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The Residual and its Use for Partial Structure Evaluation. A Critical Note on the Discriminator Function

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The value of the residual $\langle(I_{\rm obs}-I_{\rm calc})^2\rangle/\langle I^2{}_{\rm obs}\rangle$ will change when one or more atoms are added to an incomplete model of the structure looked for. It is possible to calculate statistically the expected values of the residual both for correct and (randomly) incorrect placing of a new fragment. The results then show that the correctness of the new atomic position(s) cannot be proved, but only estimated by means of the residual as a reliability criterion; the same conclusion applies to the discriminator function. Both the residual and the discriminator function, however, can be suitable in the elimination of incorrect atomic positions. In some cases even false pseudosymmetry, if any, can be eliminated from a tentative electron density map.

1. Introduction

It is necessary to have some criteria to be able to investigate the reliability of the steps to be taken in a completely automated structure evaluation.

A deconvolution of the Patterson function has been discussed previously (Lenstra & Schoone, 1973), in which, among other things, the residual $\langle(I_{\rm obs}-I_{\rm calc})^2\rangle/\langle I^2{}_{\rm obs}\rangle$ has been applied as a reliability criterion.

The residual as a means to interpret a tentative electron density map has already been stated (Lenstra, 1969). Other investigators have made use of, for instance, the discriminator function (Hackert & Jacobson, 1970; Jacobson, 1970) or a least-squares refinement (Koyama, Okada & Itoh, 1970) to locate additional atoms.

These three criteria are founded mainly on the plain fact that models obtained in this way are in agreement with the correct solutions of the structures. A theoretical explanation of the behaviour of the residual is given in the next section.

Another important point is the purport of 'correct and incorrect placing of an atom'. This will be discussed in detail in § 3; is provides some correction and completion of Wilson's (1969) treatment of the residual. It is shown that an incorrect addition of an atom under certain conditions may decrease the value of the residual. One special kind of incorrect positioning of the new atom which practically always results in a decreasing value of the residual is dealt with in § 4.

§ 5 relates the evaluation of these results for a practical automated structure determination.

In § 6 some remarks are made on the discriminator function.

2. Derivation of the values of the residual. Experimental results

For practical mathematical reasons the residual is defined as:

$$R_2\equiv\frac{\sum\limits_{H}(I_{\rm obs}-I_{\rm calc})^2}{\sum\limits_{H}I^2_{\rm obs}}$$

in which $I_{\rm obs}$ are the observed intensities and $I_{\rm calc}$ are the intensities calculated by means of the known structure model only. This implies that the observed intensities are known on absolute scale! R_2 can be written as:

$$R_2 = \langle (I^2_{\text{obs}} - I_{\text{calc}})^2 \rangle / \langle I_{\text{obs}} \rangle \equiv R / \langle I^2_{\text{obs}} \rangle ,$$

in which the angle brackets indicate averages over all values of the reciprocal vector **H**.

The structure looked for contains N atoms in the unit cell. Let us suppose that say n atoms ($n<N$) have already been located in their correct positions. After placing the $(n+1)$th atom in the position $\mathbf{r}_{n+1}$ the remaining unknown part of the structure contains u atoms. The most important factor in the R_2 function is of course the numerator; we therefore confine ourselves principally to R. The evaluation of R will be analogous to that of Wilson (1969).

(*a*) *Space group P*1

The correct structure factor that corresponds to the observed one is:

$$\mathbf{F}_1 = F_n \exp i\alpha + f_{n+1} \exp i\theta_{n+1} + F_u \exp i\chi . \qquad (1)$$

The structure factor calculated with the originally known n atom is:

$$\mathbf{F}_2 = F_n \exp i\alpha . \qquad (2)$$

The new calculated structure factor that includes the $(n+1)$th atom in a tentative position can be written as:

$$\mathbf{F}_3 = F_n \exp i\alpha + f_{n+1} \exp i\omega . \qquad (3)$$

Because $I = \mathbf{F} . \mathbf{F}^*$, we find:

$$I_1 = F_n^2 + f^2_{n+1} + F_u^2 + 2f_{n+1}F_n \cos(\alpha-\theta) + 2F_nF_u \cos(\alpha-\chi) + 2F_uf_{n+1}\cos(\theta-\chi) \qquad (4)$$

$$I_2 = F_n^2 \qquad (5)$$

$$I_3 = F_n^2 + f^2_{n+1} + 2f_{n+1}F_n \cos(\alpha-\omega) . \qquad (6)$$

From (4) and (5) we find:

$$(I_1 - I_2) = f^2_{n+1} + F_u^2 + 2f_{n+1}F_n \cos(\alpha-\theta) + 2F_nF_u \times \cos(\alpha-\chi) + 2F_uf_{n+1}\cos(\theta-\chi) . \qquad (7)$$

If the components of $\mathbf{F}_1$, $\mathbf{F}_2$ and $\mathbf{F}_3$ are independently distributed in phase, the average of $(I_{\text{obs}} - I_{\text{calc}})^2$ over a large number of the reciprocal vector **H** can be obtained by averaging each of the factors in the expression $(I_{\text{obs}} - I_{\text{calc}})^2$ seperately. We find:

$$R_o = \langle (I_1 - I_2)^2 \rangle = f^4_{n+1} + 2f^2_{n+1}\langle F_n^2 \rangle + 2\langle F_u^2 \rangle \langle F_n^2 \rangle + \langle F_u^4 \rangle + 4f^2_{n+1}\langle F_u^2 \rangle \qquad (8)$$

in which R_o represents the original R value calculated with n known atoms.

Assuming that the $(n+1)$th atom is placed correctly namely $\omega=\theta$ we find from (4) and (6) for the correct R value, denoted by R_c:

$$R_c = \langle (I_1 - I_3)^2_c \rangle = \langle F_u^4 \rangle + 2\langle F_n^2 \rangle \langle F_u^2 \rangle + 2f^2_{n+1}\langle F_u^2 \rangle . \qquad (9)$$

From the equations (8) and (9) we see that a correct addition of an atom to the known part of the structure decreases the R_2 value, because

$$\Delta R_c \equiv R_c - R_o = -f^4_{n+1} - 2f^2_{n+1}(\langle F_u^2 \rangle + \langle F_n^2 \rangle) .$$

which is clearly negative. We notice too that in an equal-atom structure ΔR_c has a constant value during the structure evaluation.

If the $(n+1)$th atom is situated in a wrong position ($\omega \neq \theta$) and ω are θ-independent of each other – specifically not related by false pseudosymmetry – we find from (4) and (6) R_f, which is the R value with a badly-misplaced added atom.

$$R_f = \langle F_u^4 \rangle + 4f^2_{n+1}\langle F_n^2 \rangle + 2\langle F_n^2 \rangle \langle F_u^2 \rangle + 2f^2_{n+1}\langle F_u^2 \rangle . \qquad (10)$$

From (8) and (10) we obtain the calculated change in R value:

$$\Delta R_f \equiv R_f - R_o = -f^4_{n+1} + 2f^2_{n+1}(\langle F_n^2 \rangle - \langle F_u^2 \rangle) .$$

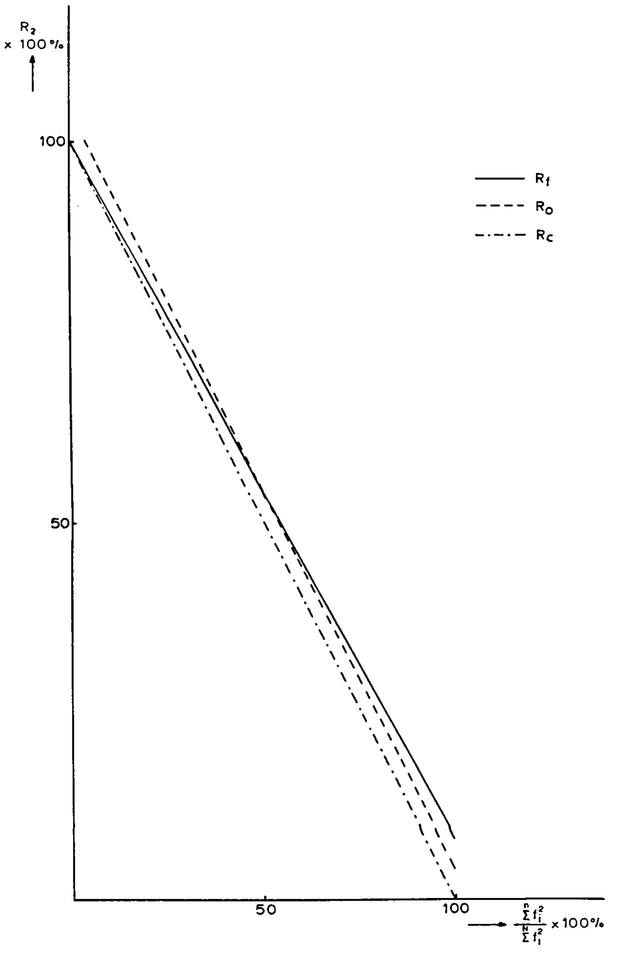

Fig. 1. The monotonic decrease of the R_2 function, when an increasing number of atoms, *e.g.* n, of the structure (containing N atoms) is correctly placed, is represented by R_c. R_o represents the R_2 function of a partly known structure, when $(n-1)$ atoms are correctly placed; if the nth atom is incorrectly placed R_2 will be equal to R_f. The numerical values are obtained from Wilson's probability distribution of F. R_0 and R_f are calculated with respect to R_c assuming a crystal structure, which contains 24 carbon atoms.

This shows that ΔR_f can be positive or negative. If we confine ourselves to heavy-atom structures, of which at least the heavy atoms are known, ΔR_f will be positive when an incorrectly placed atom is added.

The calculated R_2 values are represented in Fig. 1 as a function of the known part of the structure with respect to the total structure.

(*b*) *Space group* $P\bar{1}$

Analogous to the notations for the space group $P1$, we have:

$$\mathbf{F}_1 = \mathbf{F}_n + 2f_{n+1}\cos\theta + \mathbf{F}_u \tag{11}$$

$$\mathbf{F}_2 = \mathbf{F}_n \tag{12}$$

$$\mathbf{F}_3 = \mathbf{F}_n + 2f_{n+1}\cos\omega\,. \tag{13}$$

From these equations we easily derive:

$$R_o = \langle (I_1 - I_2)^2 \rangle = 6f^4_{n+1} + 8f^2_{n+1}\langle F^2_n \rangle + \langle F^4_u \rangle + 12f^2_{n+1}\langle F^2_u \rangle + 4\langle F^2_n \rangle \langle F^2_u \rangle \tag{14}$$

$$R_c = \langle F^4_u \rangle + 8f^2_{n+1}\langle F^2_u \rangle + 4\langle F^2_n \rangle \langle F^2_u \rangle \tag{15}$$

$$R_f = \langle F^4_u \rangle + 8f^2_{n+1}\langle F^2_u \rangle + 4\langle F^2_n \rangle \langle F^2_u \rangle + 4f^4_{n+1} + 16f^2_{n+1}\langle F^2_n \rangle\,. \tag{16}$$

From (14) and (15) we see that a correct positioning of the new atom decreases the R_2 value. However, if the new atom is misplaced the R_2 value will change with

$$\Delta R_f = -2f^4_{n+1} + 4f^2_{n+1}(2\langle F^2_n \rangle - \langle F^2_u \rangle)\,.$$

This shows again that ΔR_f can be positive or negative; if we confine ourselves to heavy-atom structures ΔR_f will be positive.

(*c*) *Experimental test of* R_c *and* R_f

Our statistical approach to the residual gives a general insight into this function. Our aim is only to check this insight for some heavy-atom compounds, of which the crystal structures are already known.

The crystal structures used for this purpose were nickel hydrogen malate, space group $P4_12_12$ (Lenstra, 1974) and potassium hydrogen mesotartrate, space group $P\bar{1}$ (Kroon & Kanters, 1972). The possible atomic positions of the lighter atoms were selected from a heavy-atom Fourier synthesis. The electron densities of these positions were nearly equal.

A typical result of the tests made is given in Table 1. For both structures the experimental results fit in with the statistical description of the R_2 value.

This strongly suggests that the R_2 value can be used as a reliability criterion in a structure evaluation procedure. For this reason a better understanding of the factors influencing the R_2 value is necessary.

3. The interpretation of R_c and R_f

If from an equal-atom structure all atoms but one are correctly placed the R_2 values calculated for the space groups $P1$ and $P\bar{1}$ are in agreement with those obtained by Wilson (1969). However, if we locate all atoms in a wrong position – which is not really possible in the space group $P1$ – we shall find $R_2 \simeq 1{\cdot}00$. This conclusion is not consistent with the experimental results. A correct derivation of the expected R_2 value should be analogous to Wilson's (1950) article about the likely largest value for the reliability index.

Table 1. *Test of the residual using nickel hydrogen malate* ($P4_12_12$)

The R_2 values are calculated with 800 independent reflexions with $0 < \sin\theta/\lambda < 0{\cdot}71$.

Added atom	Experimental R_2 value %	
–	18·12	Original structure model consisting of $4Ni^{2+}$ ions and 64 light atoms.
C	19·11	Incorrect atomic site.
C	19·16	Incorrect atomic position.
C	17·18	Correct atomic site.
C	17·27	Correct atomic site.

The behaviour of the statistically calculated R_2 value appears to be not very different from that of the actual R_2 value [see *e.g.* § 4(*b*)]. In the automated heavy-atom structure analysis proposed by Koyama *et al.* (1970) use is made of the monotonic decrease in the actual R_2 value. Yet, this behaviour of R_2 is only a statistical one. This implies that we are not able to obtain a decisive prediction of the R_2 value calculated for the actual addition of a specified atom to a specified structure model.

The question arises whether the discrepancies between the statistical and the 'actual' R_2 value – at least partly – are due to systematical reasons or not.

Leaving experimental errors out of consideration we applied an important approximation in the averaging process. In equation (1), for instance, the phase angles α and χ depend on the positional parameters of n and u atoms respectively. The tentative phase $\omega(=2\pi\mathbf{H}\,.\,\mathbf{r}_{n+1})$ and any other phase angle $\theta_i(=\pi 2\mathbf{H}\,.\,\mathbf{r}_i)$ are not necessarily 'randomly' independent of each other. They are dependent if the interatomic vector $(\mathbf{r}_i - \mathbf{r}_{n+1})$ happens to be present in the calculated Patterson function and is not explained by the first n atoms.

By rewriting

$$R \equiv \sum_H (I_{\text{obs}} - I_{\text{calc}})^2$$

we find this equal to

$$R = \int_v (P_{\text{obs}} - P_{\text{calc}})^2 \mathrm{d}V\,.$$

If n atoms of the structure are correctly placed, n^2 interatomic vectors (P_{calc}) will be explained and they disappear from the difference Patterson map. In locating the $(n+1)$th atom $(2n+1)$ new vectors have to be present in the difference Patterson ($P_{\text{obs}} - P_{\text{calc}}$).

If each of these $(2n+1)$ vectors occurs in this Patterson function they too disappear from the difference Patterson, and the expected R value will correspond to R_c.

We find R_f if only the origin peak is accounted for and consequently $2n$ negative peaks appear in the difference Patterson map.

If some of the $(2n+1)$ vectors occur in the Patterson function, or rather if some of them occur in the difference Patterson with n atoms included in P_{calc}, we shall find intermediate values for R. In some measure this always occurs through partial overlap in the difference Patterson. If pseudosymmetry is present we will recognize it as occuring systematically.

According to Wilson (1969) an atomic position is incorrect if the phase difference $\Delta\omega(\equiv 2\pi\mathbf{H}\,.\,\Delta\mathbf{r})$ between a correct phase and the tentative one changes by at least 2π as $\mathbf{H}$ takes on all orientations, meaning that $\langle\cos\Delta\omega\rangle=0$.

This condition does not take care of the above-mentioned non-randomness, and as a consequence it is not sufficiently strict. This means that the value of the residual with an incorrect positioning of say only the last atom is not necessarily too big for it to be overlooked.

In a normal selection of a possible atomic position at least some Patterson vectors will be explained. Consequently R_c and R_f represent extrema of the residual.

Of course we want to know the influence upon the residual of the number and kind of interatomic vectors which happen to be present in the observed Patterson function. Fortunately a systematic approach is possible by using pseudosymmetry.

4. The derivation of R_p; the experimental test of R_c and R_p

(*a*) In the case of pseudosymmetry an exact relation exists between the correct position of the new fragment of the structure and the pseudosymmetry related one(s).

We will discuss an example in the space group $P1$. The structure contains N atoms, of which n atoms are known and which are situated in such a way that a pseudo-inversion centre will coincide with the origin.

The observed structure factor is:

$$\mathbf{F}_1=\mathbf{F}_n+f_{n+1}\exp i\theta_{n+1}+f_{n+2}\exp i\theta_{n+2}+F_u\exp i\chi. \tag{17}$$

The possible atomic positions are selected from a calculated Fourier function, of which the phases of the structure amplitudes are based on F_n. After the correct location of the $(n+1)$th atom the calculated structure factor is:

$$\mathbf{F}_1=\mathbf{F}_n+f_{n+1}\exp i\theta_{n+1} \tag{18}$$

in which $\theta_{n+1}\neq 0$ or π, so that the pseudo-inversion centre disappears.

The addition of the $(n+2)$th atom on either of the pseudosymmetry related positions gives different values of F.

In the case of a correct position we find:

$$\mathbf{F}_3=\mathbf{F}_n+f_{n+1}\exp i\theta_{n+1}+f_{n+2}\exp i\theta_{n+2}\,. \tag{19}$$

If the atom is located on its inverse position we have

$$\mathbf{F}_4=\mathbf{F}_n+f_{n+1}\exp i\theta_{n+1}+f_{n+2}\exp -i\theta_{n+2}\,. \tag{20}$$

From these equations we easily obtain:

$$\begin{aligned}R_o=\langle(I_1-I_2)^2\rangle=\langle F_u^4\rangle+f_{n+2}^4+2f_{n+1}^2f_{n+2}^2+2f_{n+1}^2\langle F_u^2\rangle\\+2f_{n+2}^2\langle F_u^2\rangle+2\langle F_u^2\rangle\,\langle F_n^2\rangle+2f_{n+2}^2\langle F_n^2\rangle\end{aligned} \tag{21}$$

$$\begin{aligned}R_c=\langle(I_1-I_3)^2\rangle=\langle F_u^4\rangle+2f_{n+1}^2\langle F_u^2\rangle+2f_{n+2}^2\langle F_u^2\rangle\\+2\langle F_u^2\rangle\,\langle F_n^2\rangle\end{aligned} \tag{22}$$

$$\begin{aligned}R_p=\langle(I_1-I_4)^2\rangle=\langle F_u^4\rangle+2f_{n+1}^2\langle F_u^2\rangle+2f_{n+2}^2\langle F_u^2\rangle\\+2\langle F_u^2\rangle\,\langle F_n^2\rangle+4f_{n+1}^2f_{n+2}^2\,.\end{aligned} \tag{23}$$

From (22) and (23) we see: $R_p=R_c+4f_{n+1}^2f_{n+2}^2$.
From (8) and (10) we find: $R_f=R_c+4f_{n+1}^2\langle F_n^2\rangle$.

It is now clear that in general R_p has a value between R_c and R_f, which we expected. From (23) and (21) we see that in practice R_p is smaller than R_o.

(*b*) *Experimental results*

Although the difference between R_c and R_p is very small if one adds only one atom to the known structure model, we tried to verify that R_c is smaller than R_p. The test compounds were the structure of zinc malate, space group $P2_1$ (Lenstra, 1973) and a bromopregnane deri-

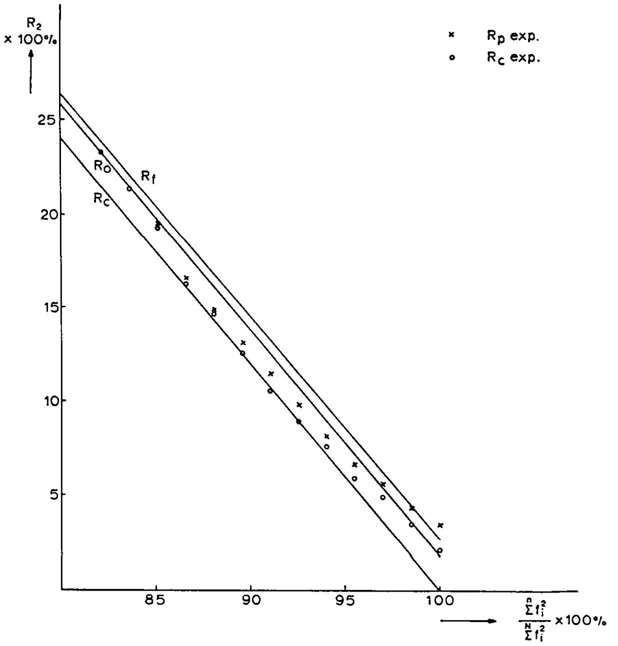

Fig. 2. The theoretical values of the residual R_2 are represented by three solid lines, namely R_c, R_o and R_f. The experimental values of R_2 by locating the atoms of zinc malate at their correct position are given by dots. If the last added atom is placed at its pseudosymmetrically related position the experimental R_2 value is represented as a cross. The discrepancies between the dots and the solid line R_c are not only the result of experimental errors in, for instance, the atomic coordinates and the measured intensities, but also of the application of the simple Wilson F distribution to a heavy atom compound.

vate, space group $P2_12_12_1$ (Ohrt, Haner, Cooper & Norton, 1968).

If only the heavy atoms are located, the former structure will contain a pseudo-inversion centre and the latter compound show a pseudo-mirror plane.

The possible atomic positions were selected from the Fourier function calculated with phases based on the heavy-atom positions only. The results obtained in both investigations showed that if a new atom is located on its pseudosymmetry-related position the calculated R_2 value will be somewhat higher than the R_2 value corresponding to the correctly placed atom. This suggests that the residual can be applied to eliminate pseudosymmetry in a structure evaluation procedure.

A survey of the results obtained in the case of zinc malate is shown in Table 2. The R_2 values (Fig. 2) are calculated with the scaling factor and the thermal parameter derived from a Wilson plot.

Table 2. *Quantitative test of R_c and R_p by means of zinc malate ($P2_1$)*

The R_2 value is calculated for 600 reflexions with $0{\cdot}33 < \sin\theta/\lambda < 0{\cdot}64$. Excepting the Zn^{2+} ions all atoms were assumed to be carbon.

Number of atoms in the structure model	R_2 value		ΔR_2 value		
	Theor.	Exp.	ΔR_2*	ΔR_2†	ΔR_{pc}‡
2	21·43	23·21	–	–	–
4	19·64	21·29	1·92	2·45	–
6	17·86	19·25	2·04	3·34	+0·04
8	16·07	16·22	3·03	1·77	+0·34
10	14·28	14·63	1·59	1·29	+0·21
12	12·50	12·54	2·09	1·73	+0·57
14	10·71	10·52	2·02	1·67	+0·92
16	8·93	8·87	1·65	1·97	+0·92
18	7·14	7·58	1·29	1·88	+0·59
20	5·36	5·87	1·71	1·37	+0·75
22	3·57	4·88	1·00	2·08	+0·73
24	1·78	3·46	1·42	1·16	+0·84
26	0·00	2·08	1·38	1·49	+1·34

* ΔR_2: average of the experimental ΔR_2 values, calculated by locating a trial atom at each of the remaining correct atomic sites; the theoretical value of $\Delta R_2 = 1{\cdot}78$.

† ΔR_2: actual value of ΔR_2. A trial atom is located at a particular correct atomic site.

‡ ΔR_{pc}: experimental value of $(R_p - R_c)/\langle I^2_{obs}\rangle$; this quantity has to be positive everywhere.

The discrepancies between the statistically calculated and the experimental R_2 values are due to many factors. Theoretically we have to include a F probability distribution proposed by Sim (1961) instead of the simple F distribution given by Wilson, since we confined ourselves to heavy-atom structures. The experimental errors, such as small displacements of the atoms in the structure model and measuring errors, influence the R_2 value. They have been discussed in detail by Wilson (1969) and Luzatti (1952).

5. A structure evaluation procedure

We tried to evaluate the crystal structure from a Fourier synthesis calculated with the phases of some atoms only. The structure factors were calculated with the scaling factor and 'overall' temperature parameter obtained from a Wilson plot.

(a) *Selection of the possible atomic positions*

If no pseudosymmetry is involved the calculated Fourier synthesis compared with the final Fourier function will show:

1. enhanced peaks – weight τf – at the positions of the known atoms
2. reduced peaks – weight χf – at the sites of unknown atoms
3. background peaks .

The weighting factors τ and χ have been calculated by Luzatti (1953) and Ramachandran (1964). These factors enable us to define a significance level in the calculated electron density map; peaks above this level are expected to correspond to real atoms.

The possible atomic positions were refined by interpolation in the calculated electron density function.

(b) *A straightforward structure evaluation; R_c and R_f*

The experimental results (see § 2) showed that if the R_2 value increased the newly added atom would not correspond to an atomic position.

We therefore formulated a 'negative' criterion, namely a criterion to eliminate incorrect atoms. If $(R_{\text{new}} - R_{\text{original}}) > 0$, the related atom will be incorrect. This criterion is necessary, but not sufficient.

Each possible atomic position that was not eliminated, was accepted as a correct one and consequently added to the known part of the structure looked for.

We tested this negative criterion with the crystal structure of nickel hydrogen malate and potassium hydrogen mesotartrate. The structures resulting from the proposed procedure were in both cases complete and correct. They were refined without any difficulty.

(c) *Structure evaluation combined with the elimination of pseudosymmetry*

Once we know a small part of the structure, it is easy to detect the pseudosymmetry, if any. If pseudosymmetry does occur we still demand of the proposed procedure that it yield not only a complete, but also a unique solution of the crystal structure. This means that the criterion $(R_{\text{new}} - R_{\text{original}}) > 0$ for the elimination of incorrect atomic positions is not sufficient, because not only R_c but also R_p has a value smaller than R_o (see §4). We therefore needed one more criterion.

From each group of possible atomic positions related by the known pseudosymmetry only one position, corresponding to the lowest R_2 value, was accepted as a correct one. This criterion is of course not always correct, but will for the moment suffice.

The combination of the two formulated criteria was tested on several compounds.

1. Zinc malate, space group $P2_1$. The pseudosymmetry element is an inversion centre. The distribution of E values $P(E)$ (Ramachandran & Srinivasan, 1959)

corresponds clearly to a non-centrosymmetric space group. The evaluation procedure yielded the complete and unique structure.

2. Bromopregnane derivate, space group $P2_12_12_1$. The pseudosymmetry element is a mirror plane. The $P(E)$ function corresponds to a non-centrosymmetric space group. The structure was found without any trouble and did refine perfectly.

3. Potassium hydrogen monofluormalonate (Lenstra & Spek, 1974), space group $Pca2_1$. The pseudosymmetry involved is a pseudo-C-centring of the structure. The $P(E)$ function corresponds neither to a centrosymmetric nor to a noncentrosymmetric space group. The experimentally determined structure was found to be incorrect only for the F atom, which appeared to be placed in a pseudosymmetry related F position. The least-squares refinement procedure proposed by Koyama *et al.* (1970) also failed to identify the incorrectly placed atom.

4. Benzeetimide hydrobromide (Spek & Lenstra, 1974), space group $P1$, $Z=2$. The structure contains 56 atoms per unit cell. The pseudosymmetry element is an inversion centre. The $P(E)$ function is clearly centrosymmetric. The structure resulting from the program was incorrect. Most accepted atomic positions, however, were found to be correct; all other accepted positions appeared to be related to their correct sites through the pseudo-inversion centre. The structure model was not complete. This was due to our criterion for the elimination of the pseudosymmetry. In some situations both atomic positions, of which only one was accepted, were correct.

The last two mentioned structures were not known beforehand. The correct structure could easily be derived from the experimentally determined atomic positions by taking into account the pseudosymmetry involved and the chemical knowledge of the molecules searched for.

6. A comparison of the discriminator function D and the residual R_2

Hackert & Jacobson (1970) describe a discriminator function D for testing the correctness of a partial structure. The D value depends on the difference between the observed Patterson function P_{obs} and the Patterson map P_{calc} related to the partial structure. Algebraically expressed the discriminator function is based on:

$$S=\int_v |P_{\text{obs}}-P_{\text{calc}}|\,\mathrm{d}V\,.$$

The value of D is calculated from:

$$D\equiv\frac{\Delta S_t-\Delta S_o}{\Delta S_t}$$

in which ΔS is the change in S value caused by the addition of a new fragment to the known part of the structure and the subscripts t and o are theoretically calculated and practically observed respectively.

From these author's Tables 1 and 2 the reader may conclude that the discriminator function D is a better criterion than the common R value. The calculated D value results from ΔS_o and ΔS_t. The calculated R value is the experimental one, whereas the theoretical value has been left out of the discussion. In this situation it is of course obvious to prefer the D value.

We employed the R_2 value as a criterion which corresponds to

$$R=\int_v (P_{\text{obs}}-P_{\text{calc}})^2\mathrm{d}V\,.$$

The necessary, but not sufficient, condition for a correct fragment is R or S showing a minimum value. We are now able to calculate the theoretical change in R_2 value, and compare the D value with, for instance, R', in which R' is defined as:

$$R'\equiv\frac{\Delta R_{2,t}-\Delta R_{2,o}}{\Delta R_{2,t}}\,.$$

In this situation I prefer R', because a time-consuming Patterson calculation for the known fragment is then avoided.

According to Hackert & Jacobson the residual is a sensitive criterion only if nearly all atoms are placed in reasonably correct positions. They therefore proposed using the D value in the situation with a small initial fragment.

In solving equal-atom structures and using only small initial fragments it is highly probably that nearly the complete vector set related to this model happens to be present in the observed Patterson function. This is the result of the immense amount of vector overlap (see, *e.g.* Braun, Hornstra & Leenhonts, 1969). Our conclusion is that both the R_2 value and the S value – and hence the D function – suffer from the same kind of insensitivity.

In Table 3 of Hackert & Jacobson the D value shows a greater sensitivity to incorrect positioning of the new fragment than does the common R value. This is true, but not only because of the difference between these functions. To calculate the D value the authors use Patterson functions that have been calculated with sharpened intensities.

This means that high-order reflexions have a greater weight in the D function than in the R function. The relation between high-order reflexions and the accuracy of a structure determination is well known. The influence is clearly stated, for instance, by Wilson (1969) and Luzatti (1952). From their discussion we see that in using sharpened intensities the residual R_2 and also the common R will be sensitive to incorrect positioning of the newly added fragment.

Our final conclusion is that in a structure evaluation the D function and the residual R_2 are both useful. The functions are expected to have nearly the same properties. According to their nature the best way to employ them is in eliminating incorrect atomic positions. To formulate, however, the best possible criteria with the R_2 or D function is not yet possible, because the distribution functions $P(R_2)$ or $P(D)$ are still unknown.

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Polytypism in Silver Iodide

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Synthetic crystals of silver iodide are shown to form polytypes other than the previously reported wurtzite-type β-AgI and sphalerite-type γ-AgI. Four new polytypes have been discovered and their layer sequences determined by X-ray diffraction. The constant of proportionality between percentage hexagonality and birefringence of AgI polytypes has been established.

Introduction

Silver iodide is reported to be trimorphic at atmospheric pressure (*e.g.* Burley, 1963*a*). Below a transition temperature of 147 °C the structure may be of the sphalerite-type (γ-AgI) or the wurtzite-type (β-AgI). These transform to a body-centred cubic structure (α-AgI) in which the silver ions are disordered (Strock, 1934).

Single crystals of β-AgI have been grown by several methods: Helmholz (1935), Cochrane (1967), Mills, Perrott & Fletcher (1970), Suri, Henisch & Faust (1970). The most detailed investigation of the hexagonal form is due to Burley (1963*b*), and his crystallographic data are summarized as follows:

Space group $P6_3mc$
Cell dimensions $a_0=4{\cdot}592$, $c_0=7{\cdot}510$ Å
I at $(\frac{1}{3},\frac{2}{3},0)$, $(\frac{2}{3},\frac{1}{3},\frac{1}{2})$
Ag at $(\frac{1}{3},\frac{2}{3},u)$, $(\frac{2}{3},\frac{1}{3},\frac{1}{2}+u)$ with $u=0{\cdot}6253$
Isotropic temperature factors $B_{\rm I}=1{\cdot}8$, $B_{\rm Ag}=3{\cdot}4$ Å^2.

The very existence of the low-cubic polymorph γ-AgI has been disputed by Majumdar & Roy (1959). If it does exist it is almost certainly metastable at all temperatures below the $\gamma\rightarrow\alpha$ transition at 555 °C (Burley, 1963*a*). Fridrichsons & Mathieson (1962) have described γ-AgI as a metastable disordered polytype of β-AgI produced by crushing the latter. Certainly we are not aware of any successful attempts to grow single crystals of γ-AgI, and structural investigations of the β-AgI–γ-AgI system have been performed with powder samples only (Bloch & Möller, 1931; Manson, 1956; Majumdar & Roy, 1959; Burley, 1963*a*, 1964). Conflicting conclusions have been drawn from these studies concerning the stability relations between the putatively coexisting γ and β forms. Bloch & Möller (1931) found that the sphalerite form was stable at low temperatures and they imply an equilibrium transformation $\gamma\rightleftharpoons\beta$ at about 135 °C. Manson (1956) reports that the transition $\gamma\rightarrow\beta$ occurred rapidly at all temperatures above 120 °C and that the transformation was partially reversible. Burley (1963*a*, 1964) found that the phase change