The reaction yielding the ferrous complex which takes place in solution upon addition of 2,2′-bipyridine to a solution of a ferrous salt can only lead to the formation of a stable five-membered ring consisting of N_2–C_1–C_1'–N_2' and the Fe^{++} ion if the two nitrogen atoms are in the *cis* positions. Since in the solid crystalline form the nitrogen atoms lie in the *trans* positions, there must be rotation about the C_1–C_1' bond in solution in order for complex formation to be possible. The observed length of this bond would indicate that such rotation would be easily possible in solution.

The molecules in the unit cell of 2,2′-bipyridine show no unusually close approaches. The shortest intermolecular distances are 3·11 Å between the H_8 bonded to the C_4 in one ring and the C_3'' of the next molecule, and 3·12 Å between H_9 bonded to C_5 in one molecule and H_7'' bonded to C_3'' in the next molecule. Since the van der Waals radius of a carbon atom is about 1·7 Å and that of a hydrogen atom is about 1·3 Å, this indicates that the only forces between the molecules in the crystal are weak van der Waals forces. This is supported by the low melting point (69·5° C.) of this compound and also by the tendency of these crystals to sublime slowly in air at room temperatures.

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An Improvement of the 'Heavy-Atom' Method of Solving Crystal Structures

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For the normal heavy-atom method of solving crystal structures the Fourier series, whose coefficients are given in moduli by the observed intensities and in phase by the heavy-atom contribution, is summed. It is shown that a Fourier series with coefficients quite different from these shows the unknown part of the structure more clearly. A criterion for determining the degree of resolution of a structure is given and the advantage of the new series is demonstrated both theoretically and by means of practical examples.

Introduction

The 'heavy-atom' method of solving crystal structures is most frequently used for centrosymmetrical structures when one pair of atoms is sufficiently heavy to be detected by the Patterson function. With the observed structure amplitudes and phases given by the contribution of the known atom, a Fourier synthesis is calculated from which the position of the remaining atoms may be found. If the known atom is not heavy enough to dominate the phases of the complete structure, the remaining atoms will not show themselves. On the other hand, if the known atom is too heavy the relative contributions of the unknown atoms to the structure factors will be comparable in size with the experimental errors of the latter. The peaks of the Fourier synthesis due to random errors will then be of the same order as a peak height for one of the unknown atoms, whose positions will not be determined with any certainty.

Luzzati (1953) has given a theoretical treatment of the heavy-atom method as part of a more general

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paper which deals with the resolution of crystal structures when the positions of some atoms are known. The cases he considered are:

(*a*) two known atoms in a centrosymmetrical structure;
(*b*) many known atoms in a centrosymmetrical structure;
(*c*) many known atoms in a non-centrosymmetrical structure.

Luzzati suggested a criterion for deciding the degree of resolution which would be obtained in each of these cases.

The present paper deals primarily with case (*a*), and will briefly mention case (*b*). It will be shown that a Fourier synthesis with amplitudes and phases different from those normally used resolves the structure more clearly than the usual 'heavy-atom' synthesis. A criterion, different from that used by Luzzati, will be used to compare the resolution of structures in the two cases, both in theory and by means of practical examples. It will be assumed that there are no experimental errors in the observed data.

Derivation and properties of the new Fourier series

We shall consider a centrosymmetrical structure with N atoms per unit cell and with two atoms (related by a crystallographic centre of symmetry) in known positions. The atoms are assumed to have the same shape so that, for the jth atom,

$$n_j = f_j / \sum_{j=1}^{N} f_j$$

is a constant throughout reciprocal space.

We may write

$$f_j = \theta_{\mathbf{h}} n_j , \qquad (1)$$

where $\theta_{\mathbf{h}}$ is a function of $\sin\theta$, or alternatively of the position in reciprocal space denoted by the vector $\mathbf{h}$.

Then

$$F_{\mathbf{h}} = \sum_{j=1}^{N} f_j \cos 2\pi\mathbf{h}\cdot\mathbf{r}_j = \theta_{\mathbf{h}} \sum_{j=1}^{N} n_j \cos 2\pi\mathbf{h}\cdot\mathbf{r}_j = \theta_{\mathbf{h}} U_{\mathbf{h}} ,$$

where $U_{\mathbf{h}}$ is the unitary structure factor.

However,

$$U_{\mathbf{h}} = \sum_{j=3}^{N} n_j \cos 2\pi\mathbf{h}\cdot\mathbf{r}_j + 2n_H \cos 2\pi\mathbf{h}\cdot\mathbf{r}_H ,$$

where the subscript H denotes the value of the quantity for the atoms of known position.

Then

$$\sum_{j=3}^{N} n_j \cos 2\pi\mathbf{h}\cdot\mathbf{r}_j = U_{\mathbf{h}} - C_{\mathbf{h}} ,$$

where

$$C_{\mathbf{h}} = 2n_H \cos 2\pi\mathbf{h}\cdot\mathbf{r}_H .$$

The sign of $U_{\mathbf{h}}$ is unknown, but if $U_{\mathbf{h}}C_{\mathbf{h}}$ is positive and S_c is the sign of $C_{\mathbf{h}}$ then

$$\sum_{j=3}^{N} n_j \cos 2\pi\mathbf{h}\cdot\mathbf{r}_j = S_c\{|U_{\mathbf{h}}| - |C_{\mathbf{h}}|\} , \qquad (2)$$

while if $U_{\mathbf{h}}C_{\mathbf{h}}$ is negative

$$\sum_{j=3}^{N} n_j \cos 2\pi\mathbf{h}\cdot\mathbf{r}_j = -S_c\{|U_{\mathbf{h}}| + |C_{\mathbf{h}}|\} . \qquad (3)$$

The ratio of the probability that $U_{\mathbf{h}}C_{\mathbf{h}}$ is positive, $P_+(U_{\mathbf{h}}C_{\mathbf{h}})$, divided by the probability that $U_{\mathbf{h}}C_{\mathbf{h}}$ is negative, $P_-(U_{\mathbf{h}}C_{\mathbf{h}})$, may be found from the probability distribution of structure factors given by Wilson (1949), and is

$$\frac{P_+(U_{\mathbf{h}}C_{\mathbf{h}})}{P_-(U_{\mathbf{h}}C_{\mathbf{h}})} = \frac{\exp\left\{-\frac{1}{2\varepsilon'}(|U_{\mathbf{h}}| - |C_{\mathbf{h}}|)^2\right\}}{\exp\left\{-\frac{1}{2\varepsilon'}(|U_{\mathbf{h}}| + |C_{\mathbf{h}}|)^2\right\}} = \exp\left(\frac{2}{\varepsilon'}|U_{\mathbf{h}}C_{\mathbf{h}}|\right),$$

where

$$\varepsilon' = \sum_{j=3}^{N} n_j^2 .$$

Since

$$P_+(U_{\mathbf{h}}C_{\mathbf{h}}) + P_-(C_{\mathbf{h}}U_{\mathbf{h}}) = 1 ,$$

we find

$$P_+(U_{\mathbf{h}}C_{\mathbf{h}}) = \tfrac{1}{2} + \tfrac{1}{2}\tanh\left(\frac{|U_{\mathbf{h}}C_{\mathbf{h}}|}{\varepsilon'}\right) \qquad (4)$$

and

$$P_-(U_{\mathbf{h}}C_{\mathbf{h}}) = \tfrac{1}{2} - \tfrac{1}{2}\tanh\left(\frac{|U_{\mathbf{h}}C_{\mathbf{h}}|}{\varepsilon'}\right) . \qquad (5)$$

For a given pair of values $|U_{\mathbf{h}}|$ and $C_{\mathbf{h}}$, the average value of

$$\sum_{j=3}^{N} n_j \cos 2\pi\mathbf{h}\cdot\mathbf{r}_j$$

will be

$$S_c\{|U_{\mathbf{h}}| - |C_{\mathbf{h}}|\}P_+(U_{\mathbf{h}}C_{\mathbf{h}}) - S_c\{|U_{\mathbf{h}}| + |C_{\mathbf{h}}|\}P_-(U_{\mathbf{h}}C_{\mathbf{h}}) ,$$

or

$$\overline{\sum_{j=3}^{N} n_j \cos 2\pi\mathbf{h}\cdot\mathbf{r}_j} = S_c\left\{|U_{\mathbf{h}}| \tanh\left(\frac{|U_{\mathbf{h}}C_{\mathbf{h}}|}{\varepsilon'}\right) - |C_{\mathbf{h}}|\right\} .$$

In the case where the sign of $U_{\mathbf{h}}$ is indicated by the value of $C_{\mathbf{h}}$ it can be seen that the quantity

$$S_c\left\{|U_{\mathbf{h}}| \tanh\left(\frac{|U_{\mathbf{h}}C_{\mathbf{h}}|}{\varepsilon'}\right) - |C_{\mathbf{h}}|\right\}$$

is playing the same role, in a statistical sense, for the $N-2$ unknown atoms as $U_{\mathbf{h}}$ normally plays for all the atoms.

This leads us to examine the properties of the Fourier series

$$\sigma_{\mathbf{r}} = \sum_{T} \theta_{\mathbf{h}} S_c\left\{|U_{\mathbf{h}}| \tanh\left(\frac{|U_{\mathbf{h}}C_{\mathbf{h}}|}{\varepsilon'}\right) - |C_{\mathbf{h}}|\right\} \cos 2\pi\mathbf{h}\cdot\mathbf{r} , \qquad (6)$$

where the summation is over T reflexions, the total number available. It is actually proved in Appendix III that these values for the Fourier coefficients give the best resolution for the unknown atoms according to the criterion of resolution given in the following section.

When there is no atom of known position, but $U_{\mathbf{h}}$ is known in sign and magnitude, the expected value of $\cos 2\pi\mathbf{h}\cdot\mathbf{r}_j$ is given by

$$\overline{\cos 2\pi\mathbf{h}\cdot\mathbf{r}_j} = \frac{n_j}{\varepsilon} U_{\mathbf{h}} ,$$

where

$$\varepsilon = \sum_{j=1}^{N} n_j^2 ,$$

a result given by Cochran & Woolfson (1955).

Similarly, we see that when the heavy-atom position is known the expected value of $\cos 2\pi\mathbf{h}\cdot\mathbf{r}_j$ is

$$\overline{\cos 2\pi\mathbf{h}\cdot\mathbf{r}_j} = \frac{n_j}{\varepsilon'} S_c \left\{ |U_{\mathbf{h}}| \tanh\left(\frac{|U_{\mathbf{h}}C_{\mathbf{h}}|}{\varepsilon'}\right) - |C_{\mathbf{h}}| \right\} . \qquad (7)$$

The expected value of $\sigma_{\mathbf{r}}$ at the centre of the jth atom is

$$\begin{aligned}\overline{\sigma_{\mathbf{r}_j}} &= \overline{\sum_T \theta_{\mathbf{h}} S_c \left\{ |U_{\mathbf{h}}| \tanh\left(\frac{|U_{\mathbf{h}}C_{\mathbf{h}}|}{\varepsilon'}\right) - |C_{\mathbf{h}}| \right\} \cos 2\pi\mathbf{h}\cdot\mathbf{r}_j} \\ &= \frac{n_j}{\varepsilon'} \overline{\theta_{\mathbf{h}}}^h \sum_T \left\{ |U_{\mathbf{h}}| \tanh\left(\frac{|U_{\mathbf{h}}C_{\mathbf{h}}|}{\varepsilon'}\right) - |C_{\mathbf{h}}| \right\}^2 \\ &= \frac{n_j}{\varepsilon'} \overline{\theta_{\mathbf{h}}}^h T \overline{\left\{ |U_{\mathbf{h}}| \tanh\left(\frac{|U_{\mathbf{h}}C_{\mathbf{h}}|}{\varepsilon'}\right) - |C_{\mathbf{h}}| \right\}^2}^{U,C} . \qquad (8)\end{aligned}$$

The symbols to the right of the averaging bars are the variables over which the averages are taken.

The probability $P(U, C)\,dU\,dC$ that $|U_{\mathbf{h}}|$ lies between U and $U+dU$, while at the same time $|C_{\mathbf{h}}|$ lies between C and $C+dC$, is found in Appendix I.

Then

$$\begin{aligned}&\overline{\left\{ |U_{\mathbf{h}}| \tanh\left(\frac{|U_{\mathbf{h}}C_{\mathbf{h}}|}{\varepsilon'}\right) - |C_{\mathbf{h}}| \right\}^2}^{U,C} \\ &\quad = \int_{U=0}^{1} \int_{C=0}^{2n_H} P(U, C) \left\{ U \tanh\left(\frac{UC}{\varepsilon'}\right) - C \right\}^2 dU\,dC ,\end{aligned}$$

the modulus brackets having been dropped on the right-hand side of this equation because the quantities U and C are constrained to be positive by the limits of the integration.

From this we find

$$\begin{aligned}\sigma_{\mathbf{r}_j} &= 2\sqrt{\left(\frac{2}{\pi^3\varepsilon'^3}\right)} n_j \overline{\theta_{\mathbf{h}}}^h T \int_{U=0}^{1} \int_{C=0}^{2n_H} \left\{ U \tanh\left(\frac{UC}{\varepsilon'}\right) - C \right\}^2 \\ &\times \exp\left(-\frac{U^2+C^2}{2\varepsilon'}\right) \cosh\left(\frac{UC}{\varepsilon'}\right) (4n_H^2 - C^2)^{-\frac{1}{2}}\, dU\,dC . \qquad (9)\end{aligned}$$

Substituting

$$U = \sqrt{(\varepsilon')}X, \quad C = 2n_H \sin\varphi \quad \text{and} \quad 2n_H/\sqrt{\varepsilon'} = \alpha ,$$

we have

$$\begin{aligned}\sigma_{\mathbf{r}_j} &= 2\sqrt{\left(\frac{2}{\pi^3}\right)} n_j \overline{\theta_{\mathbf{h}}}^h T \\ &\times \int_{X=0}^{1/\sqrt{\varepsilon'}} \int_{C=0}^{\pi/2} \{X \tanh(X\alpha \sin\varphi) - \alpha \sin\varphi\}^2 \\ &\times \exp\left(-\frac{X^2+\alpha^2 \sin^2\varphi}{2}\right) \cosh(X\alpha \sin\varphi)\, dX\, d\varphi . \qquad (10)\end{aligned}$$

It may be shown that if $\varepsilon'^{-\frac{1}{2}}$ (which is of the order $N^{\frac{1}{2}}$) is greater than 3 the upper limit of X in (10) may be replaced by ∞ without appreciable error. Then

$$\overline{\sigma_{\mathbf{r}_j}} = n_j \overline{\theta_{\mathbf{h}}}^h T \psi(\alpha) , \qquad (11)$$

where $\psi(\alpha)$ is a function of α given by

$$\begin{aligned}\psi(\alpha) &= 2\sqrt{\left(\frac{2}{\pi^3}\right)} \int_{X=0}^{\infty} \int_{\varphi=0}^{\pi/2} \{X \tanh(X\alpha \sin\varphi) - \alpha \sin\varphi\}^2 \\ &\times \exp\left(-\frac{X^2+\alpha^2 \sin^2\varphi}{2}\right) \cosh(X\alpha \sin\varphi)\, dX\, d\varphi . \qquad (12)\end{aligned}$$

For a Fourier synthesis with coefficients $\theta_{\mathbf{h}}U_{\mathbf{h}}$, correct in amplitude and phase, the value at the centre of the jth atom is $n_j\overline{\theta_{\mathbf{h}}}^h T$. The value of $\psi(\alpha)$ is thus the ratio of the expected height of an atomic peak given by the function $\sigma_{\mathbf{r}}$ to that given by the Fourier synthesis with correct amplitudes and phases.

Luzzati (1953) showed that the expected height of an atomic peak given by the straightforward application of the heavy-atom method is χ times the true height, where χ is a function of α; χ is tabulated by Luzzati in terms of the variable φ ($= \frac{1}{2}\alpha^2$). A comparison of $\psi(\alpha)$ and χ for various values of α is given in Table 1. This table shows that for values of α less than about unity the normal application of the heavy-atom method gives higher peaks for the unknown atoms than does $\sigma_{\mathbf{r}}$. But this alone cannot be used as a criterion of resolution: the size of peaks may be doubled by doubling all the coefficients without any gain in resolution whatsoever. The fair comparison of

Table 1

α	$\psi(\alpha)$	χ	$\xi(\alpha)$	$\mu_\sigma/\mu_{\sigma'}$
0·00	0·000	0·000	1·000	2·00
0·25	0·057	0·128	0·869	1·74
0·50	0·187	0·246	0·795	1·57
0·75	0·330	0·359	0·746	1·38
1·00	0·454	0·457	0·724	1·25
1·50	0·632	0·609	0·761	1·14
2·00	0·733	0·715	0·802	1·07
3·00	0·832	0·818	0·870	1·04
4·00	0·873	0·870	0·911	1·02
6·00	0·918	0·915	0·939	1·02
8·00	0·939	0·936	0·954	1·01
∞	1·000	1·000	1·000	1·00

the resolution in the two cases is dealt with in the next section.

The criterion of resolution

The criterion of resolution for a particular atom, as shown by a function $\varrho_{\mathbf{r}}$, which will be used here, is similar to one proposed by Cochran (1952). This is expressed as the value of

$$\mu = \frac{\overline{\varrho_{\mathbf{r}j} - \overline{\varrho_{\mathbf{r}}}^{r}}}{\left\{\overline{(\varrho_{\mathbf{r}} - \overline{\varrho_{\mathbf{r}}})^2}^{r}\right\}^{\frac{1}{2}}} . \tag{13}$$

The greater the value of μ, the more the atom stands out in comparison to the root-mean-square fluctuation of the function about its mean value.

For the function $\sigma_{\mathbf{r}}$ given by (7) it can be shown that

$$\overline{(\sigma_{\mathbf{r}} - \overline{\sigma_{\mathbf{r}}}^{r})^2}^{r} = T\overline{\theta_{\mathbf{h}}^2}^{h}\overline{\left\{|U_{\mathbf{h}}|\tanh\left(\frac{|U_{\mathbf{h}}C_{\mathbf{h}}|}{\varepsilon'}\right) - |C_{\mathbf{h}}|\right\}^2}^{u,c} . \tag{14}$$

The application of the results of equations (8), (11) and (14) to (13) gives

$$\mu = n_j\overline{\theta_{\mathbf{h}}}^{h}\left\{\frac{T\psi(\alpha)}{\varepsilon'\overline{\theta_{\mathbf{h}}^2}^{h}}\right\}^{\frac{1}{2}} . \tag{15}$$

It should be noted that $\sigma_{\mathbf{r}}$ has the characteristics of a difference synthesis: the heavy atom does not contribute to the Fourier coefficients and so does not appear. In the case of $\gamma_{\mathbf{r}}$, the function produced by the Fourier series with coefficients $S_c|U_{\mathbf{h}}|$, the heavy atom does appear, enhanced in fact above its normal size. If the value of μ was found for this function the value would be greatly affected by the large contribution of the heavy-atom peak to the divisor of equation (15). This can be avoided by considering the value of μ for $\gamma'_{\mathbf{r}}$, the Fourier coefficients of which are $S_c\{|U_{\mathbf{h}}| - |C_{\mathbf{h}}|\}$. This will be identical with $\gamma_{\mathbf{r}}$ with the heavy-atom peak removed.

It is shown in Appendix II that

$$\mu_{\gamma'} = n_j\overline{\theta_{\mathbf{h}}}^{h}\chi\left\{\frac{T}{\varepsilon'\overline{\theta_{\mathbf{h}}^2}^{h}\xi(\alpha)}\right\}^{\frac{1}{2}} , \tag{16}$$

where $\xi(\alpha)$ is a function of α. The efficiency of $\sigma_{\mathbf{r}}$ compared with $\gamma'_{\mathbf{r}}$ in resolving atoms may be expressed as

$$\frac{\mu_\sigma}{\mu_{\gamma'}} = \frac{\{\psi(\alpha)\xi(\alpha)\}^{\frac{1}{2}}}{\chi} , \tag{17}$$

which is tabulated in Table 1, together with $\xi(\alpha)$.

It can be seen that for small values of α the function $\sigma_{\mathbf{r}}$ is substantially better than $\gamma'_{\mathbf{r}}$ (or $\gamma_{\mathbf{r}}$). For larger values of α the two functions become more equal in efficiency, each approximating to the completely correct answer.

Practical examples

The example considered here is a two-dimensional structure containing 12 atoms per unit cell with space group $P\bar{1}$. There are 2 known atoms related by the centre of symmetry for which

$$f_H = n_H \exp\left[-\sin^2\theta\right] ,$$

and 10 others for which

$$f_j = n_j \exp\left[-\sin^2\theta\right] .$$

The three cases considered are, $n_H = n_j$, $n_H = 2n_j$ and $n_H = 3n_j$, for each of which the functions $\sigma_{\mathbf{r}}$ and $\gamma_{\mathbf{r}}$ are calculated and shown in Fig. 1. The indices of the reflexions used are those for which $h^2+k^2 \leq 100$. The values of $\mu_{\gamma'}$ and μ_σ for the jth atom are as follows:

$n_H = n_j$: $\mu_{\gamma'} = 1{\cdot}66$, $\mu_\sigma = 2{\cdot}43$;
$n_H = 2n_j$: $\mu_{\gamma'} = 3{\cdot}00$, $\mu_\sigma = 3{\cdot}51$;
$n_H = 3n_j$: $\mu_{\gamma'} = 3{\cdot}70$, $\mu_\sigma = 4{\cdot}00$.

It will be noticed from Fig. 1 that the values of μ do give a good indication of the resolution to be expected. The critical value of μ at which an atom becomes clearly seen is about 3. This example shows clearly the advantage of using the function $\sigma_{\mathbf{r}}$ rather than $\gamma_{\mathbf{r}}$ for finding the unknown atoms. The theoretical values of μ enable one to predict whether or not the structure will be found from the position of the known atom.

More than two known atoms

It is fairly evident that the coefficients to be used in this case are, as before,

$$S_c\theta_{\mathbf{h}}\left\{|U_{\mathbf{h}}|\tanh\left(\frac{|U_{\mathbf{h}}C_{\mathbf{h}}|}{\varepsilon'}\right) - |C_{\mathbf{h}}|\right\} ,$$

where

$$C_{\mathbf{h}} = \sum_k n_j \cos 2\pi\mathbf{h}\cdot\mathbf{r}_j$$

and is the contribution of the k known atoms. The calculations for μ have not been carried out in this case, although it is expected that the advantage factor will be of the same order as in the case of $k = 2$. The quantity corresponding to α will now be

$$(2\sum_k n_i^2 / \sum_{N-k} n_j^2)^{\frac{1}{2}} .$$

Conclusions

An examination of Fig. 1 shows the advantages of $\sigma_{\mathbf{r}}$ compared with $\gamma_{\mathbf{r}}$ for finding the unknown atoms. Part of the improvement may be due to the fact that $\sigma_{\mathbf{r}}$ excludes the heavy atom and the diffraction ripples associated with it. However, this will only interfere with the recognition of a structure if one of the lighter atoms is close to the heavy atom, and the theory comparing the efficacy of the two functions

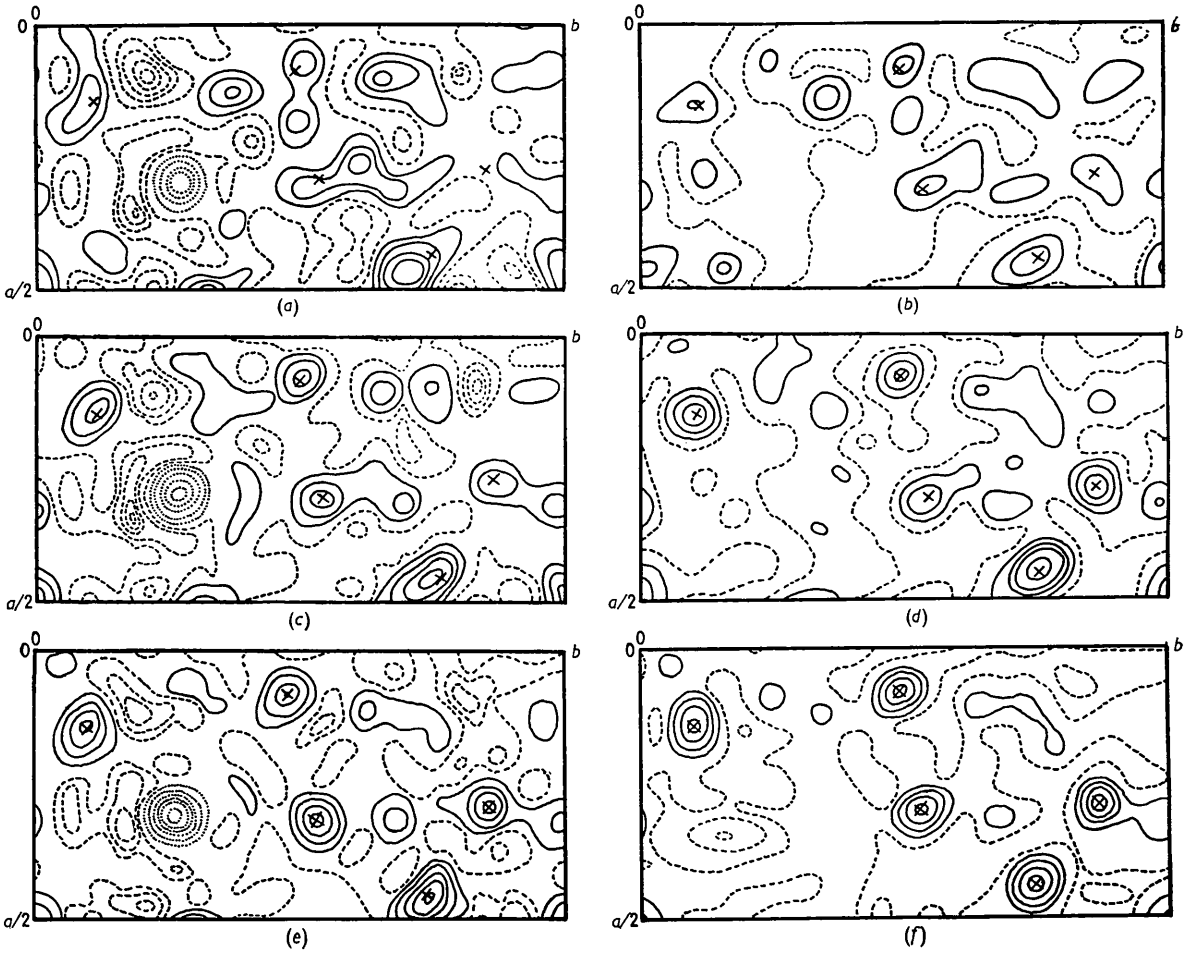

Fig. 1. The functions shown are as follows:

(*a*) $\gamma_{\mathbf{r}}$ for $n_H = n_j$; (*b*) $\sigma_{\mathbf{r}}$ for $n_H = n_j$;
(*c*) $\gamma_{\mathbf{r}}$ for $n_H = 2n_j$; (*d*) $\sigma_{\mathbf{r}}$ for $n_H = 2n_j$;
(*e*) $\gamma_{\mathbf{r}}$ for $n_H = 3n_j$; (*f*) $\sigma_{\mathbf{r}}$ for $n_H = 3n_j$.

The contours are drawn at unit intervals of these functions. The zero and negative contours are drawn as dashed lines. Dotted contours are drawn round the 'heavy' atom at 3, 6, 9, ... etc. units.

has allowed for the removal of the heavy atom from $\gamma_{\mathbf{r}}$ to give the function $\gamma'_{\mathbf{r}}$. The advantage of $\sigma_{\mathbf{r}}$ may, in fact, be more evident in theory than in practice. If $\mu_{\gamma'}$ and μ_{σ} are both low then, albeit that $\mu_{\sigma}/\mu_{\gamma'}$ may be fairly large, neither function will reveal the structure; if they are both large the structure may be clearly seen in $\sigma_{\mathbf{r}}$ and in $\gamma_{\mathbf{r}}$ and again there is no real advantage. It is for intermediate values of μ that some practical advantage may be obtained. Another point to be considered in this respect is that $\gamma_{\mathbf{r}}$ itself is not often calculated; when the indication of a sign is weak because $|C_{\mathbf{h}}|$ is small the appropriate term is usually omitted from the Fourier series. It can be seen that the determination of the Fourier coefficients for $\sigma_{\mathbf{r}}$ really amounts to putting discretion on to a mathematical basis. If $|C_{\mathbf{h}}|$ is small the term goes in with small amplitude whereas if $|C_{\mathbf{h}}|$ is large the amplitude approximates to $S_c\{|U_{\mathbf{h}}|-|C_{\mathbf{h}}|\}$, which is the value it would have if the sign was given with certainty. For this reason $\sigma_{\mathbf{r}}$ may not be so much better than the function one would normally calculate, although there can be little doubt that it would be better to some extent. A point which is definitely clarified by the results of this paper is that the indiscriminate acceptance of signs hinders the process of structure determination: it does not pay to put in all the Fourier coefficients in the first place, a practice which is not unknown amongst crystallographers.

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APPENDIX I

The probability that $|C_{\mathbf{h}}|$ lies between C and $C+dC$ is the probability that $\cos 2\pi\mathbf{h}\cdot\mathbf{r}_H$ lies between $C/2n_H$ and $(C+dC)/2n_H$. This is

$$P_{|C|}dC = \frac{2}{\pi}(4n_H^2-C^2)^{-\frac{1}{2}}dC\,.$$

The value of

$$\sum_{j=3}^{N} n_j \cos 2\pi\mathbf{h}\cdot\mathbf{r}_j$$

must then be either $S_c\{|U_{\mathbf{h}}|-|C_{\mathbf{h}}|\}$ or $-S_c\{|U_{\mathbf{h}}|+|C_{\mathbf{h}}|\}$ to give $|U_{\mathbf{h}}| = U$, depending on whether $U_{\mathbf{h}}C_{\mathbf{h}}$ is positive or negative.

From the distribution of structure factors given by Wilson (1949) the probability that $|U_{\mathbf{h}}|$ will lie between U and $U+dU$ for a fixed value of C is then

$$P_{|U|}dU = (2\pi\varepsilon')^{-\frac{1}{2}}\left[\exp\left\{-\frac{(|U|+|C|)^2}{2\varepsilon'}\right\} + \exp\left\{-\frac{(|U|-|C|)^2}{2\varepsilon'}\right\}\right]dU\,.$$

The probability that $|C_{\mathbf{h}}|$ will be between C and $C+dC$ while at the same time $|U_{\mathbf{h}}|$ is between U and $U+dU$ is thus $P(U,C)dU\,dC = P_{|U|}P_{|C|}dU\,dC$.

Then

$$P(U,C)dU\,dC = \sqrt{\left(\frac{2}{\pi^3\varepsilon'}\right)}\left[\exp\left\{-\frac{(|U|+|C|)^2}{2\varepsilon'}\right\} + \exp\left\{-\frac{(|U|-|C|)^2}{2\varepsilon'}\right\}\right](4n_H^2-C^2)^{-\frac{1}{2}}dU\,dC$$
$$= 2\sqrt{\left(\frac{2}{\pi^3\varepsilon'}\right)}\exp\left(-\frac{U^2+C^2}{2\varepsilon'}\right)\cosh\left(\frac{UC}{\varepsilon'}\right) \times (4n_H^2-C^2)^{-\frac{1}{2}}dU\,dC\,.$$

APPENDIX II

$$\gamma'_{\mathbf{r}} = \sum_{T} S_c\theta_{\mathbf{h}}(|U_{\mathbf{h}}|-|C_{\mathbf{h}}|)\cos 2\pi\mathbf{h}\cdot\mathbf{r}\,.$$

Since the terms on the right-hand side occur in equivalent pairs ($\mathbf{h}$ and $-\mathbf{h}$) we may write

$$2\sum_{\frac{1}{2}T} S_c\theta_{\mathbf{h}}(|U_{\mathbf{h}}|-|C_{\mathbf{h}}|)\cos 2\pi\mathbf{h}\cdot\mathbf{r}\,,$$

the summation now being over half the total number of reflexions.

Then

$$(\gamma'_{\mathbf{r}})^2 = 4\Big\{\sum_{\frac{1}{2}T} S_c\theta_{\mathbf{h}}(|U_{\mathbf{h}}|-|C_{\mathbf{h}}|)\cos 2\pi\mathbf{h}\cdot\mathbf{r}\Big\}^2$$
$$= 4\sum_{\frac{1}{2}T}\theta_{\mathbf{h}}^2(|U_{\mathbf{h}}|-|C_{\mathbf{h}}|)^2\cos^2 2\pi\mathbf{h}\cdot\mathbf{r} + 2\sum_{\frac{1}{4}T^2-\frac{1}{2}T}\theta_{\mathbf{h}}\theta_{\mathbf{h}'}(|U_{\mathbf{h}}|-|C_{\mathbf{h}}|)(|U_{\mathbf{h}'}|-|C_{\mathbf{h}'}|) \times\{\cos 2\pi(\mathbf{h}+\mathbf{h}')\cdot\mathbf{r}+\cos 2\pi(\mathbf{h}-\mathbf{h}')\cdot\mathbf{r}\}\,.$$

We now use the results

$$\overline{\cos^2 2\pi\mathbf{h}\cdot\mathbf{r}}^r = \tfrac{1}{2} \quad\text{and}\quad \overline{\cos 2\pi\mathbf{h}\cdot\mathbf{r}}^r = 0\,.$$

Then

$$\overline{\gamma'^2_{\mathbf{r}}}^r = 2\sum_{\frac{1}{2}T}\theta_{\mathbf{h}}^2(|U_{\mathbf{h}}|-|C_{\mathbf{h}}|)^2 = T\overline{\theta_{\mathbf{h}}^2}^h\overline{(|U_{\mathbf{h}}|-|C_{\mathbf{h}}|)^2}^h\,.$$

If we assume that the values of $U_{\mathbf{h}}$ and $C_{\mathbf{h}}$ which occur for the structure have the expected theoretical distributions, we may replace $\overline{(|U_{\mathbf{h}}|-|C_{\mathbf{h}}|)^2}^h$ by $\overline{(|U_{\mathbf{h}}|-|C_{\mathbf{h}}|)^2}^{u,c}$.

Dropping the subscripts, we may write

$$\overline{(|U|-|C|)^2}^{u,c} = \overline{U^2}^u + \overline{C^2}^c - 2\overline{|UC|}^{u,c}\,.$$

Now

$$\overline{U^2}^u = \sum_{j=1}^{N} n_j^2 = \varepsilon\,,$$
$$\overline{C^2}^c = 2n_H^2$$

and

$$UC = \Big\{\sum_{j=1}^{N} n_j\cos 2\pi\mathbf{h}\cdot\mathbf{r}_j\Big\}(2n_H\cos 2\pi\mathbf{h}\cdot\mathbf{r}_H)$$
$$= 4n_H^2\cos^2 2\pi\mathbf{h}\cdot\mathbf{r}_H + 2\sum_{j=3}^{N} n_Hn_j\cos 2\pi\mathbf{h}\cdot\mathbf{r}_H\cos 2\pi\mathbf{h}\cdot\mathbf{r}_j\,.$$

If we consider a fixed value of C, then by the application of the central-limit theorem we may find the probability that UC lies between UC and $UC+dUC$. This is

$$P(UC)dUC = (2\pi\varepsilon' X)^{-\frac{1}{2}}\exp\left\{-\frac{(UC-2X)^2}{2X\varepsilon'}\right\}dUC\,,$$

where $X = 2n_H^2\cos^2 2\pi\mathbf{h}\cdot\mathbf{r}_H$.

From this we find that

$$P(|UC|)d|UC| = (2\pi\varepsilon' X)^{-\frac{1}{2}}\left[\exp\left\{-\frac{(|UC|-2X)^2}{2X\varepsilon'}\right\} + \exp\left\{-\frac{(|UC|+2X)^2}{2X\varepsilon'}\right\}\right]d|UC|\,.$$

The mean value of $|UC|$ for a fixed value of C is then

$$\overline{|UC|}^u = (2\pi\varepsilon' X)^{-\frac{1}{2}}\int_{|UC|=0}^{\infty}\left[\exp\left\{-\frac{(|UC|-2X)^2}{2X\varepsilon'}\right\} + \exp\left\{-\frac{(|UC|+2X)^2}{2X\varepsilon'}\right\}\right]|UC|\,d|UC|$$
$$= \left(\frac{X\varepsilon'}{2\pi}\right)^{\frac{1}{2}}\exp\left(-\frac{2X}{\varepsilon'}\right) + 4X\varphi\left(2\sqrt{\frac{X}{\varepsilon'}}\right)\,,$$

where

$$\varphi(x) = (2\pi)^{-\frac{1}{2}}\int_{t=0}^{x}\exp(-\tfrac{1}{2}t^2)\,dt$$

is the probability integral which may be found tabulated in Uspensky (1937).

Then

$$\overline{|UC|}^{u,c} = \overline{\left(\frac{X\varepsilon'}{2\pi}\right)^{\frac{1}{2}} \exp\left(-\frac{2X}{\varepsilon'}\right)}^{c} + \overline{4X\varphi\left(2\sqrt{\frac{X}{\varepsilon'}}\right)}^{c}$$

$$= \frac{2}{\pi}\left(\frac{\varepsilon'}{\pi}\right)^{\frac{1}{2}} n_H \int_{\theta=0}^{\frac{\pi}{2}} \cos\theta \exp(-\alpha^2\cos^2\theta)\,d\theta$$

$$+ \frac{16n_H^2}{\pi}\int_{\theta=0}^{\frac{\pi}{2}} \cos^2\theta\,\varphi(\sqrt{2}\alpha\cos\theta)\,d\theta\,.$$

From this we find

$$\overline{(|U|-|C|)^2}^{u,c} = \varepsilon + 2n_H^2$$

$$-\frac{4}{\pi}\left(\frac{\varepsilon'}{\pi}\right)^{\frac{1}{2}} n_H \int_{\theta=0}^{\frac{\pi}{2}} \cos\theta \exp(-\alpha^2\cos^2\theta)\,d\theta$$

$$-\frac{32n_H^2}{\pi}\int_{\theta=0}^{\frac{\pi}{2}} \cos^2\theta\,\varphi(\sqrt{2}\alpha\cos\theta)\,d\theta\,,$$

and, since $\varepsilon = \varepsilon' + 2n_H^2$, this becomes

$$\overline{(|U|-|C|)^2}^{u,c}$$

$$= \varepsilon'\left[1+\alpha^2\left\{1-\frac{8}{\pi}\int_{\theta=0}^{\frac{\pi}{2}} \cos^2\theta\,\varphi(\sqrt{2}\alpha\cos\theta)\,d\theta\right\}\right.$$

$$\left.-\frac{4\alpha}{\pi^{\frac{3}{2}}}\int_{\theta=0}^{\frac{\pi}{2}} \cos\theta\exp(-\alpha^2\cos^2\theta)\,d\theta\right] = \varepsilon'\xi(\alpha)\,,$$

where $\xi(\alpha)$ is a function of α. This has been calculated for various values of α by normal methods of numerical analysis and is given for these values in Table 1.

When

$$\overline{\gamma_{\mathbf{r}}'^2}^{r} = T\overline{\theta_{\mathbf{h}}^2}^{h}\varepsilon'\xi(\alpha)$$

the expected value of $\gamma_{\mathbf{r}_j}'$ is given by

$$\overline{\gamma_{\mathbf{r}_j}'} = \overline{\gamma_{\mathbf{r}_j}} = n_j\overline{\theta_{\mathbf{h}}}^{h} T\chi\,,$$

and hence we find

$$\mu_{\gamma'} = n_j\overline{\theta_{\mathbf{h}}}^{h}\chi\left\{\frac{T}{\varepsilon'\overline{\theta_{\mathbf{h}}^2}^{h}\xi(\alpha)}\right\}^{\frac{1}{2}}.$$

APPENDIX III

When the position of the heavy atom is known the expected value of $\cos 2\pi\mathbf{h}\cdot\mathbf{r}$ at the centre of the jth atom is given by (7) as

$$\overline{\cos 2\pi\mathbf{h}\cdot\mathbf{r}_j} = \frac{n_j}{\varepsilon'}S_c\left\{|U_{\mathbf{h}}|\tanh\left(\frac{|U_{\mathbf{h}}C_{\mathbf{h}}|}{\varepsilon'}\right) - |C_{\mathbf{h}}|\right\}$$

$$= x_{\mathbf{h}}\,,\ \text{say}\,.$$

If we consider the function

$$\sigma_{\mathbf{r}} = \sum_T A_{\mathbf{h}}\cos 2\pi\mathbf{h}\cdot\mathbf{r}\,,$$

then

$$\overline{\sigma_{\mathbf{r}_j}\sigma_{\mathbf{r}}} = \sum_T A_{\mathbf{h}}x_{\mathbf{h}}$$

and

$$\left\{\overline{(\sigma_{\mathbf{r}_j}-\overline{\sigma_{\mathbf{r}}})^2}^{r}\right\}^{\frac{1}{2}} = \left(\sum_T A_{\mathbf{h}}^2\right)^{\frac{1}{2}}.$$

The value of μ_{σ_j} is then found from (13) and is

$$\mu_{\sigma_j} = \sum_T A_{\mathbf{h}}x_{\mathbf{h}}/\left(\sum_T A_{\mathbf{h}}^2\right)^{\frac{1}{2}}.$$

Since multiplying all the A's by a common factor does not affect the value of μ_{σ_j}, the problem of maximizing μ_{σ_j} may be expressed as finding the maximum value of $\sum_T A_{\mathbf{h}}x_{\mathbf{h}}$ for a fixed value $\sum_T A_{\mathbf{h}}^2$.

Now

$$d\left(\sum_T A_{\mathbf{h}}x_{\mathbf{h}}\right) = \sum_T x_{\mathbf{h}}\,dA_{\mathbf{h}} = 0 \quad \text{for} \quad \sum_T A_{\mathbf{h}}x_{\mathbf{h}}$$

to be a maximum

and

$$d\left(\sum_T A_{\mathbf{h}}^2\right) = 2\sum_T A_{\mathbf{h}}\,dA_{\mathbf{h}} = 0 \quad \text{for} \quad \sum_T A_{\mathbf{h}}^2$$

to be a constant.

The values of $x_{\mathbf{h}}$ will thus satisfy the first condition if $A_{\mathbf{h}}/x_{\mathbf{h}}$ is a constant for all $\mathbf{h}$.

The function given by (6) takes the value of this constant as unity.

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