

## The Use of General Programmes for Crystallographic Calculations on the Manchester University Electronic Digital Computer (Mark II)

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A general programme is described for computing Patterson and Fourier syntheses. It can be applied to centrosymmetric and non-centrosymmetric space groups without modification so that there is no need to check programmes for different space groups. Examples with times of computation are given. An application of the programme to diffraction-broadening corrections of superlattice reflexions is also described.

The second general programme computes structure factors in zones of reflexions of triclinic, monoclinic and orthorhombic space groups. The computing time is 2–3 sec. per reflexion, and printing out of indices and structure factor takes 2.4 sec.

### 1. Introduction

The use of electronic digital computers for crystallographic calculations has been described by Bennett & Kendrew (1952), Ahmed & Cruickshank (1953), and Thompson, Carminer, Fantl, Wright & King (1954). Bennett & Kendrew describe the use of the Cambridge machine EDSAC for two- and three-dimensional Fourier syntheses; Ahmed & Cruickshank are concerned with the computation of differential Fourier syntheses on the Manchester machine; Thompson *et al.* discuss the application of LEO, the machine built by J. Lyons and Co., to the refinement of structures by differential Fourier syntheses and by the method of steepest descents. The foregoing procedures ('programmes' in computer language) for structure refinement were originally developed for particular space groups, and modifications have to be made for other space groups. The coding of new programmes, and the subsequent checking of them, take up the major part of the time spent on a problem. To obtain some reduction in this 'programming' time, Ahmed & Cruickshank have devised a quick method of checking programmes for centrosymmetric structures. In the present paper a general programme is described which can be used without modification for the calculation of Fourier and Patterson syntheses in both centrosymmetric and non-centrosymmetric space groups. The same programme can also be applied to the Fourier summations required to determine the diffraction broadening of superlattice reflexions in alloys. A general programme is also described for the calculation of structure factors for a particular zone.

The Manchester machine has been described in full by Kilburn (1949, 1951), and briefly by Ahmed & Cruickshank (1953). It is sufficient for the present paper to state that the storage facilities are made up of a high speed electronic store of eight 'pages' and a large magnetic store of 256 'tracks'.

In this paper it is not intended to give an account of programming for a digital computer; full details for the Manchester machine will be found in the Manchester University *Programmer's Handbook* (1953). Problems for a computing machine are first broken down into a series of simple mathematical processes. A routine is constructed for each process. The programme consists of a master routine together with a number of other routines. The order of use of the routines is specified by the master routine. It is possible to construct a routine to do two similar processes, e.g. to calculate sines or cosines; such a routine will have two starting or entry points depending on which process is required. The entry point of a routine is given by its 'cue', and a 'directory of cues' is made for the complete programme. The general programmes described in the present paper are made up of multipurpose routines which enable the calculations for the different space groups to be carried out by changing the 'directory of cues'; a maximum of five short lines in the directory are changed for Fourier and Patterson syntheses and one only for structure factors.

### 2. Two-dimensional Patterson and Fourier syntheses

Patterson and Fourier syntheses can be calculated in two ways for a network of points in a two-dimensional projection: (i) The coefficients are stored in the machine and used to calculate the value for each point. (ii) The coefficients are used to compute preliminary tables; these are stored in the machine and used to compute the values for the final table.

The second method is similar to that described by Lipson & Beevers (1936) for hand computation by the 6° strips. Both these methods were tried on the machine, and the conclusions of Bennett & Kendrew

(1952) that the second method is faster and better were verified.

### 2.1. *The machine programme*

The complete programme for the second method is made up of the following routines:

- (i) Master.
- (ii) Input coefficients.
- (iii) Compute preliminary table.
- (iv) Read or write preliminary table.
- (v) Compute final table.
- (vi) Print or punch final table.

The functions of these routines can be explained as follows:

(i) *Master routine*.—The main function of the master routine has already been explained in the introduction. It contains the counting instructions to use a group of routines in a closed loop for a definite numbers of cycles. There are two points of entry to the master routine for either Patterson or Fourier syntheses.

(ii) *Input coefficients*.—The coefficients and indices are punched on teleprinter tape in groups with one index constant. A group of coefficients and indices is taken into the machine by this routine and stored on page 7 of the electronic store.

(iii) *Compute preliminary table*.—The group of coefficients and indices on page 7 is used by this routine to compute a line of the preliminary table on page 4. The preliminary table line can have a maximum of 64 values, since there are 64 'short lines' on a page of the electronic store. Each 'short line' contains both the value of the running total for the preliminary table and the value of the constant index. Cosines or sines are not calculated directly but read off from a table of cosines (from 0 to 90° at intervals of 90°/32) held on page 2 of the electronic store.

The routine has four points of entry and will compute

$$C(hk) = \pm \sum F(hk) \cos 2\pi(hx/a) \quad \text{and} \\ S(hk) = \pm \sum F(hk) \sin 2\pi(hx/a),$$

using the nomenclature of Lipson & Beevers (1936).

(iv) *Read or write preliminary table*.—A line of the preliminary table for a constant index computed on page 4 is written up into the magnetic store by one entry point of this routine. The other entry point enables the line of the preliminary table to be read down from the magnetic store to page 4 for computation of the final table.

The master routine uses routines (ii), (iii) and the 'write' part of (iv) in a closed looped until all the lines of the preliminary table are written into the magnetic store.

(v) *Compute final table*.—A line of the final table is computed for a constant value of coordinate, say  $x$ , by bringing in turn each line of the preliminary table

from the magnetic store to page 4 by the 'read' part of routine (iv), reading it at the correct  $x$  value and adding the line of computed  $y$  values to those already stored on pages 6 and 7. The line of the final table can be made up to a maximum of 128 points. The four entry points of this routine compute

$$\pm \sum C(hk) \cos 2\pi(ky/b) \quad \text{and} \quad \pm \sum S(hk) \sin 2\pi(ky/b)$$

for variable  $y$ .

(vi) *Print or punch final table*.—The final routine either prints out or punches out in tape the line of the final table stored on pages 6 and 7 and at the same time clears these pages for the next summation. Machine time is saved by punching out the information since it is two and a half times as fast as printing; the tape can afterwards be printed out on a teleprinter.

The 'read' part of routine (iv), together with routines (v) and (vi), are used in a closed loop by the master routine until all the lines of the final table are completed.

### 2.2. *Input tapes*

The first stage in a Fourier synthesis is to make a table of  $F(hk)$  coefficients with the  $F(00)$ ,  $F(h0)$  and  $F(0k)$  terms suitably weighted; for certain space groups sum and difference tables of  $F(hk) + F(h\bar{k})$  and  $F(hk) - F(h\bar{k})$  are more convenient. The data of these tables are punched out. It is convenient to confine the largest summations to the shorter preliminary tables, i.e. to have as few lines as possible in the preliminary tables. The data tape carries values of  $F(hk)$ , or of  $A(hk)$  and  $B(hk)$  when the structure is not centrosymmetric, in a sequence which depends on the indices.

The other tapes required are: (i) The 'Directory of cues', which depends on the structure. (ii) A 'Table of constants', which specifies the range of the unit cell, the interval for calculation, the number of lines in the preliminary tables and the magnetic tracks used for their storage, and finally the arrangement of the printed results.

### 2.3. *Checks*

The input of data and computation of preliminary tables can be checked by repeating the process with the writing current to the magnetic store switched off. This means each line of the preliminary table will be computed but cannot be written on the magnetic drum. The computed line is compared with that already in the magnetic store and if agreement is obtained the programme proceeds to the next line; otherwise the machine indicates if the check fails for the particular line.

The final table can be checked only by repeating from the preliminary table and comparing the result. In general, this is not found to be necessary if good magnetic tracks are used for the preliminary tables.

Errors that do occur can usually be detected by inspection of the final table. Faulty lines in the final table can be re-computed by setting the hand controls of the machine.

#### 2.4. Application to crystal structures

*Example A: Fourier synthesis of *m*-tolidine dihydrochloride.*—The structure of *m*-tolidine dihydrochloride was published by Fowweather & Hargreaves (1950). The space group is *I*2 so that the *b*-axis projection is centrosymmetrical. It was computed for  $33 \times 33 = 1089$  points (intervals of  $a/32$ ,  $c/128$ ). The preliminary tables of 13 lines were computed in 3 min. 55 sec. from the 145 coefficients. Each point in the final table was computed in 0.73 sec. and printed in 0.82 sec. or punched in 0.33 sec.

The time required for the punching and checking of the input tape was approximately 20 min. The computing time including both checking of preliminary tables and printing out of the final table was 36 min., making the total time for the Fourier synthesis 56 min.

*Example B: Fourier synthesis of  $\beta$ -uranium.*—The non-centrosymmetrical structure of  $\beta$ -uranium, space group *P*4 $mm$ , was computed for Thewlis & Steeple (1954). 63 terms (32*A*'s and 31*B*'s) are involved in the *b*-axis projection, computed for  $33 \times 17 = 561$  points (intervals of  $a/64$ ,  $c/32$ ). The preliminary tables took 2 min. 12 sec. to calculate and the time per point of the final table, including printing, was 1.85 sec. Total machine time was 22 min., including both the checking of the preliminary table and the printing out of the final tables.

#### 2.5. Application to instrumental broadening

The general programme was applied to the Fourier summations required to determine the diffraction broadening of the superlattice reflexions of the alloy CdMg. A two-dimensional extension (Edmunds & Hinde, 1952) of a correction method due to Stokes (1948) was used. The method requires that the particular reflexion should also be observed when sharp, that is, from a perfectly ordered crystal.

The intensity distribution in the central section of the reciprocal lattice spot, both for the broad and sharp reflexions, is expressed as a two-dimensional Fourier summation. The real and imaginary components of coefficients  $G_{yz}$  and  $H_{yz}$  are calculated from the intensities  $g(vw)$  and  $h(vw)$ , read off at regular intervals round the reciprocal-lattice point, as follows:

$$\text{Broad spot: } G_{yz} = \Sigma \Sigma g(vw) \exp 2\pi i(vy + wz); \quad (1)$$

$$\text{Sharp spot: } H_{yz} = \Sigma \Sigma h(vw) \exp 2\pi i(vy + wz); \quad (2)$$

where  $v$  and  $w$  are coordinates in reciprocal space.

The true intensity distribution  $I(vw)$  in the diffuse reflexion is then given by the summation whose coefficients  $K_{yz}$  are the quotients  $H_{yz}/G_{yz}$ , where

$$I(vw) = \Sigma \Sigma K_{yz} \exp 2\pi i(vy + wz). \quad (3)$$

Six Fourier summations are required in the correction of one reflexion and take a considerable time using Beavers-Lipson strips. These six summations require only two directories of cues; no modification of routines is necessary although the last two summations will have to be added together by hand for the final answer. A considerable saving of time was obtained by preparing two new master routines for this problem; these require negligible checking since they only specify the order in which the other routines are used. This problem requires only a limited number of values in the preliminary tables, and the new master routines make it possible to compute the cosine preliminary tables on one half of page 4 of the electronic store and the sine preliminary tables on the other half. The first master routine used for equations (1) and (2) computes and prints the real components of  $G_{yz}$  and  $H_{yz}$ , and immediately follows with the imaginary components from the same preliminary tables. The second master routine combines the real and imaginary contributions of  $K_{yz}$  (equation (3)) in each line of the preliminary tables, thus reducing the last two Fourier summations to one. The input tape has to be punched so that a group of coefficients for the real components of one constant index is followed by the imaginary components of the same constant index. The machine time with these new master routines is approximately 2 hr.

### 3. Computation of structure factors

The programming of the problem is simplified by treating each reflexion separately. The contributions of the different atoms to a reflexion are computed and added together, the result is printed out and the process repeated for the next reflexion. This treatment is different from that described by Ahmed & Cruickshank (1953), who found it quicker to compute the contributions of one atom to all the reflexions and then repeat for other atoms, adding the contributions to the running totals for each reflexion. The time lost in the present work by the alternative method is partly offset by reading the trigonometric functions from a table stored in the machine, instead of computing them. The extra time required for a general programme is only 1 sec. per reflexion, which is negligible compared with the time necessary for the preparation and checking of programmes for particular space groups.

#### 3.1. The programme

The programme is made up of the following routines:—

- (i) Master.
- (ii) Input co-ordinates.
- (iii) Input ( $h, k, f_i$ ).
- (iv) Compute structure factor.
- (v) Print.

The functions of these routines can be briefly explained as follows:

The master routine decides the order in which the other routines are used. It first causes the atomic co-ordinates to be taken into a page of the electronic store and writes them up into the magnetic store for future reference. Each co-ordinate is stored in a short line of 20 digits; there are 64 short lines on a page so that the maximum number of atoms in the asymmetric unit is 32. The values of the co-ordinates must be expressed fractionally in the range 0.5000 to -0.5000.

The second input routine takes in the indices and atomic scattering factors for the reflexion to be computed. There are six entry points to the structure factor routine enabling the following expressions to be calculated:

- (i)  $\sum_i f_i \cos 2\pi(hx_i/a) \cos 2\pi(ky_i/b)$ .
- (ii)  $\sum_i f_i \sin 2\pi(hx_i/a) \sin 2\pi(ky_i/b)$ .
- (iii)  $\sum_i f_i \cos 2\pi(hx_i/a + ky_i/b)$ .
- (iv)  $\sum_i f_i \sin 2\pi(hx_i/a + ky_i/b)$ .
- (v)  $\sum_i f_i \sin 2\pi(hx_i/a) \cos 2\pi(ky_i/b)$ .
- (vi)  $\sum_i f_i \cos 2\pi(hx_i/a) \sin 2\pi(ky_i/b)$ .

The above expressions cover the triclinic, monoclinic and orthorhombic space groups. The trigonometric functions are not computed but read from a table of cosines; the cosines are evaluated at intervals of  $90^\circ/64$  (i.e.  $1/256$ ths). The value of  $hx/a$  or  $ky/b$  is calculated to the nearest  $1/256$ th before the table is read; there is no loss of accuracy for the higher indices. Running totals are kept of the trigonometric function for atoms of the same scattering power. These totals are multiplied by the atomic scattering factors and summed for the different types of atoms.

The structure factor is finally obtained by multiplying the above expressions by a numerical factor which depends on the space group and can be either positive or negative. The multiplication is done by the print routine and the results are printed out in the form  $h \pm k \pm F(hk) \pm$ . The indices and scattering factors of the next reflexion are then taken in the machine and the process is repeated.

### 3.2. Input tapes

Four tapes are required for each structure: (i) Directory of cues, which decides the type of trigonometric expression used. (ii) Co-ordinates input tape. (iii) Indices and atomic scattering factor input tape. (iv) Constants representing the total number of atoms in the asymmetric unit, the number of different types of atoms and the number in each type, and the numerical constant used by the print routine.

The programme is limited to 32 atoms in the asymmetric unit with a maximum of 12 different atomic scattering factors.

Only the short co-ordinate input tape has to be re-punched for re-calculation of structure factors after a change in co-ordinates.

### 3.3. Applications

(i) *m-Tolidine dihydrochloride*.—Structure factors were calculated for reflexions in the  $h0l$  zone, for which the trigonometric expressions are of form  $\sum \cos \cos$  or  $\sum \sin \sin$ . There are nine atoms of three different types in the asymmetric unit. Input of indices and scattering factors and computation of the structure factor takes 1.9 sec. per reflexion; the printing out of  $h, k, F$  took 2.4 sec. The time taken for punching the input tape for 140 reflexions was 20 min., so that the total time taken for the zone of 140 reflexions was 30 min.

(ii) *m-Tolidine*.—*m-Tolidine* has sixteen atoms in the asymmetric unit with two different atomic scattering factors. The computing time was 2.6 sec. per reflexion.

(iii) *Triphenylene*.—There are eighteen atoms of one type in the asymmetric unit. The computing time per reflexion was 2.9 sec.

(iv) *Non-centrosymmetrical space groups*.—A modified master routine is used in these cases. This enables  $A(hk) = F(hk) \cos \alpha$  and  $B(hk) = F(hk) \sin \alpha$  to be calculated and printed out with the indices. The structure factors and phase angles  $\alpha$  are then computed by hand methods.

## 4. Conclusions

Electronic digital machines have more profitable application to structure-factor calculations than to electron-density computations. A considerable amount of printing is involved in the electron-density computations and the printing time is found to be of the order of the computing time, but in spite of this the results described here represent a considerable increase in speed over existing methods. In addition, digital machines have the great advantage of accuracy.

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## A New Modification of L-Glutamic Acid and its Crystal Structure

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A new modification of L-glutamic acid has been found. Its unit cell has a close relationship in dimensions to the other modification reported by Bernal. The crystal structure of this new form has been determined by means of electron-density projections on (100) and (001). Three N-H...O and one O-H...O hydrogen bonds link molecules in three dimensions. An indication of the configuration of the zwitterion is obtained from the dimensions of the carboxylic groups and also from the projected maps of difference series. The carbon-chain configuration is compared with those of two similar compounds, L-glutamine and DL-glutamic acid hydrochloride.

### Introduction

In the course of preparing monosodium glutamate, the present author found crystals which had not hitherto been reported. Though the result of chemical analysis and the measurement of specific rotation\* showed that they were glutamic acid, the preliminary X-ray test revealed that the dimensions of the unit cell were different from those for L-glutamic acid investigated by Bernal (1931). We shall call Bernal's modification the  $\alpha$ -form and the present modification the  $\beta$ -form. As the  $\beta$ -form has one rather short axis it seemed to be promising for the structure determination, and so it was decided to analyse this newly found form as a part of a current program of research in this laboratory on the crystal structures of the fundamental substances composing high polymers.

### Crystallographic data

While the  $\alpha$ -form reported by Bernal (1931) has  $a = 7.06$ ,  $b = 10.3$  and  $c = 8.75$  kX., space group  $P2_12_12_1$ ,  $Z = 4$ , the present form is also orthorhombic but has

$$a = 5.17, b = 17.34 \text{ and } c = 6.95 \text{ \AA} \quad (\text{all } \pm 0.2\%), \\ Z = 4.$$

From the systematic absences  $h00$ ,  $0k0$  and  $00l$  for  $h, k, l$  odd, the space group was found to be  $P2_12_12_1$ . The calculated density ( $1.56 \text{ g.cm.}^{-3}$ ) is in agreement with that observed ( $1.57 \text{ g.cm.}^{-3}$ ). Thus there is seen a simple relation between the dimensions of the two unit cells:

\*  $[\alpha]_D^{20} = +31.7^\circ$  (2N HCl solution).

$$a (\beta\text{-form}) \cong \frac{1}{2}b (\alpha\text{-form}), \quad b (\beta\text{-form}) \cong 2c (\alpha\text{-form}), \\ c (\beta\text{-form}) \cong a (\alpha\text{-form}).$$

Cu  $K\alpha$  radiation was used throughout the investigation, and intensity data for  $0kl$ ,  $h0l$  and  $hk0$  reflexions, which were recorded on zero-level Weissenberg and oscillation photographs about the three principal axes, were estimated visually. Correction for absorption was neglected because crystals were cut and ground carefully into rods of cross-sections less than 0.2 mm. After being corrected for Lorentz and polarization factors the intensities were roughly converted to an absolute scale by comparing the calculated average values with those observed (Wilson, 1942).

### Determination of the structure

The Patterson projections along the three principal axes were computed from the  $0kl$ ,  $h0l$  and  $hk0$  intensity data. As we were not successful in deriving atomic coordinates from these projections, the minimum-function method (Buerger, 1951) was applied. The  $M_2$  and  $M_4$  maps showed up a number of possible atomic positions, from which several reasonable structures were derived. Inequality relations (Harker & Kasper, 1948; Okaya & Nitta, 1952) gave signs of 26  $F_{(0kl)}$ 's and 35  $F_{(hko)}$ 's, from which preliminary Fourier series were synthesized. Comparing  $M_2$  and  $M_4$  maps with these Fourier projections, an approximate disposition of the molecule was obtained. The locations of atoms were checked by the trial-and-error method on the assumption of a plausible molecular model for glutamic acid. The atomic coordinates were refined in the usual manner by successive two-dimensional Fourier