

mit Zeichenprogrammen von K. Anzenhofer, München.

3. Kleinste Quadrate

Von uns zur unmittelbar anschliessenden Berechnung einer (F_o)- oder ($F_o - F_c$)-Fouriersynthese geändertes Programm von W. R. Busing und H. A. Levy, Oak Ridge.

4. Atomabstände usw.

Von uns erweitertes Programm von W. R. Busing und H. A. Levy, Oak Ridge.

Für die Unterstützung dieser Arbeit sind wir der Deutschen Forschungsgemeinschaft, dem Fonds der Chemischen Industrie und der Badischen Anilin- und

Sodafabrik, Ludwigshafen, zu besonderem Dank verpflichtet.

Literatur

- MÜLLER, E., HOPPE, W., HAGENMAIER, H., HAISS, H., HUBER, R., RUNDEL, W. & SUHR, H. (1963). *Chem. Ber.* **96**, 1712.
 COCHRAN, W. (1951). *Acta Cryst.* **4**, 408.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 747.
 MERRIT, L. L. & LANTERMAN, E. (1952). *Acta Cryst.* **5**, 811.
 HALL, D. & LLEWELLYN, F. J. (1956). *Acta Cryst.* **9**, 108.
 CARON, A., PALENIK, G. J., GOLDISH, E. & DONOHUE, J. (1964). *Acta Cryst.* **17**, 102.
 BAUER, S. H. (1947). *J. Amer. Chem. Soc.* **69**, 3104.
 NISHIKAWA, T., ITOH, T. & SHIMODA, K. (1955). *J. Chem. Phys.* **23**, 1735.

Acta Cryst. (1965). **18**, 473

The Correlation Method. A Systematic Use of the Interrelationship between Sign Relations

BY A. DE VRIES

Laboratorium voor Kristalchemie der Rijksuniversiteit, Utrecht, The Netherlands

(Received 13 April 1964)

The method discussed is based on the interrelationship between sign relations, and aims at obtaining a closer estimate of which sign relations are most likely to be correct. This method was developed especially for work with projection data in cases where the number of strong reflexions is relatively small. An example of the application of the method is given.

1. Introduction and definitions

The correlation method was developed in the course of the crystal structure determination of L-asparagine monohydrate, where only the projections were centrosymmetric and the projection data contained a relatively small number of strong reflexions. Although the method presents its greatest advantages under these circumstances it may be quite useful in other cases as well.

The method may be regarded either as an extension of the coincidence method or as an extension of the use of relationships between sign relations, as described by Woolfson (1961, p. 80). It is treated here as an extension of the coincidence method.

The definitions of some of the symbols used are:

- $s(hkl)$ The sign of the structure factor of the reflexion hkl .
 S_n The sign of sign relation number n , written in the form $s(hkl) \times s(h'k'l') \times s(h+h', k+k', l+l')$ = S_n .
 P_+ The probability that a sign relation is correct, calculated from the U values of the reflexions

in that sign relation (see *e.g.* Woolfson, 1961, p. 50).

$$P_- = 1 - P_+.$$

P_+^* The probability that a sign relation is correct, including the influence of the relations with other sign relations.

$$P_-^* = 1 - P_+^*.$$

2. Coincidences of a different kind

A coincidence of the usual type (we shall call this a *coincidence of the first kind*) is formed by a pair of sign relations $s(hkl) \times s(h'k'l') \times s(h+h', k+k', l+l') \approx +$ that have *two* structure factors in common; such a pair indicates that the remaining two structure factors have probably the same sign (this will be called the *indication* from the coincidence). For instance, the sign relations

$$\begin{aligned} s(0, 5, 6) \times s(0, 2, 0) \times s(0, 7, 6) &\approx + \\ s(0, 2, 0) \times s(0, 7, 6) \times s(0, 9, 6) &\approx + \end{aligned}$$

form a coincidence, the indication being

$$s(0, 5, 6) \approx s(0, 9, 6).$$

The general procedure in using coincidences is to search for the indication that has the highest probability of being correct. This indication is then accepted and the result thus obtained is introduced into the sign relations, and again one searches for the indication that will now have the highest probability of being correct, and so on.

Unfortunately the probability that an indication is correct, *i.e.* the probability that the two sign relations involved are either both correct or both incorrect, is always lower than the probability that either of the two sign relations is correct; so, in general, the reliability of the indications is not high. The situation will improve, however, when an indication is given by more than one coincidence: the more coincidences yield the same indication, the higher the probability that this indication will be correct. It is therefore important to note that there are coincidences of another type, which occur more frequently than the coincidences of the first kind and thus give higher probabilities. These coincidences we shall call *coincidences of the second kind*.

A coincidence of the second kind is formed by a pair of sign relations that have *one* structure factor in common; such a pair indicates that the product of the signs of the other four structure factors is probably positive. For instance, the sign relations

$$\begin{aligned}s(0, 2, 4) \times s(0, 6, 2) \times s(0, 8, 6) &\approx + \\ s(0, 2, 4) \times s(0, 3, 4) \times s(0, 5, 8) &\approx +\end{aligned}$$

form a coincidence of the second kind, the indication being

$$s(0, 6, 2) \times s(0, 8, 6) \approx s(0, 3, 4) \times s(0, 5, 8).$$

(It should be noted that a coincidence of the first kind can be regarded as a special case of a coincidence of the second kind).

3. The correlation equation

The reliability of the coincidence method, already having been improved by the introduction of the coincidences of the second kind, in the preceding section, can be increased further by a more effective way of making use of coincidences that give the same indication.

Suppose there are two pairs of sign relations with one structure factor in common (instead of

$$s(hkl) \times s(h'k'l') \times s(h+h', k+k', l+l') \approx +$$

we shall use here the form

$$s(hkl) \times s(h'k'l') \times s(h+h', k+k', l+l') = S$$

where S is more likely to be positive):

$$\begin{aligned}s(0, 0, 4) \times s(0, 8, 2) \times s(0, 8, 6) &= S_1 \\ s(0, 0, 4) \times s(0, 10, 2) \times s(0, 10, 6) &= S_2\end{aligned}$$

and

$$\begin{aligned}s(0, 2, 0) \times s(0, 8, 2) \times s(0, 10, 2) &= S_3 \\ s(0, 2, 0) \times s(0, 8, 6) \times s(0, 10, 6) &= S_4\end{aligned}$$

which give the same indication:

$$s(0, 8, 2) \times s(0, 8, 6) \approx s(0, 10, 2) \times s(0, 10, 6).$$

If this indication is true, then both S_1S_2 and S_3S_4 have to be positive; if it is false then both S_1S_2 and S_3S_4 have to be negative; in either case $S_1S_2 = S_3S_4$.

Now this relation $S_1S_2 = S_3S_4$ (which we shall call a *correlation equation*) influences the probabilities of positive or negative of each of its constituent signs S . To demonstrate this for the sign S_1 we write the correlation equation as

$$S_1 = S_2S_3S_4.$$

From this equation it is seen that S_1 can be positive only if $S_2S_3S_4$ is positive and that S_1 can be negative only if $S_2S_3S_4$ is negative, and since every S is always more likely to be positive than negative, this increases the probability that $S_1 = +$.

To give an example, we shall calculate this increase for the case that all the P_+ values involved are 0.8. From the probabilities for the different sign combinations in $S_2S_3S_4$ given in Table 1 it follows that the probability that $S_2S_3S_4$ is positive is 0.608, and the probability that it is negative is 0.392, so the ratio P_+/P_- for $S_2S_3S_4$ is 1.55. For S_1 itself the ratio P_+/P_- is 4.0. Since S_1 must always have the same sign as $S_2S_3S_4$, the ratio P_+^*/P_-^* for S_1 (the ratio of the probabilities, taking into account the influence of the correlation equation) is the product of the ratio P_+/P_- for S_1 and the ratio P_+/P_- for $S_2S_3S_4$. So P_+^*/P_-^* for S_1 is $4.0 \times 1.55 = 6.2$.

Table 1. Probabilities for the different sign combinations in $S_2S_3S_4$ (assuming $P_+ = 0.8$ for all three sign relations)

	P
All three signs positive (1 possibility)	0.512
Two signs positive, one negative (3 possibilities)	0.384
One sign positive, two negative (3 possibilities)	0.096
All three signs negative (1 possibility)	0.008
	$\Sigma P = 1.000$

If there are more correlation equations containing S_1 , the calculation will be completely analogous. Assume that there are the following four correlation equations:

$$\begin{aligned}S_1 &= S_2S_3S_4 \\ &= S_5S_6S_7 \\ &= S_8S_9S_{10} \\ &= S_8S_{10}S_{11}.\end{aligned}$$

For each triple product of signs and for S_1 itself one may calculate the ratio P_+/P_- , and next the ratio P_+^*/P_-^* for S_1 is obtained simply as the product of all these separate P_+/P_- values. Taking again $P_+ = 0.8$ for all the sign relations involved we get:

$$P_+^*/P_-^* \text{ for } S_1 = 4.0 \times (1.55)^4 = 23.1.$$

So every correlation equation containing S_1 will increase the probability that S_1 is positive, and by combining all those equations one may obtain very high probabilities indeed. For instance, from the sign relations between the $0kl$ reflexions with $U \geq 0.20$ from L-asparagine monohydrate we calculated that the most probable sign relation had a chance of only 0.1% of being incorrect, whereas the most likely indication obtained from coincidences of the first kind still had an 11% chance of being incorrect (De Vries, 1963).

4. The procedure of the sign determination

It will be clear from the preceding section that in our method we determine the signs S of the sign relations rather than the signs s of the structure factors. The way in which this is done is:

- (a) Calculate for the most promising sign relations the probability that they hold, taking into account the correlation equations.
- (b) Take the sign relation with the highest probability as correct, and substitute a + for its sign in the correlation equations.
- (c) Continue as under (a) until the probabilities get too low and/or until enough sign relations have been assumed to be correct.

5. Correction of the probabilities

One important aspect of the method of successively taking sign relations as correct has not been discussed yet. We know that, at the start, out of the total number of sign relations a certain number is incorrect. So by assuming some sign relations to be correct we imply that the relative abundance of incorrect sign relations in the remaining ones increases and therefore also that for each sign relation the chance of being incorrect increases. This effect can be taken account of by increasing the P_- values of the remaining sign relations, as may be shown as follows.

Suppose we start with 100 sign relations, out of which 20 are incorrect. Suppose also that ΣP_- (the statistical value for the number of incorrect sign relations) corresponds to the true number of incorrect relations, so $\Sigma P_- = 20$. At the stage where we have assumed 30 sign relations to be correct (this means that we take for these $P_+ = 1$ and $P_- = 0$) we calculate ΣP_- again and find say, $\Sigma P_- = 16$, meaning that the probability function we used corresponds now to a total of 16 incorrect relations. Since the true number of incorrect relations is still 20, we have to correct the probability function so as to give again $\Sigma P_- = 20$; we can do this by multiplying every P_- by $\frac{5}{4}$. This correction may seem small, but its effect can be considerable. For instance, when a sign relation occurs in four correlation equations, its P_-^* increases by a factor of approximately $(\frac{5}{4})^5 \approx 3$.

Applying the correction factor discussed above we get a gradual increase of the P_-^* values when more and more of the sign relations are assumed to be correct, and at a certain stage the lowest P_-^* left will be so large as to give us an indication that we had better make no further assumptions.

A final remark has to be made on this point. If the sign relations assumed to be correct come largely from a special group of sign relations, it will be advisable to use a separate correction factor for this group; we used for instance different correction factors for the group of sign relations between reflexions with $k+l = \text{even}$ and the group containing reflexions with $k+l = \text{odd}$.

6. An example of the application of the method

To illustrate the use of the correlation method we shall give the results of the application of the method to the $0kl$ reflexions with $U \geq 0.20$ of L-asparagine monohydrate (De Vries, 1963). The pertinent data

Table 2. List $0kl$ reflexions with $U \geq 0.15$

k	l	U	k	l	U
0	4	+22	5	11	-34
0	8	+50	5	13	-34
1	5	+26	6	1	+22
2	0	-30	6	6	-24
2	3	+15	6	7	-19
2	4	-21	6	10	-16
2	8	-15	6	12	-20
2	11	+15	7	1	-18
2	12	+19	7	6	-22
2	13	-16	7	7	-21
2	14	-20	7	8	+20
3	1	-18	7	10	-27
3	3	+27	8	0	-18
3	4	+21	8	2	-26
3	5	+26	8	3	+20
3	11	+23	8	5	-26
3	13	+27	8	6	-23
4	2	+15	9	6	+32
4	4	-17	9	9	-17
4	5	+15	10	0	+23
4	10	+15	10	2	+20
4	12	-26	10	6	+25
5	1	-17	10	9	-19
5	5	-28	11	2	-15
5	6	+29	12	1	+28
5	9	-21			

are: space group $P2_12_12_1$; 40 atoms per unit cell, barring the hydrogen atoms; 148 $0kl$ reflexions; data on U -values and sign relations are given in Tables 2 and 3; 90 correlation equations were found† for the sign relations given in Table 3.

Table 4 lists the signs of sign relations successively assumed to be positive, and for the first two assumptions in this Table we give the procedure in some detail below.

† A paper describing a convenient way of finding the correlation equations is in preparation.

Table 3. List of all sign relations between the $0kl$ reflexions with $U \geq 0.20$

	Sign relation*	$P_{-}\dagger$		Sign relation*	$P_{-}\dagger$		Sign relation*	$P_{-}\dagger$
1	$0,4 \times 2,0 \times 2,4$	0.25	31	$2,0 \times 4,12 \times 6,12$	0.22	61	$\bar{3},4 \times 7,10 \times 10,6$	0.25
2	$5,5 \times 5,9$	0.27	32	$5,6 \times 7,6$	0.18	62	$3,5 \times 3,11 \times 6,6$	0.25
3	$5,9 \times 5,13$	0.22	33	$6,6 \times 8,6$	0.21	63	$4,12 \times 7,7$	0.25
4	$7,6 \times 7,10$	0.27	34	$7,6 \times 9,6$	0.16	64	$5,11 \times 8,6$	0.17
5	$8,2 \times 8,2$	0.32	35	$8,2 \times 10,2$	0.22	65	$6,1 \times 9,6$	0.19
6	$8,2 \times 8,6$	0.27	36	$8,6 \times 10,6$	0.21	66	$7,7 \times 10,2$	0.30
7	$10,2 \times 10,2$	0.38	37	$2,4 \times 3,5 \times 5,9$	0.30	67	$9,6 \times 12,1$	0.14
8	$10,2 \times 10,6$	0.33	38	$3,13 \times 5,9$	0.28	68	$3,11 \times 5,5 \times 8,6$	0.24
9	$0,8 \times 0,4 \times 0,4$	0.22	39	$5,6 \times 7,10$	0.22	69	$5,6 \times \bar{8},5$	0.21
10	$2,4 \times 2,4$	0.25	40	$5,11 \times 7,7$	0.24	70	$5,9 \times 8,2$	0.27
11	$3,3 \times 3,5$	0.06	41	$6,1 \times \bar{8},3$	0.33	71	$5,13 \times 8,2$	0.17
12	$3,3 \times 3,11$	0.08	42	$6,1 \times 8,5$	0.28	72	$3,13 \times 5,11 \times 8,2$	0.12
13	$3,4 \times 3,4$	0.25	43	$6,6 \times 8,2$	0.27	73	$7,7 \times 10,6$	0.25
14	$3,5 \times 3,13$	0.06	44	$7,10 \times 9,6$	0.19	74	$4,12 \times 5,6 \times \bar{9},6$	0.12
15	$5,5 \times 5,13$	0.02	45	$8,2 \times 10,2$	0.30	75	$6,6 \times 10,6$	0.22
16	$8,2 \times 8,6$	0.08	46	$8,2 \times 10,6$	0.25	76	$6,12 \times 10,0$	0.28
17	$8,3 \times 8,5$	0.11	47	$8,6 \times 10,2$	0.32	77	$5,5 \times 5,11 \times 10,6$	0.12
18	$10,2 \times 10,6$	0.12	48	$2,14 \times 3,3 \times 5,11$	0.19	78	$7,6 \times 12,1$	0.21
19	$1,5 \times 2,0 \times 3,5$	0.17	49	$3,5 \times 5,9$	0.30	79	$5,6 \times 7,7 \times \bar{12},1$	0.21
20	$5,6 \times 6,1$	0.21	50	$5,6 \times \bar{7},8$	0.28	80	$5,9 \times 5,11 \times 10,2$	0.25
21	$5,11 \times 6,6$	0.16	51	$6,12 \times 8,2$	0.32	81	$7,8 \times \bar{12},1$	0.28
22	$6,1 \times 7,6$	0.27	52	$7,8 \times 9,6$	0.27	82	$7,10 \times 12,1$	0.22
23	$6,12 \times 7,7$	0.30	53	$3,3 \times 5,5 \times 8,2$	0.17	83	$5,11 \times 5,13 \times 10,2$	0.14
24	$7,7 \times 8,2$	0.25	54	$5,6 \times 8,3$	0.22	84	$7,10 \times \bar{12},1$	0.11
25	$7,8 \times 8,3$	0.32	55	$5,9 \times 8,6$	0.27	85	$6,6 \times 3,3 \times 3,3$	0.28
26	$7,10 \times 8,5$	0.19	56	$\bar{3},4 \times 3,5 \times 6,1$	0.28	86	$10,0 \times 5,5 \times \bar{5},5$	0.28
27	$2,0 \times 1,5 \times 1,5$	0.25	57	$4,12 \times 7,8$	0.30	87	$5,6 \times \bar{5},6$	0.27
28	$3,5 \times 5,5$	0.15	58	$5,6 \times 8,2$	0.22	88	$5,9 \times 5,9$	0.38
29	$3,11 \times 5,11$	0.14	59	$5,9 \times 8,5$	0.30	89	$5,11 \times 5,11$	0.19
30	$3,13 \times 5,13$	0.09	60	$7,6 \times 10,2$	0.33	90	$5,13 \times 5,13$	0.19

* For simplicity $s(0kl)$ is represented by the indices k and l only. Also use has been made of the relation $s(0\bar{k}l) = (-1)^{k+l} \times s(0kl)$.
 † The P_{-} values are calculated by means of the formulae given by Woolfson (1961) in the approximation for equal atoms.

Table 4. Results of the application of the correlation method

The structure factors included are: the two structure factors determining the origin, and those contained in all the sign relations assumed to be correct at each stage. The number of possibilities indicates how many different choices can be made for the set of signs of the structure factors included at each stage.

Signs assumed to be positive	P_{-}^* of the signs	Structure factors included	Possibilities
S_{16}	0.001	5	4
S_{15}	0.0015	7	8
$S_{68} = S_{71}$	0.001	8	8
S_{14}	0.007	9	8
$S_{28} = S_{30}$	0.001	10	8
$S_{29} = S_{64} = S_{72}$	0.002	11	8
$S_{35} = S_{83}$	0.004	12	8
$S_{18} = S_{36} = S_{77}$	0.004	13	8
$S_{12} = S_{53}$	0.006	14	8
$S_{46} = S_{47}$	0.008	15	8
$S_{37} = S_{55} = S_{70} = S_{80}$	0.010	16	8
S_{39}	0.028	17	8
S_{32}	0.009	18	8
$S_{34} = S_{44}$	0.007	19	8
$S_{67} = S_{78} = S_{82}$	0.010	20	8

Sign relation 16 had the correlation equations:

$$S_{16} = S_9 S_{45} S_{47} = S_{12} S_{53} S_{68} = S_{12} S_{55} S_{70} = S_{14} S_{64} S_{72} \\ = S_{15} S_{68} S_{71} = S_{18} S_6 S_8 = S_{18} S_{35} S_{36} = S_{18} S_{46} S_{47} .$$

In addition to this we had $S_9 = S_{10} = -S_{13}$. From these relations P_{-}^* for S_{16} was calculated as 0.001, and this

being the lowest P_{-}^* , sign relation 16 was assumed to hold:

$$s(0, 0, 8) \times s(0, 8, 2) \times s(0, 8, 6) = + .$$

When we take $s(0, 0, 8) = a$ and $s(0, 8, 2) = b$ then $s(0, 8, 6) = ab$. So together with the two structure factors determining the origin (we chose $s(0, 3, 5) = s(0, 5, 6) = +$) we had 5 structure factors, with 4 possibilities for their signs (both a and b can be $+$ as well as $-$).

For sign relations 15 we had now:

$$S_{15} = S_9 S_2 S_3 = S_{12} S_{53} S_{71} = S_{14} S_{28} S_{30} = S_{18} S_{77} S_{83} \\ = S_{68} S_{71}$$

(the last product contains only two signs because $S_{16} = +$ could be left out). Again using $S_9 = S_{10} = -S_{13}$ this yielded P_{-}^* for S_{15} as 0.0015, and S_{15} was assumed to be positive:

$$s(0, 0, 8) \times s(0, 5, 5) \times s(0, 5, 13) = + .$$

We had already $s(0, 0, 8) = a$; so, taking $s(0, 5, 5) = c$ we get $s(0, 5, 13) = ac$. We thus had now 7 structure factors with 8 possibilities for their signs.

As these first two sign relations assumed to be correct happened to occur together in one correlation equation, the result of these first two assumptions was that the other two sign relations in this equation had to have the same sign. This considerably increased the probability that this sign would be positive,

and so this sign was the next one to be assumed to be positive. With only three exceptions all the following assumptions were related to signs found to be the same for two or more sign relations.

After the last assumption listed in Table 4 the lowest P_* left was 0.065, much higher therefore than any of the P_* values listed in the Table. For this reason and also because the signs of 20 structure factors had already been included, this was considered a good point at which to stop. (Indeed it was found that further calculations would not have yielded much useful information.) From the sign relations between the signs of one medium ($0.20 > U \geq 0.15$) and two large structure factors the sign of one medium structure factor could be determined with a P_* of 0.0025. We thus had a total of 21 structure factors, the signs of which could be expressed in three sign symbols, a , b and c , hence with 8 possibilities for their signs (Table 5). For one of the possible choices for a , b and c ($a=b=c=+$) all 21 signs were positive, so this possibility could be discarded right away. For one of the others ($a=+, b=c=-$) all 21 signs appeared to be correct; it was possible to solve the corresponding Fourier synthesis.

Table 5. Signs for the 21 structure factors, expressed in the sign symbols a , b and c

k = even l = even	k = odd l = odd	k = odd l = even	k = even l = odd
k l Sign	k l Sign	k l Sign	k l Sign
0 8 a	3 3 bc	5 6 $+$	12 1 $+$
2 0 c	3 5 $+$	7 6 c	
2 4 ac	3 11 abc	7 10 ac	
2 8 ac	3 13 a	9 6 $+$	
8 2 b	5 5 c		
8 6 ab	5 9 ac		
10 2 bc	5 11 ab		
10 6 abc	5 13 ac		

7. Gradual development of new correlation equations

One minor point has yet to be mentioned here. When a number of sign relations has been taken as correct and the information contained in these sign relations is introduced in the remaining sign relations, this might lead to new correlation equations, and these new correlation equations might have considerable influence upon the probabilities of the correctness of further assumptions. For this reason it is advisable to interrupt the calculations when a substantial part of the signs has been determined, and to make a new list of the correlation equations that can be found at this stage; preferably one should make a separate list for each of the possible sets of signs of the structure factors included at this stage.

It is quite clear that the new correlation equations (containing four signs) mentioned here have proceeded from already existing ones which contained initially six, eight, or more signs. Strictly speaking these

correlation equations of 'higher degree' should have been included in the calculations right from the beginning. There are, however, reasons for not doing so:

1. The influence of the correlation equations upon the probabilities decreases rapidly as the degree of the equations increases.
2. The omission of correlation equations of higher degree will counteract the effect mentioned in the Appendix.
3. The introduction of correlation equations of higher degree would complicate the calculations.

8. Summary

When the method developed here is compared with the coincidence method the following differences are noted:

1. Apart from the coincidences of the first kind the coincidences of the second kind are also used.
2. Instead of taking indications of coincidences as correct we take sign relations as correct.

As a result the probabilities that the assumptions are correct are far greater than with the coincidence method. Consequently structures too complicated to be solved by the coincidence method may indeed be solved by the correlation method, as has been demonstrated for L-asparagine monohydrate (De Vries, 1963).

The procedure for the calculations is as follows:

1. Make a list of all sign relations between all strong (and medium) reflexions.
2. Make a list of all correlation equations for those sign relations.
3. Calculate the probability to hold for the most promising sign relations, taking into account the correlation equations.
4. Take the sign relation with the highest probability as correct and substitute a $+$ for its sign in the correlation equations.
5. Proceed as under (3) until the probabilities get too low, applying a correction factor to take account of the gradual relative increase of failures in the remaining sign relations.
6. It is advisable to stop the first round of calculations when a substantial part of the signs has been determined, as new correlation equations develop gradually. A second round of calculations (taking also into account the new correlation equations) may then be started for each of the possible sets of signs separately.

Advantages in comparison with other direct methods are:

1. Probabilities are high, so the chance of mistakes is slight.
2. Large amounts of information are used for making the decisions.

3. It is a multiple-solution method.
4. The calculations can easily be done on a desk calculator, and are also well adaptable to computer programming.

The method proved successful for a projection of the structure of L-asparagine monohydrate (De Vries, 1963), for projections of the structures of three modifications of mesotartaric acid (Bootsma & Schoone, 1965) and for a projection of the structure of tartronic acid (Kroon, Kanters & Van Eyck, 1965).

APPENDIX

The value 23.1 obtained in § 3 for the P_+^*/P_-^* ratio for S_1 is actually somewhat too high, since three of the triple products involved are not independent, because S_3 and S_8 are each present in two different triple products. The correct value of P_+^*/P_-^* , which can be obtained by calculating the probabilities for the various sign combinations in a way analogous to that followed in Table 1, is 21.7.

For each of the signs S_3 and S_8 separately, its influence may easily be calculated as is shown here for S_3 . Instead of

$$S_2S_3S_4 = S_3S_8S_9$$

we write

$$S_3 \times (S_2S_4 = S_8S_9).$$

The term between brackets may now be considered as one single sign, the P_+/P_- ratio of which is equal to the product of the P_+/P_- ratios of S_2S_4 and S_8S_9 . From here on the calculation of P_+^*/P_-^* for S_1 proceeds as in § 3.

Since S_3 and S_8 occur together in one triple product, this trick can not be used for the calculation of the influence of the two signs together. However, in most cases the error made when the procedure of § 3 is followed (which ignores the effect of the interrelation between the correlation equations) is rather small.

It is a pleasure to thank Prof. J. M. Bijvoet and Prof. A. F. Peerdeman for their continuous interest and valuable criticism.

References

- BOOTSMA, G. A. & SCHOONE, J. C. (1965). To be published.
- DE VRIES, A. (1963). Thesis, University of Utrecht, The Netherlands.
- KROON, J., KANTERS, J. A. & VAN EYCK, B. P. (1965). To be published.
- WOOLFSON, M. M. (1961). *Direct methods in crystallography*. Oxford: Clarendon Press.

Acta Cryst. (1965). **18**, 478

On the Proper Modes of Propagation of X-rays*

BY EDWARD J. SACCOCIO† AND ALFRED ZAJAC‡

Polytechnic Institute of Brooklyn, Brooklyn, New York 11201, U.S.A.

(Received 19 August 1963 and in revised form 4 March 1964)

The modes of propagation of an X-ray wave field for single diffraction are evaluated at the Bragg angle as an illustration of a method which can be applied to simultaneous diffraction.

Introduction

The methods of the dynamical theory of X-ray diffraction are presented extensively in established texts (James, 1954; Zachariasen, 1945) and recently have been subjected to some reviews (James, 1963). The general theoretical treatment deals with cases when any number of reciprocal lattice points enter the Ewald sphere. However, applications of the general results of the dynamical theory to situations observed in practice are almost exclusively limited to two fields, *i.e.* to the case when only two reciprocal

lattice points (one of which is the origin) are on the sphere of reflection. Such theory has been worked out in detail. The starting and most important part is the evaluation of the equations of the dispersion sheets.

When considering a larger number of fields, say three or four, the usual procedure is unwieldy. It is rather difficult to obtain the dispersion sheets. Considerable information can, however, be obtained when one works exclusively under conditions when Bragg's law is fulfilled exactly. These conditions correspond to the diameter points of the dispersion sheets.

In addition, it seems to us that in the case of a larger number of fields it is necessary to evaluate the normal modes of vibration of the electric field vector of the X-ray wave fields. Considerable insight

* Supported by National Science Foundation.

† Present address: Physics Department, St. John's University, Jamaica, New York, U.S.A.

‡ Present address: Physics Department, Adelphi University, Garden City, L.I., New York, U.S.A.