Likewise, the elimination of the noise of the refinement of the mean structure from the A matrix may be performed in a similar manner as before.

The pseudosymmetry operator which gives high covariance between parameters need not always allow a sensible selection of combination of parameters. An example is the pseudosymmetry operators $(\frac{1}{3}+x,\ y,\ \frac{1}{2}-z)$, $(\frac{2}{3}+x,\ y,\ \frac{1}{2}-z)$. A refinement procedure for a crystal structure with these pseudosymmetry operators is currently being investigated, and will be published elsewhere.

We have seen earlier that a full-matrix solution tends to overweight the changes in the 'difference' structure whereas a block diagonal approach overweights the changes in the 'mean' structure but underweights the 'difference' structure, and so other refinement procedures may be considered.

As stated in the Introduction, the refinement of the 'difference' structure is only possible as $(\sin\theta)/\lambda$ increases. Thus the simplest method to reduce covariance between highly covarying parameters is to use high-angle data or to weight data according to $(\sin\theta)/\lambda$. Similarly, if there is an index condition so that only the 'difference' structure contributes to certain reflexions then the weight of these reflexions can be increased.

A combination of a full-matrix approach and a diagonal approach can be considered. This is simply brought about by multiplying the diagonal elements a_{ii} of the A matrix by a constant, k_1, greater than 1, and the elements of the column matrix B by a constant k_2. The constant k_2 should be less than k_1, otherwise the refinement of the 'mean' structure will be overweighted. A down weighting of the refinement of the 'difference' structure is brought about by a reduction of the apparent covariance between parameters. The shifts of highly covarying parameters are reduced more than the shifts in parameters which are less covariant. A read-out/read-in interruption to the least-squares refinement program prior to the inversion of the A matrix allows any number of modifications to be tested without re-evaluating the A matrix each time.

This final method has a lot to recommend it. Consider our simple two-variable example again. The equation

$$\sqrt{a_{11}}\,\Delta u_1=\frac{\beta}{2-\delta}+\frac{\gamma}{\delta}$$

becomes

$$\frac{k_1}{k_2}\sqrt{a_{11}}\,\Delta u_1=\frac{\beta}{2-\delta'}+\frac{\gamma}{\delta'}=\omega_1\beta+\omega_2\gamma$$

where

$$1-\delta'=k_1^{-1}\,(1-\delta)\,;\quad k_1>1\,.$$

δ'/δ varies from ∞ for $\delta=0$ to 1 for $\delta=1$. Also $(2-\delta)/\delta$ varies from ∞ for $\delta=0$ to 1 for $\delta=1$, whereas $\omega_2/\omega_1=(2-\delta')/\delta'$ varies from $(k_1+1)/(k_1-1)$ for $\delta=0$ to 1 for $\delta=1$.

Thus we have a built-in discrimination against those parameters of the 'difference' structure which are least accurately determined. If we choose k_1 as 1·4 say, then ω_2/ω_1 varies between 6 and 1. This procedure will also work when a larger set of covarying variables is considered.

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The Use of Phase Relationships between Quartets of Reflexions

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Phase relations between quartets of reflexions can be found either directly from a generalized Hughes expression or by elimination of the phase of a reflexion common to two $\sum_2$ relationships. By combining the information from both types, strengthened quartet relationships (SQR) can be constructed, which are comparable to the $\sum_2$ relations in reliability and number. Most of the reliable SQR's involve the strong reflexions only. The phases of these reflexions are related by a highly overdetermined system of equations leading in a simple manner to a good starting set.

List of symbols

$F(H)$	Structure factor of reflexion H
E_H	Normalized structure factor
U_H	Unitary structure factor
f	Atomic scattering factor
g	Scattering factor of the squared electron density of an atom
N	Number of atoms in the unit cell
V	Volume of the unit cell
$S(H)$	The sign of reflexion H
φ_H	The phase of reflexion H

Introduction

For structures containing but one kind of atom Sayre (1952) derived the expression

$$\frac{g}{f}F(H)=\frac{1}{V}\sum_{H'}F(H')F(H-H')\,. \qquad (1)$$

Hughes (1953) found the related formula

$$U_{H+K}=N\quad\overline{U_HU_K}^{\,H+K} \qquad (2)$$

where the average is taken keeping $H+K$ constant. In an analogous way Simerska (1956) derived the general expression

$$U_{H1+H2+\dots+Hm} = N^{m-1}\,\overline{U_{H1}U_{H2}\dots U_{Hm}}^{\,(H1+H2+\dots+Hm)}\,. \qquad (3)$$

From equations (1) and (2) it follows that:

$$S(H)S(K)S(H-K) = +1 \text{ for large } |U_HU_KU_{H-K}|\,. \qquad (4)$$

Table 1. *The number of triplets H, K, H−K and quartets H, K, L, H−K−L as a function of the magnitudes* $E_4=\sigma_3\sigma_2^{-3/2}\,|E_{000}E_HE_KE_{H-K}|$ *and* $E_4=\sigma_3\sigma_2^{-3/2}|E_HE_KE_LE_{H-K-L}|$ *respectively together with the relative percentages of correct sign information*

E_4 value	Number of triplets $H, K, H-K$ above the E_4 value of column 1	Number of triplets with $S(H)S(K)$ $S(H-K)$ $=+1$	Number of triplets with $S(H)S(K)$ $S(H-K)$ $=-1$	Relative percentage of correct information of the triplets	Number of quartets H, K, L $H-K-L$ above the E_4 value of column 1	Number of quartets with $S(H)$ $S(K)S(L)$ $S(H-K-L)$ $=+1$	Number of quartets with $S(H)$ $S(K)S(L)$ $S(H-K-L)$ $=-1$	Relative percentage of correct information of the quartets
40·25	2	2	0	100				
37·50	3	3	0	100				
33·75	5	5	0	100				
30·00	12	12	0	100				
26·25	25	25	0	100				
22·50	49	49	0	100				
21·00	66	66	0	100				
19·50	91	91	0	100				
18·00	124	124	0	100	0	0	0	
16·50	174	174	0	100	1	1	0	100
15·00	266	266	0	100	7	7	0	100
14·25	318	318	0	100	10	10	0	100
13·50	394	394	0	100	14	14	0	100
12·75	481	481	0	100	23	23	0	100
12·00	597	597	0	100	43	43	0	100
11·25	771	766	5	99·4	74	74	0	100
10·50	961	953	8	99·2	114	114	0	100
9·75	1236	1224	12	99·0	192	189	3	98·4
9·00	1597	1570	27	98·3	316	311	5	98·4
8·25	2098	2047	51	97·6	502	492	10	98·0
7·50	2782	2694	88	96·8	837	804	33	96·1
6·75	3798	3633	165	95·7	1525	1441	84	94·5
6·00	5299	4991	308	94·2	2848	2639	209	92·7
5·25	7509	6883	626	91·7	5683	5123	560	90·1

Table 2. *Number of quartets H, K, L H−K−L for groups of different size containing the strongest reflexions*

The percentage of correct information is indicated for each group.

Number of the strongest reflexions N	Number of quartets with $E_4>5$ within the group of N reflexions	Total sum of E_4 within this group	Mean value of E_4 per quartet	Percentage of correct sign information within the group
10	0	0	0	
20	21	272	13·0	100
30	91	1011	11·1	95·7
40	212	2072	9·8	93·3
50	471	3993	8·5	91·8
60	834	6468	7·8	91·8
70	1237	9050	7·3	91·1
80	1839	12817	7·0	90·8
90	2336	15880	6·8	90·1
100	2825	18886	6·7	89·7

From equation (3) more complex sign relationships can be found. Simerska showed that

$$S(H)S(K)S(L)S(H-K-L) = +1 \qquad (5)$$

with a reliability proportional to the weight

$$|U_H U_K U_L U_{H-K-L}|$$

should be helpful in phase determining processes.

In the program system of Stewart (1970) relations of type (5) are used, not, however, in the original form. Stewart derives the relation

$$S(H)S(K)S(L)S(H-K-L) = +1\,, \qquad (5a)$$

a so-called relation of the second kind, from two triplet relationships (4):

$$\left.\begin{array}{l} S(H-K)S(H)S(K) = +1 \\ S(H-K)S(L)S(H-K-L) = +1 \end{array}\right\} \qquad (5b)$$

by elimination of $S(H-K)$. Of course (5*a*) is less reliable than any of the triplets (5*b*). Germain, Main & Woolfson (1970) report the use of phase relations of a similar kind, also derived from the original $\sum_2$ listing.

In this paper the weights of the relations (5) and (5*a*) are combined into a strengthened quartet relationship (SQR), which appears to be very useful in the first stage of a phase determination.

Quartet relation

From equation (3) with $m=3$ the expression

$$U_{H+K+L} = N^2\, \overline{U_H U_K U_L}^{\,H+K+L} \qquad (6)$$

is obtained. This leads to the sign relation

$$S(H)S(K)S(L)S(H-K-L) = +1 \qquad (7)$$

for large $|E_H E_K E_L E_{H-K-L}|$. The ordinary $\sum_2$ relation can be considered as a special case of (7) where $E_L = E_{000}$:

$$S(H)S(K)S(H-K) = +1 \qquad (8)$$

for large $|E_H E_K E_{000} E_{H-K}|$. We have tested (7) and (8) for a recently solved structure of space group $P2_1/c$ with 56 carbon and oxygen atoms in the unit cell (Schenk, 1972*a*), and the results are summarized in Tables 1, 2 and 3. As could be expected, in both cases the percentage of failures follows the same trend with

$$E_4 = \sigma_3\sigma_2^{-3/2}|E_H E_K E_L E_{H-K-L}| \text{ (see Table 1).}$$

In the quartet list (7) most of the reliable sign relations (large E_4) are found within the group of 30 reflexions of highest E. The reliable relations of type 8 are spread over the strongest 300 reflexions.

Quartet relationships of the second kind

If in a $\sum_2$ list two triplets with one reflexion in common are present:

$$S(H)S(K)S(H-K) = +1$$
$$\text{with } E_4^{H,K} = |E_{000}E_H E_K E_{H-K}|\sigma_3\sigma_2^{-3/2} \qquad (9)$$

and

$$S(H)S(L)S(H-L) = +1$$
$$\text{with } E_4^{H,L} = |E_{000}E_H E_L E_{H-L}|\sigma_3\sigma_2^{-3/2}, \qquad (10)$$

then by elimination of $S(H)$ a quartet relation of the second kind

$$S(K)S(H-K)S(L)S(H-L) = +1 \qquad (11)$$

is formed (Stewart, 1970). The reliability of equation (11) is smaller than that of the original relations (9) and (10). If relations (9) and (10) have probabilities of P_1 and P_2 respectively of being correct then the probability of (11) is given by

$$P_3 = P_1P_2 + (1-P_1)(1-P_2) \qquad (12)$$

and thus

$$P_3 < P_1\,, P_2\,. \qquad (13)$$

P_1 and P_2 can be calculated using the well known probability formula:

$$P_+(H) = \tfrac{1}{2} + \tfrac{1}{2}\tanh\left(\sigma_3\sigma_2^{-3/2}|E_H|E_K E_{H-K}\right). \qquad (14)$$

In our experience equation (13) often gives overestimates of the proper probabilities so that we prefer to work with weights based on E values. We use therefore an approximation to (13):

$$E_4^{H,K,L} < E_4^{H,K}\,, \quad E_4^{H,L} \qquad (15)$$

Table 3. *Number of triplets H, K, H−K for groups of different size containing the strongest reflexions*

Number of the strongest reflexions N	Number of triplets within the group of N reflexions ($E_4 > 5{\cdot}25$)	Total sum of E_4 within this group	Mean value of E_4 per triplet	Percentage of correct sign information within the group
10	2	82	41·2	100
20	11	375	34·1	100
30	24	720	30·0	100
40	42	1140	27·1	100
50	63	1537	24·4	100
60	94	2062	21·9	100
70	131	2685	20·5	100
80	184	3480	18·9	100
90	233	4162	17·9	99·8
100	298	5047	16·9	99·9

which is certainly fullfiled by the weights

$$E_4^{H,K,L}=E_4^{H,K}\frac{|E_LE_{H-L}|}{E_{000}^2}$$
$$=\left|\frac{E_H}{E_{000}}E_KE_{H-K}E_LE_{H-L}\right|\sigma_3\sigma_2^{-3/2}. \quad (16)$$

Strengthened quartet relationships

The pure quartet relationships (7) can be strengthened by the relations of the second kind. A quartet H, K, L and $H-K-L$ can be split into two triplets in the following three ways:

$$\left.\begin{array}{lll} H-K & H & K \\ H-K & L & H-K-L \end{array}\right\} \quad (17)$$

$$\left.\begin{array}{lll} H-L & H & L \\ H-L & K & H-K-L \end{array}\right\} \quad (18)$$

$$\left.\begin{array}{lll} K+L & H & H-K-L \\ K+L & K & L \end{array}\right\}. \quad (19)$$

The weight E_4^* of the strengthened quartet relationship (SQR) is then given by the sum of the weights of (7), (17), (18) and (19):

$$E_4^*=\sigma_3\sigma_2^{-3/2}\left(\frac{|E_{H-K}|+|E_{H-L}|+|E_{K+L}|}{E_{000}}+1\right)$$
$$\times|E_HE_KE_LE_{H-K-L}|. \quad (20)$$

The reliability of these weights E_4^* can be judged by comparing the percentage failures as a function of E_4^* with the percentage failures of the triplet relation as a function of $E_4=\sigma_3\sigma_2^{-3/2}|E_{000}E_HE_KE_{H-K}|$. For our test structure there is complete agreement (see Table 4). From Tables 1 and 4 it can be seen that the number of reliable SQR's is much greater than that of the pure quartet relations.

Unreliable SQR's

Some quartet relationships are not invariant under the symmetry operations. This happens when one of the sums $H-K$, $H-L$, $K+L$ corresponds to a space group extinction. Then two different quartet relationships involving H, K, L and $H-K-L$ give opposite phase indications.

An example in space group $P2_1c$: the reflexions 523, 222, 111 and $2\bar{1}0$ form a quartet and $S(222)=S(111)=S(210)=+1$. Then $S(523)\ S(222)\ S(111)\ S(2\bar{1}0)=+1\ldots(a)$, but also $S(523)\ S(222)\ S(1\bar{1}1)\ S(210)=+1\ldots(b)$. Thus from ($a$) $S(523)=-1$ and from (b) $S(523)=+1$.

The quartet relations

$$H, K, L\ H-K-L \quad \text{with} \quad L=\lambda_1H+\lambda_2K$$

are not useful, as discussed previously for the case $\lambda_1=0$, $\lambda_2=1$ (Schenk, 1972*b*). As pure quartet relations they cannot disturb the phase determination because their number is small and their E_4 values are not

Table 4. *The number of* SQR'*s as a function of* E_4^* *together with the percentage of correct information*

The percentage of correct triplet information (see Table 1) is given as a reference value.
From $E_4^*=8$ the listing is complete, below this value terms are lacking.

E_4^* value	Number of strengthened quartet relations above the E_4 value	Number of quartets with $S(H)S(K)S(L)$ $S(H-K-L)=+1$	Number of quartets with $S(H)S(K)S(L)$ $S(H-K-L)=-1$	Relative percentage of correct information of the strengthened quartets	Relative percentage of correct information of the triplets (see Table 1)
40·25					
37·50					
33·75					
30·00	2	2	0	100	100
26·25	9	9	0	100	100
22·50	17	17	0	100	100
21·00	29	29	0	100	100
19·50	56	56	0	100	100
18·00	88	88	0	100	100
16·50	140	140	0	100	100
15·00	259	259	0	100	100
14·25	331	331	0	100	100
13·50	435	435	0	100	100
12·75	554	554	0	100	100
12·00	738	735	3	99·6	100
11·25	985	980	5	99·5	99·4
10·50	1387	1377	10	99·3	99·2
9·75	1989	1968	21	98·9	99·0
9·00	2787	2742	45	98·4	98·3
8·25	3833	3733	100	97·4	97·6
7·50	5078	4892	186	96·3	96·8
6·75	6108	5764	344	94·4	95·7
6·00	6820	6252	568	91·7	94·2
5·25	7118	6385	733	89·7	91·7

large compared to those of the triplet relations. After strengthening however, their E_4^* values may be enhanced and hence these SQR's should preferably be avoided. This can easily be achieved by imposing an additional condition for reliable SQR's:

$$\det \begin{pmatrix} H \\ K \\ L \end{pmatrix} \neq 0 \, .$$

Non-centrosymmetric structures

For non-centrosymmetric structures phases can be obtained from the $\sum_2$ relation:

$$\varphi_H = \frac{\sum\limits_K |E_H E_K E_{H-K}| \, (\varphi_K + \varphi_{H-K})}{\sum\limits_K |E_H E_K E_{H-K}|} \qquad (21)$$

or from the even more useful tangent formula

$$\tan \varphi_H = \frac{\sum\limits_K |E_H E_K E_{H-K}| \sin (\varphi_K + \varphi_{H-K})}{\sum\limits_K |E_H E_K E_{H-K}| \cos (\varphi_K + \varphi_{H-K})} \, . \qquad (22)$$

The corresponding expressions involving quartets of structure factors are easily found:

$$\varphi_H = \frac{\sum\limits_K \sum\limits_L E_4 \, (\varphi_K + \varphi_L + \varphi_{H-K-L})}{\sum\limits_K \sum\limits_L E_4} \qquad (23)$$

and

$$\tan \varphi_H = \frac{\sum\limits_K \sum\limits_L E_4 \sin (\varphi_K + \varphi_L + \varphi_{H-K-L})}{\sum\limits_K \sum\limits_L E_4 \cos (\varphi_K + \varphi_L + \varphi_{H-K-L})} \, . \qquad (24)$$

In (23) and (24) the triplets and SQR's can be employed simultaneously by using, for SQR's:

$$E_4 = \varphi_3 \varphi_2^{-3/2} \left(\frac{|E_{H-K}| + |E_{H-L}| + |E_{K+L}|}{E_{000}} + 1 \right) \times |E_H| \, |E_K| \, |E_L| \, |E_{H-K-L}|$$

and for triplets, relations

$$E_4 = \sigma_3 \sigma_2^{-3/2} \, |E_H| \, |E_K| E_{000} |E_{H-K}| .$$

For (23) and (24) refinement criteria can be found in the same way as for (21) and (22) (Schenk, 1972*c*). The criterion of (23) is:

$$\mathrm{CCQ}_2 = \sum_H \sum_K \sum_L E_4 | -\varphi_H + \varphi_K + \varphi_L + \varphi_{H-K-L} |^2 \qquad (25)$$

with

$$-\pi < -\varphi_H + \varphi_K + \varphi_L + \varphi_{H-K-L} \leq \pi$$

and the criterion of (24) is:

$$\mathrm{CCQT}_2 = \sum_H \sum_K \sum_L E_4 \sin^2 \tfrac{1}{2} (-\varphi_H + \varphi_K + \varphi_L + \varphi_{H-K-L}) \, . \qquad (26)$$

The forms of (25) and (26) show that all trivialities resulting from space-group symmetry (Schenk, 1972*c*) also occur with the quartet relationships.

In the centrosymmetric case (23) and (24) reduce to the sign relationship:

$$S(H) = S\{ \sum_K \sum_L E_4 S(K) S(L) S(H-K-L) \} \qquad (27)$$

with the refinement – (or consistency-) criterion:

$$\sum_H \sum_K \sum_L E_4 \{ 1 - S(H) S(K) S(L) S(H-K-L) \} \, . \qquad (28)$$

The use of SQR's

It is well known that the triplet relations are very useful in order to find correct phases of a large number of reflexions on the basis of a correct starting set. However, often it appears to be very difficult to obtain such a starting set with triplet relations. The reason is that the reliable triplet relationships are distributed over a large group of reflexions.

By means of the SQR's it should be easy to find a good starting set of phases and symbolic phases. From

Table 5. *Number of* SQR'*s with* $E_4^* > 5$ *and* $E_4^* > 10$ *respectively for groups of different size containing the strongest reflexions*

	$E_4^* > 5$				$E_4^* > 10$			
Number of the strongest reflexions N	Number of quartets with $E_4^* > 5$ within the group of N reflexions	Total sum of E_4^* within this group	Mean value of $E_4^* \langle E_4^* \rangle$	Percentage of correct sign information	Number of quartets with $E_4^* > 10$ within the group of N reflexions	Sum total of E_4^*	Mean value of $E_4^* \langle E_4^* \rangle$	Percentage of correct sign information
10	0	0			0	0		
20	21	425	20·2	100·0	21	425	20·2	100
30	91	1562	17·2	97·0	86	1516	17·6	99·2
40	212	3145	14·8	95·2	178	2842	16·0	99·2
50	471	5945	12·6	93·7	296	4410	14·9	99·0
60	834	9494	11·4	93·6	398	5754	14·5	98·7
70	1237	13349	10·8	93·1	476	6860	14·4	98·9
80	1839	18953	10·3	92·8	583	8308	14·3	98·9
90	2336	23254	10·0	92·2	661	9296	14·1	98·9
100	2825	27566	9·8	91·8	728	10174	14·0	99·0

Table 5 it can be seen that the strongest 50 reflexions of the test structure contain 296 reliable SQR's with $E_4^* > 10$, their mean value being 14·9. This means that the 50 phases are correlated by a highly overdetermined system of relations so that a reliable starting set can easily be constructed. The SQR's cannot be used for extending the set of phases to say 200 or 300, because the new phases are linked by a small number of rather weak SQR's to the starting set.

Thus the properties of triplet-relations and SQR's are complementary. By using the two types of relations at the same time the advantages of both can be combined.

Practical procedure for structure determinations

We have adopted the following procedure in our computer programs:

1. Calculating triplet relations and SQR's.
2. Convergence mapping (Germain, Main & Woolfson, 1970) applied to the *n* strongest reflexions only with the following modifications:
   a. The reliability of a phase is estimated by

$$R_H = \underset{\substack{K \\ \text{triplets}}}{\sum} E_4^2 + \underset{\substack{K \\ \text{SQR's}}}{\sum} \underset{L}{\sum} E_4^{*2}.$$

   b. If all E_4^* and E_4 values contributing to an R_H are below a limit value (approximately 30% of the maximum E_4) this R_H is set equal to zero.
   c. No prior choice of origin-defining reflexions is made.
3. The output reflexions of the convergence mapping form the starting group of phases. Some of them are used for the definition of the origin and other are given symbolic phases.
4. Extension of the group of symbolically phased reflexions.
5. Finding the most reliable solution on the basis of the appropriate criterion (Schenk, 1972*c*).

The method was applied to a structure in $P2_1/c$, for which previously only after two failures a proper starting set could be found. By the new method this starting set was obtained automatically. In another structure determination, for which our former phasing process failed several times, a new starting set, found by means of the above procedure, lead to the correct solution.

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The Dependence of the Debye–Waller Temperature Factors on the Atomic Masses

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The question of how the Debye–Waller temperature factors depend on the atomic masses is discussed in terms of lattice dynamics.

1. Introduction

Recently Huiszoon & Groenewegen (1972) investigated whether or not the Debye–Waller factors depend on the atomic masses. We quote their result: '... a theorem will be derived which states that Debye–Waller *B* values of individual atoms in a crystal lattice do not depend on the atomic masses when the temperature of the crystal is above its Debye temperature'. The equations derived by Huiszoon & Groenewegen are correct; we believe, however, that their equations should be interpreted in another manner.

Huiszoon & Groenewegen (1972) base their interpretation on their equations (15) and (18). We quote equation (18) for reference as

$$\langle u_i\left(\begin{smallmatrix} l \\ r \end{smallmatrix}\right) u_k\left(\begin{smallmatrix} l \\ r \end{smallmatrix}\right)\rangle = U_r^{ik} = \frac{k_BT}{N} \sum_{\mathbf{q}} (L^{-1})_{ik}\left(\begin{smallmatrix} \mathbf{q} \\ rr \end{smallmatrix}\right) + \frac{\hbar^2\delta_{ik}}{12k_BTm_r}$$

$$- \frac{\hbar^4}{720k_B^3T^3m_r^2N} \sum_{\mathbf{q}} L_{ik}\left(\begin{smallmatrix} \mathbf{q} \\ rr \end{smallmatrix}\right) + \ldots, \; T > \Theta_D/2\,. \qquad (1)$$