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Strengthening of the Triplet Relationship: a New Probabilistic Approach in $P\bar{1}$

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A new probabilistic approach is described which can improve the reliability of the triplet relationships. The terms $|E_{\mathbf{K}}|, |E_{\mathbf{H}_1+\mathbf{K}}|, |E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}|$ are tested in order to give the probability of the sign of $E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}$ rather than the 'exact' value of the invariant, as made in preceding approaches, *e.g.* $B_{3,0}$ formula [Karle & Hauptman, *Acta Cryst.* (1958), **11**, 264–269] the modified triple product [Hauptman, *Acta Cryst.* (1964), **17**, 1421–1433; Hauptman, Fisher, Hancock & Norton, *Acta Cryst.* (1969), B**25**, 811–814] and *M–D–K–S* formula [Hauptman, New Orleans Meet. Amer. Cryst. Assoc., 2 March. (1970), Abstract *B*8].

1. Introduction

The most widely used direct method for solving crystal structures is based on the use of the phase relationship

$$\sin(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}+\mathbf{k}})\simeq 0\,. \tag{1}$$

(1) leads to $\sum_2$ and tangent formulae (Karle & Hauptman, 1953, 1958) which are able to extend and refine a number of plausible basis sets of phases. The process is a 'stepwise' one: the procedures usually introduce a number of ambiguities, assigning them initial numerical values and proceeding with tangent refinement and extension. Completely wrong answers, nevertheless, may result when one or more 'bad' triplets [*i.e.* triplets for which (1) is violated] occur in the early stages of the process. Four different ways are currently used for overcoming this difficulty.

(1) Increase of the number of ambiguities in the basic set of phases. Unfortunately the size of the starting set is limited by the number of the phase combinations it is practical to explore.

(2) Enlargement of the starting set by the introduction of a number of phases previously determined. In order to achieve this, several additional formulae may be used: we quote the $\sum_1$ formula (Karle & Hauptman, 1953), strengthened $\sum_1$ formulae (Giacovazzo, 1975*a*), the coincidence methods (Grant, Howells & Rogers, 1957; Debaerdemaeker & Woolfson, 1972).

(3) The 'magic integers' approach (White & Woolfson, 1975; Declercq, Germain & Woolfson, 1975). The method is not a 'stepwise' one and should not be too sensitive to 'bad' triplets in the early stages of the procedure.

(4) The quartet method (Schenk, 1974; Hauptman, 1975*a*, *b*; Green & Hauptman, 1976; Hauptman & Green, 1976; Giacovazzo, 1975*b*, 1976*a*, *b*, *c*). When triplet and quartet relationships are used concurrently in the procedures for the crystal structure solution, a larger number of reliable relations are available, thus decreasing the probability of using 'bad' relations in the early stages of the process.

All the above mentioned methods may reduce the influence of the 'bad' triplets but are not able to identify them. It seems then that the procedures based on the cosine invariant computation (Hauptman, Fisher, Hancock & Norton, 1969; Hauptman, Fisher & Weeks, 1971) could play an important role in the process for the solution of complex crystal structures. From a formal point of view the method has the great advantage of using all the structure factors in the phase generation: for example (Karle & Hauptman, 1957)

$$\begin{aligned}&|E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}|\cos(\varphi_{\mathbf{h}_1}+\varphi_{\mathbf{h}_2}+\varphi_{\mathbf{h}_3})\\&\simeq(N^{3/2}/2)\,\langle(|E_{\mathbf{k}}|^2-1)\,(|E_{\mathbf{h}'+\mathbf{k}}|^2-1)\,(|E_{-\mathbf{h}_3+\mathbf{k}}|^2-1)\rangle_{\mathbf{k}}\\&+N^{-1/2}(|E_{\mathbf{h}_1}|^2+|E_{\mathbf{h}_2}|^2+|E_{\mathbf{h}_3}|^2-2)\,,\end{aligned} \tag{2}$$

where $\mathbf{h}'=\mathbf{h}_1$ or $\mathbf{h}_2$ and $\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=0$.

Relation (2) is formally able to give the exact value of the invariant phase rather than equating it to zero as is done in the tangent method. (2) however, is exact only when the structure consists of N identical point atoms and when no rational dependence of atomic coordinates occurs. Its practical application therefore requires some conditions whose nature deserves to be discussed. Formally speaking, the measure of the cosine invariant may be obtained just by allowing the $\mathbf{k}$ vector to range uniformly throughout reciprocal space. As all the computed averages are, of necessity, only estimates of the true averages and are based on the finite number of data available from the experiment, the problem of the variance caused by the finite sampling may constitute a severe restriction. A partial answer to this problem was given by Hauptman, Fisher, Hancock & Norton (1969) who proposed the phase relation

$$\begin{aligned}&|E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}|\cos(\varphi_{\mathbf{h}_1}+\varphi_{\mathbf{h}_2}+\varphi_{\mathbf{h}_3})\\&\simeq G\langle(|E_{\mathbf{k}}|^{1/2}-\langle|E|^{1/2}\rangle)\,(|E_{\mathbf{h}_1+\mathbf{k}}|^{1/2}\\&-\langle|E|^{1/2}\rangle)\,(|E_{-\mathbf{h}_3+\mathbf{k}}|^{1/2}-\langle|E|^{1/2}\rangle)\rangle_{\mathbf{k}}+R_3\,,\end{aligned}$$

where

$$\begin{aligned}R_3=\frac{\sigma_3}{4\sigma_2^{3/2}}\,[\tfrac{3}{2}(|E_{\mathbf{h}_1}E_{\mathbf{h}_2}|^2+|E_{\mathbf{h}_2}E_{\mathbf{h}_3}|^2+|E_{\mathbf{h}_3}E_{\mathbf{h}_1}|^2)+|E_{\mathbf{h}_1}|^2\\+|E_{\mathbf{h}_2}|^2+|E_{\mathbf{h}_3}|^2-\tfrac{7}{2}]\,,\end{aligned}$$

$\langle|E|^{1/2}\rangle=\langle|E_{\mathbf{k}}|^{1/2}\rangle_{\mathbf{k}}$, and G is an empirical scale factor.

The sampling problem nevertheless was still unsolved. Its importance is the more relevant since the computation of the cosine invariants is time consuming even on very fast computers. Thus approximate formulae are widely used which make various restrictions on the range of **k** (Karle, 1970; Hauptman, Fisher & Weeks, 1971). The most recent is the *M*(*D*–*KS*) formula (Hauptman, 1970; Fisher, Hancock & Hauptman, 1970):

$$\cos(\varphi_{\mathbf{h}_1}+\varphi_{\mathbf{h}_2}+\varphi_{\mathbf{h}_3})=M(D\text{–}KS)\,, \tag{3}$$

where

$$D=\frac{\sum_{i=1}^{3}m_iD_i}{\sum_{i=1}^{3}m_i}\,,$$

$$D_i=\langle(|E_{-\mathbf{h}_i+\mathbf{k}}|^2-1)\;|\;|E_\mathbf{k}|>t,|E_{\mathbf{h}_j+\mathbf{k}}|>t\rangle_\mathbf{k}\,,$$

$$i=1,2,3;\quad j=2,3,1\,,$$

$$S=\frac{\sum_{i=1}^{3}n_iS_i}{\sum_{i=1}^{3}n_i}$$

$$S_i=2\langle(|E_{-\mathbf{h}_i+\mathbf{k}}|^2-1)\;|\;|E_\mathbf{k}|>t\rangle_\mathbf{k}\,,$$

t is an arbitrary number exceeding unity and K and M are empirical parameters dependent on the distribution of the invariant cosines. Even if the *M*(*D*–*KS*) formula improves the preceding ones, it is not able to estimate the variance of the computed cosines: so cosine values exceeding unity are unfortunately frequent.

So far we have stressed just one aspect of the sampling problem, that is 'given the finite number of experimental available data, what is the reliability of the calculated cosine invariant when we average over indices of specific combinations of the structure factors?' An answer to this problem, of course, can only be given by means of probabilistic methods. Now a more interesting problem is whether the probability methods are able to answer this more subtle question: 'The expected value of $\cos(\varphi_{\mathbf{h}_1}+\varphi_{\mathbf{h}_2}+\varphi_{\mathbf{h}_3})$ is given by (Hauptman, 1972)

$$\langle\cos(\varphi_{\mathbf{h}_1}+\varphi_{\mathbf{h}_2}+\varphi_{\mathbf{h}_3})\rangle=\frac{I_1(G)}{I_0(G)}\,, \tag{4}$$

where

$$G=2|E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}|/\sqrt{N}\,,$$

and the variance by

$$\operatorname{var}[\cos(\varphi_{\mathbf{h}_1}+\varphi_{\mathbf{h}_2}+\varphi_{\mathbf{h}_3})]=1-\frac{I_1(G)}{GI_0(G)}-\frac{I_1^2(G)}{I_0^2(G)}\,. \tag{5}$$

In what way does the value of the single triple ($|E_\mathbf{k}|$, $|E_{\mathbf{h}_1+\mathbf{k}}|,|E_{-\mathbf{h}_3+\mathbf{k}}|$) change the effective value of G as given by the triplet relationship alone?'

If we are able to provide an answer to this question the immediate consequence is the well grounded hope of moderating in a simple way the disastrous influence of the negative cosines during the phase determining process. In fact the theory should permit us to use directly in the tangent formula a value of G which uses also the information contained in all reciprocal space. This new value of G may in principle even reverse the positivity required by the expected cosine value defined by the triplet relationship. This probabilistic approach should present further advantages in the multisolution procedures. The more accurate value of G in fact should allow a better choice of the starting set of reflexions by the convergence method (Germain, Main & Woolfson, 1970) and should improve the accuracy of the final phases obtained by refinement with the tangent formula (Busetta & Comberton, 1974).

In conclusion, in accordance with our new probabilistic point of view, all the information provided by the cosine invariant computation method should yield the expected value of the cosine invariant and its variance, rather than the 'exact' value of the cosine, whose estimate is in practice unobtainable given the finite number of experimentally available data. If (4) and (5) remain formally valid in this probabilistic approach some consequences of the method may be: (1) The expected values of the cosine invariant will always be allowed values, *i.e.* $|\langle\cos\varphi_{\mathbf{h}_1}+\varphi_{\mathbf{h}_2}+\varphi_{\mathbf{h}_3}\rangle|<1$. The values of the variance will always be positive: the confidence in the expected value of the cosine will be derived from the experimental data and not defined *a priori* (see Busetta & Comberton, 1974). (2) The ability to calculate the expectation value of a cosine invariant, whatever the number of combinations $|E_\mathbf{k}|$, $|E_{\mathbf{h}_1+\mathbf{k}}|,|E_{-\mathbf{h}_3+\mathbf{k}}|$ may be, allows us to make various restrictions on the range of **k**, thus saving computing time. (3) The increased effectiveness of the tangent procedure for the determination of initial phases should reduce the computing time required to implement the least-squares procedure suggested by Hauptman *et al.* (1969) in the early stages of the phasing procedure. It may be noted, moreover, that this new type of direct approach to the phase problem opens new prospects in the problem of enlarging the starting set. In fact probabilistic considerations similar to those here developed for the cosine invariant $\cos(\varphi_{\mathbf{h}_1}+\varphi_{\mathbf{h}_2}+\varphi_{\mathbf{h}_3})$ are applicable to other invariants and seminvariants whose usefulness in the direct process for phase determination has been proved. Our unpublished results obtained in this field are sufficient to encourage their use in the procedures for the solution of large structures.

2. The mathematical preliminaries

The method to be described requires the derivation of a variety of conditional probability distributions. If we denote by $P(E_1,E_2,\ldots,E_n)$ the joint probability function of n normalized structure factors, its characteristic function (Klug, 1958) may be expanded in a

Gram–Charlier series:

$$C(u_1,u_2,\ldots,u_n)=\exp\left[-\tfrac{1}{2}(u_1^2+u_2^2+\ldots+u_n^2)\right]$$
$$\times\left[1+S_3/t^{3/2}+(S_4/t^2+S_3^2/2t^3)+(S_5/t^{5/2}+S_3S_4/t^{7/2}\right.$$
$$\left.+S_3^3/6t^{9/2})+\ldots\right], \tag{6}$$

where $u_i, i=1,\ldots,n$ are carrying variables associated with E_i, t is the number of independent atoms in the unit cell,

$$S_v=t\sum_{r+s+\ldots+w=v}\frac{\lambda_{rs\ldots w}}{r!s!\ldots w!}(iu_1)^r(iu_2)^s\ldots(iu_n)^w,$$

and

$$\lambda_{rs\ldots w}=\frac{K_{rs\ldots w}}{m^{(r+s+\ldots+w)/2}}\,.$$

$K_{rs\ldots w}$ are the cumulants of the distribution and m is the order of the space group. To obtain the probability distribution $P(E_1,E_2,\ldots,E_n)$, the formula

$$\frac{1}{2\pi}\int_{-\infty}^{+\infty}(iu)^v\exp\left[-\tfrac{1}{2}u^2\right]\exp\left[-iux\right]\mathrm{d}u=H_v(x)\varphi(x)\,,$$

finds frequent application. Here $\varphi(x)$ is the standardized Gaussian function

$$\varphi(x)=(2\pi)^{-1/2}\exp\left(-x^2/2\right),$$

and $H_v(x)$ is the Hermite polynomial of vth order defined by the equation

$$H_v(x)=(-1)^v\exp\left(\frac{x^2}{2}\right)\frac{\mathrm{d}^v}{\mathrm{d}x^v}\exp\left[-\tfrac{1}{2}x^2\right].$$

3. The joint probability distribution $P(E_{\mathbf{H}_1},E_{\mathbf{H}_2}, E_{\mathbf{H}_1+\mathbf{H}_2},E_{\mathbf{K}},E_{\mathbf{H}_1+\mathbf{K}},E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}})$

We introduce the abbreviation

$$E_1=E_{\mathbf{H}_1},\ E_2=E_{\mathbf{H}_2},\ E_3=E_{\mathbf{H}_1+\mathbf{H}_2},\ E_4=E_{\mathbf{K}},$$
$$E_5=E_{\mathbf{H}_1+\mathbf{K}},\ E_6=E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}\,.$$

In order to determine (6) we find

$$S_3/t^{3/2}=\frac{1}{\sqrt{N}}\left[(iu_1)(iu_2)(iu_3)+(iu_1)(iu_4)(iu_5)\right.$$
$$\left.+(iu_2)(iu_5)(iu_6)+(iu_3)(iu_4)(iu_6)\right],$$

$$S_4/t^2=-\frac{1}{8N}\left[(iu_1)^4+(iu_2)^4+\ldots+(iu_6)^4\right]$$
$$+\frac{1}{N}\left[(iu_1)(iu_2)(iu_4)(iu_6)\right.$$
$$+(iu_2)(iu_3)(iu_4)(iu_5)$$
$$\left.+(iu_1)(iu_3)(iu_5)(iu_6)\right],$$

$$S_5/t^{5/2}=-\frac{1}{2N\sqrt{N}}\left[(iu_1)^3(iu_2)(iu_3)\right.$$
$$+(iu_1)(iu_2)^3(iu_3)+(iu_1)(iu_2)(iu_3)^3$$
$$+(iu_1)^3(iu_4)(iu_5)+\text{cyclic terms}$$
$$+(iu_2)^3(iu_5)(iu_6)+\text{cyclic terms}$$
$$\left.+(iu_3)^3(iu_4)(iu_6)+\text{cyclic terms}\right].$$

The form of the probability distribution function $P(E_1,E_2,\ldots,E_6)$ is shown in Appendix A. From the calculations there performed we obtain

$$P_+(E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2})\simeq\tfrac{1}{2}+\tfrac{1}{2}\tanh G_{\mathbf{H}_1,\mathbf{H}_2}\,, \tag{7}$$

where

$$G_{\mathbf{H}_1,\mathbf{H}_2}=\frac{1}{\sqrt{N}}\left|E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}\right|\left(1+\frac{A}{B}\right),$$

$$A=(E_{\mathbf{K}}^2-1)\,(E_{\mathbf{H}_1+\mathbf{K}}^2-1)\,(E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}^2-1)/N$$

and

$$B=1+\left[(E_{\mathbf{K}}^2-1)\,(E_{\mathbf{H}_1+\mathbf{K}}^2-1)+(E_{\mathbf{K}}^2-1)\,(E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}^2-1)\right.$$
$$\left.+(E_{\mathbf{H}_1+\mathbf{K}}^2-1)\,(E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}^2-1)+3\right]/N$$
$$-\left[H_4(E_{\mathbf{K}})+H_4(E_{\mathbf{H}_1+\mathbf{K}})+H_4(E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}})\right]/8N\,.$$

Formally speaking, (7) preserves the tangent formulation provided by the Cochran–Woolfson relation

$$P_+\simeq\tfrac{1}{2}+\tfrac{1}{2}\tanh\frac{1}{\sqrt{N}}\left|E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}\right|, \tag{8}$$

but seems able to improve (8) when one or more triples $(|E_{\mathbf{K}}|,|E_{\mathbf{H}_1+\mathbf{K}}|,|E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}|)$ are known *a priori.*

In particular, knowledge of the moduli $|E_{\mathbf{K}}|$, $|E_{\mathbf{H}_1+\mathbf{K}}|$, $|E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}|$ affects the probability values provided by (8) for the triplet $E_{\mathbf{H}_1},E_{\mathbf{H}_2},E_{\mathbf{H}_1+\mathbf{H}_2}$ in terms of the ratio A/B. This ratio is of order $1/N\sqrt{N}$: so, when N is large enough, knowledge of only a single triple $(|E_{\mathbf{K}}|,|E_{\mathbf{H}_1+\mathbf{K}}|,|E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}|)$ is not able to modify significantly the probability values provided by the Cochran–Woolfson formula. However, for fixed $\mathbf{H}_1$ and $\mathbf{H}_2$ vectors, numerous triples $\mathbf{K},\mathbf{H}_1+\mathbf{K},\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}$ exist in general in the set of measured reflexions; it seems useful then to study more general probability distributions which are able to take into account a larger number of contributors.

4. The joint probability distribution $P(E_{\mathbf{H}_1},E_{\mathbf{H}_2},E_{\mathbf{H}_1+\mathbf{H}_2}, E_{\mathbf{K}_1},E_{\mathbf{H}_1+\mathbf{K}_1},E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}_1},E_{\mathbf{K}_2},E_{\mathbf{H}_1+\mathbf{K}_2},E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}_2},\ldots$

The study of this distribution leads us once more to (7), but now

$$A\simeq\sum_{\mathbf{K}}(E_{\mathbf{K}}^2-1)\,(E_{\mathbf{H}_1+\mathbf{K}}^2-1)\,(E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}^2-1)/N\,, \tag{9}$$

$$B\simeq1+\sum_{\mathbf{K}}\left[(E_{\mathbf{K}}^2-1)\,(E_{\mathbf{H}_1+\mathbf{K}}^2-1)+(E_{\mathbf{K}}^2-1)\right.$$
$$\times\,(E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}^2-1)+(E_{\mathbf{H}_1+\mathbf{K}}^2-1)$$
$$\left.+\,(E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}^2-1)\right]/N$$
$$-\sum_{\mathbf{K}}\left[H_4(E_{\mathbf{K}})+H_4(E_{\mathbf{H}_1+\mathbf{K}})+H_4(E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}})\right]/8N\,. \tag{10}$$

If the summations in (9) and (10) involve a sufficient number of triples $(E_{\mathbf{K}},E_{\mathbf{H}_1+\mathbf{K}},E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}})$ (7) may strongly affect the positivity required by (8). Thus triplets whose signs are defined to be negative by (7) with high probability should be particularly useful in the procedures for phase solution retaining their character of negativity. In these cases

$$S(E_{\mathbf{H}_1+\mathbf{H}_2}) \simeq -S(E_{\mathbf{H}_1})S(E_{\mathbf{H}_2}) .$$

From now on when we refer to (7) it will be understood that A and B are defined by (9) and (10).

5. The estimation of A and B

From the algebraic form of (7) one should deduce that triplets strongly defined to be positive are marked by large positive values of A and small values of B. Triplets strongly defined to be negative will arise from large negative values of A and small values of B. On the other hand large positive values of A and B should not greatly affect the Cochran–Woolfson relation.

If we write

$$B=1+Q ,$$

we observe that the function A/B presents a discontinuity when $Q=-1$. This behaviour has no physical meaning and is due to including in (7) only terms up to $1/N^{3/2}$. In fact we have represented the probability distributions as asymptotic Gram–Charlier series and the actual values of probability we obtain will be correct to the degree of approximation we choose.

In order to understand the role played by each of the summations in A and B it seems useful to derive, given a triplet $E_{\mathbf{H}_1}, E_{\mathbf{H}_2}, E_{\mathbf{H}_1+\mathbf{H}_2}$, their expected values. If the summations in (9) and (10) involve a large number of terms, their estimates will be related to the following mean values:

$$\langle (E^2_{\mathbf{K}}-1)\,(E^2_{\mathbf{H}_1+\mathbf{K}}-1)\,(E^2_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}-1)\rangle \simeq \frac{8}{P}\,\frac{E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}}{N\sqrt{N}} , \tag{11}$$

$$\begin{aligned}\langle (E^2_{\mathbf{K}}-1)\,(E^2_{\mathbf{H}_1+\mathbf{K}}-1)+(E^2_{\mathbf{K}}-1)\,(E^2_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}-1)\\ +(E^2_{\mathbf{H}_1+\mathbf{K}}-1)\,(E^2_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}-1)\rangle\\ \simeq \frac{2}{P}\,(E^2_{\mathbf{H}_1}+E^2_{\mathbf{H}_2}+E^2_{\mathbf{H}_1+\mathbf{H}_2}-3)\\ \times\left(\frac{1}{N}+\frac{E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}}{N\sqrt{N}}\right) ,\end{aligned} \tag{12}$$

$$\langle H_4(E_{\mathbf{K}})+H_4(E_{\mathbf{H}_1+\mathbf{K}})+H_4(E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}})\rangle \simeq -\frac{9}{N} , \tag{13}$$

where P is a function of $E_{\mathbf{H}_1}, E_{\mathbf{H}_2}, E_{\mathbf{H}_1+\mathbf{H}_2}$ not defined because it is not relevant for our present purpose.

Whereas (11) clarifies the meaning of A (its sign should coincide with that of $E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}$), suitable estimation of B requires some observations. (*a*) The first term of (12) depends on the sign of $E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}$: in particular, it should assume small values when that sign is negative. This behaviour suggests that negative triplets should be marked by large negative values of (11) and small positive values of (12), so giving rise to strong corrections of the Cochran–Woolfson formula. (*b*) If N is large enough and $E^2_{\mathbf{H}_1}+E^2_{\mathbf{H}_2}+E^2_{\mathbf{H}_1+\mathbf{H}_2}>3$, the value of (12) is always positive. One should then set the first term of (12) equal to zero when it has been calculated negative. (*c*) The estimation of (13) involves Hermite polynomials of order four. The values of these polynomials are also sensitive to experimental errors in the estimation of the $|E|$'s (see Fig. 1). Furthermore, (13) does not contain any information on the sign of $E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}$. Its estimation therefore may be omitted in the procedures for phase solution, as much in the interest of simplification as in the expectation that its effect will be negligible.

6. Strengthened Σ_1 relationship

From the joint probability distribution $P(E_{\mathbf{H}}, E_{2\mathbf{H}}, E_{\mathbf{K}}, E_{\mathbf{H}+\mathbf{K}}, E_{2\mathbf{H}+\mathbf{K}})$ we obtain

$$P_+[(E^2_{\mathbf{H}}-1)E_{2\mathbf{H}}] \simeq 0{\cdot}5 + 0{\cdot}5 \tanh \frac{|(E^2_{\mathbf{H}}-1)E_{2\mathbf{H}}|}{2\sqrt{N}}\left(1+\frac{C}{D}\right) , \tag{14}$$

where

$$\begin{aligned}C &\simeq 2 \sum_{\mathbf{K}} (E^2_{\mathbf{K}}-1)\,(E^2_{\mathbf{H}+\mathbf{K}}-1)\,(E^2_{2\mathbf{H}+\mathbf{K}}-1)/N ,\\ D &\simeq 1+\{2 \sum_{\mathbf{K}} [(E^2_{\mathbf{K}}-1)\,(E^2_{\mathbf{H}+\mathbf{K}}-1)\\ &\quad +(E^2_{\mathbf{H}+\mathbf{K}}-1)\,(E^2_{2\mathbf{H}+\mathbf{K}}-1)]\\ &\quad +\sum_{\mathbf{K}} (E^2_{\mathbf{K}}-1)\,(E^2_{2\mathbf{H}+\mathbf{K}}-1)\}/N .\end{aligned}$$

(14) is derived in Appendix *B*.

7. Experimental results

Four model structures ($P\bar{1}$) have been used in order to test (7). The first contains 35 atoms at random positions in the asymmetric unit ($N=70$); the second, third

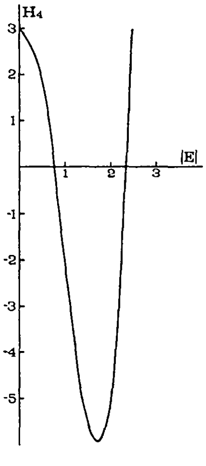

Fig. 1. The Hermite polynomial of order four plotted in the range of the observed $|E|$'s.

and fourth structures contain 100, 200, 300 atoms in the unit cell respectively. In Tables 1–4 the reliability of (7) is compared with that of the Cochran–Woolfson relation (8): $\sum_1$ relations were excluded from the calculations. In accordance with the observations made in § 5, the value of B is calculated omitting the Hermite polynomials of order four. In the tables the number of relations and the percentage of correct ones are given along with the corresponding values of the arguments of the hyperbolic tangent. As may be observed, the percentages of correct relations calculated by (7) are markedly better than the percentages obtained by the Cochran–Woolfson formula. Our approach seems then advisable in the more difficult structures where (8) may fail.

Table 1. *Number of triplet relations* (*nr*) *and percentage of correct relations for a* 70-*atom model structure*

tanh	Equation (8)		Equation (7)		Equation (15)	
|arg|	nr.	%	nr.	%	nr.	%
0·6	1099	92·4	982	96·7	967	96·9
0·8	951	94·1	868	98·7	888	97·7
1·0	578	96·7	708	99·6	779	99·0
1·2	348	98·9	529	100	651	99·5
1·4	170	99·4	380	100	504	99·8
1·6	77	100	242	100	379	100
2·0	13	100	97	100	189	100
2·4	4	100	36	100	95	100
2·8			9	100	40	100
3·2			1	100	18	100
3·4					10	100

Table 2. *Number of triplet relations* (*nr*) *and percentage of correct relations for a* 100-*atom model structure*

tanh	Equation (8)		Equation (7)		Equation (15)	
|arg|	nr.	%	nr.	%	nr.	%
0·6	1319	92·1	1265	96·0	1242	96·4
0·8	1134	93·2	1086	98·0	1134	97·4
1·0	784	95·8	862	99·4	990	98·6
1·2	460	97·0	651	100	802	99·1
1·4	262	98·9	468	100	648	99·5
1·6	152	100	325	100	499	100
2·0	45	100	167	100	295	100
2·4	13	100	67	100	169	100
2·8	2	100	31	100	97	100
3·2			13	100	50	100
3·4			9	100	42	100
3·8			3	100	18	100

Table 3. *Number of triplet relations* (*nr*) *and percentage of correct relations for a* 200-*atom model structure*

tanh	Equation (8)		Equation (7)		Equation (15)	
|arg|	nr.	%	nr.	%	nr.	%
0·6	1298	86·7	1092	90·6	1079	89·6
0·8	758	89·2	769	93·2	843	91·3
1·0	364	90·9	491	93·9	596	93·8
1·2	127	89·0	277	97·1	362	95·6
1·4	52	82·7	167	97·6	224	96·4
1·6	5	100	88	96·6	128	96·9
2·0			24	100	41	95·1
2·4			4	100	12	100
2·8			2	100	4	100
3·2					4	100
3·4					4	100

Table 4. *Number of triplet relations* (*nr*) *and percentage of correct relations for a* 300-*atom model structure*

tanh	Equation (8)		Equation (7)		Equation (15)	
|arg|	nr.	%	nr.	%	nr.	%
0·6	885	86·0	710	90·8	733	90·0
0·8	668	91·5	566	94·3	625	92·8
1·0	333	89·5	416	96·6	475	95·4
1·2	130	90·0	268	97·8	331	98·2
1·4	55	100	170	97·1	229	97·8
1·6	9	100	92	97·8	150	98·0
2·0			50	100	61	100
2·4			22	100	36	100
2·8			11	100	16	100
3·2			5	100	1	100
3·4			4	100	1	100

8. A constrained formula

In order to define the sign of $E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}$, (7) requires the availability of a number of triples ($E_{\mathbf{K}}$, $E_{\mathbf{H}_1+\mathbf{K}}, E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}$). The data shown in Tables 1–4 were calculated by allowing $\mathbf{K}$ to vary over all the available set of reflexions. 3055, 4617, 7799, 13921 independent normalized structure factors constitute the sets of reflexions generated for the model structures with $N=70$, 100, 200, 300 respectively (see Table 5).

Table 5. *Application of* (7) *and* (15) *to the four model structures*: *some experimental data*

N	Number of independent reflexions used for (7)	Number of independent reflexions available for (15) when $\alpha=0{\cdot}8$	Values of (16) when $\alpha=0{\cdot}0$	Values of (16) when $\alpha=0{\cdot}8$
70	3055	1604	0·327	0·651
100	4617	2365	0·296	0·632
200	7799	4035	0·324	0·558
300	13921	7319	0·396	0·578

In order to reduce computing time, a modification of (7) would be desirable which permits the use of a limited subset of the experimental data in obtaining the sign of the triplets without too great a penalty. In this connexion we observe that the more $(E^2_{\mathbf{K}}-1)$ $(E^2_{\mathbf{H}_1+\mathbf{K}}-1)$ $(E^2_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}-1)$ differs from zero the more the triples $E_{\mathbf{K}}, E_{\mathbf{H}_1+\mathbf{K}}, E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}$ help (in a probabilistic sense) in determining the sign of $E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}$. Therefore a basis for selecting a properly chosen subset of data should be the requirement that, for each $E_{\mathbf{K}}$, $E_{\mathbf{H}_1+\mathbf{K}}, E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}$,

$$|E^2-1|>\alpha\,.$$

The constrained probability value defined under these conditions will be

$$P_+(E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}\,|\,|E^2_{\mathbf{K}}-1|>\alpha\,,\quad |E^2_{\mathbf{H}_1+\mathbf{K}}-1|>\alpha\,,\quad |E^2_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}-1|>\alpha)\,. \qquad (15)$$

It has been an empirical observation in this laboratory that good accuracy in the determination of the signs of the triplets may be obtained even when $\alpha\geq 0{\cdot}8$. Therefore (15) has been calculated when $\alpha=0{\cdot}8$ for all the model structures: the outcome is shown in Tables 1–4. Under this condition the number of reflexions available for (15) for each model structure is shown in Table 5. From Tables 1–4 we deduce that the constrained formula improves the Cochran–Woolfson relation even if it is a little worse than (7). Its use seems advisable mostly when computer time must be saved by the crystallographer. It should be emphasized that (15) is not the only way of obtaining constrained formula, *i.e.* in the $M(D-KS)$ formula (3), which also purports to be an improvement over (8), a different constraint is suggested. However (3) and (15) [or (7)] are well correlated: specifically, if **K** is such that the $|E_{\mathbf{K}}|$ and $|E_{\mathbf{H}_1+\mathbf{K}}|$ are both large, then both (3) and (15) yield positive or negative estimates for $E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}$ according to whether $|E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}|$ is mostly large or mostly small, respectively. In order to simplify this paper we will deal with this kind of theoretical aspect in a following paper, where the non-centrosymmetric case will be explored.

9. The limits of our approach

For a given structure (7) may improve (8) only marginally when the set of experimental data is confined to very low scattering angles. In this case in fact the average number of triples $(|E_{\mathbf{K}}|, |E_{\mathbf{H}_1+\mathbf{K}}|, |E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}|)$ available for use in (7) for each triplet $E_{\mathbf{H}_1}, E_{\mathbf{H}_2}, E_{\mathbf{H}_1+\mathbf{H}_2}$ will not be large enough to improve the Cochran–Woolfson relation significantly. An *a posteriori* measure of this correction may be deduced from the quantity

$$\sum_{\mathbf{H}_1,\mathbf{H}_2} |A_{\mathbf{H}_1,\mathbf{H}_2}| \Big/ \sum_{\mathbf{H}_1,\mathbf{H}_2} B_{\mathbf{H}_1,\mathbf{H}_2}\,, \qquad (16)$$

where the summation is to be taken over the set of the estimated triplets.

In Table 5 we give the experimental values of (16) for the four model structures when (7) and (15) are calculated. In our experience, values of (16) greater than or equal to 0·15 normally lead to notable gains in reliability in comparison with the Cochran–Woolfson relation. So (7) should make the solution of a crystal structure easier when the number of available reflexions (expanded to include all equivalent reflexions) is larger than $40N$.

A question arises: '(7) draws its advantage from the fact that it is able to use the information contained in all reciprocal space. Is then its effectiveness independent of the structural complexity, provided a sufficiently large number of reflexions is available ($\sim 100\ N$)?' An affirmative answer to the question would require the following statement: 'the effectiveness of (7) is directly related to the value of (16). If the number of available reflexions is large enough to yield large values of (16), the effectiveness of (7) is secured independently of the structural complexity'. This statement has not in reality been verified.

We observe in this connexion: (*a*) in spite of the values of (16), (7) is more effective in the model structures with $N=70$, 100 rather than when $N=200$, 300, and (*b*) the values of (16) arising from the use of (15) are larger than the corresponding values obtained by (7). In other words, in spite of the smaller number of triples $(|E_{\mathbf{K}}|, |E_{\mathbf{H}_1+\mathbf{K}}|, |E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}|)$ checked by the constrained formula, the Cochran–Woolfson relation is more severely modified by (15) than by (7). (7) nevertheless, is more reliable than (15).

A theoretical answer to the lack of effectiveness of (7) as a function of the structural complexity may be given in terms of the probability theory. As the atomic coordinates were assumed in our approach to be independent random variables which are uniformly distributed, all the E factors involved in the distribution can be themselves considered random variables. The quantity $(E^2_{\mathbf{K}}-1)\,(E^2_{\mathbf{H}_1+\mathbf{K}}-1)\,(E^2_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}-1)$ is then a function of random variables whose conditional distribution, for fixed $|E_{\mathbf{H}_1}|, |E_{\mathbf{H}_2}|, |E_{\mathbf{H}_1+\mathbf{H}_2}|$, may be easily derived from (A1). Also the quantity

$$\langle A\rangle = \sum_{\mathbf{K}} (E^2_{\mathbf{K}}-1)\,(E^2_{\mathbf{H}_1+\mathbf{K}}-1)\,(E^2_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}-1)$$

is a function of random variables, for which we obtain

$$P_+[S(\langle A\rangle)S(E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2})] \simeq 0{\cdot}5 + 0{\cdot}5 \text{ than } \frac{|\langle A\rangle\,.\,E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}|}{N\sqrt{N}}\,. \qquad (17)$$

The left-hand side of (17) denotes the probability that the sign of $\langle A\rangle$ coincide with that of the triplet. It is evident from (7) that the more complex the structure becomes, the smaller, in the average sense, is the probability of the sign coincidence between $\langle A\rangle$ and the corresponding triplet.

In conclusion, (7) enlarges the range of the structures to which direct methods may be succesfully applied. (7) in fact is less sensitive than (8) to the structural complexity and to structural regularities, since it makes use also of the information in all reciprocal space. Its effectiveness nevertheless decreases with N: the more complex the structure the less the values of $\langle A\rangle$ are closely distributed around the corresponding $E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}$ values. In our opinion, structures with up to 100 atoms in the asymmetric unit may in favourable conditions be solved routinely by (7) in a multisolution procedure.

10. A procedure for the quadrupole methods

Burzlaff & Böhme (1975) recently described a formula which is used to derive from the P_+ values of the triplets which constitute quadrupoles an improved probability value for a chosen triplet. The method would be of great advantage in large structures if a significant percentage of the negative triplets would present input values of $P_+ \leq 0{\cdot}50$. Although (7) seems more suitable than (8), the percentage of the triplets defined to be negative by (7) is in general too small. Furthermore, for a given structure we do not know *a priori* the real percentage of negative triplets. However from the triplet theory the expected value P_t of this percentage may be derived, whatever the structure may be. The set of experimental G values provided by (7) should then be modified in such a way as to yield a percentage of negative triplets close to P_t.

A simple way is to modify each value $G_{\mathbf{H}_1,\mathbf{H}_2}$ by a quantity proportional to

$$Q_{\mathbf{H}_1,\mathbf{H}_2} \simeq \frac{1}{\sqrt{N}} |E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}| \, (A_{\mathbf{H}_1,\mathbf{H}_2}/B_{\mathbf{H}_1,\mathbf{H}_2})$$

so that the set of values

$$G'_{\mathbf{H}_1,\mathbf{H}_2} = G_{\mathbf{H}_1,\mathbf{H}_2} + Q_{\mathbf{H}_1,\mathbf{H}_2}\theta$$

yields a percentage of negative triplets close to P_t. This procedure, emphasizing the role of the terms $|E_{\mathbf{K}}|, |E_{\mathbf{H}_1+\mathbf{K}}|, |E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}|$, may introduce errors in the probability values. These errors may subsequently be corrected by application of the quadrupole method.

The determination of the factor θ is a trivial task if P_t is known. In its turn P_t may be easily defined for a given structure for any threshold value E_s (only the $|E| > E_s$ are used to obtain the $\sum_2$ relationships).

Let us denote by Ω the set of the couples ($E_{\mathbf{K}}$, $E_{\mathbf{H}+\mathbf{K}}$) which (*a*) lie in the third quadrant of the plane ($E_{\mathbf{K}}, E_{\mathbf{H}+\mathbf{K}}$); (*b*) have moduli larger than E_s; (*c*) form triplets with a fixed **H** reflexion whose $|E|$ is larger than E_s.

Then the integral (Giacovazzo, 1974)

$$I(E_{\mathbf{H}}, E_s, N) = \int_{-\infty}^{-E_s} \int_{\infty-}^{-E_s} P(E_{\mathbf{K}}, E_{\mathbf{H}+\mathbf{K}}) \mathrm{d}E_{\mathbf{K}} \mathrm{d}E_{\mathbf{H}+\mathbf{K}}$$
$$= \sum_{\nu=0}^{\infty} \frac{[\Phi^{(\nu)}(-E_s)]^2}{\nu!} \left(\frac{E_{\mathbf{H}}}{\sqrt{N}}\right)^{\nu}$$

represents the population of the normalized structure factors which belong to Ω. $\Phi^{(\nu)}$ is the νth derivative of

$$\Phi(x) = \frac{1}{\sqrt{(2\pi)}} \int_{-\infty}^{x} \exp(-t^2/2) \mathrm{d}t \, .$$

In its turn

$$Y_1(E_s, N) = \frac{1}{\sqrt{(2\pi)}} \int_{E_s}^{\infty} \exp(-E_{\mathbf{H}}^2/2) \times \sum_{\nu=0}^{\infty} \frac{[\Phi^{(\nu)}(-E_s)]^2}{\nu!} \left(\frac{E_{\mathbf{H}}}{\sqrt{N}}\right)^{\nu} \mathrm{d}E_{\mathbf{H}} \qquad (18)$$

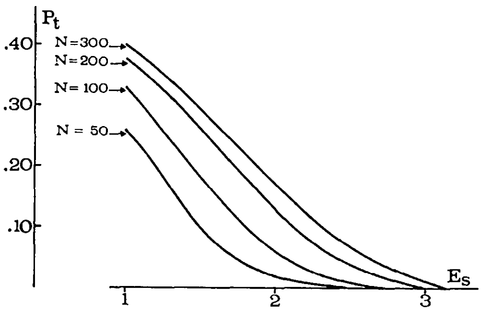

Fig. 2. Percentage of negative triplets as a function of the threshold value E_s.

represents the population of the couples ($E_{\mathbf{K}}, E_{\mathbf{H}+\mathbf{K}}$) belonging to Ω which form positive triplets with all the $E_{\mathbf{H}}$ factors whose moduli lie in the range (E_s, ∞).

The population of the couples belonging to Ω which form positive and negative triplets with all the $E_{\mathbf{H}}$ factors whose moduli lie in the range (E_s, ∞) is (Giacovazzo, 1974)

$$Y_2(E_s, N) = \frac{1}{\sqrt{(2\pi)}} \int_{E_s}^{\infty} \exp(-E_{\mathbf{H}}^2/2) \times \sum_{\nu=0}^{\infty} \frac{[\Phi^{(\nu)}(-E_s)]^2}{\nu!} \left(\frac{E_{\mathbf{H}}}{\sqrt{N}}\right) [1-(1)^{\nu}] \mathrm{d}E_{\mathbf{H}} \, . \qquad (19)$$

From (18) and (19) the expected percentage of the negative triplets when only the normalized structure factors with $|E| > E_s$ are used is

$$P_t(E_s, N) = 1 - Y_1/Y_2 \, .$$

Owing to the fast convergence of the series involved, Y_1 and Y_2 are easily computable. When the first eight terms in the summations in Y_1 and Y_2 are calculated, 0·04 s should be consumed by an IBM 370/158 in order to calculate P_t. In Fig. 2 we have plotted some curves, each corresponding to a single value of N. So, for a structure with $N = 100$, the expected percentage of negative triplets when $E_s = 2{\cdot}2$ is 0·03; this percentage increases to 0·15 when $E_s = 1{\cdot}60$.

11. Conclusions

A probabilistic theory is described which may be used to derive from the distribution $P(E_{\mathbf{H}_1}, E_{\mathbf{H}_2}, E_{\mathbf{H}_1+\mathbf{H}_2}, E_{\mathbf{K}}, E_{\mathbf{H}_1+\mathbf{K}}, E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}})$ a probability value for the sign of $E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}$. The reliability of the sign indication depends on a statistical moment of order

$$\frac{1}{\sqrt{N}} \left(i.e. \; \frac{E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}}{\sqrt{N}}\right),$$

one or more moments of order

$$1/N \{i.e. \sum_{\mathbf{K}} [(E_{\mathbf{K}}^2-1)(E_{\mathbf{H}_1+\mathbf{K}}^2-1) + (E_{\mathbf{K}}^2-1)(E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}^2-1) + (E_{\mathbf{H}_1+\mathbf{K}}^2-1)(E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}^2-1)]\},$$

one or more moments of order $1/N\sqrt{N}$

$$[i.e. \sum_{\mathbf{K}} (E_{\mathbf{K}}^2-1)(E_{\mathbf{H}_1+\mathbf{K}}^2-1)(E_{\mathbf{H}_1+\mathbf{H}_2+\mathbf{K}}^2-1)] \, .$$

The phase relations so stated markedly improve the Cochran–Woolfson relation and seem especially suitable to the structures in which the latter relation fails. The new formulae consume much more computing time than the Cochran–Woolfson relation. Nevertheless new computing techniques such as that described by Busetta & Comberton (1974) seem able to reduce this disadvantage.

APPENDIX *A*

The Fourier transform of (6) gives

$$
\begin{aligned}
P(E_1,E_2,\ldots,E_6) &= \frac{1}{(2\pi)^3} \\
&\times \exp\left[-\tfrac{1}{2}(E_1^2+E_2^2+\ldots+E_6^2)\right]\{1 \\
&+\frac{1}{\sqrt{N}}[E_1E_2E_3+E_1E_4E_5+E_2E_5E_6+E_3E_4E_6] \\
&-\frac{1}{8N}[H_4(E_1)+H_4(E_2)+\ldots+H_4(E_6)] \\
&+\frac{1}{N}[E_1E_2E_4E_6+E_2E_3E_4E_5+E_1E_3E_5E_6] \\
&+\frac{1}{2N}[(E_1^2-1)(E_2^2-1)(E_3^2-1) \\
&+(E_1^2-1)(E_4^2-1)(E_5^2-1) \\
&+(E_2^2-1)(E_5^2-1)(E_6^2-1) \\
&+(E_3^2-1)(E_4^2-1)(E_6^2-1)+2(E_1^2-1)E_2E_3E_4E_5 \\
&+2E_1(E_2^2-1)E_3E_5E_6+2E_1E_2(E_3^2-1)E_4E_6 \\
&+2E_1E_2E_4(E_5^2-1)E_6+2E_1E_3(E_4^2-1)E_5E_6 \\
&+2E_2E_3E_4E_5(E_6^2-1)] \\
&+\frac{1}{6N\sqrt{N}}[H_3(E_1)H_3(E_2)H_3(E_3) \\
&+H_3(E_1)H_3(E_4)H_3(E_5)+H_3(E_2)H_3(E_5)H_3(E_6) \\
&+H_3(E_3)H_3(E_4)H_3(E_6)+3H_3(E_1)(E_2^2-1)(E_3^2-1) \\
&+E_4E_5+3H_3(E_1)E_2E_3(E_4^2-1)(E_5^2-1) \\
&+3(E_1^2-1)H_3(E_2)(E_3^2-1)E_5E_6 \\
&+3E_1H_3(E_2)E_3(E_5^2-1)(E_6^2-1) \\
&+3(E_1^2-1)(E_2^2-1)H_3(E_3)E_4E_6 \\
&+3E_1E_2H_3(E_3)(E_4^2-1)(E_6^2-1) \\
&+3(E_1^2-1)E_2(E_4^2-1)H_3(E_5)E_6 \\
&+3E_1(E_2^2-1)E_4H_3(E_5)(E_6^2-1) \\
&+3(E_1^2-1)E_3H_3(E_4)(E_5^2-1)E_6 \\
&+3E_1(E_3^2-1)H_3(E_4)E_5(E_6^2-1) \\
&+3(E_2^2-1)E_3E_4(E_5^2-1)H_3(E_6) \\
&+3E_2(E_3^2-1)(E_4^2-1)E_5H_3(E_6) \\
&+6(E_1^2-1)(E_2^2-1)E_3E_4(E_5^2-1)E_6 \\
&+6(E_1^2-1)E_2(E_3^2-1)(E_4^2-1)E_5E_6 \\
&+6E_1(E_2^2-1)(E_3^2-1)E_4E_5(E_6^2-1) \\
&+6E_1E_2E_3(E_4^2-1)(E_5^2-1)(E_6^2-1)] \\
&-\frac{1}{2N\sqrt{N}}[H_3(E_1)E_2E_3+E_1H_3(E_2)E_3+E_1E_2H_3(E_3) \\
&+H_3(E_1)E_4E_5+\text{cyclic terms} \\
&+H_3(E_2)E_5E_6+\text{cyclic terms} \\
&+H_3(E_3)E_4E_6+\text{cyclic terms}] \\
&+\frac{1}{N\sqrt{N}}[(E_1^2-1)(E_2^2-1)E_3E_4E_6 \\
&+E_1(E_2^2-1)(E_3^2-1)E_4E_5+(E_1^2-1)E_2(E_3^2-1)E_5E_6 \\
&+(E_1^2-1)E_2(E_4^2-1)E_5E_6+E_1E_2E_3(E_4^2-1)(E_5^2-1) \\
&+(E_1^2-1)E_3E_4(E_5^2-1)E_6+E_1(E_2^2-1)E_4E_5(E_6^2-1) \\
&+(E_2^2-1)E_3E_4(E_5^2-1)E_6+E_1E_2E_3(E_5^2-1)(E_6^2-1) \\
&+E_1E_2E_3(E_4^2-1)(E_6^2-1)+E_2(E_3^2-1)(E_4^2-1)E_5E_6 \\
&+E_1(E_3^2-1)E_4E_5(E_6^2-1)] \\
&-\frac{1}{8N\sqrt{N}}[H_5(E_1)E_2E_3+H_5(E_1)E_4E_5 \\
&+H_4(E_1)E_2E_5E_6 \\
&+H_4(E_1)E_3E_4E_6+E_1H_5(E_2)E_3+E_1H_4(E_2)E_4E_5 \\
&+H_5(E_2)E_5E_6+H_4(E_2)E_3E_4E_6+E_1E_2H_5(E_3) \\
&+E_1H_4(E_3)E_4E_5+E_2H_4(E_3)E_5E_6+H_5(E_3)E_4E_6 \\
&+E_1E_2E_3H_4(E_4)+E_1H_5(E_4)E_5+E_2H_4(E_4)E_5E_6 \\
&+E_3H_5(E_4)E_6+E_1E_2E_3H_4(E_5)+E_1E_4H_5(E_5) \\
&+E_2H_5(E_5)E_6+E_3E_4H_4(E_5)E_6+E_1E_2E_3H_4(E_6) \\
&+E_1E_4E_5H_4(E_6)+E_2E_5H_5(E_6)+E_3E_4H_5(E_6)]\}
\end{aligned}
\qquad (A1)
$$

The conditional joint probability distribution $P(E_1,E_2,E_3 \mid E_4,E_5,E_6)$ is easily obtained from (*A*1):

$$
\begin{aligned}
&P(E_1,E_2,E_3 \mid E_4,E_5,E_6) \\
&\quad = \frac{P(E_1,E_2,E_3,E_4,E_4,E_5,E_6)}{\displaystyle\iiint_{-\infty}^{+\infty} P(E_1,E_2,\ldots,E_6)\mathrm{d}E_1\mathrm{d}E_2\mathrm{d}E_3}\,.
\end{aligned}
\qquad (A2)
$$

The denominator of (*A*2), after some calculation, becomes

$$
\begin{aligned}
&\frac{1}{(2\pi)^3}\exp\left[-\tfrac{1}{2}(E_4^2+E_5^2+E_6^2)\right](\sqrt{2\pi})^3 \\
&\qquad \times\{1-[H_4(E_4)+H_4(E_5)+H_4(E_6)]/8N\}\,.
\end{aligned}
$$

Finally, we obtain the conditional expected value

$$
\begin{aligned}
&\langle E_1E_2E_3 \mid E_4,E_5,E_6\rangle \\
&=\iiint_{-\infty}^{+\infty} E_1E_2E_3P(E_1,E_2,E_3 \mid E_4,E_5,E_6)\mathrm{d}E_1\mathrm{d}E_2\mathrm{d}E_3 \\
&=\frac{1}{1-[H_4(E_4)+H_4(E_5)+H_4(E_6)]/8N} \\
&\times\frac{1}{\sqrt{N}}\left\{1+\frac{1}{N}[(E_4^2-1)(E_5^2-1)(E_6^2-1)\right. \\
&+(E_4^2-1)(E_5^2-1)+(E_4^2-1)(E_6^2-1) \\
&+(E_5^2-1)(E_6^2-1)] \\
&\left.-\frac{1}{8N}[H_4(E_4)+H_4(E_5)+H_4(E_6)]\right\}.
\end{aligned}
\qquad (A3)
$$

Likewise

$$\begin{aligned}\langle E_1^2E_2^2E_3^2|E_4,E_5,E_6\rangle &= \frac{1}{1-[H_4(E_4)+H_4(E_5)+H_4(E_6)]/8N}\\ &\times\{1-[H_4(E_4)+H_4(E_5)+H_4(E_6)]/8N\\ &+[(E_4^2-1)(E_5^2-1)+(E_4^2-1)(E_6^2-1)\\ &+(E_5^2-1)(E_6^2-1)+4]/N\}\,. \end{aligned}\qquad (A4)$$

Since the conditional probability distribution of the random variable $R=E_1E_2E_3$ may be expanded in a Gram–Charlier series (Cramér, 1951), we may write

$$P(R|E_4,E_5,E_6)=\frac{1}{\sigma\sqrt{(2\pi)}}\exp\left[\frac{-(R-\langle R\rangle)^2}{2\sigma^2}\right]+\ldots$$

where R is given by (A3) and

$$\begin{aligned}\sigma^2 &= \langle E_1^2E_2^2E_3^2|E_4,E_5,E_6\rangle-\langle E_1E_2E_3|E_4,E_5,E_6\rangle^2\\ &= \frac{1}{1-[H_4(E_4)+H_4(E_5)+H_4(E_6)]/8N}\\ &\times\{1-[H_4(E_4)+H_4(E_5)+H_4(E_6)]/8N\\ &+[(E_4^2-1)(E_5^2-1)+(E_4^2-1)(E_6^2-1)\\ &+(E_5^2-1)(E_6^2-1)+3]/N\}\,. \end{aligned}\qquad (A5)$$

For the sake of simplicity we have neglected in (A5) the $1/N^2$ and higher-order terms arising in $\langle E_1E_2E_3|E_4,E_5,E_6\rangle^2$ and have employed also

$$\begin{aligned}&\{1-[H_4(E_4)+H_4(E_5)+H_4(E_6)]/8N\}^{-2}\\ &\qquad\simeq\{1-[H_4(E_4)+H_4(E_5)+H_4(H_6)]/8N\}^{-1}.\end{aligned}$$

These approximations may occasionally result in some error, but in practice are not critical.

As $P_+=(P_-/P_++1)^{-1}$, we obtain

$$\begin{aligned}P_+ &= \tfrac{1}{2}+\tfrac{1}{2}\tanh\frac{1}{\sqrt{N}}\,|E_1E_2E_3|\\ &\times\frac{1}{Q}\left\{1+\frac{1}{N}(E_4^2-1)(E_5^2-1)(E_6^2-1)\right.\\ &+\frac{1}{N}[(E_4^2-1)(E_5^2-1)+(E_4^2-1)(E_6^2-1)\\ &+(E_5^2-1)(E_6^2-1)]\\ &\left.-\frac{1}{8N}[H_4(E_4)+H_4(E_5)+H_4(E_6)]\right\}, \end{aligned}\qquad (A6)$$

where

$$\begin{aligned}Q &= 1+\frac{1}{N}[(E_4^2-1)(E_5^2-1)+(E_4^2-1)(E_6^2-1)\\ &+(E_5^2-1)(E_6^2-1)+3]\\ &-\frac{1}{8N}[H_4(E_4)+H_4(E_5)+H_4(E_6)]\,.\end{aligned}$$

APPENDIX *B*

From the joint probability distribution $P(E_{\mathbf{H}},E_{2\mathbf{H}},E_{\mathbf{K}},E_{\mathbf{H}+\mathbf{K}},E_{2\mathbf{H}+\mathbf{K}})$ we obtain

$$\begin{aligned}\langle R\rangle &= \langle(E_{\mathbf{H}}^2-1)E_{2\mathbf{H}}|E_{\mathbf{K}},E_{\mathbf{H}+\mathbf{K}},E_{2\mathbf{H}+\mathbf{K}}\rangle\simeq 1/\sqrt{N}\\ &+\{2(E_{\mathbf{K}}^2-1)(E_{\mathbf{H}+\mathbf{K}}^2-1)(E_{2\mathbf{H}+\mathbf{K}}^2-1)\\ &+E_{\mathbf{K}}E_{2\mathbf{H}+\mathbf{K}}(E_{\mathbf{H}+\mathbf{K}}^2-1)[(E_{\mathbf{K}}^2-1)+(E_{2\mathbf{H}+\mathbf{K}}^2-1)]\\ &-[H_4(E_{\mathbf{K}})+H_4(E_{\mathbf{H}+\mathbf{K}})+H_4(E_{2\mathbf{H}+\mathbf{K}})]/8\\ &+2(E_{\mathbf{K}}^2-1)(E_{\mathbf{H}+\mathbf{K}}^2-1)+2(E_{\mathbf{H}+\mathbf{K}}^2-1)(E_{2\mathbf{H}+\mathbf{K}}^2-1)\\ &+(E_{\mathbf{K}}^2-1)(E_{2\mathbf{H}+\mathbf{K}}^2-1)\}/N\sqrt{N}\,, \end{aligned}\qquad (B1)$$

$$\begin{aligned}\sigma^2 &\simeq \langle(E_{\mathbf{H}}^2-1)^2E_{2\mathbf{H}}^2|E_{\mathbf{K}},E_{\mathbf{H}+\mathbf{K}},E_{2\mathbf{H}+\mathbf{K}}\rangle\\ &\simeq 2\{1+3/2N-[H_4(E_{\mathbf{K}})+H_4(E_{\mathbf{H}+\mathbf{K}})\\ &+H_4(E_{2\mathbf{H}+\mathbf{K}})]/8N\\ &+2E_{\mathbf{K}}E_{2\mathbf{H}+\mathbf{K}}[3+2(E_{\mathbf{H}+\mathbf{K}}^2-1)]/N\\ &+2[(E_{\mathbf{K}}^2-1)(E_{\mathbf{H}+\mathbf{K}}^2-1)\\ &+(E_{\mathbf{H}+\mathbf{K}}^2-1)(E_{2\mathbf{H}+\mathbf{K}}^2-1)]/N\\ &+(E_{\mathbf{K}}^2-1)(E_{2\mathbf{H}+\mathbf{K}}^2-1)/N\}\,. \end{aligned}\qquad (B2)$$

As in Appendix A, we calculate here the expression for $|R|\langle R\rangle/\sigma^2$. In the numerator as well as in the denominator of this expression a seminvariant appears (*i.e.* $E_{\mathbf{K}}E_{2\mathbf{H}+\mathbf{K}}$) whose sign is unknown. In the quartet theory (Giacovazzo, 1975*b*) a similar effect occurred (*i.e.* the seminvariant $E_{\mathbf{h}+\mathbf{k}}E_{\mathbf{h}+\mathbf{l}}E_{\mathbf{k}+\mathbf{l}}$ appeared): we showed in that paper that the sign of the seminvariant does not affect too heavily the sign of the quartet. On this ground it is easy to derive (14) from (B1) and (B2).

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On Maximal Subgroups with Increased Unit Cells

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According to Hermann [*Z. Kristallogr.* (1929), **69**, 533] the crystallographic space groups *G* have two kinds of maximal subgroups *H*, isotranslational ('zellengleich') and isoclass ('klassengleich'), *i.e.* subgroups of the same class but with different translation lattices. The maximal subgroups of index two are easily found from the existing tabulations of magnetic space groups. The paper focuses mainly on isoclass subgroups with increased unit cells. Also, a method is described for deriving directly from the crystallographic space groups all maximal isoclass subgroups of index two and of index four with increased unit cells.

Introduction

Hermann (1929) was first to distinguish between two categories of maximal subgroups *H* of space groups *G*: (*a*) subgroups *H* having the same translation lattice as *G* ('zellengleich'), (*b*) subgroups *H* having a different translation lattice, but belonging to the same crystal class as *G* ('klassengleich').

Subgroups of category (*a*) were first presented by Hermann in *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (1935), so many crystallographers will be familiar with them. Subgroups of category (*b*) look more mysterious. It might even be surprising to learn from this paper that maximal subgroups of category (*b*) were first tabulated nearly 20 years ago although in a form in which the fact is difficult to recognize. Indeed, we shall show in Part I that, with little calculation, maximal subgroups of category (*b*) can be read directly from the known tabulation of magnetic space groups having an antitranslation element (Opechowski & Guccione, 1965; Belov, Neronova & Smirnova, 1957; abbreviated OG and B respectively).

In Part II, we state the rules for deriving maximal subgroups of category (*b*) directly from the crystallographic space groups. The subgroups considered are of index two and four.

Part I

I. 1. *Definitions*

Two cases are to be considered under category (*b*): (*b*1) the subgroup *H* has an increased unit cell; this case mainly will be considered here [for completeness the other cases, (*a*) and (*b*2) are dealt with in the last remarks of § I. 4.], (*b*2) the space group *G* is centred while *H* has partly or wholly lost the centring, the case for which the unit cells remain the same. In this respect the wording 'zellengleich' for category (*a*) is not particularly satisfactory. We would recommend the terminology 'isotranslation' and 'isoclass' subgroups for 'zellengleich' and 'klassengleich' respectively.

Let *G* be a group, *H* a subgroup of *G*, *g* an element of *G*, but not contained in *H*. If

$$G = H + gH , \qquad (1.\ 1)$$

H is a maximal subgroup of index two of *G*.

(*a*) If *G* is a space group and $g = (\alpha|\tau_\alpha)$, a space group element, where α is a rotation, τ_α a translation, then *H* is a subgroup of category (*a*).

(*b*) If *G* is a space group and $g = (e|\mathbf{t}_G)$ where *e* is the identity element and $\mathbf{t}_G$ a (non-zero) lattice translation, not contained in *H*, then *H* is a subgroup of category (*b*).