(BAM), Berlin, sowie der Deutschen Forschungsgemeinschaft, Bonn-Bad Godesberg, für deren freundliche Unterstützung.

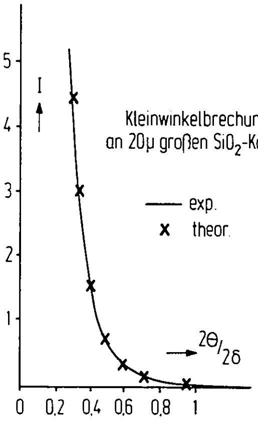

Fig. 13. Brechung der Cu $K\alpha$-Strahlung an 20 µm großen SiO_2-Körnern, aufgenommen mit der Lochblendenkammer 'Feldschlange II' (volle Kurve). Theoretische Berechnung durch Gleichung (27): $I_K(2\theta) = I_B(2\theta)/\pi b$.

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Computer-Aided Derivation of Theoretical Joint Probability Distributions of Normalized Structure Factors

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Abstract

A general theoretical and practical procedure is presented for deriving joint probability distributions of any number of structure factors in any space group. The distributions include all higher-order terms up to a preset order of N and thus may be used at any approximation. The procedure combines and extends the two different methods introduced by Naya, Nitta & Oda [*Acta Cryst.* (1964), **17**, 421-433; *Acta Cryst.* (1965), **19**, 734-747] for deriving joint probability distributions of phase-restricted and not-phase-restricted normalized structure factors respectively. The general algorithm for deriving joint probability distributions of structure factors has been implemented in a computer program, thus resulting in the possibility of computer-aided derivations of probabilistic relations for any set of structure factors. Optionally, the program transforms the resulting series-expansion form of the joint probability distribution into an exponential expression. In low-order approximation these exponential expressions usually turn out to be identical to expressions known from the literature.

Introduction

The phase-determining expressions used in present direct methods are almost exclusively joint probability distributions (j.p.d.'s) of normalized structure factors (n.s.f.'s) in exponential form, *e.g.* the triplet phase sum distribution of Cochran (1955) and the quartet phase sum expressions of Hauptman (1975, 1976) and Giacovazzo (1976). These exponential expressions are approximations since, for mathematical reasons, only a limited number of terms can be included in their derivation. The method, initiated by Bertaut (1955*a*, *b*, 1960), Klug (1958) and later systematized by Naya, Nitta & Oda (1964, 1965), leads to better approximations, but has never been used in practical direct methods because the associated calculations are complex. This method allows the use of higher-order terms and leads to j.p.d.'s in series-expansion form, involving Laguerre or Hermite polynomials, for distributions of not-phase-restricted and phase-restricted structure factors (s.f.'s) respectively. Naya *et al.* handle j.p.d.'s of phase-restricted and not-phase-restricted s.f.'s separately, whilst in the practice of direct methods in many space groups these

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two different types of s.f.'s both occur and consequently they also appear simultaneously in a vast number of phase relationships. Those relations in particular play a crucial role in phase determination because they couple the constrained phases to the unconstrained ones. Therefore a more general procedure for deriving j.p.d.'s, allowing for any combination of s.f.'s, is necessary. Another drawback of series-expansion expressions is the slow convergence of the series, although the employment of Taylor-series expansions should finally guarantee this. However, to reach convergence the number of terms to be included in the series must be very large. It has been shown recently for special triplet and quartet distributions that bringing the derivation algorithm into the form of a computer program solves these problems (Peschar & Schenk, 1986, 1987).

The aim of this paper is twofold. Firstly, a general method is presented for deriving j.p.d.'s of s.f.'s. This procedure combines and generalizes the two distribution types of Naya *et al.* (1964, 1965) so that all combinations of phase-restricted and/or not-phase-restricted s.f.'s can be handled. It will be shown how the j.p.d.'s are derived, discussing the most important steps in detail and paying attention to the way in which the theoretical calculations are performed in practice. In contrast to the procedures of Naya *et al.*, no *a priori* selection of n.s.f.'s is introduced. As it turns out from the general expression for the j.p.d. of s.f.'s, an *a posteriori* transformation to j.p.d.'s of selected n.s.f.'s is easily carried out.

Secondly, it will be shown that, under the usual assumption of a uniform *a priori* distribution of variables for the atomic coordinates, the derivation algorithm can be incorporated in a computer program, leading to computer-aided derivations of the desired j.p.d.'s.

Finally, it will be demonstrated that a simple transformation of low-order approximations of the series-expansion expressions, an automated procedure as well, leads to known exponential expressions for the j.p.d.'s.

1. Outline of the method of deriving j.p.d.'s

A general method for deriving j.p.d.'s for any combination of n.s.f.'s needs to use crystallographic symmetry explicitly. This symmetry is most simply expressed in matrix notation, in which each symmetry operation consists of a rotational matrix R and a translational vector T. In the case that m symmetry operations are present and N atoms are situated in the unit cell the structure factor is a sum of $n = N/m$ terms,

$$F_H = \sum_{j=1}^{n} \xi_j(\mathbf{H}) = \sum_{j=1}^{n} \eta_j(\mathbf{H}) + i \sum_{j=1}^{n} \zeta_j(\mathbf{H}) = A_H + iB_H. \tag{1}$$

$\xi_j(\mathbf{H})$ is a sum of m contributions or, equivalently, a sum of τ_H different symmetry-operated terms, each with a multiplicity m_H (≥ 1) ($m = \tau_H m_H$; * in R_s^* denotes transpose):

$$\xi_j(\mathbf{H}) = m_H \sum_{s=1}^{\tau_H} f_j(\mathbf{H}) \exp[2\pi i(R_s^* \mathbf{H} r_j + \mathbf{H} T_s)]. \tag{2}$$

In the course of the derivation it will be necessary to distinguish between not-phase-restricted s.f.'s. for which both A_H and B_H are present, on the one hand, and phase-restricted s.f.'s on the other. For the latter only two phase values Δ_1 and $\Delta_1 + \pi$ are possible with $0 \leq \Delta_1 < \pi$, so (1) reduces to a simpler expression. By multiplying the actual phase-restricted structure factor F'_H by $\exp(-i\Delta_1)$ a real-valued structure factor F_H is defined,

$$F_H = \exp(-i\Delta_1) F'_H = \sum_{j=1}^{n} \xi_j(\mathbf{H}). \tag{3}$$

This simple transformation, necessary since the calculation of j.p.d.'s requires real-valued variables, brings any phase-restricted structure factor to the same form. In the end, the final result can easily be transformed back to the original phase restrictions.

The determination of the j.p.d. of n random variables $x_1, \ldots, x_n$,

$$\begin{aligned} P(x_1, \ldots, x_n) &= (2\pi)^{-n} \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} \exp[-i(u_1 x_1 + \ldots + u_n x_n)] \\ &\quad \times C(u_1, \ldots, u_n)\, \mathrm{d}u_1 \ldots \mathrm{d}u_n, \end{aligned} \tag{4}$$

amounts to the calculation of its Fourier transform, the characteristic function $C(u_1, \ldots, u_n)$, which in turn can be expressed as

$$\begin{aligned} C(u_1, \ldots, u_n) &= \langle \exp[i(u_1 x_1 + \cdots + u_n x_n)] \rangle_{\text{random variables}}. \end{aligned} \tag{5}$$

The real and imaginary parts of the not-phase-restricted s.f.'s, A_H and B_H respectively, and the phase-restricted s.f.'s F_H as defined in (3) serve as the random variables. The shorthand notations A_i, B_i and F_i are employed for A_{H_i}, B_{H_i} and F_{H_i}. For convenience not-phase-restricted s.f.'s and variables corresponding to them are from now on referred to *via* the subscript ν only while the subscript μ is used exclusively for the phase-restricted s.f.'s; so the j.p.d. of l_c (≥ 0) not-phase-restricted and l_r (≥ 0) phase-restricted s.f's can be expressed as

$$\begin{aligned} P(A_1, \ldots, A_{l_c}, B_1, \ldots, B_{l_c}, F_1, \ldots, F_{l_r}) &= (2\pi)^{-(2l_c + l_r)} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\left\{ -i\left[\sum_{\nu=1}^{l_c} (A_\nu v_\nu + B_\nu w_\nu) \right.\right. \\ &\quad \left.\left. + \sum_{\mu=1}^{l_r} (F_\mu u_\mu) \right]\right\} \\ &\quad \times C(v_1, \ldots, v_{l_c}, w_1, \ldots, w_{l_c}, u_1, \ldots, u_{l_r}) \\ &\quad \times \mathrm{d}v_1 \ldots \mathrm{d}v_{l_c}\, \mathrm{d}w_1 \ldots \mathrm{d}w_{l_c}\, \mathrm{d}u_1 \ldots \mathrm{d}u_{l_r} \end{aligned} \tag{6}$$

and its characteristic function as

$$C=\left\langle\exp\left(i\sum_{j=1}^{n}\left\{\sum_{\nu=1}^{l_c}[\eta_j(\mathbf{H}_\nu)v_\nu+\zeta_j(\mathbf{H}_\nu)w_\nu]\right.\right.\right.$$
$$\left.\left.\left.+\sum_{\mu=1}^{l_r}\xi_j(\mathbf{H}_\mu)u_\mu\right\}\right)\right\rangle. \tag{7}$$

Since the random variables A_i, B_i and F_i are functions of the atomic coordinates, the average in (7) can also be calculated by taking the position vectors r_j to be the primitive random variables and averaging over their allowable values. If one uses $C=\exp[\ln(C)]$, changes the integration variables for the not-phase-restricted s.f.'s by means of

$$u_\nu=\rho_\nu\exp(i\theta_\nu)=v_\nu+iw_\nu\quad \nu=1,\ldots,l_c \tag{8}$$

and assumes the position vectors r_j to be independent, the following expression for the characteristic function is obtained:

$$C=\exp\left\{\sum_{j=1}^{n}\left[\ln\left\langle\exp\left(i\left\{\sum_{\nu=1}^{l_c}\tfrac{1}{2}[u_\nu^*\xi_j(\mathbf{H}_\nu)\right.\right.\right.\right.\right.$$
$$+u_\nu\xi_j^*(\mathbf{H}_\nu)]$$
$$\left.\left.\left.\left.\left.+\sum_{\mu=1}^{l_r}\xi_j(\mathbf{H}_\mu)u_\mu\right\}\right)\right\rangle_{\mathbf{r}_j}\right]\right\} \tag{9}$$

in which the * denotes complex conjugation.

A second change of variables,

$$\left.\begin{array}{l}A_\nu=R_\nu\cos(\Phi_\nu)\\ B_\nu=R_\nu\sin(\Phi_\nu)\end{array}\right\}\quad\text{for }\nu=1,\ldots,l_c \tag{10}$$

transforms (6) into the more useful j.p.d. of the magnitudes R_H and phases Φ_H for the not-phase-restricted s.f.'s

$$P(R_1,\ldots,R_{l_c},\Phi_1,\ldots,\Phi_{l_c},F_1,\ldots,F_{l_r})$$
$$=R_1\ldots R_{l_c}(2\pi)^{-2l_c-l_r}$$
$$\times\int_{-\infty}^{\infty}\ldots\int_{-\infty}^{\infty}\ldots\int_{0}^{2\pi}\ldots\int_{0}^{2\pi}\ldots\int_{0}^{\infty}\ldots\int_{0}^{\infty}\rho_1\ldots\rho_{l_c}$$
$$\times\exp\left[-i\left\{\sum_{\nu=1}^{l_c}[\rho_\nu R_\nu\cos(\theta_\nu-\Phi_\nu)]+\sum_{\mu=1}^{l_r}F_\mu u_\mu\right\}\right]$$
$$\times C(\rho_1,\ldots,\rho_{l_c},\theta_1,\ldots,\theta_{l_c},u_1,\ldots,u_{l_r})$$
$$\times d\rho_1\ldots d\rho_{l_c}\,d\theta_1\ldots d\theta_{l_c}\,du_1\ldots du_{l_r}, \tag{11}$$

with $C(\rho_1,\ldots,u_{l_r})$ as defined in (9). From (9) and (11), four important steps in the derivation of j.p.d.'s of s.f.'s follow:

(i) A Taylor-series expansion of the exponential expression inside the average brackets in (9), followed by the averaging over r_j term by term (the moments calculation) yields a series expansion in the integration variables ρ_ν, θ_ν and u_μ with the moments as coefficients.

(ii) Then the logarithm of the series expansion of step (i) is calculated. This transformation leads to another series in the integration variables ρ, θ and u, the cumulants, which are expressible in the already calculated moments (the moments–cumulants transformation).

(iii) Expression (9) shows further that after summation of the cumulants the characteristic function is obtained.

(iv) The Fourier transform of the characteristic function leads to the j.p.d. aimed at [see (11)].

In the following sections the four steps will be discussed in detail.

2. The calculation of the moments

In order to be able to average (9) over the single primitive random variable r_j, the exponential argument of the logarithm is expanded first by a Taylor-series expansion. The resulting series can be written as

$$\sum_{n\max=0}^{\infty}U_{n\max}(m^{\beta_1,\ldots,\beta_{l_c}}_{\alpha_1,\ldots,\alpha_{l_c},\gamma_1,\ldots,\gamma_{l_r}}) \tag{12}$$

in which the moments m, defined as

$$m^{\beta_1,\ldots,\beta_{l_c}}_{\alpha_1,\ldots,\alpha_{l_c},\gamma_1,\ldots,\gamma_{l_r}}$$
$$=\left\langle\prod_{\nu=1}^{l_c}\{[\xi_j(\mathbf{H}_\nu)]^{\alpha_\nu}[\xi_j^*(\mathbf{H}_\nu)]^{\beta_\nu}\}\prod_{\mu=1}^{l_r}[\xi_j(\mathbf{H}_\mu)]^{\gamma_\mu}\right\rangle_{\mathbf{r}_j}, \tag{13}$$

are the coefficients in the series expansion $U_{n\max}$:

$$U_{n\max}$$
$$=\sum_{\substack{\alpha_1,\ldots,\gamma_{l_r},\beta_1,\ldots\beta_{l_c}=0\\ \alpha_1+\ldots+\alpha_{l_c}+\beta_1+\ldots+\beta_{l_c}+\gamma_1+\ldots\gamma_{l_r}=n\max}}^{n\max}\ \prod_{\nu=1}^{l_c}\left\{\frac{(i\rho_\nu)^{\alpha_\nu+\beta_\nu}}{2^{\alpha_\nu+\beta_\nu}\alpha_\nu!\beta_\nu!}\right.$$
$$\left.\times\exp[i\theta_\nu(\beta_\nu-\alpha_\nu)]\right\}$$
$$\times\prod_{\mu=1}^{l_r}\left\{\frac{(iu_\mu)^{\gamma_\mu}}{\gamma_\mu!}\right\}m^{\beta_1,\ldots,\beta_{l_c}}_{\alpha_1,\ldots,\alpha_{l_c},\gamma_1,\ldots,\gamma_{l_r}}. \tag{14}$$

The evaluation of (13) needs to be performed for moments involving not-phase-restricted s.f.'s only, because when one or more phase-restricted s.f.'s are involved the moments can be constructed easily from the former.

Moments involving not-phase-restricted structure factors only

From Naya *et al.* (1964, 1965), the first step in the calculation of the expression for the moments of l not-phase-restricted s.f.'s,

$$m^{\beta_1,\ldots,\beta_l}_{\alpha_1,\ldots,\alpha_l}=\left\langle\prod_{\nu=1}^{l}\{[\xi_j(\mathbf{H}_\nu)]^{\alpha_\nu}[\xi_j^*(\mathbf{H}_\nu)]^{\beta_\nu}\}\right\rangle_{\mathbf{r}_j}, \tag{15}$$

is the consequent application of the multinomial-coefficients-generating expression ($A1$) (see

Appendix) to each of the $2l$-fold $[\xi_j(\mathbf{H}_\nu)]^\alpha$ expressions. This leads to

$$m^{\beta_1,\ldots,\beta_l}_{\alpha_1,\ldots,\alpha_l} = \sum_{\substack{\alpha_{11},\ldots,\alpha_{1\tau_1}=0\\ \sum_{s=1}^{\tau_1}\alpha_{1s}=\alpha_1}}^{\alpha_1} \cdots \sum_{\substack{\beta_{l1},\ldots,\beta_{l\tau_l}=0\\ \sum_{s=1}^{\tau_l}\beta_{ls}=\beta_l}}^{\beta_l} \frac{\prod_{\nu=1}^{l}\alpha_\nu!\beta_\nu!}{\prod_{\nu=1}^{l}\prod_{s=1}^{\tau_\nu}\alpha_{\nu s}!\beta_{\nu s}!}$$

$$\times \prod_{\nu=1}^{l}\{[f_j(\mathbf{H}_\nu)m_{H_\nu}]^{\alpha_\nu+\beta_\nu}\}$$

$$\times \exp\left\{2\pi i\left[\sum_{\nu=1}^{l}\sum_{s=1}^{\tau_\nu}(\alpha_{\nu s}-\beta_{\nu s})\mathbf{H}_\nu T_s\right]\right\}$$

$$\times \left\langle \exp\left\{2\pi i\left[\sum_{\nu=1}^{l}\sum_{s=1}^{\tau_\nu}R^*_s(\alpha_{\nu s}-\beta_{\nu s})\mathbf{H}_\nu\right].\mathbf{r}_j\right\}\right\rangle_{\mathbf{r}_j}. \tag{16}$$

To proceed from (16) an assumption has to be made concerning the *a priori* distribution $p(\mathbf{r}_j)$ of the primitive random variable $\mathbf{r}_j$, in order to perform averaging in (16) as the integral

$$\int \exp\left\{2\pi i\left[\sum_{\nu=1}^{l}\sum_{s=1}^{\tau_\nu}R^*_s(\alpha_{\nu s}-\beta_{\nu s})\mathbf{H}_\nu\right].\mathbf{r}_j\right\}p(\mathbf{r}_j)\,\mathrm{d}\mathbf{r}_j. \tag{17}$$

In this paper only the uniform distribution $p(\mathbf{r}_j)=1$ for all $\mathbf{r}_j$ is considered, for which (17) results in a delta function,

$$\delta\left[\sum_{\nu=1}^{l}\sum_{s=1}^{\tau_\nu}R^*_s(\alpha_{\nu s}-\beta_{\nu s})\mathbf{H}_\nu\right]. \tag{18}$$

Hence, a non-zero contribution to the moments (16) exists only when the restrictive condition

$$\sum_{\nu=1}^{l}\sum_{s=1}^{\tau_\nu}R^*_s(\alpha_{\nu s}-\beta_{\nu s})\mathbf{H}_\nu=\mathbf{0} \tag{19}$$

with

$$\sum_{s=1}^{\tau_\nu}\alpha_{\nu s}=\alpha_\nu \quad\text{and}\quad \sum_{s=1}^{\tau_\nu}\beta_{\nu s}=\beta_\nu \tag{20}$$

is fulfilled.

Moments involving one or more phase-restricted structure factors

It will be shown now how the moments involving one or more phase-restricted s.f.'s follow from expression (16). As an example the moments involving one phase-restricted structure factor will be discussed but the generalization to more phase-restricted s.f.'s is obvious.

For each structure factor F_H as defined in (3), the ξ_j can be expressed as

$$\xi_j(\mathbf{H})=m_H[\exp(-i\Delta_1)\xi'_j(\mathbf{H})+\exp(i\Delta_1)\xi'^*_j(\mathbf{H})] \tag{21}$$

with the complex-valued $\xi'_j(\mathbf{H})$,

$$\xi'_j(\mathbf{H})=\sum_{s=1}^{\tau'_H}f_j(\mathbf{H})\exp[2\pi i(R^*_s\mathbf{H}\mathbf{r}_j+\mathbf{H}T_s)] \tag{22}$$

For the definition of ξ'_j in (22) those $\tau'_H=\tau_H/2$ operations should be selected from the τ_H operations of $\xi_j(\mathbf{H})$ such that $R^*_{s_1}\mathbf{H}\neq -R^*_{s_2}\mathbf{H}$ with $s_1,s_2\in\{1,\ldots,\tau_H\}$.

Then application of expression $(A1)$ to the γ-fold product of $\xi_j(\mathbf{H})$ leads to

$$[\xi_j(\mathbf{H})]^\gamma=(m_H)^\gamma\sum_{\substack{r_1,r_2=0\\ r_1+r_2=\gamma}}^{\gamma}\frac{\gamma!}{r_1!r_2!}[\xi'_j(\mathbf{H})]^{r_1}[\xi'^*_j(\mathbf{H})]^{r_2}$$

$$\times\exp[i\Delta_1(r_2-r_1]. \tag{23}$$

After multiplication of both sides by

$$\prod_{\nu=1}^{l}[\xi_j(\mathbf{H}_\nu)]^{\alpha_\nu}[\xi^*_j(\mathbf{H}_\nu)]^{\beta_\nu}$$

and use of the moments definition (15), the moments of l not-phase-restricted s.f.'s and one phase-restricted structure factor are given by

$$m^{\beta_1,\ldots,\beta_l}_{\alpha_1,\ldots,\alpha_l,\gamma}=(m_H)^\gamma\sum_{\substack{r_1,r_2=0\\ r_1+r_2=\gamma}}^{\gamma}\frac{\gamma!}{r_1!r_2!}m^{\beta_1,\ldots,\beta_l,r_2}_{\alpha_1,\ldots,\alpha_l,r_1}$$

$$\times\exp[i\Delta_1(r_2-r_1)]. \tag{24}$$

Hence, phase-restricted s.f.'s can be handled similarly to the not-phase-restricted ones, provided that in the moments calculations (16) for the phase-restricted s.f.'s only those τ'_H symmetry operations are selected which do not lead to reciprocal vectors which are related through a centre of symmetry. After application of (24) for each phase-restricted structure factor, the actual moments are automatically obtained.

Calculation of moments in practice

In order to obtain a j.p.d. correct up to $N^{-\mathrm{Norde}}$, $\mathrm{Norde}\geq 0$, moments with all possible numerical combinations of integers $(\alpha_1,\ldots,\alpha_{l_c},\ \beta_1,\ldots,\beta_{l_c},\ \gamma_1,\ldots,\gamma_{l_r})$ with $\alpha_1+\ldots+\beta_{l_c}+\ldots+\gamma_{l_r}\leq 2\,(\mathrm{Norde}+1)$ should be considered, as will be verified after discussing the Fourier transform.

Fortunately, the number of moments to be calculated as indicated by expressions (19) and (20) can be reduced appreciably. A first reduction is obtained when in expression (16) all $\mathbf{H}_\nu$ are changed into $-\mathbf{H}_\nu$. This leads to an interchange of α_ν's and β_ν's and hence only to a sign change of the argument of the phase factor

$$\sum_{\nu=1}^{l}\sum_{s=1}^{\tau_\nu}(\alpha_{\nu s}-\beta_{\nu s})\mathbf{H}_\nu T_s. \tag{25}$$

Consequently, a limited number of integer combinations needs to be used for the evaluation of (19) only, since the remaining combinations follow directly. A further reduction results from the choice of the uniform *a priori* distribution. With the notations r_{ijs} $(i,j=1,2,3)$ for the elements of the 3×3 rotational matrix R_s^* and $h_{1\nu}$, $h_{2\nu}$ and $h_{3\nu}$ for the indices of the reflection $\mathbf{H}_\nu$, the three conditions (19), which must be satisfied simultaneously, are

$$\sum_{\nu=1}^{l}\sum_{s=1}^{\tau_\nu}(r_{i1s}h_{1\nu}+r_{i2s}h_{2\nu}+r_{i3s}h_{3\nu})(\alpha_{\nu s}-\beta_{\nu s})=0 \quad \text{for } i=1,2,3. \tag{26}$$

For any negative term on the left-hand side of (26), $-h_{i\nu}(\alpha_{\nu s}-\beta_{\nu s})$, twice its absolute value is added to both sides of (26). From (20), this leads to the conditions

$$\sum_{\nu=1}^{l}(t_{i1}h_{1\nu}+t_{i2}h_{2\nu}+t_{i3}h_{3\nu})(\alpha_\nu-\beta_\nu)=\text{even} \quad \text{for } i=1,2,3 \tag{27}$$

with

$$t_{ij}=\begin{cases}+1 & \text{if any of the } r_{ijs} \text{ can be } +1 \text{ or } -1\\ 0 & \text{if all } r_{ijs} \text{ are } 0.\end{cases} \tag{28}$$

In the case of one structure factor in a triclinic, monoclinic or orthorhombic space group the conditions (27) reduce to

$$h_i(\alpha-\beta)=\text{even} \quad \text{for } i=1,2,3. \tag{29}$$

So for moments with $(\alpha-\beta)$ odd to exist, all three indices should be even. If only one structure factor is involved, the stronger condition that moments with $\alpha-\beta=\text{odd}$ must vanish can be proved (Foster & Hargreaves, 1963).

Once an $(\alpha_1,\ldots,\beta_{l_c})$ combination, *i.e.* a potential non-zero moment, has been selected under the conditions described, condition (19) should be checked for all possible contributing $(\alpha_{1s},\ldots,\beta_{l_cs})$ combinations. From (19) it can be seen that only summations over symmetry-related reciprocal vectors must be performed. In view of the preceding for each reflection $\mathbf{H}_\nu$ only those symmetry operations should be selected with $\xi_j(R_{s1}^*\mathbf{H})\neq\xi_j(\pm R_{s2}^*\mathbf{H})$ for $(s1,s2)\in(1,\tau_\nu)$. In the computer program for each selected $R_s^*\mathbf{H}_\nu$ vector a unique and positive code word is calculated. Condition (19) can now simply be evaluated by adding for every $(\alpha_{1s},\ldots,\beta_{l_cs})$ combination the respective code words and comparing the resulting sum with the code word for the null vector. Whenever a contributing combination is encountered, its weight is calculated from the factorial products in expression (16). In a similar way the arguments of the phase factors [see (25)] are added and finally reduced to a unique interval. After incorporating the multiplicities m_H and the extra weight and phase factors due to phase-restricted s.f.'s each moment can be characterized by: (i) the $(\alpha_1,\ldots,\beta_{l_c})$ combination; (ii) a numerical weight; (iii) a code number for an extra phase shift x in $\exp(2\pi ix)$.

It should be remarked that in the moments defined this way for each (α_ν,β_ν) a product of scattering factors $[f_j(\mathbf{H}_\nu)]^{\alpha_\nu+\beta_\nu}$ is also present. As it appears there is at this point no need to calculate these factors numerically, so the $(\alpha_1,\ldots,\beta_{l_c})$ combination serves also to indicate their implicit presence. For the storage of each variable α or β four bits are reserved, which is sufficient for j.p.d.'s correct up to order N^{-6} (see the section on the Fourier transform). In the 60-bit Cyber-750 CDC machine, which was used to perform the calculations, in this way two computer words are necessary to store the moments code $(\alpha_1,\ldots,\beta_{15})$ of 15 s.f.'s. In the present program at most four computer words can be reserved for the storage of the moments code $(\alpha_1,\ldots,\beta_{l_c})$, though this is not a strict upper limit and may be changed in future versions. Hence, at present multivariate moments of up to 15 s.f.'s in any space group can be obtained in an automated way.

3. The calculation of the cumulants

The next step is the calculation of the logarithm of the series expansion (12). While the functional form of (12) is to be retained, new arguments for $U_{n\max}$ must be calculated, the so-called cumulants, from the known moments. Since $U_0=1$, this procedure, the moments–cumulants transformation, is given by

$$\sum_{n\max=1}^{\infty}U_{n\max}(k^{\beta_1,\ldots,\beta_{l_c}}_{\alpha_1,\ldots,\alpha_{l_c},\gamma_1,\ldots,\gamma_{l_r}})$$
$$=\ln\left[1+\sum_{n\max=1}^{\infty}U_{n\max}(m^{\beta_1,\ldots,\beta_{l_c}}_{\alpha_1,\ldots,\alpha_{l_c},\gamma_1,\ldots,\gamma_{l_r}})\right]. \tag{30}$$

Upon expansion of both sides of (30), identical series must appear. In order to explain the computational aspects of this transformation, the right-hand side of (30) is expanded, using the series expansion for the logarithm ($A2$) and the multinomial-generating function ($A1$). This results in

$$\sum_{n=0}^{\infty}(-1)^n n!\sum_{\substack{r_1,\ldots,r_p=0\\ r_1+\ldots+r_p=n+1\\ \lim p\to\infty}}^{n+1}\frac{U_1^{r_1}\ldots U_p^{r_p}}{r_1!\ldots r_p!}. \tag{31}$$

From (14), each U_m in (31) is a series in itself with moments

$$m^{\beta_1,\ldots,\beta_{l_c}}_{\alpha_1,\ldots,\alpha_{l_c},\gamma_1,\ldots,\gamma_{l_r}} \quad \text{with } \alpha_1+\ldots+\beta_{l_c}+\ldots+\gamma_{l_r}=m$$

as coefficients. If one now represents each term in U_m by a different variable x_{jm} and supposes that each U_m consists of q_m of these terms, then

$$U_m=\sum_{j=1}^{q_m}x_{jm}. \tag{32}$$

Subsequent application of $(A1)$ to the U_m then leads to:

$$\sum_{n=0}^{\infty} (-1)^n n! \sum_{\substack{r_1,\dots,r_p=0 \\ r_1+\dots+r_p=n+1 \\ \lim p\to\infty}}^{n+1} \times \prod_{i=1}^{p} \left(\sum_{\substack{t_{1i},\dots,t_{q_i i}=0 \\ t_{1i}+\dots+t_{q_i i}=r_i}}^{r_i} \frac{X_{1i}^{t_{1i}} \dots X_{q_i i}^{t_{q_i i}}}{t_{1i}! \dots t_{q_i i}!} \right). \qquad (33)$$

This expression indicates that under restriction of the summation conditions

$$\sum_{i=1}^{p} r_i = n+1$$

and (34)

$$\sum_{j=1}^{q_i} t_{ji} = r_i \quad \text{for } i=1,\dots,p$$

all possible products of x's should be calculated. Each x is associated with a product of integration variables and a moment, both characterized by the integer combination $(\alpha_1,\dots,\beta_{l_c},\gamma_1,\dots,\gamma_{l_r})$. Therefore, multiplication of x's can be achieved by the following operation: for each integration variable the corresponding powers are summed, which is done in the computer program by simply adding the code words for the $(\alpha_1,\dots,\beta_{l_c},\dots,\gamma_{l_r})$ combination. Because only four bits of storage are used for each of the variables α, β and γ, in the 60-bit Cyber computer 15 of these variables can be handled simultaneously. The second operation involved is the multiplication of the weights, taking into account the extra weights which arise from the expansions $(A1)$ and $(A2)$. Finally the phase factors are summed as well and then reduced to a unique interval. After performing these operations for each possible product of x's and collecting terms with identical sums of code words the left-hand side of (30) is obtained.

4. The characteristic function

The last step to obtain the characteristic function consists of the summation of the cumulants contributions of the n different primitive random variables for each of the $(\alpha_1,\dots,\beta_{l_c},\dots,\gamma_{l_r})$ combinations present, so

$$\sum_{j=1}^{n} \left[\sum_{n\text{max}=1}^{\infty} U_{n\text{max}}(k^{\beta_1,\dots,\beta_{l_c}}_{\alpha_1,\dots,\alpha_{l_c},\gamma_1,\dots,\gamma_{l_r}}) \right]$$

$$= \sum_{n\text{max}=1}^{\infty} U_{n\text{max}} \left[\sum_{j=1}^{n} (k^{\beta_1,\dots,\beta_{l_c}}_{\alpha_1,\dots,\alpha_{l_c},\gamma_1,\dots,\gamma_{l_r}}) \right]. \qquad (35)$$

If one assumes that the atoms have similarly formed scattering-factor curves:

$$f_j(\mathbf{H}_\nu) = f(\mathbf{H}_\nu) z_j \qquad (36)$$

and defines

$$Z_{n\text{max}} = \sum_{j=1}^{N} z_j^{n\text{max}} = m \sum_{j=1}^{n} z_j^{n\text{max}} \qquad (37)$$

(the factor m can easily be incorporated into the weight of the cumulants), the final characteristic function can be expressed as

$$C = \exp \left[\sum_{n\text{max}=1}^{\infty} Z_{n\text{max}} U_{n\text{max}}(k'^{\beta_1,\dots,\beta_{l_c}}_{\alpha_1,\dots,\alpha_{l_c},\gamma_1,\dots,\gamma_{l_r}}) \right], \qquad (38)$$

in which the prime indicates that the scattering-factor product present for each term has been changed into

$$\left\{ \prod_{\nu=1}^{l_c} [f(\mathbf{H}_\nu)^{\alpha_\nu+\beta_\nu} \right\} . \left\{ \prod_{\mu=1}^{l_r} [f(\mathbf{H}_\mu)]^{\gamma_\mu} \right\}. \qquad (39)$$

5. The Fourier transform of the characteristic function

In order to obtain the expression for the j.p.d. of s.f.'s, the expression for the characteristic function should be substituted in (11) and the integrations, constituting the Fourier transformations, performed. In general, there is no analytical solution for this problem; however, there are two approximation methods for handling it.

The first, most widely used, method preserves the exponential form of the characteristic function, but when performing the integrations all terms with $n\text{max} > 3$ which consist of ρ- and θ-dependent products, other than $\prod \rho_t \exp i\theta_t$ with $\theta_{t_1} \neq \theta_{t_2}$, are neglected. This approximation procedure leads to the familiar exponential expressions for j.p.d.'s of n.s.f.'s [see *e.g.* Giacovazzo (1980), chapter 7].

The second method (Naya *et al.*, 1964, 1965), applied in this paper, incorporates all terms up to a certain order. In this procedure only terms are retained in the exponential for which $n\text{max} \leq 2$. The exponential including all other terms is expanded by means of a Taylor series. The resulting series in combination with the exponential can then be integrated term by term.

The result of the Taylor expansion and subsequent application of $(A1)$ to expression (38) is

$$\sum_{n=0}^{\infty} \left[\sum_{\substack{r_3,\dots,r_p=0 \\ r_3+\dots+r_p=n \\ \lim p\to\infty}}^{n} \frac{(Z_3U_3)^{r_3} \dots (Z_pU_p)^{r_p}}{r_3! \dots r_p!} \right]. \qquad (40)$$

Comparison of (40) with (31) shows that apart from the weight factor $(-1)^n n!$ and the presence of the Z_n they are similar. This means that the operations to be performed are almost identical to those for the moments-cumulants transformations: the code words for the cumulants should be added as well as the corresponding phase-factors codes. Furthermore, the cumulant weights should be multiplied. Then multiplication of the Z_n values is performed in a similar way. On the basis of the subscript n of Z_n, a code number is calculated by assigning each different n a different storage place in a computer word. Summation of the respective Z_n codes then yields a code for the number and type of Z_n present. This expansion leads to

$$C_{n\max\geq 3} = 1 + \sum_{n\max=3}^{\infty} U_{n\max}(l^{\beta_1,\dots,\beta_{l_c}}_{\alpha_1,\dots,\alpha_{l_c},\gamma_1,\dots,\gamma_{l_r}})$$
$$= \exp\left[\sum_{n\max=3}^{\infty} Z_{n\max} U_{n\max}(k'^{\beta_1,\dots,\beta_{l_c}}_{\alpha_1,\dots,\alpha_{l_c},\gamma_1,\dots,\gamma_{l_r}})\right] \tag{41}$$

where the $(\alpha_1, \dots, \beta_{l_c}, \dots, \gamma_{l_r})$ combinations on the left-hand side of (41) have been composed by summing those on the right-hand side. The final argument $l^{\beta_1,\dots,\beta_{l_c}}_{\alpha_1,\dots,\alpha_{l_c},\gamma_1,\dots,\gamma_{l_r}}$ represents the following quantities:

(a) the code word(s) for

$$(\alpha_1, \dots, \beta_{l_c}, \dots, \gamma_{l_r});$$

(b) the numerical weight

$$w^{\beta_1,\dots,\beta_{l_c}}_{\alpha_1,\dots,\alpha_{l_c},\gamma_1,\dots,\gamma_{l_r}};$$

(c) the phase factor δ in

$$\exp(2\pi i\delta^{\beta_1,\dots,\beta_{l_c}}_{\alpha_1,\dots,\alpha_{l_c},\gamma_1,\dots,\gamma_{l_r}});$$

(d) a code word for the Z_n values present, denoted as $Z(n_1, \dots, n_p)$;

(e) the product of scattering-factor constants [see (39)];

(f) the product of integration variables.

Therefore the expanded part of the characteristic function can be expressed as

$$C_{n\max\geq 3} = 1 + \sum_{n\max=3}^{\infty} \sum^{n\max}_{\substack{\alpha_1,\dots,\gamma_{l_r},\beta_1,\dots,\beta_{l_c}=0\\ \alpha_1+\dots+\alpha_{l_c}+\beta_1+\dots+\beta_{l_c}+\gamma_1+\dots+\gamma_{l_r}=n\max}}$$
$$\times \prod_{\nu=1}^{l_c}\left\{\frac{[i\rho_\nu f(\mathbf{H}_\nu)]^{\alpha_\nu+\beta_\nu}}{2^{\alpha_\nu+\beta_\nu}\alpha_\nu!\beta_\nu!}\right.$$
$$\left.\times \exp[i\theta_\nu(\beta_\nu-\alpha_\nu)]\right\} \prod_{\mu=1}^{l_r}\left\{\frac{[iu_\mu f(\mathbf{H}_\mu)]^{\gamma_\mu}}{\gamma_\mu!}\right\}$$
$$\times Z(n_1, \dots, n_p)\, W^{\beta_1,\dots,\beta_{l_c}}_{\alpha_1,\dots,\alpha_{l_c},\gamma_1,\dots,\gamma_{l_r}}$$
$$\times \exp(2\pi i\delta^{\beta_1,\dots,\beta_{l_c}}_{\alpha_1,\dots,\alpha_{l_c},\gamma_1,\dots,\gamma_{l_r}}). \tag{42}$$

The only non-zero contributions to the not-expanded exponential part of the characteristic function are when

$$\alpha_\nu = \beta_\nu = 1 \quad \text{for } \nu = 1, \dots, l_c$$
$$\text{and} \tag{43}$$
$$\gamma_\mu = 2 \qquad \text{for } \mu = 1, \dots, l_r.$$

For these contributions the phase factors are 0, all $Z(n_1, \dots, n_p)$ can be expressed as $\sum_{j=1}^N z_j^2$ and the corresponding weights can be simplified to $W(\mathbf{H})$. Since no mixed moments with α_i, β_j are non-zero for $i \neq j$, the approximation (36) appears not to be necessary for Z_2 so it may be denoted

$$Z_2(\mathbf{H}_\nu) = \sum_{j=1}^{N} [f_j(\mathbf{H}_\nu)]^2. \tag{44}$$

Consequently, the exponential part of the characteristic function can be written as

$$C_{n\max\leq 2} = \exp\left\{-\tfrac{1}{4}\sum_{\nu=1}^{l_c}[Z_2(\mathbf{H}_\nu)W(\mathbf{H}_\nu)\rho_\nu^2]\right.$$
$$\left.-\tfrac{1}{2}\sum_{\mu=1}^{l_r}[Z_2(\mathbf{H}_\mu)W(\mathbf{H}_\mu)u_\mu^2]\right\}. \tag{45}$$

After insertion of the complete characteristic function, the product of expressions (45) and (42) in (11), two types of integrals must be calculated, those involving complex-valued s.f.'s and those involving phase-restricted s.f.'s.

Complex-valued structure factors

After a change of variables,

$$\rho_\nu = y_\nu\{W(\mathbf{H}_\nu)[Z_2(\mathbf{H}_\nu)]\}^{-1/2} \quad \nu = 1, \dots, l_c, \tag{46}$$

and if the subscript ν is dropped for simplicity, this type of integral is

$$(i/2)^{\alpha+\beta}[W(\mathbf{H})Z_2(\mathbf{H})]^{-(\alpha+\beta+2)/2}$$
$$\times \int_0^{2\pi}\int_0^{\infty} y^{\alpha+\beta+1}\exp\{-y^2/4 - i\theta(\alpha-\beta)$$
$$- iyR_H[W(\mathbf{H})Z_2(\mathbf{H})]^{-1/2}$$
$$\times \cos(\theta_H - \Phi_H)\}\,\mathrm{d}y\,\mathrm{d}\theta. \tag{47}$$

The evaluation of (47) has been given by Naya *et al.* (1965) and results in

$$4\pi\exp[-R_H^2 Z_2^{-1}(\mathbf{H})][W(\mathbf{H})Z_2(\mathbf{H})]^{-(\alpha+\beta+2)/2}$$
$$\times R_{\alpha,\beta}\{R_H[W(\mathbf{H})Z_2(\mathbf{H})]^{-1/2}\}$$
$$\times \exp[-i(\alpha-\beta)\Phi_H] \tag{48}$$

in which the function $R_{\alpha,\beta}$ can be expressed in Laguerre polynomials.

Phase-restricted structure factors

With a similar change of variables as in (46),

$$u_\mu = y_\mu[W(\mathbf{H}_\mu)Z_2(\mathbf{H}_\mu)]^{-1/2}, \tag{49}$$

this type of integral is

$$[W(\mathbf{H})Z_2(\mathbf{H})]^{-(\alpha+1)/2}$$
$$\times \int_{-\infty}^{\infty} (iy)^\alpha \exp\{-\tfrac{1}{2}y^2 - iyF_H[W(\mathbf{H})Z_2(\mathbf{H})]^{-1/2}\}\,\mathrm{d}y. \tag{50}$$

The calculation of (50) can be performed with an expression given by Klug [(1958), equation (I.16)] and this results in

$$(2\pi)^{1/2}[W(\mathbf{H})Z_2(\mathbf{H})]^{-(\alpha+1)/2}$$
$$\times\exp[-\tfrac{1}{2}F_H^2 Z_2(\mathbf{H})]H_\alpha\{F_H[W(\mathbf{H})Z_2(\mathbf{H})]^{-1/2}\} \qquad (51)$$

H_α is the Hermite polynomial [(*A*4) in Appendix].

The j.p.d. of normalized structure factors

Expressions (48) and (51) show that the actual arguments of the j.p.d. of s.f.'s are the n.s.f.'s. After a simple transformation to the normalized variables,

$$\begin{aligned}|E_{H_\nu}| &= R_{H_\nu}[W(\mathbf{H}_\nu)Z_2(\mathbf{H}_\nu)]^{-1/2} \quad \nu=1,\ldots,l_c\\ E_{H_\mu} &= F_{H_\mu}[W(\mathbf{H}_\mu)Z_2(\mathbf{H}_\mu)]^{-1/2} \quad \mu=1,\ldots,l_r,\end{aligned} \qquad (52)$$

the final j.p.d. of the magnitudes $|E_H|$ and phases Φ_H of the not-phase-restricted s.f.'s and the normalized variables E_H for the phase-restricted s.f.'s can be written

$$\begin{aligned}&P(|E_1|,\ldots,|E_{l_c}|,\Phi_1,\ldots,\Phi_{l_c},E_1,\ldots,E_{l_r})\\
&=\prod_{\nu=1}^{l_c}[\pi^{-1}|E_{H_\nu}|\exp(-|E_{H_\nu}|^2)]\\
&\quad\times\prod_{\mu=1}^{l_r}\left\{\left[\frac{Z_2(\mathbf{H}_\mu)}{2\pi}\right]^{1/2}\exp(-\tfrac{1}{2}E_{H_\mu}^2)\right\}\\
&\quad\times\Bigg(1+\sum_{n\max=3}^{\infty}\ \sum_{\substack{\alpha_1,\ldots,\gamma_{l_r},\beta_1,\ldots,\beta_{l_c}=0\\ \alpha_1+\ldots+\alpha_{l_c}+\beta_1+\ldots+\beta_{l_c}+\gamma_1+\ldots+\gamma_{l_r}=n\max}}^{n\max}\\
&\quad\times\prod_{\nu=1}^{l_c}\Big\{R_{\alpha_\nu,\beta_\nu}(|E_{H_\nu}|)[W(\mathbf{H}_\nu)Z_2(\mathbf{H}_\nu)]^{-(\alpha_\nu+\beta_\nu)/2}\\
&\quad\times\exp[i\Phi_\nu(\beta_\nu-\alpha_\nu)]\Big\}\\
&\quad\times\prod_{\mu=1}^{l_r}\Big\{H_{\alpha_\mu}(E_{H_\mu})[W(\mathbf{H}_\mu)Z_2(\mathbf{H}_\mu)]^{-\alpha_\mu/2}\Big\}\\
&\quad\times Z(n_1,\ldots,n_p)\,W^{\beta_1,\ldots,\beta_{l_c}}_{\alpha_1,\ldots,\alpha_{l_c},\gamma_1,\ldots,\gamma_{l_r}}\\
&\quad\times\exp(2\pi i\delta^{\beta_1,\ldots,\beta_{l_c}}_{\alpha_1,\ldots,\alpha_{l_c},\gamma_1,\ldots,\gamma_{l_r}})\Bigg).\end{aligned} \qquad (53)$$

For equal-atom structures, the relation between the order up to which (53) is correct and the maximum α, β or γ value involved is now readily established. From (37), the quotient of the Z_n factors in (53) can be noted as $N^{\frac{1}{2}-n\max+p}$ with p the number of Z_n values in the product $Z(n_1,\ldots,n_p)$. Therefore, the relation between the order Norde in $N^{-\mathrm{Norde}}$, $n$max and the individual α's, β's and γ's can be obtained as

$$\alpha_1+\ldots+\beta_{l_c}+\ldots+\gamma_{l_r}=n\max=2(\mathrm{Norde}+p). \qquad (54)$$

For example, for distributions correct up to order N^{-6}, each individual α, β and γ should be less than 14.

To summarize, for the identification of each term in (53) the following quantities are necessary:

(1) the code word(s) for $(\alpha_1,\ldots,\beta_{l_c},\ldots,\gamma_{l_r})$, representing the products of Laguerre and/or Hermite polynomials;

(2) the numerical weight $w^{\beta_1,\ldots,\beta_{l_c}}_{\alpha_1,\ldots,\alpha_{l_c},\gamma_1,\ldots,\gamma_{l_r}}$;

(3) the phase-factor argument $\delta^{\beta_1,\ldots,\beta_{l_c}}_{\alpha_1,\ldots,\alpha_{l_c},\gamma_1,\ldots,\gamma_{l_r}}$;

(4) the code word for the product of Z_n values, $Z(n_1,\ldots,n_p)$.

With items (1) to (4) for each term the j.p.d. is completely coded. The calculation has been automated with the help of a computer program which outputs the quantities (1) to (4) and stores them on disk. J.p.d.'s correct to at maximum N^{-6} can be calculated, since for each of the variables only four bits are reserved.

6. Transformation of the series-expansion distributions into exponential expressions

In order to compare the new j.p.d.'s with the familiar exponential expressions for the (conditional) j.p.d.'s of n.s.f.'s known from the literature, the linear part of (53),

$$\left(1+\sum_{n\max=3}^{\infty}\{\ldots\}\right), \qquad (55)$$

is transformed into an exponential expression by employing the equality $x=\exp[\ln(x)]$. This transformation has been applied before, *e.g.* by Bertaut (1956), Karle (1972) and by Karle & Gilardi (1973) for the triplet phase-sum distribution in $P1$ and by Giacovazzo (1976) for a conditional quartet phase-sum distribution also in $P1$. Expression (55) changes in this way to

$$\begin{aligned}&\exp\left\{\ln\left[1+\sum_{n\max=3}^{\infty}V'_{n\max}(x_1,\ldots,x_{qn\max})\right]\right\}\\ &=1+\sum_{n\max=3}^{\infty}V_{n\max}(x_1,\ldots,x_{qn\max}),\end{aligned} \qquad (56)$$

in which the notation $V_{n\max}(x_1,\ldots,x_{qn\max})$ is a shorthand for the collection of all qnmax different terms for which $\alpha_1+\ldots+\beta_{l_c}+\ldots+\gamma_{l_r}=n\max$. Expressions (30) and (56) show a striking similarity and since (30) can be evaluated by a computer program, (56) may be evaluated by computer too. The operations to be performed are partly similar to those discussed in connection with the cumulants calculation; in particular the steps involved in (30) up to (34) apply to (56) as well. The handling of the code words can also be carried out similarly: the weights are multiplied and the phase-factor codes and the code words for $Z(n_1,\ldots,n_p)$ are summed. The summation of the $(\alpha_1,\ldots,\beta_{l_c},\ldots,\gamma_{l_r})$ combinations involves now only the symbolic multiplication of phase-dependent parts like $\exp[-i(\alpha-\beta)\Phi_H]$. For the symbolic multiplication of the magnitude-dependent parts, as represented by the functions $R_{\alpha,\beta}(|E_H|)$ and $H_\alpha(E_H)$, a different procedure must be adopted. Both $R_{\alpha,\beta}(|E_H|)$ and $H_\alpha(E_H)$ consist of series expansions in $|E_H|$, and E_H respectively. Multiplication of such series involves not only multiplying normalized structure-factor products of the same structure factor but of different s.f.'s as well,

$$C_1|E_{H_i}|^{b_1}C_2|E_{H_j}|^{b_2} \quad \text{with } i=j \text{ or } i\neq j. \qquad (57)$$

The real-valued coefficients C_1 and C_2 can simply be multiplied. In order to obtain products like $|E_{H_i}|^{b_1}|E_{H_j}|^{b_2}$ in which both $i\neq j$ and $i=j$ terms may be present, each term in a series expansion $R_{\alpha,\beta}$ or H_α, $|E_{H_i}|^b$, is coded by storing the power b of each H_i at a different place in a computer word. For each $n$max value in (56), each individual integer power b is always smaller or equal to $n$max [see *e.g.* for the $R_{\alpha,\beta}$ function Appendix V of Naya *et al.* (1965)] so up to the order $N^{-5/2}$ a four-bit storage assignment for each structure factor suffices. Consequently, on a 60-bit machine 15 powers of b_i can be packed in one word and handled simultaneously and for 30 structure factors only two words of storage are necessary. The multiplication of the $R_{\alpha,\beta}(|E_H|)$ and $H_\alpha(E_H)$ products can thus be performed by adding the respective code words for the powers since then automatically powers of corresponding structure factors, stored at the same place, will be added. In this way, for each $Z(n_1,\ldots,n_p)$ combination up to a predetermined order, in the exponential expression the corresponding magnitude and phase expressions can be obtained solely by simple symbolic manipulations, adding and multiplying. As it turns out almost all exponential j.p.d.'s which rely on the uniform *a priori* assumption can be reproduced by this routine from expression (55).

7. Concluding remarks

With the procedures discussed in the preceding paragraphs, incorporated in a Fortran V computer program, it is possible:

(i) To derive j.p.d.'s for any choice of n.s.f.'s in any space group under the assumption of a uniform *a priori* distribution of the primitive random variables, the atomic coordinates. The order up to which the series-expansion expression is correct can be specified and is limited in practice only by the amount of computer time available.

(ii) To transform the series-expansion j.p.d. to an exponential expression. At low order, the familiar exponential expressions are obtained as given *e.g.* by Giacovazzo (1980) in chapters 7 and 8.

The computer program enables systematic investigations into:

(i) the reliability of estimates of phase relationships based on j.p.d.'s at different levels of approximation in order to trace the optimum reliability for practical direct methods;

(ii) the difference in reliability of estimates of phase relations of different mixes of phase-restricted and not-phase-restricted reflections in one and the same structure;

(iii) the comparison of the reliabilities of estimates of phase relations resulting from the known and the new j.p.d.'s;

(iv) the comparison of the reliabilities of estimates of phase relations in different space groups;

(v) the derivation of new j.p.d.'s for invariants and seminvariants and checking them by using known structures.

In all cases the computer program will generate the relevant j.p.d.'s and write their functional form to disk. Then a second program will be used to calculate with the disk j.p.d. as basis the phase-sum estimates and compare these values with the actual values.

In future papers various distributions obtained with the above procedure and their test results will be discussed and compared with those of known expressions.

APPENDIX
Some definitions

The multinomial-coefficients-generating expression is

$$(a_1+a_2+\ldots+a_n)^m = \sum_{\substack{r_1,\ldots,r_n=0 \\ r_1+\ldots+r_n=m}}^{m} m!\,\frac{a_1^{r_1}\ldots a_n^{r_n}}{r_1!\ldots r_n!}. \qquad (A1)$$

The series expansion for the logarithm is

$$\ln(1+x) = \sum_{n=0}^{\infty} \frac{(-1)^n x^{n+1}}{n+1} \quad \text{for } |x|<1 \text{ or } x=1. \qquad (A2)$$

The function $R_{n,n^*}(|E|)$ has been defined by Naya *et al.* (1965) as

$$R_{n,n^*}(|E|) = \sum_{\tau=0}^{n^*} (-1)^\tau \tau! \binom{n}{\tau}\binom{n^*}{\tau}(|E|)^{n+n^*-2\tau} \qquad (A3)$$

for $n\geq n^*$ and with $R_{n,n^*}=R_{n^*,n}$.

The Hermite polynomial can be expressed (Watson, 1952) as

$$H_n(E) = n!\sum_{k=0}^{[n/2]} \frac{(-1)^k E^{n-2k}}{k!2^k(n-2k)!} \qquad n=0,1,2,\ldots \qquad (A4)$$

with $[n/2]$ the nearest smaller integer of $n/2$.

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Comments on Absorption in Takagi–Taupin Equations

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Abstract

The Takagi–Taupin theory of X-ray diffraction leaves an ambiguity in the choice of the wave vector inside the crystal. This holds also for its imaginary part which describes absorption. One consequence of this ambiguity is that the wave vector $\mathbf{k}_0$ inside the crystal need not always satisfy the continuity conditions for the tangential component of the wave vector at the entrance surface. But if the direction of the imaginary part is once fixed then it determines the particular manner of solution of the Takagi–Taupin equations. Thus a direction of the imaginary part of the wave vector in the crystal parallel to the reflecting net planes will in general ensure that the continuity condition is not satisfied; only a wave vector with an imaginary part perpendicular to the crystal surface can satisfy this condition.

1. Introduction

Dynamical X-ray diffraction in perfect and distorted crystals may be described by the Takagi–Taupin equations (Takagi, 1962, 1969; Taupin, 1964). An important feature of this theory is that the 'amplitudes' $D_h(\mathbf{r})$ of the generalized Bloch waves are not constant but are slowly varying functions of position. This fact leaves an ambiguity in the choice of the wave vector $\mathbf{k}_0$ inside the crystal. After Takagi a convenient choice is that the magnitude of $\mathbf{k}_0$ is given by

$$|\mathbf{k}_0| = k = nK, \tag{1a}$$

where n is the mean refractive index and $K = 1/\lambda$, the wave number in vacuum, and sometimes that

$\mathbf{k}_0$ may satisfy the continuity condition for the tangential component of the wave vector at the entrance surface. (1*b*)

The Takagi–Taupin equations are also applicable in the case of an absorbing crystal, provided that all relevant quantities now assume complex values. The real and imaginary parts of $\mathbf{k}_0$ are called $\mathbf{k}_{0r}$ and $\mathbf{k}_i$, respectively, so that

$$\mathbf{k}_0 = \mathbf{k}_{0r} + i\mathbf{k}_i. \tag{2}$$

The direction of $\mathbf{k}_i$ may be chosen arbitrarily. However, this choice influences the particular manner of solution of the equations. Hence it determines whether or not $\mathbf{k}_0$ satisfies the continuity condition (1*b*) and whether or not the parameter β_h [(4)] may be chosen equal to zero. In principle these problems are solved in the literature but they have never been pointed out explicitly.

2. Takagi–Taupin equations and boundary conditions

Let us recall the well known equations, for simplicity in the case of a perfect crystal and for the two-beam case:

$$\begin{aligned} \frac{\partial}{\partial s_0} D_0(\mathbf{r}) &= -i\pi K\chi_{\bar{h}}CD_h(\mathbf{r}) \\ \frac{\partial}{\partial s_h} D_h(\mathbf{r}) &= -i\pi K\chi_h CD_0(\mathbf{r}) + 2\pi iK\beta_h D_h(\mathbf{r}) \end{aligned} \tag{3}$$

where χ_h and $\chi_{\bar{h}}$ are the Fourier coefficients of the dielectric susceptibility; C is the polarization factor; s_0 and s_h are unit vectors along the refracted and reflected directions;

$$\beta_h = (\mathbf{k}_h^2 - \mathbf{k}_0^2)/2\mathbf{K}^2 \tag{4}$$

where $\mathbf{k}_0$ and $\mathbf{k}_h$ are vectors inside the crystal and $\mathbf{K}$ is the wave vector in vacuum. The extremities of both wave vectors $\mathbf{k}_0$ and $\mathbf{k}_h$ are matched through the value of β_h.

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