

The intermolecular linkages seem to provide good evidence in favour of the theory of mesohydric tautomerism given by Hunter (1946), but a full discussion of the resonance phenomena cannot be attempted here. It is hoped to present this, together with the results of further work on the anhydrous form of this compound, at a later date.

The author is indebted to Dr C. H. Carlisle for much helpful advice and encouragement throughout the course of this work. Acknowledgement is also due to the Department of Scientific and Industrial Research for a maintenance grant.

References

- BOOTH, A. D. (1947). *Nature, Lond.*, **160**, 196.
 CLEWS, C. J. B. & COCHRAN, W. (1947). *Nature, Lond.*, **159**, 264.
 CLEWS, C. J. B. & COCHRAN, W. (1948). *Acta Cryst.* **1**, 4.
 COREY, R. B. (1938). *J. Amer. Chem. Soc.* **60**, 1598.
 DE HAAN, T. (1908). *Rec. Trav. chim. Pays-Bas*, **27**, 162.
 HUGHES, E. W. (1940). *J. Amer. Chem. Soc.* **62**, 1258.
 HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
 HUNTER, L. (1946). *Rep. Progr. Chem.* **141**.
 JAEGER, F. M. (1908). *Z. Krystallogr.* **44**, 569.
 KNAGGS, I. E. (1935). *Proc. Roy. Soc. A*, **150**, 576.
 ROBERTSON, J. M. (1936). *Proc. Roy. Soc. A*, **157**, 79.
 ROBERTSON, J. M. (1938). *Proc. Roy. Soc. A*, **167**, 122.

Acta Cryst. (1948). **1**, 174

The Application of the Harker-Kasper Method of Phase Determination

BY J. GILLIS

Department of Applied Mathematics, Weizmann Research Institute, Rehovot, Palestine

(Received 4 October 1947 and in revised form 19 April 1948)

The Harker-Kasper inequalities and related ones are applied to the data on oxalic acid dihydrate given by Robertson and Woodward. The technique of obtaining some forty signs of the structure amplitudes is developed in detail. Some general remarks on the method conclude the paper.

1. Introduction

1.1. The main purpose of this paper is the application of the method of inequalities, due to Harker & Kasper (1948), to the determination of the phases of some of the structure factors in an actual case. We discuss in § 2 the data on oxalic acid dihydrate given by Robertson & Woodward (1936). The working will be shown in some detail to bring out the various technical ideas which have had to be used in the process. In § 3 we discuss some general considerations which emerge from the work of § 2, and also some of the wider possibilities of the method as well as its limitations. These points are further illustrated by another example in § 4.

1.2. For the sake of completeness we recall here the necessary definitions. If F_{hkl} represents a general structure factor, we define the *unitary structure amplitudes*, U_{hkl} , by

$$U_{hkl} = F_{hkl} / f_{hkl}. \quad (1.1)$$

Here f_{hkl} is a suitable mean atomic scattering factor for the hkl direction normalized to make

$$U_{000} = 1. \quad (1.2)$$

U_{hkl} is in fact no other than the quantity ${}^a\hat{F}_{hkl}$ introduced by Harker & Kasper and also called \hat{F}_{hkl} by the present writer (Gillis, 1948). The new symbol has been introduced for reasons of typographic simplicity.

If we know the values of $|F_{hkl}|$, we can easily calculate those of $|U_{hkl}|$. Our purpose will be to use this latter information to deduce also the *phases* of the U_{hkl} 's, and these are, of course, the same as the phases

of the corresponding F_{hkl} 's. In this paper we shall be concerned only with real F_{hkl} 's, so that all we have to determine is their signs.

We shall often use a single capital letter to denote a triplet; e.g. U_H for U_{hkl} . Then U_{2H} will represent $U_{2h, 2k, 2l}$, $U_{H+H'}$ will stand for $U_{h+h', k+k', l+l'}$, etc. We shall use the symbol $[hkl]$ to denote the sign of F_{hkl} , i.e. if the phase of F_{hkl} is α

$$[hkl] = e^{i\alpha}. \quad (1.3)$$

As we have already remarked, we shall be dealing in this paper only with cases in which $[hkl] = \pm 1$.

1.3. Our argument will depend on the following inequalities. They are asserted here for the $h0l$ terms of a crystal of space group $P2_1/n$, except for (d) which is asserted for the $0kl$ terms. (a), (b), (c), (e) and (f) are, however, in fact true of *all* the terms of a centrosymmetric crystal, and this fact will be used in § 3. Proofs of (a), (b), (c) and (d) have been given by Harker & Kasper (1948), and of (e) and (f) by the writer (Gillis, 1948):

$$(a) \quad U_H^2 \leq \frac{1}{2}(1 + U_{2H}).$$

$$(b) \quad (U_H + U_{H'})^2 \leq (1 + U_{H+H'}) (1 + U_{H-H'}).$$

$$(c) \quad (U_H - U_{H'})^2 \leq (1 - U_{H+H'}) (1 - U_{H-H'}).$$

$$(d) \quad U_{0kl}^2 \leq \frac{1}{4}(1 \pm U_{0,2k,0} \pm U_{0,0,2l} + U_{0,2k,2l}),$$

the \pm sign being taken according as $k+l$ is even or odd.

$$(e) \quad |U_{3H} + 3U_H|^3 \leq \frac{1}{2}(1 + U_{2H})(3 + 4U_{2H} + U_{4H})^2.$$

$$(f) \quad |U_{3H} - 3U_H| \leq 2(1 + U_{2H}).$$

2. Oxalic acid dihydrate

2.1. We consider here the data of Robertson & Woodward (1936). We shall be interested in the $h0l$ terms, and we list the values of U_{h0l} below in Table 2. (The reason for grouping the terms in this way will be explained in § 2.4.) These values were computed from the observed $|F_H|$'s and a mean f_H -curve interpolated to the values given in Table 1. Robertson & Woodward have found this f -curve to be suitable for organic crystals of this general type. It is obtained by interpolation from the atomic scattering factors of oxygen and carbon.

The crystal has space group $C_{2h}^5-P2_1/n$. The molecular formula is $C_2H_2O_4 \cdot 2H_2O$. The molecules are centro-symmetric and there are two of them per unit cell. This makes $F_{000}=132$, and we normalize the f_H -function accordingly. The lattice constants are

$$a = 6.12 \pm 0.02, \quad b = 3.60 \pm 0.01, \quad c = 12.03 \pm 0.03 \text{ \AA.}$$

$$\beta = 106.2^\circ.$$

Table 1. Mean f_H -values

$\sin \theta$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
f_{hkl}	132	106	86	70	57	45	34	25	16

2.2. We now examine these data in the light of relation (a). We observe that (a) implies that

$$U_{2H} \geq 2U_H^2 - 1,$$

and so U_{2H} is certainly positive if

$$|U_{2H}| > 1 - 2U_H^2.$$

Applying this test to all relevant pairs ($H, 2H$) we see that the condition is satisfied in the case $H=202$. Hence $U_{404} = +0.66$.

2.3. The relations (e) and (f) are, in this case, quickly disposed of. We can use them only to test H -values such that U_H, U_{2H}, U_{3H} all occur in Table 2. This limits us to $H=200, 002, 004, 103, 101, 101, 103, 202$. We get from (e) the following result: If $[202] = -1$, then $[101] = -[303]$. We shall see later that, in fact, $[202] = -1$, and so the result holds. None of the other relevant values of H yields any result at all.

2.4. We now come to relations (b) and (c). To use them we first note that the observed $h0l$ intensities all have $h+l$ even. Now $H+H', H-H'$ differ by $2H'$, i.e. by a set $(2h'.0.2l')$ in which $2h'+2l'$ is a multiple of 4. On this basis we can divide up our set of H 's into four separate groups with the property that h_10l_1, h_20l_2 belong to the same group if and only if h_1-h_2, l_1-l_2 , and $\frac{1}{2}\{(h_1-h_2)+(l_1-l_2)\}$ are all even. Then in any application of (b) and (c) both of the U terms on the right-hand side must come from the same group. The groups are listed in Table 2, each in descending order of magnitude of $|U_H|$.

We introduce the scheme set out in Table 3. Entry (i) is fairly typical of the argument embodied in this scheme and should make the meaning clear. We take

$50\bar{7}$ and $1.0.\bar{1}\bar{1}$ as our $H+H', H-H'$ respectively. Then, by (b) and (c),

$$(U_{30\bar{5}} \pm U_{202})^2 \leq (1 \pm U_{50\bar{7}})(1 \pm U_{1.0.\bar{1}\bar{1}}).$$

Table 2. The four independent groups of U_{h0l} -values

Group 1		Group 2		Group 3		Group 4	
H	$ U_H $	H	$ U_H $	H	$ U_H $	H	$ U_H $
1.0. $\bar{1}\bar{1}$	0.88	503	0.52	408	0.67	0.0.10	0.65
507	0.76	107	0.51	404	0.66	204	0.64
309	0.66	1.0.11	0.50	202	0.57	402	0.63
505	0.33	105	0.49	206	0.50	006	0.57
501	0.33	309	0.45	606	0.47	604	0.40
503	0.30	103	0.37	008	0.39	208	0.37
107	0.30	303	0.31	0.0.12	0.31	600	0.31
305	0.27	109	0.24	2.0. $\bar{1}\bar{0}$	0.29	200	0.30
101	0.25	505	0.21	400	0.26	204	0.23
105	0.22	301	0.20	404	0.12	402	0.18
303	0.08	101	0.16	206	0.07	002	0.11
301	0.07	307	0.13	004	0.01	208	0.0
103	0.05	3.0. $\bar{1}\bar{1}$	0.0	202	0.01	2.0. $\bar{1}\bar{2}$	0.0
307	0.0	1.0. $\bar{1}\bar{3}$	0.0	2.0.10	0.0	406	0.0
109	0.0	305	0.0	408	0.0	406	0.0
5.0. $\bar{1}\bar{1}$	0.0	501	0.0	4.0. $\bar{1}\bar{2}$	0.0	4.0. $\bar{1}\bar{0}$	0.0
		509	0.0	602	0.0	608	0.0
				602	0.0		

Now there are four possible values for the right-hand side depending on the signs which we allocate to the terms. In the penultimate column, then, we enter

$$(1 + 0.76)(1 + 0.88) = 3.32,$$

$$(1 + 0.76)(1 - 0.88) = 0.21,$$

$$(1 - 0.76)(1 + 0.88) = 0.45,$$

$$(1 - 0.76)(1 - 0.88) = 0.03.$$

If $[30\bar{9}] = [202]$, we have by (b),

$$(U_{30\bar{5}} + U_{202})^2 \leq (1 + U_{50\bar{7}})(1 + U_{1.0.\bar{1}\bar{1}}),$$

and the left-hand side is $(0.66 + 0.57)^2 = 1.51$. Hence the only possible value for the right-hand side is 3.32, i.e. $[50\bar{7}] = [1.0.\bar{1}\bar{1}] = +1$. On the other hand, if $[30\bar{9}] = -[202]$, we can apply (c). Then

$$1.51 = (U_{30\bar{5}} - U_{202})^2 \leq (1 - U_{50\bar{7}})(1 - U_{1.0.\bar{1}\bar{1}}),$$

and, by a similar argument, $[50\bar{7}] = [1.0.\bar{1}\bar{1}] = -1$. The whole result can be summed up in the formula

$$[50\bar{7}] = [1.0.\bar{1}\bar{1}] = [30\bar{9}][202].$$

In making the entries in the penultimate column of Table 3 we shall always list

$$(1 + |U_{H+H'}|)(1 + |U_{H-H'}|),$$

$$(1 + |U_{H+H'}|)(1 - |U_{H-H'}|),$$

$$(1 - |U_{H+H'}|)(1 + |U_{H-H'}|),$$

$$(1 - |U_{H+H'}|)(1 - |U_{H-H'}|),$$

in that order.

As a second example consider (iii). If

$$[50\bar{7}] = [505] = +1,$$

then

$$(U_{50\bar{1}} - U_{006})^2 = 0.32 \leq (1 - 0.76)(1 - 0.33) = 0.16,$$

and this is obviously untrue. Similarly, if

$$[50\bar{7}] = [505] = -1,$$

then $(U_{50\bar{1}} + U_{006})^2 = 0.32 \leq 0.16$.

From these two contradictions we see that

$$[50\bar{7}] = -[505].$$

We proceed with the formal tabulation. After (xi) of Group 1 we break off the work on this group since we appear to have exhausted the $H + H'$, $H - H'$ pairs which can yield information. In the tabulated work on Groups 2, 3 and 4 we omit those pairs which have been found to lead to no conclusion; thirty-five such pairs were in fact examined.

was needed to decide on which of the symbols to choose in this way.) Then we can use the results obtained in Table 3 to express a number of $[h0l]$ -values in terms of a, b, c, d, e, f . Thus we soon see that $[30\bar{3}] = d$, $[400] = -f$, $[101] = ac$, etc. One interesting fact is that we can deduce two forms for the value of $[10\bar{5}]$, viz. ae and $bcde$. Hence $ae = bcde$, i.e. $d = abc$. This enables us to express our signs in terms of a, b, c, e, f alone. The result is tabulated in List 1 of Table 4. The zero terms are also indicated by 0. Subsequent determinations will be listed in the other columns which we shall enter from time to time at suitable stages of the work. The values of $|U_H|$ have been included in this table for convenience.

Table 3. Systematic application of relations (b) and (c)

	$H + H'$	$H - H'$	H	H'		Conclusion
Group 1						
(i)	50 $\bar{7}$	1.0.11	30 $\bar{5}$	202	1.51 \leq 3.32, 0.21, 0.45, 0.03	$[50\bar{7}] = [1.0.11] = [30\bar{5}] [202]$
(ii)	50 $\bar{7}$	30 $\bar{9}$	40 $\bar{8}$	101	0.06 \leq 2.92, 0.60, 0.38, 0.10	None
(iii)	50 $\bar{7}$	505	50 $\bar{1}$	006	0.32 \leq 2.34, 1.18, 0.32, 0.16	$[50\bar{7}] = -[505]$
(iv)	50 $\bar{7}$	501	50 $\bar{3}$	004	0.096 \leq 2.34, 1.18, 0.32, 0.16	None
(v)	1.0.11	30 $\bar{9}$	2.0.10	101	0.29 \leq 3.12, 0.64, 0.20, 0.04	$[1.0.11] = [2.0.10] [101]$
(vi)	1.0.11	505	30 $\bar{3}$	208	0.46 \leq 2.5, 1.25, 0.16, 0.08	$[1.0.11] = [30\bar{3}] [208]$
(vii)	1.0.11	501	30 $\bar{5}$	206	0.59 \leq 2.5, 1.25, 0.16, 0.08	$[1.0.11] = [30\bar{5}] [206]$
(viii)	1.0.11	50 $\bar{3}$	30 $\bar{7}$	204	0.13 \leq 2.44, 1.32, 0.16, 0.08	None
(ix)	1.0.11	10 $\bar{7}$	10 $\bar{9}$	002	—	None
(x)	50 $\bar{7}$	503	50 $\bar{5}$	002	—	None
(xi)	50 $\bar{7}$	10 $\bar{7}$	30 $\bar{7}$	200	—	None
Group 2						
(i)	309	10 $\bar{5}$	202	107	1.17 \leq 2.16, 0.74, 0.82, 0.28	$[309] = [10\bar{5}] = [202] [107]$
(ii)	503	1.0.11	307	204	0.41 \leq 2.27, 0.76, 0.72, 0.24	$[503] = -[1.0.11]$
(iii)	503	10 $\bar{9}$	30 $\bar{3}$	206	0.66 \leq 1.89, 1.16, 0.60, 0.12	$[503] = [30\bar{3}] [206]$
(iv)	107	30 $\bar{3}$	202	10 $\bar{5}$	1.12 \leq 1.98, 1.04, 0.64, 0.34	$[107] = [202] [10\bar{5}]$
(v)	1.0.11	10 $\bar{9}$	101	0.0.10	0.81 \leq 1.86, 1.11, 0.62, 0.37	$[1.0.11] = [101] [0.0.10]$
(vi)	1.0.11	301	206	10 $\bar{5}$	0.98 \leq 1.8, 1.2, 0.6, 0.4	$[206] = [1.0.11] [301]$
(vii)	10 $\bar{5}$	30 $\bar{3}$	204	101	0.79 \leq 1.95, 1.03, 0.67, 0.35	$[10\bar{5}] = [204] [101]$
Group 3						
(i)	408	400	404	004	0.42 \leq 1.91, 1.12, 0.42, 0.26	$[408] = -[400]$
(ii)	404	008	206	20 $\bar{2}$	0.24 \leq 2.31, 1.02, 0.46, 0.20	$[008] = -[404] (= -1)$
(iii)	404	0.0.12	208	20 $\bar{4}$	1.02 \leq 2.18, 1.14, 0.44, 0.23	$[208] = [204] [404] (= [204])$
(iv)	404	2.0.10	30 $\bar{3}$	107	0.67 \leq 2.14, 1.18, 0.43, 0.24	$[30\bar{3}] = [107]$
(v)	202	60 $\bar{6}$	40 $\bar{2}$	20 $\bar{4}$	1.61 \leq 2.31, 0.83, 0.63, 0.23	$[202] = [60\bar{6}] = [40\bar{2}] [204]$
(vi)	202	0.0.12	107	10 $\bar{5}$	1.0 \leq 2.6, 1.08, 0.56, 0.30	$[202] = [107] [10\bar{5}]$
(vii)	202	2.0.10	204	006	1.46 \leq 2.15, 1.11, 0.55, 0.31	$[202] = [2.0.10] = [204] [006]$
Group 4						
(i)	0.0.10	200	105	10 $\bar{5}$	0.50 \leq 2.14, 1.16, 0.46, 0.22	$[0.0.10] = [105] [10\bar{5}]$
(ii)	20 $\bar{4}$	208	202	006	1.30 \leq 2.24, 1.03, 0.49, 0.23	$[20\bar{4}] = [208] = [202] [006]$
(iii)	20 $\bar{4}$	600	40 $\bar{2}$	202	1.44 \leq 2.15, 1.13, 0.48, 0.25	$[20\bar{4}] = [600] = [40\bar{2}] [202]$
(iv)	40 $\bar{2}$	006	202	20 $\bar{4}$	1.46 \leq 2.56, 0.70, 0.58, 0.16	$[40\bar{2}] = [006] = [202] [20\bar{4}]$
(v)	60 $\bar{4}$	204	400	20 $\bar{4}$	0.81 \leq 1.72, 1.08, 0.74, 0.46	$[60\bar{4}] = [400] [20\bar{4}]$

2.5. In some of the cases where we obtained no conclusion we could in fact have deduced some partial results. However, these would have been of little use and would in any event have been superseded by the more complete results which we shall obtain in due course. It will be seen that a number of our conclusions were superfluous in that they are included in earlier results, but it seemed better at this stage to follow the method through as a routine and leave till later the sorting out of the conclusions. That point has now been reached.

To begin with set $[0.0.10] = a$, $[006] = b$, $[1.0.11] = c$, $[107] = d$, $[105] = e$, and $[408] = f$. (Some trial and error

2.6. Up to this point we have made no reference to terms whose magnitudes have not actually been observed. However, we may apply the inequalities to obtain information about Fourier coefficients farther out on the reciprocal lattice (which might have been measured with shorter wave-length radiation) and then use this information to derive signs of actual terms. We now give an example of this procedure, and several further examples will occur later.

Since $[404] = +1$, $[408] = f$,

we have $(U_{404} + fU_{408})^2 = (1.33)^2 = 1.77$.

Hence $1.77 \leq (1 + fU_{004})(1 + fU_{8.0.12})$,
 and so $1 + fU_{8.0.12} \geq 1.77/1.01 = 1.75$,
 i.e. $1 - fU_{8.0.12} \leq 0.25$.

It follows that

$$\begin{aligned} (U_{503} - fU_{309})^2 &\leq (1 - fU_{206})(1 - fU_{8.0.12}) \\ &\leq 1.07 \times 0.25 \\ &= 0.27. \end{aligned}$$

Table 4. Stages in the determination of the signs of U_{H01}

H	U_H	List 1	List 2	List 3	List 4
200	0.30	—	—	—	-a
400	0.26	-f	ace	+1	+1
600	0.31	ce	ce	a	a
002	0.11	—	—	—	-a
004	0.01	—	—	—	—
006	0.57	b	b	-a	-a
008	0.39	-1	-1	-1	-1
0.0.10	0.65	a	a	a	a
0.0.12	0.31	—	—	—	-1
1.0.11	0.50	c	c	c	c
109	0	—	—	—	0
107	0.51	abc	abc	-c	-c
105	0.22	e	e	ac	ac
103	0.37	—	—	—	-c
101	0.25	ac	ac	ac	ac
101̄	0.16	—	—	—	-c
103̄	0.05	—	—	—	—
105̄	0.49	ae	ae	c	c
107̄	0.30	—	—	—	-ac
109̄	0.24	—	—	—	c
1.0.11̄	0.88	abe	abe	-ac	-ac
1.0.13̄	0	—	—	—	0
2.0.10	0	—	—	—	0
208	0.37	ce	ce	a	a
206	0.50	-ab	-ab	+1	+1
204	0.23	—	—	—	—
202	0.57	bce	bce	-1	-1
202̄	0.01	—	—	—	—
204̄	0.64	ce	ce	a	a
206̄	0.07	—	—	—	—
208̄	0	—	—	—	0
2.0.10̄	0.29	bce	bce	-1	-1
2.0.12̄	0	—	—	—	0
309	0.45	ae	ae	c	c
307	0	—	—	—	0
305	0	—	—	—	0
303	0.08	—	—	—	-ac
301	0.20	-abc	-abc	c	c
301̄	0.07	—	—	—	—
303̄	0.31	abc	abc	-c	-c
305̄	0.27	—	—	—	-ac
307̄	0.13	—	—	—	c
309̄	0.66	ac	ac	ac	ac
3.0.11̄	0	—	—	—	0
3.0.13̄	0	—	—	—	0
408	0.67	f	-ace	-1	-1
406	0	—	—	—	0
404	0.66	+1	+1	+1	+1
402	0.18	—	—	—	a
402̄	0.63	b	b	-a	-a
404̄	0.12	—	—	—	—
406̄	0	—	—	—	0
408̄	0	—	—	—	0
4.0.10̄	0	—	—	—	0
4.0.12̄	0	—	—	—	0
505	0.33	—	—	—	ac
503	0.52	-c	-c	-c	-c
501	0.33	—	—	—	ac
501̄	0	—	—	—	0
503̄	0.30	—	—	—	-c
505̄	0.21	—	—	—	-c
507	0.76	abe	abe	-ac	-ac
509	0	—	—	—	0
5.0.11̄	0	—	—	—	0
602	0	—	—	—	0
602̄	0	—	—	—	0
604̄	0.40	-cef	a	a	a
606̄	0.47	bce	bce	-1	-1
608̄	0	—	—	—	0

A C I

By the familiar argument we deduce that $[503] = f[309]$.

Comparing this with List 1 we see that $-c = aef$, i.e. $f = -ace$. Substitution of this value of f in List 1 gives us List 2.

With these results one can easily continue and derive many more signs. The fundamental step is a repeated 'trial-and-error' application of relations (b) and (c), though with experience one soon learns to reduce the number of errors and so the total number of trials. Essentially what one strives for is the art of knowing which pairs are likely to repay investigation.

2.7. We proceed with the argument.

(i) Since $[107] = -[301]$, we have

$$(U_{107} - U_{301})^2 = 0.50.$$

$$\begin{aligned} \text{Hence } 1 - U_{408} &\geq 0.50/(1 - U_{206}) \\ &\geq 0.50/1.07 \\ &= 0.47. \end{aligned}$$

But $|U_{408}| = 0.67$ and hence $[408] = -1$. It follows incidentally that $ace = +1$, i.e. $e = ac$.

(ii) By a similar argument,

$$\begin{aligned} 1 - bU_{204} &\geq (U_{206} - bU_{0.0.10})^2 / (1 - bU_{2.0.16}) \\ &\geq 1.32/2, \text{ using List 2 and the fact that} \end{aligned}$$

$$\begin{aligned} |U_H| &\leq 1 \text{ for every } H, \\ &= 0.66. \end{aligned}$$

$$\text{Hence } [204] = -b.$$

It follows from List 2 that $b = -ce$, i.e. $e = -bc$. By comparison with (i) we see that $b = -a$. These results enable us to express all our signs in terms of a and c , and, for the sake of simplicity, we do so in List 3.

$$\text{(iii) } (U_{101} - U_{503})^2 \leq (1 - U_{602})(1 - U_{404}) = 0.34,$$

$$\text{and so } [101] = [503] = -c.$$

$$\begin{aligned} \text{(iv) } 1 - U_{10.0.6} &\geq (U_{402} - U_{604})^2 / (1 - U_{202}) \\ &\geq (1.03)^2 / 1.01 = 1.05, \end{aligned}$$

$$\text{and so } 1 + U_{10.0.6} \leq 0.95.$$

$$\begin{aligned} \text{Hence } (U_{501} + U_{50})^2 &\leq (1 + U_{008})(1 + U_{10.0.6}) \\ &\leq 0.61 \times 0.95 = 0.58. \end{aligned}$$

It follows that $[501] = -[507] = ac$.

(v) By the now familiar arguments,

$$[503] = -ac[408] = ac,$$

$$\text{and } [103] = -[105] = -c.$$

$$\begin{aligned} \text{(vi) } 1 - cU_{903} &\geq (U_{404} - cU_{501})^2 / (1 - cU_{105}) \\ &= (0.66)^2 / 0.51 = 0.85, \end{aligned}$$

$$\text{and so } 1 + cU_{903} \leq 1.15.$$

$$\begin{aligned} \text{Hence } (U_{505} + cU_{402})^2 &\leq (1 + cU_{903})(1 + cU_{107}) \\ &\leq 1.15 \times 0.49 = 0.56, \end{aligned}$$

and it follows that

$$[505] = -c[402] = ac.$$

(vii) Since we know that $[202] = -1$, we deduce from § 2.3 that $[303] = -[101] = -ac$.

(viii) By arguments which are now quite familiar we can show that

$$\begin{aligned} [200] &= -a, & [0.0.12] &= -1, \\ [30\bar{5}] &= -ac, & [307] &= c, \\ [10\bar{7}] &= -ac, & [002] &= -a, \\ [402] &= a, & [50\bar{5}] &= c. \end{aligned}$$

$$\begin{aligned} \text{(ix) } 1 - cU_{1.0.21} &\geq (U_{1.0.11} - cU_{0.0.10})^2 / (1 - cU_{10\bar{1}}) \\ &= (1.53)^2 / 1.16 = 2.00. \end{aligned}$$

Hence $|U_{1.0.21}| = 1$ and $[1.0.2\bar{1}] = -c$. It follows that $(U_{10\bar{9}} + cU_{0.0.12})^2 = 0$ and therefore $[10\bar{9}] = -c[0.0.12] = c$.

We must point out here that we have nowhere used more than two places of decimals. Indeed, the approximate nature of the assumptions underlying our whole theory would have rendered futile any higher accuracy of arithmetic. In these circumstances the assertion that $|U_{1.0.21}| = 1$ need not perhaps be as startling as it may at first appear. The physical significance of the result will be discussed in § 3.1.

2.8. We have tabulated in List 4 of Table 4 the information accumulated at this stage. It will be seen that the signs of all except the smallest of the terms U_H have been established, at least in terms of the unknown quantities a and c . The question of the values of these unknown quantities will be discussed in §§ 3.2 and 3.3.

2.9. *Alternative derivation.* In the above analysis we could have obtained the sign of $[008]$ directly at the beginning by applying inequality (d) of § 1.3 to U_{014} . We can compute from the original data the following values:

H	$ U_H $
014	0.48
020	0.18
028	0

and we already know that $|U_{008}| = 0.39$. Hence $0.23 \leq \frac{1}{4}(1 \pm 0.18 \pm 0.39)$, and this cannot be satisfied unless the sign of the 0.39 term is positive, i.e.

$$[008] = -1.$$

Since the whole theory is based on approximations, it is useful to get such confirmations from independent inequalities.

3. Some general considerations

3.1. *Application of the method to structure determination.* There is a rather curious incidental way in which this method may provide direct preliminary information before any Fourier summation has been performed. We saw above in § 2.7 that—to the accuracy of the theory— $|U_{1.0.21}| = 1$. Physically this means that

almost all of the scattering matter is concentrated very near to the $1.0.2\bar{1}$ planes. Such inexact and incomplete information can never solve a structure, but it may well be of valuable assistance as a guide, and it is interesting that we can use the method of inequalities to derive this knowledge about a set of planes whose reciprocal-lattice point did not intersect the sphere of reflexion.

In this case the information can be verified directly from the solved structure. A point lies near one of the $1.0.2\bar{1}$ planes if its lattice co-ordinates are such that $x/a - 21z/c$ is nearly an integer. In Table 5 we quote from the paper of Robertson & Woodward the co-ordinates of certain specified atoms. In the last column we give the value of the linear form under discussion. The other atoms of the structure are obtained from those listed by the operations of the symmetry elements of the space group, and so will give values for the expression differing by an integer from \pm the quantities in the last column. The agreement is seen to be fairly good

Table 5. *Co-ordinates of certain atoms in oxalic acid dihydrate*

Atom	x	y	z	$x/a - 21z/c$
C	-0.22	0.12	0.61	-1.1
O (1)	0.52	-0.20	1.78	-3.0
O (2)	-1.39	0.77	0.42	-1.0
H ₂ O (3)	-2.76	-1.41	2.15	-4.2

3.2. *The value of c .* The fact is that c is not determinable by these or any other algebraic methods. It is clear from the forms of the inequalities of § 1.3 that we cannot derive the sign of any U_{h0l} with odd h, l unless we already know the sign of at least one such term. In fact, if we have a set of signs for the odd terms such that all the inequalities are satisfied, then the inequalities will remain satisfied if we change the signs of all these odd terms.

Physically this corresponds to the fact that to multiply all the odd terms by -1 would not change the structure but would simply change the origin to a different centre of symmetry. We should always get such indeterminate signs in cases where the space group operations give several equivalent centres of symmetry in the one unit cell.

If we give c the value -1 , we see that all our signs agree with those derived from the structure by Robertson & Woodward.

3.3. *Patterson's ambiguities.* The existence of these ambiguities (Patterson, 1939, 1944; Pauling & Shappell, 1930; Robertson, 1945) precludes any hope that we might be able, by suitably extending these or similar methods, to solve a structure directly from the $|F_H|$'s by algebraic processes alone. However, what might still happen in practice is that we might be able to express a number of the signs in terms of unknown quantities a, b, \dots , etc. The ambiguities may well be expressed by the fact that some or all of these quantities are not algebraically determinable. In that case we

should have to use other (chemical, etc.) information to find some of the signs and so deduce the values of a, b, \dots . Alternatively, if there are not too many of these quantities, we might be able to test the various possibilities separately to see which made chemical sense.

Either of these methods would suffice to determine a in the case discussed in § 2 above.

3.4. *The margin of inequality.* There were many instances during the work in § 2 in which both signs satisfied an inequality, one by a comfortable margin and the other by a relatively narrow margin. In almost all such cases it was the former sign which was the correct one. This suggests that the method may have 'reserves of power' in the sense that stronger inequalities than those used are in fact satisfied.

One possible explanation is that a temperature effect reduces the total number of electrons taking part in a reflexion. The result would presumably be to make the observed value of $|F_H|$ less than that predicted by the trigonometric polynomial by a factor of the form

$$\exp[-M\{(\sin \theta)/\lambda\}^2],$$

where M is some positive constant. We should then be justified, before applying our inequalities, in first multiplying each $|U_H|$ by

$$\exp[+M\{(\sin \theta)/\lambda\}^2].$$

The difficulty is, of course, that we cannot know the correct value of M so long as we know nothing of the structure, and it is precisely when we start from such a state of ignorance that we most need the inequalities method. However, it should not be difficult to exercise judgement. There is an obvious upper limit set to M by the fact that none of the $|U_H|$'s, when multiplied, may exceed 1. Moreover, experience of a number of trials has led the writer to the conclusion that an excessive value of M will inevitably reveal itself by leading to mutually inconsistent derivations of signs. So long as the results have been entirely self-consistent they have always proved to be correct.

4. Phosphorus pentachloride

4.1. In considering the data of Clark, Powell & Wells (1942) on phosphorus pentachloride we tried increasing the $|U_H|$'s by the factor $\exp[1.6\{(\sin \theta)/\lambda\}^2]$.

It was then possible to proceed with methods much like those described in § 2, though the higher symmetry of the tetragonal space group yielded some extra inequalities which proved useful.

4.2. One further point which emerged seems worth noting. We had, among others, the following values:

H	$ U_H $
002	0.04
004	0.79
006	0.41

Now it was possible to show by an argument of the familiar type that $[004] = -1$. We could then apply inequality (e) of § 1.3.

$$\begin{aligned} |3U_{002} + U_{006}| &\leq 2(1 + U_{004}) \\ &= 0.42, \end{aligned}$$

and so $[002] = -[006]$.

This illustrates an important feature of inequalities like (d) and (e). The U_H with lowest suffix is multiplied by some coefficient greater than 1 (in this case 3). This may enable U_H to play a significant role also itself quite small. The effect is important for the lower order terms since, for small values of θ , f_H may be large and so $|U_H|$ will be small although $|F_H|$ itself may be relatively large and its sign correspondingly important.

In conclusion, the writer must express his gratitude for some editorial advice which led to the introduction of what system there is in the working of § 2. Also some of the remarks in § 3.2 were suggested by observations made by Sir Lawrence Bragg and others at a discussion in the Cavendish Laboratory.

References

- CLARK, D., POWELL, H. M. & WELLS, A. F. (1942). *J. Chem. Soc.* p. 642.
 GILLIS, J. (1948). *Acta Cryst.* **1**, 76.
 HARKER, D. & KASPER, J. S. (1948). *Acta Cryst.* **1**, 70.
 PATTERSON, A. L. (1939). *Nature, Lond.*, **143**, 939.
 PATTERSON, A. L. (1944). *Phys. Rev.* **65**, 195.
 PAULING, L. & SHAPPELL, M. D. (1930). *Z. Kristallogr.* **75**, 128.
 ROBERTSON, J. M. (1945). *Ann. Rep. Progr. Chem.* p. 46.
 ROBERTSON, J. M. & WOODWARD, I. (1936). *J. Chem. Soc.* p. 1817.