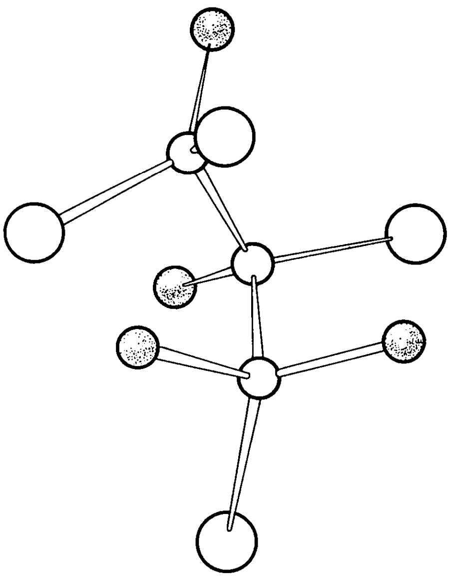

Fig. 6. The orthogonal projection of the three water molecules O(4), O(5) and O(6) with their tetrahedrally coordinated neighbours. The large spheres are chloride ions and the small ones are the water molecules. The dotted spheres are water molecules belonging to magnesium octahedra.

It is probable that the hydrogen atoms do not lie very far from the line of centers of the heavier atoms, since the hydrogen-bond angles, assuming linearity of the bond, do not deviate by more than 16° from tetrahedral. This approximately tetrahedral environment of the three four-coordinated water molecules, O(4), O(5) and O(6) is illustrated in Figs. 5 and 6.

This is clearly a very reasonable structure for a hydrated phase in which the stoichiometry is such that each ion can have a complete hydration polyhedron and there is no direct anion-cation contact. It is interesting to note that all the distortions from regularity necessary to form this pattern of associated octahedra are to be found in the hydrogen-bonded [Cl^- . $6H_2O$] octahedra, and that this distortion has an enantiomorphic sense even though the whole crystal structure is centrosymmetrical. The more tightly bound ionic [Mg^+ . $6H_2O$] octahedra are completely undistorted within the accuracy of the structure determination.

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The Evaluation of Phases for Structure Determination by Neutron Diffraction

By J. Karle

U.S. Naval Research Laboratory, Washington, D.C. 20390, *U.S.A.*

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The formulas for phase determination often used for X-ray diffraction data are not immediately applicable to neutron diffraction data when atoms with both positive and negative scattering factors are present. A formula is presented from which normalized structure factors for the squared structure may be calculated from the normalized scattering data, as obtained from a neutron diffraction experiment. Since the squared structure is defined as the structure which scatters with the square of the scattering factor for each atom in the original structure, the computed structure factors for the squared structure will always represent a positive structure and the formulas for phase determination used for X-ray data will be applicable. Test calculations are presented.

Introduction

The positions of the atoms in the unit cell of a crystal can be calculated by Fourier series methods, provided that both the amplitudes and phases of the scattered neutron waves are known. The amplitudes and phases form the coefficients of a Fourier series representing the neutron scattering density in the unit cell, and the main maxima of such a function correspond to the positions of the atomic nuclei. Fourier series methods have been employed for several years starting with the investigations of Bacon & Pease (1953) and Peterson, Levy &

Simonsen (1953, 1954). When the coefficients of the series are corrected for thermal effects, they correspond to point scatterers and give rise to Fourier maps which are comparable to E-maps in X-ray diffraction. These latter E-maps are computed with the normalized structure factors, E, as coefficients, which are obtained from the X-ray intensity data by correcting for thermal motion and concentrating the scattering power of the atomic electrons into single points located approximately at the atomic centers. The meaning of such maps in terms of the probability of locating atomic positions has been discussed (Karle, Hauptman, Karle & Wing, 1958).

As in the case of X-rays, only the amplitudes of the scattered waves may be directly obtained from experiment. However a simple procedure, the symbolic addition procedure, for obtaining the required phases from the measured intensities has been developed for X-rays when a center of symmetry is present (Karle & Karle, 1963, 1964*a*, 1965), and some progress has been made in generalizing this procedure to noncentrosymmetric crystals (Karle & Karle, 1964*b*). Although many neutron diffraction studies have been facilitated by a previous knowledge of the structure from X-ray studies, the question naturally arises whether a procedure similar to the symbolic addition procedure for X-ray diffraction might not be developed for neutron diffraction, thereby affording a direct method of analysis of the neutron data. This would be particularly useful when X-ray data were either not available, or when available, not sufficiently detailed concerning light atom positions.

It will be seen in the subsequent analysis that an immediate application of the phase determining procedure to neutron diffraction data is not generally feasible. The underlying cause is the fact that certain atoms have negative scattering factors for neutrons (Bacon, 1962), whereas this does not occur for X-rays. It is possible, however, that the problem associated with the neutron data can be overcome, since a set of intensities may be calculated from these data which are closely related to those which would have been obtained in a neutron diffraction experiment if all the atoms scattered positively. In fact, the calculated set of intensities correspond approximately to the data which would be obtained from a structure in which all the atoms scatter with the square of their scattering factors. Such a structure is referred to as the squared structure. After standard renormalization procedures, there is little difference between the intensities corresponding to a structure with positive scattering factors for the atoms and those corresponding to the squared structure. When the scattering factors are the same for all the atoms present, the so-called normalized structure factors for the structure and its square are identical.

As the result, then, of computing intensities for the squared structure directly from the experimental neutron diffraction data, a set of intensities would be obtained which correspond approximately to a structure whose atoms scatter positively and whose positions have not changed. The next step would involve the application of a procedure for phase determination to these calculated intensities in order to calculate a Fourier map for locating the atomic positions. Atom identification would reveal which ones have contributed a negative scattering factor to the original intensity data.

We proceed now with an analysis of the phase problem for neutrons. In addition, a formula will be derived for calculating the normalized structure factor magnitudes for the squared structure and test calculations will be presented.

Analysis of the problem

The phase problem for neutron diffraction can be readily clarified by deriving a phase determining formula comparable to one employed for X-ray data. We define the quasi-normalized structure factor, $\varepsilon_{\mathbf{k}}$, for neutron diffraction,

$$\varepsilon_{\mathbf{k}}=\beta_2^{-1/2}\sum_{j=1}^{N} b_j \exp(2\pi i\mathbf{k}\,.\,\mathbf{r}_j)\,, \tag{1}$$

where

$$\beta_n=\sum_{j=1}^{N} b_j^n\,, \tag{2}$$

b_j is the scattering factor for neutrons of the jth atom in a unit cell containing N atoms, $\mathbf{r}_j$ is a vector whose components are the coordinates of the jth atom, and $\mathbf{k}=h, k, l$ is a vector whose components are the Miller indices of a reflection.*

We define the squared structure as that structure which is identical with the original structure except that each atom scatters with the square of the actual atomic scattering factor for neutrons. The quasi-normalized structure factor $\varepsilon'_{\mathbf{k}}$ for the squared structure is then

$$\varepsilon'_{\mathbf{k}}=\beta_4^{-1/2}\sum_{j=1}^{N} b_j^2 \exp(2\pi i\mathbf{k}\,.\,\mathbf{r}_j)\,. \tag{3}$$

It follows from (1) that

$$\begin{aligned}\varepsilon_{\mathbf{k}}\varepsilon_{\mathbf{h}-\mathbf{k}}=&\beta_2^{-1}\sum_{j=1}^{N} b_j^2 \exp(2\pi i\mathbf{h}\,.\,\mathbf{r}_j)\\ &+\beta_2^{-1}\sum_{\substack{j=1\\ j\neq k}}^{N}\sum_{k=1}^{N} b_j b_k \exp[2\pi i(\mathbf{k}\,.\,\mathbf{r}_j+(\mathbf{h}-\mathbf{k})\,.\,\mathbf{r}_k)]\,.\end{aligned} \tag{4}$$

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* For the case that none of the indices is zero, the quasi-normalized structure factors, ε, are the same as the normalized structure factors, E. When there are systematic absences due to space group extinctions among reflections for which at least one of the indices is zero, the quasi-normalized structure factors have to be rescaled to equal the normalized structure factors. If, for example, half of the reflections are extinctions within a particular set, such as the $h0l$ reflections in space group $P2_1/c$, then the appropriate quasi-normalized structure factors must be divided by $2^{\frac{1}{2}}$, *i.e.* $\varepsilon_{h0l}/2^{\frac{1}{2}}=E_{h0l}$. The rule is $|\varepsilon|^2(1-q)=|E|^2$, where q is the fraction of reflections in the set which are space group extinctions. We are considering here only primitive unit cells.

If we average over all vectors $\mathbf{k}$, the double sum in (4) averages to zero, and we obtain with the use of (3),

$$\varepsilon'_{\mathbf{h}}=\beta_2\beta_4^{-1/2}\langle\varepsilon_{\mathbf{k}}\varepsilon_{\mathbf{h}-\mathbf{k}}\rangle_{\mathbf{k}}\,. \tag{5}$$

Equation (5) is the algebraic equivalent of a family of formulas in X-ray diffraction, *e.g.* the third inequality of Karle & Hauptman (1950), the Sayre equation (1952), and the algebraic equation of Hughes for equal atoms (1953). It is clear from inspection of equation (5) that averages taken over structure factors for the original structure give structure factors for the squared structure. In the comparable phase determining relations for X-ray diffraction, this matter, though generally true, can be quite safely ignored, since X-ray scattering factors for atoms are always positive numbers* and, in addition, the application of the equivalent of equation (5) in X-ray diffraction is ordinarily limited to those terms involving only the largest structure factor magnitudes. In such cases the distinction between the phases for the original and squared structures is of no consequence. In fact, it is easy to show that when all the atoms are alike the quasi-normalized, structure factors for X-ray scattering are the same for the original and for the squared structure.

In the case of neutron diffraction where some atoms may be scattering with positive scattering factors and others with negative scattering factors, the phases and magnitudes of the structure factors for the squared structure may readily differ from those for the original structure. The symbolic addition procedure for phase determination in X-ray diffraction utilizes formulas related to (5) and proceeds in a step-wise fashion starting with some phases of known value and others denoted by symbols. As the determination proceeds new phases are added to the list of known phases, since the phases determined for the squared structure can be used to represent those for the original structure. Since this is not the case in neutron diffraction when a significant number of atoms have scattering factors of opposite sign, it is not apparent how the phase determination can proceed in a step-wise fashion. Clearly, a different approach is required for neutron diffraction.

If we knew the magnitudes of the quasi-normalized structure factors for the squared structure, we could apply the preocdure for phase determination, since all atoms would have positive scattering factors as in the case of X-rays. The squared structure could then be calculated from the phases so determined and, once it was known, the original structure could be derived. In the next section it will be shown how the magnitudes of the structure factors for the squared structure can be determined from the magnitudes of the structure factors for the original structure obtained in a neutron diffraction experiment.

Structure factors for the squared structure

We now carry out an analysis, similar to that of Hauptman (1964) for the X-ray case, with a view toward obtaining a general formula, defining the magnitudes of the quasi-normalized structure factors for the squared structure in terms of those for the original structure, which is applicable to all the space groups.

It follows from (1) that

$$|\varepsilon_{\mathbf{k}}|^2-1=\beta_2^{-1}\sum_{\substack{j=1\\j\neq k}}^{N}\sum_{k=1}^{N}b_jb_k\exp(2\pi i\mathbf{k}\,.\,\mathbf{r}_{jk})\,, \tag{6}$$

where

$$\mathbf{r}_{jk}=\mathbf{r}_j-\mathbf{r}_k\,.$$

Also,

$$|\varepsilon'_{\mathbf{k}}|^2-1=\beta_4^{-1}\sum_{\substack{j=1\\j\neq k}}^{N}\sum_{k=1}^{N}b_j^2b_k^2\exp(2\pi i\mathbf{k}\,.\,\mathbf{r}_{jk})\,. \tag{7}$$

From (6), we have

$$(|\varepsilon_{\mathbf{k}}|^2-1)(|\varepsilon_{\mathbf{h}-\mathbf{k}}|^2-1)=\beta_2^{-2}\sum_{\substack{j=1\\j\neq k}}^{N}\sum_{k=1}^{N}\sum_{\substack{j'=1\\j'\neq k'}}^{N}\sum_{k'=1}^{N}$$

$$\times b_jb_kb_{j'}b_{k'}\exp\{2\pi i[\mathbf{h}\,.\,\mathbf{r}_{jk}+\mathbf{k}\,.\,(\mathbf{r}_{j'k'}-\mathbf{r}_{jk})]\}\,. \tag{8}$$

If equation (8) is averaged over all vectors $\mathbf{k}$, all terms on the right vanish except those for which $\mathbf{r}_{j'k'}-\mathbf{r}_{jk}=0$. There is always at least one pair (j',k') for which the latter equation is satisfied, namely $j'=j$ and $k'=k$.

We now define

$$\alpha_{jk}=\frac{\sum\limits_{j'\neq k'}b_{j'}b_{k'}}{b_jb_k}\,, \tag{9}$$

where the summation is taken over all pairs (j',k') which satisfy $\mathbf{r}_{j'k'}-\mathbf{r}_{jk}=0$. Also if $j=k$, α_{jk} is defined to be zero. Unlike the X-ray case where $\alpha_{jk}\geq 1$ if $j\neq k$, α_{jk} for neutron diffraction can be less than one as well as larger than one. When there is no overlap in the Patterson function $\alpha_{jk}=1$ if $j\neq k$ for both X-rays and neutrons.

It follows from (8) and (9) that

$$\langle(|\varepsilon_{\mathbf{k}}|^2-1)(|\varepsilon_{\mathbf{h}-\mathbf{k}}|^2-1)\rangle_{\mathbf{k}}$$

$$=\beta_2^{-2}\sum_{\substack{j=1\\j\neq k}}^{N}\sum_{k=1}^{N}b_j^2b_k^2\alpha_{jk}\exp(2\pi i\mathbf{h}\,.\,\mathbf{r}_{jk})\,. \tag{10}$$

The right side of (10) resembles the right side of (7). In order to facilitate an approximation involving (7), we rewrite (10) in the form

$$\langle(|\varepsilon_{\mathbf{k}}|^2-1)(|\varepsilon_{\mathbf{h}-\mathbf{k}}|^2-1)\rangle_{\mathbf{k}}=\beta_2^{-2}\sum_{j=1}^{N}\sum_{k=1}^{N}b_j^2b_k^2\alpha_{jk}$$

$$\times\left[\frac{\sum\limits_{j=1}^{N}\sum\limits_{k=1}^{N}b_j^2b_k^2\alpha_{jk}\exp(2\pi i\mathbf{h}\,.\,\mathbf{r}_{jk})}{\sum\limits_{j=1}^{N}\sum\limits_{k=1}^{N}b_j^2b_k^2\alpha_{jk}}\right],j\neq k\,. \tag{11}$$

The coefficient in front of the bracketed term (11) is found from (10) when $\mathbf{h}=0$ to be

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* This assumes that the X-ray frequency is not near an absorption edge, in which case the scattering factor would be a complex number.

$$\beta_2^{-2}\sum_{\substack{j=1\\ j\neq k}}^{N}\sum_{k=1}^{N} b_j^2 b_k^2 \alpha_{jk} = \langle(|\varepsilon_{\mathbf{k}}|^2-1)^2\rangle_{\mathbf{k}}\,. \tag{12}$$

An approximation is now made replacing the weighted average given by the bracketed term by

$$\frac{\displaystyle\sum_{\substack{j=1\\ j\neq k}}^{N}\sum_{k=1}^{N} b_j^2 b_k^2 \exp(2\pi i\mathbf{h}\,.\,\mathbf{r}_{jk})}{\displaystyle\sum_{\substack{j=1\\ j\neq k}}^{N}\sum_{k=1}^{N} b_j^2 b_k^2} = \frac{\beta_4(|\varepsilon_{\mathbf{h}}'|^2-1)}{\beta_2^2-\beta_4} \tag{13}$$

using (7) and (2).

Up to this point the analysis has essentially followed that of Hauptman (1964) for the X-ray diffraction case. The difference occurs in expression (13). In the X-ray case the bracketed term was replaced by an average involving the first powers of the atomic scattering factors bringing in the structure factor magnitudes of the original structure as defined in (6). This is legitimate in the X-ray case owing to the close relationship between structure factors for the original structure and those for the squared structure when all the atomic scattering factors are positive. However, for the case of neutron diffraction, the approximation used for X-ray diffraction cannot be used. Instead, it is necessary and, as it turns out, desirable to approximate the expression in the bracket of (11) by an average which includes the squares of the atomic scattering factors, equation (13). We thus obtain an expression for the structure factor magnitudes of the squared structure in terms of those for the original structure by substituting (12) and (13) into (11),

$$|\varepsilon_{\mathbf{h}}'|^2-1 \simeq (\beta_2^2\beta_4^{-1}-1)\,\frac{\langle(|\varepsilon_{\mathbf{k}}|^2-1)(|\varepsilon_{\mathbf{h}-\mathbf{k}}|^2-1)\rangle_{\mathbf{k}}}{\langle(|\varepsilon_{\mathbf{k}}|^2-1)^2\rangle_{\mathbf{k}}}\,. \tag{14}$$

In analogy to the integrated formulas derived for the X-ray case (Karle & Hauptman, 1959), the following formula is suggested as a possible alternative to (14),

$$|\varepsilon_{\mathbf{h}}'|^2-1 \simeq (\beta_2^2\beta_4^{-1}-1)\,\frac{\langle A_{t,\mathbf{k}}A_{t,\mathbf{h}-\mathbf{k}}\rangle_{\mathbf{k}}}{\langle A_{t,\mathbf{k}}^2\rangle_{\mathbf{k}}}\,, \tag{15}$$

where

$$A_{t,\mathbf{k}} = \left(\frac{|\varepsilon_{\mathbf{k}}|^t-1}{\log|\varepsilon_k|} - M_t\right)\,, \tag{16}$$

and

$$M_t = \left\langle\frac{|\varepsilon_{\mathbf{k}}|^t-1}{\log|\varepsilon_{\mathbf{k}}|}\right\rangle_{\mathbf{k}}. \tag{17}$$

Application

Several test caluclations were performed in order to determine how best to apply formulas (14) and (15), whether either appears to be superior, and the reliability with which the larger $|\varepsilon'|$ can be determined from these formulas. The calculations were performed on naphthalene in space group $P2_1/a$ (Abrahams, Robertson & White, 1949; Cruickshank, 1957), myoinositol in space group $P2_1/c$ (Rabinowitz & Kraut, 1964), and sucrose in space group $P2_1$ (Brown & Levy, 1963), having 36, 192 and 90 atoms per unit cell, respectively. Values of the magnitudes of quasi-normalized structure factors $|\varepsilon|$, were computed from the published structures and the neutron scattering factors for atoms employing equation (1). The number computed corresponded approximately to the number of independent data obtained from the copper sphere of scattering for X-rays, 767 for naphthalene, 2975 for myoinositol and 2749 for sucrose. In applying (14) and (15) the basic deck of independent data is expanded to include all reflections according to the space group equivalences, including the space group absences. Quasi-normalized structure factor magnitudes for the squared structure, $|\varepsilon'|$, were computed from (3) in order to compare the results from (14) and (15) with the correct $|\varepsilon'|$ for the given structures. On present day fast computers, $|\varepsilon'|$ can be computed from (14) or (15) for all the independent reflections mentioned above in less than an hour for each substance.

In computing (14) and (15) the averages,

$$\langle(|\varepsilon_{\mathbf{k}}|^2-1)^2\rangle_{\mathbf{k}}\,, \tag{18}$$

and

$$\langle A_{t,\mathbf{k}}^2\rangle_{\mathbf{k}} \tag{19}$$

are computed from the data deck, rather than from theoretical considerations. In order to compensate further for possible statistical variation in the sample of data, it is suggested that in computing the averages $\langle(|\varepsilon_{\mathbf{k}}|^2-1)(|\varepsilon_{\mathbf{h}-\mathbf{k}}|^2-1)\rangle_{\mathbf{k}}$ in (14) and $\langle A_{t,\mathbf{k}}A_{t,\mathbf{h}-\mathbf{k}}\rangle_{\mathbf{k}}$ in (15), the number of terms, ν, be obtained from

$$\nu = \frac{\sum_{\mathbf{k}}[(|\varepsilon_{\mathbf{k}}|^2-1)^2+(|\varepsilon_{\mathbf{h}-\mathbf{k}}|^2-1)^2]}{2\langle(\varepsilon_{\mathbf{k}}|^2-1)^2\rangle_{\mathbf{k}}}\,, \tag{20}$$

and

$$\nu = \frac{\sum_{\mathbf{k}}(A_{t,\mathbf{k}}^2+A_{t,\mathbf{h}-\mathbf{k}}^2)}{2\langle A_{t,\mathbf{k}}^2\rangle_{\mathbf{k}}} \tag{21}$$

respectively instead of using the actual numerical count. Theoretical values are to be used for the denominators in (20) and (21). Thus, when the sample of data is a good statistical sample, expressions (20) and (21) coincide with the actual numerical count. The denominator of (20) is 2 for space group $P1$ and 4 for centrosymmetric crystals. An appropriate intermediate value should be used for noncentrosymmetric crystals having centrosymmetric projections. This value is readily calculated from the proportion of centrosymmetric and noncentrosymmetric reflections in the data. The value $t=3$ has been employed here. The denominator of (21) when $t=3$ is 11·29 for space group $P1$ and 24·28 for centrosymmetric crystals*.

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* These values are obtained by carrying out the calculations of the expected values, employing the probability distributions of Wilson (1949) for space groups $P1$ and $P\bar{1}$, in which the transformation of variable, $\varepsilon = F/(\sum_{j=1}^{N} b_j^2)^{\frac{1}{2}}$, has been made.

Tables 1 and 2 show some typical calculations of structure factors for the squared structure, $|\varepsilon'|_c$, using (15) for naphthalene and myoinositol respectively. The results for sucrose were similar. In the course of the calculations it was found that the results were improved for myoinositol by using (20) or (21) instead of the actual numerical count and that the largest $|\varepsilon'|$ values for myoinositol were computed somewhat more accurately by the integrated formula, (15), rather than by (14). None of these differences were observed for naphthalene or sucrose. At the end of the calculations, the results were listed in decreasing order of the values of $|\varepsilon'|_c$. The column labeled $|\varepsilon|$ shows the structure factor magnitudes which would be observed from an experiment with neutrons, the column labeled $|\varepsilon'|_o$ shows the magnitudes which would be observed for the squared structure and the column labeled $|\varepsilon'|_c$ shows the structure factor magnitudes for the squared structure calculated by use of (15) from a knowledge of the $|\varepsilon|$ values. The last column shows the actual number of terms contributing to the calculation.

Table 1. *Comparison of the* $|\varepsilon|$ *which would be observed from experiment, the* $|\varepsilon'|_o$ *which would be observed from the squared structure and the* $|\varepsilon'|_c$ *which were calculated by* (15) *from the* $|\varepsilon|$ *for napthalene*

The last column gives the number of terms contributing to (15). The values shown were chosen from among the largest $|\varepsilon'|_c$.

hkl	$\lvert\varepsilon\rvert$	$\lvert\varepsilon'\rvert_o$	$\lvert\varepsilon'\rvert_c$	no.
$60\bar{8}$	1·93	4·80	4·65	445
$40\bar{7}$	3·30	3·03	3·16	604
$60\bar{4}$	0·78	2·42	3·05	643
$60\bar{7}$	2·83	2·60	3·02	494
210	0·86	2·46	2·88	1104
$52\bar{1}$	0·87	2·76	2·66	719
547	0·69	1·98	2·62	349
136	1·40	2·93	2·58	615
$41\bar{1}$	2·29	2·52	2·54	879
$21\bar{7}$	2·86	2·50	2·54	649
$35\bar{2}$	1·10	2·40	2·42	539
$73\bar{2}$	1·28	2·41	2·39	479
258	0·70	0·45	2·35	350
713	1·06	2·47	2·34	559

Table 2. *Comparison of the* $|\varepsilon|$ *which would be observed from experiment, the* $|\varepsilon'|_o$ *which would be observed from the squared structure and the* $|\varepsilon'|_c$ *which were calculated by* (15) *from the* $|\varepsilon|$ *for myoinositol*

The last column gives the number of terms contributing to (15). The values shown were chosen from anomg the largest $|\varepsilon'|_c$.

hkl	$\lvert\varepsilon\rvert$	$\lvert\varepsilon'\rvert_o$	$\lvert\varepsilon'\rvert_c$	no.
$5\ 0\ \overline{10}$	3·79	9·13	7·22	2874
$5\ 0\ \bar{6}$	3·82	5·84	5·47	3426
4 8 5	3·07	3·54	4·57	2519
$1\ 10\ \overline{15}$	0·37	3·00	4·54	1650
$1\ 6\ \overline{13}$	4·75	4·22	4·31	2430
$4\ 0\ \overline{12}$	1·49	4·02	4·18	2817
4 6 7	4·92	3·48	4·15	2634
4 11 5	0·88	3·23	4·13	2015
5 9 10	3·29	3·61	4·05	1749
4 10 5	0·87	1·84	4·00	2183
5 6 13	0·04	1·32	3·97	1818
5 6 12	1·82	2·48	3·96	1920
$6\ 4\ \bar{1}$	2·96	3·53	3·89	3115
7 0 6	1·61	3·66	3·89	2851
$3\ 9\ \bar{6}$	4·56	1·54	3·81	2435
$4\ 4\ \overline{15}$	2·77	2·91	3·80	1956

The listings in Tables 1 and 2 were chosen from among the 28 largest $|\varepsilon'|_c$ values for naphthalene and the 44 largest values for myoinositol, resp. They were chosen to show the general trend and the extremes in agreement between $|\varepsilon'|_o$ and $|\varepsilon'|_c$. Several conclusions are apparent:

1. The largest $|\varepsilon'|_o$ are well reproduced by the calculated $|\varepsilon'|_c$.
2. The largest values of $|\varepsilon'|_o$ and $|\varepsilon'|_c$ are often associated with smaller values of $|\varepsilon|$.
3. Occasionally large values of $|\varepsilon'|_c$ are associated with small values of $|\varepsilon'|_o$.

In an actual application to structure determination the investigator would have only $|\varepsilon|$ and $|\varepsilon'|_c$ values available. It would not be apparent then when large $|\varepsilon'|_c$ are associated with small $|\varepsilon'|_o$. We note in Table 1 that the first such case for naphthalene occurs for $\mathbf{h}=(2,5,8)$, the twenty-seventh vector in the complete listing. Some moderate values of $|\varepsilon'|_o$ associated with large $|\varepsilon'|_c$ are seen to occur for myoinositol in Table 2. If the entire listings were available to the reader, it would be noted that such discrepancies increase in number and severity as one proceeds down the listing. Since the introduction of several large $|\varepsilon'|_c$ which really should be small, as indicated by the associated $|\varepsilon'|_o$, is undesirable in a phase determining procedure, it is important to consider how this might be avoided. There are several criteria which may be effectively employed, particularly in the initial stages of the phase determination, as follows:

(*a*) The results for $|\varepsilon'|_c$ may be accepted as given only down to some chosen cut-off value for $|\varepsilon'|_c$.

(*b*) Below the cut-off value for $|\varepsilon'|_c$, a minimum value for the $|\varepsilon|$, which are observed from experiment, would be required before accepting the computed quantity $|\varepsilon'|_c$.

(*c*) The somewhat smaller $|\varepsilon'|_c$ values associated with the largest values of $|\varepsilon|$ may be accepted.

The justification for criterion (*a*) is that generally there is good agreement between the very largest $|\varepsilon'|_c$ and their corresponding $|\varepsilon'|_o$. Criterion (*b*) implies that if a particular value of $|\varepsilon|$ is observed to be quite small, it is unlikely that the corresponding $|\varepsilon'|_o$ would reach an unusually large value. Similar considerations relate to criterion (*c*). The proper application of criterion (*b*) has the desired effect of eliminating most of the $|\varepsilon'|_c$ which are calculated to be much too large compared with the corresponding $|\varepsilon'|_o$, and only a few of the significant ones. An effective application of criteria (*a*) and (*b*) to naphthalene would involve, for example, the acceptance of all $|\varepsilon'|_c$ down to a cut-off value of 2·2 and the elimination of $|\varepsilon'|_c$ below this point for which $|\varepsilon| > 0{\cdot}5$. It would make little difference if the elimination criterion $|\varepsilon| > 0{\cdot}5$ were applied at the beginning of the listing. Criterion (*c*) could be implemented by specifying, for example, that all $|\varepsilon'|_c > 1{\cdot}7$ be accepted if $|\varepsilon| > 2{\cdot}0$. Similarly for myoinositol, all $|\varepsilon'|_c$ could be accepted down to a cut-off value of 4·0, and below this value the $|\varepsilon'|_c$ would be eliminated if $|\varepsilon| < 1 \cdot 0$ and accepted down to $|\varepsilon'|_c > 2 \cdot 8$ if $|\varepsilon| > 3 \cdot 0$. The numbers used for criteria (*a*), (*b*) and (*c*) with myoinositol are larger than those for napthalene because the number of atoms in the asymmetric unit is larger and the $|\varepsilon'|_c$ values are larger for myoinositol. The numbers used here in the application of the criteria are evidently somewhat arbitrary but should serve as a guide. It is not clear at this point how useful the introduction of additional statistical considerations would be for the present, and therefore the investigation of such matters is deferred. It might be pointed out however that further study along such lines would include considerations such as the number of atoms in the asymmetric unit, the relative amount of negative scattering matter, the number of terms contributing to a particular calculation and the variance of the individual terms.

Procedures for phase determination are particularly dependent in their initial stages on relationships among the largest $|\varepsilon'|$ values. Also, it is desirable to have at least ten phases among the larger $|\varepsilon'|$ values per atom in the asymmetric unit for the computation of a Fourier series. Thus the success of a procedure for structure determination, based upon the calculations presented here, depends on how well the computed larger $|\varepsilon'|_c$ are correlated with the larger $|\varepsilon'|_o$.

Aside from phase considerations, it is apparent that useful information should derive from comparing Patterson functions computed from the coefficients $|\varepsilon|^2$ and $|\varepsilon'|^2$ when both positive and negative scattering matter are present.

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An Alternative Method of Solving the Layer Scaling Equations of Hamilton, Rollett and Sparks

By G.C. Fox
Theoretical Nuclear Physics Group, Cavendish Laboratory, Cambridge, England

and K.C. Holmes
Laboratory of Molecular Biology, Hills Road, Cambridge, England

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The relationship between the methods of Dickerson (1959), Rollett & Sparks (1960), and Hamilton, Rollett & Sparks (1965) (HRS) is discussed, together with a short account of why the first two methods are unsatisfactory. An alternative iterative method (the method of 'shortest path') of solving the layer scaling equations of HRS is given which converges faster than the solution given by HRS. An exact solution of the equations of HRS is given which may be applied to situations where a simple weighting scheme may be used. The method of 'shortest path' may be important in protein crystallography where setting up the normal matrix may mean scanning 100000 reflexions and therefore the speed of convergence is of paramount importance.

Introduction

The purpose of this paper is threefold:

(*a*) To give an account of the relationship between the methods of Dickerson (1958), Rollett & Sparks (1960), and Hamilton, Rollett & Sparks (1965).

(*b*) To present an alternative iterative method (the method of 'shortest path') of solving the scaling equations of Hamilton, Rollett & Sparks (1965; we will refer to this paper as HRS), which converges faster than the solution given by these authors. The method of shortest path has the additional advantages that no fudge