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Calculation of Geometrical Structure Factors for Space Groups of Low Symmetry. I

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This paper describes a simple calculator for the function cos $(hx+ky+lz)$. Values of this function can be read directly from tables of cos hx, provided that the origin of the latter can be shifted an amount $(ky+lz)$ at will. A simple mechanical device to do this is described.

Introduction

The geometrical structure factor for all space groups is

$$\sum_j \cos(hx_j+ky_j+lz_j)+i\sum_j \sin(hx_j+ky_j+lz_j),$$

where the summation is over symmetry-equivalent atoms. This sum is often rewritten as a product or sum of products of cosine or sine factors, each involving only one of the coordinates x, y, z, by making use of any symmetry present; but it can equally well be calculated in the above form if we have some device which assists in rapidly tabulating $\cos(hx_j+ky_j+lz_j)$ and $\sin(hx_j+ky_j+lz_j)$. The present device is designed for this purpose.

The principle* of the device is as follows. Suppose that $\cos(hx+ky+lz)$ is tabulated for one plane in reciprocal space at a time, working across the plane, row by row. That is, l is kept constant for a large number of (h, k); and k is kept constant for, say, h from -15 to $+15$. If we were reading values of $\cos(hx+ky+lz)$ from a cosine curve then we would move a distance l_1z from the origin along the abscissa for all (h, k, l_1), and a further distance k_1y for all (h, k, l_1). From this point (k_1y+l_1z) we move a distance hx, and read off the value of the cosine; this last step is repeated for successive h.

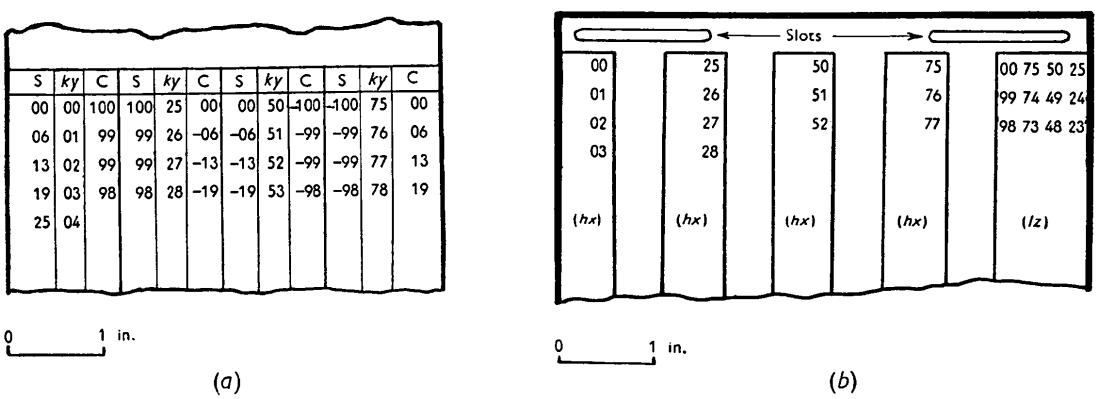
In actual use it would be faster to move the abscissa scale relative to the cosine curve so that the zero point on the *scale* is at the position corresponding to $\cos(k_1y+l_1z)$ on the *curve*. The point hx on the abscissa scale now corresponds to $\cos(hx+k_1y+l_1z)$ on the curve. If we replace the cosine curve by a table of values of cosines then it is a simple matter to move the abscissa column mechanically, relative to the cosine column, by any desired amount l_1z or (k_1y+l_1z). An immediate practical difficulty is that such a device would be too long, and therefore in any practicable design the tables must be broken up. The present device is described below.

* Bunn (1945) has described a slide-rule using the same basic principle, but with a different mechanical arrangement.

Description

Three kinds of tables are used: (1) tables of angular intervals, given as decimal fractions of a cycle, at intervals of 0·01 (i.e. 3·6°) from 0·00 to 0·99; (2) tables of sines of these angles; (3) tables of cosines of these angles.

The moving chart consists of a strip of tracing linen 4½ in. wide, and about 45 in. long. It carries tables of sines and cosines, and one table of angular intervals under the heading '*ky*' (see Fig. 1(*a*)). The tables are



(*a*) (*b*)

Fig. 1. (*a*) Section of movable chart, showing arrangement of sine (S), cosine (C), and *ky* tables. Values of *ky* given in decima fractions of a cycle; sines and cosines to two-figure accuracy, and at 3·6° intervals.
(*b*) Arrangement of *hx* and *lz* scales on perspex cover.

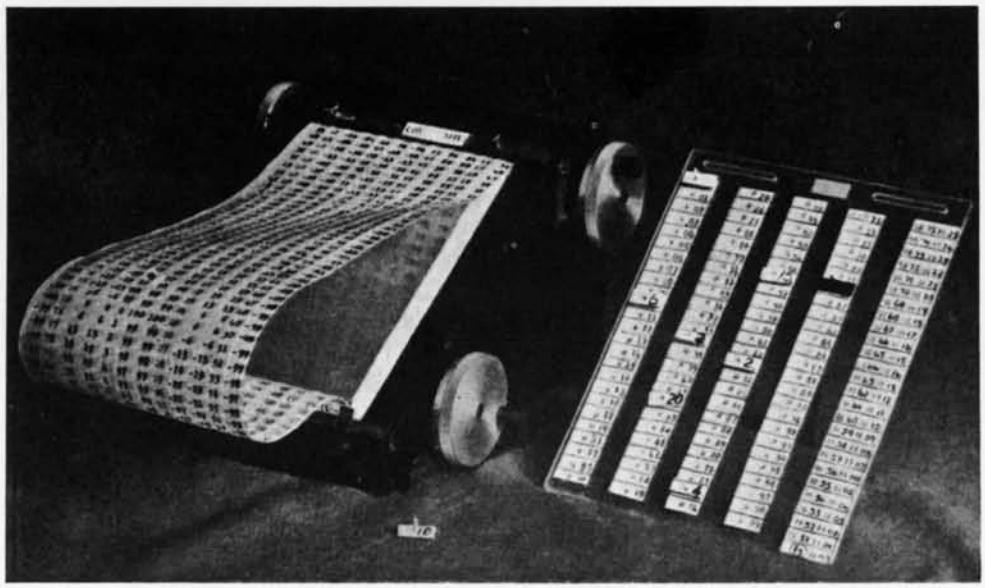


Fig. 2. Photograph of the device. The perspex cover is removed and placed (with one of the marking pins) alongside the box.

arranged vertically, the spacing between the rows being $\frac{1}{4}$ in., a spacing which can be conveniently set on a typewriter. The spacing of the columns is given in Fig. 1(*a*).

The three tables on the chart are in four blocks. In the left-hand block the *ky* table with its corresponding sine and cosine tables runs from $\theta = 0$ to $\theta/2\pi = 1{\cdot}25$; the other three blocks begin at $\theta/2\pi =$ 0·25, 0·50, 0·75, respectively, and each runs through $1\frac{1}{4}$ cycles.

The chart is mounted in a suitable box with a sloping front panel and two winding drums (Fig. 2). The drums move independently, one being used for forward and one for backward winding. Small fibre washers prevent them running too freely. A flat metal plate, curved at the ends, supports the chart close to a perspex cover, and leads it on to the drums. The box is designed so that a quarter of a cycle in each column can be seen, i.e. an area of $4\frac{1}{2}$ in. by 7 in., which is a convenient size. (In fact the sole reason for having more than one block of tables is to reduce the device to these dimensions.) Thus a full table of values of cosines (or sines, or *ky*) always appears on the visible area of the chart.

The perspex cover carries fixed scales of angular intervals, labelled '*hx*' and '*lz*' respectively, on paper glued to its lower surface (Fig. 1(*b*)). The *hx* scale is typed on four strips equally spaced ($\frac{1}{2}$ in. apart, and $\frac{5}{8}$ in. wide). The numbers on these run from top to bottom, and the strips from left to right. The *lz* scale (on the single wider strip on the right) is similar, but the numbers run from bottom to top, and from right to left. Faint horizontal lines have been ruled on the perspex to guide the eye.

The cover is loosely held by thumbscrews through horizontal slots in its upper edge, to allow sideways movement of a little more than 1 in. The clear sections of the cover, between the *hx* scales, allow the tables on the chart to be seen; and the dimensions have been chosen so that only one set of figures on the chart (i.e. *either* the cosine, *or* the *ky*, *or* the sine table) can be seen at once, depending on the position of the cover.

Small holes are drilled in the perspex at the position of each value of '*hx*', into which can be inserted flat markers mounted on a short pin. The markers are numbered 1, 2, 3, ..., corresponding to values of h, and there are two sets, with black and red figures on a white background, for h and $\bar{h}$. A similar marker painted red is used to indicate the origin. These markers are not essential, but are an aid to quick reading.

The device is used as follows. Coordinates (x, y, z) known to any desired accuracy can be used as starting-point, and the integral multiples hx, ky, lz, are formed to the same accuracy. These quantities are *then* rounded off to the nearest 0·01. The red (origin) marker is now placed in the appropriate hole on the cover, using the '*lz*' table on the right. Thus if l_1z is in the first column on the *lz* table then the origin marker is in the first column of holes (counting from the *right*), and in the same horizontal row as l_1z on the *lz* scale. Next the '*h*' markers are placed at the tabulated values of *hx*; and it will be noted that these '*h*' pins are not moved as long as this atom is being considered. The cover is now moved to expose the *ky* scales, and the chart is wound on until k_1y is at the origin marker (reading k_1y on the table to the right of the marker). Then the cover is shifted to expose the cosine table; the values of the cosines opposite the '*h*'

markers are values of $\cos(hx+k_1y+l_1z)$ for $h = 1, 2, 3, \ldots$. (Likewise the cover can be shifted, if necessary, to expose the corresponding values of $\sin(hx+k_1y+l_1z)$.) Once all the values of $\cos(hx+k_1y+l_1z)$ have been written down, the chart is moved to bring k_2y to the origin marker, then k_3y, etc. Finally the whole process is repeated, by shifting the origin marker, to deal with l_2z, then l_3z, etc.

Discussion

A device of this kind must be judged by considering (1) simplicity and cheapness of construction, (2) simplicity and directness in use, (3) speed in calculation, (4) universality, i.e. usefulness for many different calculations, (5) accuracy.

The present device is simple and cheap to make. It is also simple and direct to use, for two reasons. First, the structure-factor formula is evaluated in its most general, and at the same time most straightforward, form; the device simply carries out the calculations in the way represented in the formula, without prior re-arrangement in some 'sum-of-products' form. Secondly, the only accessory table needed for each calculation is a table of hx, ky and lz; and the device uses these quantities in a very simple way. (It can be used by unskilled computers as readily as a table of cosines.)

Any simple device dealing with one atom at a time must be slower than more elaborate machines which deal with atoms in groups. A test of this little box, however, showed it to be surprisingly speedy to use. An atom with coordinates $x = 0{\cdot}2777$, $y = 0{\cdot}1639$ and $z = 0{\cdot}5500$ was chosen, and $\cos(hx+ky+lz)$ was tabulated for $l = 3$, $k = 0, 1, \ldots, 19$, and $h = 0, 2, 4, 6, \ldots, 20$, or $h = 1, 3, 5, 7, \ldots, 19$. The time for tabulating hx, ky and lz, and for setting the markers, was 6 min.; but this is, of course, done only once for each atom. The time for writing down $\cos(hx+ky+lz)$ for the 220 values of (h, k, l) mentioned above was 16 min.; and this speed could be maintained for a long period. It seems unlikely that $\cos(hx+ky+lz)$ can be calculated by hand faster than this. (It should be mentioned, however, that a larger device using the same basic principle is now being constructed which directly assists the hand computation of

$$\sum_{j=1}^{N} \cos(hx_j+ky_j+lz_j)$$

rather than $\cos(hx+ky+lz)$; it will be described in Part II of this paper.)

The question of speed cannot be discussed without reference to the form in which the geometrical structure factor is expressed. As mentioned earlier, this direct form is often rewritten, where possible, as a single product term for purposes of evaluation. This is convenient for two reasons: (*a*) it means that one term only need be evaluated for the whole set of symmetry-equivalent atoms, (*b*) many desk machines and mathematical tables can more easily be used to evaluate a product of cosines than the cosine of a sum. If, however, the geometrical structure factor can be expressed only as the sum of two or more product terms, and the number of symmetry-equivalent atoms is low, the first advantage is reduced or disappears. This is notably the case in the triclinic system, where the sum of four product terms is needed. In this case, direct evaluation is obviously preferable. In the monoclinic system, for a general hkl structure factor, the sum of two product terms is needed, but each includes the contribution of two atoms; hence the total number of terms to be evaluated by either method is the same. In the orthorhombic and higher systems the direct evaluation of one term for each atom becomes increasingly inefficient.

It is worth specifically pointing out the universality of this device, since this is one of the advantages it has over most strip methods. The box is complete in itself, and is used *as it stands*. The use of high indices in a calculation involves no more preparation than the tabulation of hx; ky and lz—a few minutes' work. Thus the labour of any calculation is simply proportional to the number of reflexions considered, no matter how large the indices along any axes. Likewise the extra labour in changing from three-figure to four-figure accuracy in (x, y, z) lies only in the tabulation of hx, ky and lz, and is trivial.

Inaccuracies in calculations on devices of this kind arise from three causes: (1) physical inaccuracies in construction of the device, (2) inaccuracies due to 'rounding-off' hx, ky and lz, (3) inaccuracies due to finite interval-size in cosine table.

Since the box is not an analogue device no inaccuracies arise from its construction, in which, therefore, there is no necessity for fine tolerances. The other two sources of error are interdependent. It should first be noted that the maximum error introduced by the use of this device into hx, ky and lz will be no more than 0·005, whatever the value of h, k and l. In the Appendix to this paper a short account of the standard-deviations of 'rounding-off' errors has been given. This shows that the process of rounding-off hx, ky and lz separately before adding (as is done here) gives about twice the standard error when compared with rounding off the sum, $(hx+ky+lz)$; but that *both* methods are in general more accurate than using the product form.

It would be quite practicable to halve the error by constructing a slightly larger box in which the interval of the tables was 0·005 cycles, rather than 0·01 cycles, since the figures on the present tables are quite reasonably spaced out. Indeed, a box with tables at 0·002 cycles, and with sines and cosines to three figures, need not be inconveniently large; but problems requiring subdivision at smaller intervals than 0·005 probably warrant other and more powerful methods of calculation.

It is believed that this calculating device may be of

service in laboratories where larger machines are not readily available; even where they are available it is proving useful for those exploratory 'trial-and-error' calculations which arise at some point or another in most structure determinations.*

This work has been done during the tenure of a C.S.I.R.O. Overseas Studentship. The writer has pleasure in acknowledging helpful discussions with Dr Helen D. Megaw.

APPENDIX

By Helen D. Megaw

Rounding-off errors

It is assumed that angles, expressed in cycles, are rounded off to two decimal places; where the third digit is 5, it is rounded off to make the second digit even. Values of $\cos\theta$ or $\sin\theta$ are rounded off to two decimal places. We require to know the standard deviation of the geometrical structure factor. Suppose there are $2p$ symmetry-related atoms in general positions in a centrosymmetric structure.

(i) If the geometrical structure factor is evaluated by summing hx, ky, lz, rounding off the sum, and evaluating the cosine for each of the p atoms separately, the s.d. of θ for a single atom is $0{\cdot}01\times 1/\sqrt{12}$ cycles. The s.d. of $\cos\theta$ due to this is $1/\sqrt{2}\times 2\pi\times 0{\cdot}01/\sqrt{12} = 0{\cdot}013$; the effect of rounding-off errors in $\cos\theta$ itself is negligible. For $2p$ atoms, the s.d. of their sum of cosines is $2\sqrt{p}\times 0{\cdot}013$.

(ii) If the terms hx, ky, lz are rounded off before adding, then for $\cos(hx+ky)$ the s.d. is 0·019, for $\cos(hx+ky+lz)$ it is 0·022; as before, the s.d. for $2p$ atoms is proportional to $2\sqrt{p}$.

(iii) If the geometrical structure factor can be expressed in the form

$$2p\begin{Bmatrix}\cos\\ \sin\end{Bmatrix}hx.\begin{Bmatrix}\cos\\ \sin\end{Bmatrix}ky \quad \text{(one index zero)}$$

or

$$2p\begin{Bmatrix}\cos\\ \sin\end{Bmatrix}hx.\begin{Bmatrix}\cos\\ \sin\end{Bmatrix}ky.\begin{Bmatrix}\cos\\ \sin\end{Bmatrix}lz \quad \text{(no index zero)},$$

its s.d. is $2p\times 0{\cdot}013$ or $2p\sqrt{(3/2)}\times 0{\cdot}013$ respectively. If it can be expressed only as the sum of n such terms, its s.d. is $2p\sqrt{n}\times 0{\cdot}013$ or $2p\sqrt{n}\sqrt{(3/2)}=0{\cdot}013$ respectively.

The ratio of the s.d.'s resulting from methods (ii) and (iii) is thus

$$\frac{1}{\sqrt{(pn)}}\times\frac{0{\cdot}19}{0{\cdot}13} \quad \text{(one index zero)}$$

or

$$\sqrt{\left(\frac{2}{3pn}\right)}\times\frac{0{\cdot}22}{0{\cdot}13} \quad \text{(no index zero)}.$$

Where no index is zero, pn is never less than 4, and method (iii) is therefore less accurate than method (ii). The same holds good where one index is zero, except for triclinic crystals and for monoclinic crystals in the zones $hk0$ and $0kl$; here pn is 2, and the methods are of equal accuracy. The case when two indices are zero can be treated similarly, but is not of as much importance in practice.

* *Note added in proof.*—The device is now manufactured by Crystal Structures Ltd, 339 Cherryhinton Road, Cambridge, England.

Reference

Bunn, C. W. (1945), *Chemical Crystallography*, p. 270. Oxford: Clarendon Press.