elements B_{ij} are restricted to integers for which $|\mathbf{B}| = 1$. The algorithm yields the five cells given in Table 1.

Conclusions

In the previous section only a few examples of the application of the algorithm have been illustrated. Many more could have been given. The method represents a practical tool to study inter- and intra-lattice relationships and, for this reason, is particularly suited to carry out research on published crystallographic data. Applications of the procedure, under-way or planned, comprise cross-referencing of the single-crystal and powder data files, routine identification and registration procedures, and a systematic study of twinning, especially to clarify the relationship between the geometrical and structural aspects of twins.

References

CASSELS, J. W. S. (1971). *An Introduction to the Geometry of Numbers.* New York: Springer-Verlag.
DeCAMP, W. H. (1976). *Acta Cryst.* B**32**, 2257–2258.
DELAUNAY, B. (1933). *Z. Kristallogr.* **84**, 109–149.
DONNAY, J. D. H. & ONDIK, H. M. (1972). *Crystal Data Determinative Tables*, Third edition. US Department of Commerce, National Bureau of Standards and the JCPDS, International Center for Diffraction Data, Swarthmore, PA.
GRUBER, B. (1973). *Acta Cryst.* A**29**, 433–440.
HUBBARD, C. R., HIMES, V. L., MIGHELL, A. D. & PAGE, S. W. (1980). *Acta Cryst.* In the press.
International Tables for X-ray Crystallography (1969). Vol. I. Birmingham: Kynoch Press.
MORRIS, M. C., McMURDIE, H. F., EVANS, E. H., PARETZKIN, B., deGROOT, J. H., WEEKS, B. S. & NEWBERRY, R. J. (1978). *Natl Bur. Stand. (US) Monogr.* 25, Section 15.
SANTORO, A. (1974). *Acta Cryst.* A**30**, 224–231.
SANTORO, A. & MIGHELL, A. D. (1970). *Acta Cryst.* A**26**, 124–127.
SANTORO, A. & MIGHELL, A. D. (1972). *Acta Cryst.* A**28**, 284–287.
SANTORO, A. & MIGHELL, A. D. (1973). *Acta Cryst.* A**29**, 169–175.
VISSER, J. W. (1969). *J. Appl. Cryst.* **2**, 89–95.

The Expected Values of Triplet Invariants. Acentric Case

BY JEROME KARLE

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC 20375, USA

Abstract

A formula for the expected values of triplet phase invariants is derived in the acentric case from third-order determinantal joint probability distributions. Theoretical calculations based on this and earlier formulae are compared with expected values observed for a roughly equal-atom structure and one containing a heavy atom.

Introduction

The expected value of a triplet phase invariant is affected by the knowledge of the magnitudes of appropriate structure factors. It is possible to obtain expressions for such expected values from joint probability distributions involving the triplet invariants of interest and certain associated structure-factor magnitudes. A general joint probability distribution function has been derived recently (Karle, 1978) that is based on the determinants that provide the necessary and sufficient conditions that a Fourier series representing a crystal structure be non-negative (Karle & Hauptman, 1950). These determinantal joint probability distributions have already been applied in the fourth order (Karle, 1979, 1980) to obtain conditional distributions for the triplet invariants $\varphi_{\mathbf{k}_1-\mathbf{k}_2} + \varphi_{-\mathbf{k}_1+\mathbf{k}_3} + \varphi_{\mathbf{k}_2-\mathbf{k}_3}$, given the structure-factor magnitudes $|\mathscr{E}_{\mathbf{k}_1-\mathbf{k}_2}|$, $|\mathscr{E}_{-\mathbf{k}_1+\mathbf{k}_3}|$, $|\mathscr{E}_{\mathbf{k}_2-\mathbf{k}_3}|$ and many sets of $|\mathscr{E}_{\mathbf{k}_1}|$, $|\mathscr{E}_{\mathbf{k}_2}|$, $|\mathscr{E}_{\mathbf{k}_3}|$.

The third-order determinants and determinantal joint probability distributions give the main formulae for phase determination, $\sum_2$ and the sum of angles formula. One question of interest is how well the new distributions represent the expected values of the triplet phase invariants, $\varphi_{\mathbf{k}_1} + \varphi_{-\mathbf{k}_2} + \varphi_{-\mathbf{k}_1+\mathbf{k}_2}$, given the three magnitudes $|\mathscr{E}_{\mathbf{k}_1}|$, $|\mathscr{E}_{-\mathbf{k}_2}|$, $|\mathscr{E}_{-\mathbf{k}_1+\mathbf{k}_2}|$. Such expected values have been investigated in some detail previously (Karle, 1972; Karle & Gilardi, 1973) in connection with other forms for the appropriate joint probability

distributions. An earlier investigation was carried out by Tsoucaris (1970). The interest in making a further study here with the third-order determinantal distributions derives not only from the test of a new expression but also from the fact that it affords an opportunity to assess the validity of a scaling factor for these distributions that was introduced heuristically. A confirmation of the validity of the scaling factor has already been obtained for fourth-order distributions in the above-mentioned investigations (Karle, 1979, 1980).

Triplet probability distribution and expected values

This derivation begins with expression (15) of the general theory (Karle, 1978) which gives the joint probability distribution of the variates in an mth-order determinant, $D_{m,p}$, for the acentric case. For the third order, we have

$$P_{3,\ell}(|\mathscr{E}_{k_1}|, |\mathscr{E}_{-k_2}|, |\mathscr{E}_{-k_1+k_2}|, \varphi_{k_1}, \varphi_{-k_2}, \varphi_{-k_1+k_2})$$

$$= N_{3,\ell} \exp\left[\mathscr{E}_0^2 D_{3,p} \cdot \left\langle \frac{\Delta_{3,p,q}}{\Delta_{1,3,p,q}\Delta_{2,3,p,q}} \right\rangle_q \right],\quad (1)$$

where the $\mathscr{E}_k = |\mathscr{E}_k| \exp(i\varphi_k)$ are quasi-normalized structure factors with magnitudes $|\mathscr{E}_k|$ and phases φ_k, $N_{3,\ell}$ is a normalizing constant, $\mathscr{E}_0 \equiv \mathscr{E}_{000}$,

$$D_{3,p} = \begin{vmatrix} \mathscr{E}_0 & \mathscr{E}_{-k_1} & \mathscr{E}_{-k_2} \\ \mathscr{E}_{k_1} & \mathscr{E}_0 & \mathscr{E}_{k_1-k_2} \\ \mathscr{E}_{k_2} & \mathscr{E}_{-k_1+k_2} & \mathscr{E}_0 \end{vmatrix},\quad (2)$$

p refers to a specific set of k_1 and k_2 and the Δ's in the average term of the exponential function are principal minors of $D_{3,p}$. The manner of formation of the Δ's is described in detail in Karle (1972). The average term in (1) is a constant whose value is increased as the $|\mathscr{E}|$'s involved in (2) are increased in value. It may be written

$$\left\langle \frac{\Delta_{3,p,q}}{\Delta_{1,3,p,q}\Delta_{2,3,p,q}} \right\rangle_q = \mathscr{E}_0^{-3} V_{3,p},\quad (3)$$

where the term $\mathscr{E}_0^{-3}$ is formed by factoring out all the diagonal terms from the Δ's.

The smallest value for $V_{3,p}$ is unity, occurring when the magnitudes of the off-diagonal $\mathscr{E}$ approach zero. Its value increases as the magnitudes increase becoming usually fractionally larger than unity.

The right side of (1) can be written

$$N_3' \exp[2(\sigma_3/\sigma_2^{3/2}) V_{3,p}|\mathscr{E}_{k_1}\mathscr{E}_{-k_2}\mathscr{E}_{-k_1+k_2}|\cos\varPhi],\quad (4)$$

where

$$V_{3,p} = \frac{(1 - |U_{k_1}|^2) + (1 - |U_{-k_2}|^2) + (1 - |U_{-k_1+k_2}|^2)}{3(1 - |U_{k_1}|^2)(1 - |U_{-k_2}|^2)(1 - |U_{-k_1+k_2}|^2)},\quad (5)$$

$$U_h = (\sigma_2^{1/2}/\sigma_1)\,\mathscr{E}_h,\quad (6)$$

$$\cos\varPhi \equiv \cos(\varphi_{k_1} + \varphi_{-k_2} + \varphi_{-k_1+k_2}),\quad (7)$$

$$\sigma_n = \sum_{j=1}^{N} Z_j^n,\quad (8)$$

N_3' is a normalizing constant and Z_j is the atomic number of the jth atom in a unit cell containing N atoms. The factor $\sigma_3/\sigma_2^{3/2} = Q_3$ replaces $\mathscr{E}_0^{-1}$ in (4) in order to account for the possible presence of atoms of unequal atomic number.

Except for the factor $V_{3,p}$, the probability function given by (4) resembles that obtained from other methods for deriving this function. The term $V_{3,p}$ arises from the average term in (1). It had been noted in earlier studies that a term such as $V_{3,p}$ is needed to give improved accuracy when the magnitudes $|\mathscr{E}_{k_1}|$, $|\mathscr{E}_{-k_2}|$ and $|\mathscr{E}_{-k_1+k_2}|$ are large. Such terms replace higher-order terms in the probability distribution function that could serve a similar purpose.

As noted above, $V_{3,p}$ is usually fractionally larger than unity when the structure-factor magnitudes are large and thereby has the effect of enhancing prob-
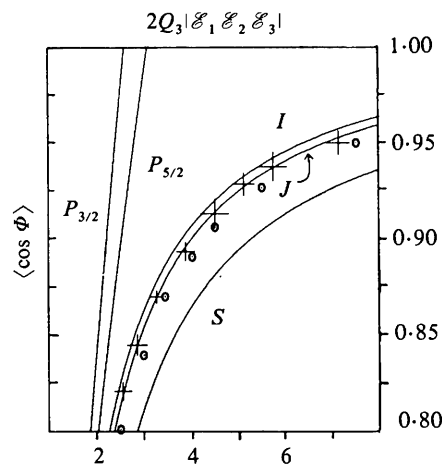

Fig. 1. Variation of expected values of the triplet cosine invariants with $2|\mathscr{E}_{k_1-k_2}\mathscr{E}_{-k_1+k_2}\mathscr{E}_{k_1-k_2}|\sigma_3/\sigma_2^{3/2}$ for N-acetylneuraminic acid (space group $P2_1$). The crosses represent values computed from a large number of invariants and the arms of the crosses, measured from the crossover point, represent three standard deviations. The solid curves represent the variation of several theoretical formulae obtained previously (Karle & Gilardi, 1973). The exponential form of the joint probability distribution carried to the $N^{-1/2}$ term, equation (29) of Karle & Gilardi (1973), give curve S, carried to the $N^{-3/2}$ term, equation (30) of Karle & Gilardi (1973), gives curve J and modified by means of the inequality theory, equation (31) of Karle & Gilardi (1973), gives curve I. The curves $P_{3/2}$ and $P_{5/2}$ are calculated from the series form of the joint distribution carried to the $N^{-3/2}$ and $N^{-5/2}$ terms, respectively. The latter curves show the unsatisfactory divergence of the series form. The points marked by circles were computed from equation (9) of this paper. In contrast, curve S is obtained if the additional contributions from $|\mathscr{E}_{k_1}|$, $|\mathscr{E}_{-k_2}|$ and $|\mathscr{E}_{-k_1+k_2}|$ are ignored, i.e. if $V_{3,p}$ is replaced by unity in (9).

ability measures, *e.g.* expected values. This focuses special interest on the behavior of $V_{3,p}$ and the scale on which it and the general $V_{n,p}$ ($n = 3, 4, \cdots$) have been introduced into the determinantal joint probability distributions on the basis of a heuristic argument. In the special case of $V_{3,p}$, the factor three in the denominator of (5) is an expression of the heuristic scaling. In a more general but equivalent way the $V_{n,p}$ (Karle, 1978, equation 15) were scaled by an averaging over the ratios of determinants. Equation (3) is a special case of this.

The expected value of $\cos \Phi$ is readily obtained from (4). It is

$$\langle \cos \Phi \rangle = I_1(W)/I_0(W), \qquad (9)$$

where I_0 and I_1 are Bessel functions of imaginary argument and

$$W = 2(\sigma_3/\sigma_2^{3/2}) \, V_{3,p} |\mathscr{E}_{k_1} \mathscr{E}_{-k_2} \mathscr{E}_{-k_1+k_2}|. \qquad (10)$$

Calculations and results

A number of calculations have been performed (Karle & Gilardi, 1973) to test a variety of forms for W that derive from exponential and series forms for the joint
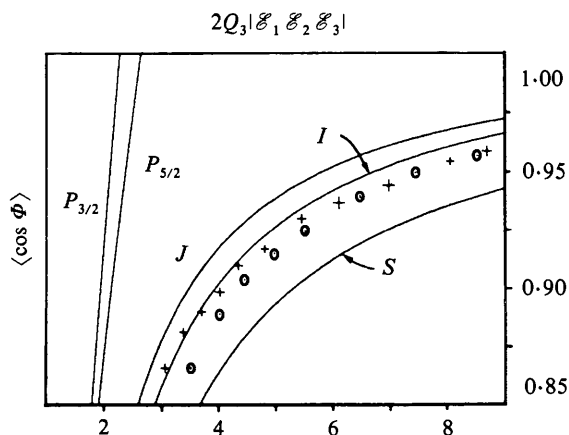

Fig. 2. Variation of expected values of the triplet cosine invariants with $2|\mathscr{E}_{k_1-k_2} \mathscr{E}_{-k_1+k_2} \mathscr{E}_{k_1-k_2}|\sigma_3/\sigma_2^{3/2}$ for a bromine derivative of N-acetylneuraminic acid (space group $P2_1$). The crosses represent values computed from a large number of invariants and the arms of the crosses, measured from the crossover point, represent three standard deviations. The labels for the solid curves are the same as those for Fig. 1. The points marked by circles were computed from equation (9).

probability distribution for $\mathscr{E}_{k_1}$, $\mathscr{E}_{-k_2}$ and $\mathscr{E}_{-k_1+k_2}$. In some of the forms for W, functions appear that are comparable to $V_{3,p}$ in (10) that take into account the larger magnitudes of $|\mathscr{E}_{k_1}|$, $|\mathscr{E}_{-k_2}|$ and $|\mathscr{E}_{-k_1+k_2}|$. The tests were made by computing $\langle \cos \Phi \rangle$ as given in (9) and making comparisons with average values obtained from crystal structures. The calculations were performed for an almost equal-atom structure, N-acetyl-neuraminic acid and a bromine derivative of this compound. The details of the earlier calculations can be found in a previous publication (Karle & Gilardi, 1973). To these earlier calculations were added the results of using the definition for W given by (10). The totality of these calculations giving the variation of the expected values of the triplet cosine invariants, $\langle \cos \Phi \rangle$, with $2|\mathscr{E}_{k_1} \mathscr{E}_{-k_2} \mathscr{E}_{-k_1+k_2}|\sigma_3/\sigma_2^{3/2}$ for N-acetyl-neuraminic acid and a bromine derivative of this compound are shown in Figs. 1 and 2, respectively. The computations based on the crystal structures are indicated by crosses and those from the definition of W given by (10) are indicated by circles. In the region of $2|\mathscr{E}_{k_1} \mathscr{E}_{-k_2} \mathscr{E}_{-k_1+k_2}|\sigma_3/\sigma_2^{3/2}$ that is displayed, (10) is seen to give quite accurate results for the higher values. For the lower values, (10) gives results that fall somewhat below the experimental points. Reference to the vertical scale, however, indicates that the discrepancies do not exceed 0.015 and are usually much less. A much improved fit both at the lower and higher values of $2|\mathscr{E}_{k_1} \mathscr{E}_{-k_2} \mathscr{E}_{-k_1+k_2}|\sigma_3/\sigma_2^{3/2}$ is obtained if the value of $V_{3,p}$ is enhanced by five percent. The scaling of the expression for $V_{3,p}$ appearing in the definition of W given by (10) is apparently close to optimal for the substances studied. Curve S would be obtained if the factor $V_{3,p}$ in (10) were replaced by unity.

References

Karle, J. (1972). *Acta Cryst.* B**28**, 3362–3369.
Karle, J. (1978). *Proc. Natl Acad. Sci. USA*, **75**, 2545–2548.
Karle, J. (1979). *Proc. Natl Acad. Sci. USA*, **76**, 2089–2093.
Karle, J. (1980). *Proc. Natl Acad. Sci. USA*, **77**, 5–9.
Karle, J. & Gilardi, R. D. (1973). *Acta Cryst.* A**29**, 401–407.
Karle, J. & Hauptman, H. (1950). *Acta Cryst.* **3**, 181–187
Tsoucaris, G. (1970). *Acta Cryst.* A**26**, 492–499.