so as to cause the water–water separation across the twofold axis to be only 2·63 Å in calcium phosphate, whilst it is 3·2 Å in gypsum. The latter change lends support to the idea that the hydrogen is between the water molecules in the dihydrogen phosphate and that the resulting bond contraction is responsible for the slight general rearrangement.

As has been previously reported (MacLennan & Beevers, 1956), the structure of monocalcium phosphate monohydrate shows the same corrugated sheets of $CaPO_4$ as in the structure now being described. It therefore seems possible that these sheets are a common feature of calcium phosphate structures. They may occur, for example, in $Ca_3(PO_4)_2$ (Mackay, 1953), a structure which shows vectors of 3·8 Å, which is approximately equal to the shortest Ca–Ca distance in the corrugated sheets. However, the sheets do not seem to be present in the structure of $Sr_3(PO_4)_2$ (Zachariasen, 1948).

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An Equation between Structure Factors for Structures Containing Unequal or Overlapped Atoms. I. The Equation and its Properties

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An equation between structure factors has been developed which holds precisely for centrosymmetric resolved structures containing not more than two types of atom. The form of the equation is

$$F_{\mathbf{h}} = A_{\mathbf{s}} \cdot \frac{1}{V} \sum_{\mathbf{h}'} F_{\mathbf{h}'} F_{\mathbf{h}+\mathbf{h}'} + B_s \cdot \frac{1}{V^2} \sum_{\mathbf{h}'} \sum_{\mathbf{h}''} F_{\mathbf{h}'} F_{\mathbf{h}''} F_{\mathbf{h}+\mathbf{h}'+\mathbf{h}''} ,$$

where $A_{\mathbf{s}}$ and $B_{\mathbf{s}}$ are functions of $\mathbf{s}$, the position vector of $\mathbf{h}$ in reciprocal space, and V is the volume of the unit cell. The equation may also be applied to resolved projections if V is replaced by A, the area, or l, the length, of the projection.

It is shown that the same equation will approximately hold in some cases of projections containing partially or completely overlapped equal atoms and also for resolved structures containing more than two types of atom.

The theory of the equation is fully developed and its applicability to various types of structure is illustrated by numerical examples.

1. Introduction

Sayre (1952) was the first to show that, for a structure containing equal resolved atoms, the structure factors are quantitatively related to each other. This relationship is in the form of the equation

$$F_{\mathbf{h}} = A_{\mathbf{s}} \frac{1}{V} \sum_{\mathbf{h}'} F_{\mathbf{h}'} F_{\mathbf{h}+\mathbf{h}'} , \tag{1}$$

the $\mathbf{h}'$ under the summation sign indicating that the summation is taken over all values of $\mathbf{h}'$. The equation may also be applied to two-dimensional or one-dimensional data if V, the volume of the unit cell, is replaced by either A, the area, or l, the length of the projection.

The equation was derived by Sayre in the following way. For a structure containing equal resolved atoms the operation of squaring the electron density, $\varrho_{\mathbf{r}}$, retains the condition of equal resolved atoms but changes the shape of each atom. It may be shown in the case of a centrosymmetrical structure that

$$\frac{1}{V} \sum_{\mathbf{h}'} F_{\mathbf{h}'} F_{\mathbf{h}+\mathbf{h}'}$$

equals the hth Fourier coefficient of $\varrho_{\mathbf{r}}^2$. The factor $A_{\mathbf{s}}$, a function of the distance $\mathbf{s}$ of the point $\mathbf{h}$ from the origin of reciprocal space, corrects for the difference of shape of the atoms with electron distribution $\varrho_{\mathbf{r}}$ and $\varrho_{\mathbf{r}}^2$, so that

$$A_{\mathbf{s}}\cdot\frac{1}{V}\sum_{\mathbf{h}'}F_{\mathbf{h}'}F_{\mathbf{h}+\mathbf{h}'}\,,$$

is made equal in value to $F_{\mathbf{h}}$.

Sayre's equation was the inspirational source of sign relationships (Cochran, 1952; Zachariasen, 1952) but the equation itself has been of much less practical value than its progeny. Direct methods of structure determination are most frequently applied to projections of structures where the condition of equal resolved atoms is the exception rather than the rule.

In Part I of this paper is developed an equation between structure factors, which is often valid for structures containing unequal or overlapped atoms. The properties and limitations of the equation will be demonstrated both theoretically and by means of numerical examples.

Part II will be devoted to the application of the equation as a fairly powerful tool for structure determination.

2. The equation

Let us consider a centrosymmetrical structure containing resolved isotropic atoms of two types, P and Q. The electron distribution for these two types of atom is such that at distance u from their centres the electron densities are $(\varrho_u)_P$ and $(\varrho_u)_Q$ respectively. Let the scattering factors of atoms P and Q be represented by the functions of $\mathbf{s}$, f_P and f_Q.

Now let us consider a point $\mathbf{s}$ in reciprocal space and form a function of the electron density, $\varrho'_{\mathbf{r},\,\mathbf{s}}$, given by

$$\varrho'_{\mathbf{r},\,\mathbf{s}} = A_{\mathbf{s}}\varrho_{\mathbf{r}}^2 + B_{\mathbf{s}}\varrho_{\mathbf{r}}^3\,, \tag{2}$$

where $A_{\mathbf{s}}$ and $B_{\mathbf{s}}$ are functions of $\mathbf{s}$.

The function $\varrho'_{\mathbf{r},\,\mathbf{s}}$ will represent atoms P and Q with the modified electron distribution

$$(\varrho'_u)_P = A_{\mathbf{s}}(\varrho_u)_P^2 + B_{\mathbf{s}}(\varrho_u)_P^3 \tag{3}$$

and

$$(\varrho'_u)_Q = A_{\mathbf{s}}(\varrho_u)_Q^2 + B_{\mathbf{s}}(\varrho_u)_Q^3\,. \tag{4}$$

The scattering factor for the transformed atom P will be

$$f'_P = A_{\mathbf{s}}(f^2)_P + B_{\mathbf{s}}(f^3)_P\,, \tag{5}$$

where $(f^2)_P$ and $(f^3)_P$ are the scattering factors corresponding to atoms with radial distributions $(\varrho_u)_P^2$ and $(\varrho_u)_P^3$. Similarly

$$f'_Q = A_{\mathbf{s}}(f^2)_Q + B_{\mathbf{s}}(f^3)_Q\,. \tag{6}$$

For any particular value of $\mathbf{s}$ it is always possible to find values of $A_{\mathbf{s}}$ and $B_{\mathbf{s}}$ such that $f'_P = f_P$ and $f'_Q = f_Q$. With these values of $A_{\mathbf{s}}$ and $B_{\mathbf{s}}$ it is evident that the structure factor of index $\mathbf{h}$, $F_{\mathbf{h}}$, equals the Fourier coefficient of index $\mathbf{h}$ of $\varrho'_{\mathbf{r},\,\mathbf{s}}$, where $\mathbf{s}$ is the position vector corresponding to $\mathbf{h}$ in reciprocal space. If the $\mathbf{h}$th Fourier coefficients of $\varrho_{\mathbf{r}}^2$ and $\varrho_{\mathbf{r}}^3$ are $G_{\mathbf{h}}$ and $H_{\mathbf{h}}$ respectively, then

$$F_{\mathbf{h}} = A_{\mathbf{s}}G_{\mathbf{h}} + B_{\mathbf{s}}H_{\mathbf{h}}\,. \tag{7}$$

We have already mentioned the result

$$G_{\mathbf{h}} = \frac{1}{V}\sum_{\mathbf{h}'}F_{\mathbf{h}'}F_{\mathbf{h}+\mathbf{h}'} \tag{8}$$

and it may similarly be shown that

$$H_{\mathbf{h}} = \frac{1}{V}\sum_{\mathbf{h}'}F_{\mathbf{h}'}G_{\mathbf{h}+\mathbf{h}'} = \frac{1}{V^2}\sum_{\mathbf{h}'}\sum_{\mathbf{h}''}F_{\mathbf{h}'}F_{\mathbf{h}''}F_{\mathbf{h}+\mathbf{h}'+\mathbf{h}''}\,. \tag{9}$$

There is then an equation between structure factors

$$F_{\mathbf{h}} = A_{\mathbf{s}}\cdot\frac{1}{V}\sum_{\mathbf{h}'}F_{\mathbf{h}'}F_{\mathbf{h}+\mathbf{h}'} + B_{\mathbf{s}}\cdot\frac{1}{V^2}\sum_{\mathbf{h}'}\sum_{\mathbf{h}''}F_{\mathbf{h}'}F_{\mathbf{h}''}F_{\mathbf{h}+\mathbf{h}'+\mathbf{h}''} \tag{10}$$

which may be applied to a structure consisting of isotropic resolved atoms of two types.

3. A test of the equation

In order to test equation (10) we shall, following Sayre's example, consider a one-dimensional model structure containing atoms with a Gaussian distribution of electron density. The centrosymmetrical structure taken as a model, for which the unit cell is of length 20 Å, contains eight atoms of electron distribution

$$(\varrho_u)_P = 6\sqrt{2}\,.\exp\,[-2\pi u^2]$$

with coordinates ±0·0625, ±0·1428, ±0·2500 and ±0·4500, and two atoms of electron distribution

$$(\varrho_u)_Q = 12\sqrt{2}\,.\exp\,[-2\pi u^2]$$

with coordinates ±0·3333.

For the atoms of type P the scattering factor, f_P, which is the Fourier transform of $(\varrho_u)_P$, is given by

$$f_P = \int_{-\infty}^{\infty}(\varrho_u)_P\cos 2\pi us\,.du = 6\exp\,[-\tfrac{1}{2}\pi s^2]\,, \tag{11}$$

and similarly

$$f_Q = 12\exp\,[-\tfrac{1}{2}\pi s^2]\,. \tag{12}$$

Values of ϱ_u^2, ϱ_u^3, (f^2) and (f^3) for P and Q are given in Table 1.

Table 1

Function	Atom P	Atom Q
ϱ_u^2	$72\exp\,[-4\pi u^2]$	$288\exp\,[-4\pi u^2]$
ϱ_u^3	$432\sqrt{2}\,.\exp\,[-6\pi u^2]$	$3456\sqrt{2}\,.\exp\,[-6\pi u^2]$
(f^2)	$36\exp\,[-\tfrac{1}{4}\pi s^2]$	$144\exp\,[-\tfrac{1}{4}\pi s^2]$
(f^3)	$144\sqrt{3}\,.\exp\,[-\tfrac{1}{6}\pi s^2]$	$1152\sqrt{3}\,.\exp[-\tfrac{1}{6}\pi s^2]$

Table 2

h	s	A_s	$-B_s$	G_h	H_h	$A_sG_h+B_sH_h$	F_h	A'_sG_h
0	0·00	0·250	0·0120	567·9	5779	72·5	72·0	55·0
1	0·05	0·250	0·0120	−99·1	−1591	−5·6	−4·9	−9·6
2	0·10	0·248	0·0119	−119·4	−1768	−8·6	−8·2	−11·5
3	0·15	0·245	0·0118	201·6	3272	10·8	10·3	19·1
4	0·20	0·242	0·0116	−108·1	−1671	−6·8	−6·7	−10·2
5	0·25	0·238	0·0113	−176·5	−2152	−17·7	−17·4	−16·3
6	0·30	0·233	0·0110	171·4	3003	7·0	6·2	15·5
7	0·35	0·227	0·0107	−85·3	−1501	−3·3	−3·3	−7·5
8	0·40	0·220	0·0103	−136·6	−1845	−11·1	−11·0	−11·7
9	0·45	0·213	0·0098	227·5	3313	16·0	15·7	19·8
10	0·50	0·205	0·0093	−323·7	−3178	−36·8	−36·8	−25·7
11	0·55	0·197	0·0088	−131·2	−1809	−9·9	−9·8	−10·0
12	0·60	0·188	0·0082	207·7	3111	13·6	13·2	15·1
13	0·65	0·179	0·0077	−19·9	−893	−3·3	−3·6	−1·4
14	0·70	0·170	0·0071	−79·0	−1349	−3·8	−3·3	−5·2
15	0·75	0·161	0·0066	248·9	3365	17·9	17·4	15·5
16	0·80	0·151	0·0061	6·6	−591	4·5	4·8	0·3
17	0·85	0·142	0·0056	−97·2	−1437	−5·7	−6·0	−5·3
18	0·90	0·132	0·0051	130·4	2311	5·4	5·2	6·7
19	0·95	0·123	0·0046	−89·4	−1330	−4·9	−4·6	−4·3
20	1·00	0·114	0·0041	19·8	−383	3·8	4·0	0·9
21	1·05	0·105	0·0037	104·4	1993	3·6	3·5	4·3
22	1·10	0·097	0·0033	−56·9	−1007	−2·2	−2·3	−2·1
23	1·15	0·088	0·0030	−89·5	−1336	−3·9	−4·0	−3·1
24	1·20	0·081	0·0026	73·4	1582	1·8	1·7	2·3
25	1·25	0·074	0·0023	−75·0	−1163	−2·9	−2·8	−2·2
26	1·30	0·066	0·0020	−76·7	−1206	−2·7	−2·6	−2·0

Values of A_s and B_s such that $f'_P=f_P$ and $f'_Q=f_Q$ satisfy the equations

$$36 \exp[-\tfrac{1}{4}\pi s^2]A_s+144\sqrt{3}.\exp[-\tfrac{1}{6}\pi s^2]B_s = 6\exp[-\tfrac{1}{2}\pi s^2]$$

and

$$144 \exp[-\tfrac{1}{4}\pi s^2]A_s+1152\sqrt{3}.\exp[-\tfrac{1}{6}\pi s^2]B_s = 12\exp[-\tfrac{1}{2}\pi s^2]\,,$$

for which the solution is

$$A_s = \tfrac{1}{4}\exp[-\tfrac{1}{4}\pi s^2] \text{ and } B_s = -\frac{1}{48\sqrt{3}}\exp[-\tfrac{1}{3}\pi s^2]\,.$$

Structure factors, F_h, were calculated for the model structure with indices up to the limit permitted by Cu $K\alpha$ radiation. Values of G_h and H_h were then found by the application of equations (8) and (9). These are shown in Table 2, together with the values of $A_sG_h+B_sH_h$, which may be compared with the adjacent values of F_h. It will be seen that they compare remarkably well; the agreement expressed in terms of the normally defined reliability index is 2·9%. The small differences in the two sets of figures may be attributed to the slight overlap of Gaussian atoms, for which the electron density does not fall to zero at a finite distance from the centre, and also to the limitation of the maximum value of **h** imposed by the wavelength of Cu $K\alpha$ radiation.

It is interesting to see how well Sayre's equation can be made to apply to this example. It is, of course, impossible to find a factor A'_s such that $F_h = A'_sG_h$ since this would imply values of A'_s such that

$$f_P = A'_s(f^2)_P \tag{13}$$

and

$$f_Q = A'_s(f^2)_Q \tag{14}$$

simultaneously. To satisfy (13) and (14) we require $A'_s = \frac{1}{6}\exp[-\frac{1}{4}\pi s^2]$ and $A'_s = \frac{1}{12}\exp[-\frac{1}{4}\pi s^2]$ respectively. A factor $A'_s = K\exp[-\frac{1}{4}\pi s^2]$ is taken such that

$$\sum_h |F_h| = K\sum_h \exp[-\tfrac{1}{4}\pi s^2]|G_h|$$

and the values of A'_sG_h are given in the last column of Table 2. The agreement with the values of F_h expressed as a reliability index is 33%, which is, as would be expected, agreement of a much lower order than that obtained by the application of equation (10).

4. Overlapped atoms

For a structure considered in three dimensions there is only a slight overlap of the electron content of different atoms at relatively large distances from the atomic centres. However, for structures considered in projection, as they usually are, overlap of a much more severe character may occur. One type of projection frequently encountered is that of a structure containing approximately equal atoms (carbon, nitrogen and oxygen) projected down an axis of between 4·5 Å and 7·5 Å. In such projections atoms are observed in aspects varying from being completely isolated to being completely overlapped. At the latter extreme the pair of overlapped atoms would present the same appearance as an isolated atom of double weight. There are also intermediate situations where atoms may be partially overlapped in varying degrees.

We shall now investigate the possibility of applying

Table 3

	$r = 0{\cdot}0$ Å		$r = 0{\cdot}2$ Å		$r = 0{\cdot}4$ Å		$r = 0{\cdot}6$ Å		$r = 0{\cdot}8$ Å		$r = 1{\cdot}0$ Å	
s (Å^{-1})	$\varphi_{\mathbf{s}}$	$\varphi'_{\mathbf{s}}$	$\varphi_{\mathbf{s}}$	$\varphi'_{\mathbf{s}}$	$\varphi_{\mathbf{s}}$	$\varphi'_{\mathbf{s}}$	$\varphi_{\mathbf{s}}$	$\varphi'_{\mathbf{s}}$	$\varphi_{\mathbf{s}}$	$\varphi'_{\mathbf{s}}$	$\varphi_{\mathbf{s}}$	$\varphi'_{\mathbf{s}}$
0·0	12·00	12·00	12·00	12·92	12·00	13·61	12·00	13·70	12·00	13·15	12·00	12·51
0·2	11·32	11·32	10·98	11·43	10·57	12·60	9·83	11·40	8·70	9·66	7·43	7·81
0·4	9·37	9·37	8·73	9·35	7·14	8·67	5·01	6·08	2·82	3·32	0·89	1·02
0·6	6·80	6·80	5·38	6·59	3·65	4·44	1·36	1·81	0·03	0·07	0·65	0·55
0·8	4·38	4·38	3·34	3·74	1·31	1·74	0·03	0·08	0·79	0·89	2·87	2·69
1·0	2·50	2·50	1·64	1·88	0·24	0·41	0·24	0·06	1·64	1·36	2·49	2·36
1·2	1·24	1·24	0·66	0·74	0·00	0·00	0·51	0·33	1·23	1·05	0·82	0·76
1·4	0·55	0·55	0·23	0·28	0·03	0·00	0·44	0·31	0·48	0·40	0·06	0·04

equation (10) to this type of projection. If the values taken for $A_{\mathbf{s}}$ and $B_{\mathbf{s}}$ are those which satisfy equation (10) for single-weight and double-weight atoms, then atoms which are either isolated or completely overlapped in projection will cause no error in the equation. We shall now assess the error caused by a pair of partially overlapped atoms by comparing the Fourier transform of the original electron density with that of the electron-density function given by equation (2).

Once more we shall, for mathematical convenience, use atoms of Gaussian electron distribution

$$\varrho_u = K \exp\left[-2\pi u^2\right] . \tag{15}$$

Consider two such atoms at O and O' with centres separated by the vector $\mathbf{r}$. The total electron density at the point X, a vector distance $\mathbf{R}$ from O is

$$\varrho_{\mathbf{R}} = K \exp\left[-2\pi(\mathbf{R})^2\right] + K \exp\left[-2\pi(\mathbf{r}+\mathbf{R})^2\right] . \tag{16}$$

The Fourier transform of the pair of atoms at the point $\mathbf{s}$ in reciprocal space is

$$\begin{aligned}\varphi_{\mathbf{s}} &= \int_{\mathbf{R}=-\infty}^{\infty} \varrho_{\mathbf{R}} \cos 2\pi\mathbf{R}.\mathbf{s}\,d\mathbf{R} \\ &= \frac{1}{\sqrt{2}} K \exp\left[-\tfrac{1}{2}\pi s^2\right](1+\cos 2\pi\mathbf{r}.\mathbf{s}) .\end{aligned} \tag{17}$$

Now

$$\begin{aligned}\varrho^2_{\mathbf{R}} = K^2 \{&\exp\left[-4\pi(\mathbf{R})^2\right] + \exp\left[-4\pi(\mathbf{R}+\mathbf{r})^2\right] \\ &+ 2 \exp\left[-2\pi(\mathbf{R})^2\right] \exp\left[-2\pi(\mathbf{R}+\mathbf{r})^2\right]\}\end{aligned} \tag{18}$$

and

$$\begin{aligned}\varrho^3_{\mathbf{R}} = K^3 \{&\exp\left[-6\pi(\mathbf{R})^2\right] + \exp\left[-6\pi(\mathbf{R}+\mathbf{r})^2\right] \\ &+3 \exp\left[-4\pi(\mathbf{R})^2\right] \exp\left[-2\pi(\mathbf{R}+\mathbf{r})^2\right] \\ &+3 \exp\left[-2\pi(\mathbf{R})^2\right] \exp\left[-4\pi(\mathbf{R}+\mathbf{r})^2\right]\} .\end{aligned} \tag{19}$$

The Fourier transforms of $\varrho^2_{\mathbf{R}}$ and $\varrho^3_{\mathbf{R}}$ are

$$\begin{aligned}(\varphi^2)_{\mathbf{s}} = {}&\tfrac{1}{2} K^2 \exp\left[-\tfrac{1}{4}\pi s^2\right] \\ &\times\{1+\cos 2\pi\mathbf{r}.\mathbf{s} + 2 \exp\left[-\pi r^2\right] \cos \pi\mathbf{r}.\mathbf{s}\}\end{aligned} \tag{20}$$

and

$$\begin{aligned}(\varphi^3)_{\mathbf{s}} = {}&\frac{1}{\sqrt{6}} K^3 \exp\left[-\tfrac{1}{6}\pi s^2\right]\{1+\cos 2\pi\mathbf{r}.\mathbf{s} \\ &+3 \exp\left[-\tfrac{4}{3}\pi r^2\right] (\cos \tfrac{2}{3}\pi\mathbf{r}.\mathbf{s} + \cos \tfrac{4}{3}\pi\mathbf{r}.\mathbf{s})\} .\end{aligned} \tag{21}$$

The Fourier transform of the electron-density function (2) for the pair of atoms is

$$\varphi_{\mathbf{s}}' = A_{\mathbf{s}}(\varphi^2)_{\mathbf{s}} + B_{\mathbf{s}}(\varphi^3)_{\mathbf{s}} . \tag{22}$$

To show how $\varphi_{\mathbf{s}}$ and $\varphi'_{\mathbf{s}}$ compare in a practical case we shall take $K = 6\sqrt{2}$, which corresponds to atoms of the type used in the previous example. In fact $\varphi_{\mathbf{s}}$ and $\varphi'_{\mathbf{s}}$ are functions or r, s and $\mathbf{r}.\mathbf{s}$, but in Table 3 values of $\varphi_{\mathbf{s}}$ and $\varphi'_{\mathbf{s}}$ are compared for various values of r and s with $\mathbf{r}.\mathbf{s}$ always taken equal to rs. This table shows that the maximum differences between $\varphi_{\mathbf{s}}$ and $\varphi'_{\mathbf{s}}$ occur when r is about 0·5 Å. For this value of r, values of $\varphi_{\mathbf{s}}$ and $\varphi'_{\mathbf{s}}$ are compared in Table 4 for varying s in the four cases $\mathbf{r}.\mathbf{s} = rs$, $\mathbf{r}.\mathbf{s} = \frac{2}{3}rs$, $\mathbf{r}.\mathbf{s} = \frac{1}{3}rs$ and $\mathbf{r}.\mathbf{s} = 0$.

Table 4

$r = 0{\cdot}5$ Å

	$\mathbf{r}.\mathbf{s} = rs$		$\mathbf{r}.\mathbf{s} = \frac{2}{3}rs$		$\mathbf{r}.\mathbf{s} = \frac{1}{3}rs$		$\mathbf{r}.\mathbf{s} = 0$	
s (Å^{-1})	$\varphi_{\mathbf{s}}$	$\varphi'_{\mathbf{s}}$	$\varphi_{\mathbf{s}}$	$\varphi'_{\mathbf{s}}$	$\varphi_{\mathbf{s}}$	$\varphi'_{\mathbf{s}}$	$\varphi_{\mathbf{s}}$	$\varphi'_{\mathbf{s}}$
0·0	12·00	13·91	12·00	13·91	12·00	13·91	12·00	13·91
0·2	10·21	11·92	10·72	12·43	11·06	12·79	11·26	13·00
0·4	6·10	7·34	7·85	9·08	8·84	10·20	9·30	10·72
0·6	2·35	3·10	4·46	5·42	6·19	7·25	6·82	7·92
0·8	0·42	0·76	1·97	2·48	3·70	4·32	4·38	5·08
1·0	0·00	0·00	0·68	0·92	1·89	2·29	2·52	2·98
1·2	0·12	0·01	0·12	0·21	0·83	1·02	1·26	1·48
1·4	0·19	0·09	0·01	0·02	0·30	0·37	0·54	0·63

In Table 5 the maximum differences between $\varphi_{\mathbf{s}}$ and $\varphi'_{\mathbf{s}}$ for various values of $\mathbf{s}$ are compared with $f_{\mathbf{s}}$ for a single atom and it can be seen that these differences amount to the contribution of about one-third of an atom.

For the projection of a structure containing mostly isolated but a few overlapped atoms, equation (10) might be expected to apply reasonably well, although not so well as it does in the case of completely resolved atoms.

Table 5

s (Å^{-1})	$(\varphi'_{\mathbf{s}}-\varphi_{\mathbf{s}})_{\text{max.}}$	$f_{\mathbf{s}}$ for single atom	$(\varphi'_{\mathbf{s}}-\varphi_{\mathbf{s}})_{\text{max.}}/f_{\mathbf{s}}$
0·0	1·91	6·00	0·32
0·2	1·74	5·66	0·31
0·4	1·42	4·68	0·30
0·6	1·10	3·40	0·32
0·8	0·70	2·19	0·32
1·0	0·46	1·25	0·37
1·2	0·22	0·62	0·35
1·4	0·09	0·28	0·32

5. A test of the equation with overlapped atoms

To test equation (10) for a structure with overlapped atoms we shall once again consider a one-dimensional model. The unit cell is of length 20 Å, as in the previous example, and contains ten atoms of electron distribution

$$\varrho_u = 6\sqrt{2}.\exp\,[-2\pi u^2]$$

with coordinates $\pm 0{\cdot}0625$, $\pm 0{\cdot}1000$, $\pm 0{\cdot}2500$, $\pm 0{\cdot}4444$ and $\pm 0{\cdot}4500$.

Two pairs of atoms are partially overlapped in each asymmetric unit, the interatomic distances being 0·75 Å and 0·112 Å respectively. Values of $F_{\mathbf{h}}$, $G_{\mathbf{h}}$ and $H_{\mathbf{h}}$ have been calculated for those reflexions allowed by Cu $K\alpha$ radiation and, with the same $A_{\mathbf{s}}$ and $B_{\mathbf{s}}$ as used in the example of § 3, values of $F_{\mathbf{h}}$ and $A_{\mathbf{s}}G_{\mathbf{h}}+B_{\mathbf{s}}H_{\mathbf{h}}$ are compared in Table 6. The agreement between these two sets of figures, expressed as a reliability index, is 10·3 %, an agreement inferior to that obtained in the previous example but still quite satisfactory. The conclusions drawn from the calculations of § 4 are thus confirmed.

Table 6

$\mathbf{h}$	$G_{\mathbf{h}}$	$H_{\mathbf{h}}$	$A_{\mathbf{s}}G_{\mathbf{h}}+B_{\mathbf{s}}H_{\mathbf{h}}$	$F_{\mathbf{h}}$
0	519·6	5509	63·7	60·0
1	−119·3	−2446	− 0·4	− 1·9
2	233·4	3097	21·2	18·9
3	−143·8	−1969	−12·0	−11·8
4	67·0	844	6·4	7·6
5	− 90·4	− 560	−15·2	−13·2
6	−296·0	−2891	−37·2	−34·5
7	72·8	1595	− 0·6	1·3
8	−209·5	−3028	−14·9	−13·3
9	224·4	3224	16·2	16·0
10	−256·3	−3401	−20·9	−21·1
11	228·6	3097	17·9	15·9
12	− 49·8	−1296	1·2	0·0
13	95·3	1339	6·7	5·0
14	− 55·2	− 484	− 6·0	− 6·8
15	− 47·0	− 722	− 2·8	− 2·9
16	136·9	1806	9·7	9·9
17	−107·0	−1890	− 4·6	− 3·5
18	121·4	2093	5·3	6·1
19	− 98·5	−1970	− 3·0	− 2·0
20	166·6	2449	9·0	9·3
21	− 71·8	−1407	− 2·3	− 2·0
22	16·4	648	− 0·5	− 0·7
23	− 41·4	− 579	− 1·9	− 2·4
24	− 18·5	− 278	− 0·8	− 1·2
25	− 1·0	321	− 0·8	− 1·2
26	− 85·4	−1416	− 2·8	− 3·0

6. Atoms of more than two types

With appropriate values of the two parameters $A_{\mathbf{s}}$ and $B_{\mathbf{s}}$, equation (10) will always hold precisely, or nearly so, for structures containing isolated atoms of only two types. For structures containing more than two types of atom it is obviously impossible to choose values of $A_{\mathbf{s}}$ and $B_{\mathbf{s}}$ such that $f' = f$ for all the atoms simultaneously. There are two ways in which we might seek to overcome this difficulty. We could replace the function of the electron density, $\varrho'_{\mathbf{r}}$, as given by (2), by a function containing a greater number of adjustable parameters such as

$$\varrho''_{\mathbf{r},\mathbf{s}} = A_{\mathbf{s}}\varrho_{\mathbf{r}}^2+B_{\mathbf{s}}\varrho_{\mathbf{r}}^3+C_{\mathbf{s}}\varrho_{\mathbf{r}}^4+\ldots\,,$$

where the number of terms taken in the series equals the number of types of atom in the structure. This leads to an equation between structure factors of the form

$$F_{\mathbf{h}} = \frac{A_{\mathbf{s}}}{V}\sum_{\mathbf{h}'} F_{\mathbf{h}'}F_{\mathbf{h}+\mathbf{h}'}+\frac{B_{\mathbf{s}}}{V^2}\sum_{\mathbf{h}'}\sum_{\mathbf{h}''} F_{\mathbf{h}'}F_{\mathbf{h}''}F_{\mathbf{h}+\mathbf{h}'+\mathbf{h}''}$$
$$+\frac{C_{\mathbf{s}}}{V^3}\sum_{\mathbf{h}'}\sum_{\mathbf{h}''}\sum_{\mathbf{h}'''} F_{\mathbf{h}'}F_{\mathbf{h}''}F_{\mathbf{h}'''}F_{\mathbf{h}+\mathbf{h}'+\mathbf{h}''+\mathbf{h}'''}+\ldots\,. \qquad (23)$$

Although this gives an exact equation for any structure containing isolated atoms we shall not consider this type of equation any further. It will be shown in Part II of this paper that equation (10) can be a useful tool for structure determination when used in such a way that great precision in the equality of the two sides is not required. In these circumstances the extra precision offered by equation (23) is more than offset by its greater complexity.

The other method of attempting to overcome the shortage of parameters is to choose values for $A_{\mathbf{s}}$ and $B_{\mathbf{s}}$ in such a way that f' is approximately equal to f for all the atoms simultaneously. Let us consider a structure containing atoms of several types but all of the same form, so that $(\varrho_u)_K = K\psi(u)$ for an atom of weight K, where $\psi(u)$ is a function of the distance u from the centre of the atom.

Then

$$(\varrho_u)_K^2 = K^2\{\psi(u)\}^2 \quad\text{and}\quad (\varrho_u)_K^3 = K^3\{\psi(u)\}^3\,.$$

Let $\eta_{\mathbf{s}}$, $\pi_{\mathbf{s}}$ and $\theta_{\mathbf{s}}$ be the values of the Fourier transforms of $\psi(u)$, $\{\psi(u)\}^2$ and $\{\psi(u)\}^3$ at the point $\mathbf{s}$ in reciprocal space. If the parameters $A_{\mathbf{s}}$ and $B_{\mathbf{s}}$ are chosen so that

$$f'_{K_1} = f_{K_1} \quad\text{and}\quad f'_{K_2} = f_{K_2}$$

then

$$K_1\eta_{\mathbf{s}} = A_{\mathbf{s}}K_1^2\pi_{\mathbf{s}}+B_{\mathbf{s}}K_1^3\theta_{\mathbf{s}} \qquad (24)$$

and

$$K_2\eta_{\mathbf{s}} = A_{\mathbf{s}}K_2^2\pi_{\mathbf{s}}+B_{\mathbf{s}}K_2^3\theta_{\mathbf{s}}\,. \qquad (25)$$

The solution of (24) and (25) gives

$$A_{\mathbf{s}} = \frac{(K_1+K_2)}{K_1K_2}\frac{\eta_{\mathbf{s}}}{\pi_{\mathbf{s}}} \quad\text{and}\quad B_{\mathbf{s}} = -\frac{1}{K_1K_2}\frac{\eta_{\mathbf{s}}}{\theta_{\mathbf{s}}}\,.$$

With these values of the two parameters, we have for an atom of weight K

$$f'_K = A_{\mathbf{s}}K^2\pi_{\mathbf{s}}+B_{\mathbf{s}}K^3\theta_{\mathbf{s}} = \frac{K^2}{K_1K_2}(K_1+K_2-K)\eta_{\mathbf{s}}\,.$$

For the same atom we have $f_K = K\eta_{\mathbf{s}}$, so that

$$\frac{f'_K}{f_K} = \frac{K(K_1+K_2-K)}{K_1K_2} = \gamma_{K,\,K_1,\,K_2}\,. \tag{26}$$

It will be noticed that $\gamma_{K,\,K_1,\,K_2}$ is not a function of $\mathbf{s}$, which shows that the modified atom acts as an atom with the same form of scattering factor as the original atom but of different weight. The closeness of the value of $\gamma_{K,\,K_1,\,K_2}$ to unity gives an indication of the extent to which f'_K approximates to f_K. The general form of $\gamma_{K,\,K_1,\,K_2}$ as a function of K is shown in Fig. 1. The diagram is symmetrical about the ordinate $K = \frac{1}{2}(K_1+K_2)$, for which value of K there is a maximum value of $\gamma_{K,\,K_1,\,K_2}$.

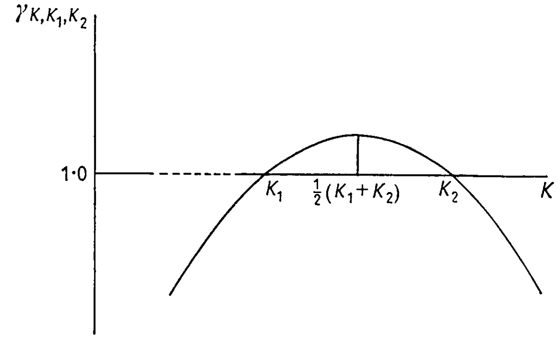

Fig. 1. The form of $\gamma_{K,\,K_1,\,K_2}$ as a function of K.

Let us take as an example $K_1 = 6$ and $K_2 = 12$. The values of $\gamma_{K,\,K_1,\,K_2}$ corresponding to various values of K are shown below:

K	$\gamma_{K,\,6,\,12}$	K	$\gamma_{K,\,6,\,12}$
2	0·44	10	1·11
3	0·62	11	1·07
4	0·78	12	1·00
5	0·90	13	0·90
6	1·00	14	0·78
7	1·07	15	0·62
8	1·11	16	0·44
9	1·12		

For atoms with weights in the range 5–13, f'_K and f_K do not differ by more than $\pm 12\%$.

In practice it is not often required that f'_K should approximate to f_K for the whole of a range of values of K. As an example, we may consider a structure containing atoms of relative weights 6:7:8:17.

If we choose $K_1 = 7$, $K_2 = 17$ then

$$\gamma_{6,7,17} = 0{\cdot}91,\ \gamma_{7,7,17} = 1{\cdot}00,\ \gamma_{8,7,17} = 1{\cdot}07,$$
$$\gamma_{17,7,17} = 1{\cdot}00\,,$$

and, for all the atoms of the structure, f'_K and f_K will agree tolerably well. It should be noted that for an atom of weight 12, in the range 6–17,

$$\gamma_{12,7,17} = 1{\cdot}21\,,$$

but since atoms of this weight do not occur in the structure the comparatively poor agreement between f'_{12} and f_{12} is of no consequence as far as equation (10) is concerned.

It is not always possible to find values of $A_{\mathbf{s}}$ and $B_{\mathbf{s}}$ such that f'_K and f_K agree tolerably well for all the atoms of a structure. If an atom of weight 12 *was* present in the previous example, then, by choosing $K_1 = 8$ and $K_2 = 16$, we have

$$\gamma_{6,8,16} = 0{\cdot}84,\ \gamma_{7,8,16} = 0{\cdot}93,\ \gamma_{8,8,16} = 1{\cdot}00\,,$$
$$\gamma_{12,8,16} = 1{\cdot}12,\ \gamma_{17,8,16} = 0{\cdot}93\,.$$

This spreads the discrepancies between f'_K and f_K fairly uniformly among the various types of atom, but whether or not this is the best thing to do will depend on the composition of the structure. If there are n_K atoms of weight K, then the average contribution of this group of atoms to a structure factor is proportional to $K\sqrt{n_K}$. The most sensible values of $A_{\mathbf{s}}$ and $B_{\mathbf{s}}$ would clearly be those which gave the least f'_K-f_K discrepancy for the type of atom for which $K\sqrt{n_K}$ is greatest, and vice versa. It is not always possible to satisfy this condition.

7. A test of the equation with atoms of more than two types

The one-dimensional model structure used for this test has the unit-cell dimension 20 Å and contains atoms for which the electron distribution has the form

$$(\varrho_u)_K = K\sqrt{2}\,.\exp\,[-2\pi u^2]\,.$$

The unit cell contains

6 atoms with $K = 6$ and coordinates $\pm 0{\cdot}025$, $\pm 0{\cdot}200$ and $\pm 0{\cdot}245$,
4 atoms with $K = 8$ and coordinates $\pm 0{\cdot}100$ and $\pm 0{\cdot}470$,
2 atoms with $K = 12$ and coordinates $\pm 0{\cdot}150$

and

4 atoms with $K = 17$ and coordinates $\pm 0{\cdot}330$ and $\pm 0{\cdot}420$.

The values of $K\sqrt{n_K}$ are 14·7, 16·0, 17·0 and 34·0 for K = 6, 8, 12 and 17 respectively. Choosing $K_1 = 8$ and $K_2 = 17$ we have

$$\gamma_{6,8,17} = 0{\cdot}84,\ \gamma_{8,8,17} = 1{\cdot}00,\ \gamma_{12,8,17} = 1{\cdot}15\,,$$
$$\text{and } \gamma_{17,8,17} = 1{\cdot}00\,.$$

In Table 7 the values of $A_{\mathbf{s}}G_{\mathbf{h}}+B_{\mathbf{s}}H_{\mathbf{h}}$ and $F_{\mathbf{h}}$ are compared for the range of $\mathbf{h}$ within the limits imposed by Cu $K\alpha$ radiation. It will be seen that the agreement is quite good, the conventional reliability index being 12·1%.

Table 7

h	$G_{\mathbf{h}}$	$H_{\mathbf{h}}$	$A_sG_{\mathbf{h}}+B_sH_{\mathbf{h}}$	$F_{\mathbf{h}}$
0	1950·2	15281	163·8	160·0
1	−271·0	−2454	−18·6	−14·9
2	608·4	6544	28·5	25·3
3	−328·6	−4405	− 4·2	− 8·3
4	− 80·9	− 788	− 4·7	− 2·1
5	−782·8	−8565	−34·0	−29·9
6	74·6	418	7·9	4·0
7	−586·4	−5663	−33·8	−29·2
8	340·9	3857	13·3	9·9
9	285·2	2966	13·9	13·6
10	360·1	3765	17·1	18·1
11	481·9	5266	20·9	18·6
12	−108·8	− 691	− 8·9	− 7·7
13	−103·3	− 442	−10·0	− 8·8
14	−376·0	−4352	−14·4	−18·6
15	−444·5	−3243	−29·7	−29·2
16	−587·4	−6528	−22·7	−23·4
17	397·8	3594	20·1	22·3
18	−463·1	−4289	−21·7	−22·8
19	429·7	5798	10·6	9·9
20	53·3	526	2·2	0·4
21	298·5	4246	6·5	7·7
22	− 34·1	− 983	0·9	1·1
23	127·6	1834	2·4	2·4
24	−338·9	−4604	− 7·4	− 7·4
25	− 13·3	− 44	− 0·6	− 0·8
26	−168·4	−2976	− 2·0	− 1·5

8. The application of the equation to non-Gaussian atoms

So far, the atoms considered in this paper have been of simple Gaussian shape and, where two or more types of atom have been present in the same structure, they have been assumed as having the same shape, differing only in magnitude. However, when there are only two types of resolved atoms in a structure, values of A_s and B_s can always be found to simultaneously satisfy equations (5) and (6) whatever the shapes of the atoms. Equation (10) can thus be used with no loss of accuracy.

For structures containing unresolved atoms all of one type, such as the model structure in § 4, the observed structure factors may be modified to correspond to atoms of any shape, including Gaussian if so desired. An example of this procedure was given by Sayre (1952).

Structures containing atoms of more than two types are a little more complicated. Values of A_s and B_s may be chosen to satisfy equations (5) and (6) for any two types of atom present in the structure but, if this is done, the values of γ_{K,K_1,K_2} for the remaining atoms will vary with the vector $\mathbf{s}$. It is nevertheless quite possible to find γ_{K,K_1,K_2} as a function of $\mathbf{s}$, should this be required, as the scattering factors for the various types of atom are usually known. However, as has been previously stated, equation (10) is normally used only in a non-precise way and variations in the values of γ_{K,K_1,K_2} will not be too important as long as they stay within reasonable limits.

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