

The Determination of Structure Invariants. I. Quadrupoles and Their Uses

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The triple-phase relationships (tpr) involving a particular set of reflexions can, in general, be related to each other since they form an interdependent set. A particular form of relationship, called a quadrupole, involves the sum of four tpr's and this sum can either be 0 or some other value, usually π , if there is translational symmetry. A tpr involved in a number of quadrupoles with zero sum has an enhanced probability of being close to zero whereas if it is involved in many quadrupoles with sum π then it may be expected that this tpr will deviate significantly from zero. An analysis of the quadrupoles can lead to a selection of tpr's which is more reliable than one selected on the basis of the three values of $|E|$ alone. Such tpr's can be used in the early stages of phase determination to increase the probability of getting through the first critical stages without serious error. A few tpr's which deviate significantly from zero may also be detected from the quadrupoles.

Introduction

A structure invariant is a quantity which does not change in value with change of origin. One fairly obvious type of structure invariant is $|E_{\mathbf{h}}|$ or $|E_{\mathbf{h}}|^2$. The latter quantity is the Fourier coefficient of a point-atom Patterson function and if there are no overlapped Patterson peaks or peaks with related positions (Hauptman, 1964; Simonov, 1969) then, with a large enough data set, theoretically infinite, the structure can be solved.

Another type of structure-invariant quantity is the sum of the phases of a number of structure factors the sum of whose indices is zero. In the most frequently occurring form, involving three reflexions, this appears as

$$\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_3} = \zeta_{\mathbf{h}_1, \mathbf{h}_2} \quad (1)$$

where

$$\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 = 0.$$

The knowledge of a sufficient number of ζ 's, as many as there are unknown φ 's, will enable the φ 's to be determined as long as the equations of the form given by (1) are linearly independent. However the quantities ζ , unlike $|E|$ or $|E|^2$, do not in general have known values but rather a known probability density which, for general phases, takes the form given by Cochran (1955):

$$P(\zeta) = [2\pi I_0(\kappa)]^{-1} \exp(\kappa \cos \zeta) \quad (2)$$

where I_0 is a modified Bessel function,

$$\kappa = 2\sigma_3\sigma_2^{-3/2}|E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}|, \quad \sigma_n = \sum_{j=1}^N Z_j^n$$

and Z_j is the atomic number of the j th atom of the structure with N atoms in the unit cell.

For a centrosymmetric structure the structure factors are real and ζ can have one of the two values, 0

or π (modulo 2π). We shall be considering only non-centrosymmetric structures in the present paper.

An implicit assumption of a great deal of recent work, particularly by Hauptman (*e.g.* 1972) has been that it should be possible to deduce one type of structure invariant from another and in particular from that set which constitutes the observed data, the $|E|$'s. It is easy to show that one cannot, even in principle, derive the ζ 's from the $|E|$'s. If one considers a non-centrosymmetric structure and also its enantiomorph then they have identical sets of $|E|$'s. But the phases of the enantiomorph structure are the negatives of those of the original structure and hence the corresponding values of ζ for the two structures will be the negatives of each other. We thus see that no function of $|E|$ can be expected to give the correct values of ζ .

There are however quantities which are both structure and enantiomorph invariant and these are the values of $|\zeta|$ and $\cos \zeta$. In 1964 Hauptman proposed the use of the formula

$$\begin{aligned} & |E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}| \cos(\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_3}) \\ & \simeq \frac{\sigma_1^3 - 3\sigma_1\sigma_2 + 2\sigma_3}{\sigma_2^{3/2} \langle (|E_1|^2 - 1)^3 \rangle_1} \langle (|E_1|^2 - 1)(|E_{\mathbf{h}_1+\mathbf{h}_1}|^2 - 1) \\ & \times (|E_{-\mathbf{h}_3+\mathbf{h}_1}|^2 - 1) \rangle_1 + \sigma_3\sigma_2^{-3/2} \\ & \times (|E_{\mathbf{h}_1}|^2 + |E_{\mathbf{h}_2}|^2 + |E_{\mathbf{h}_3}|^2 - 2), \end{aligned} \quad (3)$$

where \mathbf{l} ranges over all vectors corresponding to observed intensities. This formula seems to be very sensitive to experimental errors in the data and a modified formula was used by Hauptman, Fisher, Hancock & Norton (1969) which, for N equal atoms in the unit cell, is

$$\begin{aligned} & |E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}| \cos(\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_3}) \\ & \simeq K \langle (|E_1|^{1/2} - |E|^{1/2})(|E_{\mathbf{h}_1+\mathbf{h}_1}|^{1/2} - |E|^{1/2}) \\ & \times (|E_{-\mathbf{h}_3+\mathbf{h}_1}|^{1/2} - |E|^{1/2}) \rangle + \frac{1}{4} N^{-1/2} \{ \frac{3}{2} (|E_{\mathbf{h}_1}E_{\mathbf{h}_2}|^2 \\ & + |E_{\mathbf{h}_2}E_{\mathbf{h}_3}|^2 + |E_{\mathbf{h}_3}E_{\mathbf{h}_1}|^2) + |E_{\mathbf{h}_1}|^2 + |E_{\mathbf{h}_2}|^2 \\ & + |E_{\mathbf{h}_3}|^2 - \frac{7}{2} \} \end{aligned} \quad (4)$$

where K is an empirically determined function of κ which makes the cumulative distribution of the computed values of $\cos \xi$ agree with a theoretical distribution.

Another expression, the so-called MDKS formula by Hauptman (1972), uses conditional averages of the $|E|^2 - 1$ type of quantity and includes two arbitrary parameters which are so adjusted as to give agreement between the calculated and theoretical distributions of $\cos \xi$.

The characteristics of all these equations are firstly that they are rather demanding of computer time and, secondly, that for the majority of invariants examined, where ξ does not differ appreciably from 0 (modulo 2π), the value of $\cos \xi$ must be computed very accurately indeed to give a small error in $|\xi|$. Thus if the computed value is 0.80 but the real value is 1.00 the corresponding error in the estimate of $|\xi|$ is 47° . What can be very valuable is if a number of *reliable* values of $\cos \xi$ appreciably different from unity can be found. Alternatively if that class of calculated values of $\cos \xi$ which are negative actually contains a large proportion of 'bad' relationships these can then be excluded from a symbolic-addition or similar structure-solving process and the probability of finding the correct solution will be enhanced.

The quadrupole-relationship method

Woolfson (1958) showed that sign relationships could be related and so could have interdependent probabilities. It is possible to extend this idea to phase relationships.

Consider three phase relationships of the form

$$\varphi_{h_1} + \varphi_{h_4} + \varphi_{h_5} + b_1 \simeq 0,$$

$$\varphi_{h_2} - \varphi_{h_4} + \varphi_{h_6} + b_2 \simeq 0$$

and

$$\varphi_{h_3} - \varphi_{h_5} - \varphi_{h_6} + b_3 \simeq 0, \quad (5)$$

where the constant angles, b , arise because of translational elements of symmetry.

These may be combined to give a fourth invariant

$$\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3} + (b_1 + b_2 + b_3) \simeq 0. \quad (6)$$

To illustrate the idea we take the following example from the space group $P2_12_12_1$,

$$\varphi_{2,1,3} - \varphi_{2,4,10} + \varphi_{4,5,7} + \pi = \xi_1 \simeq 0,$$

$$-\varphi_{4,3,9} + \varphi_{2,1,1} + \varphi_{2,4,10} + \pi = \xi_2 \simeq 0$$

and

$$\varphi_{6,4,6} - \varphi_{4,5,7} + \varphi_{2,1,1} + \pi = \xi_3 \simeq 0 \quad (7)$$

which combine to give

$$-\varphi_{2,1,3} + \varphi_{4,3,9} - \varphi_{6,4,6} + \pi = \xi_4 \simeq 0. \quad (8)$$

Similarly the set of relationships

$$\varphi_{2,1,3} - \varphi_{2,4,8} + \varphi_{4,5,5} + \pi = \xi'_1 \simeq 0,$$

$$-\varphi_{4,3,9} - \varphi_{2,1,1} + \varphi_{2,4,8} = \xi'_2 \simeq 0$$

and

$$\varphi_{6,4,6} - \varphi_{4,5,5} + \varphi_{2,1,1} = \xi'_3 \simeq 0 \quad (9)$$

also leads to relationship (8).

The phase relationship (8) is itself just a normal relationship which could be found independently of the others. We call four relationships which combine together as (7) with (8) or as (9) with (8) a *quadrupole*. These two quadrupoles are 'consistent' in that not only is the expectation value of each ξ equal to zero from the normal statistics of ξ but there is also the *exact* relationship

$$\xi_1 + \xi_2 + \xi_3 + \xi_4 = 0. \quad (10)$$

However, one can also find cases of inconsistent quadrupoles - for example

$$-\varphi_{2,1,1} + \varphi_{4,5,7} - \varphi_{6,4,8} = \xi_1 \simeq 0,$$

$$\varphi_{2,1,1} - \varphi_{6,1,8} + \varphi_{4,0,7} = \xi_2 \simeq 0,$$

$$-\varphi_{4,5,7} + \varphi_{2,4,1} + \varphi_{6,1,8} + \pi = \xi_3 \simeq 0$$

and

$$\varphi_{6,4,8} - \varphi_{4,0,7} - \varphi_{2,4,1} = \xi_4 \simeq 0 \quad (11)$$

but with

$$\xi_1 + \xi_2 + \xi_3 + \xi_4 = \pi. \quad (12)$$

If a given ξ appears in a number of relationships of type (12) then it suggests that this ξ may depart appreciably from its expectation value of zero.

Let us now consider a situation where ξ_1 appears in M quadrupoles of the form

$$\xi_1 + \xi_{2,r} + \xi_{3,r} + \xi_{4,r} = C_r \quad (r=1 \text{ to } M). \quad (13)$$

If $C_r = 0$ then

$$\xi_1 = -(\xi_{2,r} + \xi_{3,r} + \xi_{4,r}) \quad (14)$$

and if $C_r = 0$ for $r=1$ to R then these R relationships give

$$R\xi_1 = -\sum_{r=1}^R (\xi_{2,r} + \xi_{3,r} + \xi_{4,r}). \quad (15)$$

Each of the ξ 's on the right-hand side of (15) has an expectation value of 0 and so these relationships alone indicate that the expectation value of ξ_1 is

$$\langle \xi_1 \rangle = 0. \quad (16)$$

We can also estimate the variance of ξ_1 , $\sigma_{\xi_1}^2$, if all the ξ 's on the right-hand side of (15) are different. This will be

$$\sigma_{\xi_1}^2 = \frac{1}{R^2} \sum_{r=1}^R (V_{2,r} + V_{3,r} + V_{4,r}), \quad (17)$$

where V is the variance of a relationship as given by Karle & Karle (1966).

In fact with many contributors on the right-hand side of (15) it is likely that some ξ 's will appear several times. If we change our notation slightly and write (15) as

$$R\xi_1 = - \sum_{i=1}^Q \alpha_i \xi_i \quad (18)$$

where there are Q independent ξ 's on the right-hand side of (15) and ξ_i appears in the summation with coefficient α_i , then

$$q_0^2 = \frac{1}{R^2} \sum_{i=1}^Q \alpha_i^2 V_i. \quad (19)$$

In a similar fashion one can group together those indications for which $C_r = \pi$ and these give $\langle \xi_1 \rangle = \pi$ with variance q_π^2 .

How then can we combine together the complete set of equations (13)? What we cannot do is to take some weighted average of the indications $\langle \xi_1 \rangle = 0$ and $\langle \xi_1 \rangle = \pi$ to give an intermediate value. This is because of the usual 2π ambiguity situation which appears in this case as an inability to distinguish between $\langle \xi_1 \rangle = \pi$ and $\langle \xi_1 \rangle = -\pi$.

What we have done in practice is to take the total variance for all the quadrupole-derived relationships as

$$V_q = |q_0^{-2} - q_\pi^{-2}|^{-1} \quad (20)$$

with $\langle \xi_1 \rangle = 0$ if $q_0^2 > q_\pi^2$ and $\langle \xi_1 \rangle = \pi$ otherwise.

A more precise technique of combining the indications $\xi = 0$ and $\xi = \pi$ is possible. If one assumes that the central-limit theorem is almost applicable in this case then the distributions about 0 and π are approximately Gaussian. The product of the two Gaussian functions in the range $\pi \geq \xi > -\pi$ would then give the overall probability distribution if a suitable normalization factor is applied. The combined probability density for ξ would be an even function and in general would be bimodal. An expectation value for $\langle |\xi| \rangle$ would have to be found by numerical methods.

We feel that this procedure, which would take several times as long as our present technique, is not justified in view of the overall precision attained in the calculation of the expectation values of $|\xi|$.

Some numerical tests

1. Estradiol urea, space group $P2_12_12_1$

This is a known structure solved by Hauptman, Fisher & Weeks (1971). A total of 813 triple-phase invariants were used and gave rise to 10255 consistent quadrupoles and 358 inconsistent ones. The invariants were divided into groups, according to their calculated values of V_q and the actual values of ξ were examined within each group.

It was found, not unexpectedly, that for small values of V_q the actual values of ξ clustered closely about zero. Thus there were 120 calculated values of $V_q < 0.10$ and the mean deviation of the actual values of ξ , $\langle |\xi| \rangle$, was 21° . The largest value of $|\xi|$, $|\xi_{\max}|$ was 99° but the next smaller value was 55° .

It was clear that when the variance became moderately large and positive not much definite information could be gained. However there were two indications where $q_\pi^2 > q_0^2$ and for these the actual values of $|\xi|$ were 140 and 175° .

2. A photolysis product, space group $P2_12_12_1$

This known structure was solved by Karle, Karle & Estlin (1967). A total of 697 triple-phase invariants gave rise to 3086 consistent and 55 inconsistent quadrupoles. The variances were much larger on average than those found for estradiol urea. There were 17 with $V_q < 0.30$ giving $\langle |\xi| \rangle = 25^\circ$ and $|\xi|_{\max} = 62^\circ$. There were five indications for which $q_\pi^2 > q_0^2$ and the value of $|\xi|$ for these were $65, 88, 106, 125, 169^\circ$.

Conclusions

There is undoubtedly some information content in the quadrupole relationships and our tests so far suggest that they enable one to make a selection of relationships which is significantly more reliable than one picked on the basis of the magnitudes of the structure factors alone. For estradiol urea the top 120 relationship, chosen on the basis of values of $|E_{h_1}E_{h_2}E_{h_3}|$, give $\langle |\xi| \rangle = 24^\circ$ and there are nine values of $|\xi|$ greater than $55^\circ - 150, 104, 99, 76, 71, 66, 66, 58$ and 56° . The difference in the value of $\langle |\xi| \rangle$ for this set of relationships and the one chosen by the quadrupole method is not too significant, but what is important is the absence from the set of a number of poor relationships.

For the photolysis product the best 17 relationships chosen on the basis of value of $|E_{h_1}E_{h_2}E_{h_3}|$ gave $\langle |\xi| \rangle = 24^\circ$, a slightly lower figure than that of the quadrupole-selected set, but the value of $|\xi|_{\max}$ was 99° .

We are proposing to try the quadrupole procedure on a large number of known structures to check that it enables a better selection of relationships to be made - better in the sense that fewer relationships are included with large values of $|\xi|$. These relationships can then be used with greater confidence in the early stages of phase determination by symbolic addition or the phase-permutation method. It is a matter of experience that the early stages of phase determination are very critical and that if one can negotiate the first twenty or so phase determinations without large error then the development of further phases is usually reliable. Thus the matter of excluding bad relationships, even very few of them, can be very important from the point of view of solving crystal structures.

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Large Extinction Effects in Magnesium Oxide

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Integrated intensities from a large crystal of magnesium oxide are shown to be affected by primary extinction. The intensities are found to fit the solutions of the dynamic theory of X-ray diffraction for both the Laue and the Bragg cases. A mosaic block size of 3.56×10^{-3} cm has been found.

Introduction

Many authors, *e.g.* Weiss (1966), have pointed out the importance of investigating extinction experimentally and experimental studies have been carried out by varying the wavelength of the incidental radiation (Zachariasen, 1968*a, b*); the degree of polarization of the incident beam (Chandrasekhar, 1960); and the crystal size (Cochran, 1953; Denne, 1972). Recently, Lawrence (1972) has investigated extinction in a large crystal of lithium fluoride which allows a variation in the incident and diffracted path lengths in the crystal, and similar experiments carried out on magnesium oxide are described here.

Magnesium oxide has the sodium chloride-type structure and therefore the positions of the ions in the structure are known. The thermal parameters were obtained from a separate experiment (Lawrence, 1973), using high-order structure factors measured from a small single crystal using molybdenum $K\alpha$ radiation. They were found to be 0.30 and $0.34A^2$ for the magnesium and oxygen ions respectively. Depending, therefore, on the accuracy of the theoretical scattering factors, the calculated structure factors are known and can be assumed to be equal to the kinematic structure factors.

Following Zachariasen (1967), the extinction factor y can be defined as

$$y = (F_o/F_k)^2$$

where F_o and F_k are the observed and kinematic structure factors respectively. Four equations for y have been suggested, each of which can be expanded as an infinite series. They are

$$y = (1 + 2x)^{-1/2} \quad (1)$$

$$y = \frac{\tan h\sqrt{3x}}{\sqrt{3x}} \quad (2)$$

$$y = \frac{\tan^{-1}\sqrt{3x}}{\sqrt{3x}} \quad (3)$$

$$y = \frac{\sum J_{2n+1}(2\sqrt{3x})}{\sqrt{3x}} \quad (4)$$

These equations represent Zachariasen's solution for a small spherical crystal (1) and the solution for dynamic theory for the Bragg and Laue cases, (2) and (4). (3) is an equation whose behaviour is similar to the others.

The parameter x is the sum of the primary and secondary extinction and is given by

$$x = AF_k^2 t^2 + r^* Q \bar{T}$$

A and r^* are constants, t is the mean path length through a single crystal block, Q is the reflectivity of the plane and \bar{T} is the effective path length through the crystal.

For small values of x , the four equations for y are the same, giving $y = 1 - x$, but for large x , y tends to different values. On theoretical grounds, all solutions for y are likely and it was decided to test the validity of the equations experimentally using a large crystal of magnesium oxide, magnesium oxide being chosen since it was known to exhibit large extinction effects.