SOME TECHNIQUES FOR STRUCTURE FACTOR CALCULATIONS

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Abstract

Although the computations involved in crystal structure analysis by X-ray methods are very well known, certain procedural techniques in effecting the same have been found to economise both time and effort. In this paper, some of the techniques for calculating two and three dimensional structure factors are described.

Introduction

The computational work involved in crystal structure analysis by X-ray methods consists in the main two types of calculations. Given a set of Fourier co-efficients, called the structure factors, the electron density $\rho\,(x, y, z)$ in the unit cell is obtained by the sum:

$$\rho_{(xyz)} = \frac{1}{V} \int_{h} \int_{k} \int_{l}{}_{-\infty}^{\infty} F_{hkl} \cos \{2\pi (hx + ky + lz) + a_{hkl}\} \tag{1}$$

Without any loss of generality, we confine ourselves to centrosymmetric structures only. The phase $\pm$ of the Fourier coefficients is then implied in the definition of structure factor.

The other type of calculation involved is as follows: Given the fractional co-ordinates (x_i, y_i, z_i) of the various atoms in the unit cell, the structure factor F_{hkl} for the reflection from the plane (hkl) is computed from the formula

$$F_{hkl} = \sum_{i} f_i \cos 2\pi (hx_i + ky_i + lz_i) \tag{2}$$

where i runs over all the atoms in the unit cell and the atom is situated at (x_i, y_i, z_i). While Equation (2) is the most general form for a centrosymmetric structure, it often reduces to one or other of the following forms (or forms similar to these):—

$$F_{hkl} = \sum_{i} f_i \, {}^{\cos}_{\sin}\, 2\pi (hx_i + ky_i) \, {}^{\cos}_{\sin}\, 2\pi \, lz_i \tag{2 a}$$

$$F_{hkl} = \sum_{i} f_i \, {}^{\cos}_{\sin}\, 2\pi hx_i \, {}^{\cos}_{\sin}\, 2\pi ky_i \, {}^{\cos}_{\sin}\, 2\pi lz_i \tag{2 b}$$

Since most of the work is done using two dimensional projections the more important forms of (2) are:—

$$F_{hk0} = \sum_i f_i \begin{smallmatrix}\cos\\ \sin\end{smallmatrix}\, 2\pi\,(hx_i + ky_i) \tag{2 c}$$

$$F_{hk0} = \sum_i f_i \begin{smallmatrix}\cos\\ \sin\end{smallmatrix}\, 2\pi hx_i \begin{smallmatrix}\cos\\ \sin\end{smallmatrix}\, 2\pi ky_i \tag{2 d}$$

The magnitude of the work is often considerable, depending on the number of atoms in the unit cell and the number of reflections observed. To calculate the trigonometric factors in the above formulæ various machines are in use such as the I.B.M. and the Hollerith machines of the digital variety and the S-FAC[1] of the analogue type, existing in Professor Pepinsky's laboratory. Many other mechanical devices of a more modest type have also been designed by various workers to do the same. Numerical tables listing the values of cosine or sine for values of x from 0 to 1·00 divided into suitable equal parts and h running from 0 to about 30 have been published by Buerger[2] and others. Pepinsky and his co-workers devised an elegant table[3] for calculating the trigonometric factors of the type

$$\pm \begin{smallmatrix}\cos\\ \sin\end{smallmatrix}\, 2\pi hx_i \begin{smallmatrix}\cos\\ \sin\end{smallmatrix}\, 2\pi ky_i \tag{2 e}$$

$$\pm \begin{smallmatrix}\cos\\ \sin\end{smallmatrix}\, 2\pi hx_i \begin{smallmatrix}\sin\\ \cos\end{smallmatrix}\, 2\pi ky_i \tag{2 f}$$

During the course of our work, it was found that this table can be extended in its use, by adopting certain procedural techniques to economise the labour involved. These methods are described below.

Computational Methods

Before proceeding further, it is necessary to explain how the table, reproduced below (Table I), is constructed. Putting $\cos 2\pi hx = \cos 2\pi\theta$, the interval of $(0-1)$ for θ completes one full cycle for the argument of the cosine. This interval is divided into 100 equal parts and the cosine for each is tabulated in the first horizontal row (Row 1, Table I). Similarly taking $\cos 2\pi ky = \cos 2\pi\phi$ the value of $\cos 2\pi\phi$ for values of ϕ at intervals of $1/100$ is tabulated in the first vertical column (Column 1, Table I). The product $\cos 2\pi hx \cdot \cos 2\pi ky$ for any $hx = \theta$ and $ky = \phi$ is then evaluated and written at the intersection of the respective values of θ and ϕ in the Table. Remembering that

$$\cos 2\pi\theta = -\cos 2\pi\,(\theta + \tfrac{1}{2}) = +\cos 2\pi\,(\theta + 1)$$

we can easily see that if θ lies between ·25 and ·75 the value of the cosine is negative and at all other places it is positive. A simple colour code is adopted in the table to indicate this. The argument hx in intervals of ·01 is typed in four rows (Table I C) with the first and the fourth rows in black type and the second and the third rows in red. (Here the second and the third rows are printed in bold face.) If θ is in red, the value of the cosine is negative and if in black, it is positive. In evaluating $\cos 2\pi\, hx \cdot \cos 2\pi\, ky$ therefore, if both the arguments agree in colour, the product is positive and if they disagree, the product is negative. Remembering this colour code, one can therefore find out all such products from Table I. In practice, the argument ϕ is typed in four vertical columns, the middle columns

TABLE I

Number Field for Structure Factor Calculations

cos $2\pi hx$

(C)	100	99	98	97	96	95	94	93	92	91	90	89	88	87	86	85	84	83	82	81	80	79	78	77	76	75
	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
	50	49	48	47	46	45	44	43	42	41	40	39	38	37	36	35	34	33	32	31	30	29	28	27	26	25
	00	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
	100	100	99	98	97	95	93	90	88	84	81	77	73	68	64	59	54	48	43	37	31	25	19	13	06	00
	100	100	99	98	97	95	93	90	88	84	81	77	73	68	64	59	54	48	43	37	31	25	19	13	06	00
	99	99	98	97	96	94	92	90	87	84	80	76	72	68	63	58	53	48	42	36	31	25	19	12	06	00
	98	98	97	96	95	93	91	89	86	83	79	76	72	67	62	58	53	47	42	36	30	24	18	12	06	00
	97	97	96	95	94	92	90	88	85	82	78	75	71	66	62	57	52	47	41	36	30	24	18	12	06	00
	95	95	94	93	92	90	88	86	83	80	77	73	69	65	60	56	51	46	41	35	29	24	18	12	06	00
	93	93	92	91	90	88	86	84	81	78	75	72	68	64	59	55	50	45	40	34	29	23	17	12	06	00
	90	90	90	89	88	86	84	82	79	76	73	70	66	62	58	53	48	44	39	33	28	23	17	11	06	00
	88	88	87	86	85	83	81	79	77	74	71	67	64	60	56	52	47	42	37	32	27	22	16	11	06	00
	84	84	84	83	82	80	78	76	74	71	68	65	61	58	54	50	45	41	36	31	26	21	16	11	05	00
	81	81	80	79	78	77	75	73	71	68	65	62	59	55	52	48	43	39	34	30	25	20	15	10	05	00
	77	77	76	76	75	73	72	70	67	65	62	59	56	53	49	45	41	37	33	28	24	19	14	10	05	00
	73	73	72	72	71	69	68	66	64	61	59	56	53	50	46	43	39	35	31	27	23	18	14	09	05	00
	68	68	68	67	66	65	64	62	60	58	55	53	50	47	44	40	37	33	29	25	21	17	13	09	04	00
	64	64	63	62	62	60	59	58	56	54	52	49	46	44	40	37	34	31	27	23	20	16	12	08	04	00
	59	59	58	58	57	56	55	53	52	50	48	45	43	40	37	35	32	28	25	22	18	15	11	07	04	00
	54	54	53	53	52	51	50	48	47	45	43	41	39	37	34	32	29	26	23	20	17	13	10	07	03	00
	48	48	48	47	47	46	45	44	42	41	39	37	35	33	31	28	26	23	21	18	15	12	09	05	03	00
	43	43	42	42	41	41	40	39	37	36	34	33	31	29	27	25	23	21	18	16	13	11	08	05	03	00
	37	37	36	36	36	35	34	33	32	31	30	28	27	25	23	22	20	18	16	14	11	09	07	05	02	00
	31	31	31	30	30	29	29	28	27	26	25	24	23	21	20	18	17	15	13	11	10	08	06	04	02	00
	25	25	25	24	24	24	23	23	22	21	20	19	18	17	16	15	13	12	11	09	08	06	05	03	02	00
	19	19	19	18	18	18	17	17	16	16	15	14	14	13	12	11	10	09	08	07	06	05	04	02	01	00
	13	13	12	12	12	12	12	11	11	11	10	10	09	09	08	07	07	05	05	05	04	03	02	02	01	00
	06	06	06	06	06	06	06	06	06	05	05	05	05	04	04	04	03	03	03	02	02	02	01	01	00	00
	00	00	00	00	00	00	00	00	00	00	00	00	00	00	00	00	00	00	00	0·	00	00	00	00	00	00
(S)	25	24	23	22	21	20	19	18	17	16	15	14	13	12	11	10	09	08	07	06	05	04	03	02	01	00
	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	49	48	50
	75	74	73	72	71	70	69	68	67	66	65	64	63	62	61	60	59	58	57	56	55	54	53	52	51	50
	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100

sin $2\pi hx$

[printed in bold face in Table II (a)] being actually typed in red, on a small strip of the same size as shown in Table II (a) and II (b). If it is desired to calcualte $-\cos 2\pi\, hx \cos 2\pi ky$, the colours in the above strip, Table II, are interchanged. Actually a single strip with the four columns typed on both sides, one side having the outer columns in black and the other side having the outer columns in red serve to represent $ky = \phi$ for $+\cos 2\pi ky$ and $-\cos 2\pi ky$ respectively. Likewise to evaluate $\pm \sin 2\pi\, \theta \sin 2\pi\, ky$ another strip with the columns as arranged in Table II (c) and II (d) is preprared with the bold face as indicated in the above tables. When evaluating $\sin 2\pi\theta \sin 2\pi\, \phi$ the horizontal rows marked (S) in Table I are used.

TABLE II

+cos (a)				+sin (b)				−cos (c)				−sin (d)			
100	**50**	**50**	00	**75**	**75**	25	25	**100**	50	50	**00**	75	75	**25**	**25**
99	**51**	**49**	01	**76**	**74**	26	24	**99**	51	49	**01**	76	74	**26**	**24**
98	**52**	**48**	02	**77**	**73**	27	23	**98**	52	48	**02**	77	73	**27**	**23**
97	**53**	**47**	03	**78**	**72**	28	22	**97**	53	47	**03**	78	72	**28**	**22**
96	**54**	**46**	04	**79**	**71**	29	21	**96**	54	46	**04**	79	71	**29**	**21**
95	**55**	**45**	05	**80**	**70**	30	20	**95**	55	45	**05**	80	70	**30**	**20**
94	**56**	**44**	06	**81**	**69**	31	19	**94**	56	44	**06**	81	69	**31**	**19**
93	**57**	**43**	07	**82**	**68**	32	18	**93**	57	43	**07**	82	68	**32**	**18**
92	**58**	**42**	08	**83**	**67**	33	17	**92**	58	42	**08**	83	67	**33**	**17**
91	**59**	**41**	09	**84**	**66**	34	16	**91**	59	41	**09**	84	66	**34**	**16**
90	**60**	**40**	10	**85**	**65**	35	15	**90**	60	40	**10**	85	65	**35**	**15**
89	**61**	**39**	11	**86**	**64**	36	14	**89**	61	39	**11**	86	64	**36**	**14**
88	**62**	**38**	12	**87**	**23**	37	13	**88**	62	38	**12**	87	63	**37**	**13**
87	**63**	**37**	13	**88**	**62**	38	12	**87**	63	37	**13**	88	62	**38**	**12**
86	**64**	**36**	14	**89**	**61**	39	11	**86**	64	36	**14**	89	61	**39**	**11**
85	**65**	**35**	15	**90**	**60**	40	10	**85**	65	35	**15**	90	60	**40**	**10**
84	**66**	**34**	16	**91**	**59**	41	09	**84**	66	34	**16**	91	59	**41**	**09**
83	**67**	**33**	17	**92**	**58**	42	08	**83**	67	33	**17**	92	58	**42**	**08**
82	**68**	**32**	18	**93**	**57**	43	07	**82**	68	32	**18**	93	57	**43**	**07**
81	**69**	**31**	19	**94**	**56**	44	06	**81**	69	31	**19**	94	56	**44**	**06**
80	**70**	**30**	20	**95**	**55**	45	05	**80**	70	30	**20**	95	55	**45**	**05**
79	**71**	**29**	21	**96**	**54**	46	04	**79**	71	29	**21**	96	54	**46**	**04**
78	**72**	**28**	22	**97**	**53**	47	03	**78**	72	28	**22**	97	53	**47**	**03**
77	**73**	**27**	23	**98**	**52**	48	02	**77**	73	27	**23**	98	52	**48**	**02**
76	**74**	**26**	24	**99**	**51**	49	01	**76**	74	26	**24**	99	51	**49**	**01**
75	**75**	**25**	25	**100**	**50**	50	00	**75**	75	25	**25**	100	50	**50**	**00**

The mode of evaluating any product is thus obvious. To illustrate the method the following example is given. For the sake of simplicity, two dimensional data are taken up and we shall assume that it is desired to evaluate the structure factors of the type $hk0$, for a fixed h, ($h = 3$ say) and a running k. Let us suppose that h and k run from 0 to 10 and the trigonometric factor in F_{hkl} is of the type $\cos 2\pi hx_i \cos 2\pi ky_i$. Let $x = \cdot 12$ and $y = \cdot 15$. The following Table III is prepared. In evaluating hx it is obvious that only the non-integral portion of hx or ky need be taken. Thus hx for $h = 9$ and $x = \cdot 12$ is actually $-1 \cdot 08$. But $\cos 2\pi = (1 \cdot 08)$ $\cos 2\pi\,(\cdot 08)$.

TABLE III

h or k	$x = \cdot 12$ hx	$y = \cdot 15$ ky
0	0	0
1	12	15
2	24	30
3	36	45
4	48	60
5	60	75
6	72	90
7	84	05
8	96	20
9	08	35
10	20	50

The strip [Table II (*a*)] is placed at $\cdot 36$ in the horizontal row and values of $\cos 2\pi (3x) \cos 2\pi ky$ are read off by noting the value against 0, $\cdot 15$, $\cdot 30$, etc., on the vertical strip. The proper sign is to be attached by following the colour code: thus $\cos 2\pi (\cdot 36) \cos 2\pi (\cdot 15)$ is negative, equal to $- \cdot 37$ while $\cos 2\pi (\cdot 36) \cos 2\pi (\cdot 60)$ is positive equal to $\cdot 52$ because $\cdot 36$ is in red, $\cdot 15$ is in black and $\cdot 60$ is in red. It is found that preparing an initial table for every atom with co-ordinates (x_i, y_i, z_i) of the values of hx_i and ky_i as in Table III is quite expeditious in later work. Often one has to separate, say, the even and odd h's and k's. The odd ones may be marked off in the coloured pencil so that one can readily identify the required type of h or k.

This table is devised for the evaluation of products. It is often customary to evaluate $\cos 2\pi (hx_i + ky_i)$ by using a different machine or by expanding the expression and writing it down as the sum of the products of cosines and sines. The purpose of this paper is to show that Table I can be used for calculating any type of structure factor for two or three dimensional work. In fact, with the procedure outlined in what follows, this table is found to be much more expedient for the evaluation of the factors of the type $\cos 2\pi (hx_i + ky_i + lz_i)$. The procedure given below is with the aid of the Marchant calculating machine; but it can be adopted for any other standard calculating machine.

(1) *Calculation of the Type* $\cos 2\pi (hx_i + ky_i)$: For the sake of simplicity, two dimensional data is taken up first. We shall assume that h is constant and k is the running index. The machine is operated in the "stop" position so that the carriage does not move. First, the non-integral portion of hx_i is punched into the machine. Then the value of y_i is locked in the panel of the machine. Then by repeated punching on the addition (+) key, one gets the value of $(hx_i + y_i)$, $(hx_i + 2y_i)$, etc. Taking the non-integral portion of the same, one can directly read off the value of the cosine from the very first row of Table I. After a little practice, one usually remembers the first row, so that with each punching of the ky_i value one can write down the value of the cosine itself, even without referring to the table. After exhausting all ky_i, the machine is cleared, the next value of hx, *i.e.*, $(h + 1)\,x$ is put in and the process repeated, till all the h's are completed. The same procedure is adopted for all the atoms in the unit cell, or as done in practice, for the asymmetric unit.

(2) *Type* $\cos 2\pi (hx_i + ky_i + lz_i)$: It is easy to see that the above process can be extended without difficulty to the three dimensional structure factors. All that is necessary is to keep two of the indices constant and use the third as the running index, a procedure which should be adopted in any computation. Hence taking the l index as the running index, the value of $(hx_i + ky_i)$ is punched into the machine and then for getting $(hx_i + ky_i + lz_i)$ assuming O to L the maximum value l, the procedure is the same as in case (1).

If it is desired to calculate $\sin 2\pi (hx_i + ky_i + lz_i)$ the procedure is similar using of course the horizontal rows (S).

(3) *Type* $\begin{smallmatrix}\cos\\ \sin\end{smallmatrix} 2\pi hx_i \begin{smallmatrix}\cos\\ \sin\end{smallmatrix} 2\pi ky_i \begin{smallmatrix}\cos\\ \sin\end{smallmatrix} 2\pi lz_i$: A trigonometric product of this type can be calculated in many ways. But in practice we found the following as ultimately less time-consuming. Every product of the above type can be written as the sum of four cosines or sines. Thus for example

$$\begin{aligned}&\cos A \cos B \cos C\\ &\quad = \tfrac{1}{4}\,[\cos (A + B + C) + \cos (A + B - C)\\ &\qquad + \cos (A - B + C) + \cos (A - B - C)]\end{aligned}$$

Hence the procedure is only a slight variation of the one in case (2). This leaves us with only four additions ultimately which is far simpler in operation than multiplications every time.

A variation for this case, which may sometimes be found easier, is to list the values of $\cos 2\pi hx_i$, $\cos 2\pi ky_i$, $\cos 2\pi lz_i$ for all the values of h, k and l separately from the first row of Table I and then effect the multiplication.

REFERENCES

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