

X-ray scattering factor for NH_4^+ at rest from the observed radial scattering factors f_0, f_4 . Such a result yields, however, only the qualitative conclusion, already reached in the X-ray analysis, that the one-centre SCF calculations do not give large enough non-spherical components, *i.e.*, they do not yield a sharp enough concentration of charge around the hydrogen atoms. Observations on another dynamical state (*e.g.* temperature variation, isotopic replacement ND_4) would give, at least in principle, complementary information on the physical basis of this deviation. Such studies would gain substantially from theoretical scattering factors of free NH_4^+ , with the observed bond length and with some internal dynamics included to account for the observed average bond vibrations. The anisotropy of chlorine vibrations is, in any case, far too small to cause observable effects in the X-ray scattering factor of chlorine.

We are indebted to Dr. R. Tellgren for providing the single crystal used for the neutron diffraction work, and to Miss S. Rosten for her invaluable help with the computational work. This study was financially supported by the National Council for Science, Finland (K.K-S. and M.M.) and by the University of Helsinki (M.M.).

References

- BACON, G. E. (1972). *Acta Cryst.* A28, 357–358.
 BOIKO, A. A. (1970). *Sov. Phys. Crystallogr.* 14, 539–543.
 COPPENS, P. (1970). *Thermal Neutron Diffraction*, Edited by B. T. M. WILLIS, pp. 82–100. Oxford Univ. Press.
 COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A26, 71–83.
 COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* 18, 1035–1038.
 COULSON, C. A. (1970). *Thermal Neutron Diffraction*, Edited by B. T. M. WILLIS, pp. 68–81. Oxford Univ. Press.
 GOLDSCHMIDT, G. H. & HURST, D. G. (1951). *Phys. Rev.* 83, 88–94.
International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press.
 KURKI-SUONIO, K. (1967). *Ann. Acad. Sci. Fenn. A VI*, 263.
 KURKI-SUONIO, K. & RUUSKANEN, A. (1971). *Ann. Acad. Sci. Fenn. A VI*, 358.
 LAGE, F. C. VON DER & BETHE, H. A. (1947). *Phys. Rev.* 71, 612–622.
 LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* A30, 580–584.
 LEVY, H. A. & PETERSON, S. W. (1952). *Phys. Rev.* 86, 766–770.
 MOCCIA, R. J. (1964). *J. Chem. Phys.* 40, 2176–2185.
 PESONEN, A. (1971). *Ann. Acad. Sci. Fenn. A VI*, 378.
 PRESS, W. (1973). *Acta Cryst.* A29, 257–263.
 PRESS, W. (1976). *Acta Cryst.* A32, 170.
 PRESS, W. & HÜLLER, A. (1973). *Acta Cryst.* A29, 252–256.
 VAHVASELKÄ, A. & KURKI-SUONIO, K. (1975). *Phys. Fenn.* 10, 87–99.
 YELON, W. B., COX, D. E. & KORTMAN, P. J. (1974). *Phys. Rev.* B9, 4843–4856.
 ZACHARIASEN, W. H. (1967). *Acta Cryst.* 23, 558–564.

Acta Cryst. (1976). A32, 115

Restriction of the Number of Terms in the Sayre–Hughes Equation Connected with a Criterion to Establish the Absence of Atomic Overlap in Projection

BY J. J. L. HEINERMAN AND J. KROON

Laboratorium voor Structuurchemie, Rijksuniversiteit, Padualaan 8, Utrecht, The Netherlands

(Received 28 July 1975; accepted 1 August 1975)

In the Sayre–Hughes equation the variable reciprocal-lattice vector ranges over the whole reciprocal net. It is shown that under the condition that a projection along a zone axis has no overlapping atoms the variable reciprocal-lattice vector can be restricted to range over a plane of the reciprocal net. *A fortiori* if a projection on an axis is free from overlap the variable vector can be restricted to range over a row of the reciprocal net. Criteria to determine the projections for which these conditions are best fulfilled are given. These criteria involve the absolute values of the structure factors only. The theory is illustrated by a test employing normalized structure factors calculated from atomic coordinates.

Introduction

It is always possible to determine the three-dimensional structure from any two resolved two-dimensional projections for which the projection on their intersecting line is resolved. In the case that only one two-

dimensional projection is resolved use can be made of generalized projections to find the three-dimensional structure.

For reciprocal space it follows that under the conditions mentioned above, a restricted number of structure factors determines the others (at the given

resolution). In this paper we shall first show that under these circumstances the number of terms in the Sayre–Hughes equation can be restricted. The resulting equations will be called reduced Sayre–Hughes equations. Secondly we shall show how to find those projections for which the conditions of no atomic overlap are best fulfilled. Only the absolute values of structure factors enter into this procedure.

Reduced Sayre–Hughes equations

Denote by N the number of atoms in the unit cell, by Z_j the number of electrons of atom j , and define

$$\sigma_n = \sum_{j=1}^N Z_j^n. \quad (1)$$

Define the normalized structure factor $E_{\mathbf{h}}$ and the normalized structure factor of the squared structure $E_{\mathbf{h}}^s$ by

$$E_{\mathbf{h}} = \sum_{j=1}^N \frac{Z_j}{\sigma_2^{1/2}} \exp 2\pi i \mathbf{h} \cdot \mathbf{r}_j \quad (2)$$

and

$$E_{\mathbf{h}}^s = \sum_{j=1}^N \frac{Z_j^2}{\sigma_4^{1/2}} \exp 2\pi i \mathbf{h} \cdot \mathbf{r}_j \quad (3)$$

respectively.

With these definitions the Sayre–Hughes equation (Sayre, 1952; Hughes, 1953) is written as

$$E_{\mathbf{h}}^s = \frac{\sigma_2}{\sigma_4^{1/2}} \langle E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}} \rangle_{\mathbf{k}}, \quad (4)$$

where \mathbf{k} is a vector which ranges throughout the reciprocal net. We shall show that if certain conditions, to be specified below, are fulfilled, it suffices if \mathbf{k} ranges over planes or rows of the reciprocal net.

(a) If there are no atoms with the same x coordinate, $\delta_{x_i x_j} = \delta_{ij}$, $i, j = 1, \dots, N$, then

$$\begin{aligned} \langle E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}} \rangle_{\mathbf{k}_1} &= \frac{1}{\sigma_2} \sum_{i=1}^N \sum_{j=1}^N Z_i Z_j \\ &\quad \times \langle \exp 2\pi i [\mathbf{h} \cdot \mathbf{r}_j + \mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)] \rangle_{\mathbf{k}_1} \\ &= \frac{1}{\sigma_2} \sum_{i=1}^N \sum_{j=1}^N Z_i Z_j \{ \exp 2\pi i [\mathbf{h} \cdot \mathbf{r}_j \\ &\quad + k_2(y_i - y_j) + k_3(z_i - z_j)] \} \delta_{x_i x_j} = \frac{\sigma_4^{1/2}}{\sigma_2} E_{\mathbf{h}}^s, \\ E_{\mathbf{h}}^s &= \frac{\sigma_2}{\sigma_4^{1/2}} \langle E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}} \rangle_{\mathbf{k}_1}. \end{aligned} \quad (5a)$$

(b) If there are no atoms with the same (x, y) coordinates, $\delta_{x_i x_j} \delta_{y_i y_j} = \delta_{ij}$, $i, j = 1, \dots, N$, then

$$E_{\mathbf{h}}^s = \frac{\sigma_2}{\sigma_4^{1/2}} \langle E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}} \rangle_{\mathbf{k}_1 \mathbf{k}_2}. \quad (6a)$$

Equations (5a) and (6a) will be referred to as the reduced Sayre–Hughes equations.*

In (5a) k_2 and k_3 are fixed. For $k_2=0$ and $k_3=h_3$, only projection reflexions are needed to calculate $E_{\mathbf{h}}^s$. If all the projection reflexions $E_{h_1 0 h_3}$ and $E_{h_1 h_2 0}$ are known, all the $E_{\mathbf{h}}^s$ can be calculated. This means that the three-dimensional structure can be obtained from the \mathbf{b} and \mathbf{c} projections.

In (6a) k_3 is fixed. If all the $E_{h_1 h_2 1}$ are known (then the $E_{h_1 h_2 \bar{1}}$ are also known) all the $E_{h_1 h_2 0}^s$ and the $E_{h_1 h_2 2}^s$ can be calculated. Next for equal-atom structures ($E_{\mathbf{h}}^s = E_{\mathbf{h}}$), all the $E_{h_1 h_2 3}$ etc. can be calculated: the generalized projection for $k_3=1$ suffices to calculate the three-dimensional structure. Again for equal-atom structures it can be seen that if all the $E_{h_1 h_2 h_3}$ with h_3 fixed are known, all the $E_{h_1 h_2 n h_3}$ for all integers n can be calculated. For structures consisting of unequal atoms we can use

$$E_{\mathbf{h}}^s \approx \frac{\sigma_3}{\sigma_2^{1/2} \sigma_4^{1/2}} E_{\mathbf{h}} \quad (7)$$

(Cochran & Woolfson, 1955). These results can be interpreted as follows. The electron density is given by

$$\varrho(x, y, z) = \frac{1}{c} \sum_{k_3} \varrho_{k_3}(x, y) \exp -2\pi i k_3 z, \quad (8)$$

where the generalized projections $\varrho_{k_3}(x, y)$ along \mathbf{c} are non-zero only if $(x, y) = (x_j, y_j)$, $j = 1, \dots, N$. From the condition $\delta_{x_i x_j} \delta_{y_i y_j} = \delta_{ij}$, $i, j = 1, \dots, N$, it follows that $\varrho(x, y, z)$ is non-zero only if $z = z_j$. Therefore the real parts of the terms in the right-hand side of (8) with $k_3 \neq 0$ have at least a maximum for $z = z_j$. For $k_3 = 0$ no information about the value for z_j can be obtained. For $k_3 = 1$ there is only one maximum. The position of this maximum gives the value for z_j . In general the term with $k_3 \neq 0$ has $|k_3|$ maxima which lead to $|k_3|$ possible values for z_j . Further, we note that from (6a) it can be shown that a generalized projection of the squared structure is proportional to the product of two generalized projections.

In considering the similarity between the modulus projections $|\varrho_{k_3}(x, y)|$ and the projection with $k_3=0$, especially when there are no atoms which overlap in the \mathbf{c} projection, Vainshtein (1959a, b) was led to equalities which interrelate the structure factors of parallel reciprocal-lattice planes. Analogously he has found equalities which interrelate the structure factors of parallel reciprocal-lattice rows for the case that no atoms overlap in the projection on an axis. In fact his equalities can be obtained from special cases of the reduced Sayre–Hughes equations.

When (5a) and (6a) are compared with (4) it is seen that the stronger the conditions for the \mathbf{r}_j , the more the part of the reciprocal net through which \mathbf{k} ranges

* A probabilistic approach leads to (4) containing conditional averages (Hauptman, 1970). Analogous results can be obtained for (5a) and (6a).

can be restricted. If in (5a) k_2 and k_3 are not fixed but take on a restricted number of values then the condition $\delta_{x_i x_j} = \delta_{i j}$ is relaxed. The same holds for the condition $\delta_{x_i x_j} \delta_{y_i y_j} = \delta_{i j}$ if in (6a) k_3 takes on a restricted number of values. We shall give an example. Assume that only atoms 1 and 2 have the same (x, y) coordinates. Then

$$\begin{aligned} \langle E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}} \rangle_{\substack{k_1 k_2 \\ k_3 = k_{31}, k_{32}}} &= \frac{1}{\sigma_2} \sum_{i=1}^N \sum_{j=1}^N Z_i Z_j \\ &\times \{ \exp 2\pi i \mathbf{h} \cdot \mathbf{r}_j \} \delta_{x_i x_j} \delta_{y_i y_j} \\ &\times \langle \exp 2\pi i k_3 (z_i - z_j) \rangle_{k_3 = k_{31}, k_{32}} \\ &= \frac{\sigma_4^{1/2}}{\sigma_2} E_{\mathbf{h}}^s + \frac{Z_1 Z_2}{\sigma_2} \{ \exp 2\pi i (h_1 x_1 + h_2 y_1) \} \\ &\times \{ \exp 2\pi i h_3 z_2 \langle \exp 2\pi i k_3 (z_1 - z_2) \rangle_{k_3 = k_{31}, k_{32}} \\ &+ \exp 2\pi i h_3 z_1 \langle \exp 2\pi i k_3 (z_2 - z_1) \rangle_{k_3 = k_{31}, k_{32}} \}. \end{aligned} \quad (9)$$

If k_{31} and k_{32} are chosen in such a way that

$$k_{31}(z_1 - z_2) = k_{32}(z_1 - z_2) + \frac{1}{2} \pmod{1},$$

then the result is

$$E_{\mathbf{h}}^s = \frac{\sigma_2}{\sigma_4^{1/2}} \langle E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}} \rangle_{\substack{k_1 k_2 \\ k_3 = k_{31}, k_{32}}}, \quad (10)$$

which should be compared with (6a).

Overlap criteria

For $\mathbf{h} = \mathbf{0}$ we find from the reduced Sayre-Hughes equations

$$\langle |E_{\mathbf{k}}|^2 \rangle_{k_1} = 1 \quad \text{if} \quad \delta_{x_i x_j} = \delta_{i j}, \quad i, j = 1, \dots, N, \quad (11)$$

and

$$\langle |E_{\mathbf{k}}|^2 \rangle_{k_1 k_2} = 1 \quad \text{if} \quad \delta_{x_i x_j} \delta_{y_i y_j} = \delta_{i j}, \quad i, j = 1, \dots, N. \quad (12)$$

Compare with

$$\langle |E_{\mathbf{k}}|^2 \rangle_{\mathbf{k}} = 1. \quad (13)$$

Equating the mean values in (12) for different values of k_3 a relation between the absolute values of structure factors is obtained. Vainshtein (1959a, b) has pointed out that the fulfilment of such a relation indicates the absence of atomic overlap in projection and the validity of his equalities between the structure factors of parallel reciprocal-lattice planes. It also indicates the validity of the reduced Sayre-Hughes equation (6a). As quantitative criteria we define

$$K_1 = \langle \{ \langle |E_{\mathbf{k}}|^2 \rangle_{k_1} - 1 \}^2 \rangle_{k_2 k_3}, \quad (14)$$

which approaches zero if there is no atomic overlap on the a axis, and

$$K_{12} = \langle \{ \langle |E_{\mathbf{k}}|^2 \rangle_{k_1 k_2} - 1 \}^2 \rangle_{k_3}, \quad (15)$$

which approaches zero if there is no atomic overlap in the c projection. For comparison define

$$K = \langle \{ |E_{\mathbf{k}}|^2 - 1 \}^2 \rangle_{\mathbf{k}}. \quad (16)$$

We shall show that K_1 and K_{12} give an impression of the overlap in the projections on a and along c respectively. An interpretation of K has been given by Hauptman (1964). Here we shall show its connexion with K_1 and K_{12} .

If only two atoms i and j have the same x coordinate then

$$\langle |E_{\mathbf{k}}|^2 \rangle_{k_1} = 1 + \frac{2Z_i Z_j}{\sigma_2} \cos 2\pi [k_2 (y_i - y_j) + k_3 (z_i - z_j)], \quad (17)$$

and

$$\begin{aligned} K_1 &= \frac{4Z_i^2 Z_j^2}{\sigma_2^2} \langle \cos^2 2\pi [k_2 (y_i - y_j) + k_3 (z_i - z_j)] \rangle_{k_2 k_3} \\ &= \frac{2Z_i^2 Z_j^2}{\sigma_2^2} (1 + \delta_{2y_i 2y_j} \delta_{2z_i 2z_j}), \end{aligned} \quad (18)$$

where the subscripts $2y_i$ etc. are shorthand notations for $2y_i \pmod{1}$ etc. In this case the minimum value of K_1 is $2Z_i^2 Z_j^2 / \sigma_2^2$. It can be shown that every pair of atoms with the same x coordinate gives a contribution to K_1 of at least $2Z_i^2 Z_j^2 / \sigma_2^2$. If all atoms have the same x coordinate then the minimum value of K_1 is

$$\sum_{i=1}^N \sum_{j=1}^N \sum_{i < j} 2Z_i^2 Z_j^2 / \sigma_2^2 = 1 - \sigma_4 / \sigma_2^2. \quad (i)$$

Next we consider the additional effect of a centre of symmetry. If two atoms i and j , related by a centre of symmetry, have the same x coordinate, this pair of atoms will give a contribution to K_1 of at least $2Z_i^4 / \sigma_2^2$. If two independent atoms i and j have the same x coordinate not equal to zero or to a half then there are two pairs of atoms which contribute to K_1 . These two pairs together give a contribution of at least $8Z_i^2 Z_j^2 / \sigma_2^2$. If the x coordinates of two independent atoms i and j are equal to zero (half) then the centrosymmetrically related atoms also have x coordinates equal to zero (half). These four atoms together give a contribution to K_1 of at least $(2Z_i^4 + 2Z_j^4 + 16Z_i^2 Z_j^2) / \sigma_2^2$. If all atoms have the same x coordinate, whence $x_j = 0(\frac{1}{2})$ for all j , the minimum value of K_1 can be shown to be

$$\left(\sum_{j=1}^{N/2} 2Z_j^4 + \sum_{i=1}^{N/2} \sum_{j=1}^{N/2} \sum_{i < j} 16Z_i^2 Z_j^2 \right) / \sigma_2^2 = 2 - 3\sigma_4 / \sigma_2^2. \quad (ii)$$

The same results hold for K_{12} if not only the x coordinates, but also the corresponding y coordinates are equal.

Hauptman (1964) found that the value of K is equal to (i) for structures without coinciding interatomic vectors and to (ii) if there are only coinciding interatomic vectors as a consequence of a centre of symmetry. Clearly these values for K can be interpreted as the result of the overlap of all atoms, i.e. the result of projecting on a point.

The contributions to K_1 and K_{12} contain the squares of the $Z_i Z_j$. Therefore K_1 and K_{12} are related to atomic overlap in projections of the squared structure. Also, they indicate the reliability of the $E_{\mathbf{h}}^s$ calculated with

the reduced Sayre–Hughes equations in the case that the conditions are not fulfilled.

Different projection directions

In the preceding only the conditions of no overlap in the projection on a and no overlap in the c projection have been considered. These conditions lead to the reduced Sayre–Hughes equations (5a) and (6a). Of course the absence of atomic overlap in other one- and two-dimensional projections leads to analogous results.

Define

$$\begin{aligned} \mathbf{a}' &= u_1 \mathbf{a} + u_2 \mathbf{b} + u_3 \mathbf{c}, \\ \mathbf{b}' &= v_1 \mathbf{a} + v_2 \mathbf{b} + v_3 \mathbf{c}, \\ \mathbf{c}' &= w_1 \mathbf{a} + w_2 \mathbf{b} + w_3 \mathbf{c}, \end{aligned}$$

where u_1, \dots, w_3 are integers so that $V'_{\text{cell}} = V_{\text{cell}}$. If no atoms overlap in the projection on \mathbf{a}' then, analogous to (5a),

$$E_{\mathbf{h}}^s = \frac{\sigma_2}{\sigma_4^{1/2}} \langle E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}} \rangle_{\mathbf{k}}, \quad (5b)$$

$$\begin{aligned} k_1 v_1 + k_2 v_2 + k_3 v_3 &= n_v \\ k_1 w_1 + k_2 w_2 + k_3 w_3 &= n_w \end{aligned}$$

where n_v and n_w are fixed integers [to be compared with k_2 and k_3 in (5a)]. If no atoms overlap in the \mathbf{c}' projection then, analogous to (6a),

$$E_{\mathbf{h}}^s = \frac{\sigma_2}{\sigma_4^{1/2}} \langle E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}} \rangle_{\mathbf{k}}, \quad (6b)$$

$$k_1 w_1 + k_2 w_2 + k_3 w_3 = n_w$$

where n_w is a fixed integer [to be compared with k_3 in (6a)]. The corresponding overlap criteria are

$$K_1 = \langle \{ \langle |E_{\mathbf{k}}|^2 \rangle_{\mathbf{k}} - 1 \}^2 \rangle_{n_v n_w} \quad (14b)$$

$$\begin{aligned} k_1 v_1 + k_2 v_2 + k_3 v_3 &= n_v \\ k_1 w_1 + k_2 w_2 + k_3 w_3 &= n_w \end{aligned}$$

and

$$K_{12} = \langle \{ \langle |E_{\mathbf{k}}|^2 \rangle_{\mathbf{k}} - 1 \}^2 \rangle_{n_w} \quad (15b)$$

$$k_1 w_1 + k_2 w_2 + k_3 w_3 = n_w$$

respectively.

The optimum value for n_w in (6b)

Fig. 1 shows two limiting spheres I and II. The origin of II is shifted over the vector \mathbf{h} with respect to the origin of I. Let the lattice point $(l_1 l_2 l_3)$ in I be connected with E_1 and in II with E_1^* . Then the coinciding points pertaining to \mathbf{k} in I and to $-(\mathbf{h}-\mathbf{k})$ in II are associated with terms $E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}$ in the Sayre–Hughes equation. Only half of these coinciding points supply independent terms, because the lattice points pertaining to \mathbf{k} in I and to $-(\mathbf{h}-\mathbf{k})$ in II correspond to the same terms as do the lattice points related to $\mathbf{h}-\mathbf{k}$ in I and to $-\mathbf{k}$ in II.

Coinciding lattice points lying on a plane correspond to terms in the reduced Sayre–Hughes equation (6b) [coinciding lattice points lying on a row correspond to terms in the reduced Sayre–Hughes equation (5b)]. It can be shown that the plane parallel to the $\mathbf{a}'^* \mathbf{b}'^*$ plane for which the surface inside both sphere I and sphere II

is as large as possible is obtained for $n_w = \frac{1}{2}q$, where $q = h_1 w_1 + h_2 w_2 + h_3 w_3$. If q is odd then this plane does not contain lattice points (n_w must be an integer). So the optimum value for n_w , giving in general the largest number of terms in (6b), is $n_{w0} = \frac{1}{2}q \pm \frac{1}{2}$ (q odd). Both values give the same set of terms $E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}$. If q is even then for $n_w = \frac{1}{2}q$ only half the terms are independent. Consequently the optimum value for n_w is in general $n_{w0} = \frac{1}{2}q \pm 1$ (q even). Again both values give the same set of terms $E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}$.

The determination of the optimum pair $(n_v, n_w)_o$ in (5b) is more intricate. However, the requirement of no atomic overlap on an axis will seldom be fulfilled and there is little practical need to pursue this aspect.

A test

The dimethyl ester of *meso*-tartaric acid (Kroon & Kanters, 1973), space group $P\bar{1}$, with six O and six C atoms in the asymmetric unit was used to test the theory in the preceding sections. From the atomic coor-

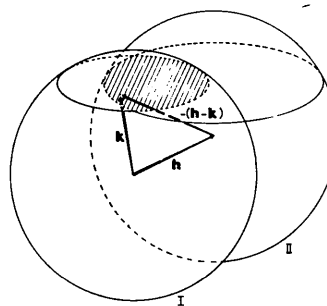


Fig. 1. Two limiting spheres I and II with an intersecting reciprocal-lattice layer. The origin of II is shifted over the vector \mathbf{h} with respect to the origin of I. The reciprocal-lattice vectors \mathbf{k} and $-(\mathbf{h}-\mathbf{k})$ correspond to terms $E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}$ in the Sayre–Hughes equation.

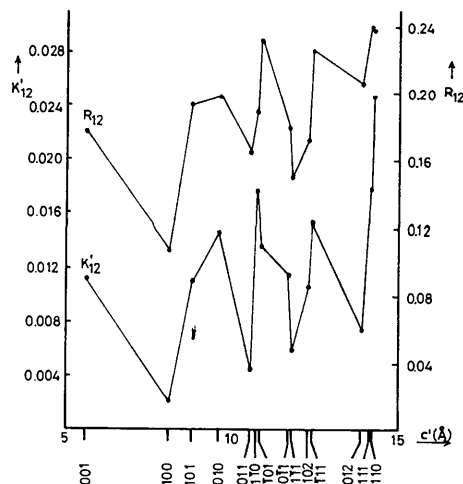


Fig. 2. K'_{12} and R_{12} values plotted against the length of the (w_1, w_2, w_3) axis.

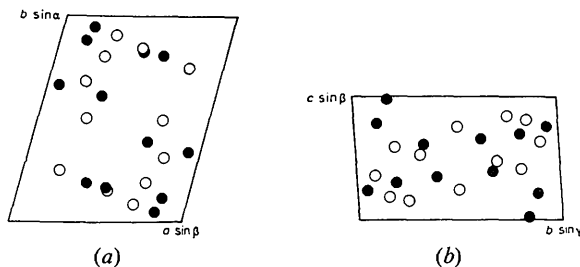


Fig. 3. The [001] projection (a) and the [100] projection (b).
○ Carbon atom; ● Oxygen atom.

dinates 1868 normalized structure factors (Cu $K\alpha$ sphere) were calculated. Next, for 14 projection directions (w_1, w_2, w_3) we calculated the overlap criterion

$$K'_{12} = \frac{\sum_{n_w} W_{n_w} \{ \langle |E_{\mathbf{k}}|^2 \rangle_{\mathbf{k}} - 1 \}^2}{\sum_{n_w} W_{n_w}} \quad (14c)$$

The weighting factor W_{n_w} is equal to the number of terms $|E_{\mathbf{k}}|^2$ with n_w fixed and copes with the different standard deviations for the $\langle |E_{\mathbf{k}}|^2 \rangle$. For the corresponding reduced Sayre-Hughes equations having optimum values for n_w , we calculated the residual

$$R_{12} = \frac{\sum |E_{\mathbf{h}} - \frac{\sigma_2^{3/2}}{\sigma_3} \langle E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}} \rangle_{\mathbf{k}}|}{\sum |E_{\mathbf{h}}|} \quad (19)$$

where the summation extends over the largest 500 $|E_{\mathbf{h}}|$'s.

In Fig. 2 the values of K'_{12} and R_{12} are plotted against the length of the (w_1, w_2, w_3) axis. It is seen that the general behaviour of R_{12} is the same as that of K'_{12} . Further it should be noted that the minimum of R_{12} corresponds to the minimum of the overlap criterion. In this minimum R_{12} is equal to 0.107; this value is not much larger than 0.078, which is obtained if in (19) no restrictions are imposed on \mathbf{k} .

The values for K'_{12} are related to atomic overlap in projections. Fig. 3 gives the projections along the

two shorter axes. Owing to the limited number of structure factors, point atoms are smeared out in a Fourier projection. Taking into account only the first diffraction ring (James, 1962), in such a way that the entire electron density of an atom is supposed to lie inside this ring, the standard deviation for the radius of an atom can be calculated to be 0.25 Å (Cu $K\alpha$ sphere). This value is used for the atomic radii in Fig. 3. The [001] projection [Fig. 3(a)] contains two pairs of almost completely overlapping atoms. For the case of complete overlap they would give a contribution to the overlap criterion of at least $8Z_C^2 Z_O^2 / \sigma_2^2 = 0.0128$ (Z_C and Z_O are the atomic numbers of C and O respectively). The K'_{12} value for the [001] projection is equal to 0.0112. Clearly this value is related to the two pairs of almost completely overlapping atoms. The minimum of K'_{12} (Fig. 2), equal to 0.0021, corresponds to the [100] projection. From Fig. 3(b) it is seen that in this projection there is no atomic overlap.

It appears that for these examples the overlap criterion quite well reflects the actual atomic overlap in projection and that it gives an indication about the reliability of the corresponding reduced Sayre-Hughes equations.

We thank Dr H. Krabbendam and Professor A. F. Peerdeman for critical reading of the manuscript.

References

- COCHRAN, W. & WOOLFSON, M. M. (1955). *Acta Cryst.* **8**, 1-12.
 HAUPTMAN, H. (1964). *Acta Cryst.* **17**, 1421-1433.
 HAUPTMAN, H. (1970). Seminar, CECAM workshop, Orsay, September 1970.
 HUGHES, E. W. (1953). *Acta Cryst.* **6**, 871.
 JAMES, R. W. (1962). *The Crystalline State*, Vol. II, 396-401. London: Bell.
 KROON, J. & KANTERS, J. A. (1973). *Acta Cryst.* **B29**, 1278-1283.
 SAYRE, D. (1952). *Acta Cryst.* **5**, 60-65.
 VAINSHTEIN, B. K. (1959a). *Dokl. Akad. Nauk SSSR*, **124**, 87-90. [Engl. Trans. *Sov. Phys. Dokl.* (1959). **4**, 12-15.]
 VAINSHTEIN, B. K. (1959b). *Kristallografiya*, **4**, 3-12. [Engl. Trans. *Sov. Phys. Crystallogr.* (1960). **4**, 1-9.]