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Probabilistic Theory of the Structure Invariants: Extension to the Unequal Atom Case with Application to Neutron Diffraction

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Recent methods in the probabilistic theory of the structure invariants and seminvariants are here generalized to include the case that not all atoms in the unit cell are identical. The presence of unequal atoms, in particular a few heavy atoms, is thus clearly seen to enhance the power of the direct method. Since the method permits the presence of negative scatterers, the application to neutron diffraction is immediate. Only the conditional probability distributions associated with the first neighborhood of the three-phase structure invariant and the first two neighborhoods of the four-phase structure invariant in $P1$ and $P\bar{1}$ are treated here. However the methods are clearly sufficiently general to cope with structure invariants and seminvariants in general.

1. Introduction

In recent months a new method in the probabilistic theory of the structure invariants was introduced (Hauptman, 1975*a*,*b*). For a fixed crystal structure it is assumed that one or more reciprocal vectors $\mathbf{h},\mathbf{k},\ldots$, are the primitive random variables uniformly distributed over well defined subsets of reciprocal space. Then a structure invariant or seminvariant, as a function of the primitive random variables $\mathbf{h},\mathbf{k},\ldots$, is itself a random variable and its conditional probability distribution, given the values of a suitable set of structure factor magnitudes, can then be found. In this way a probabilistic estimate for the structure invariant or seminvariant in terms of an appropriately chosen set of structure factor magnitudes may be derived. Finally, the concept of 'neighborhood of a structure invariant or seminvariant' has been introduced and its central importance stressed. However the method was limited by the requirement that the crystal structure consist of N identical atoms in the unit cell. It appears now that the restriction to identical atoms was not essential. In the present paper the methods recently obtained are generalized to include the case that not all atoms are identical. In fact the formalism is of sufficient generality to include also the case that some of the atomic scattering factors are negative, so that the extension to neutron diffraction is automatic.

In the space group $P1$ the normalized structure factor is defined by

$$E_{\mathbf{h}}=|E_{\mathbf{h}}|\exp(i\varphi_{\mathbf{h}})=\frac{1}{\sigma_2^{1/2}}\sum_{j=1}^{N}f_j\exp(2\pi i\mathbf{h}\,.\,r_j) \quad (1.1)$$

in which f_j and r_j are the zero-angle atomic scattering factor and position vector respectively of the atom labeled j, N is the number of atoms in the unit cell and

$$\sigma_n=\sum_{j=1}^{N}f_j^n\,. \quad (1.2)$$

In the recent work (Hauptman, 1975*a*,*b*) the mathematical formalism required to find the various conditional probability distributions of the structure invariants and seminvariants has been described in some detail. In order to save space here it is assumed that the reader is thoroughly familiar with these recent papers, and the present paper is heavily dependent on them. The mathematical Appendixes I and II contain only the few necessary guideposts which the interested reader will find helpful in his attempt to understand or recreate the analysis appropriate to the unequal atom case. In addition, equations (I.5) and (II.5) of these Appendixes, the joint probability distributions of three and seven structure factors respectively, are of major importance in themselves, and will surely play a central role in further developments. For the reader interested in studying all details of the derivations, these are given for $P1$ in the long Appendix III.*

2. The conditional probability distribution of the structure invariant $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}$, given the three magnitudes $|E_{\mathbf{h}}|,|E_{\mathbf{k}}|,|E_{\mathbf{l}}|$

Suppose that a crystal structure in $P1$ is fixed. Specify also the three non-negative numbers R_1,R_2,R_3. The threefold Cartesian product $W\times W\times W$ of reciprocal space W with itself is defined to be the collection of all ordered triples $(\mathbf{h},\mathbf{k},\mathbf{l})$ of reciprocal vectors $\mathbf{h},\mathbf{k},\mathbf{l}$. Suppose finally that the primitive random variable $(\mathbf{h},\mathbf{k},\mathbf{l})$ is uniformly distributed over the subset of $W\times W\times W$ defined by

$$|E_{\mathbf{h}}|=R_1,\ |E_{\mathbf{k}}|=R_2,\ |E_{\mathbf{l}}|=R_3 \quad (2.1)$$

and

$$\mathbf{h}+\mathbf{k}+\mathbf{l}=0\,. \quad (2.2)$$

* Appendix III has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31742 (93 pp., 2 microfiches). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1 NZ, England. Appendix III is also available from the author as a technical report issued by the Medical Foundation of Buffalo.

Strictly speaking, in order to ensure that the domain of the primitive random variable be non-vacuous, it is necessary to interpret the exact equality $|E_{\mathbf{h}}|=R_1$ of (2.1), for example, as the inequalities $R_1 \le |E_{\mathbf{h}}| \le R_1+\mathrm{d}R_1$, where $\mathrm{d}R_1$ is a small positive quantity, *etc.* Then the linear combination of phases

$$\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}} \tag{2.3}$$

is a structure invariant which, as a function of the primitive random variables $\mathbf{h},\mathbf{k},\mathbf{l}$, is itself a random variable. Denote by $P(\Phi|R_1,R_2,R_3)$ the conditional probability distribution of φ, given (2.1). The major result of this section is the formula

$$P(\Phi|R_1,R_2,R_3)\simeq \frac{1}{K}\exp(A\cos\Phi) \tag{2.4}$$

where

$$A=\frac{2\sigma_3}{\sigma_2^{3/2}}R_1R_2R_3\,, \tag{2.5}$$

σ_n is defined by (1.2), and the normalizing parameter K is given by

$$K=2\pi I_0(A) \tag{2.6}$$

where I_0 is the modified Bessel function. In the special case that all atoms are identical, (2.4) was first obtained by Cochran (1955), using a different probabilistic background. Appendix I contains only the briefest sketch of the derivation of (2.4), and complete familiarity with earlier work is assumed (Hauptman, 1975*a*,*b*). However, see Appendix III for complete details, in particular equation (*B*.44).

3. The conditional probability distribution of the structure invariant $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}$, given the four magnitudes $|E_{\mathbf{h}}|,|E_{\mathbf{k}}|,|E_{\mathbf{l}}|,|E_{\mathbf{m}}|$

Suppose that a crystal structure in $P1$ is fixed and that the four non-negative numbers R_1,R_2,R_3,R_4 are also specified. The fourfold Cartesian product $W\times W\times W\times W$ is defined to be the collection of all ordered quadruples $(\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m})$ of reciprocal vectors $\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m}$. It is assumed finally that $(\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m})$ is the primitive random variable which is uniformly distributed over the subset of $W\times W\times W\times W$ for which

$$|E_{\mathbf{h}}|=R_1,\ |E_{\mathbf{k}}|=R_2,\ |E_{\mathbf{l}}|=R_3,\ |E_{\mathbf{m}}|=R_4\,, \tag{3.1}$$

and

$$\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}=0\,. \tag{3.2}$$

Again, the exact equality $|E_{\mathbf{h}}|=R_1$ of (3.1) is to be interpreted as $R_1\le|E_{\mathbf{h}}|\le R_1+\mathrm{d}R_1$, *etc.* Then the structure invariant

$$\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}} \tag{3.3}$$

is a function of the random variables $\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m}$ and is therefore itself a random variable. The conditional probability distribution of φ, given (3.1), the chief result of this section, turns out to be [equation (*C*.50) of Appendix III]

$$P(\Phi|R_1,R_2,R_3,R_4)\simeq \frac{1}{L}\exp(B\cos\Phi) \tag{3.4}$$

where

$$B=\frac{2\sigma_4}{\sigma_2^2}R_1R_2R_3R_4\,, \tag{3.5}$$

$$L=2\pi I_0(B)\,, \tag{3.6}$$

and σ_n is defined by (1.2).

The close parallel between §§2 and 3 has been emphasized and is such that not even a brief sketch of the derivation of (3.4) is necessary here (but Appendix III contains complete details). However there is a major difference between (2.4) and (3.4) which must also be stressed. In the case of X-ray diffraction the f_j are the atomic numbers Z_j and are all positive. Hence the parameters A and B, (2.5) and (3.5) respectively, are also positive so that (2.4) and (3.4) have only a single maximum at $\Phi=0$ and the larger the values of A or B the smaller the standard deviation and the more reliable the estimate of the structure invariant φ, zero in this case. In the presence of unequal atoms, in particular a small number of heavy atoms, the parameters A and B may increase greatly and the reliability of the estimate for φ correspondingly increased. If, on the other hand, negative scatterers are also present, as in the case of neutron diffraction, then the value of the parameter A will be reduced since A is proportional to σ_3 which is the sum of the cubes of the atomic scattering factors. In this case the reliability of the estimate for the three-phase invariant (2.3) is reduced accordingly. In the extreme case that $\sigma_3\simeq 0$, a situation which appears never to occur in practice, φ, (2.3), is approximately uniformly distributed. The parameter B, on the other hand, is not reduced in the presence of negative scatterers since B varies directly with σ_4, the sum of the fourth powers of the atomic scattering factors. Hence the distribution (3.4) can only be favorably affected in the presence of unequal atoms, whether in the X-ray or neutron diffraction case. It should however be mentioned that (3.4) is in general not as useful as (2.4) since B values (of order $1/N$) tend to be smaller than A values (of order $1/N^{1/2}$), at least for large values of N. Hence remarks like these are more meaningful for the distributions associated with the second and higher neighborhoods of the three- and four-phase structure invariants φ [(2.3) and (3.3), respectively]. The seven magnitude neighborhood of the four-phase structure invariant (3.3) is studied next with results not completely anticipated.

4. The conditional probability distribution of the structure invariant $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}$, given the seven magnitudes $|E_{\mathbf{h}}|,|E_{\mathbf{k}}|,|E_{\mathbf{l}}|,|E_{\mathbf{m}}|,|E_{\mathbf{h}+\mathbf{k}}|,|E_{\mathbf{k}+\mathbf{l}}|,|E_{\mathbf{l}+\mathbf{h}}|$

Fix the seven non-negative numbers $R_1,R_2,R_3,R_4,,R_{12}$, R_{23},R_{31} and make the same hypotheses as in §3. Suppose that the ordered quadruple $(\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m})$ is the primitive

random variable which is now uniformly distributed over the subset of $W\times W\times W\times W$ defined by

$$|E_{\mathbf{h}}|=R_1,\ |E_{\mathbf{k}}|=R_2,\ |E_{\mathbf{l}}|=R_3,\ |E_{\mathbf{m}}|=R_4\ , \tag{4.1}$$

$$|E_{\mathbf{h}+\mathbf{k}}|=R_{12},\ |E_{\mathbf{k}+\mathbf{l}}|=R_{23},\ |E_{\mathbf{l}+\mathbf{h}}|=R_{31}\ , \tag{4.2}$$

and

$$\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}=0\ . \tag{4.3}$$

As before, the exact equality $|E_{\mathbf{h}}|=R_1$ of (4.1) is to be understood as $R_1\le|E_{\mathbf{h}}|\le R_1+\mathrm{d}R_1$, *etc.* Then the structure invariant

$$\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}\ , \tag{4.4}$$

a function of the primitive random variables $\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m}$, is itself a random variable, and its conditional probability distribution, given (4.1) and (4.2), the major result of this paper, turns out to be [equation (*D*.94) of Appendix III],

$$\begin{aligned}P(\Phi|R_1,R_2,R_3,R_4,R_{12},R_{23},R_{31})&\\ \simeq\frac{1}{M}\exp(-2B'\cos\Phi)I_0\left(\frac{2\sigma_3}{\sigma_2^{3/2}}R_{12}Y_{12}\right)&\\ \times I_0\left(\frac{2\sigma_3}{\sigma_2^{3/2}}R_{23}Y_{23}\right)I_0\left(\frac{2\sigma_3}{\sigma_2^{3/2}}R_{31}Y_{31}\right)&\end{aligned} \tag{4.5}$$

where

$$B'=\frac{1}{\sigma_2^3}(3\sigma_3^2-\sigma_2\sigma_4)R_1R_2R_3R_4\ , \tag{4.6}$$

$$Y_{12}=[R_1^2R_2^2+R_3^2R_4^2+2R_1R_2R_3R_4\cos\Phi]^{1/2}\ , \tag{4.7}$$

$$Y_{23}=[R_2^2R_3^2+R_1^2R_4^2+2R_1R_2R_3R_4\cos\Phi]^{1/2}\ , \tag{4.8}$$

$$Y_{31}=[R_3^2R_1^2+R_2^2R_4^2+2R_1R_2R_3R_4\cos\Phi]^{1/2}\ , \tag{4.9}$$

$$M=2\pi\sum_{\mu,\nu,\varrho=-\infty}^{\infty}(-1)^{\mu+\nu+\varrho}\mathcal{Q}_{\mu\nu\varrho}I_{\mu+\nu+\varrho}(2B')\ , \tag{4.10}$$

where $\mathcal{Q}_{\mu\nu\varrho}$ is defined by

$$\begin{aligned}\mathcal{Q}_{\mu\nu\varrho}=I_\mu\left(\frac{2\sigma_3}{\sigma_2^{3/2}}R_{12}R_1R_2\right)I_\mu\left(\frac{2\sigma_3}{\sigma_2^{3/2}}R_{12}R_3R_4\right)&\\ \times I_\nu\left(\frac{2\sigma_3}{\sigma_2^{3/2}}R_{23}R_2R_3\right)I_\nu\left(\frac{2\sigma_3}{\sigma_2^{3/2}}R_{23}R_1R_4\right)&\\ \times I_\varrho\left(\frac{2\sigma_3}{\sigma_2^{3/2}}R_{31}R_3R_1\right)I_\varrho\left(\frac{2\sigma_3}{\sigma_2^{3/2}}R_{31}R_2R_4\right)\ ,&\end{aligned} \tag{4.11}$$

and I is the modified Bessel function. Appendix II contains only the briefest sketch of the derivation of (4.5) with heavy dependence on recent work (Hauptman, 1975*a*,*b*), but Appendix III contains a detailed analysis. As pointed out in the earlier work (Hauptman, 1975*b*), it is not necessary in the applications to calculate M from the triple sum (4.10), a lengthy computation. It is much faster to calculate the normalizing parameter M, if desired, numerically from the distribution (4.5) directly, and the most probable value of $|\varphi|$, which may lie anywhere between 0 and π, may also be found directly from (4.5).

In the special case that all atoms are identical, it is readily verified that the present distribution (4.5) reduces to the one derived earlier [(3.2) of Hauptman (1975*b*)]. In the case of unequal atoms however, particularly when one or more heavy atoms are present, the parameters B' and $\sigma_3/\sigma_2^{3/2}$ may be significantly greater than their earlier counterparts, $2/NR_1R_2R_3R_4$ and $1/N^{1/2}$, respectively, in the X-ray diffraction case. The resulting sharpening of the distribution (4.5) yields a more reliable estimate for the value of the quartet φ.

In the neutron diffraction case, however, the values of B' and $\sigma_3/\sigma_2^{3/2}$ tend to be reduced, resulting in a flattening of the distribution (4.5) and a correspondingly less reliable estimate for the value of φ. It is of interest to observe in fact that in the extreme case that $\sigma_3\simeq 0$, then $B'\simeq B/2$, and (4.5) reduces to (3.4) so that only the zero estimate for φ is possible and nothing is gained in going from the first to the second neighborhood. Since this is precisely the case that (2.4) yields no information, one may speculate that more reliable estimates for the cosine invariants, in particular those whose values are probably negative, are to be obtained in this case by going to the higher neighborhoods of the three- and four-phase invariants or through an investigation of the five- or even six-phase structure invariants. It should be stressed however that in the actual applications to real structures this extreme appears never to be realized so that (4.5) and its generalizations will almost certainly prove to be useful in the applications.

It should be pointed out finally that in the special case that

$$R_{12}\simeq R_{23}\simeq R_{31}\simeq 0 \tag{4.12}$$

then (4.5) reduces to

$$\begin{aligned}P(\Phi|R_1,R_2,R_3,R_4;R_{12}\simeq R_{23}\simeq R_{31}\simeq 0)&\\ \simeq\frac{1}{M}\exp(-2B'\cos\Phi)&\end{aligned} \tag{4.13}$$

where

$$M=2\pi I_0(2B')\ , \tag{4.14}$$

so that, as already pointed out earlier in the equal atom case (Hauptman, 1974, 1975*b*), in this special case the most probable value of φ is π, and the larger the value of B' the more likely it is that φ is close to π.

5. Space group $P\bar{1}$

In view of recently derived results in $P\bar{1}$ (Green & Hauptman, 1976; Hauptman & Green, 1976) and the work described in §§1–4, the analogues of (2.4), (3.4), and (4.5) in the space group $P\bar{1}$, obtained by analogy, are briefly described here.

5.1. *The conditional probability distribution of the structure invariant* $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}$, *given the three magnitudes* $|E_{\mathbf{h}}|,|E_{\mathbf{k}}|,|E_{\mathbf{l}}|$

Make the same assumptions and use the same notation as in §2. Note however that, since the space

group now is $P\bar{1}$, the structure invariant

$$\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}} \tag{5.1}$$

takes on only the two values of 0 and π. Hence its probability distribution is discrete. Denote by $P_3^{\pm}=P_3^{\pm}(R_1,R_2,R_3)$ the conditional probability that $\varphi=0$ or π (or that $\cos\varphi=\pm 1$) respectively, given the three magnitudes (2.1). Then

$$P_3^{\pm}\simeq\frac{1}{K}\exp\left(\pm\frac{A}{2}\right), \tag{5.2}$$

where

$$K=2\cosh\frac{A}{2}, \tag{5.3}$$

which should be compared with (2.4) and (2.6). Again A and σ_n are defined by (2.5) and (1.2) respectively, and N is the number of atoms in the whole unit cell. In the special case of equal atoms (5.2) was first obtained by Woolfson (1954) who used a different probabilistic background.

5.2. *The conditional probability distribution of the structure invariant $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}$, given the four magnitudes $|E_{\mathbf{h}}|,|E_{\mathbf{k}}|,|E_{\mathbf{l}}|,|E_{\mathbf{m}}|$*

Use the notation and hypotheses of §3 but note that the structure invariant

$$\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}} \tag{5.4}$$

now takes on only the two values $0,\pi$. Denote by $P_4^{\pm}=P_4^{\pm}(R_1,R_2,R_3,R_4)$ the conditional probability that $\varphi=0$ or π (or that $\cos\varphi=\pm 1$) respectively, given the four magnitudes (3.1). Then

$$P_4^{\pm}\simeq\frac{1}{L}\exp\left(\pm\frac{B}{2}\right), \tag{5.5}$$

where

$$L=2\cosh\frac{B}{2}, \tag{5.6}$$

which should be compared with (3.4) and (3.6). Again B is defined by (3.5), σ_n by (1.2), and N is the number of atoms in the whole unit cell. If all atoms are identical (5.5) reduces to (4.1) of Hauptman & Green (1976).

5.3. *The conditional probability distribution of the structure invariant $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}$, given the seven magnitudes $|E_{\mathbf{h}}|,|E_{\mathbf{k}}|,|E_{\mathbf{l}}|,|E_{\mathbf{m}}|,|E_{\mathbf{h}+\mathbf{k}}|,|E_{\mathbf{k}+\mathbf{l}}|,|E_{\mathbf{l}+\mathbf{h}}|$*

Refer to §4 for notation and hypotheses and denote by $P_7^{\pm}=P_7^{\pm}(R_1,R_2,R_3,R_4,R_{12},R_{23},R_{31})$ the conditional probability that the four-phase structure invariant (5.4) be 0 or π (or that $\cos\varphi=\pm 1$) respectively, given the seven magnitudes (4.1) and (4.2). Then

$$P_7^{\pm}\simeq\frac{1}{M}\exp(\mp B')\cosh\left(\frac{\sigma_3}{\sigma_2^{3/2}}R_{12}Y_{12}^{\pm}\right)\times\cosh\left(\frac{\sigma_3}{\sigma_2^{3/2}}R_{23}Y_{23}^{\pm}\right)\cosh\left(\frac{\sigma_3}{\sigma_2^{3/2}}R_{31}Y_{31}^{\pm}\right) \tag{5.7}$$

where

$$Y_{12}^{\pm}=R_1R_2\pm R_3R_4\,, \tag{5.8}$$

$$Y_{23}^{\pm}=R_2R_3\pm R_1R_4\,, \tag{5.9}$$

$$Y_{31}^{\pm}=R_3R_1\pm R_2R_4\,, \tag{5.10}$$

$$M=\exp(-B')\cosh\left(\frac{\sigma_3}{\sigma_2^{3/2}}R_{12}Y_{12}^{+}\right)\cosh\left(\frac{\sigma_3}{\sigma_2^{3/2}}R_{23}Y_{23}^{+}\right)\times\cosh\left(\frac{\sigma_3}{\sigma_2^{3/2}}R_{31}Y_{31}^{+}\right)+\exp(+B')\cosh\left(\frac{\sigma_3}{\sigma_2^{3/2}}R_{12}Y_{12}^{-}\right)\times\cosh\left(\frac{\sigma_3}{\sigma_2^{3/2}}R_{23}Y_{23}^{-}\right)\cosh\left(\frac{\sigma_3}{\sigma_2^{3/2}}R_{31}Y_{31}^{-}\right), \tag{5.11}$$

and B' and σ_n are defined by (4.6) and (1.2) respectively. Equations (5.7)–(5.11) should be compared with their analogues in $P1$, equations (4.5)–(4.11). If all atoms are identical (5.7) reduces to (3.13) of Hauptman & Green (1976).

5.4. *The special case that $R_{12}\simeq R_{23}\simeq R_{31}\simeq 0$*

If

$$R_{12}\simeq R_{23}\simeq R_{31}\simeq 0\,, \tag{5.12}$$

(5.7) and (5.11) reduce to

$$P_7^{\pm}\simeq\frac{1}{M}\exp(\mp B')\,, \tag{5.13}$$

$$M=2\cosh B'\,, \tag{5.14}$$

so that, as observed previously in the equal atom case (Hauptman, 1974; Hauptman & Green, 1976), in this special case φ is probably equal to π and the larger the value of B' the more likely it is that $\varphi=\pi$.

6. Concluding remarks

The recently secured probabilistic theory of the structure invariants and seminvariants has been generalized here to include the case that not all atoms in the unit cell are identical. It has been shown how the presence of unequal atoms, in particular a few heavy atoms, increases the power of the direct method, a fact long known but now quantitatively expressed, at least in the cases treated in this paper. Since the generalization described here permits the presence of negative scatterers, the application to neutron diffraction is also immediate. On the basis of the analysis presented in this work it seems almost certain that the extension to unequal atoms, described here only for the three- and four-phase structure invariants, will carry over without essential change to higher neighborhoods and to the structure invariants and seminvariants in general.

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APPENDIX I
Derivation of (2.4)

In order to derive the conditional probability distribution (2.4) it is necessary first to obtain the joint probability distribution $P_3=P(R_1,R_2,R_3;\Phi_1,\Phi_2,\Phi_3)$ of the magnitudes $|E_\mathbf{h}|,|E_\mathbf{k}|,|E_\mathbf{l}|$ and phases $\varphi_\mathbf{h},\varphi_\mathbf{k},\varphi_\mathbf{l}$ of the three structure factors $E_\mathbf{h},E_\mathbf{k},E_\mathbf{l}$ on the basis that the ordered triple $(\mathbf{h},\mathbf{k},\mathbf{l})$ is the primitive random variable uniformly distributed over the subset of $W\times W\times W$ defined by (2.2):

$$P_3=\frac{R_1R_2R_3}{(2\pi)^6}\int_{0,0,0}^{\infty,\infty,\infty}\int_{0,0,0}^{2\pi,2\pi,2\pi}\varrho_1\varrho_2\varrho_3 \times\exp\{-i[R_1\varrho_1\cos(\theta_1-\Phi_1)+R_2\varrho_2\cos(\theta_2-\Phi_2)+R_3\varrho_3\cos(\theta_3-\Phi_3)]\}\times\prod_{j=1}^{N}g_j\,\mathrm{d}\varrho_1\mathrm{d}\varrho_2\mathrm{d}\varrho_3\mathrm{d}\theta_1\mathrm{d}\theta_2\mathrm{d}\theta_3 \tag{I.1}$$

where

$$g_j=\left\langle\exp\left\{\frac{if_j}{\sigma_2^{1/2}}[\varrho_1\cos(2\pi\mathbf{h}\,.\,\mathbf{r}_j-\theta_1)+\varrho_2\cos(2\pi\mathbf{k}\,.\,\mathbf{r}_j-\theta_2)+\varrho_3\cos(2\pi(\mathbf{h}+\mathbf{k})\,.\,\mathbf{r}_j+\theta_3)]\right\}\right\rangle_{\mathbf{h},\mathbf{k}}. \tag{I.2}$$

Following the recent method (Hauptman, 1975*a*) one finds

$$g_j=\sum_{\mu=-\infty}^{\infty}(-i)^\mu J_\mu\left(\frac{\varrho_1f_j}{\sigma_2^{1/2}}\right)J_\mu\left(\frac{\varrho_2f_j}{\sigma_2^{1/2}}\right)J_\mu\left(\frac{\varrho_3f_j}{\sigma_2^{1/2}}\right)\times\exp[i\mu(\theta_1+\theta_2+\theta_3)] \tag{I.3}$$

so that the dependence of g_j on f_j is clear. It then follows that

$$\prod_{j=1}^{N}g_j=\exp\left(\sum_{j=1}^{N}\log g_j\right)=\exp\left[-\tfrac{1}{4}(\varrho_1^2+\varrho_2^2+\varrho_3^2)-\frac{i\sigma_3}{4\sigma_2^{3/2}}\varrho_1\varrho_2\varrho_3\times\cos(\theta_1+\theta_2+\theta_3)\right]\left[1+\mathrm{O}\left(\frac{1}{N}\right)\right] \tag{I.4}$$

where $\mathrm{O}(1/N)$ represents terms of order $1/N$ or higher in which the terms of order $1/N$ are independent of the θ's. Substituting from (I.4) into (I.1) and carrying out the indicated sixfold integration in accordance with recently described techniques (Hauptman, 1975*a*) one finally obtains the desired joint probability distribution of three structure factors $E_\mathbf{h},E_\mathbf{k},E_\mathbf{l}$:

$$P_3=\frac{R_1R_2R_3}{\pi^3}\exp\left[-R_1^2-R_2^2-R_3^2+\frac{2\sigma_3}{\sigma_2^{3/2}}R_1R_2R_3\times\cos(\Phi_1+\Phi_2+\Phi_3)\right]\left[1+\mathrm{O}\left(\frac{1}{N}\right)\right] \tag{I.5}$$

where $\mathrm{O}(1/N)$ represents terms of order $1/N$ or higher in which the terms of order $1/N$ are independent of the Φ's. Hence, by fixing R_1,R_2,R_3 and multiplying by a suitable normalizing parameter (Hauptman, 1975*b*), (I.5) implies (2.4) correct up to and including terms of order $1/N$.

APPENDIX II
Derivation of (4.5)

In order to derive the conditional probability distribution (4.5) it is necessary first to obtain the joint probability distribution $P_7=P(R_1,R_2,R_3,R_4,R_{12},R_{23},R_{31};\Phi_1,\Phi_2,\Phi_3,\Phi_4,\Phi_{12},\Phi_{23},\Phi_{31})$ of the seven structure factors $E_\mathbf{h},E_\mathbf{k},E_\mathbf{l},E_\mathbf{m},E_{\mathbf{h}+\mathbf{k}},E_{\mathbf{k}+\mathbf{l}},E_{\mathbf{l}+\mathbf{h}}$ on the basis that the ordered quadruple $(\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m})$ is the primitive random variable uniformly distributed over the subset of $W\times W\times W\times W$ defined by (4.3):

$$P_7=\frac{R_1R_2R_3R_4R_{12}R_{23}R_{31}}{(2\pi)^{14}}\int_{0,0,0,0,0,0,0}^{\infty,\infty,\infty,\infty,\infty,\infty,\infty}\varrho_1\varrho_2\varrho_3\varrho_4\varrho_{12}\varrho_{23}\varrho_{31}\times\int_{0,0,0,0,0,0,0}^{2\pi,2\pi,2\pi,2\pi,2\pi,2\pi,2\pi}\varrho_1\varrho_2\varrho_3\varrho_4\varrho_{12}\varrho_{23}\varrho_{31}\times\exp\{-i[R_1\varrho_1\cos(\theta_1-\Phi_1)+R_2\varrho_2\cos(\theta_2-\Phi_2)+R_3\varrho_3\cos(\theta_3-\Phi_3)+R_4\varrho_4\cos(\theta_4-\Phi_4)+R_{12}\varrho_{12}\cos(\theta_{12}-\Phi_{12})+R_{23}\varrho_{23}\cos(\theta_{23}-\Phi_{23})+R_{31}\varrho_{31}\cos(\theta_{31}-\Phi_{31})]\}\times\prod_{j=1}^{N}g_j\,\mathrm{d}\varrho_1\mathrm{d}\varrho_2\mathrm{d}\varrho_3\mathrm{d}\varrho_4\mathrm{d}\varrho_{12}\mathrm{d}\varrho_{23}\mathrm{d}\varrho_{31}\times\mathrm{d}\theta_1\mathrm{d}\theta_2\mathrm{d}\theta_3\mathrm{d}\theta_4\mathrm{d}\theta_{12}\mathrm{d}\theta_{23}\mathrm{d}\theta_{31} \tag{II.1}$$

where

$$g_j=\left\langle\exp\left\{\frac{if_j}{\sigma_2^{1/2}}[\varrho_1\cos(2\pi\mathbf{h}\,.\,\mathbf{r}_j-\theta_1)+\varrho_2\cos(2\pi\mathbf{k}\,.\,\mathbf{r}_j-\theta_2)+\varrho_3\cos(2\pi\mathbf{l}\,.\,\mathbf{r}_j-\theta_3)+\varrho_4\cos(2\pi(\mathbf{h}+\mathbf{k}+\mathbf{l})\,.\,\mathbf{r}_j+\theta_4)+\varrho_{12}\cos(2\pi(\mathbf{h}+\mathbf{k})\,.\,\mathbf{r}_j-\theta_{12})+\varrho_{23}\cos(2\pi(\mathbf{k}+\mathbf{l})\,.\,\mathbf{r}_j-\theta_{23})+\varrho_{31}\cos(2\pi(\mathbf{l}+\mathbf{h})\,.\,\mathbf{r}_j-\theta_{31})]\right\}\right\rangle_{\mathbf{h},\mathbf{k},\mathbf{l}}. \tag{II.2}$$

Following the recent method (Appendix II, Hauptman, 1975*a*) one now finds

$$g_j = \sum_{\substack{\mu,\nu,\varrho,\sigma \\ -\infty}}^{\infty} (-i)^{\nu+\varrho+\sigma} J_{\mu+\nu+\varrho+\sigma}\left(\frac{f_j\varrho_1}{\sigma_2^{3/2}}\right) J_{\mu+\nu}\left(\frac{f_j\varrho_2}{\sigma_2^{3/2}}\right)$$
$$\times J_{\mu+\varrho}\left(\frac{f_j\varrho_3}{\sigma_2^{3/2}}\right) J_{\mu+\sigma}\left(\frac{f_j\varrho_4}{\sigma_2^{3/2}}\right) J_{\nu}\left(\frac{f_j\varrho_{12}}{\sigma_2^{3/2}}\right)$$
$$\times J_{\sigma}\left(\frac{f_j\varrho_{23}}{\sigma_2^{3/2}}\right) J_{\varrho}\left(\frac{f_j\varrho_{31}}{\sigma_2^{3/2}}\right)$$
$$\times \exp\left[i\mu(\theta_1+\theta_2+\theta_3+\theta_4)+i\nu(\theta_1+\theta_2-\theta_{12})\right.$$
$$\left.+i\sigma(\theta_1+\theta_4+\theta_{23})+i\varrho(\theta_1+\theta_3-\theta_{31})\right]. \qquad \text{(II.3)}$$

It follows that

$$\prod_{j=1}^{N} g_j = \exp\left(\sum_{j=1}^{N} \log g_j\right)$$
$$= \exp\left\{-\tfrac{1}{4}(\varrho_1^2+\varrho_2^2+\varrho_3^2+\varrho_4^2+\varrho_{12}^2+\varrho_{23}^2+\varrho_{31}^2)\right.$$
$$-\frac{i\sigma_3}{4\sigma_2^{3/2}}[\varrho_1\varrho_4\varrho_{23}\cos(\theta_1+\theta_4+\theta_{23})$$
$$+\varrho_1\varrho_3\varrho_{31}\cos(\theta_1+\theta_3-\theta_{31})$$
$$+\varrho_1\varrho_2\varrho_{12}\cos(\theta_1+\theta_2-\theta_{12})$$
$$+\varrho_2\varrho_3\varrho_{23}\cos(\theta_2+\theta_3-\theta_{23})$$
$$+\varrho_2\varrho_4\varrho_{31}\cos(\theta_2+\theta_4+\theta_{31})$$
$$+\varrho_3\varrho_4\varrho_{12}\cos(\theta_3+\theta_4+\theta_{12})]$$
$$+\frac{\sigma_4}{8\sigma_2^2}[\varrho_1\varrho_2\varrho_3\varrho_4\cos(\theta_1+\theta_2+\theta_3+\theta_4)$$
$$+\varrho_2\varrho_3\varrho_{31}\varrho_{12}\cos(\theta_2-\theta_3+\theta_{31}-\theta_{12})$$
$$+\varrho_2\varrho_4\varrho_{12}\varrho_{23}\cos(\theta_2-\theta_4-\theta_{12}-\theta_{23})$$
$$+\varrho_3\varrho_4\varrho_{23}\varrho_{31}\cos(\theta_3-\theta_4-\theta_{23}-\theta_{31})$$
$$+\varrho_1\varrho_4\varrho_{31}\varrho_{12}\cos((\theta_1-\theta_4-\theta_{31}-\theta_{12})$$
$$+\varrho_1\varrho_3\varrho_{12}\varrho_{23}\cos(\theta_1-\theta_3-\theta_{12}+\theta_{23})$$
$$\left.+\varrho_1\varrho_2\varrho_{23}\varrho_{31}\cos(\theta_1-\theta_2+\theta_{23}-\theta_{31})]\right\}$$
$$\times\left\{1+O\left(\frac{1}{N}\right)\right\} \qquad \text{(II.4)}$$

where $O(1/N)$ represents terms of order $1/N$ or higher in which the terms of order $1/N$ are independent of the θ's. Substituting from (II.4) into (II.1) and carrying out the indicated fourteenfold integration in accordance with recently secured techniques (Hauptman, 1975*a*, Appendix IV) one obtains the desired joint probability distribution of the seven structure factors $E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{l}}, E_{\mathbf{m}}, E_{\mathbf{h}+\mathbf{k}}, E_{\mathbf{k}+\mathbf{l}}, E_{\mathbf{l}+\mathbf{h}}$:

$$P_7 = \frac{R_1R_2R_3R_4R_{12}R_{23}R_{31}}{\pi}$$
$$\times \exp\left\{-R_1^2-R_2^2-R_3^2-R_4^2-R_{12}^2-R_{23}^2-R_{31}^2\right.$$
$$+\frac{2\sigma_3}{\sigma_2^{3/2}}[R_1R_2R_{12}\cos(\Phi_1+\Phi_2-\Phi_{12})$$
$$+R_3R_4R_{12}\cos(\Phi_3+\Phi_4+\Phi_{12})$$
$$+R_2R_3R_{23}\cos(\Phi_2+\Phi_3-\Phi_{23})$$
$$+R_1R_4R_{23}\cos(\Phi_1+\Phi_4+\Phi_{23})$$
$$+R_1R_3R_{31}\cos(\Phi_1+\Phi_3-\Phi_{31})$$
$$+R_2R_4R_{31}\cos(\Phi_2+\Phi_4+\Phi_{31})]$$
$$-2\left(\frac{2\sigma_3^2}{\sigma_2^3}-\frac{\sigma_4}{\sigma_2^2}\right)[R_1R_3R_{12}R_{23}\cos(\Phi_1-\Phi_3-\Phi_{12}$$
$$+\Phi_{23})+R_2R_4R_{12}R_{23}\cos(\Phi_2-\Phi_4-\Phi_{12}-\Phi_{23})$$
$$+R_2R_3R_{31}R_{12}\cos(\Phi_2-\Phi_3-\Phi_{12}+\Phi_{31})$$
$$+R_1R_4R_{31}R_{12}\cos(\Phi_1-\Phi_4-\Phi_{31}-\Phi_{12})$$
$$+R_1R_2R_{23}R_{31}\cos(\Phi_1-\Phi_2+\Phi_{23}-\Phi_{31})$$
$$+R_3R_4R_{23}R_{31}\cos(\Phi_3-\Phi_4-\Phi_{23}-\Phi_{31})]$$
$$-2\left(\frac{3\sigma_3^2}{\sigma_2^3}-\frac{\sigma_4}{\sigma_2^2}\right)R_1R_2R_3R_4$$
$$\left.\times\cos(\Phi_1+\Phi_2+\Phi_3+\Phi_4)\right\}\left\{1+O\left(\frac{1}{N}\right)\right\}, \qquad \text{(II.5)}$$

where $O(1/N)$ represents terms of order $1/N$ or higher in which the terms of order $1/N$ are independent of the Φ's. Hence, by fixing $R_1, R_2, R_3, R_4, R_{12}, R_{23}, R_{31}$, integrating (II.5) with respect to $\Phi_{12}, \Phi_{23}, \Phi_{31}$ and multiplying by a suitable normalizing parameter (Hauptman, 1975*b*) (II.5) implies (4.5), correct up to and including terms of order $1/N$.

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