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On the Reliability of Quartet Estimates

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Abstract

The conditional distributions of a quartet phase derived by Hauptman [*Acta Cryst.* (1975), A**31**, 671-679, 680-687] and by Giacovazzo [*Acta Cryst.* (1976), A**32**, 91-99, 100-104] are reconsidered. Quartets estimated negative by the Hauptman formula are unreliable for small structures.

Symbols

N: number of atoms in the primitive unit cell. In the formulas, for unequal-atom structures, N is replaced by $N_{eq} \simeq \sigma_2^3/\sigma_3^2$ where $\sigma_i = \sum_{j=1}^{N} z_j^i$. Z_j is the atomic number of the jth atom

$\Phi = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} + \varphi_{\mathbf{m}}$ with $\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}=0$

$R = |E|$

$E_1 = E_{\mathbf{h}}$, $E_2 = E_{\mathbf{k}}$, $E_3 = E_{\mathbf{l}}$, $E_4 = E_{\mathbf{m}}$

$E_5 = E_{\mathbf{h}+\mathbf{k}}$, $E_6 = E_{\mathbf{h}+\mathbf{l}}$, $E_7 = E_{\mathbf{k}+\mathbf{l}}$

$\varepsilon_i = R_i^2 - 1$

$G_{ijl} = 2R_iR_jR_l/N^{1/2}$

$B = 2R_1R_2R_3R_4/N$

$D_1(x) = I_1(x)/I_0(x)$ = ratio of modified Bessel functions of orders 1 and 0, respectively.

1. Introduction

After the pioneering work by Schenk (1973, 1974), it was soon understood that reliable estimates of quartet invariants could be obtained *via* the method of the joint probability distribution functions. Two formulas are today widely used.

(1) The Hauptman (1975) formula

$$P(\Phi) \simeq (1/L)\exp(-2B\cos\Phi) I_0(Z_5) I_0(Z_6) I_0(Z_7), \quad (1)$$

where

$$Z_5 = [G_{125}^2 + G_{345}^2 + 2G_{125}G_{345}\cos\Phi]^{1/2},$$

$$Z_6 = [G_{136}^2 + G_{246}^2 + 2G_{136}G_{246}\cos\Phi]^{1/2},$$

$$Z_7 = [G_{237}^2 + G_{147}^2 + 2G_{237}G_{147}\cos\Phi]^{1/2}.$$

Numerical methods are available for calculating: (*a*) the scaling factor L *via* the condition $\int_0^{\pi} P(\Phi)\,d\Phi = 1$; (*b*) the mode Φ_m of $P(\Phi)$; (*c*) the mean value Φ_a, given by

$$\Phi_a = \int_0^{\pi} \Phi P(\Phi)\,d\Phi;$$

(*d*) the variance, V, as given by

$$V = \int_0^{\pi} (\Phi - \Phi_a)^2 P(\Phi)\,d\Phi.$$

According to (1), Φ_m can in principle lie everywhere between 0 and π.

(2) The Giacovazzo (1976, 1980) formula

$$P(\Phi) = [2\pi I_0(G')]^{-1} \exp(G'\cos\Phi), \quad (2)$$

where

$$G' = B(1+\varepsilon_5+\varepsilon_6+\varepsilon_7)/(1+Q),$$

$$Q = [(\varepsilon_1\varepsilon_2+\varepsilon_3\varepsilon_4)\varepsilon_5 + (\varepsilon_1\varepsilon_3+\varepsilon_2\varepsilon_4)\varepsilon_6 + (\varepsilon_1\varepsilon_4+\varepsilon_2\varepsilon_3)\varepsilon_7]/2N.$$

Equation (2) is a von Mises function: it is unimodal, with $\Phi_m = 0$ or π according to whether G' is positive or negative.

Heinerman (1977) showed that the numerator of (2) (but not the denominator) may be obtained from (1) by expanding the Bessel functions $I_0(Z_i)$ according to

$$I_0(Z) = 1 + Z^2/4 + \ldots \simeq \exp(Z^2/4).$$

This result generated the idea that (2) could be considered as a less accurate approximation of (1): more precisely, Giacovazzo's statement that $\cos\Phi$ is expected to be positive when

$$R_5^2 + R_6^2 + R_7^2 > 2$$

could be considered as a rough approximation of the more complex rule given by (1) [in fact, according

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Table 1. *YONO: basis and cross magnitudes of the* 16 *quartets (found among the largest R values) for which* $\Phi_m > 60°$ *according to* (1)

For each quartet, Φ_m and Φ_a, as calculated by (1) and (2), are given. Φ_t is the true value of the quartet phase.

							From (1)		From (2)		
R_1	R_2	R_3	R_4	R_5	R_6	R_7	Φ_m	(Φ_a)	Φ_m	(Φ_a)	Φ_t
3.96	2.72	2.45	2.13	2.63	2.45	2.02	88	80	0	41	1
3.96	2.72	2.36	2.31	2.36	1.57	2.19	107	105	0	40	10
3.96	2.72	2.36	2.13	2.63	2.11	2.16	88	82	0	41	1
3.96	2.72	2.15	2.11	2.36	2.14	2.36	84	75	0	41	2
3.96	2.62	2.45	2.15	2.22	2.45	2.14	92	85	0	40	5
3.96	2.62	2.44	2.13	2.73	2.46	2.16	81	70	0	41	2
3.96	2.62	2.36	2.13	2.22	2.36	2.16	88	83	0	40	3
3.96	2.62	2.36	2.15	2.73	2.36	2.14	81	71	0	41	5
3.96	2.62	2.13	2.11	2.73	2.02	2.36	73	65	0	42	4
3.96	2.36	2.13	2.11	2.73	2.16	1.64	81	72	0	41	5
3.96	2.36	2.21	2.13	3.36	2.63	2.02	73	61	0	40	2
2.72	2.62	2.45	2.11	2.81	1.07	2.14	77	65	0	37	3
2.72	2.62	2.44	2.36	2.81	1.35	2.16	73	64	0	36	3
2.36	2.36	2.18	2.12	1.50	-	1.27	62	62	0	33	12
2.36	2.36	2.31	2.12	1.44	-	1.27	73	66	0	33	17
2.36	2.18	2.12	2.11	-	1.13	1.50	62	64	0	33	11

to (1), the sign of the quartet cosine depends on an intricate interrelationship among all the seven magnitudes $R_1, \ldots, R_7$]. However, various tests (not described here for brevity) carried out on a considerable number of crystal structures covering a large range of structural complexity (from $N \simeq 40$ to 300) and of space groups show that (1) and (2) have nearly equivalent accuracies. The problem was reanalysed by Giacovazzo (1977). He noted that (1) and (2) were obtained by different mathematical techniques: the primitive random variables are the reciprocal vectors in Hauptman's approach and the atomic positional vectors in Giacovazzo's approach. However, the different choices of the primitive random variables are not responsible for the different mathematical forms of (1) and (2), which only depend on the different approximations involved in the two approaches.

A more recent analysis of the problem (Giacovazzo, Camalli & Spagna, 1989) showed that for N sufficiently large the estimates provided by (1) and (2) coincide for all the cases of practical interest, while differences exist when N is small. Very recently, we became interested in the application of quartets to powder data. In this we handled a special class of crystal structures with $3 < N < 40$. To define our strategy for the phasing process, we made some preliminary tests to check the relative accuracies of (1) and (2). It was a great surprise for us to discover for such a class of small structures a systematic lack of accuracy for (1) and a satisfactory effectiveness for (2). Some details of our tests are given in § 2. In § 3, the centrosymmetrical case is taken into account.

A final aspect deserves to be emphasized. Our preliminary tests on powder data were aimed at checking the usefulness of the quartet invariants in a phasing process disturbed by uncertain diffraction moduli (because of diffraction-peak overlapping). We are here interested in a more basic question, the reliability of probabilistic estimates obtained when the diffraction magnitudes are certain. Thus, all the tests presented here have been performed by using the calculated structure factors, in the absence of any experimental ambiguity. We anticipate that quartet-invariant estimates can be very useful when applied to real powder data.

2. The noncentrosymmetric case: tests and applications

The structure YONO [Christensen, Nielsen, O'Reilly & Wroblewski (1992); $Y_4O(OH)_9NO_3$, $P2_1$, $Z = 2$] has been used for our tests [$N_{eq} \simeq 11$]. Among the largest 70 R values we found 7921 quartet invariants having at least two cross magnitudes in the data (this last condition will always hold in this paper).

According to (1), Φ_m is larger than 60° for as many as 1124 quartets: the average value of Φ_a is 82°, while the average of the true values is 34°. These data suggest that a large percentage of positive cosines are wrongly estimated as negative by (1). To provide the reader with a more detailed analysis we calculated the quartets among the largest 20 R values only: a total of 108 quartets were found, 16 of which had Φ_m larger than 60°. In Table 1, the basis and cross magnitudes are given for each of these quartets, together with Φ_m and Φ_a, as calculated by (1) and (2), respectively. In the last column, the true value Φ_t of Φ is shown. In Figs. 1 and 2, the distribution (1) is drawn (dashed line) for the quartets 2 and 14, respectively; they have the maximum (107°) and the minimum (62°) values of Φ_m. In the same figures, (2) is also drawn (solid line). The lack of efficiency of (1) is quite evident. In contrast, (2) correctly estimates all the cosine signs: in particular, the mode is zero for all the quartets, the value of Φ_a is relatively close to zero [Φ_a is calculated from the relation $\cos\Phi_a = D_1(G')$] and is therefore close to Φ_t.

Table 1 suggests that (1) is inefficient when the term B is too large (*e.g.* when N is very small and/or when the basis terms are very large). As a numerical example, let us suppose that $R_1 = R_2 = R_3 = R_4 = 2.8$, $R_5 = R_6 = R_7 = 2$, $N = 5$. Since the quartet is the difference of three pairs of triplets and these are expected to be very close to zero, the quartet should also be close to zero. However, according to (1), $B = 24.59$: thus the effect of the exponential term [*viz* $\exp(-49.18\cos\Phi)$] is not compensated by the product of the three I_0 functions. As a consequence, the quartet is estimated as negative by (1). The distributions (1) and (2) are shown in Fig. 3; while according to (2) Φ_a and Φ_m are 30 and 0°, respectively, according to (1) they are 131 and 132°.

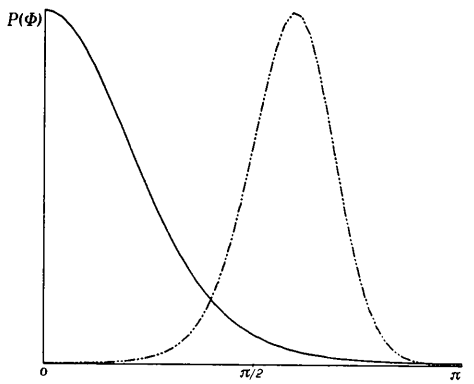

Fig. 1. YONO: distributions (1) (dashed line) and (2) (solid line) for the quartet 2 in Table 1.

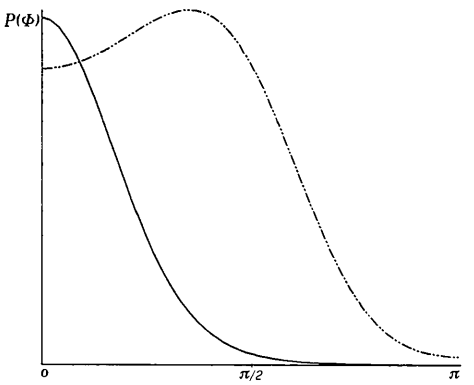

Fig. 2. YONO: distributions (1) (dashed line) and (2) (solid line) for the quartet 14 in Table 1.

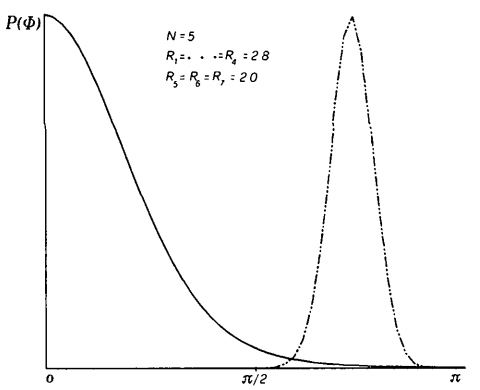

Fig. 3. Distributions (1) (dashed line) and (2) (solid line) for a hypothetical quartet (moduli given in the figure).

Table 2. *PBS: positive and negative estimated quartets*

n is the number of invariants with argument of tanh larger (in modulus) than a given argument ARG, n_w is the number of wrong estimates.

	Quartets estimated as positive		Quartets estimated as negative	
	From (3)	From (4)	From (3)	From (4)
ARG	n (n_w)	n (n_w)	n (n_w)	n (n_w)
0.0	6456 (42)	8201 (164)	1969 (1687)	224 (64)
0.4	5345 (12)	8143 (133)	1173 (952)	197 (50)
1.0	3660 (5)	8096 (128)	478 (263)	125 (23)
2.0	1889 (0)	7674 (104)	109 (86)	52 (0)
3.2	688 (0)	3874 (51)	15 (13)	22 (0)
4.2	224 (0)	601 (10)	4 (4)	9 (0)
6.0	-	143 (0)	-	2 (0)

3. The centrosymmetric case

Two probabilistic formulas are widely used for estimating the quartet signs in centrosymmetric space groups: (*a*) (Green & Hauptman, 1976; Hauptman & Green, 1976)

$$P^{\pm} \simeq (1/L)\exp(\mp B)\cosh(R_5 Z_5^{\pm}) \times \cosh(R_6 Z_6^{\pm})\cosh(R_7 Z_7^{\pm}), \qquad (3)$$

where

$$L = P^+ + P^-, \quad Z_5^{\pm} = (R_1R_2 \pm R_3R_4)/N^{1/2},$$
$$Z_6^{\pm} = (R_1R_3 \pm R_2R_4)/N^{1/2},$$
$$Z_7^{\pm} = (R_1R_4 \pm R_2R_3)/N^{1/2}.$$

(*b*) (Giacovazzo, 1975, 1980)

$$P^+ = \tfrac{1}{2} + \tfrac{1}{2}\tanh(G'/2). \qquad (4)$$

To have a common statistical parameter for our tests, we have transformed the value of P^+ obtained by (3) in an argument G'' of the function tanh, according to $G'' = 2\tanh^{-1}(2P^+ - 1)$. Equations (3) and (4) have been tested on three small structures.

PBS [Christensen, Hazell, Hewat & O'Reilly (1991); PbS_2O_3, *Pbca*, $Z = 8$; $N_{eq} \simeq 10$]. In Table 2, the quartet relationships have been ranked according to the argument (ARG) of the hyperbolic tangent: n is the number of quartets with G' or G'' larger (in modulus) than ARG, n_w is the number of wrongly estimated quartets. It should be observed that:

(*a*) quartets estimated positive by (3) or (4) are reliable [(3) seems a little more efficient than (4)];

Table 3. *HOBA: positive and negative estimated quartets*

n is the number of invariants with argument of tanh larger (in modulus) than a given argument ARG, n_w is the number of wrong estimates.

	Quartets estimated as positive		Quartets estimated as negative	
	From (3)	From (4)	From (3)	From (4)
ARG	n (n_w)	n (n_w)	n (n_w)	n (n_w)
0.0	8572 (0)	8756 (0)	198 (198)	14 (14)
0.4	8284 (0)	8748 (0)	80 (80)	9 (9)
1.0	7300 (0)	8734 (0)	19 (19)	6 (6)
2.0	5240 (0)	8450 (0)	1 (1)	
3.2	2590 (0)	6070 (0)	1 (1)	
4.2	832 (0)	1194 (0)		
6.0		13 (0)		

Table 4. *ERVO: positive and negative estimated quartets*

n is the number of invariants with argument of tanh larger (in modulus) than a given argument ARG, n_w is the number of wrong estimates.

	Quartets estimated as positive		Quartets estimated as negative	
	From (3)	From (4)	From (3)	From (4)
ARG	n (n_w)	n (n_w)	n (n_w)	n (n_w)
0.0	9014 (0)	9796 (0)	782 (782)	0 (0)
0.4	8354 (0)	9795 (0)	461 (461)	
1.0	7018 (0)	9792 (0)	173 (173)	
2.0	3573 (0)	9792 (0)	34 (34)	
3.2	313 (0)	9791 (0)	5 (5)	
4.2	0 (0)	8572 (0)	1 (1)	
6.0		124 (0)		

(*b*) distribution (3) proves completely unreliable for quartets estimated to be negative: a too high percentage of quartets are estimated negative when they are in fact positive. In contrast, (4) preserves a high degree of efficiency.

HOBA [Christensen & O'Reilly (1991); $HoBa_2Cu_{2.90}O_{6.85}$, *Pmmm*, $Z=1$; $N_{eq}\simeq 5$]. 8756 quartets are estimated positive (all correct) and 14 quartets are estimated negative (all incorrectly estimated) by (4) (see Table 3). Formula (3) estimates as positive 8572 quartets (all the estimates are correct) but as many as 198 quartets are estimated negative while they are all positive.

ERVO [Kockelmann, Schäfer & Will (1991); $ErVO_4$, $I4_1/amd$, $Z=4$; $N_{eq}\simeq 3$]. 9796 quartets were found, all of which are positive. 9014 of them are correctly estimated positive and 782 are wrongly estimated negative by application of (3) (see Table 4). On the other hand, all the 9796 quartets are correctly estimated positive by (4).

Equation (3) is more accurate for larger structures, where its ability in picking up negative quartets is comparable with that of (4). However, the tendency of (3) to overestimate the number of negative quartets is still present. The following are given as examples.

GRA4 (Crystallography group, University of York, private communication; $C_{30}H_{22}N_2O_4$, $P\bar{1}$, $Z=2$; $N_{eq}=72$). 234 quartets are estimated negative by (3): the percentage of correctly estimated quartets P_c is 0.88. When (4) is applied in the same conditions, only 149 quartets are estimated negative with $P_c=0.95$.

NEWQB [Grigg, Kemp, Sheldrick & Trotter (1978); $C_{24}H_{20}N_2O_5$, $P\bar{1}$, $Z=4$; $N_{eq}=124$]. 343 quartets are estimated negative by (3), with $P_c=0.64$. If (4) is applied, 256 quartets are estimated negative with $P_c=0.69$.

QUINOL [Wallwork & Powell (1980); $C_6H_6O_2$, $R\bar{3}$, $Z=54$; $N_{eq}=143$]. 3165 quartets are estimated negative by (3), with $P_c=0.63$. When (4) is applied under the same conditions, 3003 quartets are estimated negative, with $P_c=0.66$.

4. Additional applications

Additional tests have been made to check the usefulness (for very small structures) of the von Mises approximation to (1) recently proposed by Giacovazzo, Camalli & Spagna (1989). Accordingly, expression (2) is retained but G' is replaced by

$$G''=B+(q_5-B)+(q_6-B)+(q_7-B), \qquad (5)$$

where q_5, q_6, q_7 satisfy the equations

$$D_1(q_5)=D_1(G_{125})D_1(G_{345}),$$
$$D_1(q_6)=D_1(G_{136})D_1(G_{246}),$$
$$D_1(q_7)=D_1(G_{237})D_1(G_{147}).$$

Our tests, not described for brevity, show that the use of (5) emphasizes the drawbacks presented by (1). Readers are warned not to trust (1) or the von Mises parameter (5) for very small structures.

5. Concluding remarks

The probabilistic formulas of Hauptman (1975) [(1)] and Giacovazzo (1976, 1980) [(2)] have been tested on very small structures. While both proved efficient in the estimation of positive quartets, Hauptman's formula is unreliable for negative quartets. This systematic lack of effectiveness suggests that the probabilistic theory of the quartet invariants is far from being satisfactory. Therefore, (1) and (2) can be considered as different approximations of a still unknown quartet-phase distribution; (2) should not be considered as an approximation of (1).

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X-ray Standing Waves at Grazing Angles

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Abstract

X-ray diffraction from crystal surfaces at grazing angles gives rise to X-ray standing waves above and below the surface. Expressions are derived for the fluorescence observed from atoms located on or in a crystal as a result of excitation by the grazing-angle X-ray standing waves. In addition to the dependence of the fluorescence on the position of the atom with regard to the crystal plane that is responsible for the diffraction, the standing-wave amplitude also depends on the distance from the surface. We present standing-wave measurements from I on Ge(111) and the Ge atoms themselves which illustrate these effects.

1. Introduction

The idea of X-ray standing waves was first proposed and demonstrated by Batterman (1964, 1969), who realized that the interference between incident and diffracted beams could be used to excite atoms selectively in a crystal. The location of impurity atoms in or on the crystal is readily determined along the reciprocal-lattice vector responsible for the diffraction in the two-beam case (Golovchenko, Batterman & Brown, 1974). While X-ray standing-wave (XSW) measurements have been made in both the Bragg (Golovchenko, Batterman & Brown, 1974) and the Laue (Materlik, Frahm & Bedzyk, 1984) geometries, their principal utility has been with systems measured in the Bragg geometry.

Concurrently, the grazing-angle-diffraction (GAD) geometry has proven to be very useful for the determination of lattices on crystal surfaces, particularly the two-dimensional lattices that occur in adsorbate studies (Marra, Eisenberger & Cho, 1979; Eisenberger & Marra, 1981). In this geometry, a collimated X-ray beam is incident on a crystal surface at a grazing angle, usually close to the angle φ_c for total external reflection. The X-ray beam diffracts from a reciprocal-lattice vector approximately parallel to the crystal surface and exits the crystal at a grazing angle. The dynamical theory of X-ray diffraction has been applied to this geometry (Afanas'ev & Melkonyan, 1983; Cowan, 1985) and X-ray standing-wave effects have been observed (Afanas'ev, Imamov, Maslov & Pashaev, 1984; Cowan, Brennan, Jach, Bedzyk & Materlik, 1986; Hashizume & Sakata, 1989). X-ray standing waves have recently been used for the first determination of adsorbate-atom positions in the GAD geometry (Jach & Bedzyk, 1990). The purposes of this paper are to derive the expressions for the X-ray standing-wave fields that occur in GAD in terms of the same parameters as XSW in the Bragg geometry and to demonstrate their validity over a wide range of incidence angles near the critical angle, where the penetration of the X-ray beams varies considerably.

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