changes are for only one chemical kind of atom, the process is shortened even more. Then, all the information up to step IX for the other chemically different atoms is available from the previous calculation. Only the cards for the one kind of atom are used in the procedure up to that step.

Other information than that indicated in the outline and shown in Fig. 1, can be listed; e.g. the part of the structure factor exclusive of the atomic scattering factor, temperature factor, etc., for each chemical type of atom. This allows the evaluation of 'unitary structure factors' (Harker & Kasper, 1948; Gillis, 1948),

$$U_{hkl} = F_{hkl}/f_{hkl}.$$

Also, if desired, the individual atomic contributions to the structure factor can be listed.

We acknowledge gratefully the advice of Dr David Harker of the General Electric Research Laboratory and the technical assistance of the personnel of the IBM office at Schenectady, N.Y.

References

DONOHUE, J. & SCHOMAKER, V. (1948). Abstract of the Joint Meeting of the American Society for X-ray and Electron Diffraction and of the Crystallographic Society of America at Yale University, 31 March to 3 April.

DONOHUE, J. & SCHOMAKER, V. (1949). *Acta Cryst.* **2**, 344.

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

HARKER, D. & KASPER, J. S. (1948). *Acta Cryst.* **1**, 70.

SHAFFER, P. H., SCHOMAKER, V. & PAULING, L. (1946). *J. Chem. Phys.* **14**, 648.

Acta Cryst. (1949). **2**, 351

A Hollerith Technique for Computing Three-Dimensional Differential Fourier Syntheses in X-ray Crystal-Structure Analysis

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(*Received* 13 *April* 1949)

The paper describes the evaluation, by means of Hollerith equipment, of three-dimensional differential synthesis as used in some recent crystal-structure analyses. The method makes it possible to determine the precise positions of the maxima in the electron-density distribution with corrections for 'termination of the series' error. It can also be used for computations in the methods of least squares and steepest descents.

In the final stages of a detailed crystal-structure analysis by X-rays, a situation is reached in which both the moduli, $|F_{hkl}|$, and phase angles, α_{hkl}, of the structure factors are known, the former from experiment and the latter indirectly from calculation. It is then possible to combine these quantities by means of Fourier synthesis to give a complete electron density-distribution map of the structure. However, as was pointed out by Booth (1946*a*), this type of synthesis, although it gives a very valuable representation of the molecular structure, may not necessarily be the most sensitive method of deriving the atomic co-ordinates from the data available. In fact, for determining the positions of the maxima of the electron-density peaks as accurately as possible it is more appropriate to evaluate a differential Fourier synthesis; in practice this is done at points in the close vicinity of the maxima, and the small deviations of these points from those at which the differential synthesis equates to zero are calculated. The differential method also proves to be very convenient for applying a correction (Booth, 1946*b*) for an error intrinsic to the Fourier method, viz. displacement of atomic peaks due to the non-infinite number of coefficients used in the summations.

Our successful experience in applying Hollerith equipment to the computation of normal Fourier syntheses (Cox, Gross & Jeffrey, 1947) has led us to believe that its use can be extended to most computing problems in X-ray analysis, with great advantages in both speed and accuracy. In pursuance of this belief, we have applied the same machines to the calculation of differential syntheses in several investigations (e.g. Cruickshank, 1949; Cox, Gillot & Jeffrey, 1949) and the general features of the method used are described in this paper from the point of view of the X-ray crystallographer; as far as possible the technical details of operating the Hollerith equipment have been omitted, since these lie in the province of the professional Hollerith operator, who can supply them if the computational requirements of the problem are clearly stated. The method is necessarily more complicated than for the normal Fourier syntheses of electron density, involving as it does the use of the Hollerith tabulator for a process of multiplication as well as addition. Even so, for three-dimensional syntheses it represents a very considerable saving of labour over any method using the commonly available desk-type machines; it is inherent in the method that this saving is more marked

for structures of low symmetry, so that the calculations on a triclinic crystal are no more complicated than those on monoclinic or orthorhombic crystals.

The summations required for the differential syntheses at a point (x_r, y_r, z_r) in a centro-symmetrical structure, with the assumption of spherical symmetry around the peak maxima, are as follows (Booth, 1946*a*):

(*a*) $\sum_3 hF_{hkl}\sin 2\pi\phi_r$, $\sum_3 kF_{khl}\sin 2\pi\phi_r$, $\sum_3 lF_{hkl}\sin 2\pi\phi_r$;

(*b*) $\sum_3 h^2F_{hkl}\cos 2\pi\phi_r$, $\sum_3 k^2F_{hkl}\cos 2\pi\phi_r$, $\sum_3 l^2F_{hkl}\cos 2\pi\phi_r$,

where $\phi_r = (hx_r + ky_r + lz_r)$ and F_{hkl} is a structure factor. (The method can be extended to a non-centrosymmetric case by replacing each summation by two others containing $F_{hkl}\cos\alpha_{hkl}$ and $F_{hkl}\sin\alpha_{hkl}$ respectively in place of F_{hkl}.) Only one of the second differential summations (*b*) is strictly necessary and the others can be omitted from the computations if so desired. The approximate equality of these terms does, however, provide a check on the assumption of spherical symmetry about the peak maxima (cf. Cox *et al.* 1949).

Without the assumption of spherical symmetry, cross-terms, e.g. $hkF_{hkl}\cos 2\pi\phi_r$, are also required. In special investigations where these terms are necessary, the Hollerith method described here for the simpler computations can be extended to obtain them, but so far we have had no occasion to do this.

The computation is carried out in two distinct parts; first, the preparation of the Hollerith cards upon which are punched the relevant data, and secondly, the manipulation of these cards in order to tabulate the required sums and products of the differential synthesis.

A. Preparation of the cards

At least one Hollerith detail card is required for *every* crystallographic plane with an observed intensity except pairs related by a centre of symmetry, which are treated as one (e.g. hkl and $\bar{h}\bar{k}\bar{l}$, $h\bar{k}l$ and $\bar{h}kl$). The card will contain in its descriptive and additive fields the following information: the plane indices, hkl; values of ϕ_r for each atomic position at which the summations are required; values of $\cos 2\pi\phi_r$ and $\sin 2\pi\phi_r$; values of the observed and calculated structure factors, F^o_{hkl} and F^c_{hkl}. If the number of atoms under investigation exceeds four, then a second (or further) series of cards must be punched. The detail cards are produced by means of the following operations:

(1) *Punching the hkl indices and ϕ_r values*

A series of $x, y, z, \bar{y}, \bar{z}$ 'parameter' cards is first prepared. The lay-out of a parameter card is shown in Fig. 1 (*a*); an x-parameter card will contain a 1 punched in the h descriptive column and the x co-ordinates to three figures for all the atomic positions $a, b, c, \ldots, r, \ldots$. Similarly, every y parameter card will have 1 in a k column and the y co-ordinates. The negative parameters may be indicated either by punching the 1 in a separate column (as provided for in Fig. 1 (*a*)), or by over-punching on the positive columns.

These parameter cards can then be used to produce a set of preliminary detail cards by summary-punching; one such card is made for every required combination of h, k and l, and will have punched on it both hkl and the corresponding values of $(hx_r + ky_r + lz_r)$. As an example of the procedure, a deck of two y-cards and h x-cards on passage through a tabulator arranged to add all y-cards and add and produce *subtotals* on x-cards would print the following sequence:

h	k	l	ϕ_a	ϕ_b	ϕ_r
1	2	0	$1x_a+2y_a$	$1x_b+2y_b$	$\ldots\ 1x_r+2y_r\ \ldots$
2	2	0	$2x_a+2y_a$	$2x_b+2y_b$	$2x_r+2y_r$
	...		...	...	...
	...		...	...	...
h	2	0	hx_a+2y_a	hx_b+2y_b	hx_r+2y_r

All figures to the left of the decimal point in the ϕ values are omitted. By connecting the tabulator to a reproducing punch a detail card is produced for each line of the printed tabulation. The introduction of one z-card at the front of the deck would give detail cards of the type $h21$. A systematic extension of this procedure is used for the production of detail cards for all the observed combinations of $h, k, l, \bar{k}, \bar{l}$. The detail cards are separated into the four categories:

(1) $hx+ky+lz$, (3) $hx-ky+lz$,
(2) $hx+ky-lz$, (4) $hx-ky-lz$,

and are characterized by punching the numbers 1–4 into column 1 during the summary punching.

A certain number of redundant cards will be produced and must be removed in order to maintain the correct multiplicity relationship of the crystallographic planes. The detail cards for $(h00)$, $(0k0)$ and $(00l)$ appear only in category 1, and the $(0\bar{k}0)$ and $(00\bar{l})$ are omitted from the other packs. Similarly, the $\{hk0\}$ planes irrespective of sign should appear twice only; the $\{hkl\}$ planes are represented four times.

(2) *Punching the structure-factor values and checking*

To complete the preparation of each preliminary detail card the values of F^o_{hkl} and F^c_{hkl} are inserted by hand-punching, and the card lay-out appears as in Fig. 1 (*b*). Negative and positive values of the F's are indicated by over-punching on descriptive columns. The best method of checking the hand punching is to list the cards on the tabulator and compare the printed record with the original table of structure factors. It is also necessary to check the ϕ values, and for this purpose we use the identity

$$x\Sigma h + y\Sigma k + z\Sigma l \equiv \Sigma\phi.$$

(3) *Reproduction of the preliminary detail cards*

If there are more than four values of ϕ on the detail cards, there will not be enough columns to accommodate the cosine and sine values, and a new set of

cards must be made with a maximum of four on each, i.e. restricted to the columns 7–18. This can be done automatically by means of a reproducing punch. The cards for ϕ_a–ϕ_d, ϕ_e–ϕ_h, etc., can be distinguished either by punching in a descriptive column (e.g. by using rows to 5–9 in column 1) or by over-punching.

(4) *Punching* $\cos 2\pi\phi_r$ *and* $\sin 2\pi\phi_r$ *on the final detail cards*

The cosines and sines are transferred to the detail cards from a master pack. This consists of 1000 cards, one for each value of ϕ from 0·000 to 0·999 at intervals of 0·001. The values of ϕ, $\sin 2\pi\phi$ and $\cos 2\pi\phi$ are duplicated four times on each card and the trigonometric values (to four figures, negative values being shown as complements) are accommodated in seven-figure fields as shown in Fig. 1 (*c*). Each ϕ value on these cards is punched in the same columns as one of the ϕ_r values on the detail cards prepared by the previous operation, and the sine and cosine values fall in columns which on the detail cards are hitherto unused.

In order to transfer the appropriate sine and cosine values from the master pack to the detail cards, both packs are sorted on the columns of ϕ_a with the master pack leading. This gives a composite pack in which each ϕ master card in order is followed by those detail cards on which ϕ_a, ϕ_e, ϕ_i, etc., have the same value as on the master. When this composite pack is passed through a suitably controlled reproducing punch the correct values of $\cos 2\pi\phi$ and $\sin 2\pi\phi$ are punched on the detail cards. This operation is called intersperse gang-punching.

The master cards are then extracted and the procedure repeated for the other ϕ_r columns until all the trigonometric functions have been punched on to the detail cards, with the arrangement shown in Fig. 1 (*d*). The detail cards are now ready for the synthesis and the master pack is refiled.

B. Multiplication by the F values and summation of the synthesis

The Hollerith tabulator can multiply by numbers less than 10 by what is known as 'progressive digiting'. In order therefore to multiply by a three-figure F value, it is first necessary to produce from each detail card two more cards on which the trigonometrical functions have been multiplied by ten and by one hundred respectively and the F^o and F^c tens and hundreds figures have been displaced to the units columns thus:

	$\cos 2\pi\phi_r$	$\sin 2\pi\phi_r$	F^o	F^c
Units card	9993246	0007375	123	156
Tens card	993246–	007375–	2	5
Hundreds card	93246—	07375—	1	1

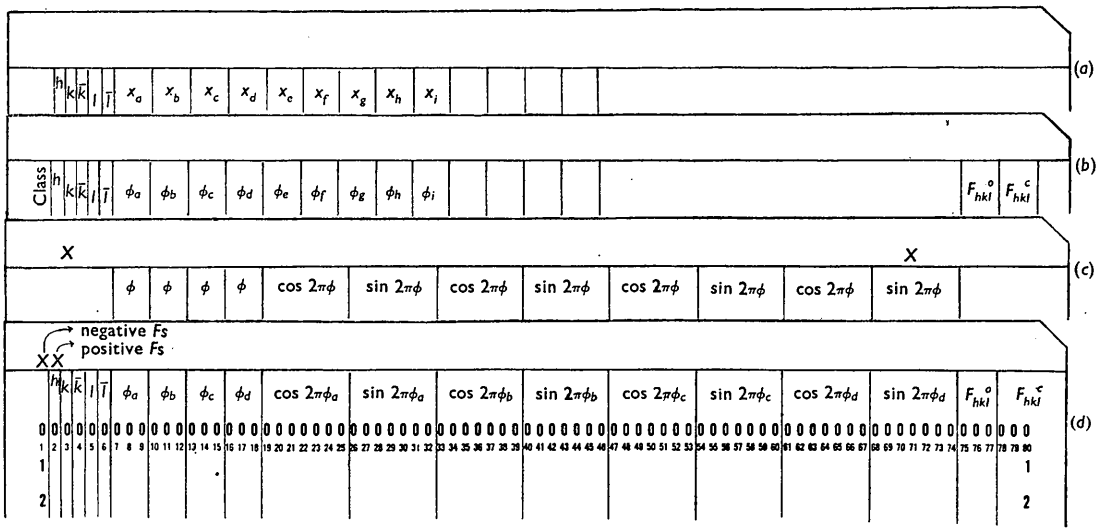

Fig. 1. (*a*) A parameter card. (*b*) A preliminary detail card. (*c*) A master card. (*d*) A final detail card.

All the multiplication of the cosine and sine values by the three-figure F's is then done by progressive digiting on the units column of the F's using three cards instead of one. The tens and hundreds detail cards can be reproduced automatically from the original units cards by means of a reproducing punch.

The detail cards are separated into packs referring to ϕ_a–ϕ_d, ϕ_e–ϕ_h, etc., and each of these packs is summed independently in two sections, one containing all cards with positive F's and the other all negatives. The positive and negative summations are carried out separately and combined at the end of the computation, as this provides the simplest means of obtaining the correct signs when multiplying by negative numbers.

The calculation of the first and second differential summations is described below for

$$\sum_3 hF_{hkl}\sin 2\pi\phi_r \quad \text{and} \quad \sum_3 h^2F_{hkl}\cos 2\pi\phi_r,$$

(where F may be F^o or F^c); these are the simplest cases because only positive values of h are involved. Selecting one of the packs into which the detail cards have been separated, e.g. that for ϕ_a—ϕ_d with F^o positive, the procedure is as follows. The cards are sorted first on

the unit column of F^o and then on the h column so that the pack when reassembled contains h groups in ascending numerical order of h; in each group the detail cards are in descending order of the numbers 9 to 1 in the F^o (units) column. It is important to remove cards in which there is a zero in this column. If in any group the complete sequence of digits 9 to 1 is not represented, a 'digiting card' is inserted in the place of the missing digit(s). The digiting card, which is put in merely to give an instruction to the tabulator, is blank except for the digit in the F^o column and the appropriate h value.

We have used two methods of tabulating, one of which, (*b*), can be used only on a rolling-total tabulator:

(*a*) The pack is inserted into the tabulator with the 9 digit cards of the $h=0$ group leading. The tabulator is controlled to print and summary-punch the subtotals $\sin 2\phi_r$ and $\cos 2\phi_r$ every time the digit in the F^o column changes. The *final total* is produced by a change in the h value. The subtotals and the final total of the groups for $h=0$, $h=1$, $h=2$, up to the maximum value of h, are printed and summary-punched in sequence. Table 1 illustrates part of this tabulation taken from an actual calculation.

Simultaneously with the printing, the information recorded in each row of the tabulation is summary-punched on a new card. The essential feature of this tabulation is that the first row of each h group corresponds to the summation of the cosine and sine values from all the cards on which h has the printed value and there is a 9 in the F^o column (i.e. $F=9$, 90 or 900), the second row is the sums from cards on which h has the same value and the F^o column is 9 and 8, and so on until on the ninth row we have the sums from cards with all F^o column digits from 9 to 1. Therefore when the summary-punched cards which correspond to this tabulation are fed back into the tabulator and summed for each h group and printed (as in Table 2, which shows the continuation of the same calculation as Table 1) the multiplication by F^o has been effected. The sums are printed, as in Tables 1 and 2, to four places of decimals, the last three of which are inaccurate. In most calculations the first figure to the right of the decimal point is also of no significance. Since it does not reduce the speed or scope of the method to print all the figures, it is preferable to round off to the significant figures at the end of the calculation.

(*b*) If a rolling-total tabulator is available the final tabulation can be obtained in a single operation without summary-punching. The cards are inserted as before but the tabulator is controlled in such a way that the *subtotal* is rolled from one counter to a second whenever there is a change in the F^o column. The total of the 9-digit cards is thus rolled nine times, the 8-digit cards eight times, and so on until the summation for the particular h group is completed, and the final totals are printed giving results in the same form as the second tabulation of the previous method. (This digiting process is explained more fully by Cox *et al.* (1947) in describing their Hollerith method for ordinary Fourier summations.)

The disadvantage of this method as compared with (*a*) is that, since the standard type of British tabulator is limited to six counters, only three summations can

Table 1. *Part of a preliminary tabulation*

h	F^o_{hkl} digit (col. 77)	$\Sigma \cos 2\pi\phi_a$	$\Sigma \sin 2\pi\phi_a$	$\Sigma \cos 2\pi\phi_b$	$\Sigma \sin 2\pi\phi_b$	$\Sigma \cos 2\pi\phi_c$	$\Sigma \sin 2\pi\phi_c$
2	9	342601	194533	95445 CB	288345 CB	448541	56166 CB
2	9+8	197273	74305	24235	344674 CB	517862	112694
2	9+8+7	290283	31596	1814 CB	314393 CB	473793	152535
2	9+...+6	118710 CB	220399	135220	522806 CB	638316	548677
2	9+...+5	277734 CB	221844	83244	433152 CB	674510	628211
2	9+...+4	249271 CB	17769	99341 CB	533497 CB	770643	228207
2	9+...+3	668497 CB	1001472	193763	755315	72982 CB	925835 CB
2	9+...+2	2199770 CB	70330 CB	151637 CB	634242	489078	3721028 CB
2	9+...+1	166706	2172409 CB	1040560 CB	2310069	5510506	4340820 CB
3	8	109230	151340	112120	117188 CB	23471	172778 CB
3	8+7	12061	127681	60671	31438 CB	19062	72878 CB
3	8+7+6	15382	96563	133362	133692	52253	266756 CB
3	8+...+5	20177 CB	86824	78443	92993	68965 CB	184955 CB
3	8+...+4	376494	76580 CB	34707	135037	77598	25668
3	8+...+3	166428	13567 CB	310068 CB	34428 CB	19918 CB	146144 CB
3	8+ +2	288583	302296 CB	62667	39868	174450 CB	408639
3	8+...+1	184608	616918	421486 CB	238897 CB	609545 CB	630735

Table 2. *Part of a final tabulation*

h	$\Sigma F^o_{hkl} \cos 2\pi\phi_a$	$\Sigma F^o_{hkl} \sin 2\pi\phi_a$	$\Sigma F^o_{hkl} \cos 2\pi\phi_b$	$\Sigma F^o_{hkl} \sin 2\pi\phi_b$	$\Sigma F^o_{hkl} \cos 2\pi\phi_c$	$\Sigma F^o_{hkl} \sin 2\pi\phi_c$
1	2612926	1523823 CB	83053 CB	1591331 CB	970943 CB	1287812
2	2517119 CB	480821 CB	952335 CB	1262759	9450267	7373525 CB
3	1132609	686883	249584 CB	20361 CB	700494 CB	221531
4	286534 CB	2726034 CB	549150 CB	5116277 CB	1416451 CB	3070481
5	3174177	449354 CB	983319 CB	1386768	2068073 CB	1393068
6	2694086 CB	1450598	1476773	595729 CB	140069	394956 CB
7	317569 CB	154424	406004 CB	297989	1831076	1217440 CB
8	62718 CB	23452 CB	239518 CB	1388006	3430125	2107877 CB

be done simultaneously, and the packs have to be re-inserted with control changes for further summations. On the other hand, the speed of tabulation is faster than when accompanied by summary-punching, fewer cards are used, and on the whole we have found it the more satisfactory method.

When the above process has been repeated for the F-negative pack the tabulations (Table 2) contain all the information necessary for the calculation of

(i) $\sum_3 F^o_{hkl}\cos 2\pi\phi_r$ (the electron density at the point (x_r, y_r, z_r), close to the peak maximum);

(ii) $\sum_3 hF^o_{hkl}\sin 2\pi\phi_r$;

(iii) $\sum_3 h^2F^o_{hkl}\cos 2\pi\phi_r$.

The arrangement of Table 2 is such that these calculations can be done quite simply by means of an ordinary desk-type multiplying machine. We have also obtained them on the Hollerith equipment by summary-punching a card for each row of Table 2 and tabulating these new cards; (i) is obtained by direct addition from the cards and (ii) by progressive digiting on the h values. The method of multiplying by h^2 using the tabulator is complicated and, being dependent upon the detailed specification of the particular tabulator, does not lend itself to a general non-technical description.

To evaluate terms containing k or l the method differs from the above description only in that the cards must be divided into four packs instead of two, in order to separate positive and negative k (or l) values. As before, the totals are combined with appropriate signs at the conclusion of the summations.

It will be noted that whereas the summations of the type (ii) and (iii) above are quite different functions according as the grouping of the cards is based on h, k or l, the summation (i) is identical in all three cases. This provides a very searching check on the sorting, tabulating and summary-punching processes in § B of the method, and we consider that it is essential to verify that all three final h, k and l summations give exactly the same value for the electron density (i). When the presence of an error has been indicated by this method, it is easily located by comparing the electron-density subtotals for various categories of cards.

The same detail cards and the same procedure can be used for evaluating the differential syntheses with the F^c_{hkl} coefficients; in the preceding description (with the arrangement in Fig. 1 (*d*)), it is merely necessary to control on the F^c column instead of the F^o column in § B. When the method was used by Cox *et al.* (1949) for the structure analysis of thiophthen, it was necessary to put *three* sets of structure factors on to the cards and all three differential syntheses were computed using the same detail cards. This was found to be a very efficient method, since the preparation and checking of the cards takes three or four times longer than the actual multiplication and summation processes.

Exactly the same technique can be used to calculate the sums of derivatives required in the methods of least squares and steepest descents. For example, to minimize the function used by Hughes (1941),

$$\Sigma w_{hkl}(F^o_{hkl}-F^c_{hkl})^2,$$

it is only necessary to punch on the cards the values of $w_{hkl}f'_{hkl}(F^o_{hkl}-F^c_{hkl})$ (where w_{hkl} is a weighting factor related to the accuracy of the intensity measurement, and f'_{hkl} is a mean unitary scattering factor) in place of or in addition to the observed and calculated structure factors. In the structure analysis of nitronium perchlorate, it has been possible to arrange the lay-out of the cards so that the same set of detail cards can be used to obtain atomic co-ordinates from both the Fourier differential method and the least squares method.

An incidental feature of the method is that the detail cards for the analysis of a structure provide a complete record of the data in a form which is permanent, easily stored, and readily accessible for further investigation.

We wish to thank the Royal Society for a grant; the British Electricity Authority, and particularly Mr W. McL. Wishart, for generously placing Hollerith equipment at our disposal; and the British Tabulating Machine Co. Ltd., for their helpful co-operation and interest.

References

Booth, A. D. (1946*a*). *Trans. Faraday Soc.* **42**, 444.
Booth, A. D. (1946*b*). *Proc. Roy. Soc.* A, **188**, 77.
Cox, E. G., Gillot, R. & Jeffrey, G. A. (1949). *Acta Cryst.* **2**, 356.
Cox, E. G., Gross, L. & Jeffrey, G. A. (1947). *Proc. Leeds Phil. Soc.* **5**, 1.
Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.
Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.