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A New Joint Probability Distribution for the Triplet Phase Sum. Inclusion of Higher-Order Terms

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Abstract

A new joint probability distribution of three normalized structure factors is derived for the case of N equal atoms in the space group $P1$. The distribution appears in a series expansion. Convergence of the series is obtained by inclusion of higher-order terms up to order N^{-5}, although with the exception of terms up to order $N^{-1/2}$ the distribution does not contain all possible terms. Test results show improved estimates of the absolute value of the triplet phase sum when compared with the Cochran distribution. In particular, the systematic errors are reduced appreciably.

1. Introduction

If a sufficient number of linear independent structure invariants (s.i.'s) $\varphi_{H_1} + \ldots + \varphi_{H_i} = \psi_i$ were known, the phases φ_H could be calculated and the structure could be solved. In practice, however, the ψ_i are not known, unless information can be obtained by anomalous scattering (Kroon, Spek & Krabbendam, 1977; Heinerman, Krabbendam, Kroon & Spek, 1978) or dynamical diffraction experiments (Post, 1977, 1979). In the absence of knowledge of the ψ_i, a possible approach to the structure determination is the estimation of $\cos\psi_3$ or $|\psi_3|$, the absolute value of the triplet phase sum ψ_3, on the basis of the $|E_H|$ values. Starting from the linearization of products of structure factors and using probabilistic calculations, several authors have shown how to employ estimated $\cos\psi_3$ values and enantiomorph-specific cosine seminvariants in practical procedures (Karle & Hauptman, 1958; Hauptman, Fisher, Hancock & Norton, 1969; Hauptman, Fisher & Weeks, 1971; Hauptman, 1972). Olthof, Sint and Schenk have shown that empirical estimates of $|\psi_3|$ can also be useful in enantiomorph-specific procedures (Olthof, Sint & Schenk, 1979; Olthof & Schenk, 1981; Olthof, 1981).

Instead of empirical estimates, theoretical estimates might also be used. Up till now, several joint probability distribution (j.p.d.) expressions involving the three complex-valued normalized structure factors (n.s.f.'s) E_{H_1}, E_{H_2} and $E_{H_1+H_2}$ have been developed from which triplet phase sum estimates may be obtained (*e.g.* Cochran, 1955; Bertaut, 1956; Karle & Hauptman, 1956, 1958; Naya, Nitta & Oda, 1965; Tsoucaris 1970; Hauptman, 1971; Giacovazzo, 1974; Heinerman, 1977; Heinerman, Krabbendam & Kroon, 1977). Recently it was shown that a further improvement might be gained by including all structure factors in the j.p.d. derivation (Giacovazzo, 1977*b*; Cascarano *et al.*, 1984). The distributions appear either in an exponential or in a series-expansion form. The exponential expressions, *e.g.* the well known Cochran distribution [Cochran (1955); see also (I.17) in Appendix I of the present paper] are correct only up to order $N^{-1/2}$ which may result in systematically incorrect estimates, in particular for smaller values of N. The j.p.d.'s in series-expansion form may also lead to incorrect estimates. These errors are the result of insufficient convergence of the series. Several procedures have been suggested to improve this convergence, for example the transformation of the series expansion into an exponential (*e.g.* Bertaut,

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1960; Karle 1972; Karle & Gilardi, 1973). The inclusion of higher-order terms, *i.e.* terms depending on higher order of $N^{-1/2}$, is another possibility to improve convergence of a series expansion. The last approach is explored in this paper.

The j.p.d.'s mentioned are in fact based on the use of the moments–cumulants transformation for obtaining the characteristic function (c.f.). With this transformation, the inclusion of higher-order moments increases quickly the number of terms to be included in the final series expansion (Klug, 1958; Naya, Nitta & Oda, 1965; Peschar & Schenk, 1986). In order to avoid this, an alternative derivation of a j.p.d. of three n.s.f.'s is presented, valid for N equal atoms in space group $P1$. The j.p.d. aimed for will be obtained *via* the calculation of the c.f. For the calculations, the atomic coordinates are chosen to be the primitive random variables (p.r.v.'s), because of the relative ease of the mathematical calculations [for a discussion of the preferable use of either the atomic coordinates or the indices as the p.r.v.'s see *e.g.* Hauptman (1975), Heinerman (1977), Giacovazzo (1977*a*, 1980)]. In contrast with existing methods, no use is made of the moments–cumulants transformation for the calculation of the c.f. Instead an approximation formula is applied such that the initial series expansion of the c.f., involving the moments, can be written in an integrable form. The resulting series expansion contains a large number of higher-order terms, although not as many as by using the moments–cumulants transformation. The derivation of successive terms in the final series-expansion expression is done with the help of a computer program. Inclusion of terms up to order N^{-5} ensures sufficient convergence, as is shown by test results. Thus, although it cannot be claimed that the resulting joint probability distribution is correct to any order of N greater than $N^{-1/2}$, the inclusion of the present selection of higher-order terms is sufficient to obtain a converging series. Finally, on the basis of test results for some model structures in space group $P1$, the new j.p.d. is shown to compare favourably with the Cochran distribution.

2. The j.p.d. of the three n.s.f.'s E_{H_1}, E_{H_2} and E_{H_3}

Suppose that in the group $P1$ the reciprocal vectors $\mathbf{H}_1$, $\mathbf{H}_2$ and $\mathbf{H}_3$ are fixed and subject to the condition

$$\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_3\equiv\mathbf{0}. \tag{1}$$

For structures consisting of N identical point atoms, the n.s.f. E_H can be defined as

$$E_H = A_H + iB_H = N^{-1/2}\sum_{j=1}^{N}\exp(2\pi i\mathbf{H}.\mathbf{r}_j). \tag{2}$$

The magnitude $|E_H|$ and the phase φ_H of E_H are assumed to be continuous random variables, denoted by R and Φ respectively. Following Karle & Hauptman (1958), the j.p.d. of the phases φ_{H_1}, φ_{H_2}, φ_{H_3} and the magnitudes $|E_{H_1}|$, $|E_{H_2}|$, $|E_{H_3}|$ of the three n.s.f.'s,

$$P = P(\Phi_1, \Phi_2, \Phi_3, R_1, R_2, R_3), \tag{3}$$

is written as a sixfold integral

$$P=[R_1R_2R_3/(2\pi)^6]\int_{\rho_1,\rho_2,\rho_3=0}^{\infty}\int_{\theta_1,\theta_2,\theta_3=0}^{2\pi}\rho_1\rho_2\rho_3 \times\exp\left[-i\sum_{\nu=1}^{3}\rho_\nu R_\nu\cos(\theta_\nu-\Phi_\nu)\right] \times C(\theta_1,\theta_2,\theta_3,\rho_1,\rho_2,\rho_3)\,d\theta_1\,d\theta_2\,d\theta_3\,d\rho_1\,d\rho_2\,d\rho_3, \tag{4}$$

while the c.f. $C(\theta_1, \theta_2, \theta_3, \rho_1, \rho_2, \rho_3)$ can be written

$$C(\theta_1,\ldots,\rho_3)=\prod_{j=1}^{N}c_j \tag{5}$$

with

$$c_j=\left\langle\exp\left[iN^{-1/2}\sum_{\nu=1}^{3}\rho_\nu\cos(2\pi\mathbf{H}_\nu.\mathbf{r}_j-\theta_\nu)\right]\right\rangle_{\mathbf{r}_j}. \tag{6}$$

In contrast with the method used by Karle & Hauptman (1958), averaging over a reciprocal vector, the average in (6) is over all possible positions of the atom labelled j. [See Appendix II for a short derivation of (4)–(6).]

After the evaluation of the average in (6), see Appendix II, the following expression for c_j is obtained.

$$c_j=\sum_{n=-\infty}^{\infty}(-i)^nJ_n(N^{-1/2}\rho_1)J_n(N^{-1/2}\rho_2)J_n(N^{-1/2}\rho_3) \times\exp[-in(\theta_1+\theta_2+\theta_3)] \tag{7}$$

with n an integer and J_n the nth-order Bessel function (see Appendix I).

Thus, the c.f. $c(\theta_1,\ldots,\rho_3)$ (5) consists of an N-fold product of summations (7), which can be written as an N-fold summation.

$$C=\sum_{n_1,\ldots,n_N=-\infty}^{\infty}(-i)^m\exp[-im(\theta_1+\theta_2+\theta_3)] \times\prod_{t=1}^{N}\prod_{\nu=1}^{3}J_{n_t}(N^{-1/2}\rho_\nu) \tag{8}$$

with

$$m=\sum_{t=1}^{N}n_t. \tag{9}$$

Now substitute (8) into (4) and integrate over θ_1, θ_2 and θ_3 using (I.7). In view of (8) and (9) a summation over m can be defined first, while next, for each value of m, summations over $n_1,\ldots,n_N$ are performed such that (9) is satisfied. This results in

$$P=[R_1R_2R_3/(2\pi)^3] \times\sum_{m=-\infty}^{\infty}\exp[-im(\Phi_1+\Phi_2+\Phi_3)]h_m(R_1,R_2,R_3) \tag{10}$$

with

$$h_m(R_1, R_2, R_3) = \sum_{\substack{n_1,\ldots,n_N=-\infty \\ n_1+n_2+\ldots+n_N=m}}^{\infty} \prod_{\nu=1}^{3} \left\{ \int_0^{\infty} \rho_\nu J_m(\rho_\nu R_\nu) \times \prod_{t=1}^{N} J_{n_t}(N^{-1/2}\rho_\nu)\, d\rho_\nu \right\}, \quad (11)$$

where the independence of the integrations over ρ_1, ρ_2 and ρ_3 has been used.

Equation (11) implies that three identical integrations have to be performed for each set of numerical values $(n_1, \ldots, n_N)$ of the N-fold summation. This formula can be somewhat simplified by introducing different summation variables in the following way. Suppose that in a certain $(n_1, \ldots, n_N)$ set the number of different n_i values is k ($k \in [1, N]$). Denote these k different values by q_λ ($\lambda \in [1, k]$). Next denote by l_λ the frequency of q_λ in a certain $(n_1, \ldots, n_N)$ set. Thus,

$$\sum_{\lambda=1}^{k} l_\lambda = N \quad (12)$$

and

$$\sum_{\lambda=1}^{k} q_\lambda l_\lambda = m. \quad (13)$$

In (11) the number of $(n_1, \ldots, n_N)$ sets which reduce to the identical product

$$\prod_{\nu=1}^{3} \prod_{\lambda=1}^{k} [J_{q_\lambda}(N^{-1/2}\rho_\nu)]^{l_\lambda}$$

can be calculated, using combinatorics, as

$$\mathrm{com}_{q,l} = N! \Big/ \prod_{\lambda=1}^{k} l_\lambda! \quad (14)$$

Hence, the N-fold summation in (11) is changed into summations over the total number of different values q, the actual values of q and the frequency l of these values q, leading to

$$h_m(R_1, R_2, R_3) = \sum_{\lambda=1}^{k} \sum_{q_1,\ldots,q_\lambda=-\infty}^{\infty} \sum_{l_1,\ldots,l_\lambda=1}^{N} \mathrm{com}_{q,l} \times \prod_{\nu=1}^{3} \left\{ \int_0^{\infty} \rho_\nu J_m(\rho_\nu R_\nu) \times \prod_{t=1}^{\lambda} [J_{q_t}(N^{-1/2}\rho_\nu)]^{l_t}\, d\rho_\nu \right\} \quad (15)$$

under the conditions (9), (12) and (13).

The integrations in (15) cannot be performed directly. Therefore, the approximation formula (I.8) has been used as well as (I.11). After integrating the approximate expression for (15), shown in detail in Appendix III, an expression for the j.p.d. can be derived, using (III.16),

$$P(\Phi_1, \Phi_2, \Phi_3, R_1, R_2, R_3) = (R_1 R_2 R_3/\pi^3) \exp[-R_1^2 - R_2^2 - R_3^2] \times \sum_{m=-\infty}^{\infty} \exp[-im(\Phi_1 + \Phi_2 + \Phi_3)] g_m(R_1, R_2, R_3) \quad (16)$$

with

$$g_m(R_1, R_2, R_3) = \sum_{\lambda=1}^{k} \sum_{q_1,\ldots,q_\lambda=-\infty}^{\infty} \sum_{l_1,\ldots,l_\lambda=1}^{N} \mathrm{com}_{q,l} \times \prod_{\nu=1}^{3} \left\{ \exp[R_\nu^2(1-D^{-2})] P_{\mu,\mu^*}(R_\nu D^{-1}) \times \left[N^{(\mu+\mu^*)/2} D^{\mu+\mu^*+2} \prod_{t=1}^{\lambda} (|q_t|!)^{l_t} \right]^{-1} \right\}. \quad (17)$$

The variables μ, μ^*, D and the function P_{μ,μ^*} are given by

$$\mu = \left(\sum_{t=1}^{\lambda} |q_t| l_t + m \right) \Big/ 2;$$

$$\mu^* = \left(\sum_{t=1}^{\lambda} |q_t| l_t - m \right) \Big/ 2; \quad (18)$$

$$D^2 = N^{-1} \sum_{t=1}^{\lambda} l_t/(|q_t|+1);$$

$$P_{\mu,\mu^*}(R/D) = \sum_{\tau=0}^{\mu^*} (-1)^\tau \tau! \binom{\mu}{\tau} \binom{\mu^*}{\tau} (R/D)^{\mu+\mu^*-2\tau} \quad (19)$$

for $\mu \geq \mu^*$ and $P_{\mu,\mu^*} = P_{\mu^*,\mu}$.

3. Conditional j.p.d. of the triplet phase sum $\psi_3 = \varphi_{H_1} + \varphi_{H_2} + \varphi_{H_3}$ with $\mathbf{H}_3 = -\mathbf{H}_1 - \mathbf{H}_2$, given the magnitudes $|E_{H_1}|$, $|E_{H_2}|$ and $|E_{H_3}|$

Use of inequality theory

Denote by Ψ_3 the random variable associated with the triplet phase sum ψ_3,

$$\psi_3 = \varphi_{\mathbf{H}_1} + \varphi_{\mathbf{H}_2} + \varphi_{\mathbf{H}_3}, \qquad \mathbf{H}_3 = -\mathbf{H}_1 - \mathbf{H}_2. \quad (20)$$

The conditional j.p.d. of Ψ_3 given the magnitudes $|E_{H_1}|$, $|E_{H_2}|$ and $|E_{H_3}|$ can easily be obtained from (16) using elementary statistics,

$$P(\Psi_3 | R_1, R_2, R_3) = L^{-1} \sum_{m=-\infty}^{\infty} \exp[-im\Psi_3] g_m(R_1, R_2, R_3), \quad (21)$$

L is the normalization constant.

A certain similarity between (16)-(17) and the Cochran distribution (I.17) can be observed when (I.17) is expanded using (I.6). The function $g_m(R_1, R_2, R_3)$ in (16) apparently plays the same role as the modified Bessel function in the Cochran expression.

From Appendix III, $g_m = g_{-m}$, thus

$$P(\Psi_3|R_1, R_2, R_3) = L^{-1}\left\{ g_0(R_1, R_2, R_3) + 2 \sum_{m=1}^{\infty} g_m(R_1, R_2, R_3) \cos(m\Psi_3) \right\}.$$

The normalization constant L is defined as

$$L = \int \left\{ g_0 + 2 \sum_{m=1}^{\infty} g_m \cos(m\Psi_3) \right\} d\Psi_3. \quad (22)$$

The integration path in (22), usually taken from $-\pi$ to π, can be defined as follows. It is well known that the non-negativity of the electron-density function implies the existence of inequalities between structure factors (Karle & Hauptman, 1950; Goedkoop, 1950). A third-order case, expressed in E values, is

$$\begin{vmatrix} E_0 & E_{-H_1} & E_{H_2} \\ E_{H_1} & E_0 & E_{H_1+H_2} \\ E_{-H_2} & E_{-H_1-H_2} & E_0 \end{vmatrix} \geq 0. \quad (23)$$

Expansion of (23) yields a restrictive condition for ψ_3,

$$\cos\psi_3 \geq p \quad (24)$$

with

$$p = (|E_{H_1}|^2 + |E_{H_2}|^2 + |E_{H_3}|^2 - N) \times (2|E_{H_1}E_{H_2}E_{H_3}|N^{-1/2})^{-1}. \quad (25)$$

$E_H \leq E_0$ implies $p \leq 1$, while of course $\cos\psi_3 = p \geq -1$. If we denote by $\min(|p|, 1)$ the smallest value of $|p|$ and 1, and introduce the notation

$$X = \arccos[\min(|p|, 1)] \quad (26)$$

the integration interval in (22) is

$$[-X, X]. \quad (27)$$

When $p \leq -1$, there is no restriction on ψ_3 and this interval becomes the commonly used interval $[-\pi, \pi]$. From (27) and (22) L is obtained,

$$L = 2g_0(R_1, R_2, R_3)X + 2 \sum_{m=1}^{\infty} \{[g_m(R_1, R_2, R_3) \sin X]/m\}. \quad (28)$$

From (21), (27) and (28) expressions for expectation values can be calculated, for example the expectation values of $|\Psi_3|$ and $|\Psi_3|^2$ given the magnitudes $|E_{H_1}|$, $|E_{H_2}|$ and $|E_{H_3}|$:

$$\langle|\Psi_3||R_1, R_2, R_3\rangle = L^{-1}\left(g_0X^2 + 2 \sum_{m=1}^{\infty} g_m\{X \sin(mX)/m + [\cos(mX) - 1]/m^2\} \right) \quad (29)$$

and

$$\langle|\Psi_3|^2|R_1, R_2, R_3\rangle = L^{-1}\left\{ \tfrac{2}{3}g_0X^3 + 2 \sum_{m=1}^{\infty} g_m[X^2 \sin(mX)/m + 2X \cos(mX)/m^2 - 2 \sin(mX)/m^3] \right\}. \quad (30)$$

From (29) and (30) the expression for the variance of $|\Psi_3|$ is obtained in a standard way.

The definition of the integration interval *via* (25)-(27) can also be used in connection with the Cochran distribution: (I.17) is easily integrated numerically from $-X$ to X.

4. The calculation of the terms of the conditional j.p.d.

For the calculation of (20), it appears to be helpful to have an expression for the order, *i.e.* the N dependence, of the terms in the series expansion (17). From (17) it can be concluded that the order of the terms of the series depends on $\text{com}_{q,l}$ and on

$$N^{-\frac{3}{2}(\mu+\mu^*)} = N^{-\frac{3}{2}\sum_{t=1}^{\lambda}|q_t|l_t}. \quad (31)$$

Defining

$$q_1 \equiv 0 \quad \text{and} \quad \begin{cases} l_1 = N, & \lambda = 1 \\ l_1 = N - \sum_{t=2}^{\lambda} l_t, & \lambda \geq 2, \lambda \in [l, k], \end{cases} \quad (32)$$

one can write $\text{com}_{q,l}$ as

$$\begin{cases} 1 & \text{for } \lambda = 1 \\ N!/\prod_{t=2}^{\lambda} l_t!\left(N - \sum_{t=2}^{\lambda} l_t\right)! & \text{for } \lambda \geq 2 \end{cases} \quad (33)$$

provided that $\sum_{t=2}^{\lambda} l_t \ll N$. Combination of this with (31) gives the order of a term in (17):

$$\begin{cases} 1 & \lambda = 1 \\ N^{-\sum_{t=2}^{\lambda} l_t(\frac{3}{2}|q_t|-1)} & \lambda \geq 2. \end{cases} \quad (34)$$

From (34) a few interesting calculation conditions can be observed for the case $\lambda \geq 2$. Suppose we want to include in our calculations all terms up to and including order $N^{-\text{SMAX}}$, with

$$\text{SMAX} = \sum_{t=2}^{\lambda} l_t(\tfrac{3}{2}|q_t| - 1), \quad \lambda \geq 2 \qquad = 0, \quad \lambda = 1. \quad (35)$$

Table 1. *Maximum values of* $|q_t|$ *and* l_t *in* (35) *for* $\lambda = 1$ (SMAX = 0·0) *and* $\lambda \geq 2$ ($t \geq 2$; SMAX ≥ 0·5) *and the cumulative number of terms up to and including* $O(N^{-\mathrm{SMAX}})$ *in* (21)

SMAX	max l	max $\|q\|$	Cumulative number of terms in (21)
0·0	N	0	1
0·5	1	1	2
1·0	2	1	4
1·5	3	1	6
2·0	4	2	10
2·5	5	2	15
3·0	6	2	22
3·5	7	3	31
4·0	8	3	45
4·5	9	3	62
5·0	10	4	85

As the minimum value of $|q_t|$ in (35) is one, the maximum obtainable l value equals 2 × SMAX. This means that at most 2 × SMAX n values of a certain $(n_1, \ldots, n_N)$ set are not equal to zero. The minimum value of l in (35) is one. This implies that the maximum individual $|q|$ value can be obtained from (35) as $[2 \times (\mathrm{SMAX}+1)/3]$, *i.e.* the smaller nearest integer of $2 \times (\mathrm{SMAX}+1)/3$.

With these conditions, a two-step algorithm has been devised to calculate expectation values. The first step consists of generating expression (17) without using actual values for N and $|E|$'s. In this step, for each term in (17) the values of μ, μ^*, D and other parts which depend on the q and l values are calculated. Thus, in fact this first step consists of the derivation of the j.p.d. (16)-(17). Although this can be done by hand, it is unpractical to do so, and instead a computer program has been written which evaluates the values μ, μ^* *etc.* of the terms in (17) and stores them on an internal or external device. The second step, the calculation of the expectation values, is now a simple summation, employing the already generated expression (17) and the current N and $|E|$ values of a certain triplet. The maximum $|q|$ and l values in (35) as well as the number of terms in (17) up to a certain SMAX value are shown in Table 1. When terms up to and including $O(N^{-5})$ are included in the distribution, the computer time needed to calculate the expectation values is about the same as the time needed to calculate expectation values by integrating the Cochran distribution numerically.

In Tables 2, 3, 4 and 5 test results are shown for four randomly generated equal-atom structures in space group $P1$. From comparison of the tables, it can be observed that the mean systematic difference Av1 is considerably lower for the new distribution when compared with the Cochran distribution. As might be expected, this trend gets less strong when the number of atoms increases. The same observations can be made in the case of the mean absolute difference Av2, although these results are less significant. Comparable results have been obtained for

Table 2. *Cumulative means Av*1 *and Av*2, *both in mcycles, for a randomly generated equal-atom structure,* $N = 15$, *space group* $P1$

$\langle|\Psi_3|\rangle$ calculated from (29) (New) and *via* numerical integration of (I.17) (Cochran). $E_3 = |E_{H_1} E_{H_2} E_{-H_1-H_2}| N^{-1/2}$. Strongest 200 $|E_H|$ values used, $|E_H| \geq 1{\cdot}23$.

Under limit E_3	Number triplets	New Av1	New Av2	Cochran Av1	Cochran Av2
2·3	10	−3	23	−16	27
1·8	52	−14	28	−26	34
1·6	103	−10	31	−23	36
1·4	216	−12	34	−25	40
1·1	481	−10	38	−24	43
1·0	654	−12	41	−26	45
0·9	857	−11	44	−26	47
0·8	1092	−8	48	−24	50
0·7	1309	−9	50	−25	52
0·6	1501	−9	53	−25	55

Table 3. $N = 25$, *space group* $P1$, *Av*1 *and Av*2 *in mcycles*

Strongest 250 $|E_H|$ values used, $|E_H| \geq 1{\cdot}38$.

Under limit E_3	Number triplets	New Av1	New Av2	Cochran Av1	Cochran Av2
1·7	35	−18	30	−28	36
1·5	78	−7	36	−17	39
1·3	194	−2	45	−12	48
1·2	308	−7	44	−17	47
1·1	460	−7	48	−17	52
1·0	698	−8	50	−19	54
0·9	970	−7	53	−18	57
0·8	1298	−7	55	−19	59
0·7	1671	−7	59	−19	62

Table 4. $N = 50$, *space group* $P1$, *Av*1 *and Av*2 *in mcycles*

Strongest 250 $|E_H|$ values used, $|E_H| \geq 1{\cdot}59$.

Under limit E_3	Number triplets	New Av1	New Av2	Cochran Av1	Cochran Av2
1·8	21	3	32	−3	30
1·6	43	−7	34	−13	35
1·4	103	−9	42	−16	44
1·2	202	−13	45	−20	47
1·0	446	−7	53	−14	56
0·9	666	−4	58	−12	60
0·8	867	−4	61	−11	63
0·7	1093	−3	64	−10	66
0·5	1214	−3	66	−10	68

Table 5. $N = 100$, *space group* $P1$, *Av*1 *and Av*2 *in mcycles*

Strongest 250 $|E_H|$ values, $|E_H| \geq 1{\cdot}58$.

Under limit E_3	Number triplets	New Av1	New Av2	Cochran Av1	Cochran Av2
1·1	28	−11	46	−15	48
1·0	44	−15	52	−20	54
0·9	92	−11	57	−16	58
0·8	175	−4	70	−9	72
0·7	314	−5	74	−10	75
0·6	544	0	80	−4	81
0·5	834	−2	84	−6	85
0·4	935	−6	86	−10	87

Table 6. $N=30$, *space group P*1, *realistic model structure* (*Kanters & van Veen*, 1973; *slightly modified*)

Strongest 300 $|E_H|$ values, $|E_H| \geq 1{\cdot}43$.

Under limit E_3	Number triplets	New Av1	New Av2	Cochran Av1	Cochran Av2
2·3	25	+1	26	−6	26
2·1	49	−1	29	−9	29
1·9	104	−11	32	−19	35
1·7	201	−10	33	−18	36
1·5	379	−14	34	−22	38
1·3	692	−13	38	−23	42
1·1	1181	−17	42	−27	46
0·9	1952	−19	48	−29	52
0·7	2690	−21	53	−31	58
0·5	2852	−22	54	−31	59

a realistic model structure in $P1$ [Kanters & van Veen (1973), changed into an equal-atom structure], shown in Table 6.

It has been shown that it is possible to obtain reliable estimates of $|\Psi_3|$ *via a* j.p.d. in a series-expansion form. However, the inclusion of a vast number of higher-order terms, successively calculated by a computer program, is essential to obtain sufficient convergence. It must be noted that, owing to the approximation as applied here, not all higher-order terms are present but a selection of them only. Our results show that this selection is broad enough to reach the same goal, a converging series. Our results show further that in particular the systematic differences between the expectation values of $|\Psi_3|$ and the calculated $|\Psi_3|$ values are lower for the new distribution, when compared with the results obtained *via* the Cochran distribution. This may find future application in enantiomorph-specific procedures, such as those described by Olthof & Schenk (1981).

Test results and conclusions

As indicated in the *Introduction*, j.p.d.'s in a series-expansion form can suffer from insufficient convergence. The convergence of the distribution can be examined by looking at the changes in expectation values when higher-order terms are included in the distribution. In Table 7, the convergence of the distribution (21) can be observed for five examples *via* $\langle|\Psi_3|\rangle$ and $\sigma^2(|\Psi_3|)$, the expectation value and the variance of $|\Psi_3|$. It appears that when terms up to and including $O(N^{-5})$ are present in the distribution no further significant changes in $\langle|\Psi_3|\rangle$ and $\sigma^2(|\Psi_3|)$ occur. For comparison the values obtained *via* numerical integration of the Cochran distribution (I.17) are shown.

Further numerical tests have been performed in order to compare the present distribution with the Cochran distribution. For both distributions the expectation values $\langle|\Psi_3|\rangle$ have been compared with the $|\Psi_3|$ values as calculated from the structure. The overall differences between $\langle|\Psi_3|\rangle$ and $|\Psi_3|$ on the basis of the structure can be examined *via* the cumulative averages,

$$\mathrm{Av1} = \left\{ \sum_{\text{Triplets}} (|\Psi_3| - \langle|\Psi_3|\rangle) \right\} \Big/ \sum_{\text{Triplets}} \text{in mcycles} \quad (36)$$

and

$$\mathrm{Av2} = \left\{ \sum_{\text{Triplets}} \| \Psi_3| - \langle|\Psi_3|\rangle| \right\} \Big/ \sum_{\text{Triplets}} \text{in mcycles.} \quad (37)$$

Av1 and Av2 can be interpreted as the cumulative systematic and cumulative differences respectively. In the summation of (36) and (37) only those triplets are included with an $|E_{H_1}E_{H_2}E_{-H_1-H_2}|N^{-1/2}$ value above a certain limit. Sorting of the triplets on the basis of the variances $\sigma^2(|\Psi_3|)$, as calculated from the distribution, instead of the $|E_{H_1}E_{H_2}E_{-H_1-H_2}|N^{-1/2}$ value yields a similar ordering of the triplets.

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APPENDIX I

Basic formulas

The generating function for the Bessel functions of the first kind and order n, $J_n(Z)$, is

$$\exp[(Z/2)(t-1/t)] = \sum_{n=-\infty}^{\infty} t^n J_n(Z), \quad (I.1)$$

n integer (Watson, 1952, p. 14). Substitution of $t = i\exp(i\varphi)$ in (I.1) yields (Watson, 1952, p. 22)

$$\exp[iZ\cos\varphi] = \sum_{n=-\infty}^{\infty} i^n J_n(Z)\exp[in\varphi]. \quad (I.2)$$

If t is changed into $-t^{-1}$ in (I.1) (Watson, 1952, p. 15),

$$J_{-n}(Z) = (-1)^n J_n(Z), \quad (I.3)$$

n integer. Expansion of (I.1) in ascending powers of Z leads to (Watson, 1952, p. 40)

$$J_n(Z) = \sum_{m=0}^{\infty} (-1)^m (Z/2)^{n+2m}/m!(n+m)! \quad (I.4)$$

The modified Bessel function of the first kind, $I_n(Z)$, is defined as (Watson, 1952, p. 77)

$$I_n(Z) = i^{-n} J_n(iZ). \quad (I.5)$$

Table 7. *Convergence of* (21) *monitored via* $\langle|\Psi_3|\rangle$ *and* $\sigma^2(|\Psi_3|)$ $\langle|\Psi_3|\rangle$ *calculated from* (29), $\sigma^2(|\Psi_3|)$ *from* (29) *and* (30), *both containing terms up to and including* $O(N^{-\mathrm{SMAX}})$

$\langle|\Psi_3|\rangle$ and $\sigma^2(|\Psi_3|)$ of Cochran distribution calculated *via* numerical integration of (II.12). $\langle|\Psi_3|\rangle$ in rad $\times 1000/2\pi$, rounded off. $\sigma^2(|\Psi_3|)$ in squared rad $\times 1000/2\pi$, rounded off. p calculated from (25).

$N=25$			A		B		C		D		E	
$\lvert E_{H_1}\rvert$			1·50		2·0		2·5		2·5		3·0	
$\lvert E_{H_2}\rvert$			1·50		2·0		2·5		3·0		3·0	
$\lvert E_{-H_1-H_2}\rvert$			1·50		2·0		2·5		3·0		3·0	
$N^{-1/2}\lvert E_{H_1}E_{H_2}E_{-H_1-H_2}\rvert$			0·675		1·60		3·125		4·5		5·2	
p			−13·52		−4·06		−1·00		−0.08		0·192	
SMAX	0·5	1·0	1·5	2·0	2·5	3·0	3·5	4·0	4·5	5·0	Cochran	
A $\langle\lvert\Psi_3\rvert\rangle$	115	127	125	125	125	125	125	125	125	125	136	
$\sigma^2(\lvert\Psi_3\rvert)$	17	70	68	68	69	69	69	69	69	69	78	
B $\langle\lvert\Psi_3\rvert\rangle$	−37	103	68	69	68	68	68	68	68	68	78	
$\sigma^2(\lvert\Psi_3\rvert)$	−385	83	12	22	20	20	20	20	20	20	25	
C $\langle\lvert\Psi_3\rvert\rangle$	−238	148	9	58	44	45	44	44	44	44	53	
$\sigma^2(\lvert\Psi_3\rvert)$	−1363	169	−129	36	2	10	8	8	8	8	11	
D $\langle\lvert\Psi_3\rvert\rangle$	99	68	49	44	42	38	36	36	36	35	43	
$\sigma^2(\lvert\Psi_3\rvert)$	27	10	1	5	8	5	4	5	5	5	7	
E $\langle\lvert\Psi_3\rvert\rangle$	92	72	54	43	38	36	34	33	32	32	39	
$\sigma^2(\lvert\Psi_3\rvert)$	22	15	7	2	3	5	5	4	4	4	6	

Application of (I.5) to (I.2) leads to

$$\exp[Z\cos\varphi]=\sum_{n=-\infty}^{\infty} I_n(Z)\exp[in\varphi]. \quad \text{(I.6)}$$

From (I.2), with the procedure of Watson (1952, p. 20)

$$\int_0^{2\pi}\exp[iZ\cos(\theta-\varphi)-im\theta]\,\mathrm{d}\theta = 2\pi i^m\exp[-im\varphi]J_m(Z). \quad \text{(I.7)}$$

For small values of Z, $J_n(Z)$ can be approximated (Watson, 1952, p. 421) by

$$J_n(Z)\simeq[(Z/2)^n/n!]\exp[-Z^2/4(n+1)], \quad \text{(I.8)}$$

for small Z.

The Weber-Sonine integral (Watson, 1952, p. 393) is given by

$$\int_0^{\infty} J_\nu(at)\exp[-p^2t^2]t^{\mu-1}\,\mathrm{d}t = \{\Gamma[(\nu+\mu)/2](a/2p)^\nu\exp(-a^2/4p^2)/2p^\mu\Gamma(\nu+1)\} \times {}_1F_1[(\nu-\mu)/2+1;\,\nu+1;\,a^2/4p^2] \quad \text{(I.9)}$$

for $\mathrm{Re}\,(\nu+\mu)>0$; $|\arg(p)|<\pi/4$. The confluent hypergeometric function ${}_1F_1(-n;\,\alpha+1;\,x)$ is related to the generalized Laguerre polynomial $L_n^\alpha(x)$ *via*

$${}_1F_1(-n;\,\alpha+1;\,x)=\frac{n!\,\Gamma(\alpha+1)}{\Gamma(\alpha+n-1)}L_n^\alpha(x). \quad \text{(I.10)}$$

(I.9) can therefore be rewritten as

$$\int_0^{\infty} J_\nu(at)\exp[-p^2t^2/4]t^{\mu-1}\,\mathrm{d}t = \{2^{\mu-1}[(\mu-\nu)/2-1]!\,a^\nu/p^{\mu+\nu}\} \times\exp[-a^2/p^2]L^\nu_{(\mu-\nu)/2-1}(a^2p^{-2}). \quad \text{(I.11)}$$

A particular case of (I.11) is given by

$$\int_0^{\infty} J_n(at)\exp[-p^2t^2/4]t^{n+1}\,\mathrm{d}t = [2^{n+1}a^n/(p^2)^{n+1}]\exp[-a^2/p^2]. \quad \text{(I.12)}$$

$\mathrm{Ln}(1+x)$ can be written

$$\mathrm{Ln}(1+x)=\sum_{n=0}^{\infty}(-1)^n x^{n+1}/(n+1) \quad \text{for } |x|<1 \text{ or } x=1. \quad \text{(I.13)}$$

An elementary trigonometric formula (Hauptman, 1971) is

$$\sum_\lambda A_\lambda\exp\{i(\varphi+\alpha_\lambda)\}=x\exp\{i(\varphi+\xi)\} \quad \text{(I.14)}$$

with

$$x=\left\{\sum_{\lambda,\mu}A_\lambda A_\mu\cos(\alpha_\lambda-\alpha_\mu)\right\}^{1/2} \quad \text{(I.15)}$$

and

$$x\exp(i\xi)=\sum_\lambda A_\lambda\exp(i\alpha_\lambda). \quad \text{(I.16)}$$

The Cochran distribution (Cochran, 1955) is

$$P(\Psi_3|R_1,R_2,R_3|) = L^{-1}\exp[2R_1R_2R_3N^{-1/2}\cos\Psi_3], \quad \text{(I.17)}$$

with the notation L normalization constant, Ψ_3 random variable associated with the triplet phase sum, R_i random variable associated with the absolute value of the n.s.f. E_i.

APPENDIX II

Brief derivation of equations (4)–(6)

Denote by X and Y the random variables associated with the real and imaginary parts A_H and B_H, respectively, of a n.s.f. E_H. According to the notation of Karle & Hauptman (1958), the expression for the j.p.d. of A_{H_1}, A_{H_2}, A_{H_3}, B_{H_1}, B_{H_2} and B_{H_3} can be written

$$\begin{aligned} &P(X_1, X_2, X_3, Y_1, Y_2, Y_3) \\ &= (2\pi)^{-6} \int_{x_1,x_2,x_3,y_1,y_2,y_3=-\infty}^{\infty} \exp\left[-i \sum_{\nu=1}^{3} X_\nu x_\nu + Y_\nu y_\nu\right] \\ &\quad \times C(x_1, x_2, x_3, y_1, y_2, y_3) \\ &\quad \times \mathrm{d}x_1\, \mathrm{d}x_2\, \mathrm{d}x_3\, \mathrm{d}y_1\, \mathrm{d}y_2\, \mathrm{d}y_3. \end{aligned} \tag{II.1}$$

The expression for the c.f. $c(x_1, \ldots, y_3)$ is

$$\begin{aligned} &C(x_1, x_2, x_3, y_1, y_2, y_3) \\ &= \int_{X_1,\ldots,Y_3=-\infty}^{\infty} \exp\left[+i \sum_{\nu=1}^{3} X_\nu x_\nu + Y_\nu y_\nu\right] \\ &\quad \times P(X_1, \ldots, Y_3)\, \mathrm{d}X_1, \ldots, \mathrm{d}Y_3 \\ &= \left\langle \exp\left[i \sum_{\nu=1}^{3} (A_{H_\nu} x_\nu + B_{H_\nu} y_\nu)\right]\right\rangle_{\text{atomic coord.}} \end{aligned} \tag{II.2}$$

The average in (II.2) is over all possible positions of the atomic coordinates, the p.r.v.'s. Substitute (2) into (II.2) and assume that the p.r.v.'s are independent of each other. Then,

$$\begin{aligned} &C(x_1, \ldots, y_3) \\ &= \prod_{j=1}^{N} \left\langle \exp\left\{ iN^{-1/2} \sum_{\nu=1}^{3} [x_\nu \cos(2\pi \mathbf{H}_\nu . \mathbf{r}_j) \right.\right. \\ &\quad \left.\left. + y_\nu \sin(2\pi \mathbf{H}_\nu . \mathbf{r}_j)]\right\} \right\rangle_{\mathbf{r}_j}. \end{aligned} \tag{II.3}$$

The average in (II.3) is over the possible positions of each atom separately.

After application of transformations from Cartesian to polar coordinates,

$$\begin{aligned} X_\nu &= R_\nu \cos \Phi_\nu, & Y_\nu &= R_\nu \sin \Phi_\nu \\ x_\nu &= \rho_\nu \cos \theta_\nu, & y_\nu &= \rho_\nu \sin \theta_\nu, \end{aligned} \tag{II.4}$$

(II.1) is changed to (4), and (II.3) to (5).

Derivation of c_j, expression (7)

Employing (I.2) and $\mathbf{H}_3 = -\mathbf{H}_1 - \mathbf{H}_2$, one can write (6) as

$$\begin{aligned} c_j = &\sum_{n_1,n_2,n_3=-\infty}^{\infty} i^{n_1+n_2+n_3} J_{n_1}(N^{-1/2}\rho_1) J_{n_2}(N^{-1/2}\rho_2 \\ &\times J_{n_3}(N^{-1/2}\rho_3) \exp[-i(n_1\theta_1 + n_2\theta_2 + n_3\theta_3)] \\ &\times \langle \exp\{2\pi i \mathbf{r}_j . [\mathbf{H}_1(n_1 - n_3) \\ &+ \mathbf{H}_2(n_2 - n_3)]\}\rangle_{\mathbf{r}_j}. \end{aligned} \tag{II.5}$$

The average in (II.5) can be evaluated by integrating (II.5) over x_j, y_j and z_j using the integration interval $[0, 1]$, assuming independence of and uniform distributions for x_j, y_j and z_j.

In general, the integrations in (II.5) yield zero, unless

$$\mathbf{H}_1(n_1 - n_3) + \mathbf{H}_2(n_2 - n_3) = \mathbf{0}. \tag{II.6}$$

If one excludes the possibility of a linear dependence for $\mathbf{H}_1$ and $\mathbf{H}_2$, the only non-zero contribution in (II.5) is for

$$n_1 = n_2 = n_3. \tag{II.7}$$

Hence, the threefold summation in (II.5) is reduced to a single summation and (7) is obtained.

APPENDIX III

The calculation of $\int_0^\infty \rho J_m(\rho R) \prod_{t=1}^{\lambda} [J_{q_t}(N^{-1/2}\rho)]^{l_t}\, \mathrm{d}\rho$

For the calculation of

$$\int_0^\infty \rho J_m(\rho R) \prod_{t=1}^{\lambda} [J_{q_t}(N^{-1/2}\rho)]^{l_t}\, \mathrm{d}\rho, \tag{III.1}$$

with m defined in (13), it appears to be useful if m and all orders q_t of the Bessel functions in (III.1) are positive. Let us deal with $m \geq 0$ (I) and $m < 0$ (II) separately.

I. $m \geq 0$. With respect to the q values two possibilities exist.

(a) All $q_t \geq 0$ for $t \in [1, \lambda]$. All orders m and q_t positive, (III.1) remains unchanged.

(b) Some $q_t < 0$, $t \in [1, \lambda]$. Let us divide the summation (13) into three parts:

$$m = \sum_{t_1} q_{t_1} l_{t_1} + \sum_{t_2} q_{t_2} \alpha_{t_2} + \sum_{t_2} q_{t_2} \beta_{t_2} \tag{III.2}$$

in which the summation over t_1 involves all negative q values. Both the second and the third summations run over all positive q values. The rational positive coefficients α_{t_2} and β_{t_2} add up to l_{t_2}. The zero-q-value term does not contribute to m and has therefore been omitted. Select now α_{t_2} and β_{t_2} such that

$$\sum_{t_1} q_{t_1} l_{t_1} + \sum_{t_2} q_{t_2} \alpha_{t_2} = 0. \tag{III.3}$$

This expression is equal to

$$-\sum_{t_1} |q_{t_1}| l_{t_1} + \sum_{t_2} |q_{t_2}| \alpha_{t_2} = 0. \tag{III.4}$$

Hence, (III.2) reduces to

$$m = \sum_{t_2} q_{t_2} \beta_{t_2} = \sum_{t_2} |q_{t_2}| \beta_{t_2} \geq 0. \tag{III.5}$$

Equations (III.4) and (III.5) imply that

$$\begin{aligned} \sum_{t=1}^{\lambda} |q_t| l_t &= \sum_{t_1} |q_{t_1}| l_{t_1} + \sum_{t_2} |q_{t_2}| \alpha_{t_2} + \sum_{t_2} |q_{t_2}| \beta_{t_2} \\ &= 2 \sum_{t_1} |q_{t_1}| l_{t_1} + m. \end{aligned} \tag{III.6}$$

Employing (I.3) and (III.6), one can write (III.1) as

$$(-1)^{(\sum_{t=1}^{\lambda}|q_t|l_t-m)/2}\int_0^\infty \rho J_{|m|}(\rho R)\prod_{t=1}^{\lambda}[J_{|q_t|}(N^{-1/2}\rho)]^{l_t}\,d\rho,$$

$$m=\sum_{t=1}^{\lambda}|q_t|l_t. \qquad \text{(III.7)}$$

Evidently, the case that all q values are positive is included in (III.7) as well.

II. $m<0$. Application of (I.3) to (III.1) yields

$$(-1)^m(-1)^{\sum_{t=1}^{\lambda}q_tl_t}\int_0^\infty \rho J_{|m|}(\rho R)\prod_{t=1}^{\lambda}[J_{-q_t}(N^{-1/2}\rho)]^{l_t}$$

$$=\int_0^\infty \rho J_{|m|}(\rho R)\prod_{t=1}^{\lambda}[J_{-q_t}(N^{-1/2}\rho)]^{l_t}\,d\rho \qquad \text{(III.8)}$$

because of (13). Obviously, (III.8) can be treated along the lines of case I, again resulting in (III.7).

It remains to integrate (III.7). This equation can be transformed into a directly integrable form by application of the approximation formula (I.8),

$$\text{(III.7)}\simeq\left\{(-1)^{(s-m)/2}\Big/2^sN^{s/2}\prod_{t=1}^{\lambda}(|q_t|!)^{l_t}\right\}$$

$$\times\int_0^\infty \rho^{s+1}J_m(\rho R)\exp[-\rho^2D^2/4]\,d\rho \qquad \text{(III.9)}$$

where we have introduced the variables

$$S=\sum_{t=1}^{\lambda}|q_t|l_t \qquad \text{(III.10)}$$

and

$$D^2=N^{-1}\sum_{t=1}^{\lambda}l_t/(|q_t|+1). \qquad \text{(III.11)}$$

The remaining integration in (III.9) can be performed using (I.11), resulting in

$$\{2\times(-1)^{(s-m)/2}[(s-m)/2]![R/D]^m\exp[-R^2/D^2]\}$$

$$\times\left[N^{s/2}D^{s+2}\prod_{t=1}^{\lambda}(|q_t|!)^{l_t}\right]^{-1}L^m_{(s-m)/2}[R^2/D^2] \qquad \text{(III.12)}$$

with $L^m_{(s-m)/2}$ the associated Laguerre polynomial.

After the introduction of new variables,

$$\mu=(s+m)/2 \text{ and } \mu^*=(s-m)/2 \qquad \text{(III.13)}$$

and the function $P_{\mu,\mu^*}(RD^{-1})$,

$$P_{\mu,\mu^*}(RD^{-1})$$

$$=(-1)^{\mu^*}\mu^*!(R/D)^{\mu-\mu^*}L^{\mu-\mu^*}_{\mu^*}(R^2D^{-2}) \qquad \text{(III.14)}$$

for $\mu\geq\mu^*$, $P_{\mu^*,\mu}=P_{\mu,\mu^*}$, the final result is

$$\int_0^\infty \rho J_m(\rho R)\prod_{t=1}^{\lambda}[J_{q_t}(N^{-1/2}\rho)]^{l_t}\,d\rho$$

$$\simeq\{2\exp[-R^2/D^2]P_{\mu,\mu^*}(RD^{-1})\}$$

$$\times\left[N^{(\mu+\mu^*)/2}D^{\mu+\mu^*+2}\prod_{t=1}^{\lambda}(|q_t|!)^{l_t}\right]^{-1}. \qquad \text{(III.15)}$$

$P_{\mu,\mu^*}(RD^{-1})$ is the same function as $R_{n,n^*}(E)$ which was introduced by Naya, Nitta & Oda (1965). Examples and numerical values can be found in their Appendix V, Tables 2 and 3. Explicit expressions for $P_{\mu,\mu^*}(RD^{-1})$ can be generated by means of their formula (IV-7),

$$P_{\mu,\mu^*}(RD^{-1})=\sum_{\tau=0}^{\mu}(-1)^\tau\tau!\binom{\mu}{\tau}\binom{\mu^*}{\tau}(RD^{-1})^{\mu+\mu^*-2\tau} \qquad \text{(III.16)}$$

($\mu\geq\mu^*$ and $P_{\mu,\mu^*}=P_{\mu^*,\mu}$).

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