Acta Cryst. (1975). A31, 731

The Joint Probability Distribution of $E_{\mathbf{k}}$, $E_{\mathbf{h}+\mathbf{k}}$ and $\cos 2\pi(\mathbf{h}/2+\mathbf{k})\cdot\mathbf{U}$ – where U is a Single Patterson Vector – and Related Conditional Averages: Space Group $P\bar{1}$

BY J. J. L. HEINERMAN, H. KRABBENDAM AND J. KROON

Laboratorium voor Structuurchemie, Rijksuniversiteit, Padualaan 8, Utrecht, The Netherlands

(*Received* 22 *April* 1975; *accepted* 26 *April* 1975)

In order to establish a generalized form of an earlier derived algebraic relation between a structure factor, triple products and a single Patterson vector U, the joint probability distribution $P(X_0, X_1, M)$ of $E_{\mathbf{k}}$, $E_{\mathbf{h}+\mathbf{k}}$ and $\cos 2\pi(\mathbf{h}/2+\mathbf{k})\cdot\mathbf{U}$ with h fixed, is derived for space group $P\bar{1}$. From this distribution the desired generalized equations are obtained. The sign probability formula for triple products is adapted to the case that $\cos 2\pi(\mathbf{h}/2+\mathbf{k})\cdot\mathbf{U}$ is known. A numerical check on the expression for the conditional average $\langle\cos 2\pi(\mathbf{h}/2+\mathbf{k})\cdot\mathbf{U}\,||E_{\mathbf{k}}|>t, |E_{\mathbf{h}+\mathbf{k}}|>t\rangle_{\mathbf{k}}$, showed that for an artificial structure the set of signs of the structure factors obtained from this expression was better than that calculated from heavy-atom positions related by U.

Introduction

For structures with centrosymmetric space groups Krabbendam & Kroon (1971) derived a relation between a structure factor, triple products and a resolved single Patterson vector,

$$F_{\mathbf{h}}=\frac{\sum_{\mathbf{k}} F_{\mathbf{h}}F_{\mathbf{k}}F_{\mathbf{h}+\mathbf{k}}\cos 2\pi\mathbf{k}\cdot\mathbf{U}}{\cos 2\pi\mathbf{h}\cdot\frac{\mathbf{U}}{2}\sum_{\mathbf{k}} f_1(\mathbf{k})f_1(\mathbf{h}+\mathbf{k})}, \qquad (1)$$

in which $\mathbf{k}$ ranges uniformly throughout the reciprocal net and $f_1(\mathbf{k})$ and $f_1(\mathbf{h}+\mathbf{k})$ are the form factors (including temperature factors) of the two atoms related by the single Patterson vector $\mathbf{U}=2\mathbf{r}_1$. With the sign probabilities for triple products (Cochran & Woolfson, 1955)

$$P_+ - P_- = \tanh\frac{\varepsilon_3}{\varepsilon_2^3}|U_{\mathbf{h}}U_{\mathbf{k}}U_{\mathbf{h}+\mathbf{k}}|, \qquad (2)$$

(1) was modified to

$$F_{\mathbf{h}}=\frac{\sum_{\mathbf{k}}|F_{\mathbf{h}}F_{\mathbf{k}}F_{\mathbf{h}+\mathbf{k}}|(P_+-P_-)\cos 2\pi\mathbf{k}\cdot\mathbf{U}}{\cos 2\pi\mathbf{h}\cdot\frac{\mathbf{U}}{2}\sum_{\mathbf{k}} f_1(\mathbf{k})f_1(\mathbf{h}+\mathbf{k})}. \qquad (3)$$

With the aid of an R value based on (3) and on the symmetry relations between structure factors, we were able to locate single vectors by scanning through Patterson space. Then the structure factors were calculated with (3) (Krabbendam & Kroon, 1971). However, the scanning procedure takes a lot of computing time. For this reason in two structures heavy-atom single vectors were searched for by calculating R for those Patterson peaks that are larger than a preset value (Kroon & Krabbendam, 1974; Heinerman, Kroon & Krabbendam, 1976).

Some difficulty arose owing to the fact that the calculated value of $F_{\mathbf{h}}$ became very inaccurate when $\cos 2\pi\mathbf{h}\cdot\mathbf{U}/2$, in the denominator, approached zero. The use has been proposed (Kroon & Krabbendam, 1974) in these cases of an equivalent formula, with cosines replaced by sines. An easier way out, followed here, is to dispose of the denominator by replacing in (1) $\mathbf{k}$ by $-\mathbf{h}-\mathbf{k}$ and adding this equation to the original one. The result is, now in terms of normalized structure factors,

$$E_{\mathbf{h}}=\left(\frac{Z_1^2}{\sigma_2}\right)^{-1}\langle E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}\cos 2\pi\left(\frac{\mathbf{h}}{2}+\mathbf{k}\right)\cdot\mathbf{U}\rangle_{\mathbf{k}} \qquad (4)$$

and by introduction of $P_+ - P_-$

$$E_{\mathbf{h}}=\left(\frac{Z_1^2}{\sigma_2}\right)^{-1}\langle|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|(P_+-P_-)\times\cos 2\pi\left(\frac{\mathbf{h}}{2}+\mathbf{k}\right)\cdot\mathbf{U}\rangle_{\mathbf{k}}, \qquad (5)$$

where Z_j is the number of electrons of atom j and $\sigma_2=\sum_{j=1}^{N} Z_j^2$.

A major problem in the application of (3) appeared to be the fact that the equations needed a large number of terms. In this paper we develop a generalization of (4) and (5) on a statistical basis, in analogy to Hauptman's (1970) generalization of the Sayre–Hughes equation (Sayre, 1952; Hughes, 1953), which enables us to reduce the number of terms in the equations. First we derive the joint probability distribution $P(X_0, X_1, M)$ of $E_{\mathbf{k}}$, $E_{\mathbf{h}+\mathbf{k}}$ and $\cos 2\pi(\mathbf{h}/2+\mathbf{k})\cdot\mathbf{U}$. From this the sign probability of triple products is found for the case that not only $\mathbf{h}$, $|E_{\mathbf{k}}|$ and $|E_{\mathbf{h}+\mathbf{k}}|$, but also $\cos 2\pi(\mathbf{h}/2+\mathbf{k})\cdot\mathbf{U}$, is given. In fact, in (5) P_+-P_- stands for this sign probability. Next the generalized expression of (4) is derived. From the conditional probability distribution $P(M\,||E_{\mathbf{k}}|, |E_{\mathbf{h}+\mathbf{k}}|)$ its first and second moments are obtained, which will lead to the generalized form of (5). It is argued that in practical

applications the first moment, extended to the area $|E_{\mathbf{k}}|>t$ and $|E_{\mathbf{h}+\mathbf{k}}|>t$, is to be preferred to the generalized form of (5). The applicability to sign determination of this first moment is checked by a numerical example.

Notation

$\mathbf{r}_j$ position vector of the jth atom
$\mathbf{U}=2\mathbf{r}_1$ single vector
N number of atoms in the unit cell
Z_j number of electrons associated with atom j
$\sigma_n=\sum_{j=1}^{N} Z_j^n$
$\mathbf{h},\mathbf{k}$ reciprocal-lattice vectors
$E_{\mathbf{h}}=\sum_{j=1}^{N/2} \frac{2Z_j}{\sigma_2^{1/2}} \cos 2\pi\mathbf{h}\,.\,\mathbf{r}_j$ normalized structure factor
$s_{\mathbf{h}}$ sign of $E_{\mathbf{h}}$
$E_{\mathbf{h}}^s=\sum_{j=1}^{N/2} \frac{2Z_j^2}{\sigma_4^{1/2}} \cos 2\pi\mathbf{h}\,.\,\mathbf{r}_j$ normalized structure factor of the squared structure
$E_{\mathbf{h}}^f=\sum_{j=1}^{N/2} \frac{2Z_j^4}{\sigma_8^{1/2}} \cos 2\pi\mathbf{h}\,.\,\mathbf{r}_j$ normalized structure factor of the structure to the fourth power
P_+,P_- sign probabilities of $E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}$
P_+^c,P_-^c as P_+,P_- where $\mathbf{h}$, $|E_{\mathbf{k}}|$, $|E_{\mathbf{h}+\mathbf{k}}|$ and $\cos 2\pi\mathbf{h}(\mathbf{h}/2+\mathbf{k})\,.\,\mathbf{U}$ are given
$P(X,\ldots)$ joint probability distribution of $X,\ldots$
$P(X,\ldots\,|\,Y,\ldots)$ is $P(X,\ldots)$ where $Y,\ldots$ are given
$q_j(x,\ldots)$ characteristic function of the joint probability distribution $p_j(\xi,\ldots)$
$\langle X(\mathbf{k})\rangle_{\mathbf{k}}$ mean value of $X(\mathbf{k}),\mathbf{k}$ ranges throughout the whole reciprocal net
$\langle X(\mathbf{k})\,|\,Y,\ldots\rangle_{\mathbf{k}}$ is $\langle X(\mathbf{k})\rangle_{\mathbf{k}}$ where $Y,\ldots$ are given
$\langle X(\mathbf{k})\rangle_{\mathbf{k}_r}$ is $\langle X(\mathbf{k})\rangle_{\mathbf{k}}$ where the conditions still have to be specified.

The joint probability distribution $P(X_0,X_1,M)$

For structures with space group $P\bar{1}$ the method of Hauptman (1971) will be used to derive the joint probability distribution $P(X_0,X_1,M)$ of $E_{\mathbf{k}}$, $E_{\mathbf{h}+\mathbf{k}}$ and $\cos 2\pi(\mathbf{h}/2+\mathbf{k})\,.\,\mathbf{U}$, where $\mathbf{h}$ is fixed, $\mathbf{k}$ is variable and $\mathbf{U}$ is a single Patterson vector.

For $P\bar{1}$ the expression for the normalized structure factor is

$$E_{\mathbf{h}}=\sum_{j=1}^{N/2} \frac{2Z_j}{\sigma_2^{1/2}} \cos 2\pi\mathbf{h}\,.\,\mathbf{r}_j\,, \tag{6}$$

in which N is the number of atoms in the unit cell. Suppose there is a resolved Patterson peak at $\mathbf{U}=2\mathbf{r}_1$. By $p_1(\xi_0,\xi_1,\xi_M)$ we denote the joint probability distribution of $(2Z_1/\sigma_2^{1/2})\cos 2\pi\mathbf{k}\,.\,\mathbf{r}_1$, $(2Z_1/\sigma_2^{1/2})\cos 2\pi(\mathbf{h}+\mathbf{k})\,.\,\mathbf{r}_1$ and $\cos 2\pi(\mathbf{h}/2+\mathbf{k})\,.\,2\mathbf{r}_1$, and by $p_j(\xi_0,\xi_1)$, $j=2,\ldots,N/2$, the joint probability distribution of $(2Z_j/\sigma_2^{1/2})\cos 2\pi\mathbf{k}\,.\,\mathbf{r}_j$ and $(2Z_j/\sigma_2^{1/2})\cos 2\pi(\mathbf{h}+\mathbf{k})\,.\,\mathbf{r}_j$. The characteristic functions $q_1(x_0,x_1,x_M)$ and $q_j(x_0,x_1)$, $j=2,\ldots,N/2$, corresponding to $p_1(\xi_0,\xi_1,\xi_M)$ and the $p_j(\xi_0,\xi_1)$ respectively, are given by

$$q_1(x_0,x_1,x_M)=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp\left[i(x_0\xi_o+x_1\xi_1+x_M\xi_M)\right] \times p_1(\xi_0,\xi_1,\xi_M)\mathrm{d}\xi_0\mathrm{d}\xi_1\mathrm{d}\xi_M \tag{7}$$

and

$$q_j(x_0,x_1)=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp\left[i(x_0\xi_0+x_1\xi_1)\right]p_j(\xi_0,\xi_1)\mathrm{d}\xi_0\mathrm{d}\xi_1\,, \quad j=2,\ldots,\frac{N}{2}\,. \tag{8}$$

Assuming $p_1,\ldots,p_{N/2}$ to be independent, $P(X_0,X_1,M)$ can be obtained from the product of the q's (see *e.g.* Cramér, 1971):

$$P(X_0,X_1,M)=\frac{1}{(2\pi)^3}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp\left[-i(X_0x_0+X_1x_1+Mx_M)\right] \times q_1(x_0,x_1,x_M)\prod_{j=2}^{N/2} q_j(x_0,x_1)\mathrm{d}x_0\mathrm{d}x_1\mathrm{d}x_M\,. \tag{9}$$

Formulae (7) and (8) can be written as

$$q_1(x_0,x_1,x_M)=\left\langle \exp\left[i\left(x_0\frac{2Z_1}{\sigma_2^{1/2}}\cos 2\pi\mathbf{k}\,.\,\mathbf{r}_1 + x_1\frac{2Z_1}{\sigma_2^{1/2}}\cos 2\pi(\mathbf{h}+\mathbf{k})\,.\,\mathbf{r}_1 + x_M\cos 2\pi\left(\frac{\mathbf{h}}{2}+\mathbf{k}\right).2\mathbf{r}_1\right)\right]\right\rangle_{\mathbf{k}} \tag{10}$$

and

$$q_j(x_0,x_1)=\left\langle \exp\left[i\left(x_0\frac{2Z_j}{\sigma_2^{1/2}}\cos 2\pi\mathbf{k}\,.\,\mathbf{r}_j + x_1\frac{2Z_j}{\sigma_2^{1/2}}\cos 2\pi(\mathbf{h}+\mathbf{k})\,.\,\mathbf{r}_j\right)\right]\right\rangle_{\mathbf{k}}, \quad j=2,\ldots,\frac{N}{2}\,. \tag{11}$$

The sum of the two cosines in (11) is replaced by one cosine, following Hauptman (1970),

$$x_0\frac{2Z_j}{\sigma_2^{1/2}}\cos 2\pi\mathbf{k}\,.\,\mathbf{r}_j + x_1\frac{2Z_j}{\sigma_2^{1/2}}\cos 2\pi(\mathbf{h}+\mathbf{k})\,.\,\mathbf{r}_j = \frac{2Z_j}{\sigma_2^{1/2}}A_j\cos(2\pi\mathbf{k}\,.\,\mathbf{r}_j+\varepsilon_j)\,, \tag{12}$$

where

$$A_j=(x_0^2+x_1^2+2x_0x_1\cos 2\pi\mathbf{h}\,.\,\mathbf{r}_j)^{1/2}, \tag{13}$$

$$\cos\varepsilon_j=A_j^{-1}(x_0+x_1\cos 2\pi\mathbf{h}\,.\,\mathbf{r}_j) \tag{14}$$

and

$$\sin\varepsilon_j=A_j^{-1}x_1\sin 2\pi\mathbf{h}\,.\,\mathbf{r}_j\,. \tag{15}$$

Next, for the exponentional form we use the following expansion into Bessel functions* (Watson, 1966, p. 22),

$$\exp(iz\cos\theta)=J_0(z)+2\sum_{n=1}^{\infty}i^nJ_n(z)\cos n\theta\,. \quad (16)$$

The expression for $q_j(x_0,x_1)$ becomes, after averaging,

$$q_j(x_0,x_1)=J_0\left(\frac{2Z_j}{\sigma_2^{1/2}}A_j\right),\quad j=2,\ldots,\frac{N}{2}, \quad (17)$$

where it is assumed that there are no atoms j with $j=2,\ldots,N/2$, which have three rational coordinates. The sum of three cosines in (10) could be replaced by one cosine. However, in this case A and ε are no longer independent of $\mathbf{k}$. Therefore, only the first two cosines are combined, and then

$$\exp[i(2Z_1/\sigma_2^{1/2})A_1\cos(2\pi\mathbf{k}\,.\,\mathbf{r}_1+\varepsilon_1)]$$

and

$$\exp[ix_M\cos 2\pi(\mathbf{h}/2+\mathbf{k})\,.\,2\mathbf{r}_1]$$

are expanded in Bessel functions. After averaging, assuming that the three coordinates of atom 1 are not all rational, it is found that

$$q_1(x_0,x_1,x_M)=J_0\left(\frac{2Z_1}{\sigma_2^{1/2}}A_1\right)J_0(x_M)+2\sum_{n=1}^{\infty}i^{3n}\times J_{2n}\left(\frac{2Z_1}{\sigma_2^{1/2}}A_1\right)J_n(x_M)\cos 2n\left(2\pi\frac{\mathbf{h}}{2}\,.\,\mathbf{r}_1-\varepsilon_1\right)\,. \quad (18)$$

Next the expressions for $q_1(x_0,x_1,x_M)$ and $q_j(x_0,x_1)$ are substituted into (9). The integration with respect to x_M can be done exactly (Watson, 1966, p. 405):

$$\begin{aligned}P(X_0,X_1,M)=&\frac{1}{(2\pi)^2}P(M)\\&\times\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp[-i(X_0x_0+X_1x_1)]\\&\times\left\{J_0\left(\frac{2Z_1}{\sigma_2^{1/2}}A_1\right)+2\sum_{n=1}^{\infty}(-1)^nJ_{4n}\left(\frac{2Z_1}{\sigma_2^{1/2}}A_1\right)\right.\\&\times\cos(2n\arcsin M)\cos 4n\left(2\pi\frac{\mathbf{h}}{2}\,.\,\mathbf{r}_1-\varepsilon_1\right)\\&+2\sum_{n=1}^{\infty}(-1)^nJ_{4n-2}\left(\frac{2Z_1}{\sigma_2^{1/2}}A_1\right)\\&\times\sin[(2n-1)\arcsin M]\\&\left.\times\cos\left[(4n-2)\left(2\pi\frac{\mathbf{h}}{2}\,.\,\mathbf{r}_1-\varepsilon_1\right)\right]\right\}\\&\times\prod_{j=2}^{N/2}J_0\left(\frac{2Z_j}{\sigma_2^{1/2}}A_j\right)\mathrm{d}x_0\mathrm{d}x_1\,,\end{aligned} \quad (19)$$

* For space group $P\bar{1}$ Hauptman & Karle (1958) made use of an expansion into moments, whereas for space group $P1$ Karle & Hauptman (1958) applied for the first time an expansion in Bessel functions, which simplified their calculations. Details for $P1$ have been given by Hauptman (1970).

where $P(M)$ is the probability distribution of $\cos 2\pi(\mathbf{h}/2+\mathbf{k})\,.\,2\mathbf{r}_1$,

$$P(M)=\frac{1}{\pi(1-M^2)^{1/2}}\,. \quad (20)$$

It can be shown that the expression between the accolades can be written as the sum of four exponentials. Next, the product

$$\prod_{j=2}^{N/2}J_0\left(\frac{2Z_j}{\sigma_2^{1/2}}A_j\right)$$

is expanded (Hauptman, 1970, 1971) and the integrations are performed. The resulting expression for $P(X_0,X_1,M)$ can be written as

$$\begin{aligned}P(X_0,X_1,M)=&P(X_0,X_1)P(M)\\&\times\left\{1+\frac{Z_1^2}{\sigma_2}M\left[(X_0^2+X_1^2-2)\cos 2\pi\mathbf{h}\,.\,\frac{\mathbf{U}}{2}+2X_0X_1\right]\right.\\&-\frac{\sigma_4^{1/2}}{\sigma_2^2}Z_1^2E_{\mathbf{h}}^sM\left[2(X_0^2+X_1^2-1)\right.\\&\left.\left.+4X_0X_1\cos 2\pi\mathbf{h}\,.\,\frac{\mathbf{U}}{2}\right]+\ldots\right\},\end{aligned} \quad (21)$$

where

$$\sigma_n=\sum_{j=1}^{N}Z_j^n\,, \quad (22)$$

$$E_{\mathbf{h}}^s=\sum_{j=1}^{N/2}\frac{2Z_j^2}{\sigma_4^{1/2}}\cos 2\pi\mathbf{h}\,.\,\mathbf{r}_j\,, \quad (23)$$

$$E_{\mathbf{h}}^f=\sum_{j=1}^{N/2}\frac{2Z_j^4}{\sigma_8^{1/2}}\cos 2\pi\mathbf{h}\,.\,\mathbf{r}_j \quad (24)$$

and

$$\begin{aligned}P(X_0,X_1)=&\frac{1}{2\pi\left(1-\frac{\sigma_4}{\sigma_2^2}E_{\mathbf{h}}^{s2}\right)^{1/2}}\\&\times\exp\left[-\frac{1}{2\left(1-\frac{\sigma_4}{\sigma_2^2}E_{\mathbf{h}}^{s2}\right)}\right.\\&\left.\times\left(X_0^2+X_1^2-2\frac{\sigma_4^{1/2}}{\sigma_2}E_{\mathbf{h}}^sX_0X_1\right)\right]\\&\times\left\{1-\frac{\sigma_4}{\sigma_2^2}[\tfrac{1}{8}(X_0^4+4X_0^2X_1^2+X_1^4)\right.\\&-\tfrac{5}{4}(X_0^2+X_1^2)+\tfrac{5}{4}]\\&-\frac{\sigma_8^{1/2}}{\sigma_2^2}[E_{\mathbf{h}}^f(\tfrac{1}{2}X_0^3X_1+\tfrac{1}{2}X_0X_1^3-3X_0X_1)\\&+\tfrac{1}{4}E_{2\mathbf{h}}^f(X_0^2X_1^2-X_0^2-X_1^2+1)]\\&\left.+\frac{\sigma_4^{3/2}}{\sigma_2^3}[E_{\mathbf{h}}^s(\tfrac{3}{2}X_0^3X_1+\tfrac{3}{2}X_0X_1^3-7X_0X_1)]+\ldots\right\}\end{aligned} \quad (25)$$

denotes the joint probability distribution of $E_{\mathbf{k}}$ and $E_{\mathbf{h}+\mathbf{k}}$.† In (21) the interdependence of the variables $E_{\mathbf{k}}$ and $E_{\mathbf{h}+\mathbf{k}}$ on the one hand and the variable $\cos 2\pi(\mathbf{h}/2+\mathbf{k})\,.\,\mathbf{U}$ on the other is contained in the series between accolades. $E^s_{\mathbf{h}}$ can be approximated by

$$E^s_{\mathbf{h}} \approx \frac{\sigma_3}{\sigma_2^{1/2}\sigma_4^{1/2}} E_{\mathbf{h}} \text{ (Cochran \& Woolfson, 1955).} \quad (26)$$

For $E^f_{\mathbf{h}}$ the same method leads to

$$E^f_{\mathbf{h}} \approx \frac{\sigma_5}{\sigma_2^{1/2}\sigma_8^{1/2}} E_{\mathbf{h}}\,. \quad (27)$$

In the case that all atoms are identical, (25) reduces to the $P(X_0, X_1)$ as derived by Hauptman & Karle (1958). These authors have also calculated terms of the order $1/N^2$. They state that their formula is valid in the case of dissimilar atoms when N is replaced by σ_2^3/σ_3^2. However, this appears to be compatible only with the main term of our (25).

Sign probabilities for triple products

The sign probabilities P^c_+ and P^c_- for triple products, where $\mathbf{h}$, $|E_{\mathbf{k}}|$, $|E_{\mathbf{h}+\mathbf{k}}|$ and $\cos 2\pi(\mathbf{h}/2+\mathbf{k})\,.\,\mathbf{U}$ are given, can be calculated from $P(X_0, X_1, M)$:

$$\begin{aligned} P^c_+ - P^c_- &= s_{\mathbf{h}} \frac{\sum_{q=0}^{1}\sum_{r=0}^{1}(-1)^{q+r}P\left((-1)^q|E_{\mathbf{k}}|,(-1)^r|E_{\mathbf{h}+\mathbf{k}}|,\cos 2\pi\left(\frac{\mathbf{h}}{2}+\mathbf{k}\right).\mathbf{U}\right)}{\sum_{q=0}^{1}\sum_{r=0}^{1}P\left((-1)^q|E_{\mathbf{k}}|,(-1)^r|E_{\mathbf{h}+\mathbf{k}}|,\cos 2\pi\left(\frac{\mathbf{h}}{2}+\mathbf{k}\right).\mathbf{U}\right)} \\ &= P_+ - P_- + 8s_{\mathbf{h}}\frac{Z_1^2}{\sigma_2}P_+P_-|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|\cos 2\pi\left(\frac{\mathbf{h}}{2}+\mathbf{k}\right).\mathbf{U} \\ &\quad - 16s_{\mathbf{h}}\frac{\sigma_4^{1/2}}{\sigma_2^2}Z_1^2E^s_{\mathbf{h}}P_+P_-|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|\cos 2\pi\left(\frac{\mathbf{h}}{2}+\mathbf{k}\right).\mathbf{U}\cos 2\pi\mathbf{h}\,.\,\frac{\mathbf{U}}{2}+\ldots, \end{aligned} \quad (28)$$

where P_+ and P_- are the sign probabilities for triple products, $\mathbf{h}$, $|E_{\mathbf{k}}|$ and $|E_{\mathbf{h}+\mathbf{k}}|$ given,

$$\begin{aligned} P_+ - P_- &= s_{\mathbf{h}}\frac{\sum_{q=0}^{1}\sum_{r=0}^{1}(-1)^{q+r}P((-1)^q|E_{\mathbf{k}}|,(-1)^r|E_{\mathbf{h}+\mathbf{k}}|)}{\sum_{q=0}^{1}\sum_{r=0}^{1}P((-1)^q|E_{\mathbf{k}}|,(-1)^r|E_{\mathbf{h}+\mathbf{k}}|)} \\ &= \tanh\frac{\frac{\sigma_4^{1/2}}{\sigma_2}s_{\mathbf{h}}E^s_{\mathbf{h}}|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|}{1-\frac{\sigma_4}{\sigma_2^2}E^{s2}_{\mathbf{h}}} \\ &\quad + \left\{1-\left(\tanh\frac{\frac{\sigma_4^{1/2}}{\sigma_2}|E^s_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|}{1-\frac{\sigma_4}{\sigma_2^2}E^{s2}_{\mathbf{h}}}\right)^2\right\} \\ &\quad \times\left\{-\frac{\sigma_8^{1/2}}{\sigma_2^2}s_{\mathbf{h}}E^f_{\mathbf{h}}(\tfrac{1}{2}|E^3_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}| + \tfrac{1}{2}|E_{\mathbf{k}}E^3_{\mathbf{h}+\mathbf{k}}| - 3|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|)\right. \\ &\quad \left.+\frac{\sigma_4^{3/2}}{\sigma_2^3}s_{\mathbf{h}}E^s_{\mathbf{h}}(\tfrac{3}{2}|E^3_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}| + \tfrac{3}{2}|E_{\mathbf{k}}E^3_{\mathbf{h}+\mathbf{k}}| - 7|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|)\right\}+\ldots\,. \end{aligned} \quad (29)$$

In (28) the first term is $P_+ - P_-$. The higher-order terms in (28) express the influence of the known value of $\cos 2\pi(\mathbf{h}/2+\mathbf{k})\,.\,\mathbf{U}$. For equal atoms the first part of (29) reduces to the $P_+ - P_-$ derived by Tsoucaris (1970), which is to be preferred to the one given by Cochran & Woolfson, if $\mathbf{h}$ is fixed and $|E_{\mathbf{h}}|$ is large.

Generalized equations

In the Sayre–Hughes equation $E^s_{\mathbf{h}} = \sigma_2/\sigma_4^{1/2}\langle E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}\rangle_{\mathbf{k}}$ the vector $\mathbf{k}$ ranges uniformly over all vectors of the reciprocal net. Hauptman (1970) has derived a generalized form of this equation for space group $P1$, in which only a restricted set of E's, in practice the larger ones, is involved. We will derive generalized forms of our (4) and (5). First we derive the generalized Sayre–Hughes equation for space group $P\bar{1}$; the generalization of (4) is then obvious.

Let r denote one of the following conditions:

$$t_1 < |E_{\mathbf{k}}| < t_2 \wedge t_3 < |E_{\mathbf{h}+\mathbf{k}}| < t_4\,,$$

or

$$t_1 < |E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}| < t_2\,,$$

or *e.g.*

$$t_1 < |E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}| < t_2 \vee t_3 < |E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}| < t_4\,.$$

Then

$$\begin{aligned} |E_{\mathbf{h}}|\langle E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}\rangle_{\mathbf{k}_r} &= s_{\mathbf{h}}\langle E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}\rangle_{\mathbf{k}_r} \\ &= s_{\mathbf{h}}\langle|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|(P_+ - P_-)\rangle_{\mathbf{k}_r} \\ &= E_{\mathbf{h}}\langle|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|(P_+ - P_-)\rangle_{\mathbf{k}_r}, \end{aligned} \quad (30)$$

in which $P_+ - P_-$ is given by (29). From this the generalized Sayre–Hughes equation follows at once,

$$E_{\mathbf{h}} = \frac{|E_{\mathbf{h}}|}{\langle|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|(P_+ - P_-)\rangle_{\mathbf{k}_r}}\langle E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}\rangle_{\mathbf{k}_r}. \quad (31)$$

† $P(X_0, X_1)$ was derived separately from $P(X_0, X_1, M)$, again by means of an expansion in Bessel functions. (25) and (21) proved to satisfy $\int_{-1}^{1} P(X_0, X_1, M)\mathrm{d}M = P(X_0, X_1)$.

Following the same argument the generalized form of (4) is found,

$$E_{\mathbf{h}}=\frac{|E_{\mathbf{h}}|}{\left\langle |E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|(P_+^c-P_-^c)\cos 2\pi\left(\frac{\mathbf{h}}{2}+\mathbf{k}\right).\mathbf{U}\right\rangle_{\mathbf{k}_r}} \times\left\langle E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}\cos 2\pi\left(\frac{\mathbf{h}}{2}+\mathbf{k}\right).\mathbf{U}\right\rangle_{\mathbf{k}_r}. \quad (32)$$

If no conditions are imposed and if for the calculation of $\langle|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|(P_+^c-P_-^c)\cos 2\pi(\mathbf{h}/2+\mathbf{k}).\mathbf{U}\rangle_{\mathbf{k}_r}$ use is made of $P(X_0,X_1,M)$, (4) is obtained.

To derive a generalized form of (5) we proceed as follows:

$$\left\langle |E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|(P_+^c-P_-^c)\cos 2\pi\left(\frac{\mathbf{h}}{2}+\mathbf{k}\right).\mathbf{U}\right\rangle_{\mathbf{k}_r} =\left\langle\int_{-1}^{1}|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}| \times(P_+^c-P_-^c)M\,P(M\,||E_{\mathbf{k}}|,|E_{\mathbf{h}+\mathbf{k}}|)\mathrm{d}M\right\rangle_{\mathbf{k}_r}, \quad (33)$$

where

$$P(M\,||E_{\mathbf{k}}|,|E_{\mathbf{h}+\mathbf{k}}|) =\frac{\sum_{q=0}^{1}\sum_{r=0}^{1}P((-1)^q|E_{\mathbf{k}}|,(-1)^r|E_{\mathbf{h}+\mathbf{k}}|,M)}{\sum_{q=0}^{1}\sum_{r=0}^{1}P((-1)^q|E_{\mathbf{k}}|,(-1)^r|E_{\mathbf{h}+\mathbf{k}}|)}$$
$$=P(M)\left\{1+\frac{Z_1^2}{\sigma_2}M\left[(E_{\mathbf{k}}^2+E_{\mathbf{h}+\mathbf{k}}^2-2)\cos 2\pi\mathbf{h}.\frac{\mathbf{U}}{2}+2s_{\mathbf{h}}|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|(P_+-P_-)\right]\right.$$
$$-\frac{\sigma_4^{1/2}}{\sigma_2^2}Z_1^2E_{\mathbf{h}}^sM\left[2(E_{\mathbf{k}}^2+E_{\mathbf{h}+\mathbf{k}}^2-1)+4s_{\mathbf{h}}|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|(P_+-P_-)\cos 2\pi\mathbf{h}.\frac{\mathbf{U}}{2}\right]+\ldots\left.\right\}. \quad (34)$$

The evaluation of the integral in the right-hand side of (33) amounts to the evaluation of the conditional averages of $\cos 2\pi(\mathbf{h}/2+\mathbf{k}).\mathbf{U}$ and $\cos^2 2\pi(\mathbf{h}/2+\mathbf{k}).\mathbf{U}$,

$$\int_{-1}^{1}MP(M\,||E_{\mathbf{k}}|,|E_{\mathbf{h}+\mathbf{k}}|)\mathrm{d}M =\frac{Z_1^2}{\sigma_2}\left[\tfrac{1}{2}(E_{\mathbf{k}}^2+E_{\mathbf{h}+\mathbf{k}}^2-2)\cos 2\pi\mathbf{h}.\frac{\mathbf{U}}{2}+s_{\mathbf{h}}|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|(P_+-P_-)\right]$$
$$-\frac{\sigma_4^{1/2}}{\sigma_2^2}Z_1^2E_{\mathbf{h}}^s\left[E_{\mathbf{k}}^2+E_{\mathbf{h}+\mathbf{k}}^2-1+2s_{\mathbf{h}}|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|(P_+-P_-)\cos 2\pi\mathbf{h}.\frac{\mathbf{U}}{2}\right]+\ldots, \quad (35)$$

$$\int_{-1}^{1}M^2P(M\,||E_{\mathbf{k}}|,|E_{\mathbf{h}+\mathbf{k}}|)\mathrm{d}M=\tfrac{1}{2}. \quad (36)$$

The resulting generalized form of (5) is

$$E_{\mathbf{h}}=\frac{1}{W}\left\langle |E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|(P_+^c-P_-^c)\cos 2\pi\left(\frac{\mathbf{h}}{2}+\mathbf{k}\right).\mathbf{U}\right\rangle_{\mathbf{k}_r}, \quad (37)$$

where

$$W=\frac{Z_1^2}{\sigma_2}\left[\tfrac{1}{2}s_{\mathbf{h}}\langle(|E_{\mathbf{k}}^3E_{\mathbf{h}+\mathbf{k}}|+|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}^3| -2|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|)(P_+-P_-)\rangle_{\mathbf{k}_r}\cos 2\pi\mathbf{h}.\frac{\mathbf{U}}{2} +\langle E_{\mathbf{k}}^2E_{\mathbf{h}+\mathbf{k}}^2\rangle_{\mathbf{k}_r}\right]-\frac{\sigma_4^{1/2}}{\sigma_2^2}Z_1^2E_{\mathbf{h}}^s\left[s_{\mathbf{h}}\langle(|E_{\mathbf{k}}^3E_{\mathbf{h}+\mathbf{k}}| +|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}^3|-|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|)(P_+-P_-)\rangle_{\mathbf{k}_r} +2\langle E_{\mathbf{k}}^2E_{\mathbf{h}+\mathbf{k}}^2\rangle_{\mathbf{k}_r}\cos 2\pi\mathbf{h}.\frac{\mathbf{U}}{2}\right]+\ldots. \quad (38)$$

Considering the order of the terms in (37), it can be seen that for P_+-P_- (in W and in $P_+^c-P_-^c$), only the first term of (29) is needed.

The variance of

$$|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|(P_+^c-P_-^c)\cos 2\pi(\mathbf{h}/2+\mathbf{k}).\mathbf{U},$$

given $|E_{\mathbf{k}}|$ and $|E_{\mathbf{h}+\mathbf{k}}|$, depends upon $|E_{\mathbf{k}}|$ and $|E_{\mathbf{h}+\mathbf{k}}|$ (and also upon $|E_{\mathbf{h}}|$, but this is not important since $\mathbf{h}$ is fixed). On the other hand, for not too large values of Z_1^2/σ_2 the variance of $\cos 2\pi(\mathbf{h}/2+\mathbf{k}).\mathbf{U}$, given $|E_{\mathbf{k}}|$ and $|E_{\mathbf{h}+\mathbf{k}}|$, is approximately constant. Therefore, instead of (37) we prefer to use in practical applications

$$\left\langle\cos 2\pi\left(\frac{\mathbf{h}}{2}+\mathbf{k}\right).\mathbf{U}\right\rangle_{\mathbf{k}_r} =\frac{Z_1^2}{\sigma_2}\left[\tfrac{1}{2}(\langle E_{\mathbf{k}}^2+E_{\mathbf{h}+\mathbf{k}}^2\rangle_{\mathbf{k}_r}-2)\cos 2\pi\mathbf{h}.\frac{\mathbf{U}}{2} +s_{\mathbf{h}}\langle|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|(P_+-P_-)\rangle_{\mathbf{k}_r}\right]$$
$$-\frac{\sigma_4^{1/2}}{\sigma_2^2}Z_1^2E_{\mathbf{h}}^s\left[\langle E_{\mathbf{k}}^2+E_{\mathbf{h}+\mathbf{k}}^2\rangle_{\mathbf{k}_r}-1 +2s_{\mathbf{h}}\langle|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|(P_+-P_-)\rangle_{\mathbf{k}_r}\cos 2\pi\mathbf{h}.\frac{\mathbf{U}}{2}\right]+\ldots, \quad (39)$$

which can easily be obtained from (35). Note that if the equations obtained from (39) by replacing $\mathbf{U}$ by $2\mathbf{r}_i$ and by multiplying the equation by $2Z_i/\sigma_2^{1/2}$, for $i=1,\ldots,N/2$, are added together, an expression for $\langle E_{\mathbf{h}+2\mathbf{k}}\rangle_{\mathbf{k}_r}$ is found, which in the case of equal atoms reads

$$\langle E_{\mathbf{h}+2\mathbf{k}}\rangle_{\mathbf{k}_r} =\frac{1}{N^{1/2}}s_{\mathbf{h}}\left\langle|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|\tanh\frac{\frac{1}{N^{1/2}}|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|}{1-\frac{E_{\mathbf{h}}^2}{N}}\right\rangle_{\mathbf{k}_r} -\frac{1}{2N}E_{\mathbf{h}}\langle E_{\mathbf{k}}^2+E_{\mathbf{h}+\mathbf{k}}^2\rangle_{\mathbf{k}_r}+\ldots. \quad (40)$$

A numerical test

Formula (39) can be used to determine the signs of structure factors by comparing the agreement between the left and the right-hand sides of the equation, once for $s_{\mathbf{h}}=+$ and once for $s_{\mathbf{h}}=-$, and by accepting the sign that gives the best result. We applied this to an artificial structure in $P\bar{1}$ with one Mg, two O and eight C atoms in the asymmetric unit; the structure was constructed from a real one (Spek, 1975) by leaving out a few atoms in order to remove Patterson overlap on the Mg–Mg single vector (vector **U**). Normalized structure factors were calculated within the Cu $K\alpha$ sphere. The signs of all structure factors were determined with the aid of (39). For $E^s_{\mathbf{h}}$ use was made of (26). Only $|E_{\mathbf{k}}|$'s and $|E_{\mathbf{h}+\mathbf{k}}|$'s larger than 1·35 were included in the equations. Although the quantitative agreement was poor, most of the signs were determined correctly. In Fig. 1(*a*) the result is shown for the case that we used only the first-order term (order: Z_1^2/σ_2) in the equation. On the horizontal axis the structure factors are arranged in groups of 100 with decreasing $|E_{\mathbf{h}}|$ values from left to right. For each group the percentage of correctly determined signs is given (vertical axis). Fig. 1(*b*) gives the result after introduction of the second-order term [order: $(\sigma_4^{1/2}/\sigma_2^2)Z_1^2E^s_{\mathbf{h}}$]. The percentages of signs correctly determined from the heavy-atom positions are depicted in Fig. 1(*c*). Going from Fig. 1(*a*) to Fig. 1(*b*) it is seen that the result is improved by the introduction of the second-order term, except for the first 100 E's. The poor result for the very large $|E|$'s is due to the fact that the convergence of the series decreases with increasing $|E_{\mathbf{h}}|$. By comparing Fig. 1(*b*) and Fig. 1(*c*) it is evident that for this example, except for the very large $|E|$'s, our equation gives better signs than those calculated from the heavy-atom positions.

Discussion

In the derivation of $P(X_0, X_1, M)$ we assumed that $p_1, \ldots, p_{N/2}$ are independent. This holds if there are no integers m_j, two of them not zero, such that

$$\sum_{j=1}^{N/2} m_j \mathbf{r}_j = \mathbf{r}\,, \qquad (41)$$

where the three components of **r** are integers. To derive the formulae for $q_1(x_0, x_1, x_M)$ and $q_j(x_0, x_1)$, $j=2, \ldots, N/2$, we assumed that no atom has three rational coordinates. So the derivation of $P(X_0, X_1, M)$ is valid if there are no integers m_j, not all zero, such that (41) holds. The more m_j's there are that are unequal to zero and the larger they are, the less the influence of (41). If most of the m_j's are zero, and the other m_j's (m_1 inclusive) are small (consider as an example Patterson overlap on the single vector, *e.g.* $m_1=2$, $m_2=1$ and $m_3=-1$), especially the part of $P(X_0, X_1, M)$ which depends on M will be influenced.

For the largest structure factors of the artificial structure used for the numerical test, (39) is not accurate enough to predict the signs. In this case higher-order terms are needed. Possibly, better applicable formulae could be obtained with an expression for $P(X_0, X_1, M)$ where M remains in the exponent. For structures where $\sigma_4^{1/2}/\sigma_2$ is smaller than in the present numerical test we expect that more of the signs of the largest structure factors will be correct.

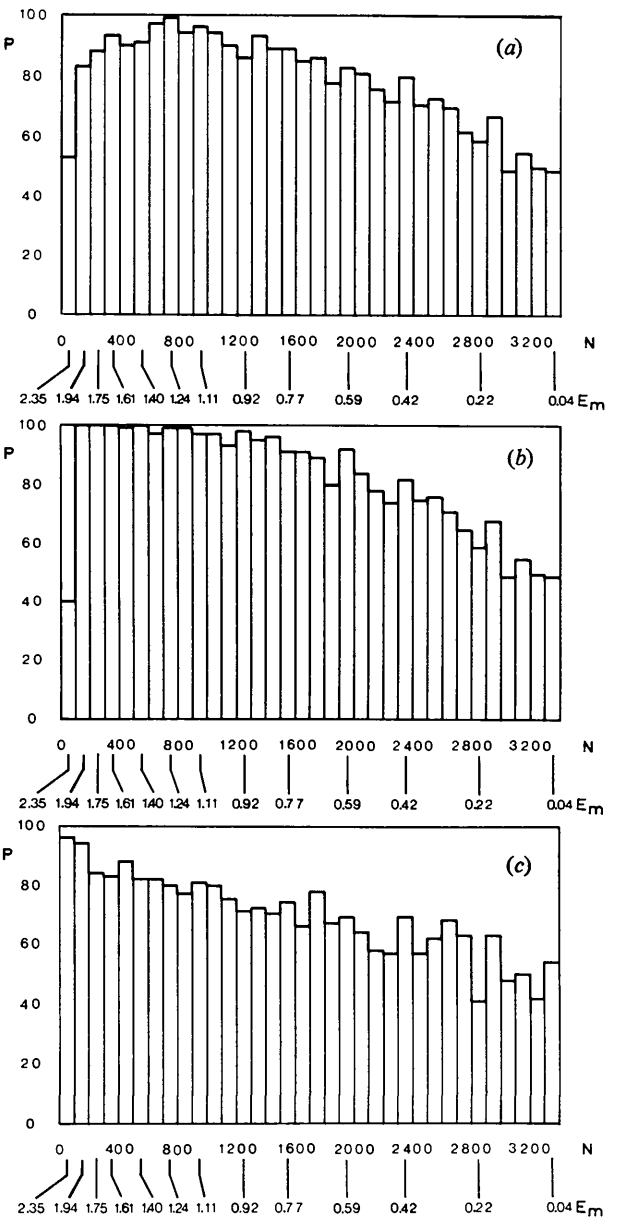

Fig. 1. Horizontal axis: Normalized structure factors arranged in groups of 100 from left to right in order of decreasing magnitude; sequence number (N) and median values (E_m) are indicated. Vertical axis: The percentage (P) of correctly predicted signs. (*a*) Sign determination with (39); only the first-order term is used. (*b*) As in (*a*), now with the second-order term included. (*c*) Sign determination from the heavy-atom positions.

We thank Dr H. Hauptman for his interest in the subject (Parma, seminar 1973) and Professor A. F. Peerdeman for stimulating discussions and critical reading of the manuscript.

References

COCHRAN, W. & WOOLFSON, M. M. (1955). *Acta Cryst.* **8**, 1–12.
CRAMÉR, H. (1971). *Mathematical Methods of Statistics.* Princeton Univ. Press.
HAUPTMAN, H. (1970). Seminar, CECAM workshop, Orsay, September 1970.
HAUPTMAN, H. (1971). *Z. Kristallogr.* **134**, 28–43.
HAUPTMAN, H. & KARLE, J. (1958). *Acta Cryst.* **11**, 149–157.
HEINERMAN, J. J. L., KROON, J. & KRABBENDAM, H. (1976). To be published.
HUGHES, E. W. (1953). *Acta Cryst.* **6**, 871.
KARLE, J. & HAUPTMAN, H. (1958). *Acta Cryst.* **11**, 264–269.
KRABBENDAM, H. & KROON, J. (1971). *Acta Cryst.* A**27**, 362–367.
KROON, J. & KRABBENDAM, H. (1974). *Acta Cryst.* B**30**, 1463–1469.
SAYRE, D. (1952). *Acta Cryst.* **5**, 60–65.
SPEK, A. L. (1975). To be published.
TSOUCARIS, G. (1970). *Acta Cryst.* A**26**, 492–499.
WATSON, G. N. (1966). *A Treatise on the Theory of Bessel Functions.* Cambridge Univ. Press.

Acta Cryst. (1975). A**31**, 737

Kinematical Theory of Mössbauer Diffraction by Magnetically Ordered Crystals

BY V. A. BELYAKOV AND R. CH. BOKUN

All Union Scientific Institute of Physical-Technical and Radiotechnical Measurements, Moscow, USSR

(*Received* 18 *October* 1972; *accepted* 21 *April* 1975)

The kinematical theory of Mössbauer diffraction by magnetically ordered crystals is developed. The case of completely resolved Zeeman splitting of a Mössbauer line is examined in detail. The expressions for coherent scattering amplitudes and scattering cross sections of γ-rays at magnetic and crystalline diffraction maxima are derived for the main types of magnetic ordering (ferromagnetic, antiferromagnetic, weak ferromagnetic and helicoidal structures) in the case of the dipole Mössbauer transition. A direct connexion between the polarization of the scattered quanta and the magnetic and crystalline structure is revealed in the expressions obtained for polarization vector and the polarization density matrix (in the cases of polarized and unpolarized incident beams respectively). The explicit form of the polarization density matrix at magnetic reflexions for an antiferromagnet is given. The applications of the present results to experimental and theoretical investigations are discussed.

In a number of theoretical (Afanas'ev & Kagan, 1965, 1973; Kagan, Afanas'ev & Perstnev, 1968; Zhdanov & Kuz'min, 1968; Hannon & Trammel, 1969; Afanas'ev & Perstnev, 1969; Belyakov & Ajvazian, 1968, 1970; Chukhovskii & Perstnev, 1972) and experimental (Voitovetskii, Korsunskii, Novikov & Pazhin, 1968; Smirnov, Sklyarevskii, Voscanyan & Artem'ev, 1969; Parak, Mössbauer, Biebl, Formanek & Hoppe, 1971; Artem'ev, Sklyarevskii, Smirnov & Stepanov, 1972; Artem'ev, Perstnev, Sklyarevskii, Smirnov & Stepanov, 1973; Mirzababaev, Smirnov, Sklyarevskii, Artem'ev, Izrailenko & Babkov, 1971) papers interesting features and possible applications of Mössbauer diffraction were revealed. In particular, the experiments on Mössbauer diffraction by magnetically ordered crystals (Smirnov *et al.*, 1969; Artem'ev *et al.*, 1972, 1973) and crystals having complicated structures of electric field gradient (EFG) (Mirzababaev *et al.*, 1971) have shown the practical feasibility of magnetic and EFG structure investigations of crystals by means of Mössbauer γ-ray diffraction. Application of Mössbauer diffraction to magnetic and crystalline structure investigations looks a promising and useful supplement to X-ray, neutron, electron diffraction methods because the Mössbauer diffraction method (Mössbauerography) has some additional advantages over conventional methods (Zhdanov & Kuz'min, 1968; Parak *et al.*, 1971; Ajvazian & Belyakov, 1969*a*,*b*; Belyakov & Ajvazian, 1969; O'Connor & Spicer, 1969; Batterman, Maracci, Merlini & Pace, 1973). Other promising fields of Mössbauer diffraction investigation are the study of the γ-ray collective interaction with nuclei, the influence of the crystal lattice on nuclear processes and related topics in nuclear physics (Afanas'ev & Kagan, 1967).

The theory of Mössbauer diffraction was developed mostly for crystals without magnetic field and EFG in the sites occupied by Mössbauer nuclei. In connexion with the above-mentioned experiments there is a need for a theory applicable to the cases of magnetically ordered crystals and crystals in which Mössbauer nuclei are situated in the sites with non-zero EFG. In the papers published on this topic the simplest cases of magnetic ordering and EFG were examined in the kinematical approximation (Belyakov & Ajvazian,