Invariants in Phase Determination (Medical Foundation of Buffalo and SUNY/Buffalo) an unknown structure has been solved with the help of a more primitive version of NQC, which will be described elsewhere (Schenk, Gartland, Einspahr & Freeman, 1974).

The author is greatly indebted to Dr Herbert Hauptman for many stimulating and fruitful discussions during the series of seminars on direct methods held in April 1973 in Parma and during the Workshop on direct methods in August 1973 in Buffalo. He thanks Professor B. O. Loopstra and Dr C. H. Stam for their critical reading of the manuscript.

References

De Jong, J. G. H., Dik-Edixhoven, C. J. & Schenk, H. (1973). *Cryst. Struct. Commun.* **2**, 33–36.
Greenberger, M. (1961). *Math. Tabl. Napn. Res. Coun.* **15**, 383–389.
Hauptman, H. A. (1972). *Crystal Structure Determination.* New York, London: Plenum Press.
Hauptman, H. A. (1974). *Acta Cryst.* A**30**, 472–476.
Schenk, H. (1973*a*). *Acta Cryst.* A**29**, 480–481.
Schenk, H. (1973*b*). *Acta Cryst.* A**29**, 77–82.
Schenk, H. & De Jong, J. G. H. (1973). *Acta Cryst.* A**29**, 31–34.
Schenk, H., Gartland, G. L., Einspahr, H. M. & Freeman, G. R. (1974). To be published.

Acta Cryst. (1974). A**30**, 481

The Joint Probability Distribution Applied to a Weak Sign Relationship

By C. Giacovazzo

Università di Bari, Istituto di Mineralogia e Petrografia, 70121 *Bari, Italy*

(*Received* 13 *November* 1973; *accepted* 2 *January* 1974)

The probability of the sign of the product $E_{\mathbf{h-k}}E_{\mathbf{h+k}}$ is derived by the mathematical device of the joint probability distribution. Some previous formulae, in contrast with Harker–Kasper inequalities, are criticized. Some experimental tests fit quite well the theory developed here.

Introduction

In a short communication, Gillis (1956) suggested the conditional sign relationship

$$S(\mathbf{h}+\mathbf{k}) \simeq -S(\mathbf{h}-\mathbf{k}) \tag{1}$$

if

$$|U_{\mathbf{h}}|^2+|U_{\mathbf{k}}|^2 \le |U_{\mathbf{h+k}}U_{\mathbf{h-k}}| \; ; \tag{2}$$

$S(\mathbf{h})$ represents the sign of $U_{\mathbf{h}}$.

Woolfson (1957) criticized this result and suggested that the most favourable condition for sign relationship (1) is that one of $U_{\mathbf{h}}$ and $U_{\mathbf{k}}$ should be large and the other small. Furthermore, by a application of the central-limit theorem, Woolfson (1957) obtained a mathematical expression of the ratio P_+/P_-, where P_+ represents the probability that $S(\mathbf{h}-\mathbf{k})S(\mathbf{h}+\mathbf{k})$ is positive while P_- is the probability that $S(\mathbf{h}-\mathbf{k})S(\mathbf{h}+\mathbf{k})$ is negative. According to Woolfson, this ratio depends on a knowledge of the signs of $U_{2\mathbf{h}}$ and $U_{2\mathbf{k}}$.

Later Woolfson (1961) derived the validity conditions for relation (1) by a suitable use of the Harker–Kasper inequalities.

From these inequalities we have

$$(U_{\mathbf{h}}+U_{\mathbf{k}})^2 \le (1+U_{\mathbf{h+k}})\,(1+U_{\mathbf{h-k}})\,, \tag{3}$$

and

$$(U_{\mathbf{h}}-U_{\mathbf{k}})^2 \le (1-U_{\mathbf{h+k}})\,(1-U_{\mathbf{h-k}})\,. \tag{4}$$

When $|U_{\mathbf{h}}|$, $|U_{\mathbf{h+k}}|$, $|U_{\mathbf{h-k}}|$ are large, $|U_{\mathbf{k}}|=0$, and

$$U_{\mathbf{h}}^2 > (1-|U_{\mathbf{h+k}}|)\,(1-|U_{\mathbf{h-k}}|)\,, \tag{5}$$

then it follows from (3) and (4) that the sign relationship (1) must hold. No use of $U_{2\mathbf{h}}$ and $U_{2\mathbf{k}}$ is made in equations (3), (4) and (5).

In a recent paper, Schenk & de Jong (1973) showed that in centrosymmetric symmorphic space groups the correct $\sum_2$ solution can be found using a new criterion (the HKC criterion), related to the sign relation (1) through the Harker–Kasper inequalities. Since the application field of the Harker–Kasper inequalities is limited, it is of some interest to draw a probability law for the sign relation (1). In this paper the mathematical device of the joint probability distribution will be used.

The joint probability distribution $P(E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{h-k}}, E_{\mathbf{h+k}})$

We introduce the abbreviation

$$E_1=E_{\mathbf{h}}\,;\; E_2=E_{\mathbf{k}}\,;\; E_3=E_{\mathbf{h-k}}\,;\; E_4=E_{\mathbf{h+k}}\,.$$

By following Klug (1958), we derive the characteristic function $C(u_1,u_2,u_3,u_4)$ of the multivariate distribution $P(E_1,E_2,E_3,E_4)$:

$$C(u_1,u_2,u_3,u_4) = \exp\left\{-\tfrac{1}{2}[u_1^2+u_2^2+u_3^2+u_4^2]\right\}\left\{1+\frac{S_3}{t^{3/2}}+\frac{S_4}{t^2}+\frac{S_3^2}{2t^3}+\dots\right\}, \tag{6}$$

where u_i, $i=1,\ldots,4$ are carrying variables associated with E_i, $t=N/2$, and

$$S_\nu = t \sum_{r+s+\ldots+w=\nu} \frac{\lambda_{rs\ldots w}}{r!s!\ldots w!}(iu_1)^r(iu_2)^s\ldots(iu_4)^w .$$

$\lambda_{rs\ldots w}$ are the standardized cumulants of the distribution.

After some calculation we find:

$$S_3 = \frac{N}{2\sqrt{2}}\{(iu_1)(iu_2)(iu_3)+(iu_1)(iu_2)(iu_4)\}$$

$$S_4 = \frac{N}{2}\left\{-\frac{3}{2}\left[\frac{(iu_1)^4}{4!}+\ldots.+\frac{(iu_4)^4}{4!}\right]\right\} + \tfrac{1}{4}[(iu_1)^2(iu_3)(iu_4)+(iu_2)^2(iu_3)(iu_4)] .$$

Finally we can write

$$\begin{aligned} &C(u_1,u_2,u_3,u_4) \\ &=\exp\{-\tfrac{1}{2}[u_1^2+\ldots+u_4^2]\}\left\{1+\frac{1}{\sqrt{N}}(iu_1)(iu_2)(iu_3)\right. \\ &+\frac{1}{\sqrt{N}}(iu_1)(iu_2)(iu_4)-\frac{1}{8N}[(iu_1)^4+\ldots+(iu_4)^4] \\ &+\frac{1}{2N}[(iu_1)^2(iu_3)(iu_4)+(iu_2)^2(iu_3)(iu_4)] \\ &+\frac{1}{2N}[(iu_1)^2(iu_2)^2(iu_3)^2+(iu_1)^2(iu_2)^2(iu_4)^2 \\ &\left.+2(iu_1)^2(iu_2)^2(iu_3)(iu_4)]+\ldots\right\}. \end{aligned} \tag{7}$$

The probability distribution is found by taking the Fourier transform of (7). We obtain the expression, correct up to and including terms of order N^{-1},

$$\begin{aligned} &P(E_1,E_2,E_3,E_4) \\ &=\frac{1}{2\pi^2}\exp[-\tfrac{1}{2}(E_1^2+E_2^2+E_3^2+E_4^2)]\left\{1+\frac{1}{\sqrt{N}}(E_1E_2E_3\right. \\ &+E_1E_2E_4)+\frac{1}{2N}[(E_1^2-1)E_3E_4 \\ &+(E_2^2-1)E_3E_4]-\frac{1}{8N}[H_4(E_1)+\ldots+H_4(E_4)] \\ &+\frac{1}{2N}[H_2(E_1)H_2(E_2)H_2(E_3) \\ &+H_2(E_1)H_2(E_2)H_2(E_4) \\ &\left.+2H_2(E_1)H_2(E_2)E_3E_4]\right\}. \end{aligned} \tag{8}$$

H_ν is the Hermite polynomial of the νth order defined by the equation

$$H_\nu(x)=(-1)^\nu \exp[\tfrac{1}{2}x^2]\frac{d^\nu}{dx^\nu}\exp[-\tfrac{1}{2}x^2] .$$

The conditional joint probability distribution $P(E_3,E_4|E_1,E_2)$ is easily obtained from (8):

$$\begin{aligned} &P(E_3,E_4|E_1,E_2) \\ &=\frac{1}{2\pi}\cdot\frac{1}{1-\frac{1}{8N}[H_4(E_1)+H_4(E_2)]}\exp[-\tfrac{1}{2}(E_3^2+E_4^2)] \\ &\times\left\{1+\frac{1}{\sqrt{N}}(E_1E_2E_3+E_1E_2E_4)+\frac{1}{2N}[(E_1^2-1)E_3E_4\right. \\ &+(E_2^2-1)E_3E_4]-\frac{1}{8N}[H_4(E_1)+\ldots+H_4(E_4)] \\ &+\frac{1}{2N}[H_2(E_1)H_2(E_2)H_2(E_3)+H_2(E_1)H_2(E_2)H_2(E_4) \\ &\left.+2H_2(E_1)H_2(E_2)E_3E_4]\right\}. \end{aligned} \tag{9}$$

The conditional expected value $\langle E_3E_4|E_1,E_2\rangle$ is defined by

$$\langle E_3E_4|E_1,E_2\rangle = \iint_{-\infty}^{+\infty} E_3E_4P(E_3,E_4|E_1,E_2)\mathrm{d}E_3\mathrm{d}E_4.$$

Then, in view of (9), we obtain

$$\begin{aligned} &\langle E_3E_4|E_1,E_2\rangle \\ &=\frac{1}{1-\frac{1}{8N}[H_4(E_1)+H_4(E_2)]}\cdot\frac{1}{2N}[2E_1^2E_2^2-E_1^2-E_2^2] . \end{aligned} \tag{10}$$

Likewise it results that

$$\begin{aligned} \langle E_3^2E_4^2|E_1,E_2\rangle &= \frac{1}{1-\frac{1}{8N}[H_4(E_1)+H_4(E_2)]} \\ &\times\left\{1-\frac{1}{8N}[H_4(E_1)+H_4(E_2)]+\frac{2}{N}H_2(E_1)H_2(E_2)\right\} \\ &\simeq 1+\frac{2}{N}H_2(E_1)H_2(E_2) . \end{aligned}$$

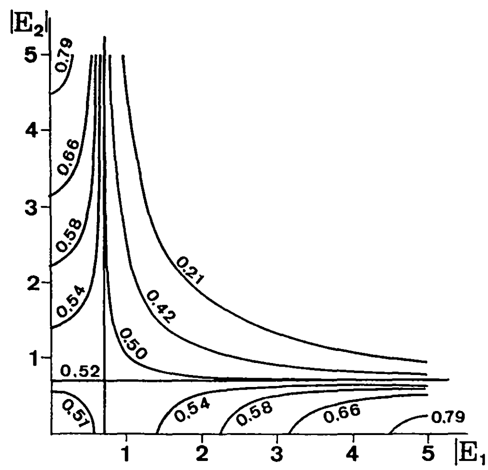

Fig. 1. Curves corresponding to equation (13).

Since the conditional probability distribution of the random variable $R=E_3E_4$ may be expanded in the form of a Gram–Charlier series (Cramér, 1951), we obtain

$$P(R|E_1,E_2)=\frac{1}{\sigma\sqrt{2\pi}}\exp\left[-\frac{(R-\langle R\rangle)^2}{2\sigma^2}\right]+\ldots,$$

where $\langle R\rangle$ is given by (10), and

$$\sigma^2=\langle E_3^2E_4^2|E_1,E_2\rangle-\langle E_3E_4|E_1,E_2\rangle^2\simeq 1+\frac{2}{N}H_2(E_1)H_2(E_2)\,.$$

As $P_+=\left(\frac{P_-}{P_+}+1\right)^{-1}$,

we find

$$P_+=\tfrac{1}{2}+\tfrac{1}{2}\tanh\left\{|E_3E_4|\times\frac{1}{\left[1+\frac{2}{N}H_2(E_1)H_2(E_2)\right]}\cdot\frac{1}{1-\frac{1}{8N}\left[H_4(E_1)+H_4(E_2)\right]}\times\frac{1}{2N}(2E_1^2E_2^2-E_1^2-E_2^2)\,.\right. \quad (11)$$

A good approximation to (11) is

$$P_+=\tfrac{1}{2}+\tfrac{1}{2}\tanh\frac{1}{2N}|E_3E_4|(2E_1^2E_2^2-E_1^2-E_2^2)\,, \quad (12)$$

and consequently

$$P_-=\tfrac{1}{2}-\tfrac{1}{2}\tanh\frac{1}{2N}|E_3E_4|(2E_1^2E_2^2-E_1^2-E_2^2)\,. \quad (13)$$

It is well known that when the atoms are not equal, one can replace N by $\sigma_3^{-2}\sigma_2^3$ in (11), (12) and (13).

In Fig. 1 we have plotted some curves corresponding to (13) for the case $N=60$ and $|E_3E_4|=4$: each curve corresponds to a single value of P_-. The behaviour of P_- function is quite clear from the Figure: in accordance with the Harker–Kasper inequalities (3), (4) and (5), large values of P_- are obtained if $|E_3|$, $|E_4|$, $|E_1|$ are large and E_2 small (or $|E_2|$ is large and $|E_1|$ small). In this connexion we wish to note explicitly that $P_-=P_+=\frac{1}{2}$ if $|E_1|=|E_2|=0$ as well as if $|E_1|=|E_2|=1$.

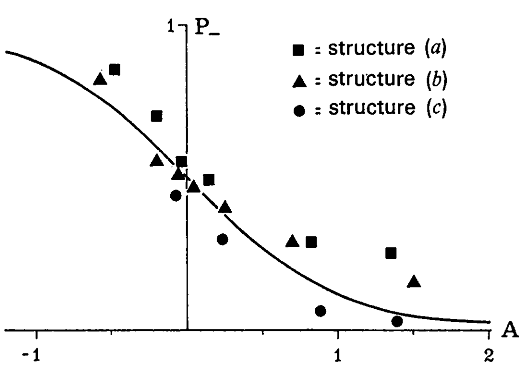

Fig. 2. $A=(2\sigma_3^{-2}\sigma_2^3)^{-1}|E_3E_4|\,(2E_1^2E_2^2-E_1^2-E_2^2)$.

A comparison with a central-limit theorem approach

The probability of the relationship (1) depends, in a central-limit theorem approach, on the probabilities P_1 and P_2 of the individual relationships

$$S(\mathbf{h})S(\mathbf{k})S(\mathbf{h}-\mathbf{k})\simeq 1\,,\quad S(\mathbf{h})S(\mathbf{k})S(\mathbf{h}+\mathbf{k})\simeq 1\,, \quad (14)$$

where P_1 and P_2 may be deduced from the well-known formula (Cochran & Woolfson, 1955,

$$P(|E_\mathbf{h}E_\mathbf{k}E_{\mathbf{h}+\mathbf{k}}|)=\tfrac{1}{2}+\tfrac{1}{2}\tanh\frac{1}{\sqrt{N}}|E_\mathbf{h}E_\mathbf{k}E_{\mathbf{h}+\mathbf{k}}|\,.$$

Then P_+ (Woolfson, 1961) reduces to

$$P'_+=P_1P_2+(1-P_1)(1-P_2)=2P_1P_2-P_1-P_2+1\,. \quad (15)$$

By expanding tanh as far as the first power, we obtain from (15)

$P'_+=\frac{1}{2}+\frac{1}{2N}|E_3E_4|E_1^2E_2^2|$, which can be approximated to

$$P'_+=\tfrac{1}{2}+\tfrac{1}{2}\tanh\frac{2|E_3E_4|E_1^2E_2^2}{2N}\,, \quad (16)$$

or

$$P'_-=\tfrac{1}{2}-\tfrac{1}{2}\tanh\frac{2|E_3E_4|E_1^2E_2^2}{2N}\,, \quad (17)$$

Thus we see that (16) is a good approximation to relation (12) if both $|E_1|$ and $|E_2|$ are very large, but may become inadequate in other cases. Furthermore the probability in equation (16) of the relation (1) is always overestimated. The formula (17) is entirely misleading when one wishes to characterize the quartets E_1, E_2, E_3, E_4 with large values of P_-. In fact, the highest value of P_- in (17) is equal to $\frac{1}{2}$, which occurs when $|E_1|=|E_2|=0$ and this is in contrast to the Harker–Kasper inequalities.

Experimental

We have tested equations (11) and (12) in three crystal structures:

(*a*) Alloxantin dihydrate (Singh, 1965): space group $P\bar{1}$, $\sigma_3^{-2}\sigma_2^3=21{\cdot}46$. 6208 quartets E_1,E_2,E_3,E_4 have been tested.

(*b*) Meso-3,3′-di-(*p*-chlorophenyl)bi-3-phthalidyl (Kalyani & Vijayan, 1969): space group $P\bar{1}$, $\sigma_3^{-2}\sigma_2^3=19{\cdot}46$. 12786 quartets have been tested.

(*c*) Mellite (Giacovazzo, Menchetti & Scordari, 1973): space group $I4_1/acd$, $\sigma_3^{-2}\sigma_2^3=156{\cdot}04$. 10524 quartets E_1,E_2,E_3,E_4 have been tested.

We have noted negligible differences between the experimental applications of (11) and (12). The comparison between the theoretical curve and the experimental results obtained by (13) is shown in Fig. 2. The agreement between theory and practice is satisfactory. In particular, in spite of the presence of a heavy atom (Cl), no serious deviation from the theory can be noted in structure (*b*). Furthermore, it is interesting to note that, owing to the presence of the factor $1/2N$ in the $\langle E_3E_4|E_1,E_2\rangle$ expression, a high percentage of quartets present A values crowded round the zero

$$[A=(2\sigma_3^{-2}\sigma_2^3)^{-1}|E_3E_4|(2E_1^2E_2^2-E_1^2-E_2^2)].$$

This behaviour is, therefore, enhanced in structure (*c*) in comparison with the structures (*a*) and (*b*).

Conclusions

In this paper, as in the Harker–Kasper inequalities (3) and (4) and in the Woolfson relation (15), no use is made of the signs $S(E_{2\mathbf{h}})$ and $S(E_{2\mathbf{k}})$. $E_{2\mathbf{h}}$ and $E_{2\mathbf{k}}$, nevertheless, are strongly correlated, as is well known, with the sign of the product $E_{\mathbf{h-k}}E_{\mathbf{h+k}}$. Consequently, from a general point of view, the probability density $P(E_{\mathbf{h}},E_{\mathbf{k}},E_{\mathbf{h-k}},E_{\mathbf{h+k}})$ worked out in this paper can be considered as a useful marginal probability function of the more exhaustive density function $P(E_{\mathbf{h}},E_{\mathbf{k}},E_{\mathbf{h-k}},E_{\mathbf{h+k}},E_{2\mathbf{h}},E_{2\mathbf{k}})$. This aspect of the problem will be considered in a further paper.

The author wishes to thank Dr A. Digennaro for many stimulating discussions.

References

Cochran, W. & Woolfson, M. M. (1955). *Acta Cryst.* **8**, 1–12.
Cramer, H. (1951). *Mathematical Methods of Statistics.* Princeton Univ. Press.
Giacovazzo, C., Menchetti, S. & Scordari, F. (1973). *Acta Cryst.* B**29**, 26–31.
Gillis, J. (1956). *Acta Cryst.* **9**, 616.
Kalyani, V. & Vijayan, M. (1969). *Acta Cryst.* B**25**, 252–260.
Klug, A. (1958). *Acta Cryst.* **11**, 515–543.
Schenk, H. & de Jong, J. G. H. (1973). *Acta Cryst.* A**29**, 31–34.
Singh, C. (1965). *Acta Cryst.* **19**, 767–774.
Woolfson, M. M. (1957). *Acta Cryst.* **10**, 635–638.
Woolfson, M. M. (1961). *Direct Methods in Crystallography.* Oxford: Clarendon Press.

Acta Cryst. (1974). A**30**, 484

Relation entre la Symétrie des Groupements $CuCl_4^{2-}$ Tétraédriques et les Propriétés Physiques des Cupritétrachlorures. I. Moment Magnétique Moyen

Par J. Lamotte-Brasseur et G. Van den Bossche

Laboratoire de Cristallographie et de Physique de l'Etat solide, Institut de Physique, Université de Liège au Sart Tilman, B-4000 Liège, Belgique

(*Reçu le* 3 *janvier* 1974, *accepté le* 11 *février* 1974)

For some crystals, the structures of which have already been determined, the flattening, D, of the $CuCl_4^{2-}$ tetrahedra has been estimated. The paramagnetic susceptibilities of many tetrachlorocuprates have been measured by the Faraday method. The mean magnetic moment decreases linearly as D increases, if D is greater than 0·2. From the known mean magnetic moment, it is therefore possible to estimate the D value of the $CuCl_4^{2-}$ tetrahedron.

Introduction

L'étude systématique de la symétrie d'un grand nombre de groupements $CuCl_4^{2-}$ tétraédriques nous a montré que leur degré de déformation peut varier très fort avec le cation coordonné. Nous traiterons ici de la relation entre cette symétrie et les moments magnétiques moyens des cristaux envisagés.

Dans le premier stade, nous estimerons les déformations pour les composés dont la structure a été déterminée. Ensuite, nous donnerons les résultats des mesures des moments magnétiques moyens de ces composés. Enfin, nous déterminerons la loi de variation du moment magnétique avec la déformation du tétraèdre et nous l'utiliserons pour prévoir la symétrie des groupements $CuCl_4^{2-}$ dans les cristaux dont la structure n'est pas encore connue.

Estimation de la déformation des tétraèdres

Helmholz & Kruh (1952) ont montré que, dans Cs_2CuCl_4, l'ion $CuCl_4^{2-}$ n'est pas un tétraèdre régulier [Fig. 1(*a*)] mais qu'il est aplati suivant l'un de ses axes de rotation–inversion [Fig. 1(*b*)].

Pour caractériser cet aplatissement, nous avons choisi comme paramètre la grandeur D définie comme suit:

$$D=\frac{L_3-L_1}{(L_1+L_2+L_3)^{1/3}},$$