for the absence of residual stresses in the heterostructure in the case of coherent growth has been obtained analytically. This condition is that the sum of the following mismatches is equal to zero: the mismatch caused by the difference between the coefficients of thermal expansion of layers and the lattice mismatch at epitaxy temperature.

The growth conditions can be satisfied with such a radius of curvature of the substrate at epitaxy temperature at which, on heterostructure straightening and cooling, the stresses caused by both the difference between the coefficients of expansion of layers and the difference between the lattice constants at epitaxy temperature are eliminated. In this case, the necessary density of dislocations is introduced.

The method of calculation has been used in analyzing the residual stresses of a 14 layer InGaAsP/InP coherently developed heterolaser with a superlattice. The moments were determined relative to the neutral plane and the middle part of each layer. It is shown that in the case of moments obtained in different ways, their total values only differ in the ninth sign and the values of stresses in the layers differ in the fourth sign. The validity of the results of calculating stresses in which the moment values are determined relative to the middle part of each layer has been confirmed.

Concluding remarks

The condition for the absence of residual stresses in superlattices has been obtained analytically for the cases of both coherent growth and misfit dislocations. In the case of pseudomorphous growth, this condition is that the sum of three mismatches is equal to zero: the lattice mismatch at epitaxy temperature, the mismatch caused by the difference between the coefficients of thermal expansion of the layers and the mismatch introduced by the misfit dislocations.

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A Multisolution Method of Phase Determination by Combined Maximization of Entropy and Likelihood. III. Extension to Powder Diffraction Data

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Abstract

The mathematical techniques used in the derivation of intensity statistics and of probabilistic relations between structure factors for single-crystal data are here extended so as to encompass the phenomenon of intensity overlap, which is encountered with diffraction data collected from microcrystalline powders or from other disordered specimens. It is shown that the loss of information caused by intensity overlap in powder diagrams may be put on the same footing as the usual loss of phase for single-crystal data by a judicious use of a multiplicity-weighted metric and of the *n*-dimensional spherical geometry associated with that metric. Structure determination from powder diffraction data is thus cast in the form of a 'hyperphase problem' in which the dimensionality varies from one data item to another. This geometric picture enables probability distributions for overlapped intensities to be derived not only under the standard assumption of a uniform distribution of random atoms - thus extending Wilson's statistics to powder data - but also for non-uniform distributions such as those occurring in maximum-entropy phase determination [Bricogne (1984). *Acta Cryst.* A**40**, 410-445]. The corresponding conditional probability distributions and likelihood functions are then derived. The possible presence of known fragments is also considered. These new distributions and likelihood functions lead to new methods of data normalization, to new statistical tests for space-group assignment, to a generalization of the 'heavy-atom' method, to the extension to powders of a new multisolution method of structure determination [Bricogne & Gilmore (1990). *Acta Cryst.* A**46**, 284-297] recently applied to single crystals [Gilmore, Bricogne & Bannister (1990). *Acta Cryst.* A**46**, 297-308] and to a new criterion for conducting crystal structure

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refinement against powder data. It is shown that these results are also applicable to other types of diffraction data corrupted by overlap, in particular to single-crystal data recorded by the Laue technique or on twinned crystals and to diffraction patterns from fibres with helical symmetry. An extensive mathematical Appendix collects the derivations and general results used in the paper, together with related material which will be used in subsequent developments. A companion paper [Gilmore, Henderson & Bricogne (1991). *Acta Cryst.* A**47**, 830-841] describes a first implementation of these results and their successful application to the *ab initio* determination of two medium-size structures from powder data.

0. Introduction

The determination of crystal structures from X-ray powder diffraction data entails not only solving the phase problem - as with single crystals - but also resolving the integrated intensity corresponding to each peak of the powder diagram into the individual intensities of the distinct Bragg reflexions contributing to that peak. Traditional direct methods are ill suited to this purpose because the three-dimensional indexing of the data on which the very structure of their formulae and procedures is predicated is spoilt by the overlap phenomenon. A number of successful structure determinations by conventional direct methods from powder data have been reported but they have been limited to cases where the small size or low symmetry of the structure or sheer instrumental prowess have resulted in a minimal proportion of overlaps.

The multisolution method based on the combined use of entropy and likelihood proposed by Bricogne (1984*a*) and developed for single-crystal data by Bricogne & Gilmore (1990) and Gilmore, Bricogne & Bannister (1990) does not suffer from this limitation. Indeed, the construction of joint probability distributions (j.p.d.'s for short) of structure factors (based on maximum-entropy distributions of atoms) on the one hand and the consultation of the experimental data through likelihood functions on the other hand are *distinct operations.* As a result, the latter can be adapted to consulting powder data without disturbing the progressive build-up of a three-dimensional picture by the former. It is therefore possible, in principle, to modify the single-crystal approach - and any computer program implementing it - so as to solve crystal structures from their powder patterns even when most or all of the integrated intensities are overlaps.

It is the purpose of this paper to present the mathematical methods and results which make this adaptation possible. The phenomenon of intensity overlap is examined in § 1. It is cast into a geometric form which makes the separation of overlapping intensities and the solution of the phase problem appear as two aspects of the same generalized 'hyperphase problem'. It is also shown that a felicitous cancellation between the effects of statistical weight, reflexion multiplicity and centric character leads to an 'equal-variance' property which greatly simplifies the associated statistical models. The derivation of probability distributions of overlapped intensities is then undertaken: first under the standard assumption of uniformly distributed atoms (§ 2), leading to an extension of intensity statistics to powder data; then in the case of non-uniformly distributed atoms and/or of the presence of known fragments (§ 3) which is fundamental to most of the subsequent applications. Probability distributions of structure factors conditioned by the knowledge of an overlapped intensity are considered in § 4 and expressions are given for their centroids. These mathematical results provide the necessary basis for an extension to powders of the main stages of a direct structure determination. Data preparation and normalization, as well as the detection of heavy atoms or known fragments in the absence of phase information, are considered in §5. Phase determination by the multisolution method mentioned above is treated in § 6. Structure completion by fragment recycling and structure refinement by the Rietveld method are examined in § 7. A first implementation of these results and its successful application to the *ab initio* determination of two medium-size structures from powder data are reported in the following paper (Gilmore, Henderson & Bricogne, 1991). Directions of further development and other possible applications of this approach - which include the Laue method and fibre diffraction - are discussed in § 8.

The work presented here draws on a great variety of mathematical techniques and results, mostly from *n*-dimensional spherical geometry and from the theories of Eulerian integrals and generalized hypergeometric series. These are found scattered in vast and heterogeneous mathematical literature where the diversity of contexts obscures their close interrelations. Direct reference in the text to this primary literature would have demanded a great deal of browsing and assimilation on the part of the reader. To ease this burden, the body of results used in this paper has been collected into a mathematical Appendix, together with extensive cross references between them and some new derivations which highlight their internal coherence; references to the primary literature are then made from within the Appendix. As it happens, the hyperphase problem considered here provides a framework within which many connections between the main techniques are displayed and exploited in a natural way and lead to very effective methods. It is hoped that the compilation of such an Appendix will enhance the usefulness of this analytical tool to future workers in the field.

1. The phenomenon of intensity overlap

1.0. *Preliminary remarks*

Each item of intensity data recorded from a single crystal by one of the standard techniques using monochromatic X-rays can be labelled by a *unique* point $\mathbf{h}$ of the reciprocal lattice and

$$I_{\mathbf{h}}^{\text{obs}} = A_{\mathbf{h}}^2 + B_{\mathbf{h}}^2 \quad \text{for an acentric reflexion} \qquad (1.1a)$$

$$I_{\mathbf{h}}^{\text{obs}} = C_{\mathbf{h}}^2 \quad \text{for a centric reflexion} \qquad (1.1b)$$

where $A_{\mathbf{h}}$ and $B_{\mathbf{h}}$ are the real and imaginary parts of a complex-valued acentric structure factor and $C_{\mathbf{h}}$ is the real coordinate of a centric structure factor measured along the direction $\theta_{\mathbf{h}}$ of one of its two allowed phases ($A2.19$).

On the other hand, each item of integrated intensity recorded from a powder specimen with monochromatic X-rays will in general be a *sum* of contributions from *several* single-crystal reflexions with identical (or instrumentally unresolvable) values of d^*. Given such an intensity data item I_u, let H_u be the collection of symmetry-unique single-crystal reflexions contributing to that integrated intensity. More specifically, let H_u^a and H_u^c be the (complementary) subsets of H_u consisting of acentric and centric reflexions respectively. Then the value of I_u is related to the structure factors of reflexions in H_u by the basic equations

$$I_u^{\text{obs}} = \sum_{\mathbf{h}\in H_u^a} p_{\mathbf{h}}[A_{\mathbf{h}}^2 + B_{\mathbf{h}}^2] + \sum_{\mathbf{k}\in H_u^c} p_{\mathbf{k}} C_{\mathbf{k}}^2. \qquad (1.2)$$

Here $p_{\mathbf{h}}$ is the multiplicity factor for reflexion $\mathbf{h}$ [Azároff & Buerger (1958), p. 201; Bacon (1962), p. 96; Warren (1969), p. 47; Wilson (1970), pp. 75-76], which is tabulated in Vol. II of *International Tables for X-ray Crystallography* (1967) (pp. 31-34).

1.1. *Geometric representation of intensity overlap*

The above relation has a simple geometric interpretation, the formulation of which requires further notation. Let the label u of an integrated intensity item be fixed so that we may dispense with the subscript u in most of what follows. Let m_a be the number of acentric reflexions in H_u^a, m_c be the number of centric reflexions in H_u^c and let $m = m_a + m_c$ be the total number of contributors to the overlap pattern. For the sake of explicitness in subsequent formulae, it is convenient to order these reflexions so that acentric reflexions are listed first ($j = 1, \ldots, m_a$) and centric reflexions next ($j = m_a + 1, \ldots, m$). For each $j = 1, \ldots, m$, let n_j be the dimension over the field $\mathbb{R}$ of real numbers of the structure factor attached to $\mathbf{h}_j$ and let n be the total dimension over $\mathbb{R}$ of the collection of structure factors contributing to I; thus,

$$n_j = 2 \quad \text{if } \mathbf{h}_j \text{ is acentric}, \qquad (1.3a)$$

$$n_j = 1 \quad \text{if } \mathbf{h}_j \text{ is centric}, \qquad (1.3b)$$

and

$$n = \sum_{j=1}^{m} n_j. \qquad (1.3c)$$

Equation (1.2) then states that I_u^{obs} is the square of the distance to the origin of a representative point in the space $\mathbb{R}^n$ when the latter is endowed with an *anisotropic* metric. The tensor of this metric with respect to the standard basis of $\mathbb{R}^n$ is represented by an $n \times n$ diagonal matrix $\mathbf{T}$ in which the multiplicity factor p_j of each reflexion j is repeated n_j times:

$$\mathbf{T} = \operatorname{diag}(p_1, p_1, p_2, p_2, \ldots, p_{m_a}, p_{m_a}, p_{m_a+1}, p_{m_a+2}, \ldots, p_m). \qquad (1.4)$$

Alternatively, we may form a vector $\mathbf{F}$ of structure-factor components in $\mathbb{R}^n$ in which the n_j components from each contributing reflexion j are weighted by the square root of the multiplicity factor p_j, according to

$$\mathbf{F} = \begin{bmatrix} p_1^{1/2} A_1 \\ p_1^{1/2} B_1 \\ p_2^{1/2} A_2 \\ p_2^{1/2} B_2 \\ \vdots \\ p_{m_a}^{1/2} A_{m_a} \\ p_{m_a}^{1/2} B_{m_a} \\ p_{m_a+1}^{1/2} C_{m_a+1} \\ p_{m_a+2}^{1/2} C_{m_a+2} \\ \vdots \\ p_m^{1/2} C_m \end{bmatrix}. \qquad (1.5)$$

The right-hand side of (1.2) is then $\|\mathbf{F}\|^2$, the square of the length of $\mathbf{F}$ in $\mathbb{R}^n$ for the *ordinary* Euclidean metric whose tensor is represented by the $n \times n$ *identity* matrix.

The geometric interpretation announced above is now obvious: (1.2) states that $\mathbf{F}$ is located on a *hypersphere* S_{n-1} in $\mathbb{R}^n$ with radius $(I^{\text{obs}})^{1/2}$ and the problem of completely specifying $\mathbf{F}$ once the associated intensity measurement is taken into account amounts to specifying the values of $n-1$ angular coordinates on that hypersphere.

1.2. *The hyperphase problem*

The problem just stated is an n-dimensional version of the usual phase problem, the latter corresponding to $n = 2$. If one reads the defining relation (1.5) backwards, it is clear that these angular coordinates perform the dual functions of (1) separating the lumped modulus into the individual moduli of the contributing reflexions and (2) specifying the phases or signs of these separate moduli. Thus the problem of resolving an overlapped intensity on the one hand and of phasing the separate moduli on the other hand appear as - so to speak - two mutually orthogonal projections of the same hyperphase problem formulated in terms of n-dimensional spherical geometry. In this terminology the hyperphase is essentially a unit vector $\boldsymbol{\omega} \in S_{n-1}$.

This viewpoint has a precedent in the classical work of Franklin, Klug, Holmes and co-workers on the structure of tobacco mosaic virus (TMV). According to the theory of diffraction by helical fibres (Cochran, Crick & Vand, 1952; Franklin & Klug, 1955; Waser, 1955*a*; Klug, Crick & Wyckoff, 1958), each item of intensity data may be written as

$$I = \sum_n |G_n|^2 \qquad (1.6)$$

where the G_n are Fourier-Bessel coefficients (usually complex valued) and where the summation is over those values of n which are allowed by the selection rules expressing the helical symmetry. This relation is identical to (1.2), except for the multiplicity weighting. Its interpretation as the equation of a hypersphere was implicit in early unpublished work by Franklin, Klug and Holmes on the applicability of the isomorphous replacement method to TMV (Holmes, 1959) and first appeared in print with the papers by Stubbs & Diamond (1975) and Holmes, Stubbs, Mandelkow & Gallwitz (1975). The latter paper alludes (p. 193) to a possible parametrization of the separation problem for two (acentric) overlapping terms by means of an extra phase angle and points out that the recovery of the two complex Fourier-Bessel coefficients '... may be formulated in a way analogous to the classic crystallographic phase problem but with three unknown parameters rather than one'. Subsequent work proceeded by the isomorphous replacement method and this viewpoint never developed beyond the level of a metaphor, but the credit for first identifying the hyperphase problem clearly belongs to these authors. The main novelty of the work about to be presented resides in a quantitative elaboration of this picture and in the derivation and exploitation of its statistical properties. In this respect, the equivalence between the resolution of overlaps and the determination of phases becomes fundamental in the integrations over hyperspheres by means of which all the subsequent statistical results are derived.

1.3. *Spherical geometry*

The geometric picture just described places n-dimensional spherical geometry in the same central rôle as that played by the geometry of the phase circle in the absence of overlap. Since this geometry for general n is less familiar and more involved than for $n = 1$ or $n = 2$, section $A1$ of the Appendix summarizes the main definitions and results required in the course of this work. The reader is invited to study § $A1$ at this point.

In the absence of overlap ($m = 1$) for single-crystal data ($p = 1$), an intensity measurement locates $\mathbf{F}$ on a zero-dimensional sphere S_0 in $\mathbb{R}^1$ (*i.e.* a pair of points, see § $A1.1$) for a centric reflexion ($n_1 = 1$) or on a one-dimensional sphere S_1 in $\mathbb{R}^2$ (*i.e.* a circle) for an acentric reflexion ($n_1 = 2$). The missing information needed to go from $(I^{\rm obs})^{1/2}$ to $\mathbf{F}$ is a sign in the centric case and a polar angle (phase) in the acentric case. At this stage, the close relationship between the phase problem and the overlap problem may be visualized in its simplest setting by noticing that there is complete identity (see § $A1.2$) between

(1) the phase problem for an acentric reflexion, where a phase between 0 and 2π must be specified [equation ($A1.7a$)];

(2) the overlap + sign problem for two overlapping centric reflexions with the same statistical weight, where a 'splitting angle' between 0 and $\pi/2$ - *i.e.* a point of the positive quadrant - describes the separation of the lumped modulus into two moduli [equation ($A1.7b$)], each of which then requires the specification of a sign [equation ($A1.7c$)].

In the presence of overlap ($m > 1$) for a general value of n, the missing coordinates are $(n-1)$ spherical polar angles which parametrize the points of a unit sphere S_{n-1} in $\mathbb{R}^n$. The definition of such angles for $n = 1, 2, 3$ is reasonably unique up to permutation of the axes. For general n, however, this is not the case, and some of the flexibility available in this choice (concerning which the reader is urged to consult §§ $A1.3$ to $A1.5$) can be used to advantage in parametrizing intensity overlap patterns.

To a crystallographer, the most natural type of polyspherical coordinate system (§ $A1.4$) for parametrizing the missing information attached to an overlapped intensity consists in solving the *overlap problem* (*i.e.* separating the m moduli) first and solving the *phase problem* (*i.e.* specifying m_a phases and m_c signs) next. By analogy with the example given above, the solution of the overlap problem entails the specification of a collection of $m-1$ splitting angles between 0 and $\pi/2$ (called *pseudophases* in what follows) defining a point of the *positive unit hyperoctant* S^+_{m-1} (§ $A1.1$); the subsequent specification of phases and signs takes place at the next level of the associated binary tree (§ $A1.3$). This parametrization amounts to using a polyspherical coordinate system in which the real and imaginary parts of each acentric structure factor have the same ancestor node.

Alternatively, we may use *zonal coordinates* (§ $A1.5$) on S^+_{m-1}, then m_a phases and m_c signs. The zonal coordinates perform the same task as the pseudophases, but they retain more symmetry than the latter and are better suited to the calculation of certain integrals over S^{+}_{m-1}, *i.e.* to integration over all possible solutions to the overlap problem.

1.4. *General statistical aspects of intensity overlap*

The geometric representation of intensity overlap makes it natural to derive probability distributions of overlapped intensities, under given assumptions, in two stages:

(1) form the j.p.d. in $\mathbb{R}^n$, under the given assumptions, of the m structure factors contributing to the chosen intensity, using the methods established for single-crystal studies;

(2) integrate out its angular dependence in $\mathbb{R}^n$ to obtain the marginal distribution of $R = \|\mathbf{F}\| = I^{1/2}$.

This integration is not only over all possible phases or signs - as in the single-crystal case - but also over the pseudophases, *i.e.* over all possible ways of separating the total intensity I into separate intensities for the m overlapping reflexions.

In this section, some general aspects of this procedure will be examined as a prelude to the derivations themselves.

1.4.1. *Change of metric.* In the transition from j.p.d.'s of single-crystal structure factors to the distribution of vector $\mathbf{F}$ defined by (1.5), the change of metric introduced in § 1.1 must be taken into account.

Let $\mathbf{F}_{sc}$ denote the vector in $\mathbb{R}^n$ with components $A_1, B_1, A_2, B_2, \ldots, A_{m_a}, B_{m_a}, C_{m_a+1}, C_{m_a+2}, \ldots, C_m$. Then (1.5) may be rewritten in the form

$$\mathbf{F} = \mathbf{T}^{1/2}\mathbf{F}_{sc} \qquad (1.7)$$

where T is defined by (1.4).

Similarly, let $\mathbf{Q}_{sc}$ denote the covariance matrix between the components of $\mathbf{F}_{sc}$ under given assumptions regarding the distribution $q(\mathbf{x})$ of random atomic positions (the calculation of $\mathbf{Q}_{sc}$ is detailed in § *A*3.2). Then the covariance matrix $\mathbf{Q}$ between the components of $\mathbf{F}$ under the same assumptions will be

$$\mathbf{Q} = \mathbf{T}^{1/2}\mathbf{Q}_{sc}\mathbf{T}^{1/2}. \qquad (1.8)$$

1.4.2. *Effect on offsets in non-central distributions.* In single-crystal studies, the distribution of $\mathbf{F}_{sc}$ becomes *non-central* (*i.e.* centred away from the origin in $\mathbb{R}^n$) whenever the distribution $q(\mathbf{x})$ is non-uniform and/or known fragments forming a partial structure are assumed to be present. The centroid of the distribution of $\mathbf{F}_{sc}$ may then be written

$$\mathbf{F}^c_{sc} = \langle \mathbf{F}_{sc} \rangle_q + \mathbf{F}^{\rm par}_{sc}. \qquad (1.9)$$

When going over to powder data, this centroid vector must be transformed according to

$$\mathbf{F}^c = \mathbf{T}^{1/2}\mathbf{F}^c_{sc} \qquad (1.10)$$

to produce the centroid of the distribution of $\mathbf{F}$.

Conversely, if a conditional centroid $\langle \mathbf{F} \rangle$ is subsequently calculated for $\mathbf{F}$ by the methods of § 4, (1.10) must be applied backwards in order to recover the corresponding single-crystal structure factors $\langle \mathbf{F}_{sc} \rangle$, *e.g.* to compute a 'centroid map' (§ 6.6).

1.4.3. *Effect on variances.* A remarkable phenomenon occurs in the calculation of the covariance matrix $\mathbf{Q}$ under the assumptions used to derive Wilson's statistics for single-crystal intensities, *i.e.* for random atoms uniformly distributed away from special positions.

In this special case (see § *A*3.3) we have, according to (*A*3.11*a*, *b*),

$$\mathbf{Q} = \sigma_2 \,\mathrm{diag}\,(p_1\varepsilon_1/2, p_1\varepsilon_1/2, \ldots, p_{m_a}\varepsilon_{m_a}/2, p_{m_a}\varepsilon_{m_a}/2,$$
$$p_{m_a+1}\varepsilon_{m_a+1}, \ldots, p_m\varepsilon_m)$$

where σ_2 is the common value of all the $\sigma_2(\mathbf{h}_j)$.

For each of the acentric reflexions ($j = 1, \ldots, m_a$) we have

$$\begin{aligned} \tfrac{1}{2}p_j\varepsilon_j &= \tfrac{1}{2}2|G\mathbf{h}_j||G_{\mathbf{h}_j}| && \text{by } (A2.20a) \text{ and } (A3.14) \\ &= |G| && \text{by } (A2.3), \end{aligned}$$

while for each of the centric reflexions ($j = m_a + 1, \ldots, m$) we have

$$\begin{aligned} p_j\varepsilon_j &= |G\mathbf{h}_j||G_{\mathbf{h}_j}| && \text{by } (A2.20b) \text{ and } (A3.14) \\ &= |G| && \text{by } (A2.3). \end{aligned}$$

Therefore the variances of all n components are equal:

$$\mathbf{Q} = \mathrm{diag}\,(\Sigma, \Sigma, \ldots, \Sigma) \qquad (1.11)$$

with

$$\Sigma = |G|\sigma_2. \qquad (1.12)$$

This remarkable 'equal-variance' property is a consequence of a double cancellation:

that between $|G_{\mathbf{h}_j}|$ and $|G\mathbf{h}_j|$, which is a general property of group actions (§*A*2.2);

that between the factor of 2 in $p_{\mathbf{h}_j}$ associated with Friedel expansion and the factor $\frac{1}{2}$ in Wilson's statistics associated with acentricity (§§ *A*2.6, *A*3.3).

This result could be rephrased into a Parseval-like theorem stating that the expected total intensity in each full orbit is the same, where a 'full orbit' (§*A*2.6) incorporates Friedel expansion.

1.4.4. *Scalar, diagonal and block-diagonal approximations.* Strictly speaking we should apply the two-stage procedure outlined at the outset (§ 1.4) starting from the j.p.d. of *all* single-crystal structure factors, to obtain the *joint* distribution of *all* the overlapped intensities present in a given powder diagram. This would retain all the correlations between overlapped intensities which result from the correlations initially present between the structure factors. This is, however, a particularly difficult task and approximations have to be made.

In the first place, we shall not seek to calculate the correlations between the integrated intensities belonging to different peaks of the diagram. This amounts to retaining only the correlations between the structure factors contributing to each peak, *i.e.* present in each matrix $\mathbf{Q}$ considered above, and may be called the block-diagonal approximation. For each item of intensity data, the associated $\mathbf{Q}$ matrix is symmetric, hence can be diagonalized in an orthonormal basis of eigenvectors. This change of basis is an orthogonal transformation which leaves invariant the hypersphere $\|\mathbf{F}\| = (I^{\text{obs}})^{1/2}$ defined by the data. Therefore, at the cost of a matrix diagonalization per data item, the block-diagonal approximation can be reduced to the diagonal approximation in which only the variances are non-zero (but can all be different). Finally, the most drastic level of approximation is to assume that $\mathbf{Q}$ is a scalar multiple of the identity matrix. As shown above in § 1.4.3, this scalar approximation is adequate under the assumptions leading to Wilson's statistics.

For practical purposes, therefore, the following cases must be considered in the ensuing derivations:

(1) the equal-variance case, *i.e.* the scalar approximation, for both central and non-central distributions;

(2) the unequal-variance case, which leads to the diagonal and block-diagonal approximations, for both central and non-central distributions.

When using the block-diagonal approximation for a non-central distribution, care must be taken to rotate the offset vector (1.10) by the diagonalizing transformation before using it in the formulae derived below.

2. Powder intensity statistics: central distributions

We are now in a position to derive the expression for the distribution of integrated intensities recorded by the powder method under the standard hypothesis that the structure consists of equal atoms uniformly and independently distributed in the asymmetric unit. In the single-crystal case, this is the assumption under which both Wilson statistics and the probabilistic phase relations of conventional direct methods are established.

2.0. *Joint distribution of the members of an overlap*

Methods described elsewhere (Wilson, 1949, 1950; Hauptman & Karle, 1953; Bertaut, 1955, 1956*a*; Klug, 1958) allow one to approximate the joint distribution of the m single-crystal structure factors contributing to an overlapped intensity by a multivariate Gaussian in n dimensions, where n is the number of degrees of freedom (1.3*c*). The assumption of uniform distribution implies, by the moment calculations of § *A*3.3, that this distribution is *central*, that its covariance matrix $\mathbf{Q}_{\text{sc}}$ is *diagonal* and that the diagonal elements are the *statistical weights* of the contributing reflexions repeated according to the number of degrees of freedom (1.3*a*, *b*) attached to each reflexion:

$$\mathbf{Q}_{\text{sc}} = \operatorname{diag}(\varepsilon_1, \varepsilon_1, \varepsilon_2, \varepsilon_2, \ldots, \varepsilon_{m_a}, \varepsilon_{m_a}, \varepsilon_{m_a+1}, \varepsilon_{m_a+2}, \ldots, \varepsilon_m). \tag{2.0}$$

When the effects of reflexion multiplicity and of centric character are taken into account (§ 1.4.3), it follows according to (1.11) that each of the n one-dimensional components F_k of the vector $\mathbf{F}$ defined in (1.5) has a Gaussian distribution with mean 0 and the *same* variance

$$\Sigma = |G| \times \sigma_2, \tag{2.1}$$

where σ_2 is the common value of all the $\sigma_2(\mathbf{h}_j)$ (the atoms are supposed to be isotropic). Furthermore, distinct components of $\mathbf{F}$ are uncorrelated. This will be called the *equal-variance case.*

In some cases the property of equal variances for all degrees of freedom is no longer satisfied. This may happen for powder data if the observational variances are incorporated into the statistical variance, but the most important instance of unequal variances will occur in the treatment of Laue data (see § 8). In this case the scattering factors, and hence the sums $\sigma_2(\mathbf{h}_j)$, will be different for the m distinct harmonics contributing to a given overlapped intensity. Moreover, these harmonics will be scattering different wavelengths of the incident polychromatic X-rays, so that the spectral composition of the incident beam, together with any wavelength dependence in the response of the detector, will cause further inequality between the variances of the raw intensities pertaining to each of these harmonics. The *unequal variance case* is thus one of genuine interest and it is also a natural intermediate in the derivation of the non-central distribution (3.11) which is of great practical importance for powders.

2.1. *The equal-variance case*

The probability density function of $\mathbf{F}$ in $\mathbb{R}^n$, which will be denoted $P_{n;\Sigma}$, is given by

$$\begin{aligned} P_{n;\Sigma}(\mathbf{F})\,\mathrm{d}^n\mathbf{F} &= \prod_{k=1}^{n} (2\pi\Sigma)^{-1/2} \exp[-F_k^2/2\Sigma]\,\mathrm{d}F_k \\ &= (2\pi\Sigma)^{-n/2} \exp[-(2\Sigma)^{-1}\|\mathbf{F}\|^2]\,\mathrm{d}^n\mathbf{F}. \end{aligned} \tag{2.2}$$

Going over to spherical polar coordinates and putting $R = \|\mathbf{F}\|$ we have

$$\mathrm{d}^n\mathbf{F} = R^{n-1}\,\mathrm{d}R\,\mathrm{d}S_{n-1}$$

where $\mathrm{d}S_{n-1}$ is the surface element on the unit sphere S_{n-1} in $\mathbb{R}^n$. Integrating over S_{n-1} we get the final expression

$$P_{n;\Sigma}(R)\,\mathrm{d}R = \Omega_n R^{n-1} (2\pi\Sigma)^{-n/2} \exp[-R^2/2\Sigma]\,\mathrm{d}R \tag{2.3}$$

in which $\Omega_n = 2\pi^{n/2}/\Gamma(n/2)$ is the surface area of S_{n-1} [see (A4.8)]. This result may be expressed directly in terms of observable intensity I:

$$P_{n;\Sigma}(I)\,\mathrm{d}I = \frac{I^{n/2-1}\exp(-I/2\Sigma)}{(2\Sigma)^{n/2}\Gamma(n/2)}\,\mathrm{d}I. \tag{2.4}$$

In terms of normalized intensity $x = R^2/\Sigma$, this may be recognized as a χ^2 distribution with n degrees of freedom:

$$P_{n;\Sigma}(x)\,\mathrm{d}x = \frac{x^{n/2-1}\exp(-x/2)}{2^{n/2}\Gamma(n/2)}\,\mathrm{d}x \tag{2.5}$$

[see *e.g.* Cramér (1946), p. 233]. For $n = 1$ and $n = 2$, these distributions coincide with the Wilson distributions for centric and acentric single-crystal reflexions respectively, provided Σ is replaced by the variances given by (A3.11a, b).

2.2. *The unequal-variance case*

To distinguish probability densities for unequal variances from those with equal variances derived in § 2.1, the latter will be denoted by $P^{(1)}_{n;\Sigma}$ and the former by $P^{(m)}_{\mathbf{n};\boldsymbol{\Sigma}}$. Here $\mathbf{n} = (n_1, n_2, \ldots, n_m)$ is a vector of numbers of degrees of freedom, and $\boldsymbol{\Sigma} = (\Sigma_1, \Sigma_2, \ldots, \Sigma_m)$ is a vector of variances for each of the m lots of degrees of freedom.

The case $m = 2$ will be treated first, as it leads to an expression involving only a well known special function. Using p.d.f.'s in terms of intensity as given by (2.4) we have

$$\begin{aligned}
P^{(2)}_{\mathbf{n};\boldsymbol{\Sigma}}(I)
&= \int_0^I P^{(1)}_{n_1;\Sigma_1}(x)P^{(1)}_{n_2;\Sigma_2}(I-x)\,\mathrm{d}x\\
&= [\exp(-I/2\Sigma_2)/(2\Sigma)^{n_1/2}(2\Sigma)^{n_2/2}\Gamma(n_1/2)\Gamma(n_2/2)]\\
&\quad \times \int_0^I x^{n_1/2-1}(I-x)^{n_2/2-1}\\
&\quad \times \exp[-(I/2)(1/\Sigma_1 - 1/\Sigma_2)]\,\mathrm{d}I.
\end{aligned}$$

Recalling that the exponential function is a ${}_0F_0$ hypergeometric series (§ A5.1) and invoking identity (A5.5), we find

$$\begin{aligned}
P^{(2)}_{\mathbf{n};\boldsymbol{\Sigma}}(I)
&= [\exp(-I/2\Sigma_2)I^{(n_1+n_2)/2-1}\\
&\quad \times \{(2\Sigma)^{n_1/2}(2\Sigma)^{n_2/2}\Gamma[(n_1+n_2)/2]\}^{-1}]\\
&\quad \times {}_1F_1[n_1/2;\,(n_1+n_2)/2;\,-\tfrac{1}{2}(1/\Sigma_1 - 1/\Sigma_2)I].
\end{aligned} \tag{2.6}$$

This expression seems at first sight to lack symmetry with respect to the permutation of indices 1 and 2, but this symmetry can be shown to hold true by means of Kummer's identity (A5.11) for the confluent hypergeometric function ${}_1F_1$. Taking $\Sigma_2 > \Sigma_1$ ensures that ${}_1F_1$ has a negative argument and hence is an alternating series. For $n_1 = n_2$, this ${}_1F_1$ is in fact closely related to a modified Bessel function of order $(n_1 - 1)/2$ [see (A6.1b)].

For $m \geq 3$ another approach is necessary, based on the use of zonal hyperspherical coordinates (§ A1.5) in p.d.f.'s of moduli. The radius R in dimension n is split into m positive radi $R\xi_j (j = 1, \ldots, m)$ by choosing a point on the positive hyperoctant S^+_{m-1} of the unit sphere S_{m-1}. By the integration formula (A1.14) in zonal coordinates (§ A1.6) we have

$$\begin{aligned}
P^{(m)}_{\mathbf{n};\boldsymbol{\Sigma}}(R) &= R^{m-1}\int_{S^+_{m-1}} P^{(1)}_{n_1;\Sigma_1}(R\xi_1)\\
&\quad \times \ldots \times P^{(1)}_{n_m;\Sigma_m}(R\xi_m)\,\mathrm{d}S_{m-1}\\
&= \left[\prod_{j=1}^{m} \Omega_{n_j} R^{n_j-1}/(2\pi\Sigma_j)^{n_j/2}\right] R^{m-1}\\
&\quad \times \int_{S^+_{m-1}} \exp\left[-\frac{R^2}{2}\left(\frac{\xi_1^2}{\Sigma_1} + \ldots + \frac{\xi_m^2}{\Sigma_m}\right)\right]\\
&\quad \times \xi_1^{n_1-1}\ldots\xi_m^{n_m-1}\,\mathrm{d}S_{m-1}.
\end{aligned} \tag{2.7}$$

The integral may be expanded by termwise integration of the power series for the exponential:

$$\begin{aligned}
&\int_{S^+_{m-1}} \exp(z_1\xi_1^2 + \ldots + z_m\xi_m^2)\xi_1^{n_1-1}\ldots\xi_m^{n_m-1}\,\mathrm{d}S_{m-1}\\
&\quad = \sum_{p_1=0}^{\infty}\ldots\sum_{p_m=0}^{\infty}\left[\int_{S^+_{m-1}} \xi_1^{2p_1+n_1-1}\ldots\xi_m^{2p_m+n_m-1}\,\mathrm{d}S_{m-1}\right]\\
&\quad\quad \times z_1^{p_1}/p_1!\ldots z_m^{p_m}/p_m!\\
&\quad = (2^{m-1})^{-1}\sum_{p_1=0}^{\infty}\ldots\sum_{p_m=0}^{\infty} B(p_1 + n_1/2, \ldots, p_m + n_m/2)\\
&\quad\quad \times z_1^{p_1}/p_1!\ldots z_m^{p_m}/p_m!
\end{aligned} \tag{2.8}$$

where the last transformation uses the expression of the moments of the hyperoctant (§ A4.5) in terms of the generalized Euler beta integral. The definition of the latter (A4.7), together with that of the Pochhammer symbol (A5.2a) and the expression (A4.8) for the area Ω_n of the hypersphere S_{n-1}, give rise to the identity

$$\begin{aligned}
&\Omega_{n_1}\ldots\Omega_{n_m}(2^{m-1})^{-1}B(p_1 + n_1/2, \ldots, p_m + n_m/2)\\
&\quad = \Omega_n \frac{(n_1/2)_{p_1}\ldots(n_m/2)_{p_m}}{(n/2)_{p_1+\ldots+p_m}}.
\end{aligned} \tag{2.9}$$

This prompts us to consider the following polyhypergeometric function in m variables:

$$\begin{aligned}
&{}_mF_1^{(m)}(\alpha_1, \ldots, \alpha_m;\, \gamma;\, z_1, \ldots, z_m)\\
&\quad = \sum_{p_1=0}^{\infty}\ldots\sum_{p_m=0}^{\infty}[(\alpha_1)_{p_1}\ldots(\alpha_m)_{p_m}/(\gamma)_{p_1+\ldots+p_m}]\\
&\quad\quad \times z_1^{p_1}/p_1!\ldots z_m^{p_m}/p_m!
\end{aligned} \tag{2.10}$$

which is further described in § A5.5.

Then, defining Σ as the geometric mean of the Σ_j:

$$\Sigma = (\Sigma_1^{n_1} \ldots \Sigma_m^{n_m})^{1/n}, \tag{2.11}$$

we may write the final expression

$$P^{(m)}_{\mathbf{n};\Sigma}(R) = \frac{\Omega_n R^{n-1}}{(2\pi\Sigma)^{n/2}}\, {}_mF_1^{(m)}\left(\frac{n_1}{2}, \ldots, \frac{n_m}{2}; \frac{n}{2}; -\frac{R^2}{2\Sigma_1}, \ldots, -\frac{R^2}{2\Sigma_m}\right). \tag{2.12}$$

A more rapidly convergent expansion may be obtained by rewriting in (2.7)

$$\exp\left[-\frac{R^2}{2\Sigma_j}\xi_j^2\right] = \exp\left[-\frac{R^2}{2\Sigma'}\xi_j^2\right]\exp\left[-\frac{R^2}{2}\left(\frac{1}{\Sigma_j}-\frac{1}{\Sigma'}\right)\xi_j^2\right] \tag{2.13}$$

for each $j = 1, \ldots, m$, which is valid for any $\Sigma' > 0$. Since $\sum_{j=1}^{m} \xi_j^2 = 1$, it follows that

$$\begin{aligned} P^{(m)}_{\mathbf{n};\Sigma}(R) = {} & \Omega_n R^{n-1}(2\pi\Sigma)^{-n/2}\exp[-R^2/2\Sigma'] \\ & \times {}_mF_1^{(m)}[n_1/2, \ldots, n_m/2; \\ & -(R^2/2)(1/\Sigma_1 - 1/\Sigma'), \ldots, \\ & -(R^2/2)(1/\Sigma_m - 1/\Sigma')]. \end{aligned} \tag{2.14}$$

The mean variance Σ' may be chosen so as to produce the fastest possible convergence of the series, *e.g.* so as to minimize $\max_j |1/\Sigma_j - 1/\Sigma'|$.

For $m = 2$, applying this procedure with $\Sigma' = \Sigma_2$ yields a ${}_2F_1^{(2)}$ with $z_2 = 0$ which reduces to ${}_1F_1$ in one variable, giving the previous formula (2.6).

3. Powder intensity statistics: non-central distributions

3.0. *Joint distribution of the members of an overlap*

When the random atoms are non-uniformly distributed, or when a partial structure is assumed to be present, the mathematical expectation $\langle \mathbf{F} \rangle$ of $\mathbf{F}$ no longer vanishes and the distribution of $\mathbf{F}$ becomes non-central. These two assumptions are not truly independent since, in any sensible statistical model, the distribution $q(\mathbf{x})$ of the random atoms must be affected by the presence of the partial structure and thus rendered non-uniform.

The construction of joint probability distributions of structure factors for a given non-uniform distribution $q(\mathbf{x})$ of random atoms has been described by the author (Bricogne, 1984*a*, 1988; Bricogne & Gilmore, 1990). The moments involved in the Gaussian approximation to these distributions are given explicitly in § A3.2 in terms of the Fourier coefficients of $q(\mathbf{x})$: equation (*A*3.3) allows the computation of the vector denoted $\langle \mathbf{F}_{\mathrm{sc}} \rangle_q$ in (1.9) while equations (*A*3.6*a*,*b*,*c*,*d*), (*A*3.7*a*,*b*) and (*A*3.8) give the elements of the covariance matrix $\mathbf{Q}_{\mathrm{sc}}$. Strictly speaking these expressions only take care of the *trigonometric* part of the statistical model and describe the distribution of unitary structure factors $\mathbf{U}$ rather than that of $\mathbf{F}$. However, it is a simple matter to incorporate the atomic scattering factors into the model [Bricogne (1988), § 1] to obtain $\langle \mathbf{F}_{\mathrm{sc}} \rangle_q$ and $\mathbf{Q}_{\mathrm{sc}}$. The additional offset due to the partial structure may then be added to form the total offset $\mathbf{F}^c_{\mathrm{sc}}$ by (1.9). These must then be subjected to the changes of metric (1.10) and (1.8) respectively to produce the vector $\mathbf{F}^c$ and matrix $\mathbf{Q}$ used below.

In the scalar approximation $\mathbf{Q}$ is assumed to be of the form $\mathbf{Q} = \operatorname{diag}(\Sigma, \ldots, \Sigma)$, leading to a non-central version of the equal-variance distribution of § 2.1. In the diagonal approximation (to which the block-diagonal approximation can always be reduced, § 1.4.4) we have instead $\mathbf{Q} = (\Sigma_1, \ldots, \Sigma_1, \Sigma_2, \ldots, \Sigma_2, \ldots, \Sigma_m, \ldots, \Sigma_m)$ where Σ_j is repeated n_j times. If the block-diagonal approximation was considered at the outset, care must be taken to rotate the offset vector $\mathbf{F}^c$ by the diagonalizing transformation before using it in the formulae derived below.

3.1. *The equal-variance case*

Introduction of the offset vector $\mathbf{F}^c$ into (2.2) yields the expression

$$\begin{aligned} P_{n;\Sigma}(\mathbf{F} \mid \mathbf{F}^c) & = (2\pi\Sigma)^{-n/2}\exp[-(2\Sigma)^{-1}\|\mathbf{F}-\mathbf{F}^c\|^2] \\ & = (2\pi\Sigma)^{-n/2}\exp[-(2\Sigma)^{-1}(\|\mathbf{F}\|^2 + \|\mathbf{F}^c\|^2)] \\ & \quad \times \exp[(\|\mathbf{F}\|\,\|\mathbf{F}^c\|/\Sigma)\cos\theta] \end{aligned} \tag{3.1}$$

where θ is the angle between $\mathbf{F}$ and $\mathbf{F}^c$:

$$\cos\theta = \mathbf{F}\,.\,\mathbf{F}^c/\|\mathbf{F}\|\,\|\mathbf{F}^c\|. \tag{3.2}$$

Using the abridged notation $R = \|\mathbf{F}\|$ and $r = \|\mathbf{F}^c\|$, we may thus write

$$\begin{aligned} P_{n;\Sigma}(\mathbf{F} \mid \mathbf{F}^c) = {} & (2\pi\Sigma)^{-n/2}\exp[-(r^2+R^2)/2\Sigma] \\ & \times \exp[(rR/\Sigma)\cos\theta]. \end{aligned} \tag{3.3}$$

To obtain the marginal distribution of R we must integrate this expression over the sphere with radius R in $\mathbb{R}^n$. For that purpose we may choose a generalized spherical polar coordinate system with the x_n axis along $\mathbf{F}^c$ and with θ as its first splitting angle. We are then in the situation to which relation (*A*1.13) of § *A*1.6 applies, giving

$$\begin{aligned} P_{n;\Sigma}(R \mid r) & = R^{n-1}(2\pi\Sigma)^{-n/2}\exp[-(r^2+R^2)/2\Sigma] \\ & \quad \times \int_{S_{n-1}} \exp[(rR/\Sigma)\cos\theta]\,\mathrm{d}S_{n-1} \\ & = R^{n-1}(2\pi\Sigma)^{-n/2}\exp[-(r^2+R^2)/2\Sigma]\Omega_{n-1} \\ & \quad \times \int_0^\pi \exp[(rR/\Sigma)\cos\theta]\sin^{n-2}\theta\,\mathrm{d}\theta. \end{aligned} \tag{3.4}$$

Now we may invoke the following classical relations:

(i) Poisson's integral [Watson (1944), pp. 24–25, 47, 79]:

$$\int_0^\pi \exp(z\cos\theta)\sin^{2\nu}\theta\,\mathrm{d}\theta = \Gamma(\nu+\tfrac{1}{2})\Gamma(\tfrac{1}{2})I_\nu(z)/(\tfrac{1}{2}z)^\nu; \qquad (3.5a)$$

(ii) relation (*A*4.9) in § *A*4.4:

$$\Omega_n/\Omega_{n-1} = \Gamma[(n-1)/2]\Gamma(\tfrac{1}{2})/\Gamma(n/2); \qquad (3.5b)$$

(iii) the expression (*A*6.1*a*) of modified Bessel functions in terms of the ${}_0F_1$ hypergeometric series:

$$I_\nu(z) = [(\tfrac{1}{2}z)^\nu/\Gamma(\nu+1)]\,{}_0F_1[-;\,\nu+1;\,(\tfrac{1}{2}z)^2]. \qquad (3.5c)$$

Combining them with $\nu = n/2-1$ allows (3.4) to be rewritten in the final form

$$P_{n;\Sigma}(R|r) = \Omega_n R^{n-1}(2\pi\Sigma)^{-n/2}\exp[-(r^2+R^2)/2\Sigma] \times {}_0F_1[-;\,n/2;\,(rR/2\Sigma)^2], \qquad (3.6a)$$

which obviously reduces to (2.3) for $r=0$. The expression of Poisson's integral in terms of ${}_0F_1$, deduced here from (3.5*a*, *b*, *c*), may be obtained directly by the method of spherical moments (see § *A*6.2).

In the particular case $n=2$, *i.e.* $\nu=0$, this expression reduces to

$$P_{2;\Sigma}(R|r) = (R/\Sigma)\exp[-(r^2+R^2)/2\Sigma]I_0(rR/\Sigma); \qquad (3.6b)$$

it even remains valid for $n=1$, *i.e.* $\nu=-\frac{1}{2}$, in which case the integration in (3.4) is over S_0 and yields $2\cosh z$ [this is related to identity (*A*6.4)]:

$$P_{1;\Sigma}(R|r) = (2/\pi\Sigma)^{1/2}\exp[-(r^2+R^2)/2\Sigma]\cosh(rR/\Sigma). \qquad (3.6c)$$

These two particular cases may be recognized as the Rice distribution (Rice, 1944, 1945) and its centric equivalent, given in equations (1.15*a*) and (1.16*a*) of Bricogne & Gilmore (1990).

If instead of (3.5*c*) we use the ${}_1F_1$ form of I_ν after Kummer transformation [equation (*A*6.1*c*), § *A*6.1]

$$I_\nu(z) = [(\tfrac{1}{2}z)^\nu e^z/\Gamma(\nu+1)]\,{}_1F_1(\nu+\tfrac{1}{2};\,2\nu+1;\,-2z), \qquad (3.5d)$$

we obtain

$$P_{n;\Sigma}(R|r) = \Omega_n R^{n-1}(2\pi\Sigma)^{-n/2}\exp[-(R-r)^2/2\Sigma] \times {}_1F_1[(n-1)/2;\,n-1;\,-2rR/\Sigma], \qquad (3.7)$$

which is better suited to the case where R and r are both large compared to $\Sigma^{1/2}$ but their difference is not.

3.2. *The unequal-variance case*

The notation introduced in § 2.2 to deal with unequal variances needs to be extended to accommodate the n-dimensional offset vector $\mathbf{F}^c$. According to (1.5) we define a vector $\mathbf{r} = (r_1, r_2, \ldots, r_m)$ of m partial multiplicity-weighted moduli by

$$r_j = p_j^{1/2}[(A_j^c)^2 + (B_j^c)^2]^{1/2} \quad \text{for } 1 \le j \le m_a \qquad (3.8a)$$

$$r_j = p_j^{1/2}|C_j^c| \quad \text{for } m_a+1 \le j \le m. \qquad (3.8b)$$

Using the same zonal hyperspherical coordinates as in § 2.2 we obtain the generalization of (2.7) in the form

$$\begin{aligned} P_{\mathbf{n};\boldsymbol{\Sigma}}^{(m)}(R|\mathbf{r}) &= R^{m-1}\int_{S_{m-1}^+} P_{n_1;\Sigma_1}^{(1)}(R\xi_1|r_1) \times\ldots\times P_{n_m;\Sigma_m}^{(1)}(R\xi_m|r_m)\,\mathrm{d}S_{m-1} \\ &= \left[\prod_{j=1}^m \frac{\Omega_{n_j}R^{n_j-1}}{(2\pi\Sigma_j)^{n_j/2}}\exp\left(-\frac{r_j^2}{2\Sigma_j}\right)\right]R^{m-1} \\ &\quad \times \int_{S_{m-1}^+}\left\{\prod_{k=1}^m \exp\left(-\frac{R^2\xi_k^2}{2\Sigma_k}\right) \times {}_0F_1\left[-;\,\frac{n_k}{2};\,\left(\frac{r_kR\xi_k}{2\Sigma_k}\right)^2\right]\xi_k^{n_k-1}\right\}\mathrm{d}S_{m-1}. \end{aligned} \qquad (3.9)$$

In order to integrate out the ξ's we must seek a power-series expansion of the integrand in which terms are collected according to the powers of these variables. For this purpose we put $u_j = r_j^2/2\Sigma_j$ and $v_j = -(R\xi_j)^2/2\Sigma_j$ and we invoke identity (*A*.5.6*a*) with $p=0$ and $q=1$:

$$e^{v_j}\,{}_0F_1(-;\,n_j/2;\,-u_jv_j) = \sum_{p_j=0}^\infty {}_1F_1(-p_j;\,n_j/2;\,u_j)v_j^{p_j}/p_j!. \qquad (3.10)$$

The integrals of monomials in the ξ's may then be written in terms of generalized beta functions. This yields an expansion of the integral into a power series in the m variables $w_j = -R^2/2\Sigma_j$. Following essentially the same steps which lead from (2.7) to (2.12) one obtains the expression

$$P_{\mathbf{n};\boldsymbol{\Sigma}}^{(m)}(R|\mathbf{r}) = \Omega_n R^{n-1}(2\pi\Sigma)^{-n/2} \times {}_mF_1^{(m)}(n_1/2,\ldots,n_m/2;\,n/2;\,\{-R^2/2\Sigma_1\},\ldots,\{-R^2/2\Sigma_m\}) \qquad (3.11)$$

where the curly brackets {.} indicate that in the series (2.10) for ${}_mF_1^{(m)}$, $z_j^{p_j}$ is to be formally replaced by

$$\{z_j^{p_j}\} = \exp(-u_j)\,{}_1F_1(-p_j;\,n_j/2;\,u_j)z_j^{p_j} \qquad (3.12a)$$

$$= {}_1F_1(p_j+n_j/2;\,n_j/2;\,-u_j)z_j^{p_j} \qquad (3.12b)$$

by Kummer's identity ($A5.11$). The ${}_1F_1$'s involved as coefficients in ($3.12a$) are, up to normalization, the associated Laguerre polynomials defined in ($A5.12$), and the identity used in (3.10) is simply the generating relation ($A5.13$). The functional expression (3.11) clearly coincides with (2.12) when $\mathbf{r} = \mathbf{0}$ since the formal substitution (3.12) then boils down to the identical substitution.

The convergence properties of expansion (3.11) may be improved by the same procedure as that described for transforming (2.10) into (2.11).

4. Conditional distributions and their centroids

In the previous two sections, the joint probability distribution in $\mathbb{R}^n$ of all m structure factors contributing to an overlap has been integrated over a hypersphere of radius R to obtain the marginal probability distribution of $R = I^{1/2}$. The present section considers the converse situation where the value of R is specified [*e.g.* $R = (I^{\text{obs}})^{1/2}$] and where it is the conditional probability distribution (c.p.d. for short) of the hyperphase $\boldsymbol{\omega} \in S_{n-1}$ which is being sought.

In the equal-variance case this distribution is uniform when $\mathbf{F}^c = \mathbf{0}$ and is unimodal with mode at $\boldsymbol{\omega}^c = \mathbf{F}^c/\|\mathbf{F}^c\|$ when $\mathbf{F}^c \neq \mathbf{0}$. In the unequal-variance case the c.p.d. can be multimodal and its maxima can be located by a Lagrange multiplier method [see *e.g.* Stubbs & Diamond (1975), pp. 715-716; Bricogne (1984*a*), § 7.1.3].

Frequently, however, it is the centroid $\langle \mathbf{F} \rangle$ of this distribution, rather than its mode(s), which is of interest for the purpose of calculating a 'centroid map' (§ 6.6). This centroid structure-factor vector is defined by

$$\langle \mathbf{F} \rangle = \int_{S_{n-1}} P(R\boldsymbol{\omega}|\mathbf{F}^c) R\boldsymbol{\omega} \, \mathrm{d}S_{n-1} \tag{4.1}$$

where P is given by ($3.6a$) or (3.11) and where the integration is over all unit vectors $\boldsymbol{\omega} \in S_{n-1}$.

4.1. *The equal-variance case*

Let $\boldsymbol{\omega}^c$ be the unit vector along $\mathbf{F}^c$, so that $\mathbf{F}^c = r\boldsymbol{\omega}^c$. By (3.1) P depends only on the angle θ between $\boldsymbol{\omega}$ and $\boldsymbol{\omega}^c$; therefore the centroid vector $\langle \mathbf{F} \rangle$ is along $\boldsymbol{\omega}^c$ and may be written

$$\langle \mathbf{F} \rangle = R \langle \cos \theta \rangle \, \boldsymbol{\omega}^c \tag{4.2}$$

with

$$\begin{aligned}\langle \cos \theta \rangle &= P_{n;\Sigma}(R|r)^{-1} \int_{S_{n-1}} P(R\boldsymbol{\omega}|\mathbf{F}^c)\boldsymbol{\omega} \,.\, \boldsymbol{\omega}^c \, \mathrm{d}S_{n-1} \\ &= \frac{\int_0^\pi \exp(X \cos \theta) \cos \theta \sin^{n-2} \theta \, \mathrm{d}\theta}{\int_0^\pi \exp(X \cos \theta) \sin^{n-2} \theta \, \mathrm{d}\theta}\end{aligned}$$

with $X = rR/\Sigma$. The numerator may be obtained from the denominator by differentiation with respect to X, so that

$$\begin{aligned}\langle \cos \theta \rangle &= \frac{\partial}{\partial X} \log {}_0F_1(-; n/2; (\tfrac{1}{2}X)^2] \\ &= \frac{\frac{1}{2}X}{n/2} \frac{{}_0F_1[-; n/2+1; (\frac{1}{2}X)^2]}{{}_0F_1[-; n/2; (\frac{1}{2}X)^2]} \qquad \text{by } (A5.7b) \\ &= \frac{\frac{1}{2}X}{n/2} \frac{\Gamma(n/2+1)}{\Gamma(n/2)} \frac{I_{n/2}(X)/(\frac{1}{2}X)^{n/2}}{I_{n/2-1}(X)/(\frac{1}{2}X)^{n/2-1}} \\ &\qquad \text{by } (A6.1a)\end{aligned} \tag{4.3}$$

Extensive cancellation occurs in this expression, using in particular ($A4.2a$), yielding the remarkably simple result:

$$\langle \mathbf{F} \rangle = R[I_{n/2}(X)/I_{n/2-1}(X)]\boldsymbol{\omega}^c \quad \text{with } X = rR/\Sigma. \tag{4.4}$$

For $n = 2$, this formula is identical to that given by Sim (1959), while for $n = 1$ it gives the centric equivalent of Sim's formula where, by virtue of ($A6.4$) and ($A6.5$), the quotient is a hyperbolic tangent (see also Cochran & Woolfson, 1955).

Once $\langle \mathbf{F} \rangle$ has been calculated in this way, the change of metric (1.7) must be applied backwards to retrieve the single-crystal structure factors required for the computation of a map.

4.2. *The unequal-variance case*

Let us use, as in § 2.2 and § 3.2, a system of zonal coordinates: a point $\boldsymbol{\xi} \in S^+_{m-1}$ defines a splitting of R into m partial radii $R\xi_j$, and to each such radius is associated a phase φ_j (zero- or one-dimensional).

The integration over S_{n-1} involved in (4.1) can be performed in two steps, according to ($A1.14$):

(i) For each value of $\boldsymbol{\xi}$ we integrate over the phases $\varphi_1, \varphi_2, \ldots, \varphi_m$ to obtain a centroid vector $\langle \mathbf{F} \rangle(\boldsymbol{\xi})$ in which the jth structure factor will be denoted $\langle F_j \rangle(\boldsymbol{\xi})$. By the previous calculation, $\langle F_j \rangle(\boldsymbol{\xi})$ has phase φ_j^c (independent of $\boldsymbol{\xi}$) and modulus

$$\begin{aligned}|\langle F_j \rangle(\boldsymbol{\xi})| &= K_j R \xi_j \langle \cos(\varphi_j - \varphi_j^c) \rangle \\ &= K_j R \xi_j \frac{\frac{1}{2} r_j R \xi_j / \Sigma_j}{n_j/2} \\ &\quad \times {}_0F_1\left[-; \frac{n_j}{2}+1; \left(\frac{1}{2}\frac{r_j R \xi_j}{\Sigma_j}\right)^2\right] \\ &= K_j R \frac{r_j R}{n_j \Sigma_j} \xi_j^2 \\ &\quad \times {}_0F_1\left[-; \frac{n_j}{2}+1; \left(\frac{1}{2}\frac{r_j R \xi_j}{\Sigma_j}\right)^2\right]\end{aligned} \tag{4.5}$$

where

$$K_j = \Omega_{n_j} R^{n_j-1}/(2\pi\Sigma_j)^{n_j/2}.$$

(2) These centroid vectors are averaged over all possible $\boldsymbol{\xi}$'s by integration over S^{+}_{m-1}, each $\boldsymbol{\xi}$ being given the weight

$$\begin{aligned}P(R\boldsymbol{\xi}|\mathbf{F}^{c}) = {}& P^{(1)}_{n_1;\Sigma_1}(R\xi_1|r_1)\\ &\times\ldots\times P^{(1)}_{n_{j-1};\Sigma_{j-1}}(R\xi_{j-1}|r_{j-1})\\ &\times P^{(1)}_{n_{j+1};\Sigma_{j+1}}(R\xi_{j+1}|r_{j+1})\\ &\times\ldots\times P^{(1)}_{n_m;\Sigma_m}(R\xi_m|r_m).\end{aligned} \tag{4.6}$$

For each j the average modulus $|\langle F_j\rangle|$ may be written as an integral similar to (3.9) but in which the ${}_0F_1$ factor for j is replaced by the r.h.s. of (4.5). The analogue of step (2.8) then produces a generalized beta function in which the jth argument is $p_j + n_j/2+1$ and (2.9) must be modified accordingly; using (A5.3) we find

$$\begin{aligned}&\Omega_{n_1}\ldots\Omega_{n_m}(2^{m-1})^{-1}B(p_1+n_1/2,\ldots,p_j+n_j/2+1,\\ &\quad\ldots,p_m+n_m/2)\\ &\qquad=\Omega_n\frac{n_j/2}{n/2}\frac{(n_1/2)_{p_1}\ldots(n_j/2+1)_{p_j}\ldots(n_m/2)_{p_m}}{(n/2+1)_{p_1+\ldots+p_m}}.\end{aligned} \tag{4.7}$$

The centroid is then obtained by dividing by $P^{(m)}_{\mathbf{n};\boldsymbol{\Sigma}}(R|\mathbf{r})$ as given by (3.11), giving

$$\begin{aligned}|\langle F_j\rangle| = R\frac{r_jR}{n_j\Sigma_j}&\left[{}_mF^{(m)}_1\left(\frac{n_1}{2},\ldots,\frac{n_j}{2}+1,\ldots,\frac{n_m}{2};\frac{n}{2}+1;\right.\right.\\ &\left.\left.\left\{-\frac{R^2}{2\Sigma_1}\right\},\ldots,\left\{-\frac{R^2}{2\Sigma_m}\right\}\right)\right]\\ &\times\left[{}_mF^{(m)}_1\left(\frac{n_1}{2},\ldots,\frac{n_j}{2},\ldots,\frac{n_m}{2};\frac{n}{2};\right.\right.\\ &\left.\left.\left\{-\frac{R^2}{2\Sigma_1}\right\},\ldots,\left\{-\frac{R^2}{2\Sigma_m}\right\}\right)\right]^{-1}\end{aligned} \tag{4.8}$$

where the formal substitution rules (3.12) apply as written for the denominator, but with the second parameter in the ${}_1F_1$ changed to $n_j/2+1$ in the numerator.

In view of the differentiation identity (A5.15) this could also be written in terms of the logarithmic derivative of ${}_mF^{(m)}_1$ with respect to z_j, underlining the formal similarity with (4.3) in the equal-variance case.

4.3. *Treatment of partial peak overlaps*

Powder diffraction diagrams often display 'massifs' of partly resolved peaks and the integrated intensities corresponding to these peaks then carry highly correlated estimation errors. In this case one cannot simply *substitute* separate values $I^{\rm obs}_1,\ldots,I^{\rm obs}_M$ into the distribution $P(\mathbf{F})$; instead one should *integrate* over a range of simultaneous values of these intensities, using as a weight their observational probability (which contains a description of the error correlations).

This procedure unfortunately does not seem to be analytically tractable, but the necessary integration can be carried out numerically from the above expressions.

5. Data preparation for direct phase determination from powder data

5.0. *Likelihood functions*

As was done previously for the single-crystal case [Bricogne (1984*a*), § 4.2.2(2); Bricogne (1988), § 0.6; Bricogne & Gilmore (1990), § 1.4], the likelihood $\Lambda(\mathscr{H})$ of a hypothesis $\mathscr{H}$ will be defined as the probability it assigned to the outcome of an observation before that observation was carried out. In the present case, let $\mathscr{H}$ be a hypothesis leading to a probability distribution $P(R_u|\mathscr{H})$ for each item u of integrated intensity. Typically $\mathscr{H}$ will consist in assuming certain values for the scale factor and the global temperature factor; for the structure factors attached to a subset of reflexions; and/or fixed locations for some structural fragments. Then, in the diagonal approximation, the distributions $P(R_u|\mathscr{H})$ for different items u are independent, so that

$$\Lambda(\mathscr{H}) = \prod_{u=1}^{N_{\rm obs}} P(R_u|\mathscr{H}). \tag{5.1}$$

The 'null hypothesis' $\mathscr{H}_0$ that all atoms are randomly and uniformly distributed (hence that there are no fragments) and that the scale and temperature factors have the values given *e.g.* by a Wilson plot may be used as a reference. Other hypotheses may then be tested against $\mathscr{H}_0$ by considering the *likelihood ratio* $\Lambda(\mathscr{H})/\Lambda(\mathscr{H}_0)$ or its logarithm, the *log-likelihood gain* $L(\mathscr{H})-L(\mathscr{H}_0)$. The distributions $P(R|\mathscr{H})$ used in forming these criteria will be (2.3), (2.12), (3.6) or (3.11) according to the nature of $\mathscr{H}$ with respect to centrality and variance equality. These criteria are thus completely specified by the derivations carried out so far.

When the powder pattern contains massifs of peaks, the remark made in § 4.3 applies and the substitutions in (5.1) must be replaced by integrations. Bayes's theorem indicates that it is the log-likelihood gain which should be integrated with respect to the observational joint distribution of the relevant $R^{\rm obs}_u$.

5.1. *Normalization of powder diffraction intensities*

Determining the global scale and temperature factors which put the raw observed intensities on an absolute scale and correct for thermal motion is an essential prerequisite to the use of statistical phasing methods. Furthermore, as structural information accrues during the phasing process, re-normalization will often be necessary to ensure that the random-atom hypothesis is being used in a quantitatively correct fashion.

Certain aspects of the normalization problem are still open issues in the single-crystal case. In this section new procedures are proposed which simultaneously solve these problems for single crystals and for powders.

5.1.1. *Normalization by maximum likelihood.* The maximization of the likelihood with respect to global scale and temperature factors constitutes the method of choice for the estimation of these parameters. It has the advantage that it uses all the information available in the expressions for the various factors $P(R_u|\mathcal{H})$ rather than that contained in the first few moments of these distributions.

For each data item u ($u=1,\ldots,N_{\rm obs}$) let s_u and $\sigma_2(u)$ be the common values of $(\sin\theta)/\lambda$ and of σ_2 for the contributing Bragg reflexions and let n_u be the total number of degrees of freedom. The hypothesis that the atoms are randomly and uniformly distributed and that k and B are such that $R_u^{\rm obs}\times k\times\exp(-Bs_u^2)$ is on an absolute scale leads to the relation

$$\Sigma_u=[|G|\sigma_2(u)/k^2]\exp(2Bs_u^2) \tag{5.2}$$

and hence, by (2.3), to the log-likelihood

$$\begin{aligned} L(k,B)&=\sum_{u=1}^{N_{\rm obs}}\log P_{n_u;\Sigma_u}(R_u^{\rm obs}) &(5.3a)\\ &=\text{constant}+\sum_{u=1}^{N_{\rm obs}}[(n_u-1)\log R_u^{\rm obs}\\ &\quad-(n_u/2)\log\Sigma_u-(R_u^{\rm obs})^2/2\Sigma_u]. &(5.3b)\end{aligned}$$

It is straightforward to maximize this expression with respect to k and B by a Newton–Raphson method, in which the derivatives of L with respect to k and B are obtained by the chain rule through (5.2) from the derivatives of (2.3) with respect to Σ.

For non-uniformly distributed random atoms and/or in the presence of a known structural fragment, let $\mathbf{F}_u^{\rm calc}$ be the offset vector on an absolute scale. For given assumed values of k and B we have the relations

$$\mathbf{F}_u^{\rm c}=k^{-1}\exp(Bs_u^2)\mathbf{F}_u^{\rm calc}. \tag{5.4}$$

In the scalar approximation (5.2) holds, although σ_2 should now be calculated by summing only over the random atoms in (*A*3.12), *i.e. excluding the atoms in the fragment.* By (3.6*a*), putting $r_u=\|\mathbf{F}_u^{\rm c}\|$, this gives the log-likelihood:

$$\begin{aligned} L(k,B)&=\sum_{u=1}^{N_{\rm obs}}\log P_{n_u;\Sigma_u}(R_u^{\rm obs}|r_u) &(5.5a)\\ &=\text{constant}+\sum_{u=1}^{N_{\rm obs}}\{(n_u-1)\log R_u^{\rm obs}\\ &\quad-(n_u/2)\log\Sigma_u-[r_u^2+(R_u^{\rm obs})^2]/2\Sigma_u\\ &\quad+\log {}_0F_1[-;n_u/2;(r_uR_u^{\rm obs}/2\Sigma_u)^2]\}. &(5.5b)\end{aligned}$$

This can also be maximized with respect to k and B by a Newton–Raphson method involving the derivatives of (3.6*a*) with respect to r as well as Σ, affording a new estimate of these parameters in the light of the extra structural assumptions made.

Similar procedures can be applied when the variances are unequal, using distributions (2.12) and (3.11) in the central and non-central cases respectively.

5.1.2. *Normalization by the method of moments.* The normalization of single-crystal data by the Wilson plot method assumes uniformly distributed random atoms and is based on relation (*A*3.13*b*)

$$\langle|F_{\mathbf{h}}|^2\rangle=\varepsilon_{\mathbf{h}}\sigma_2(\mathbf{h}) \tag{5.6a}$$

being obeyed when the F's are on an absolute scale and temperature-corrected. This procedure can be extended to powder data under the same assumptions by using instead the variance formula

$$\langle\|\mathbf{F}_u\|^2\rangle=n_u|G|\sigma_2(u) \tag{5.6b}$$

which follows from (1.11) and (1.12). Comparison of (5.6*a*) and (5.6*b*) shows that raw integrated intensities from a powder diagram, after absorption corrections, can be scaled and temperature-corrected by means of a single-crystal normalization program by simply replacing $\varepsilon_{\mathbf{h}}$ by $n_u|G|$. The same program will then produce quasi-normalized and unitary structure-factor amplitudes, defined for single-crystal data as

$$|E_{\mathbf{h}}|=|F_{\mathbf{h}}|/[\varepsilon_{\mathbf{h}}\sigma_2(\mathbf{h})]^{1/2},\qquad |U_{\mathbf{h}}|=|F_{\mathbf{h}}|/\sigma_1(\mathbf{h}) \tag{5.7a}$$

and for powder data as

$$\left.\begin{aligned}\|E_u\|&=\|\mathbf{F}_u\|/[n_u|G|\sigma_2(u)]^{1/2},\\ \|U_u\|&=\|\mathbf{F}_u\|/\sigma_1(u)\end{aligned}\right\} \tag{5.7b}$$

where σ_1 is the sum of the atomic scattering factors.

In the non-central case, *i.e.* for non-uniformly distributed atoms and/or in the presence of known fragments, it is necessary to evaluate the second moments of the distributions $P(R|\mathcal{H})$. This will be done for equal variances only, since the method of moments is only an approximation and should be viewed as a preliminary stage to maximum-likelihood scaling (§ 5.1.1). In this case the kth moment of distribution (3.6*a*) may be written

$$\begin{aligned}\langle R^k\rangle&=\Omega_n(2\pi\Sigma)^{-n/2}\exp(-r^2/2\Sigma)\\ &\quad\times\int_0^\infty\exp(-R^2/2\Sigma)R^{k+n-1}\\ &\quad\times{}_0F_1[-;n/2;(rR/2\Sigma)^2]\,{\rm d}R.\end{aligned}$$

Putting $u=r^2/2\Sigma$, $v=R^2/2\Sigma$ and using (*A*4.8) this simplifies to

$$\begin{aligned}\langle R^k\rangle&=[(2\Sigma)^{k/2}/\Gamma(n/2)]\,e^{-u}\\ &\quad\times\int_0^\infty e^{-v}v^{(k+n)/2-1}\,{}_0F_1(-;n/2;uv)\,{\rm d}v.\end{aligned}$$

Using identity (*A*5.6*b*) for $p=0$ and $q=1$ [see Rainville (1960), Ex. 4, p. 128], together with Kummer's transformation (*A*5.11), yields

$$\langle R^k\rangle=(2\Sigma)^{k/2}\{\Gamma[(k+n)/2]/\Gamma(n/2)\}$$
$$\times\,{}_1F_1(-k/2;\,n/2;\,-r^2/2\Sigma). \qquad (5.8)$$

For k even the ${}_1F_1$ in this expression is an associated Laguerre polynomial (§ *A*5.4). For $k=2$ the relation $L_1^{(\alpha)}(x)=1+\alpha-x$ with $\alpha=n/2-1$ gives

$$\langle R^2\rangle=n\Sigma+r^2 \qquad (5.9)$$

which agrees with (5.6*b*) in the central case $r=0$.

In the single-crystal case this becomes

$$\langle|F_{\mathbf{h}}|^2\rangle=\varepsilon_{\mathbf{h}}\sigma_2(\mathbf{h})+|F_{\mathbf{h}}^c|^2 \qquad (5.10)$$

where $\sigma_2(\mathbf{h})$ is calculated excluding the atoms in the fragment.

5.2. *Space group identification and lattice indexing*

The earliest applications of Wilson's statistics to single crystals were tests for centrosymmetry (Wilson, 1949, 1950) which were later extended to more subtle tests for space-group identification (Rogers, 1950). The subject has been reviewed by Hargreaves (chapter 3 in Lipson & Cochran, 1968) and Srinivasan & Parthasarathy (1976). It is easily seen that these applications are based on the fact that different hypotheses about the space group of a crystal lead to predicting different variances and numbers of degrees of freedom for the distributions of intensity in various classes of reflexions and that these predictions can be tested by inspection of the measured data through what amounts to a likelihood criterion.

For powder data, the same possibility exists: although the multiplicity factor leads to variance equalization between all the degrees of freedom, the *number* n_u of degrees of freedom for each data item u may vary for different choices of space group. If the lattice assignment itself is ambiguous [see *e.g.* Paszkowicz (1987) for a survey of indexing criteria and of methods for their optimization], different modes of indexing may lead to different predicted overlap patterns, hence to different predicted values of n_u.

Let n_u^{calc} denote the number of degrees of freedom associated to data item u under hypothesis $\mathscr{H}$ concerning the lattice and space group. Then the maximum log-likelihood *value* $L_{\max}(\mathscr{H})$ achieved after determination of k and B according to (5.3) will act as a ***figure of merit*** for $\mathscr{H}$ and the comparison of the values of $L_{\max}$ obtained for different hypotheses is the natural extension of the tests developed for single crystals.

Should discrimination remain impossible, structure determination can be undertaken for each hypothesis by the methods of § 6 and the progress of $L_{\max}$ as phase assumptions are generated and ranked will indicate which hypothesis is the most viable.

5.3. *Detection of heavy atoms and other structural fragments*

Different assumptions concerning the presence, orientation and position of a structural fragment will lead to different values of the contribution $\mathbf{F}_u^{\text{par}}$ to the offset vector of the distribution $P(R_u|r_u)$ for each data item u; this may be written formally as

$$\mathbf{F}_u^{\text{par}}=\mathbf{F}_u^{\text{par}}(\boldsymbol{\theta},\mathbf{t})$$

where $\boldsymbol{\theta}=(\theta_1,\theta_2,\theta_3)$ is a triple of Euler angles and $\mathbf{t}$ is a position vector. The most powerful test for detecting and locating a fragment [Bricogne (1988), § 4] will therefore be based on a log-likelihood gain of the form

$$\sum_{u=1}^{N_{\text{obs}}}\{\log P_{n_u;\Sigma_u}[R_u^{\text{obs}}|k,B,r_u(\boldsymbol{\theta},\mathbf{t})]$$
$$-\log P_{n_u;\Sigma_u^0}(R_u^{\text{obs}}|k_0,B_0,0)\} \qquad (5.11)$$

where k_0 and B_0 are determined by (5.3) assuming that there is no fragment (Σ_u^0 incorporates all atoms) while k and B are determined by (5.5) under the assumption that the fragment is present (Σ_u excludes the atoms in the fragment) and is placed according to $(\boldsymbol{\theta},\mathbf{t})$.

If the amplitude r of the contribution from the partial structure is assumed to be small, a differential approximation can be obtained by examining the dependence of $\log P(R|r)$ on r^2 for small r^2:

$$\frac{\partial}{\partial(r^2)}[\log P_{n;\Sigma}(R|r)]$$
$$=\frac{\partial}{\partial(r^2)}\left\{-\frac{r^2+R^2}{2\Sigma}+\log{}_0F_1\left[-;\frac{n}{2};\left(\frac{rR}{2\Sigma}\right)^2\right]\right\}$$
$$=-\frac{1}{2\Sigma}+\left(\frac{R}{2\Sigma}\right)^2\frac{1}{n/2}\,\frac{{}_0F_1[-;n/2+1;(rR/2\Sigma)^2]}{{}_0F_1[-;n/2;(rR/2\Sigma)^2]} \qquad (5.12)$$

by (*A*5.7*b*). For $r^2=0$, this reduces to

$$\frac{\partial}{\partial(r^2)}[\log P_{n;\Sigma}(R|r)\Theta]\Big|_{r^2=0}$$
$$=(2\Sigma)^{-1}(R^2/n\Sigma-1)=(2\Sigma)^{-1}(E^2-1) \qquad (5.13)$$

where (1.12) and (5.7*b*) have been used in the final rewriting. The differential approximation to the log-likelihood gain thus leads to correlating the spherically averaged Patterson of the putative heavy atom with what may be recognized as a spherically averaged origin-subtracted Patterson of the unknown structure.

This connection between log-likelihood detection and Patterson superposition will be developed more extensively elsewhere.

6. Adaptation of the tree-directed multisolution strategy to powders

All the elements are now in place for adapting to powder data the multisolution method of direct phase determination described in § 3 of Bricogne & Gilmore (1990) for single-crystal data (this paper will be referred to as I throughout this section). Most of the changes consist in using the new likelihood functions (§ 5.0) which take intensity overlap into account, so that the overall strategy (I, § 3.1) remains identical, but a number of practical difficulties can arise which require special consideration.

6.1. *Origin definition*

If sufficiently many strong non-overlapped intensities are available, the origin can obviously be defined in the same way as for single-crystal data (see I, § 3.2.1). If such is not the case, however, at least one of the origin-fixing reflexions will have to be a contributor to a strong overlapped intensity. This entails an element of hazard since it is impossible to be certain at this early stage whether it is the desired reflexion, rather than other contributors to the overlap, which is strong. The risk of an inadequate origin definition can be decreased if a strong overlap can be found in which several of the contributors would be eligible for origin definition. In particularly unfavourable cases where all the strongest normalized amplitudes are overlaps, it may be necessary to resort to 'pseudophase permutation' (§ 6.3) to create inequivalent hypotheses concerning the separation of the overlapped intensities into individual ones and to choose different origin-defining reflexions for each hypothesis; the behaviour of the log-likelihood as phasing proceeds according to § 6.3 will eventually indicate the best choice.

6.2. *Enantiomorph discrimination*

The same remarks apply to this step as to the previous one. If overlapped intensities have to be used, enantiomorph discrimination consists in *selecting a hyperhemisphere* in $\mathbb{R}^{m_a}$ for one such overlap, m_a being the number of acentric contributors to that overlap (§ 1.1). Should there be several candidates, the most efficient discriminator may be found by performing a rather fine-grained hyperphase permutation (§ 6.3) on each of them and evaluating the corresponding log-likelihood gains L. The distributions of L will all be symmetric under central inversion in the subspace $\mathbb{R}^{m_a}$ spanned by the imaginary structure-factor components, and the best candidate will be that with the highest pair of distinct peaks related by this symmetry: selecting *one* of the peaks in that pair will fix the enantiomorph.

6.3. *Hyperphase permutation*

It seems natural, in the spirit of § 1.2, to call *hyperphase permutation* the process of generating a representative sample of structure-factor values for the distinct Bragg reflexions contributing to an overlap for a given value of the total intensity. This consists in choosing a reasonably homogeneous distribution of points $\boldsymbol{\omega} \in S_{n-1}$ on the surface of the unit hypersphere in $\mathbb{R}^n$, where n is the number of degrees of freedom.

The natural generalization of sign permutation for centrics and of quadrant permutation for acentrics is what may be called *hyperoctant permutation.* This amounts to using the vertices of the inscribed hypercube of S_{n-1}, *i.e.* the 2^n points with coordinates

$$(I^{\text{obs}}/n)^{1/2}(\pm 1, \pm 1, \pm 1, \ldots, \pm 1, \pm 1) \quad (n \text{ times}).$$

This may produce too coarse a sampling of S_{n-1} for some applications, as it partitions the total intensity equally between the n degrees of freedom. Fine-grained samples can be produced by subdividing the faces of the hypercube and projecting that subdivision onto the hypersphere. More general optimal subdivisions are obtainable by means of spherical codes or spherical designs (Conway & Sloane, 1988).

In some cases (*e.g.* § 6.1) it is required to generate a sample of possible individual *amplitudes* (unphased) for the m members of an overlap. According to the terminology introduced in § 1.3, this involves *pseudophase permutation,* which is the same operation as that just described but applied to the positive hyperoctant S^+_{m-1} rather than to S_{n-1}.

6.4. *Evaluation and refinement of hyperphase assumptions*

A set of hyperphase assumptions for the reflexions of a 'basis set' completely specifies, in modulus and in phase [*via* the reverse of (1.5)], the structure factors associated with these reflexions. The situation is thus completely analogous to that considered in the single-crystal case and these assumptions define a node of the multisolution tree (I, § 3.1.1). The prior distribution of atoms $q(\mathbf{x})$ can therefore be updated to the maximum-entropy distribution $q^{\text{ME}}(\mathbf{x})$ compatible with these assumptions by the methods of I, § 2.3. The latter distribution in turn permits the evaluation of the j.p.d. of the members of each overlap (§ 3.0) and of the log-likelihood gain - and optionally its derivatives - for the second neighbourhood (closed by overlap) of the basis set with respect to a standard null hypothesis (§ 5.0). This affords precisely the same mechanism for *evaluating and refining hyperphase assumptions* as that used for single-crystal data (I, § 3.2.4, § 3.2.5, § 3.2.7). This procedure has been implemented and successfully applied and is described in more detail in Gilmore, Henderson & Bricogne (1991).

6.5. *Breaking pseudosymmetries*

When the crystal symmetry is lower than that of its lattice, the powder method causes systematic overlaps which will tend to create pseudosymmetries in the map. This difficulty can be overcome by a procedure similar to that proposed for enantiomorph discrimination (§ 6.2), in which the most effective pseudosymmetry breakers are selected by examining the sensitivity of the log-likelihood gains to hyperphase choices for overlap members deemed equivalent by the pseudosymmetry but actually inequivalent under the true symmetry.

6.6. *Centroid maps*

The use of 'centroid maps' for visual inspection (I, § 1.6) can be extended to the powder case by means of the centroid formulae derived in § 4. These maps are analogous to the 'best' maps introduced by Blow & Crick (1959) and have the property that they minimize the expected mean-square error caused by the residual hyperphase errors. The possibility of including the overlapped reflexions in the calculation of these maps has been found in practice to produce worthwhile improvements [Gilmore, Henderson & Bricogne (1991), § 3.2].

7. Completion of structure determination for powders

7.1. *Fragment detection and recycling*

The method described in § 5.3 for detecting structural fragments by calculating log-likelihood gains may be applied not only at the outset but at any stage of the phase-determination process, since (5.12) accommodates non-uniformly distributed random atoms. This detection procedure will be more sensitive in the presence than in the absence of phases and will evolve continuously from a correlation of Patterson function to a correlation of electron densities.

A fragment, once detected unambiguously in this manner, can be *recycled* by incorporation into the known partial structure. This will strengthen the offset vector $\mathbf{F}^c$ and decrease the dispersion (since the fragment atoms are withdrawn from the summation for Σ), leading to sharper conditional distributions and hence to more detailed centroid maps.

7.2. *Log-likelihood as an optimal residual for structure refinement*

At a late stage where most of the structure is described as a known fragment, the residual disagreement between calculated and observed intensities may be modelled as above through the remaining random atoms (if any) together with some 'clutter' atoms [Bricogne (1988), § 3.1]. The refinement of the parameters describing the partial structural model, the localization of the remaining atoms and the characterization of the clutter distribution can then all take place simultaneously by maximization of the global log-likelihood gain (5.11) with respect to the relevant parameters, provided the statistical variances Σ are increased to reflect the observational variances.

According to (3.7) the global log-likelihood gain will then tend to behave like a least-squares residual (the ${}_1F_1$ term becomes a small perturbation when its argument is large and negative) in which the observational variances have been incremented by the mean-square power from residual random atoms and clutter. As the level of the latter decreases, this refinement becomes a conventional least-squares refinement against integrated intensities. However, the adoption of the log-likelihood gain as a refinement criterion throughout can be expected to increase the radius of convergence of the procedure.

It would be a simple matter to incorporate the peak profile information into this statistical analysis so as to obtain the global log-likelihood criterion directly in terms of the raw (unintegrated) counts provided by the powder diffractometer. The refinement procedure just outlined would then afford an enhancement of the Rietveld method (Rietveld, 1967, 1969) as well as a connection with the phase-determination process itself. This possibility will be developed further in forthcoming publications.

8. Discussion

There have been previous attempts at overcoming the overlap problem by statistical means. Jauch (1987) used a Bayesian procedure to resolve partially overlaps in powder diagrams from membrane proteins by Wilson statistics and to use phase information from electron microscopy. His work, however, overlooked the rôle of statistical weights and the variance equalization phenomenon described in § 1.4.3, and hence had to consider centric and acentric reflexions separately. No use was made of *joint* distributions of structure factors, so that phase determination was not considered. David (1987) advocated the use of a maximum-entropy criterion applied to the Patterson function as a means of resolving overlaps and solved a two-atom structure by this procedure (David, 1990). This appeal to entropy maximization is very different from the use made here in conjunction with the saddlepoint method, as discussed elsewhere [Bricogne (1988), §§ 0.5 and 7.7; Bricogne (1990)].

The work presented here attempts to bridge the gap between single-crystal and powder methods of crystal structure determination by building a common mathematical framework within which the statistical phasing techniques developed in the former can be adapted to the latter. The essential correctness and the practical utility of this approach are demonstrated in the following paper (Gilmore, Henderson & Bricogne, 1991).

The main thrust of this paper has been directed at the powder method. It should be clear, however, that the mathematical techniques established here are applicable with only minor alterations to any type of scattering data which may be viewed as single-crystal data corrupted by overlap, by reformulating the hyperphase problem in terms of the type of overlap encountered in each case: the analytical results contained in §§ 2, 3, 4 and the Appendix are then sufficiently general to allow the computation of likelihoods and of centroid maps on which all subsequent procedures (§§ 5, 6, 7) are based. A wide variety of structure-determination techniques thus become amenable to a single unified statistical treatment, with the converse benefit that any special phasing method developed for one of them becomes available to the others. The example treated here - namely the transposition of direct methods and of the use of partial structures from single crystals to powders - illustrates this point. Other such transfers will be described in subsequent publications.

These developments belong to the second stage of a Bayesian statistical approach to structure determination initiated in a previous paper (Bricogne, 1988). In the *initial stage* of constructing joint distributions of single-crystal structure factors (§§ 2.0 and 3.0) this approach is capable

(*a*) of accommodating arbitrary scattering factors (positive, negative or complex-valued) and therefore of dealing with neutron diffraction data;

(*b*) of making use of contrast variation measurements for low-resolution phasing and of solvent flatness at higher resolution;

(*c*) of giving an improved statistical treatment of the isomorphous replacement method through the systematic use of likelihood maximization in the detection of heavy atoms and in the refinement of their parameters;

(*d*) of detecting and recycling partial structural fragments;

(*e*) of exploiting the possible occurrence of non-crystallographic symmetries and of multiple crystal forms.

In the *second stage* of consulting the available diffraction data to evaluate hypotheses relating to phase (or hyperphase) values and/or to structural or geometrical characteristics, the analytical methods of §§ 2, 3, 4 are capable of dealing with any type of intensity overlap and in particular with those produced by

(1) twinned crystals;

(2) helical fibres (*e.g.* tobacco mosaic virus, see § 1.2); an analysis of the heavy-atom parameter refinement problem associated with the use of the isomorphous replacement method on data from helical fibres may be found in Bricogne (1984*b*);

(3) poorly oriented fibres such as tubulin (Mandelkow, Thomas & Cohen, 1977; Beese, Stubbs & Cohen, 1987) which give rise to a pattern of overlap intermediate between those of fibres and of powders;

(4) two-dimensional crystalline patches of membrane proteins adsorbed on mica sheets, some of which yield rich powder diagrams [*e.g.* the 'purple membrane' from *Halobacterium halobium*, see Henderson (1975) and Jauch (1987)];

(5) the *harmonic overlap* between the multiples of reflexions with coprime indices which occurs in data recorded by Laue photography with a polychromatic X-ray beam (Moffat, Szebenyi & Bilderback, 1984; Cruickshank, Helliwell & Moffat, 1987).

The work presented here may thus be considered as a concrete illustration, in a well defined special case, of the power and flexibility of the methods available to implement the second stage of the Bayesian approach.

This theoretical work has been the basis of a collaboration with Dr C. J. Gilmore over the past three years. Its formulation has greatly benefited from the stimulation and encouragement provided by his tireless enthusiasm to turn it into practice. This collaboration was made possible by financial support from BP Research through an Extra-Mural Research Award. Discussions with Professor K. J. Packer, Dr M. J. Tricker and Dr R. C. Ward at the BP Research Centre, as well as their rôle in securing support, are gratefully acknowledged. I am most indebted to Trinity College, Cambridge, for continuing to make available ideal working conditions.

APPENDIX

The main mathematical definitions, theorems and derivations used in this work, and whose direct inclusion into the body of the paper would have disrupted the flow of the argument, have been collected into this Appendix. Each section contains back-references to those parts of the paper where the results are actually used.

*A*1. *Spherical geometry in n dimensions*

This section is fundamental to the formulation and analysis of the hyperphase problem in § 1 and to the various integrations over hyperspheres carried out in §§ 2, 3 and 4. It is bound to retain a central importance in all subsequent developments relating to other types of intensity overlap.

*A*1.1. *Balls, spheres and octants.* Let $\|\mathbf{x}\|$ denote the Euclidean norm of $\mathbf{x} \in \mathbb{R}^n$. For $n \geq 1$ the *unit n ball* B_n is defined by

$$B_n = \{\mathbf{x} \in \mathbb{R}^n \mid \|\mathbf{x}\| \leq 1\} \qquad (A1.1)$$

and the *unit* $(n-1)$ *sphere* S_{n-1} by

$$S_{n-1}=\{\mathbf{x}\in\mathbb{R}^n|\ \|\mathbf{x}\|=1\} \qquad (A1.2)$$

so that S_{n-1} is the boundary of B_n. For $n=1$, hence $n-1=0$, B_1 is the closed interval

$$B_1=[-1,+1] \qquad (A1.3)$$

and S_0, its boundary, is disconnected and consists of the two end-points

$$S_0=\{-1,+1\}. \qquad (A1.4)$$

This degenerate case is much less pathological than might be expected and various attributes of S_{n-1} defined for general n [*e.g.* the surface area Ω_n of S_{n-1}, (*A*4.8)] still give correct values for $n-1=0$ (*e.g.* $\Omega_1=2$ for a two-point space).

The *positive* (*hyper*)*octant* O_n^+ is defined as that subset of $\mathbb{R}^n$ consisting of points whose coordinates are all non-negative. The *positive unit* (*hyper*)*octant* S_{n-1}^+ is defined as the intersection of O_n^+ and S_{n-1}, *i.e.* as that subset of S_{n-1} consisting of points whose coordinates are all non-negative:

$$S_{n-1}^+=\{\mathbf{x}\in\mathbb{R}^n|x_1\geq 0, x_2\geq 0,\ldots,x_n\geq 0, \|\mathbf{x}\|=1\}. \qquad (A1.5)$$

For $n=1$ we obviously have $S_0^+=\{+1\}$. The surface area of S_{n-1}^+ is $\Omega_n/2^n$ [see (*A*4.8)], an expression which is still correct for $n=1$. The moments of S_{n-1}^+, *i.e.* the integrals over S_{n-1}^+ of monomial functions of the coordinates, are evaluated in § *A*4.5, (*A*4.10), in terms of the generalized beta integrals (*A*4.7) defined and evaluated in § *A*4.3.

A ball (or sphere or positive octant) of radius R is the set of points of the form $R\mathbf{x}$ where $\mathbf{x}$ belongs to a unit ball (or unit sphere or unit positive octant).

*A*1.2. *Spherical polar coordinates*: *low-dimensional examples.* Insight may be gained into the process of parametrizing the points of S_{n-1} by re-examining the definition of the familiar polar coordinate systems from a somewhat unusual viewpoint.

For $n=1$ we may write

$$x=R\cos\omega, \qquad \omega=0 \text{ or } \pi, \qquad (A1.6)$$

where $R=|\mathbf{x}|$ is the radius of a zero-dimensional sphere $\{-R,+R\}$ and ω is a 'zero-dimensional phase', *i.e.* essentially a sign. Both R and ω are uniquely defined, except for $x=0$.

For $n=2$ the usual polar coordinates system on the circle S_1 is defined by

$$\begin{aligned} x_1&=R\cos\varphi \\ x_2&=R\sin\varphi \end{aligned} \qquad 0\leq\varphi<2\pi \qquad (A1.7a)$$

and may be redefined as follows:

$$\begin{aligned} R_1&=R\cos\psi \\ R_2&=R\sin\psi \end{aligned} \qquad 0\leq\psi<\pi/2 \qquad (A1.7b)$$

together with

$$\begin{aligned} x_1&=R_1\cos\omega_1 \qquad &\omega_1=0 \text{ or } \pi \\ x_2&=R_2\cos\omega_2 \qquad &\omega_2=0 \text{ or } \pi. \end{aligned} \qquad (A1.7c)$$

Here R_1 and R_2 are obtained by splitting the radius R of the one-dimensional sphere S_1 by means of the 'splitting angle' ψ; they are then treated as the partial radii of two zero-dimensional spheres and are assigned the zero-dimensional phases ω_1 and ω_2. This parametrization is unique except for $x_1=0$, in which case ψ may be taken as $+\pi/2$ or $-\pi/2$.

For $n=3$ the usual spherical polar coordinate system on S_2

$$\begin{aligned} x_1&=R\sin\theta\cos\varphi \\ x_2&=R\sin\theta\sin\varphi \\ x_3&=R\cos\theta \end{aligned} \qquad \begin{aligned} 0\leq\theta<\pi \\ 0\leq\varphi<2\pi \end{aligned} \qquad (A1.8a)$$

may similarly be redefined in terms of splitting angles and zero-dimensional phases as follows:

$$\begin{aligned} R_3&=R\cos\psi_2 \\ R'&=R\sin\psi_2 \qquad & 0\leq\psi_2<\pi/2 \\ R_1&=R'\cos\psi_1 \qquad & 0\leq\psi_1<\pi/2 \\ R_2&=R'\sin\psi_1 \end{aligned} \qquad (A1.8b)$$

together with

$$\begin{aligned} x_1&=R_1\cos\omega_1 \qquad &\omega_1=0 \text{ or } \pi \\ x_2&=R_2\cos\omega_2 \qquad &\omega_2=0 \text{ or } \pi \\ x_3&=R_3\cos\omega_3 \qquad &\omega_3=0 \text{ or } \pi. \end{aligned} \qquad (A1.8c)$$

The pattern displayed by these examples will now be abstracted into a form suitable for generalization.

*A*1.3. *Spherical polar coordinates*: *binary tree representation.* Two distinct operations are seen to be involved in a general coordinate parametrization of spheres:

(*a*) the use of splitting angles, ranging from 0 to $\pi/2$, to reduce the parametrization of S_{n-1} to that of spheres of smaller dimension, thus giving a recursive 'descent' solution to the problem;

(*b*) the incorporation of the signs (zero-dimensional angles) of the terminal stages of the recursion into an extension of the range of the last splitting angle used.

A natural representation of this succession of splittings is afforded by a *binary tree* defined according to the following rules (see Fig. 1):

(1) To each node ν of the tree is associated
a dimension $n(\nu)$;
the radius $R(\nu)$ of a sphere $S_{n(\nu)-1}$;
a splitting angle $\psi(\nu)$ if $n(\nu)>1$.

(2) The root node of the tree has dimension $n(\nu)=n$ and radius R.

(3) Each node ν with $1<n(\nu)<n$, called an intermediate node, has two successors, a left successor ν_L

and a right successor ν_R, such that

$$n(\nu_L)+n(\nu_R)=n(\nu);$$

$$R(\nu_L)=R(\nu)\cos\psi(\nu);$$

$$R(\nu_R)=R(\nu)\sin\psi(\nu).$$

(4) Nodes ν with $n(\nu)=1$, called end nodes, have no successors. Each end node is labelled by the index j of the Cartesian coordinate x_j defined by the successive splittings leading from the root node to that node.

(5) The range of the splitting angle $\psi(\nu)$ associated with a node ν is defined as follows:

if neither ν_L nor ν_R is an end node,

$$0\leq\psi(\nu)<\pi/2$$

so that $R(\nu_L)$ and $R(\nu_R)$ are non-negative;

if ν_L only is an end node,

$$0\leq\psi(\nu)<\pi$$

so that coordinate $j(\nu_L)$ is unrestricted but $R(\nu_R)$ is non-negative;

if ν_R only is an end node,

$$-\pi/2\leq\psi(\nu)<\pi/2$$

so that coordinate $j(\nu_R)$ is unrestricted but $R(\nu_L)$ is non-negative;

if both ν_L and ν_R are end nodes,

$$0\leq\psi(\nu)<2\pi$$

so that both coordinates are unrestricted.

Extending in this way the range of those splitting angles leading to end nodes is a convenient way of incorporating the signs associated with the zero-dimensional phases ω used in the examples of § *A*1.2. Occasionally, however, it may be preferable to keep all splitting angles between 0 and $\pi/2$, thus parametrizing the positive octant S^+_{n-1}, and to retain the zero-dimensional angles $\omega_1,\ldots,\omega_n$ explicitly as discrete parameters.

By an elementary property of binary trees [see *e.g.* Standish (1980), pp. 53-54], there are always $n-1$ intermediate nodes (including the root node) for n end nodes; hence there are $n-1$ splitting angles in any parametrization of S_{n-1} by this method.

The examples of § *A*1.2 are then represented by the binary trees shown in Fig. 2.

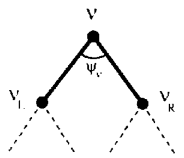


Fig. 1. The basic building block of the binary-tree representation of an n-dimensional spherical polar coordinate system consists of a node ν, whose left successor ν_L and right successor ν_R are defined by means of a splitting angle ψ_ν.

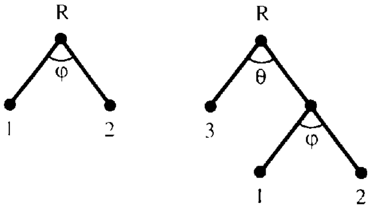
*A*1.4. *Polyspherical coordinates.* The graphical representation introduced above makes it clear that for $n\geq 4$ there are several possible polar coordinate systems, even if different ways of labelling the end nodes are considered as equivalent. This is illustrated by Fig. 3.

For $n>4$ the diversity is very great. For instance, the tree in Fig. 4 defines a parametrization of $\mathbb{R}^7$ by

$$\begin{aligned}
x_1&=R\sin\psi_1\sin\psi_3\cos\psi_5\cos\psi_6\\
x_2&=R\sin\psi_1\sin\psi_3\cos\psi_5\sin\psi_6\\
x_3&=R\sin\psi_1\sin\psi_3\sin\psi_5\\
x_4&=R\cos\psi_1\sin\psi_2\cos\psi_4\\
x_5&=R\cos\psi_1\sin\psi_2\sin\psi_4\\
x_6&=R\cos\psi_1\cos\psi_2\\
x_7&=R\sin\psi_1\cos\psi_3.
\end{aligned}\qquad (A1.9)$$

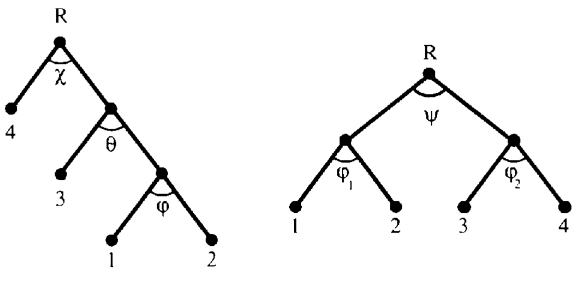
Such polyspherical coordinate systems are considered by Vilenkin (1968, pp. 495-497), who uses a general tree rather than a binary tree. This results in a complicated labelling scheme, less intelligible than the present one.

*A*1.5. *Zonal coordinates.* The method used so far is based on successive splittings of an initial radius, each splitting being defined by an angle between 0 and $\pi/2$, *i.e.* by a point of S^+_1.



(*a*) (*b*)

Fig. 2. Binary-tree representation of the usual spherical polar coordinate systems (*a*) for $n=2$ and (*b*) for $n=3$.



(*a*) (*b*)

Fig. 3. Binary-tree representations of two distinct systems of polyspherical coordinates in $n=4$ dimensions: (*a*) generalized polar coordinates, (*b*) bispherical coordinates.

Instead we may split a radius R simultaneously into m partial radii (with $m > 2$) and represent this splitting by a point $\xi \in S^+_{m-1}$ such that the m partial radii are $R\xi_1, R\xi_2, \ldots, R\xi_m$. This has the advantage of preserving a symmetry among the ξ's which would be broken if they were handled through an explicit parametrization of the splitting of hyperoctant S^+_{m-1} in terms of polar angles. This idea, introduced by Kampé de Fériet in the special case $n = m+2$ [see Appell & Kampé de Fériet (1926), p. 210], may be used recursively as was done above for $m = 2$.

A graphical representation by means of a tree is still possible (Fig. 5): a node ν to which this procedure is applied has m successors $\nu^{(1)}, \nu^{(2)}, \ldots, \nu^{(m)}$, each partial radius $R\xi_k$ belongs to a sphere $S_{n(\nu^{(k)})-1}$, and the conservation of dimension at each node reads

$$\sum_{k=1}^{m} n(\nu^{(k)}) = n(\nu).$$

The total number of angles required remains the same since

$$(m-1) + \sum_{k=1}^{m} [n(\nu^{(k)}) - 1] = n - 1.$$

As before, the zero-dimensional phases associated with the end nodes may optionally be represented by a suitable extension of the last splitting hyperoctant used.

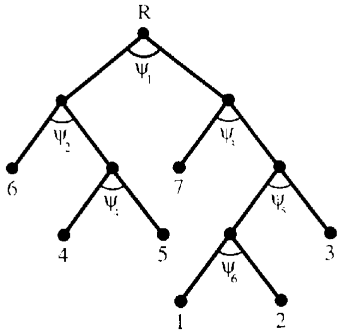


Fig. 4. A polyspherical coordinate system in $n = 7$ dimensions involving a polar radius R and six splitting angles $\psi_1, \ldots, \psi_6$.

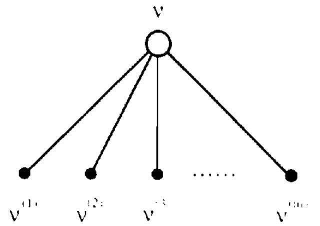


Fig. 5. The basic building block of the tree representation of an n-dimensional zonal coordinate system consists of a node ν, whose m successors $\nu^{(1)}, \nu^{(2)}, \ldots, \nu^{(m)}$ are defined by means of a point ξ belonging to the positive unit hyperoctant S^+_{m-1} rather than by $m-1$ splitting angles.

*A*1.6. *Integration over hyperspheres.* The integration of functions over S_0 and S_1 is very simple:

$$\int_{S_0} f(R\mathbf{x})\,\mathrm{d}S_0 = f(-R) + f(+R) \qquad (A1.10)$$

$$\begin{aligned}\int_{S_1} f(R\mathbf{x})R\,\mathrm{d}S_1 &= R\int_0^{2\pi} f(R\cos\varphi, R\sin\varphi)\,\mathrm{d}\varphi \\ &= R\int_0^{\pi/2}\left[\int_{S_0} f(R\cos\psi\mathbf{x}_L)\,\mathrm{d}S_0\right] \\ &\quad\times\left[\int_{S_0} f(R\sin\psi\mathbf{x}_R)\,\mathrm{d}S_0\right]\mathrm{d}\psi.\end{aligned} \qquad (A1.11)$$

From this starting point we may now define integration on spheres in any polyspherical coordinate system by induction, with the help of the binary-tree representation of that system. Reading the tree backwards from its end nodes, it suffices to specify an integral on $S_{n(\nu)-1}$ in terms of integrals over $S_{n(\nu_L)-1}$ and $S_{n(\nu_R)-1}$. At this point the burden of notation will be relieved by writing n, n_L, n_R for $n(\nu), n(\nu_L), n(\nu_R)$; R for $R(\nu)$; $\mathbf{x}, \mathbf{x}_L$ and $\mathbf{x}_R$ for $\mathbf{x}_\nu, \mathbf{x}_{\nu_L}$ and $\mathbf{x}_{\nu_R}$; and ψ for $\psi(\nu)$. The desired relation may then be written compactly as

$$\begin{aligned}&\int_{S_{n-1}} f(R\mathbf{x})R^{n-1}\,\mathrm{d}S_{n-1} \\ &= R\int_0^{\pi/2}\left[\int_{S_{n_L-1}} f(R\cos\psi\mathbf{x}_L)R^{n_L-1}\,\mathrm{d}S_{n_L-1}\right] \\ &\quad\times\left[\int_{S_{n_R-1}} f(R\sin\psi\,\mathbf{x}_R)R^{n_R-1}\,\mathrm{d}S_{n_R-1}\right] \\ &\quad\times\cos^{n_L-1}\psi\,\sin^{n_R-1}\psi\,\mathrm{d}\psi.\end{aligned} \qquad (A1.12)$$

In particular, for a spherical polar coordinate system on S_{n-1} and f depending only on the first splitting angle, say θ, we have $n(\nu_L) = 1$ and hence:

$$\int_{S_{n-1}} f(R\mathbf{x})\,\mathrm{d}S_{n-1} = \Omega_{n-1}\int_0^{\pi} f(R, \theta)\sin^{n-2}\theta\,\mathrm{d}\theta. \qquad (A1.13)$$

For a splitting over S^+_{m-1} in a system of zonal coordinates, the corresponding induction formula is easily derived. Abbreviating $n(\nu^{(k)})$ to $n^{(k)}$, we have:

$$\begin{aligned}&\int_{S_{n-1}} f(R\mathbf{x})R^{n-1}\,\mathrm{d}S_{n-1} \\ &= R^{m-1}\int_{S^+_{m-1}}\left[\prod_{k=1}^{m}\int_{S_{n^{(k)}-1}} f(R\xi_k\mathbf{x}^{(k)})R^{n^{(k)}-1}\,\mathrm{d}S_{n^{(k)}-1}\right] \\ &\quad\times\left(\prod_{k=1}^{m}\xi_k^{n^{(k)}-1}\right)\mathrm{d}S_{m-1}\end{aligned} \qquad (A1.14)$$

which obviously generalizes the previous one for $m = 2$.

In these two relations, integration is only over the totally positive hyperoctant, so that the integrations over 0-dimensional phases must be performed, as in (*A*1.11).

*A*2. *Group actions and related notions*

The books by Burnside (1911), Carmichael (1937), Hall (1959), Scott (1964) and Dixon (1973) are recommended as reference works on group theory.

*A*2.1. *Action of a group on a set.* Let G be a group with identity element e and let X be a set. An action of G on X is a mapping from $G\times X$ to X with the property that, if gx denotes the image of (g, x), then

$$\text{(i)}\ (g_1g_2)x=g_1(g_2x)\quad \text{for all } g_1, g_2\in G \text{ and all } x\in X \qquad (A2.1a)$$

$$\text{(ii)}\ ex=x \quad \text{for all } x\in X. \qquad (A2.1b)$$

An element g of G thus induces a mapping T_g of X into itself defined by $T_g(x)=gx$, with the 'representation property':

$$\text{(iii)}\ T_{g_1g_2}=T_{g_1}T_{g_2} \quad \text{for all } g_1, g_2\in G. \qquad (A2.1c)$$

Since G is a group, every g has an inverse g^{-1}; hence every mapping T_g has an inverse $T_{g^{-1}}$, so that each T_g is a permutation of X.

*A*2.2. *Orbits and isotropy subgroups.* Let x be a fixed element of the set X on which G acts. Two fundamental entities are associated with x:

(1) the subset of G consisting of all g such that $gx=x$ is a subgroup of G, called the *isotropy subgroup* of x and denoted G_x;

(2) the subset of X consisting of all elements gx with g running through G is called the *orbit* of x under G and is denoted Gx.

Through these definitions, the action of G on X can be related to the internal structure of G, as follows. Let G/G_x denote the collection of distinct left cosets of G_x in G, *i.e.* of distinct subsets of G of the form gG_x. Let $|G|$, $|G_x|$, $|Gx|$ and $|G/G_x|$ denote the numbers of elements in the corresponding sets. The number $|G/G_x|$ of distinct cosets of G_x in G is also denoted $[G:G_x]$ and is called the *index* of G_x in G; by Lagrange's theorem

$$[G:G_x]=|G/G_x|=|G|/|G_x|. \qquad (A2.2)$$

Now if g_1 and g_2 are in the same coset of G_x, then $g_2=g_1g'$ with $g'\in G_x$ and hence $g_1x=g_2x$; the converse is obviously true. Therefore, the mapping $gG_x\rightarrow gx$ from cosets to orbit elements establishes a one-to-one correspondence between the distinct left cosets of G_x in G and the elements of the orbit of x under G. It follows that the number of distinct elements in the orbit of x is equal to the index of G_x in G:

$$|Gx|=[G:G_x]=|G|/|G_x| \qquad (A2.3)$$

and that the elements of the orbit Gx of x may be listed without repetition by labelling them by the cosets of G_x in G:

$$Gx=\{\gamma x|\gamma\in G/G_x\}. \qquad (A2.4)$$

*A*2.3. *Fundamental domain and orbit decomposition.* The group properties of G imply that two orbits under G are either disjoint or equal. The set X may thus be written as the disjoint union

$$X=\bigcup_{i\in I} Gx_i \qquad (A2.5)$$

where the x_i are elements of distinct orbits and I is an indexing set labelling them. The subset $D=\{x_i\}_{i\in I}$ is said to constitute a fundamental domain (mathematical terminology) or an asymmetric unit (crystallographic terminology) for the action of G on X: it contains one representative x_i of each distinct orbit. Clearly, other fundamental domains may be obtained by choosing different representatives for these orbits.

If X is finite and if f is an arbitrary complex-valued function over X, the 'integral' of f over X may be written as a sum of integrals over the distinct orbits, yielding the orbit decomposition formula:

$$\sum_{x\in X} f(x)=\sum_{i\in I}\left[\sum_{y_i\in Gx_i} f(y_i)\right] \qquad (A2.6a)$$

$$=\sum_{i\in I}\left[\sum_{\gamma_i\in G/G_{x_i}} f(\gamma_i x_i)\right] \qquad (A2.6b)$$

$$=\sum_{i\in I}|G_{x_i}|^{-1}\left[\sum_{g_i\in G} f(g_i x_i)\right]. \qquad (A2.6c)$$

*A*2.4. *Induced action on functions.* For every action T_g of G in X, there is an associated action $T_g^{\#}$ of G on the linear space $L(X)$ of complex-valued functions over X, defined by 'change of variable':

$$[T_g^{\#}f](x)=f[(T_g)^{-1}x]=f(g^{-1}x). \qquad (A2.7)$$

Indeed for any g_1, g_2 in G,

$$\begin{aligned}\{T_{g_1}^{\#}[T_{g_2}^{\#}f]\}(x)&=[T_{g_2}^{\#}f][(T_{g_1})^{-1}x]\\&=f[T_{g_2}^{-1}T_{g_1}^{-1}x]\\&=f[(T_{g_1}T_{g_2})^{-1}x];\end{aligned}$$

since $T_{g_1}T_{g_2}=T_{g_1g_2}$, it follows that

$$T_{g_1}^{\#}T_{g_2}^{\#}=T_{g_1g_2}^{\#}. \qquad (A2.8)$$

The linear representation operators $T_g^{\#}$ on $L(X)$ provide the most natural instrument for stating and exploiting symmetry properties which a function may possess with respect to the action of G. Thus a function $f\in L(X)$ will be called G-invariant if $f(gx)=f(x)$ for all $g\in G$ and all $x\in X$. The G-invariance of f may be written

$$T_g^{\#}f=f \quad \text{for all } g\in G. \qquad (A2.9)$$

A2.5. Crystallographic group action in real space. The action of a crystallographic group Γ with point group G on a crystal with period lattice Λ may be written in terms of fractional coordinates $\mathbf{x}$ in the unit cube $[0, 1]^3$ as

$$(g, \mathbf{x}) \to S_g(\mathbf{x}) = \mathbf{R}_g\mathbf{x} + \mathbf{t}_g (\mathrm{mod}\ \Lambda) \quad (A2.10)$$

with

$$S_{g_1g_2} = S_{g_1}S_{g_2}. \quad (A2.11)$$

The notions of orbit, isotropy subgroup and fundamental domain (or asymmetric unit) for the action of G on $\mathbb{R}^3/\mathbb{Z}^3$ are inherited directly from the general setting presented above. Points $\mathbf{x}$ for which $G_\mathbf{x} \neq \{e\}$ are called *special positions* and the various types of isotropy subgroups which may be encountered in crystallographic groups have been labelled by means of Wyckoff symbols. The representation operators $S_g^{\#}$ in $L([0, 1]^3)$ have the form

$$[S_g^{\#}f](\mathbf{x}) = f[S_g^{-1}(\mathbf{x})] = f[\mathbf{R}_g^{-1}(\mathbf{x} - \mathbf{t}_g)]. \quad (A2.12)$$

The operators $R_g^{\#}$ associated with the purely rotational part of each transformation S_g will also be used.

A2.6. Crystallographic group action in reciprocal space. The representation $g \to S_g^{\#}$ of G given by its action on electron density distributions can be transposed by Fourier transformation into an action S_g^* of G on $L(\mathbb{Z}^3)$, *i.e.* on families of triply indexed Fourier coefficients' given by

$$(S_g^*F)(\mathbf{h}) = \exp(2\pi i\mathbf{h} \, . \, \mathbf{t}_g)F(\mathbf{R}_g^T\mathbf{h}) \quad (A2.13)$$

which is conjugate to the action $S_g^{\#}$ in the sense that

$$\bar{\mathscr{F}}[S_g^{\#}\rho] = S_g^*\bar{\mathscr{F}}[\rho], \qquad i.e.\ S_g^* = \bar{\mathscr{F}}S_g^{\#}\mathscr{F}. \quad (A2.14)$$

The identity $S_g^{\#}\rho = \rho$ expressing the G-invariance of ρ is then equivalent to the identity $S_g^*F = F$ between its structure factors, *i.e.* (Waser, 1955*b*)

$$F(\mathbf{h}) = \exp(2\pi i\mathbf{h} \, . \, \mathbf{t}_g)F(\mathbf{R}_g^T\mathbf{h}). \quad (A2.15)$$

If G is made to act on $\mathbb{Z}^3$ *via*

$$(g, \mathbf{h}) \to (\mathbf{R}_g^T)^{-1}\mathbf{h}, \quad (A2.16)$$

the usual notions of orbit, isotropy subgroup (denoted $G_\mathbf{h}$) and fundamental domain may be attached to this action. However, the extra shift in (A2.15) introduces a more complex behaviour than mere invariance.

A reflexion $\mathbf{h}$ is called *special* if $G_\mathbf{h} \neq \{e\}$. Then for any $g \in G_\mathbf{h}$ we have $\mathbf{R}_g^T\mathbf{h} = \mathbf{h}$ and hence

$$F(\mathbf{h}) = \exp(2\pi i\mathbf{h} \, . \, \mathbf{t}_g)F(\mathbf{h}) \quad (A2.17)$$

implying that $F(\mathbf{h}) = 0$ unless $\mathbf{h} \, . \, \mathbf{t}_g \equiv 0$ (mod 1). Special reflexions $\mathbf{h}$ for which $\mathbf{h} \, . \, \mathbf{t}_g \not\equiv 0$ (mod 1) for some $g \in G_\mathbf{h}$ are thus *systematically absent.*

A reflexion $\mathbf{h}$ is called *centric* if $G\mathbf{h} = G(-\mathbf{h})$, *i.e.* if the orbit of $\mathbf{h}$ contains $-\mathbf{h}$. Then $\mathbf{R}_\gamma^T\mathbf{h} = -\mathbf{h}$ for some coset γ in $G/G_\mathbf{h}$, so that the following relation must hold:

$$|F(\mathbf{h})| \exp(i\varphi_\mathbf{h}) = \exp(2\pi i\mathbf{h} \, . \, \mathbf{t}_\gamma)|F(-\mathbf{h})| \exp(i\varphi_{-\mathbf{h}}). \quad (A2.18)$$

In the absence of dispersion, Friedel's law gives rise to the *phase restriction*:

$$\varphi_\mathbf{h} = \theta_\mathbf{h} \equiv \pi\mathbf{h} \, . \, \mathbf{t}_\gamma (\mathrm{mod}\ \pi). \quad (A2.19)$$

The value $\theta_\mathbf{h}$ of the restricted phase is easily shown to be independent of the choice of coset representative γ.

The *full orbit* of a reflexion $\mathbf{h}$ is defined as the set-theoretical union of the orbits of $\mathbf{h}$ and of $-\mathbf{h}$. It is of particular relevance to powder diffraction and the number of its elements is the *multiplicity factor* of $\mathbf{h}$, denoted here by $p_\mathbf{h}$. If $\mathbf{h}$ is acentric, the orbits of $\mathbf{h}$ and of $-\mathbf{h}$ are disjoint and hence

$$p_\mathbf{h} = 2|G\mathbf{h}| \quad (A2.20a)$$

while if $\mathbf{h}$ is centric these two orbits are the same and

$$p_\mathbf{h} = |G\mathbf{h}|. \quad (A2.20b)$$

A3. Structure-factor algebra and statistics

The purpose of this section is to present a collection of algebraic identities between trigonometric structure-factor expressions and to demonstrate their use in calculating the moments of these expressions under assumptions of random distribution of atomic positions. The primary references for this material are Bertaut (1955, 1956*a*, *b*, 1959), Bertaut & Dulac (1956) and Bertaut & Waser (1957). The generalization of Bertaut's theory to non-uniform distributions of atoms, incorporating *inter alia* non-crystallographic symmetry, is due to Bricogne (1988).

A3.1. Bertaut's linearization formula. By the orbit decomposition formula (A2.6*c*), the contribution $\Xi(\mathbf{h}, \mathbf{x})$ of a point atom of unit scattering factor placed at $\mathbf{x}$ to the structure factor at $\mathbf{h}$ may be written

$$\Xi(\mathbf{h}, \mathbf{x}) = |G_\mathbf{x}|^{-1} \sum_{g \in G} \exp[2\pi i\mathbf{h} \, . \, S_g(\mathbf{x})]. \quad (A3.1)$$

If we consider this quantity as a function of $\mathbf{x}$ indexed by $\mathbf{h}$, the family of functions defined by $\Xi_\mathbf{h}(\mathbf{x}) = \Xi(\mathbf{h}, \mathbf{x})$ constitutes an *algebra* in the sense that products of such functions may be rewritten as linear combinations of other functions in that family, generalizing well known trigonometric identities such as $\cos a \cos b = \frac{1}{2}[\cos(a + b) + \cos(a - b)]$. This relation is given by Bertaut's linearization formula:

$$\Xi(\mathbf{h}, \mathbf{x}) \times \Xi(\mathbf{k}, \mathbf{x})$$
$$= |G_\mathbf{x}|^{-1} \sum_{g \in G} \exp(2\pi i\mathbf{k} \, . \, \mathbf{t}_g)\Xi(\mathbf{h} + \mathbf{R}_g^T\mathbf{k}, \mathbf{x}) \quad (A3.2)$$

[see § A2 of Bricogne (1988) for a proof].

*A*3.2. *Calculation of moments.* Consider the position **x** of a generic atom as a random vector distributed in the asymmetric unit D of the crystal with probability density $q(\mathbf{x})$. The trigonometric structure-factor expressions $\Xi_{\mathbf{h}}(\mathbf{x})$ then become random variables with complex or real values and the calculation of their moments is fundamental to the statistical approach to the phase problem (Hauptman & Karle, 1953; Bertaut, 1955; Klug, 1958). For our purposes, only moments of order 1 and 2 will be needed.

Let $M_{\mathbf{h}}$ [or $M(\mathbf{h})$] denote the Fourier coefficient with indices **h** of the function obtained by symmetry expanding $q(\mathbf{x})/|G_{\mathbf{x}}|$ to the whole unit cell and renormalizing it. Then the first-order moment of $\Xi_{\mathbf{h}}$ is

$$\langle \Xi_{\mathbf{h}}\rangle = |G| M_{\mathbf{h}} \qquad (A3.3)$$

while the second-order moments can be obtained, by linearizing according to (*A*3.2), as

$$\langle \Xi_{\mathbf{h}}\Xi_{\pm\mathbf{k}}\rangle = |G| \sum_{g\in G} \exp(\pm 2\pi i\mathbf{k}\,.\,\mathbf{t}_g) M(\mathbf{h}\pm\mathbf{R}_g^T\mathbf{k}). \qquad (A3.4)$$

At this point it becomes desirable to take into account the centric character of the reflexions. In the spirit of the conventions of § 1.0 and 1.1 [see also equation (*A*2.19)], define

$$\alpha_{\mathbf{h}} = \operatorname{Re}\Xi_{\mathbf{h}},\ \beta_{\mathbf{h}} = \operatorname{Im}\Xi_{\mathbf{h}} \quad \text{for } \mathbf{h} \text{ acentric} \qquad (A3.5a)$$

$$\gamma_{\mathbf{h}} = \operatorname{Re}[\exp(-i\theta_{\mathbf{h}})\Xi_{\mathbf{h}}] \quad \text{for } \mathbf{h} \text{ centric}. \qquad (A3.5b)$$

Elementary calculations according to a general procedure described in §§ *A*1 and *A*2 of Bricogne (1988) then yields the following expressions for the second-order moments:

$$\langle\alpha_{\mathbf{h}}\alpha_{\mathbf{k}}\rangle = \tfrac{1}{2}[\operatorname{Re}\langle\Xi_{\mathbf{h}}\Xi_{+\mathbf{k}}\rangle + \operatorname{Re}\langle\Xi_{\mathbf{h}}\Xi_{-\mathbf{k}}\rangle] \qquad (A3.6a)$$

$$\langle\alpha_{\mathbf{h}}\beta_{\mathbf{k}}\rangle = \tfrac{1}{2}[\operatorname{Im}\langle\Xi_{\mathbf{h}}\Xi_{+\mathbf{k}}\rangle - \operatorname{Im}\langle\Xi_{\mathbf{h}}\Xi_{-\mathbf{k}}\rangle] \qquad (A3.6b)$$

$$\langle\beta_{\mathbf{h}}\alpha_{\mathbf{k}}\rangle = \tfrac{1}{2}[\operatorname{Im}\langle\Xi_{\mathbf{h}}\Xi_{+\mathbf{k}}\rangle + \operatorname{Im}\langle\Xi_{\mathbf{h}}\Xi_{-\mathbf{k}}\rangle] \qquad (A3.6c)$$

$$\langle\beta_{\mathbf{h}}\beta_{\mathbf{k}}\rangle = \tfrac{1}{2}[\operatorname{Re}\langle\Xi_{\mathbf{h}}\Xi_{-\mathbf{k}}\rangle - \operatorname{Re}\langle\Xi_{\mathbf{h}}\Xi_{+\mathbf{k}}\rangle] \qquad (A3.6d)$$

$$\langle\alpha_{\mathbf{h}}\gamma_{\mathbf{k}}\rangle = \tfrac{1}{2}\operatorname{Re}[\exp(-i\theta_{\mathbf{h}})\langle\Xi_{\mathbf{h}}\Xi_{+\mathbf{k}}\rangle + \exp(+i\theta_{\mathbf{h}})\langle\Xi_{\mathbf{h}}\Xi_{-\mathbf{k}}\rangle] \qquad (A3.7a)$$

$$\langle\beta_{\mathbf{h}}\gamma_{\mathbf{k}}\rangle = \tfrac{1}{2}\operatorname{Im}[\exp(-i\theta_{\mathbf{h}})\langle\Xi_{\mathbf{h}}\Xi_{+\mathbf{k}}\rangle + \exp(+i\theta_{\mathbf{h}})\langle\Xi_{\mathbf{h}}\Xi_{-\mathbf{k}}\rangle] \qquad (A3.7b)$$

$$\langle\gamma_{\mathbf{h}}\gamma_{\mathbf{k}}\rangle = \tfrac{1}{2}\operatorname{Re}\{\exp[-i(\theta_{\mathbf{h}}+\theta_{\mathbf{k}})]\langle\Xi_{\mathbf{h}}\Xi_{+\mathbf{k}}\rangle + \exp[-i(\theta_{\mathbf{h}}-\theta_{\mathbf{k}})]\langle\Xi_{\mathbf{h}}\Xi_{-\mathbf{k}}\rangle\}. \qquad (A3.8)$$

These formulae, considered together with (*A*3.3) and (*A*3.4), completely specify the elements of the vector of first moments and of the covariance matrix of the trigonometric structure-factor expressions under the assumption of an arbitrary distribution $q(\mathbf{x})$ of random atoms.

*A*3.3. *Wilson statistics and statistical weight.* Let us now assume that the distribution of random atoms in the asymmetric unit is uniform, so that $M_{\mathbf{0}} = 1$ and $M_{\mathbf{h}} = 0$ for $\mathbf{h} \neq \mathbf{0}$. The general moment expressions in § *A*3.2 simplify to

$$\langle\alpha_{\mathbf{h}}\rangle = \langle\beta_{\mathbf{h}}\rangle = 0 \qquad (A3.9a)$$

$$\langle\alpha_{\mathbf{h}}\beta_{\mathbf{k}}\rangle = 0 \quad \text{for all } \mathbf{h},\mathbf{k} \qquad (A3.9b)$$

$$\langle\alpha_{\mathbf{h}}\alpha_{\mathbf{k}}\rangle = \langle\beta_{\mathbf{h}}\beta_{\mathbf{k}}\rangle = 0 \quad \text{for } \mathbf{h}\neq\mathbf{k} \qquad (A3.9c)$$

$$\langle[\alpha_{\mathbf{h}}]^2\rangle = \langle[\beta_{\mathbf{h}}]^2\rangle = \tfrac{1}{2}|G_{\mathbf{h}}|\,|G| \qquad (A3.9d)$$

and that

$$\langle\gamma_{\mathbf{h}}\rangle = 0 \qquad (A3.10a)$$

$$\langle\gamma_{\mathbf{h}}\gamma_{\mathbf{k}}\rangle = 0 \quad \text{for } \mathbf{h}\neq\mathbf{k} \qquad (A3.10b)$$

$$\langle[\gamma_{\mathbf{h}}]^2\rangle = \tfrac{1}{2}[|G_{\mathbf{h}}| + |G_{\mathbf{h}}|]|G| = |G_{\mathbf{h}}|\,|G|. \qquad (A3.10c)$$

Let $A_{\mathbf{h}}$, $B_{\mathbf{h}}$ and $C_{\mathbf{h}}$ be as defined in § 1.0. For a crystal structure consisting of uniformly distributed random atoms away from special positions, it follows from (3.9*a*, *b*, *c*, *d*) that

$$\langle[A_{\mathbf{h}}]^2\rangle = \langle[B_{\mathbf{h}}]^2\rangle = \tfrac{1}{2}|G_{\mathbf{h}}|\sigma_2(\mathbf{h}) \qquad (A3.11a)$$

and from (3.10*a*, *b*, *c*) that

$$\langle[C_{\mathbf{h}}]^2\rangle = |G_{\mathbf{h}}|\sigma_2(\mathbf{h}) \qquad (A3.11b)$$

with

$$\sigma_2(\mathbf{h}) = |G| \sum_{\text{asymmetric unit}} f(\mathbf{h})^2 = \sum_{\text{unit cell}} f(\mathbf{h})^2 \qquad (A3.12)$$

where the f's are the scattering factors. Therefore, whether **h** is acentric or centric, we have

$$\langle|F_{\mathbf{h}}|^2\rangle = |G_{\mathbf{h}}|\sigma_2. \qquad (A3.13a)$$

This expression may be compared to that used in the calculation of the normalized structure factors $E_{\mathbf{h}}$ from the ordinary structure factors $F_{\mathbf{h}}$ (assumed to have been placed on an absolute scale and corrected for thermal motion), which reads:

$$\langle|F_{\mathbf{h}}|^2\rangle = \varepsilon_{\mathbf{h}}\sigma_2, \qquad (A3.13b)$$

the quantity $\varepsilon_{\mathbf{h}}$ being called the statistical weight of reflexion **h**. It follows that

$$\varepsilon_{\mathbf{h}} = |G_{\mathbf{h}}|. \qquad (A3.14)$$

This relation was obtained by Stewart & Karle (1976) on the basis of a mostly verbal argument; the derivations above give a formal proof of it (see also Iwasaki & Ito, 1977; Stewart, Karle, Iwasaki & Ito, 1977).

*A*4. *Eulerian functions and related integrals*

Euler's gamma and beta functions are ubiquitous in classical analysis [Whittaker & Watson (1927), ch. 12; Rainville (1960), ch. 1]. Their best known properties are that they interpolate the factorial and the binomial coefficients respectively, but they occur in the present work through their rôle in the calculation of integrals of monomials over hyperspheres. This section collects those properties of Eulerian functions and of their generalizations which are directly called upon in obtaining closed expressions for probability distributions in the main body of the paper. The best reference for this selection of material is chapter 8 of Schwartz (1965).

*A*4.1. *The gamma function.* The gamma function has the well known integral representation

$$\Gamma(z)=\int_0^\infty e^{-t}t^{z-1}\,\mathrm{d}t. \qquad (A4.1a)$$

Alternatively,

$$\Gamma(z)=2\int_0^\infty e^{-t^2}t^{2z-1}\,\mathrm{d}t. \qquad (A4.1b)$$

The latter expression makes plain the relevance of Γ to the calculation of Gaussian integrals. Elementary derivations show that

$$\Gamma(z+1)=z\Gamma(z) \qquad (A4.2a)$$

$$\Gamma(n+1)=n! \quad \text{for } n\geq 0. \qquad (A4.2b)$$

*A*4.2. *The beta integral.* Products of Γ factors in the form (*A*4.1*b*) can be rearranged by going over to polar coordinates, giving rise to identities which play a fundamental rôle in the evaluation of many integrals in §§ 2 and 3. The simplest such instance occurs in the definition of the beta function:

$$\begin{aligned}\Gamma(p)\Gamma(q)&=4\int_0^\infty\int_0^\infty \exp\left[-(u^2+v^2)\right]u^{2p-1}v^{2q-1}\,\mathrm{d}u\,\mathrm{d}v \\ &\qquad\qquad \text{by } (A4.1b)\\ &=4\int_0^\infty\int_0^{\pi/2}\exp(-r^2)r^{2(p+q)-1}\\ &\qquad\times\cos^{2p-1}\theta\sin^{2q-1}\theta\,\mathrm{d}r\,\mathrm{d}\theta\\ &=\left(2\int_0^\infty\exp(-r^2)r^{2(p+q)-1}\,\mathrm{d}r\right)\\ &\qquad\times\left(2\int_0^{\pi/2}\cos^{2p-1}\theta\sin^{2q-1}\theta\,\mathrm{d}\theta\right).\end{aligned}$$

Hence

$$\begin{aligned}B(p,q)&=\Gamma(p)\Gamma(q)/\Gamma(p+q)\\ &=2\int_0^{\pi/2}\cos^{2p-1}\theta\sin^{2q-1}\theta\,\mathrm{d}\theta. \qquad (A4.3)\end{aligned}$$

In particular, for $p=q=\frac{1}{2}$,

$$[\Gamma(\tfrac{1}{2})]^2=B(\tfrac{1}{2},\tfrac{1}{2})=2\int_0^{\pi/2}\mathrm{d}\theta=\pi,$$

hence

$$\Gamma(\tfrac{1}{2})=\pi^{1/2}, \qquad (A4.4)$$

giving by (*A*4.1*b*) the value of the Gauss integral:

$$\int_0^\infty e^{-t^2}\,\mathrm{d}t=\tfrac{1}{2}\Gamma(\tfrac{1}{2})=\tfrac{1}{2}\pi^{1/2}. \qquad (A4.5)$$

The functional equation (*A*4.2*a*) for Γ then yields the values of Γ for half-odd-integer arguments:

$$\begin{aligned}\Gamma(n+\tfrac{1}{2})&=(n+\tfrac{1}{2})(n-\tfrac{1}{2})\dots\tfrac{1}{2}\Gamma(\tfrac{1}{2})\\ &=[1\times3\times5\times\dots\times(2n-1)/2^n]\pi^{1/2}\\ &=[(2n)!/2^{2n}n!]\pi^{1/2}. \qquad (A4.6)\end{aligned}$$

This identity is used in § *A*6.2 in the derivation of Poisson's integral.

*A*4.3. *Generalized beta integrals.* Application of the same procedure to n factors yields:

$$\Gamma(p_i)=2\int_0^\infty\exp(-p_i^2)u_i^{2p_i-1}\,\mathrm{d}u_i,$$

$$i=1,\dots,n \quad \text{by } (A4.1a)$$

$$\begin{aligned}\Gamma(p_1)\dots\Gamma(p_n)&=2^n\int_{O_n^+}\exp\left[-(p_1^2+\dots+p_n^2)\right]u_1^{2p_1-1}\\ &\qquad\times\dots\times u_n^{2p_n-1}\,\mathrm{d}u_1\dots\mathrm{d}u_n\\ &=\left(2^n\int_0^\infty\exp(-r^2)r^{2(p_1+\dots+p_n)-n}r^{n-1}\,\mathrm{d}r\right)\\ &\qquad\times\left(\int_{S_{n-1}^+}\xi_1^{2p_1-1}\dots\xi_n^{2p_n-1}\,\mathrm{d}S\right)\end{aligned}$$

by $u_i=r\xi_i$, where O_n^+ is the positive hyperoctant in $\mathbb{R}^n$ and S_{n-1}^+ is its intersection with the unit sphere S_{n-1} [see (*A*1.5) in § *A*1.1]. Hence the definition and integral representation of the generalized beta integral in n variables is

$$\begin{aligned}B(p_1,\dots,p_n)&=\Gamma(p_1)\dots\Gamma(p_n)/\Gamma(p_1+\dots+p_n)\\ &=2^{n-1}\int_{S_{n-1}^+}\xi_1^{2p_1-1}\dots\xi_n^{2p_n-1}\,\mathrm{d}S. \qquad (A4.7)\end{aligned}$$

The next two subsections describe two important consequences of this formula, which are used throughout §§ 2, 3 and 4.

*A*4.4. *Area of the unit sphere in R^n.* Let Ω_n denote the area of the unit sphere S_{n-1} in $\mathbb{R}^n$. Putting $p_1=p_2=\dots=p_n=\frac{1}{2}$,

$$B(\tfrac{1}{2},\dots,\tfrac{1}{2})=[\Gamma(1/2)]^n/\Gamma(n/2)=2^{n-1}\Omega_n/2^n=\tfrac{1}{2}\Omega_n$$

and hence

$$\Omega_n=\frac{2\pi^{n/2}}{\Gamma(n/2)}. \qquad (A4.8)$$

The first few terms are $\Omega_1=2$, $\Omega_2=2\pi$, $\Omega_3=4\pi$, $\Omega_4=2\pi^2$, $\Omega_5=8\pi^2/5$, $\Omega_6=\pi^3$. Note the relation

$$\begin{aligned}\Omega_n/\Omega_{n-1}&=\Gamma[(n-1)/2]\Gamma(\tfrac{1}{2})/\Gamma(n/2)\\&=B[(n-1)/2,\tfrac{1}{2}]\\&=\int\limits_0^\pi \sin^{n-2}\theta\,\mathrm{d}\theta, \qquad (A4.9)\end{aligned}$$

which has a simple geometric meaning in the context of integration [see (*A*1.13) in § *A*1.6].

*A*4.5. *Moments of the unit spherical hyperoctant.* Putting $p_i=(\alpha_i+1)/2$ in (*A*4.7) we get

$$\int\limits_{S^+_{n-1}} \xi_1^{\alpha_1}\ldots\xi_n^{\alpha_n}\,\mathrm{d}S = \frac{\Gamma[(\alpha_1+1)/2]\ldots\Gamma[(\alpha_n+1)/2]}{2^{n-1}\Gamma[(\alpha_1+\ldots+\alpha_n+n)/2]}. \qquad (A4.10)$$

This is a closed expression for the generic moments of the unit spherical hyperoctant. This result is fundamental in the derivation of (2.8) in § 2.2, of (3.11) in § 3.2 and of (4.7) in § 4.2.

*A*5. *Hypergeometric series*

Most of the multidimensional integrals evaluated in this paper yield results which are best expressed, manipulated and computed as hypergeometric series. Classical identities involving these series are used in some of the derivations in §§ 2 and 3. The best general references are Rainville (1960), Lebedev (1972), Magnus, Oberhettinger & Soni (1966).

*A*5.1. *The general hypergeometric series* ${}_pF_q$.

$$\begin{aligned}&{}_pF_q(\alpha_1,\alpha_2,\ldots,\alpha_p;\gamma_1,\gamma_2,\ldots,\gamma_q;z)\\&=\sum_{k=0}^{\infty}\left[\prod_{i=1}^{p}(\alpha_i)_k\Big/\prod_{j=1}^{q}(\gamma_j)_k\right](z^k/k!). \qquad (A5.1)\end{aligned}$$

The numbers $\alpha_1,\alpha_2,\ldots,\alpha_p,\gamma_1,\gamma_2,\ldots,\gamma_q$ are called the *parameters.* The *factorial function* $(\alpha)_n$, also called *Pochhammer's symbol*, is defined by

$$(\alpha)_k=\alpha(\alpha+1)(\alpha+2)\ldots(\alpha+k-1),\ k\geq 1 \qquad (A5.2a)$$

$$(\alpha)_0=1, \qquad \alpha\neq 0. \qquad (A5.2b)$$

and it is easily checked that

$$(1)_k=k! \qquad (A5.2c)$$

$$(\alpha)_k=\Gamma(\alpha+k)/\Gamma(\alpha) \quad \text{if } \alpha\neq 0,-1,-2,\ldots. \qquad (A5.2d)$$

If n is a positive integer,

$$(n)_k=(n+k-1)!/(n-1)! \qquad (A5.2e)$$

$$\begin{aligned}(-n)_k&=(-1)^k n!/(n-k)! &&\text{for } k\leq n,\\&=0 &&\text{for } k>n\end{aligned} \qquad (A5.2f)$$

so that if any numerator parameter α_i in (*A*5.1) is zero or a negative integer, the series terminates and gives rise to a polynomial. Either p or q, or both, may be zero; in that case, the absence of parameters is indicated by a dash. The simplest such series are:

$${}_0F_0(-;\,-;\,z)=e^z;$$

$${}_1F_0(a;\,-;\,z)=(1-z)^{-a};$$

$${}_0F_1(-;\,c;\,z)=\Gamma(c)z^{(1-c)/2}I_{c-1}(2z^{1/2}),$$

I being a modified Bessel function;

$${}_1F_1(a;\,c;\,z),$$

the confluent hypergeometric function (Kummer's function);

$${}_2F_1(a,b;\,c;\,z),$$

Gauss's hypergeometric function.

By 'pushing along' the factors in the Pochhammer symbols according to the identity

$$(\alpha)_{n+k}=(\alpha)_n(\alpha+n)_k \qquad (A5.3)$$

one can easily obtain the following differentiation formulae:

$$\begin{aligned}&\frac{\mathrm{d}^n}{\mathrm{d}z^n}\,{}_pF_q(\alpha_1,\ldots,\alpha_p;\gamma_1,\ldots,\gamma_q;z)\\&=\left[\prod_{i=1}^{p}(\alpha_i)_n\Big/\prod_{j=1}^{q}(\gamma_j)_n\right]{}_pF_q(\alpha_1+n,\ldots,\alpha_p+n;\\&\qquad\gamma_1+n,\ldots,\gamma_q+n;z). \qquad (A5.4)\end{aligned}$$

There also exist $2p+q$ linearly independent *contiguous relations* between ${}_pF_q$ as written in (*A*5.1) and its contiguous functions, *i.e.* functions in which a single parameter has been incremented by ±1, where the coefficients are polynomials at most linear in z [see Rainville (1960), pp. 80-85].

A useful recursive integral representation of ${}_pF_q$ in terms of ${}_{p-1}F_{q-1}$ is given by the following identity [Rainville (1960), theorem 28, p. 85]:

$$\begin{aligned}&{}_pF_q(\alpha_1,\ldots,\alpha_p;\gamma_1,\ldots,\gamma_q;z)\\&=[B(\alpha_1,\gamma_1-\alpha_1)]^{-1}\int\limits_0^1 t^{\alpha_1-1}(1-t)^{\gamma_1-\alpha_1-1}\\&\quad\times{}_{p-1}F_{q-1}(\alpha_2,\ldots,\alpha_p;\gamma_2,\ldots,\gamma_q;zt)\,\mathrm{d}t, \qquad (A5.5)\end{aligned}$$

which is itself a special case of another relation [Rainville (1960), theorems 37 and 38, pp. 103-104]. This identity is used in deriving (2.6) in § 2.2, with $p=q=0$.

Another important identity, special instances of which are proved in Rainville (1960, pp. 125, 201), is based on the formal rearrangement of series:

$$\left(\sum_{n=0}^{\infty} v^n/n!\right)\left[\sum_{m=0}^{\infty} A_m(-uv)^m/m!\right]$$

$$= \sum_{n=0}^{\infty}\left[\sum_{k=0}^{n} A_k(-1)^k u^k/k!(n-k)!\right]v^n$$

$$= \sum_{n=0}^{\infty}\left[\sum_{k=0}^{n} (-n)_k A_k u^k/k!\right] v^n/n! \quad \text{by } (A5.2f),$$

from which it follows readily that

$$e^v\,{}_pF_q(\alpha_1,\dots,\alpha_p;\gamma_1,\dots,\gamma_q;-uv)$$

$$= \sum_{n=0}^{\infty} {}_{p+1}F_q(-n,\alpha_1,\dots,\alpha_p;\gamma_1,\dots,\gamma_q;u)\,v^n/n! \tag{A5.6a}$$

This identity is used in the form (3.10) in § 3.2 [see also (*A*5.13)].

A related identity [Magnus, Oberhettinger & Soni (1966), p. 63] is easily proved by termwise integration of the defining series:

$$\int_0^{\infty} v^{\alpha-1}e^{-v}\,{}_pF_q(\alpha_1,\alpha_2,\dots,\alpha_p;\gamma_1,\gamma_2,\dots,\gamma_q;uv)\,\mathrm{d}v$$

$$=\Gamma(\alpha)\,{}_{p+1}F_q(\alpha_1,\alpha_2,\dots,\alpha_p,\alpha;\gamma_1,\gamma_2,\dots,\gamma_q;u). \tag{A5.6b}$$

It is used in § 5.1.2 to derive the moments (5.8) of distribution (3.6*a*).

*A*5.2. *The hypergeometric series* ${}_0F_1$. It is defined by

$$ {}_0F_1(-;\gamma;z)=\sum_{k=0}^{\infty}(\gamma)_k^{-1}z^k/k! \tag{A5.7a}$$

and is closely related to Bessel functions (see § *A*6.1). It plays a fundamental rôle in § 3.1. The differentiation identity (*A*5.4) reads

$$\frac{\mathrm{d}^n}{\mathrm{d}z^n}\,{}_0F_1(-;\gamma;z)=(\gamma)_n^{-1}\,{}_0F_1(-;\gamma+n;z) \tag{A5.7b}$$

and is used to derive (4.4).

*A*5.3. *The hypergeometric series* ${}_1F_1$. Also called the *confluent hypergeometric series* (see Slater, 1960), it is defined by

$$ {}_1F_1(\alpha;\gamma;z)=\sum_{k=0}^{\infty}[(\alpha)_k/(\gamma)_k](z^k/k!). \tag{A5.8a}$$

The differentiation identity reads

$$\frac{\mathrm{d}^n}{\mathrm{d}z^n}\,{}_1F_1(\alpha;\gamma;z)=[(\alpha)_n/(\gamma)_n]\,{}_1F_1(\alpha+n;\gamma+n;z). \tag{A5.8b}$$

There are three independent contiguous relations, namely

$$(\alpha-\gamma+1)\,{}_1F_1(\alpha;\gamma;z)=\alpha\,{}_1F_1(\alpha+1;\gamma;z)-(\gamma-1)\times{}_1F_1(\alpha;\gamma-1;z) \tag{A5.9a}$$

$$\gamma(\alpha+z)\,{}_1F_1(\alpha;\gamma;z)=\alpha\gamma\,{}_1F_1(\alpha+1;\gamma;z)-(\alpha-\gamma)z\times{}_1F_1(\alpha;\gamma+1;z) \tag{A5.9b}$$

$$\gamma\,{}_1F_1(\alpha;\gamma;z)=\gamma\,{}_1F_1(\alpha-1;\gamma;z)-z\times{}_1F_1(\alpha;\gamma+1;z). \tag{A5.9c}$$

The confluent hypergeometric function has the following integral representation:

$$ {}_1F_1(\alpha;\gamma;z)=[B(\alpha,\gamma-\alpha)]^{-1}\times\int_0^1 t^{\alpha-1}(1-t)^{\gamma-\alpha-1}e^{zt}\,\mathrm{d}t \tag{A5.10}$$

which may be deduced from (*A*5.5) by recalling that the exponential is ${}_0F_0$. The change of variable $t=1-s$, or alternatively a recourse to identity (*A*5.6*a*), readily yields Kummer's identity:

$$ {}_1F_1(\alpha;\gamma;z)=e^z\,{}_1F_1(\gamma-\alpha;\gamma;-z), \tag{A5.11}$$

which is in constant use [see *e.g.* § 2.2, remark following (2.6); § 3.1, to obtain (3.7); § 3.2, to obtain (3.12*b*); § 5.1.2, to obtain (5.8)].

*A*5.4. *The associated Laguerre polynomials.* They are defined by

$$L_n^{(\alpha)}(x)=[(\alpha+1)_n/n!]\,{}_1F_1(-n;\alpha+1;x). \tag{A5.12}$$

They are used in § 5.1.2 to calculate the moments of the non-central distributions (3.6). The polynomials for $\alpha=0$ are the simple Laguerre polynomials; those for $\alpha=\pm\frac{1}{2}$ are related to the Hermite polynomials [Lebedev (1972), p. 81].

By virtue of (*A*5.6*a*) with $p=0$ and $q=1$, the $L_n^{(\alpha)}$ have the following generating function:

$$e^t\,{}_0F_1(-;\alpha+1;-xt)=\sum_{n=0}^{\infty}L_n^{(\alpha)}(x)t^n/(\alpha+1)_n \tag{A5.13}$$

[Rainville (1960), p. 201] which is used in § 3.2.

*A*5.5. *Hypergeometric series in several variables.* There exists a natural extension of the hypergeometric series (5.1) to several variables, which was first described by Appell (1882) for the case of two variables. It consists in examining the general term in the product of two functions of one variable, namely

$$\frac{\prod_{i=1}^{p}(\alpha_i)_m}{\prod_{j=1}^{q}(\gamma_j)_m}\,\frac{\prod_{k=1}^{r}(\beta_k)_n}{\prod_{l=1}^{s}(\delta_l)_n}\,\frac{x^m}{m!}\,\frac{y^n}{n!},$$

and in identifying those inequivalent ways of replacing products such as $(\alpha_i)_m(\beta_k)_n$ or $(\gamma_j)_m(\delta_l)_n$ by $(\alpha_{ik})_{m+n}$ or $(\gamma_{jl})_{m+n}$ respectively, so as to produce a genuine function of two variables x and y rather than (say) a function of $(x+y)$. In the two-variable case with $p=r=2$ and $q=s=1$ this produces four new functions. Many more possibilities exist for higher numbers of parameters and variables and the reader is referred to the books by Appell (1925) and Appell & Kampé de Fériet (1926) for further examples.

In this work we need the following function in m variables:

$$
\begin{aligned}
&{}_mF_1^{(m)}(\alpha_1,\ldots,\alpha_m;\gamma;z_1,\ldots,z_m)\\
&\quad=\sum_{p_1=0}^{\infty}\ldots\sum_{p_m=0}^{\infty}\frac{(\alpha_1)_{p_1}\ldots(\alpha_m)_{p_m}}{(\gamma)_{p_1+\ldots+p_m}}\frac{z_1^{p_1}}{p_1!}\ldots\frac{z_m^{p_m}}{p_m!}
\end{aligned}
\tag{A5.14}
$$

(the notation is non-standard) which is most closely related to the F_D functions of Lauricella (1893). It is used in §§ 2.2 and 3.2 to calculate integrals of general multivariate Gaussians on hyperspheres. A straightforward application of identities (*A*5.3) gives the differentiation formula:

$$
\begin{aligned}
&\frac{\partial^{s_1+\ldots+s_m}}{\partial z_1^{s_1}\ldots\partial z_m^{s_m}}\,{}_mF_1^{(m)}(\alpha_1,\ldots,\alpha_m;\gamma;z_1,\ldots,z_m)\\
&\quad=\frac{(\alpha_1)_{s_1}\ldots(\alpha_m)_{s_m}}{(\gamma)_{s_1+\ldots+s_m}}\,{}_mF_1^{(m)}(\alpha_1+s_1,\ldots,\alpha_m+s_m;\\
&\qquad\gamma+s_1+\ldots+s_m;z_1,\ldots,z_m)
\end{aligned}
\tag{A5.15}
$$

which allows the maximization of log-likelihoods in the unequal-variance case (§ 5.1.2).

*A*6. *Modified Bessel functions of general order*

*A*6.1. *Expression in terms of hypergeometric series.* There exist two different representations of $I_\nu(z)$ as hypergeometric series:

$$I_\nu(z)=[(\tfrac{1}{2}z)^\nu/\Gamma(\nu+1)]\,{}_0F_1[-;\nu+1;(\tfrac{1}{2}z)^2] \tag{A6.1a}$$

$$=[(\tfrac{1}{2}z)^\nu e^{-z}/\Gamma(\nu+1)]\,{}_1F_1(\nu+\tfrac{1}{2};2\nu+1;2z) \tag{A6.1b}$$

[Abramowitz & Stegun (1965), p. 378; Rainville (1960), pp. 116, 126]. The representation in terms of ${}_0F_1$ is the most useful in this work. The representation in terms of ${}_1F_1$ may be transformed by Kummer's identity (*A*5.11) to yield

$$I_\nu(z)=[(\tfrac{1}{2}z)^\nu e^{z}/\Gamma(\nu+1)]\,{}_1F_1(\nu+\tfrac{1}{2};2\nu+1;-2z), \tag{A6.1c}$$

a form which is used to obtain (3.7) in § 3.1 and is useful for obtaining asymptotic estimates.

*A*6.2. *The Poisson integral.* The classical calculation of this integral [Watson (1944), p. 24] may be cast in a slightly different form, better suited to the context of this paper, which uses evaluations of circular moments by means of the beta function and expresses the final result as a ${}_0F_1$ hypergeometric series:

$$
\begin{aligned}
&\int_0^{\pi}\exp(z\cos\theta)\sin^{2\nu}\theta\,\mathrm{d}\theta\\
&\quad=2\int_0^{\pi/2}\cosh(z\cos\theta)\sin^{2\nu}\theta\,\mathrm{d}\theta\\
&\quad=2\sum_{p=0}^{\infty}\frac{z^{2p}}{(2p)!}\int_0^{\pi/2}\cos^{2p}\theta\sin^{2\nu}\theta\,\mathrm{d}\theta\\
&\quad=2\sum_{p=0}^{\infty}\frac{z^{2p}}{(2p)!}\frac{1}{2}\frac{\Gamma(p+\frac{1}{2})\Gamma(\nu+\frac{1}{2})}{\Gamma(p+\nu+1)}
\end{aligned}
$$

by (*A*4.3)

$$=\Gamma(\nu+\tfrac{1}{2})\Gamma(\tfrac{1}{2})\sum_{p=0}^{\infty}[\Gamma(p+\nu+1)]^{-1}[(\tfrac{1}{2}z)^{2p}/p!]$$

by (*A*4.6)

$$=\Gamma(\nu+\tfrac{1}{2})\Gamma(\tfrac{1}{2})[\Gamma(\nu+1)]^{-1}\,{}_0F_1[-;\nu+1;(\tfrac{1}{2}z)^2] \tag{A6.2}$$

by (*A*5.2*d*) and (*A*5.7*a*). By means of (*A*6.1*a*) it can be written in the more usual form (3.5*a*).

*A*6.3. *Modified Bessel functions of integer order.* The ${}_0F_1$ hypergeometric series in expression (3.6) can be conveniently written in terms of modified Bessel functions of integer order when the number n of degrees of freedom is even. Only small orders are needed. For an arbitrary argument z, $I_0(z)$ and $I_1(z)$ can be calculated to eight decimal places of accuracy by means of polynomial approximations [Abramowitz & Stegun (1965), p. 378]. For small orders greater than 1, the forward recursion relations

$$I_{n+1}(z)=I_{n-1}(z)-(2n/z)I_n(z) \tag{A6.3}$$

yield results of sufficient accuracy when z is not vanishingly small. In the latter case, the power-series expansion is an efficient method of computation.

*A*6.4. *Modified Bessel functions of half-odd-integer order.* When the number n of degrees of freedom is odd, the ${}_0F_1$ hypergeometric series in (3.6) can be written in terms of modified Bessel functions of half-odd-integer order, which can themselves be expressed in terms of elementary hyperbolic functions [see *e.g.* Abramowitz & Stegun (1965), p. 443]. The first two instances of interest here are

$$I_{-1/2}(z)=(2/\pi z)^{1/2}\cosh(z) \tag{A6.4}$$

$$I_{+1/2}(z)=(2/\pi z)^{1/2}\sinh(z) \tag{A6.5}$$

which are invoked in relating (3.6*a*) to (3.6*c*) and (4.4) to classical single-crystal results. The next few orders can be obtained to sufficient accuracy by using the forward recursion relations

$$I_{n+3/2}(z)=I_{n-1/2}(z)-[(2n+1)/z]\,I_{n+1/2}(z) \qquad (A6.6)$$

provided z is not vanishingly small.

The first few functions are

$$I_{3/2}(z)=(2/\pi z)^{1/2}[\cosh(z)+\sinh(z)/z] \qquad (A6.7)$$

$$\begin{aligned} I_{5/2}(z)=(2/\pi z)^{1/2}[&(3/z^2+1)\sinh(z)\\ &-(3/z)\cosh(z)]. \end{aligned} \qquad (A6.8)$$

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