The computation was done by the methods applied to the eighth moment (see above). The partial moments m_{kl} vanish *for all the three-dimensional space groups* including all the *hkl* subsets for which A and B have different functional forms within the same space group. It follows that the neglect of odd moments of the trigonometric structure factor (*e.g.* Shmueli & Wilson, 1981) is fully justified for three-dimensional sets of intensity data.

Non-zero values of m_{kl}, with k odd and l even, were obtained for the plane groups: *p*3, *p*3*ml*, *p*31*m*, *p*6 and *p*6*m*, only. These results are summarized in Table 2 along with the corresponding third and fifth moments of the (complex) trigonometric structure factor. An interpretation of these non-vanishing moments is given in Appendix *A* for some specific examples.

The results given in Table 2 may be of importance in the computation of intensity statistics for two-dimensional sets of data. The previously published expressions for the centrosymmetric case can be corrected (for plane groups *p*6 and *p*6*m*) by including the terms $-10m_{30}^2$ and $-56m_{50}m_{30} + 560^2_{30}m_{20}$ in the sixth and eighth cumulants of J respectively [*cf.* (7), (8), (11) and (12)], while those for the non-centrosymmetric case can be modified for the plane groups *p*3, *p*3*ml* and *p*31*m* making use of the expressions given by Foster & Hargreaves (1963) and Shmueli & Wilson (1981) for the even moments of the normalized intensity. The above modifications will be taken care of

Table 2. *Non-vanishing odd moments of the trigonometric structure factor*

All the non-zero partial moments $m_{kl} = \langle A^k B^l \rangle$, where A and B are the real and imaginary parts of J respectively and $k + l = 3$ and 5, are given in the first five rows of the table. The real parts of the total odd moments* are given by

$$\langle \mathrm{Re}(J^3) \rangle = m_{30} - 3m_{12}$$

and

$$\langle \mathrm{Re}(J^5) \rangle = m_{50} - 10m_{32} + 5m_{14};$$

the imaginary parts, containing m_{kl} with odd l, vanish.

	$p3$	$p31m$	$p3m1$	$p6$	$p6m$
m_{30}	$1\frac{1}{2}$	3	3	12	24
m_{12}	$-1\frac{1}{2}$	−3	−3	—	—
m_{50}	$11\frac{1}{4}$	$67\frac{1}{2}$	$67\frac{1}{2}$	360	2160
m_{32}	$-2\frac{1}{4}$	$-13\frac{1}{2}$	$-13\frac{1}{2}$	—	—
m_{14}	$-6\frac{3}{4}$	$-40\frac{1}{2}$	$-40\frac{1}{2}$	—	—
$\langle J^3 \rangle$	6	12	12	12	24
$\langle J^5 \rangle$	0	0	0	360	2160

* The values of the mixed partial moments m_{kl} were obtained by a direct averaging of the trigonometric expressions for the above plane groups while those of the third and fifth moment of J resulted from a zero-matrix computation (see Appendix *A*). The latter also serve as a check of internal consistency of the two computations.

in a further development of application software for intensity statistics.

APPENDIX *A*

The following considerations, related to the odd–even partial moments of the trigonometric structure factor, may prove illustrative.

It is easily seen that the sum of the rotation matrices which appear in the plane group $p3$ must be a zero matrix. For if $\mathbf{r}$ is any non-zero vector in the plane perpendicular to the threefold axis, we must have: $\mathbf{r} + \mathbf{3r} + \mathbf{3}^2\mathbf{r} = 0$ and hence the sum $\mathbf{1} + \mathbf{3} + \mathbf{3}^2$ is a zero operator.

Consider the third moment of the complex trigonometric structure factor for this plane group. We have

$$\begin{aligned}\langle J^3 \rangle &= \langle \mathrm{Re}(J^3) \rangle + i\langle \mathrm{Im}(J^3) \rangle \\ &= \sum_s \sum_t \sum_u \langle \exp[2\pi i \mathbf{h}^T(\mathbf{P}_s + \mathbf{P}_t + \mathbf{P}_u)\mathbf{r}] \rangle, \qquad (A1)\end{aligned}$$

where $\mathbf{h}^T = (hk)$, $\mathbf{r}^T = (xy)$ and $\mathbf{P}$ ranges over the 2×2 matrices which comprise the two-dimensional point group 3.

As pointed out by Shmueli & Kaldor (1981), a term in such a summation usually vanishes since the real part of the exponent can be assumed uniform in $[0,2\pi]$, except where the exponent vanishes. In the present case, for general non-zero r, this can happen only if $\mathbf{P}_s + \mathbf{P}_t + \mathbf{P}_u$ reduces to a zero matrix and, as can be seen by inspection, only the six terms in ($A1$) with $s \neq t \neq u$ will give (unit) contributions in the case of $p3$. Hence, $\langle J^3 \rangle = 6$ for this plane group.

On the other hand, writing J as $A + iB$, we have

$$\langle J^3 \rangle = m_{30} - 3m_{12} + i(3m_{21} - m_{03}), \qquad (A2)$$

where $m_{pq} = \langle A^p B^q \rangle$, in agreement with the results in Table 2. The fact that $3m_{21} - m_{03}$ is zero is consistent with a remark made by Foster & Hargreaves (1963) to the effect that m_{pq} always vanishes for odd q. This was corroborated by our computations for $p + q = 3$ and 5 (see text).

The use of symmetry in such calculations may be of some interest. For example, for the plane group $p6$, the rotation matrices correspond to the operators: $\mathbf{1}$, $\mathbf{3}$, $\mathbf{3}^2$, $-\mathbf{1}$, $-\mathbf{3}$ and $-\mathbf{3}^2$. Hence, the trigonometric structure factor for $p6$ can be written as

$$J_{p6} = J_{p3} + J^*_{p3} = 2A_{p3} \qquad (A3)$$

and its third moment is

$$\langle J^3_{p6} \rangle = m_{30}(p6) = 8m_{30}(p3) \qquad (A4)$$

as given in Table 2.

Similar factorizations of space groups may, in principle, lead to significant simplifications of the computations. However, in the case of even moments of $|J|$, all the partial moments must be evaluated and, at least for the purpose of the present study, a straightforward search for zero matrices or a treatment of the full trigonometric expressions for the real and imaginary parts of J appear to be safer and more efficient.

APPENDIX *B*

Comments on symbolic programming with Reduce

The application of symbolic programming with the Reduce language (Hearn, 1973) to an automated development of trigonometric structure factors, mentioned in the text, is a simple example of this approach which is still rather uncommon in the crystallographic literature.

Symbolic programming, as such, is one of the oldest algorithmic approaches but it was not until user-oriented preprocessors of traditional symbolic languages became available that such applications became accessible to the general user.

The 'working' language, in the present application, is Lisp and its preprocessor is Reduce (Hearn, 1973). The latter has a closely similar syntax to that of Algol and, of course, no deep understanding of the intricacies of Lisp is required in order to apply Reduce. In other words, the instructions of Reduce are translated to those of Lisp just as Fortran, with which most crystallographers are familiar, is translated to an assembly language.

Reduce recognizes a small number of elementary functions but allows the user to define his own functions and operators. For example, in the present problem we need an operator which permits the expansion of a sine and a cosine of a sum of several angles into combinations of products of these functions. Denoting sine and cosine by S and C respectively, the required definition involves the following Reduce instructions:

```
OPERATOR C,S;
FOR ALL X,Y LET C(X + Y) = C(X)*C(Y) - S(X)*S(Y);      (B1)
FOR ALL X,Y LET S(X + Y) = S(X)*C(Y) + S(Y)*C(X);.
```

The parameters X and Y may be constants, symbolic variables or functions. No numerical values are assigned, unless requested.

The space-group information can be stored in an array $R(3,N)$, where N is the order of the space groups. For example, the Reduce statements which perform this task for the space group $P4$ are:

```
R(1,1) := X;  R(2,1) := Y;  R(3,1) := Z;
R(1,2) := -X; R(2,2) := -Y; R(3,2) := Z;               (B2)
R(1,3) := -Y; R(2,3) := X;  R(3,3) := Z;
R(1,4) := Y;  R(2,4) := -X; R(3,4) := Z;,
```

and defining the hkl indices by the substitution command:

```
LET HH(1) = H, HH(2) = K, HH(3) = L;,                   (B3)
```

we can calculate the arguments $hx + ky + lz$, where the factor 2π has been included in the indices, in the following loop:

```
LET N = 4;
FOR I := 1 STEP 1 UNTIL N                               (B4)
ARG(I) := FOR J := 1 STEP 1 UNTIL 3 SUM HH(J)*R(J,I);.
```

The last two lines of ($B4$) are of course applicable to any space group provided the order N has been defined and the general equivalent positions have been stored in the array R.

The real (A) and imaginary (B) parts of the trigonometric structure factor are now obtained for the above space group as

```
A := FOR I := 1 STEP 1 UNTIL N SUM C(ARG(I));          (B5)
B := FOR I := 1 STEP 1 UNTIL N SUM S(ARG(I));,
```

and can be output (as analytic expressions) to the terminal or to a file which is subsequently processed by another program (see text). It is of interest to mention that the output can be obtained in a format which is compatible with standard Fortran and the user can thus preprocess the most tedious and error-prone sections of a Fortran program, *i.e.* lengthy expressions to be numerically evaluated, with very little effort while maintaining control over the actual arrangement of the final expression, *via* the factorization and simplification facilities offered by Reduce. Examples of Reduce algorithms, which were applied to the development of generalized intensity statistics, are given by Shmueli & Wilson (1983) and the detailed structure of the Reduce language can be found in *Reduce 2 User's Manual* (Hearn, 1973).

Such powerful tools of symbolic programming permit one, not only in principle, to obtain an analytical expression of a space-group-dependent function given the space-group symbol alone. The coordinates of the general equivalent positions can be automatically generated starting from such symbols (*e.g.* Hall, 1981; Burzlaff & Hountas, 1982; Shmueli, 1983) and the definitions of $R(I,J)$ can be readily preprogrammed.

We were encouraged by the remarks of one of the referees to include Appendix B in this paper. We certainly agree with the referee that the well established methods of symbolic programming are still not too well known, and their illustration may be of interest. We are grateful for this suggestion.

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