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One-Wavelength Technique: Some Probabilistic Formulas Using the Anomalous Dispersion Effect

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Abstract

The method of joint probability distributions has been applied to structure factors in order to assign the phases relative to the complete structure when the phases corresponding to the anomalous scatterers are known. Formulas have been obtained that generalize Sim's [*Acta Cryst.* (1959), **12**, 813-815] distribution to the case in which the anomalous dispersion effect is present.

Notation

p, q	number of anomalous and non-anomalous scatterers respectively in the unit cell
N	number of atoms in the unit cell ($N=p+q$)
$f=f'+if''$	general expression for the atomic scattering factor
F^+, F^-	structure factors of the reflexions **h** and −**h** respectively
$F_p^+, F_p^-, F_q^+, F_q^-$	structure factors of the p anomalous scatterers and of the q non-anomalous scatterers for the reflexions **h** and −**h** respectively
F'	structure factor (imaginary component of anomalous dispersion omitted)
F'_p, F''_p	contribution of anomalous scatterers due to the real and to the imaginary component of anomalous dispersion

$$F'_p=\sum_{j=1}^{p} f'_j \exp 2\pi i\mathbf{hr}_j,$$

$$F''_p=\sum_{j=1}^{p} f''_j \exp 2\pi i\mathbf{hr}_j$$

$\sum=\sum_{j=1}^{N}(f'^2_j+f''^2_j)$	average value of $\lvert F_{\mathbf{h}}\rvert^2$ at given $\lvert\mathbf{h}\rvert$
$\varphi_j=f_j/\sum^{1/2}$	normalized scattering factor of the jth atom
φ'_j, φ''_j	real and imaginary parts of φ_j
$R=F/\sum^{1/2}$	normalized structure factor

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$R^+, \theta^+, R^-, \theta^-$	normalized structure factor and phase of the reflexion **h** and −**h** respectively
$R_p = F_p/\sum^{1/2}$	pseudo-normalized structure factor ($\langle R_p^2\rangle < 1$)
$R_p^+, \theta_p^+, R_p^-, \theta_p^-$	pseudo-normalized structure factor and phase of the p anomalous scatterers for the reflexion **h** and −**h** respectively
$I_i(x)$	modified Bessel function of order i calculated at x
$D_1(x) = I_1(x)/I_0(x)$	ratio of modified Bessel functions of order 1 and 0
cs, ncs	centrosymmetric, non-centrosymmetric

Other locally used symbols are defined in the text.

1. Introduction

Joint probability distribution methods have already been applied by several authors to structure factors with complex scattering factors (see Srinivasan & Parthasarathy, 1976, and literature there quoted; Kroon, Spek & Krabbendam, 1977; Heinerman, Krabbendam, Kroon & Spek, 1978). The advent of synchrotron radiation as a tunable source for X-ray diffraction experiments has opened new prospects for the methods using anomalous dispersion, and encouraged further efforts. New probabilistic approaches have recently been described by Hauptman (1982) and Giacovazzo (1983) for the estimation of two-phase and three-phase invariants, and by Cascarano & Giacovazzo (1984) for the estimation of the 'best' coefficients for a Patterson synthesis devoted to finding the positions of the anomalous scatterers.

In this paper new probabilistic formulas are obtained, which may find useful application in the procedures for the X-ray analysis of crystals when the positions of the anomalous scatterers are known and we look for the complete structure. For the sake of brevity we will give here only the final formulas: for the mathematical approach the reader is referred to a recent book (Giacovazzo, 1980). The practical applications of the formulas are given in § 5.

2. The joint probability distribution $P(R^+, R^-, R_p^+, R_p^-, \theta^+, \theta^-, \theta_p^+, \theta_p^-)$

Let ρ^+, ρ^-, ρ_p^+, ρ_p^-, ψ^+, ψ^-, ψ_p^+, ψ_p^- be carrying variables associated with R^+, R^-, R_p^+, R_p^-, θ^+, θ^-, θ_p^+, θ_p^- respectively. By standard techniques (see Giacovazzo, 1980) we obtain the following general expression for the joint probability distribution function:

$$\begin{aligned}
&P(R^+, R^-, R_p^+, R_p^-, \theta^+, \theta^-, \theta_p^+, \theta_p^-)\\
&\simeq [R^+R^-R_p^+R_p^-/(2\pi)^8]\\
&\times\int_0^\infty \dots \int_0^\infty \int_0^{2\pi} \dots \int_0^{2\pi} \rho^+\rho^-\rho_p^+\rho_p^-\\
&\times \exp\{-i[R^+\rho^+\cos(\theta^+-\psi^+)\\
&+R^-\rho^-\cos(\theta^- - \psi^-)\\
&+R_p^+\rho_p^+\cos(\theta_p^+-\psi_p^+)+R_p^-\rho_p^-\cos(\theta_p^- - \psi_p^-)]\\
&-\tfrac{1}{4}[(\rho^+)^2+(\rho^-)^2+Z_9(\rho_p^+)^2+Z_9(\rho_p^-)^2]\\
&+\tfrac{1}{2}[-|Z_1|\rho^+\rho^-\cos(\psi^+ + \psi^- - \xi_1)\\
&-Z_9\rho^+\rho_p^+\cos(\psi^+ - \psi_p^+)\\
&-|Z_4|\rho^+\rho_p^-\cos(\psi^+ + \psi_p^- - \xi_4)\\
&-|Z_4|\rho^-\rho_p^+\cos(\psi^- + \psi_p^+ - \xi_4)\\
&-Z_9\rho^-\rho_p^-\cos(\psi^- - \psi_p^-)\\
&-|Z_4|\rho_p^+\rho_p^-\cos(\psi_p^+ + \psi_p^- - \xi_4)]\}\\
&\times d\rho^+\, d\rho^-\, d\rho_p^+\, d\rho_p^-\, d\psi^+ \dots d\psi_p^-, \qquad (1)
\end{aligned}$$

where

$$|Z_1|\exp(i\xi_1) = \sum_{j=1}^{N}\varphi_j^2 = \sum_{j=1}^{N}(\varphi_j'^2 - \varphi_j''^2) + 2i\sum_{j=1}^{N}\varphi_j'\varphi_j'',$$

$$|Z_4|\exp(i\xi_4) = \sum_{j=1}^{p}\varphi_j^2 = \sum_{j=1}^{p}(\varphi_j'^2 - \varphi_j''^2) + 2i\sum_{j=1}^{p}\varphi_j'\varphi_j'',$$

$$Z_9 = \sum_{j=1}^{p}\varphi_j\varphi_j^* = \sum_{j=1}^{p}|\varphi_j|^2 = \sum_{j=1}^{p}(\varphi_j'^2 + \varphi_j''^2).$$

Equation (1) is the source of the various distributions calculated in this paper but it will never be calculated in practice. Indeed, among the complex variates F^+, F^-, F_p^+, F_p^- algebraical relations exist depending on the actual crystal structure. Let us suppose, for example, that F^+, F^- and F_p^+ are known. Since

$$F^+ = F_p'^+ + F_q^+ + iF_p''^+,\ (F^-)^* = F_p'^+ + F_q^+ - iF_p''^+, \qquad (2)$$

where $(F^-)^*$ is the complex conjugate of F^-, we have

$$F^+ - (F^-)^* = 2iF_p''^+. \qquad (3)$$

According to (3), $F_p''^+$ is completely defined by F^+ and F^-.

In its turn F_p' is unequivocally defined by $F_p''^+$ and F_p^+, so that F_p^- is fixed too. In practice only the marginal distributions $P(E^+, E^-, E_p^+)$ or $P(E^+, E^-, E_p^-)$ or ... have to be calculated, which can be readily derived from (1) by putting to zero suitable terms of the distribution. If only one type of anomalous scatterer is present and F_p'' is known, then F_p^+ is consequently determined: $F_p^+ = (f' + if'')F_p''^+/f''$. Therefore, the distribution $P(F^+, F^-, F_p^+)$ reduces to the simpler distribution $P(F^+, F^-)\delta(F_p^+ - y)$, where $y = -i(f' + if'')\times[F^+ - (F^-)^*]/(2f'')$. For the same reasons the distribution $P(F^+, F^-, F_p^-)$ reduces to the distribution $P(F^+, F^-)$ times a suitable delta function. The above considerations find a numerical counterpart in the fact that Z_1, Z_4, Z_9 are connected by special relationships if the number of types of anomalous scatterers is smaller than two: for example, $|Z_4| = Z_9$ if only one type of anomalous scatterer is present.

In conclusion, in this paper we will derive the joint probability distributions:

(a) $P(R^+, R^-, \theta^+, \theta^-)$, $P(R^+, R_p^+, \theta^+, \theta_p^+), \ldots$ when only one type of anomalous scatterer is present;

(b) $P(R^+, R^-, R_p^+, \theta_p^+, \theta^+, \theta^-, \theta_p^+), \ldots$ when at least two types of anomalous scatterers are present.

3. Joint probability distribution functions when only one type of anomalous scatterer is present

Let us suppose that only one type of anomalous scatterer is present. Lengthy calculations led us to isolate the following joint probability distributions, whose use depends on the available *a priori* information and on the purposes one wants to achieve.

(a) $P(R^+, R^-, \theta^+, \theta^-)$

$$\simeq \frac{1}{\pi^2}\left[\frac{R^+R^-}{1-|Z_1|^2}\right] \exp\left\{-\frac{(R^+)^2}{1-|Z_1|^2} - \frac{(R^-)^2}{1-|Z_1|^2} + \frac{2|Z_1|R^+R^-}{1-|Z_1|^2}\cos(\theta^+ + \theta^- - \xi_1)\right\}. \tag{4a}$$

Equation (4a) was first derived by Hauptman (1982) and independently by Giacovazzo (1983). It appears now as one of the various distributions that our method is able to calculate.

(b) $P(R^+, R_p^+, \theta^+, \theta_p^+)$

$$\simeq \frac{1}{\pi^2}\left[\frac{R^+R_p^+}{Z_9(1-Z_9)}\right] \exp\left\{\frac{-(R^+)^2}{1-Z_9} - \frac{(R^+)^2}{Z_9(1-Z_9)} + \frac{2}{1-Z_9}R^+R_p^+\cos(\theta^+ - \theta_p^+)\right\}. \tag{4b}$$

(c) $P(R^+, R_p^-, \theta^+, \theta_p^-)$

$$\simeq \frac{1}{\pi^2}\left[\frac{R^+R_p^-}{Z_9(1-Z_9)}\right] \exp\left\{-\frac{(R^+)^2}{1-Z_9} - \frac{(R_p^-)^2}{Z_9(1-Z_9)} + \frac{2R^+R_p^-}{1-Z_9}\cos(\theta^+ + \theta_p^- - \xi_4)\right\}. \tag{4c}$$

(d) $P(R^-, R_p^+, \theta^-, \theta_p^+)$

$$\simeq \frac{1}{\pi^2}\left[\frac{R^-R_p^+}{Z_9(1-Z_9)}\right] \exp\left\{-\frac{(R^-)^2}{1-Z_9} - \frac{(R_p^+)^2}{Z_9(1-Z_9)} + \frac{2R^-R_p^+}{1-Z_9}\cos(\theta^- + \theta_p^+ - \xi_4)\right\}. \tag{4d}$$

(e) $P(R^-, R_p^-, \theta^-, \theta_p^-)$

$$\simeq \frac{1}{\pi^2}\left[\frac{R^-R_p^-}{Z_9(1-Z_9)}\right] \exp\left\{-\frac{(R^-)^2}{1-Z_9} - \frac{(R_p^-)^2}{Z_9(1-Z_9)} + \frac{2R^-R_p^-}{1-Z_9}\cos(\theta^- - \theta_p^-)\right\}. \tag{4e}$$

Numerous conditional and (or) marginal distibutions of (4a)-(4e) can be readily derived by standard techniques, which for brevity are not given here. We only quote those conditional distributions that can usefully be applied in the standard procedures for phase solution, in particular the conditional distributions of $\Phi = \theta^+ + \theta^-$, $\Phi_1 = \theta^+ - \theta_p^+$, $\Phi_2 = \theta^+ + \theta_p^-$, $\Phi_3 = \theta^- + \theta_p^+$, $\Phi_4 = \theta^- - \theta_p^-$.

Let us denote the Von Mises distribution for φ_i by

$$M(\Phi_i; q_i, Q_i) = [2\pi I_0(Q_i)]^{-1} \exp[Q_i \cos(\Phi_i - q_i)].$$

We obtain

$$\text{(a)} \qquad P(\Phi|R^+, R^-) \simeq M(\Phi; \xi_1, Q), \tag{5a}$$

where $Q = 2|Z_1|R^+R^-/(1-Z_1^2)$.

Equation (5a) has already been obtained by Hauptman (1982) and Giacovazzo (1983). It may be noted, in accordance with Cascarano & Giacovazzo (1984), that the distributions $P(F_P''|R^+, R^-)$ or $P(R_P|R^+, R^-)$ are implicitly defined by $P(\Phi|R^+, R^-)$. In particular it was found that

$$\langle |F''|^2 \,|\, |F^+|, |F^-|\rangle \simeq \tfrac{1}{4}[|F^+|^2 + |F^-|^2 - 2|F^+||F^-|D_1(Q)\cos\xi_1], \tag{6}$$

which provides probabilistic coefficients for a Patterson synthesis devoted to finding the positions of anomalous scatterers.

$$\text{(b)} \qquad P(\Phi_1|R^+, R_p^+) \simeq M(\Phi_1; 0, Q_1), \tag{5b}$$

where $Q_1 = 2R^+R_p^+/(1-Z_9)$.

$$\text{(c)} \qquad P(\Phi_2|R^+, R_p^-) \simeq M(\Phi_2; \xi_4, Q_2), \tag{5c}$$

where $Q_2 = 2R^+R_p^-/(1-Z_9)$.

$$\text{(d)} \qquad P(\Phi_3|R^-, R_p^+) \simeq M(\Phi_3; \xi_4, Q_3), \tag{5d}$$

where $Q_3 = 2R^-R_p^+/(1-Z_9)$.

$$\text{(e)} \qquad P(\Phi_4|R^-, R_p^-) \simeq M(\Phi_4; 0, Q_4), \tag{5e}$$

where $Q_4 = 2R^-R_p^-/(1-Z_9)$.

The statistical meanings of ξ_1 and ξ_4 are now clear; ξ_1 is the expected value of Φ and ξ_4 is the expected value of Φ_2 or Φ_3. The distributions (5b)-(5e) can be considered a generalization of the Sim (1959) formula (valid for real scattering factors) to the case in which the imaginary component of the anomalous dispersion is present. If this last one is vanishing, then (5b)-(5c) reduce to Sim's distribution.

4. Joint probability distribution functions where two types of anomalous scatterers are present

Let us suppose that two types of anomalous scatterers are present. Then in analogy with § 2 the more complex joint probability distribution $P(R^+, R^-,$

$R_p^+, \theta^+, \theta^-, \theta_p^+$) may be calculated. We obtain

$$\begin{aligned}
P(R^+, R^-, R_p^+, \theta^+, \theta^-, \theta_p^+) \\
&\simeq (R^+R^-R_p^+/\pi^3)(1-|Z_1|^2)^{-1}Q_{30}^{-1} \\
&\times \exp\{-Y_1(R^+)^2 - Y_2(R^-)^2 - Y_3(R_p^+)^2 \\
&+2R^+R^-Y_{11}\cos(\theta^+ + \theta^- + y_{11}) \\
&+2R^+R_p^+Y_4\cos(\theta^+ - \theta_p^+ + y_4) \\
&+2R^-R_p^+Y_5\cos(\theta^- + \theta_p^+ + y_5)\}, \qquad (7)
\end{aligned}$$

where

$$\begin{aligned}
Y_1 &= (1-|Z_1|^2)^{-1} + Q_3^2/Q_{30}; \\
Y_2 &= (1-|Z_1|^2)^{-1} + Q_9^2/Q_{30}; \\
Y_3 &= Q_{30}^{-1}; \qquad Y_4 = Q_3/Q_{30}, \quad y_4 = q_3; \\
Y_5 &= Q_9/Q_{30}, \quad y_5 = q_9; \\
Y_{11} &= \{|Z_1|^2/(1-|Z_1|^2)^2 + Q_3^2Q_9^2/Q_{30}^2 \\
&\quad -[2|Z_1|Q_3Q_9/(1-|Z_1|^2)Q_{30}] \\
&\quad \times \cos(\xi_1 + q_3 + q_9)\}^{1/2}, \\
\cos y_{11} &= \{[|Z_1|/(1-|Z_1|^2)]\cos\xi_1 \\
&\quad -(Q_3Q_9/Q_{30})\cos(q_3+q_9)\}/Y_{11}, \\
\sin y_{11} &= \{-[|Z_1|/(1-|Z_1|^2)]\sin\xi_1 \\
&\quad -(Q_3Q_9/Q_{30})\sin(q_3+q_9)\}/Y_{11}.
\end{aligned}$$

Again,

$$\begin{aligned}
Q_3 &= \{X_3^2|Z_1|^2/(1-|Z_1|^2)^2 + Z_9^2 \\
&\quad +[2X_3|Z_1|Z_9/(1-|Z_1|^2)]\cos(\xi_1+x_3)\}^{1/2}, \\
\cos q_3 &= \{[X_3|Z_1|/(1-|Z_1|^2)]\cos(\xi_1+x_3)+Z_9\}/Q_3; \\
\sin q_3 &= \{[-X_3|Z_1|/(1-|Z_1|^2)]\sin(\xi_1+x_3)\}/Q_3; \\
Q_9 &= [-X_3/(1-|Z_1|^2)], \; q_9 = x_3; \\
Q_{30} &= Z_9 - Z_9^2 - [X_3^2/(1-|Z_1|^2)]
\end{aligned}$$

and

$$\begin{aligned}
X_3 &= [|Z_1|^2Z_9^2 + |Z_4|^2 - 2|Z_1||Z_4|Z_9\cos(\xi_1-\xi_4)]^{1/2}, \\
\cos x_3 &= [|Z_1|Z_9\cos\xi_1 - |Z_4|\cos\xi_4]/X_3 \\
\sin x_3 &= [-|Z_1|Z_9\sin\xi_1 + |Z_4|\sin\xi_4]/X_3.
\end{aligned}$$

Numerous marginal and (or) conditional distributions can be derived from (7). For the sake of brevity we limit ourselves only to those that can be immediately applied in standard procedures for phase solution:

(a) $$\begin{aligned}
P(\Phi|R^+, R^-, R_p^+) \\
&\simeq L_1^{-1}\exp\{2R^+R^-Y_{11}\cos(\Phi+y_{11})\} \\
&\times I_0\{2R_p^+[(R^+)^2Y_4^2+(R^-)^2Y_5^2 \\
&+2R^+R^-Y_4Y_5\cos(\Phi+y_4+y_5)]^{1/2}\}. \qquad (8a)
\end{aligned}$$

(b) $$\begin{aligned}
P(\Phi_1|R^+, R^-, R_p^+) \\
&\simeq L_2^{-1}\exp\{2R^+R_p^+Y_4\cos(\Phi_1+y_4)\} \\
&\times I_0\{2R^-[(R^+)^2Y_{11}^2+(R_p^+)^2Y_5^2 \\
&+2R^+R_p^+Y_5Y_{11}\cos(\Phi_1+y_{11}-y_5)]^{1/2}\} \qquad (8b)
\end{aligned}$$

(c) $$\begin{aligned}
P(\Phi_3|R^+, R^-, R_p^+) \\
&\simeq L_3^{-1}\exp\{2R^-R_p^+Y_5\cos(\Phi_3+y_5)\} \\
&\times I_0\{2R^+[(R^-)^2Y_{11}^2+(R_p^+)^2Y_4^2 \\
&+2R^-R_p^+Y_4Y_{11}\cos(\Phi_3-y_4+y_{11})]^{1/2}\}. \qquad (8c)
\end{aligned}$$

L_i, $i = 1, 2, 3$, are suitable scale factors whose algebraic expression can be omitted.

Unlike distributions (5), the new conditional distributions (8a), (8b), (8c) are not of Von Mises type. They may usefully be compared with (5a), (5b) and (5d) respectively. In particular, both (5) and (8) take into account the maximal information available when one or two types of anomalous scatterers are present. However, information would be lost if (5) were applied when two types of anomalous scatterers are present.

From (7), the following conditional distribution of R_p is obtained:

$$\begin{aligned}
P(R_p^+|R^+, R^-) &\simeq 2Y_3R_p^+\exp\{-Y_3^{-1}[Y_3^2(R_p^+)^2 \\
&+ Y_4^2(R^+)^2 + Y_5^2(R^-)^2]\}A/B, \qquad (9)
\end{aligned}$$

where

$$\begin{aligned}
A &= I_0(2R^+R^-Y_{11})I_0(2R^+R_p^+Y_4)I_0(2R^-R_p^+Y_5) \\
&+2\sum_{m=1}^{\infty}\cos m(y_{11}-y_4-y_5)I_m(2R^+R^-Y_{11}) \\
&\times I_m(2R^+R_p^+Y_4)I_m(2R_p^+R^-Y_5), \qquad (10) \\
B &= I_0\{2R^+R^-[Y_{11}^2+Y_4^2Y_5^2/Y_3^2 \\
&+2(Y_4Y_5Y_{11}/Y_3)\cos(y_4+y_5-y_{11})]^{1/2}\}. \qquad (11)
\end{aligned}$$

The convergence of the series (10) is not very fast. A useful approximation of (9) is (see Appendix)

$$\begin{aligned}
P(R_p^+|R^+, R^-) \\
&\simeq L^{-1}R_p^+\exp\{-Y_3^{-1}[Y_3^2(R_p^+)^2 \\
&+\alpha\cos(y_4+y_5-y_{11})]\} \\
&\times I_0(2R^+R_p^+Y_4)I_0(2R^-R_p^+Y_5)/I_0(\alpha), \qquad (12)
\end{aligned}$$

where L is a scaling factor and α is a quantity defined by the equation

$$\begin{aligned}
D_1(\alpha) &= D_1(2R^+R^-Y_{11})D_1(2R^+R_p^+Y_4) \\
&\times D_1(2R^-R_p^+Y_5). \qquad (13)
\end{aligned}$$

Equations (9) and (12) can provide estimates of the pseudo-normalized structure factors of the p anomalous scatterers. The value $\langle R_p^+|R^+, R^-\rangle$ may be

Table 1. *A comparison of the discrepancy factors R, immediately following* (14), *for ferredoxin, for the ncs, the cs and all reflexions, using Rossmann's estimate* [(14)] *and ours* [(6)]; *n is the number of reflexions*

ncs		cs		All	
(14)	(6)	(14)	(6)	(14)	(6)
0·46	0·35	1	0·61	0·58	0·41
$n=2604$		$n=724$		$n=3328$	

Table 2. *The coordinates* ($\times 10^4$) *of the* 11 *highest peaks in the Fourier map and the corresponding intensities* (*in parentheses the published positions of the eight* Fe *atoms are given*)

x	y	z	I
7511	172	4865	1962
(7546)	(166)	(4862)	
8342	222	5156	1728
(8328)	(253)	(5142)	
9569	2508	3341	1707
(9536)	(2537)	(3354)	
418	2491	3445	1687
(407)	(2523)	(3453)	
7917	779	4828	1648
(7906)	(776)	(4773)	
9935	1908	3620	1349
(9937)	(1936)	(3614)	
38	2065	2966	1322
(5)	(2089)	(2957)	
7692	682	5409	1286
(7665)	(617)	(5402)	
7126	770	5194	677
8290	338	4477	600
6006	1396	166	586

used, as well as (6), as a Fourier coefficient in a Patterson synthesis devoted to finding the positions of the anomalous scatterers.

5. Practical applications

To gain an insight into the efficiency of the various formulas described above we applied some of them to the calculated structure factors of ferredoxin from *Peptococcus aerogenes* (Sieker, Adman & Jensen, 1972), which crystallizes in $P2_12_12_1$ with $a=30{\cdot}52$, $b=37{\cdot}75$, $c=39{\cdot}37$ Å and $M_r\simeq 6000$. There are eight iron atoms in the molecule. Attempts to locate the Fe atoms by the Patterson synthesis with $(|F^+|-|F^-|)^2$ as coefficients failed because of the noise in the map and the complexity of the Fe–S clusters. The structure was solved by Adman, Sieker & Jensen (1973) by means of heavy-atom derivatives. In our tests data up to 2 Å resolution were calculated and Fe atoms were supposed to be the anomalous scatterers with

$$f'=-1{\cdot}18, \qquad f''=3{\cdot}20.$$

In order to compare the accuracy of the estimates (6) with respect to Rossmann's (1961) estimates

$$|F''|^2\simeq\tfrac{1}{4}(|F^+|-|F^-|)^2, \tag{14}$$

Table 3. *Average values of* $|\Phi_1|$ *and* $|\Phi_2|$ *for various ranges of* Q_1 *and* Q_2 *for ferredoxin*

$n(n_1\simeq n_2)$ is the number of reflexions in the ranges in which Q_i has been divided.

Q_i	n	$\langle\lvert\Phi_1\rvert\rangle$(°)	$\langle\lvert\Phi_2\rvert\rangle$(°)	
$Q_i\geq 2$	123	24	23	
$1\leq Q_i<2$	112	33	32	cs
$0{\cdot}5\leq Q_i<1$	132	57	55	reflexions
$0\leq Q_i<0{\cdot}5$	357	76	73	
$Q_i\geq 2$	524	31	24	
$1\leq Q_i<2$	631	55	43	ncs
$0.5\leq Q_i<1$	660	72	57	reflexions
$0\leq Q_i<0{\cdot}5$	789	83	68	
$Q_i\geq 2$	747	29	24	
$1\leq Q_i<2$	743	52	42	All
$0{\cdot}5\leq Q_i<1$	792	69	57	reflexions
$0\leq Q_i<0.5$	1146	81	70	

we calculated the R factor

$$R=\sum\big||F''_{\rm true}|-|F''_{\rm calc}|\big|/\sum|F''_{\rm true}|.$$

where $|F''_{\rm calc}|$ is given by (6) or (14). The outcome is shown in Table 1. We note:

(a) estimates provided by (6) are markedly more accurate than Rossmann's estimates;

(b) according to Rossmann, $F''\equiv 0$ for cs reflexions, while better estimates are provided by (6), even if they are poorer than for the ncs case. That is because we used the distribution $P(\Phi)$ valid in $P1$ in order to estimate $|F''|^2$ for cs reflexions. It is hoped that better results will be obtained when appropriate distributions vaid for cs reflexions are available.

In spite of this drawback all the $|F''|$ estimates (cs and ncs) were elaborated by a typical run of the *SIR* program (Nunzi *et al.*, 1984). Two one-phase and 20 two-phase seminvariants were actively used in the expansion procedure together with 5439 relationships. They were strengthened by the P_{10} formula (Cascarano *et al.*, 1984). A magic-integer permutation of three reflexions led to 20 possible solutions, the third of which (in order of the combined figure of merit) revealed the correct Fe structure. In Table 2 the positions of the highest 11 peaks in the map (the published positions of the iron atoms are given in parentheses) and the corresponding intensities are shown.

If the positions of anomalous scatterers are known (the phase values θ_p^+ and θ_p^- are consequently known) then estimates of θ^+ and θ^- can be obtained by means of ($5b$)–($5e$). In order to check the efficiency of these formulas we calculated the average values $\langle|\Phi_1|\rangle$ and $\langle|\Phi_2|\rangle$ for various ranges of Q_1 and Q_2. The outcome for ferredoxin is in Table 3. We note:

(a) for ncs reflexions the relation $\theta_p\simeq\theta_p^+$ and $\theta^+\simeq-\theta_p^-$ are sufficiently accurate for $Q\geq 2$. The number of the corresponding reflexions is sufficiently large to constitute a good starting set for phase extension and refinement.

(*b*) for cs reflexions the relation $\theta^+ \simeq \theta_p^+$ and $\theta^+ \simeq -\theta_p^-$ are sufficiently accurate when $Q_i \geq 1$. Thus, information contained in cs phases proves to be not negligible compared with that provided by ncs phases.

6. Concluding remarks

The two main obstacles to overcome when one-wavelength methods are used exploiting the anomalous dispersion effect are: (*a*) finding the positions of the anomalous scatterers; (*b*) estimating phases of the complete crystal structure when the positions of the anomalous scatterers are known. In this paper a variety of new formulas has been derived, which may be used for both (*a*) and (*b*). The practical tests (on error-free diffraction data) show that the formulas are capable of making better estimates for certain magnitudes and phases, and also lead to the heavy-atom structure.

APPENDIX

In accordance with Stephens (1963) and Giacovazzo (1979) the following approximation holds:

$$1+2\sum_{m=1}^{\infty} D_m(x)D_m(y)D_m(z)\cos m(\varphi-q) \simeq 2\pi M(\varphi; q, \alpha), \qquad (A1)$$

where α is the solution of the equation

$$D_1(\alpha)=D_1(x)D_1(y)D_1(z),$$

and M is the Von Mises distribution.

In accordance with (*A*.1) we can write (10) as

$$\begin{aligned} A[I_0(2R^+R^-Y_{11})I_0(2R^+R_p^+Y_4)I_0(2R^-R_p^+Y_5)]^{-1} &= 1+2\sum_{m=1}^{\infty} D_m(2R^+R^-Y_{11})D_m(2R^+R_p^+Y_4) \\ &\quad \times D_m(2R_p^+R^-Y_5)\cos m(y_{11}-y_4-y_5) \\ &\simeq 2\pi M(y_4+y_5-y_{11}; 0, \alpha), \end{aligned} \qquad (A2)$$

where α is given by (13).

Replacing (*A*.2) in (10) and in (9) gives (12).

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Powder Diffraction with Synchrotron Radiation. I. Absolute Measurements

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Abstract

Accurate measurements of the integrated intensities of several reflections from a standard powder sample of Ni have been made using monochromatic synchrotron X-ray radiation of wavelength 1·5413 Å from a perfect double-crystal Si(111) monochromator. A perfect Ge(111) analyzer crystal was mounted on the detector arm of the diffractometer to serve as a narrow 'angular' receiving slit. The intensities were placed on an absolute scale by application of the appropriate powder diffraction expressions, which require the incident photon counts, the axial and equatorial openings of the receiving 'slit', and the polarization factor to be known. The procedure for evaluating these instrumental parameters is described in some detail. The quantitative agreement between these and previous absolute measurements on a standard Ni sample with

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