

The bond 'framework' is then filled in with two more lines. The visible ends of the bond are improved slightly by letting the middle three lines forming it run over the determined end limit by one plotter step thus providing an approximation to a cylindrical end to the bond where it cuts the spherical atom 'surface'.

The next bond is then found from the connexion matrix and so on. Figs. 1 to 3 show completed diagrams of the molecule cycloheptane (C_7H_{14}) from different viewpoints.

A program has been written in the symbolic programming language for the IBM 1620 Model II computer with 60K store using a 1627 Model II plotter (which operates at up to 200 steps per second with a step length of 0.01"). Since there is a fair amount of calculation to perform per step when drawing circles and bonds, the plotter does not work at full speed. However, an average molecule of 20 or 30 atoms, drawn 1" to 1 Å takes about eight or nine minutes to draw, which is still a considerable saving on a day's manual labour. Note that computation time is equivalent to between 3 and 4 seconds on an Atlas. It is

intended to rewrite the program for the IBM 360/44. Flow diagrams can be obtained from the authors at the St. Andrews University Computing Laboratory.

A fairly free format can be used for the atom data input and up to 200 atoms can be accommodated in one molecule. Several views can be drawn successively without reloading the atom data and stereoscopic pairs can be drawn by choosing suitable viewpoints. Any particular bond-line can be drawn as just a single-line (e.g. for 'connections' between molecules) by following a connected atom name (on the atom data cards) by an asterisk.

We are indebted to several members of staff in St. Andrews and Dundee Universities, who provided *real* molecules for testing the program.

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On the Application of the Symbolic Addition Procedure in Neutron Diffraction Structure Determination

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The conditions have been examined for the application of the symbolic addition procedure for the evaluation of signs of structure factors from neutron diffraction data for centrosymmetric crystals containing atoms with both positive and negative scattering factors. It is shown that this procedure can be used directly, without first deriving the squared structure factors, when the contribution of the negative scatterers to the total neutron scattering is less than 25%. Several examples of the use of this method are given. The results show that for $E_n \geq 1.5$, the signs of about 95% of the reflexions are determined correctly.

1. Introduction

It is well known that direct methods of solving the phase problem by the symbolic addition procedure (Karle & Karle, 1966) cannot generally be applied to neutron diffraction if the crystal under examination contains some negative scatterers of neutrons, such as hydrogen atoms, together with other positive scatterers. This is because the basic assumption for the use of direct methods, that the scattering density is always a positive quantity, is violated. To circumvent this difficulty, Karle (1966) proposed the squared-structure

approach. The squared structure is defined as one having atoms with scattering amplitudes equal to the square of the normal amplitudes, but situated at the original positions in the unit cell. Such a hypothetical crystal has positive neutron scattering density everywhere and thus the phase problems can be solved by the symbolic addition procedure. The formula for calculating the magnitudes of squared structure factors from the observed neutron intensities was also given by Karle (1966). The success of this approach was demonstrated by Ellison & Levy (1967), who used it to solve the structure of glycolic acid. Hamilton (1966) has pointed out that this approach does not utilize all the information in the data and also that the method is really not direct since one has still to use chemical

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knowledge in order to derive the atomic positions of the hydrogen atoms.

It is the purpose of this investigation to examine whether the symbolic addition procedure could be directly used in cases of crystals in which the number of negatively scattering atoms is small compared with the number of positive scatterers. Under these conditions one expects that the effect of contributions from the negative scatterers to the structure factors will be small, especially for centrosymmetric crystals where the sign of almost all the structure factors may be left unaltered. The results presented here show that in centrosymmetric crystals, even when the relative contribution of the negative scatterers is 25% of the whole, the signs can be accurately determined by the use of the symbolic addition procedure.

2. Notation

N is the number of atoms in the unit cell,
 P is the number of positive scatterers in the unit cell,
 Q is the number of negative scatterers in the unit cell,
 \mathbf{r}_j is the position vector of the j th atom,
 b_j is the scattering factor for neutrons of the j th atom,

$\langle b+ \rangle$ is the root-mean-square scattering amplitude for the positive scatterers,

$\langle b- \rangle$ is the root-mean-square scattering amplitude for the negative scatterers,

$$\beta_n = \sum_{j=1}^N b_j^n,$$

\mathbf{h} represents h, k, l ,

$E_{\mathbf{h}} = \beta_2^{-1/2} \sum_{j=1}^N b_j \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j)$ is the quasi-normalized structure factor,

$V_{\mathbf{h}} = \beta_4^{-1/2} \sum_{j=1}^N b_j^2 \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j)$ is the quasi-normalized structure factor for the squared structure.

3. Relation between $E_{\mathbf{h}}$ and $V_{\mathbf{h}}$

It has been shown by Karle (1966) that the Σ_3 relationship,

$$V_{\mathbf{h}} = \beta_2 \beta_4^{-1/2} \langle E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}} \rangle_{\mathbf{k}}, \quad (1)$$

is also valid for neutron diffraction. In the X-ray case, it has been observed that $E_{\mathbf{h}}$ and $V_{\mathbf{h}}$ of large magnitude do not differ much from each other (they are exactly

Table 1. Data for crystals for which calculations were made

Crystal	Formula	Space group	P atoms	Q atoms	σ
Potassium hydrogen chloromaleate	C Cl COOH C H COOK	$Pbcn$	80	16	0.06
Uronium nitrate	$(\text{NH}_2)_2\text{COH} + \text{NO}_3^-$	$P2_1/c$	32	20	0.14
Salicylic acid	$\text{C}_7\text{O}_3\text{H}_6$	$P2_1/a$	40	24	0.17
Biphenyl	$\text{C}_{12}\text{H}_{10}$	$P2_1/c$	24	20	0.21

Table 2. Comparison of $E_{\mathbf{h}}$ and $V_{\mathbf{h}}$ for uronium nitrate

All $E_{\mathbf{h}}$'s ≥ 2.5 .

h	k	l	$E_{\mathbf{h}}$	$V_{\mathbf{h}}$	h	k	l	$E_{\mathbf{h}}$	$V_{\mathbf{h}}$
2	7	5	-3.62	-3.67	2	7	3	-2.81	-2.72
0	8	5	-3.61	-3.59	0	6	4	-2.80	-1.91
0	0	8	3.61	4.68	8	4	1	-2.77	-2.62
0	8	3	3.37	3.36	7	7	1	2.74	3.01
II	6	5	3.37	3.02	9	2	1	2.73	2.69
2	7	3	3.26	3.24	4	4	5	2.73	2.01
0	8	1	-3.26	-3.25	0	0	4	2.73	4.15
II	6	3	-3.25	-2.88	8	4	7	2.73	2.46
I	11	2	-3.11	-3.18	0	6	2	2.72	1.80
0	0	6	-3.09	-4.35	8	4	3	2.69	2.49
0	2	7	-3.11	-3.32	0	2	3	-2.69	-2.82
1	11	0	-3.05	-3.13	6	3	2	2.68	2.31
2	7	1	-3.02	-2.95	7	7	7	2.66	2.88
6	3	4	-3.02	-2.70	7	7	1	-2.62	-2.85
0	6	6	2.95	2.09	0	2	1	2.61	2.72
8	4	1	-2.94	-2.84	8	2	7	2.60	2.75
8	2	9	-2.93	-3.10	6	5	1	-2.60	-2.30
2	7	7	-2.92	-2.87	7	7	5	-2.58	-2.78
6	5	3	2.91	2.69	7	7	3	2.57	2.77
2	7	1	2.88	2.78	6	4	9	2.53	1.48
2	9	4	2.86	3.99	I	5	8	-2.51	-1.75
8	4	9	-2.85	-2.55	0	0	2	-2.51	-4.04
0	2	5	2.85	3.01	4	4	3	-2.54	-1.63
2	7	5	2.83	2.74					

the same if all atoms are alike) even when the crystal contains atoms of considerably different atomic numbers. (1) then reduces to

$$E_h \simeq \beta_2^{3/2} \beta_3^{-1} \langle E_k E_{h-k} \rangle_k. \quad (2)$$

Equation (2) is the basis for a step-wise determination of the phases in X-ray diffraction. For centrosymmetric crystals equation (2) can be rewritten as

$$sE_h = s \sum_k E_k E_{h-k}, \quad (3)$$

where s denotes the 'sign of'. The probability that E_h has the same sign as on the right-hand side of (3) is defined as

$$P_+(h) \simeq \frac{1}{2} + \frac{1}{2} \tanh(\beta_3 \beta_2^{-3/2} |E_h| \sum_k E_k E_{h-k}). \quad (4)$$

Now if (3) is to be used for neutron diffraction, then $E_h \simeq V_h$ must hold. We have used probability considerations to show that this will be true for most structures.

Cochran & Woolfson (1955) have shown that the average probability that E_h and V_h will be alike in sign is given by

$$P_+(E_h V_h) = \frac{1}{2} + \varphi[\beta_3 E_h / (\beta_2 \beta_4 - \beta_3^2)^{1/2}], \quad (5)$$

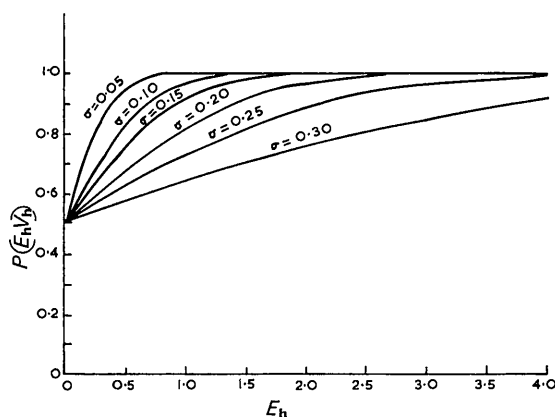


Fig. 1. The probability $P(E_h V_h)$ that E_h and V_h will be alike in sign for different values of E_h and σ .

where the function

$$\varphi(x) = (2\pi)^{-1/2} \int_0^x \exp\left(-\frac{t^2}{2}\right) dt.$$

We will evaluate the quantities β_n in terms of σ , the mean fractional contribution by the negative scatterers to the intensity, where

$$\sigma = \frac{Q \sum_{j=1}^Q b_j^2 / \sum_{j=1}^N b_j^2}{\simeq Q \langle b^- \rangle^2 / (P \langle b^+ \rangle^2 + Q \langle b^- \rangle^2)}.$$

If we further assume $P=Q$, then

$$\sigma = \langle b^- \rangle^2 / (\langle b^+ \rangle^2 + \langle b^- \rangle^2)$$

and

$$\begin{aligned} \beta_2 &\simeq Q(\langle b^+ \rangle^2 + \langle b^- \rangle^2) = Q \langle b^- \rangle^2 / \sigma, \\ \beta_3 &\simeq Q(\langle b^+ \rangle^3 - \langle b^- \rangle^3) = Q \langle b^- \rangle^3 [(1-\sigma)/\sigma]^{3/2} - 1], \\ \beta_4 &\simeq Q(\langle b^+ \rangle^4 + \langle b^- \rangle^4) = Q \langle b^- \rangle^4 [(1-\sigma)/\sigma]^2 + 1]. \end{aligned}$$

Substituting in (5) and simplifying, we get

$$P_+(E_h V_h) = \frac{1}{2} + \varphi \left[\frac{(1-\sigma)^{3/2} - \sigma^{3/2}}{(\sigma - \sigma^2 + 2\sigma^{3/2}(1-\sigma)^{3/2})^{1/2}} E_h \right]. \quad (6)$$

Fig. 1 is a plot of $P_+(E_h V_h)$ vs. E_h for σ ranging from 0.05 to 0.30. It is clear from the Figure that for σ up to 0.25, the probability is quite high that $E_h \geq 1.5$ will have the same sign as V_h .

We have also tested this on some actual crystal structures, potassium hydrogen chloromaleate (Ellison & Levy, 1965), uronium nitrate (Worsham & Levy, 1967), salicylic acid (Jude, 1968) and biphenyl (Macdonald, 1969). The values of σ and other data for these structures are given in Table 1. The values of E_h and V_h were computed from the published atomic parameters and some of these values for uronium nitrate and biphenyl are compared in Tables 2 and 3.

It can be concluded from this comparison that not only do E_h and V_h agree with each other in sign but also that large E_h are associated with large V_h . The results for potassium hydrogen chloromaleate and sali-

Table 3. Comparison of E_h and V_h for biphenyl

All E_h 's ≥ 1.5 .

h	k	l	E_h	V_h	h	k	l	E_h	V_h
6	2	2	-3.43	-3.01	8	0	2	-2.02	-1.30
6	3	1	-3.14	-3.39	1	0	2	2.01	2.08
2	3	5	2.89	3.04	3	0	8	-2.00	-2.32
3	2	6	2.56	2.47	0	6	0	1.94	2.66
5	1	4	2.42	2.05	2	3	5	-1.93	-0.81
5	3	3	-2.39	-2.63	1	4	3	-1.91	-1.66
2	1	4	2.33	1.63	5	2	4	-1.88	-2.49
0	5	1	2.31	2.25	1	1	1	1.87	1.69
7	2	0	-2.26	-2.74	8	0	2	-1.79	-1.68
0	1	1	2.21	1.98	2	3	3	1.58	0.78
1	2	3	2.18	1.68	2	2	3	1.57	1.15
4	0	6	-2.12	-2.03	3	1	3	-1.51	-1.05
1	5	1	2.10	2.25	1	3	3	1.51	0.94
3	3	5	2.05	2.03	2	3	1	1.50	2.41
4	1	1	-2.05	-1.10					

cylic acid were similar. In fact, for all these four structures, no $E_h \geq 1.5$ differed in sign from V_h . Karle (1966) found that some large V_h have small E_h values. This was also true in these structures but the reverse, that large E_h have large V_h values, was true in almost all cases, which is the only necessary condition for the application of the symbolic addition procedure.

4. Examples of application

In order to assess the applicability of the symbolic addition procedure, the calculations were done for all the structures listed in Table 1. The procedures for carrying out the sign determinations with equation (3) has been given by Karle & Karle (1966). The first step in this procedure was the computation of normalized structure factors from the observed F_h values, using the expression:

$$|E_h| = |F_h| \varepsilon^{-1} \beta_2^{-1/2} \exp(B \sin^2 \theta / \lambda^2),$$

where ε is a factor which corrects for space group absences and B is the overall temperature factor. $\sin \theta / \lambda$ values were calculated from cell constants and the value of B for each crystal was estimated from the reported temperature factors. For uronium nitrate, because observed $|F_h|$ were not available, the calculated values of E_h were used.

The next step was the generation of the ' Σ_2 ' listings for large E_h values. Both the computation of E_h and the production of these ' Σ_2 ' listing were done by a computer program written by the author.

In order to facilitate the comparison of signs determined by this procedure and from the final structures, the signs of reflexions used for defining the origin were chosen to be the same as those given by the final structures. However, these chosen reflexions satisfied the criteria given by Hauptman & Karle (1953). These, along with other reflexions which were assigned symbols in the beginning, are given in Table 4.

Table 4. Reflexions chosen for initiating the sign determination

Potassium hydrogen chloromaleate	Uronium nitrate	Salicylic acid	Biphenyl
1333+	273+	414+	235+
972+	085-	723+	326+
1231-	771+	313+	533-
885a	634a	215a	011a
1310b	294b	961b	143b
	1165c	393c	

After making the initial symbol assignments, all sign determinations using equation (3) were carried out 'by hand'. For all the structures, the signs were determined only for those reflexions with $E_h \geq 1.5$. A sign indication was accepted only if the probability calculated by equation (4) was ≥ 0.97 for a single combination of \mathbf{k} and $\mathbf{h}-\mathbf{k}$. For $E_h \sim 1.5$ when P was below 0.97, the sign symbols were accepted only if defined by at least two combinations of \mathbf{k} and $\mathbf{h}-\mathbf{k}$. The main features of these calculations and an analysis of the agreement between the signs obtained directly and from the refined structures are given in Table 5.

5. Discussion

The results given in Table 5, show that when the negative atom contribution to the scattering is below 25%, the symbolic addition procedure can be successfully applied in neutron diffraction structural analysis for centrosymmetric crystals in a fairly straightforward manner. Now, in most of the crystals, especially in organic molecules, the negatively scattering atom is the hydrogen atom ($b = -0.38 \times 10^{-12}$ cm) and when C, N, O and H atoms are present in the crystal, from scattering length considerations, it may be represented as a C_nH_n molecule. For such a hypothetical molecule, the contribution of the hydrogen atom to the total scattering will be $(0.38)^2 / (0.66)^2 + (0.38)^2$, or 25% (Hamilton & Ibers, 1968). This means that the symbolic addition procedure will be applicable in most practical cases.

It may also be pointed out that when σ is ≥ 0.20 , the inequality $F_{hkl} \leq F_{000}$ does not hold. One example of this is biphenyl (see Table 1). But even for this structure the signs are determined correctly, although the number of reflexions is not sufficient to define the structure.

Another thing which may be noted is that as σ increases, the probability given by equation (4) goes down. This is because the term β_3 contains a negative contribution from the negative scatterers. This is not serious, however; one can always start with high probability limits and once the signs of a sufficient number of reflexions have been established in terms of symbols, the alternative criterion of accepting the same symbol when defined by at least two combinations of \mathbf{k} and $\mathbf{h}-\mathbf{k}$, can be used. The problem is now being investigated for the case of non centrosymmetric crystals.

Table 5. Analysis of the agreement between the signs obtained from the symbolic addition procedure and the refined structures

Structure	Relationship between symbols	Number of independent symbols	Number of signs determined	Number of correctly determined signs
Potassium hydrogen chloromaleate	$a = b = -1$	none	96	94 (98%)
Uronium nitrate	$b = c = +1$	1(a)	226	216 (95%)
Salicylic acid	$b = c = +1$	1(a)	126	120 (95%)
Biphenyl	$a = -1$	1(b)	25	25 (100%)

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Phase Determination for Pseudo-Symmetric Centrosymmetric Crystals

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The Fourier transform of a symmetric atom group that is sampled asymmetrically by the reciprocal lattice may be deduced by inspection of the weighted reciprocal lattice. The symmetry of the atom group impresses a pseudo-symmetry on the weighted reciprocal lattice. Superposition of the pseudo-symmetric parts of the lattice gives an increased sampling of the whole Fourier transform, permits recognition of maxima and nodes, and hence provides phase information.

Introduction

The observed intensities of the X-ray diffraction maxima produced by a single crystal may be regarded as point samples of the continuous Fourier transform of the unit-cell contents (Taylor & Lipson, 1958). From some crystals, the sample interval provided by the reciprocal lattice is small enough to allow the whole transform to be deduced, as is essentially done in the 'heavy atom' method. Sample frequency may be increased by expansion of the unit cell, as in the case of horse haemoglobin (Boyes-Watson, Davidson & Perutz, 1947). In general, however, the sampling of the transform provided by the reciprocal lattice is too sparse to determine detail in the transform by examining the observed intensities.

Presence of pseudo-symmetry

A symmetric molecule or atom group has a symmetric Fourier transform. If the repeated atom groups comprising the crystal are not related by symmetry, the crystal itself will lack symmetry, and the reciprocal lattice will sample the transform asymmetrically.

Fig. 1(a) shows a hypothetical centro- and mirror-symmetric group of atoms, so arranged that the unit

cell has only centrosymmetry. The weighted reciprocal lattice [Fig. 1(c)] has approximate mirror symmetry along the $[45]^*$ direction (shown in the Figure as a broken line). Such an approximate mirror will be called a pseudo-mirror. Comparison of Fig. 1(b) and (c) shows that on either side of the pseudo-mirror, reciprocal-lattice points give samples of different parts of a symmetric transform. The sample frequency provided by the reciprocal lattice can therefore be almost doubled by superimposing on the lattice its mirror image [Fig. 1(d)]. The same result is obtained if the pseudo-mirror along the $[\bar{5}4]^*$ direction is used. There is sufficient detail provided by Fig. 1(d) to derive the full Fourier transform, and in particular the sign of the transform at the reciprocal lattice points, if it is assumed that there is a sign change across nodes.

Examples

(1) CrBr₂

The structure of CrBr₂ has been described by Tracy, Gregory & Lingafelter (1962), who have listed structure factors for the $h0l$ reciprocal lattice plane. The weighted $h0l$ reciprocal lattice in Fig. 2(a) shows pseudo-mirror symmetry about the $[103]^*$ direction. Superposition of the reciprocal lattice on its mirror