

on the same card simultaneously, thereby reducing the number of operations required.

The general outline of the scheme is sufficiently flexible to enable its application to any space group. It should be mentioned that in some cases it is better to set up the calculating scheme in accordance with the original form of the structure factor, i.e.

$$A_{hkl} = \sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j)$$

and

$$B_{hkl} = \sum_j f_j \sin 2\pi(hx_j + ky_j + lz_j),$$

obtaining the values of the argument by a cross-footing operation. In this instance it is also possible to calculate values for two reflections on one card simultaneously. In any case, the most efficient scheme for a particular job should be carefully worked out before embarking upon the calculation.

The wiring on all plugboards is of the conventional type. Wiring diagrams are available on request to these Laboratories.

This punched-card method reduces greatly the amount of time required to calculate a set of structure factors. It has thus far been applied in the calculation of the structure factors for *l*-threonine (space group $P2_12_12_1$), glycine (space group $P2_1/n$), and acetylglycine (space group $P2_1/c$). In the first case, 625 complex structure factors, depending on the parameters and form factors of eight non-equivalent atoms, were calculated in about 30 man-hours; in the second case, 250 real structure factors, involving five non-equivalent atoms, were

calculated in about 10 man-hours; and in the third case, over 1200 structure factors, involving eight non-equivalent atoms, were calculated in about 30 man-hours, excluding in all cases the time required in the preliminary operations. These times are about one-tenth of those required for the conventional method of calculation with the aid of trigonometric tables, and a motor-driven adding calculator. As pointed out above, these times are more than those which would be required if additional machines mentioned were available.

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An Improved Punched-Card Method for Crystal Structure-Factor Calculations

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Using punched cards and International Business Machines, a method of crystal structure-factor calculations has been developed, which is not only rapid and accurate, but also general for all structures. The principles and application of the scheme are discussed.

Introduction

The need for rapid and accurate means of performing laborious calculations attending a crystal-structure determination has been satisfied in great measure by Shaffer, Schomaker & Pauling (1946) with the successful application of punched-card methods, using International Business Machines. In particular, the scheme for the evaluation of Fourier series has been eminently successful. However, the method of structure-factor calculations outlined by these authors is not completely satisfactory, and a new scheme has been reported recently by Donohue & Schomaker (1948, 1949).

We wish to describe a significant improvement in the use of punched cards for this purpose, which results in a procedure that we believe to be more direct and more uniform for different crystals than any of those reported previously.

Considering the general expression for the structure factor,

$$F_{hkl} = \sum_{j=1}^N f_j \cos 2\pi(hx_j + ky_j + lz_j) + i \sum_{j=1}^N f_j \sin 2\pi(hx_j + ky_j + lz_j),$$

our basic operations are (1) to form the quantities $(hx_j + ky_j + lz_j)$, (2) to obtain their cosines (and perhaps sines), (3) to perform the multiplication of the trigonometric functions by the atomic scattering factors, f_j , and (4) to perform the indicated summations. The principle, then, is the same as that proposed originally by Shaffer *et al.* (1946).

There is a distinct advantage in basing the procedure on the general form of the structure factor, since only then is it possible to have a uniform scheme for all structures. In the scheme of Donohue & Schomaker (1948, 1949), where the structure factor is first reduced by trigonometric relations to products of sine and cosine terms, it is necessary to employ a different procedure for each space group, and for many space groups the method becomes quite complex and makes inefficient use of the machines.

However, in the practical application by Shaffer *et al.* (1946), the forming of the quantities $(hx_j + ky_j + lz_j)$ was a slow and inconvenient process, which, furthermore, could not make proper use of symmetry relations among the atomic co-ordinates (except for a center of inversion). We have found that with the IBM calculating punch (type 602) it is possible to obtain in one operation $hx_j + ky_j + lz_j$, using a deck of cards containing one card for each atom (with its x_j, y_j, z_j) for each hkl . In addition, the presence of certain symmetry elements can be used to reduce the number of parameters (and, consequently, the time of operation) without major deviation from the general scheme. This results from the fact that with the calculating punch and proper control panel *any* or *all* of the following four quantities can be obtained in one simple operation:

$$\begin{aligned} a_j &= (hx_j + ky_j + lz_j), & b_j &= (hx_j + ky_j - lz_j), \\ c_j &= (hx_j - ky_j + lz_j), & d_j &= (-hx_j + ky_j + lz_j). \end{aligned}$$

Since for many symmetry elements, the structure factor can be expressed in terms of a_j, b_j, c_j, d_j , there will be considerable reduction in the number of atomic parameters whenever such symmetry elements are present. With this phase of the problem adequately solved, we are then able to employ many of the operational techniques suggested by Donohue & Schomaker (1948, 1949), to evolve a procedure which is at the same time sufficiently rapid and general for all structures.

The effect of symmetry will be illustrated by example. For the space group $P2/m$ the general atom positions are $x, y, z; \bar{x}, \bar{y}, \bar{z}; x, \bar{y}, z; \bar{x}, y, \bar{z}$, and the structure factor can be written

$$F_{hkl} = 4 \sum_{j=1}^{\frac{1}{2}N} f_j \{ \cos 2\pi(hx_j + ky_j + lz_j) + \cos 2\pi(hx_j - ky_j + lz_j) \},$$

$$\text{or} \quad F_{hkl} = 4 \sum_{j=1}^{\frac{1}{2}N} f_j \{ \cos 2\pi a_j + \cos 2\pi c_j \}.$$

The possibility of obtaining a_j and c_j at the same time means that only the one set of parameters, x_j, y_j, z_j , are necessary in the calculations. Again, for space group

$Pmmm$, where the general positions are $x, y, z; \bar{x}, \bar{y}, \bar{z}; x, y, \bar{z}; \bar{x}, \bar{y}, z; x, \bar{y}, z; \bar{x}, y, \bar{z}; \bar{x}, y, z; x, \bar{y}, \bar{z}$, we have

$$F_{hkl} = 8 \sum_{j=1}^{\frac{1}{2}N} f_j \{ \cos 2\pi a_j + \cos 2\pi b_j + \cos 2\pi c_j + \cos 2\pi d_j \},$$

and the one set of parameters x_j, y_j, z_j is sufficient. If glide planes and screw axes are present, only a slight modification is introduced. For example, for $Pnmm$, where the general positions are

$$\begin{aligned} x, y, z; & \bar{x}, \bar{y}, \bar{z}; & \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z; & \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z; \\ \bar{x}, \bar{y}, \bar{z}; & x, y, \bar{z}; & \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z; & \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z, \end{aligned}$$

we have the two cases:

$$h + k + l = 2n,$$

$$F_{hkl} = 8 \sum_{j=1}^{\frac{1}{2}N} f_j \{ \cos 2\pi a_j + \cos 2\pi b_j + \cos 2\pi c_j + \cos 2\pi d_j \};$$

$$h + k + l = 2n + 1,$$

$$F_{hkl} = 8 \sum_{j=1}^{\frac{1}{2}N} f_j \{ \cos 2\pi a_j + \cos 2\pi b_j - \cos 2\pi c_j - \cos 2\pi d_j \}.$$

Once the quantities a_j, b_j, c_j, d_j and their cosines have been obtained, it is a simple matter to sort out (by machine) the reflections, according to whether $h + k + l$ is even or odd, and to perform the two summations above separately.

In this manner, reduction in the number of independent parameters occurs, at least partially, for all symmetry elements except 3-fold axes. We use as our unit of structure a group of atoms that may be repeated by orthorhombic symmetry elements to give the entire structure. If this is not possible, we use the full unit cell. For all crystals which are either triclinic, monoclinic or orthorhombic our unit is the irreducible minimum—the usual asymmetric unit of structure. Tetragonal and cubic crystals can be regarded conveniently as orthorhombic, and although we cannot then always take into account all the symmetry operations, our scheme is still practicable. For such cases, the total number of forms requiring computation is a fraction of that for orthorhombic crystals of comparable size of cell, and our unit is still sufficiently small. Even for rhombohedral and hexagonal space groups where the unit may be the entire cell— $C3$, for example—the ease of computing $(hx_j + ky_j + lz_j)$ makes it worth while to adhere to our general scheme.

In terms of machine operations, the simultaneous evaluation of the four quantities a_j, b_j, c_j, d_j has been made possible by the development of a proper wiring diagram, providing for storing the following products as they are computed:

$$hx_j, ky_j, lz_j, -hx_j, -ky_j, -lz_j.$$

Our present limitation to orthorhombic symmetry elements is due to the limited storage capacity of the calculator (type 602). If later models should have sufficient capacity for storing such products as

$$hy_j, kx_j, lz_j, -hy_j, -kx_j, -lz_j,$$

as well as those above, there would be many more space groups for which only the parameters of the asymmetric unit would suffice. Eventually, it may be possible to realize this situation for all space groups.

Whenever glide planes or screw axes are present, there will be alternative expressions for F_{hkl} . For instance, for the space group $Pn\bar{m}$, mentioned above, we have

$$F_{hkl} = 8 \sum_{j=1}^{\frac{1}{2}N} f_j \{A_j + B_j + C_j + D_j\}, \quad \text{for } h+k+l = 2n,$$

and

$$F_{hkl} = 8 \sum_{j=1}^{\frac{1}{2}N} f_j \{A_j + B_j - C_j - D_j\}, \quad \text{for } h+k+l = 2n+1,$$

where

$$A_j = \cos 2\pi a_j, \quad C_j = \cos 2\pi c_j,$$

$$B_j = \cos 2\pi b_j, \quad D_j = \cos 2\pi d_j.$$

It is very advantageous, for such situations, to have a means of obtaining the various combinations of $\pm A_j$, $\pm B_j$, $\pm C_j$, $\pm D_j$ in one operation. This again can be accomplished by the calculating punch with a proper wiring of a control panel. This panel, unlike the one for computing a_j , b_j , c_j and d_j , will not be the same for all problems. However, it is relatively simple for even the most complex space groups. It is also often of great aid, when $|F_{hkl}| = |F_{\bar{h}\bar{k}\bar{l}}|$, for then the two F 's consist of different combinations of $\pm A_j$, $\pm B_j$, $\pm C_j$, $\pm D_j$. Only one set of reflection cards (for hkl , but not $\bar{h}\bar{k}\bar{l}$) is necessary then until the final stages of the work.

Outline of procedure

Although the principle of our method differs from that of Donohue & Schomaker (1948, 1949), we make use of many of the operational procedures employed by them. Thus, in the following outline steps I and II and the method of obtaining the cosine or sine values (step IV) are the same as theirs.

I. Whenever any problem is to be calculated on IBM machines, the first step is always to key-punch the data on blank IBM cards. These cards have 80 columns of 10 digits each, ranging from 0 at the top to 9 at the bottom. Key-punching is the process of transferring data from the original sheets to these cards by means of a machine similar to a typewriter, which punches a hole in the card corresponding to the digit desired. For this particular problem, three sets of cards are key-punched:

(1) A deck of cards comprising a table of $\sin 2\pi\alpha$ and $\cos 2\pi\alpha$ for α ranging from 0.001 to 1.000 in intervals of 0.001. This table deck is used for all structure-factor calculations.

(2) Reflection cards for each hkl . This deck is used for the different trial calculations for a particular crystal. Each card of the deck contains, in addition to the indices hkl , the scattering factor for each kind of atom in the structure, and, if known, the temperature factor and absorption corrections.

(3) Parameter cards. A single card contains the trial

parameters x_j, y_j, z_j of one atom.* The number of such cards required is the same as the number of atoms in the unit of structure as defined previously.

From this point on, the machines perform the work; but the operator informs the machines 'what to do' and 'how to do it' by inserting a previously wired control panel for each operation. The cards are then run through that machine. This panel is easily removed and another panel inserted for the next operation.

II. 'Detail cards' are prepared by reproducing (with the automatic reproducing punch) as many sets of reflection cards as there are parameter cards. The parameters are gang-punched on these cards as they are being reproduced. As a result there is one card for each atom for each hkl .

III. At this stage, a single detail card contains the following information in the various fields:

crystal, atom, h, k, l, x_j, y_j, z_j .

With the calculating punch and the proper control panel the terms a_j, b_j, c_j, d_j are now computed and punched in four of the remaining fields of each card.

IV. By means of sorting (with the automatic sorter) and intersperse gang-punching, the cosine values of a_j, b_j, c_j, d_j are obtained from the table cards and punched on the detail cards. (If a collator is available it will be possible to speed up this procedure.) If all four terms a_j, b_j, c_j, d_j are being used, the sort must be made four times.

The detail cards are now complete and bear the following information:

crystal, atom, $h, k, l,$

$x_j, y_j, z_j, a_j, b_j, c_j, d_j, A_j, B_j, C_j, D_j,$

where $A_j = \cos 2\pi a_j$, etc.

V. With the sorter, all cards with the same hkl are grouped together, and then separated according to chemical kind of atom. Using the IBM accounting machine, with the summary punch attached, the cards are added to get the sums, $A = \sum_j A_j$, $B = \sum_j B_j$, $C = \sum_j C_j$, $D = \sum_j D_j$, for each reflection for each chemical kind of atom. These sums are punched on blank cards.

Usually, it will be necessary to have as many sets of these summary-punched cards as there are chemical kinds of atoms. Thus, for two chemically different atoms, M_1 and M_2 , there will be one set of cards containing $A_{M_1}, B_{M_1}, C_{M_1}, D_{M_1}$ and another set with $A_{M_2}, B_{M_2}, C_{M_2}, D_{M_2}$.

VI. With the calculating punch and appropriate control panel, the proper combinations of

$$\pm A \pm B \pm C \pm D$$

(which depend on hkl and the symmetry of the space group) are formed and punched on each of the summary cards.

* It is important in this procedure that all atomic parameters occur as positive numbers. If, in the unit of structure chosen, some parameters are negative, they must be given a unit translation.

VII. The results of the previous step are now transferred to one card (for each hkl). Also on this card are reproduced, from the original reflection cards, f_{hkl} for each kind of atom, the temperature factor, T_{hkl} , etc.

VIII. The products, $f_{M_1}(\pm A \pm B \pm C \pm D)_{M_1} = R_{M_1}$, etc., which represent the contribution of each chemical kind of atom to the structure factor, are obtained with the calculator and punched on this last set of cards.

IX. Also with the same cards and the calculator, the terms, R_{M_1} , are summed over all kinds of atoms, and the result is multiplied by the temperature factor and the number, P , of irreducible units of structure in the unit cell (2, 4, 8, etc.). This gives the structure factor

$$F_{hkl} = (PT_{hkl})(R_{M_1} + R_{M_2} + \dots).$$

the operator to the machine. Since it is used (with perhaps only a very slight modification) for all structures, it is kept intact once it is wired. The proper panel at step VI, for obtaining the required combinations of $\pm A \pm B \pm C \pm D$ ('cross-footing' operation) may vary considerably from problem to problem, but the wiring diagram in any case is relatively simple and can be worked out readily by an experienced operator.

In other respects, the procedure makes use of standard IBM machines and routine operations familiar to most operators. A detailed set of instructions can be prepared, so that an operator unacquainted with crystallographic problems can easily perform the calculations. Having done this once, the operator requires

Code	<i>h</i>	<i>k</i>	<i>l</i>	$\frac{1}{2}f_B$	f_H	T_{hkl}	A_B	A_H	R_B	R_H	F_{hkl}
16 1 4 1	1	1	1	705	810	957	16-	63-	226-	205-	413-
16 1 4 1	5	1	1	483	486	837	32-	189-	314-	367-	570-
16 1 4 1	9	1	1	371	213	633	125-	26-	933-	22-	576-
16 1 4 1	13	1	1	316	90	403	56-	109	357-	39	128-
16 1 4 1	3	3	1	566	618	895	79	146	899	362	1128
16 1 4 1	7	3	1	400	307	726	197	293	1577	360	1407
16 1 4 1	11	3	1	340	150	507	331	343	2251	178	1232
16 1 4 1	15	3	1	290	58	298	111	350-	646	81-	168
16 1 4 1	1	5	1	570	629	897	59-	170-	682-	430-	997-
16 1 4 1	5	5	1	437	398	788	110-	488-	962-	777-	1371-
16 1 4 1	9	5	1	362	187	602	510-	361	3693-	270	2060-
16 1 4 1	13	5	1	309	81	380	183-	430	1131-	139	377-

Fig. 1. Portion of computed data for $B_{10}H_{14}$, listed from the final set of cards (step X of procedure). Vertical lines indicate columns of decimal points.

X. These cards can now be 'listed'. This process prints the following data on a sheet of paper:

$$hkl, f_{M_1}, f_{M_2}, \dots, PT_{hkl}, R_{M_1}, R_{M_2}, \dots, F_{hkl}.$$

A portion of the listed data for an actual calculation of the structure factors for decaborane, $B_{10}H_{14}$, is shown in Fig. 1.

Discussion of procedure

The procedure, outlined above, is given in most general form, assuming that all four terms a_j, b_j, c_j, d_j need to be computed and that F_{hkl} has alternative expressions, depending on hkl . If such is not the case, only minor modifications are called for, mainly in steps V and VI. Thus, if only a_j is to be computed (e.g. space groups $P1$ and $P1$), step VI is omitted entirely, and at step III, the control panel is changed slightly to punch only a_j on the cards.

The control panels of steps III and VI form a most significant part of the equipment, and are mainly responsible for this scheme. The panel of step III, while quite complex, transfers the burden of the work from

only a few simple instructions, in order to do the calculations for a different problem.

A detailed set of instructions for following the procedure, including the wiring diagrams of the control panels for steps III and VI, has been prepared and is available to anyone interested.

Application

The scheme has been applied successfully in several calculations of the structure factors (about 500) of decaborane, $B_{10}H_{14}$. Experience has been obtained with space groups $Pn\bar{3}m$ and $C112/a$. The time required is estimated to be approximately one-tenth that taken with a manual calculating machine.

In the course of successive calculations of structure factors for a particular crystal, often only a few parameters are changed from one trial to the next. The time required for a second trial calculation, then, is much less than for the first. The new parameter cards only are used to step V of the procedure, at which point they replace the former parameter cards. If the parameter

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.

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

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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