Effects of Misplaced Atoms on the Residual $R_2$ in Space Groups of Higher Symmetry

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In space groups of symmetry higher than $P1$ misplacement of a single atom implies the misplacement of all those in the same Wyckoff position, and hence the effect on the residual is larger than in $P1$. 'Exact' values of the residual $R_2$ are obtained, with explicit allowance for dispersion.

1. Introduction

Wilson (1950) considered the values obtained for what was then called the reliability index when none of the atoms was in its right position. Because of the different degrees of dispersion of the intensity distribution functions different values were obtained for space groups $P1$ and $P\bar{1}$. Later Wilson (1969) obtained expressions for the value of three residuals when only one atom and those related to it by symmetry were misplaced. Second approximations were obtained for the space groups $P1$ and $P\bar{1}$, and a first approximation for the space group $P2/m$. He speculated that space groups of higher symmetry would lead to results of the same type, but with larger numerical coefficients. Recently there has been renewed interest in the subject (e.g. Parthasarathy & Parthasarathy, 1972; Lenstra, 1974 and private communications; Wilson, 1974b; Parthasarathy, 1975). Lenstra, in particular, has approached the subject in a new way, from the coincidence of vectors in the Patterson map, instead of basing his calculations on the intensity distribution functions. The present paper extends the work systematically to space groups of higher symmetry; the approach is through the expressions for the structure factors in **International Tables for X-ray Crystallography** (1952).

In general, the speculations of Wilson (1969) about space groups of higher symmetry are confirmed. In particular, if there are several non-equivalent misplaced atoms $R_2$ is given by

$$R_2 = 2\Sigma_{i}^{-1} \sum_{i} p_{i} f_{i}^{2} \quad (1)$$

for non-centrosymmetric space groups, and by

$$R_2 = 8(3\Sigma)^{-1} \sum_{i} p_{i} f_{i}^{2} \quad (2)$$

for centrosymmetric space groups, where $\Sigma$ is the sum of the squares of the moduli of the scattering factors of all the atoms, equal to the mean intensity of reflexion (Wilson, 1942), $p_i$ and $f_i$ are respectively the multiplicity and the modulus of the scattering factor of the $i$th misplaced atom, and the summation is over all misplaced atoms in the asymmetric unit. These expressions are in each case first approximations, valid when the scattering power of the misplaced atoms is small compared with the total scattering power of the unit cell; 'exact' expressions, involving also sums of fourth powers of the scattering factors and making allowance for dispersion, are given in (20) and §3.

A recent paper by Parthasarathy & Parthasarathy (1975) appears at first sight to be dealing with the same questions, but there are two important differences. First, they use a scaling factor that makes the average intensity for a partial structure equal to the average value for the full structure when some of the atoms are omitted because, for example, their positions are unknown. (The relation of this procedure to the scaling
of intensities is touched on in §4.) Secondly, they include the fourth-power terms for some atoms (the 'heavy' atoms in their application) and omit them for the rest (the 'light' atoms). This procedure is justifiable when there are many atoms in the second group and few in the first, but in effect they have set themselves a different problem, and the solution is correspondingly different.

Notation

The notation of this paper is similar to that of the author's previous work, but a few changes are introduced to avoid multiplicity of subscripts. In order to include dispersion bold-face type is used for complex scattering factors and signed or complex structure factors. The sum of the squares of the moduli of the scattering factors is denoted by \( Z \), as before, but the sum of the squares of the complex scattering factors is denoted by \( S \). It should be noted that the modulus of \( S \) is equal to \( Z \) only if all atoms have the same phase angle. To a first approximation

\[
\langle F^2 \rangle = \Sigma,
\]

(10)

\[
\langle F^2 \rangle = (k-1)S,
\]

(11)

where \( k \) has the value 1 for the general reflections of non-centrosymmetric space groups and the value 2 for centrosymmetric. (For zones and rows of reflections the symmetry of the corresponding projection determines the value of \( k \).) In (10) and (11) \( F \) represents \( F_1, F_2, G, H_1, H_2 \) as required, suitable subscripts being used to distinguish the corresponding values of \( Z \) and \( S \).

The mean value of the fourth powers of structure factors has been discussed by, for example, Foster & Hargreaves (1963) and Wilson (1951, 1976). In the present notation

\[
\langle F^4 \rangle = 2Z^2 + (k-1)S^2 - \sum_i [(1+k)p_i^2 - q_i]f_i^4,
\]

(12)

where \( p_i \) is the multiplicity of the Wyckoff position occupied by the \( i \)th atom, \( q_i \) is an integer depending on the space group and the Wyckoff position (actually the mean value of the fourth power of the trigonometrical structure factor for the Wyckoff position in question), and the summation is over the atoms of the asymmetric unit. Foster & Hargreaves point out that the space groups of the triclinic, monoclinic and orthorhombic systems can be arranged in seven categories for which the values of \( p \) and \( q \) are the same (within trivial factors depending on the lattice; \( Fdd2 \) and \( Fddd \) do not fit in with the scheme). The fundamental classification is presumably the point group, though \( 1, 2 \) and \( m \) all have \( p=2 \) and \( q=6 \) for the general position. Equality of the \( q \)’s holds also within each crystal class of the trigonal system, but there are many exceptions in the tetragonal, hexagonal (\textit{sensu stricto}) and cubic systems. Empirically, one might generalize to say that if the space group contains no single symmetry element of multiplicity greater than three, the value of \( q \) depends only on the point group, whereas if there is a symmetry element of multiplicity of four or six (such as \( d \) in \( Fdd2 \) and \( Fddd \) or \( 4_1 \) in \( P4_1 \)) a special calculation is necessary. The values of \( q \) have been tabulated for the general positions of many space groups by Wilson (1975b); for those common to the two listings they are equivalent.
to the coefficient of $S(4)$ in Table 1 of Foster & Har
greaves. For the space groups $P1$ ($p=q=1$) and $P\bar{T}$
($p=2$, $q=6$), (12) reduces to the familiar forms (Wil-
son, 1951)

$$\langle I^2 \rangle = 2\Sigma^2 - T$$

and

$$\langle I^2 \rangle = 2\Sigma^2 + S^2 - 3T,$$

$$= 3\Sigma^2 - 3T$$

in the absence of dispersion.

By the use of (10), (11) and (12) the average value of
the square of the difference of the intensities from the
two structures can be found. From (9), (10) and (11)
$$\langle (I_1 - I_2)^2 \rangle = \langle H_1^* \rangle - 2\Sigma_1 \Sigma_2 + \langle H_2^* \rangle$$
$$+ (k-1)S_0^*(S_1 + S_2)$$
$$+ (k-1)S_0^*(S_1^* + S_2^*)$$
$$+ 2\Sigma_0^*(\Sigma_1 + \Sigma_2)$$

where the subscript 0 refers to the atoms common to
both structures, 1 to the atoms unique to the first
structure, and 2 to the atoms unique to the second
structure. Symbols without subscript will refer to the
complete structure 1, so that, for example,
$$\Sigma = \Sigma_0 + \Sigma_1.$$  

From (12) the residual becomes

$$R_2 = \langle (I_1 - I_2)^2 \rangle / \langle I_2^2 \rangle$$

$$= \{ 2\Sigma_0^*(\Sigma_1 + \Sigma_2) + 2(\Sigma_1^2 + \Sigma_1^2 + \Sigma_2^2) + (k-1) (S_1^2 + S_2^2)$$
$$+ (k-1)S_0^*(S_0^* + S_1^* + S_2^*)S_0 \}$$
$$- \sum_{t+2} [(1+k)p_i^2 - q_i f_i]$$
$$+ \{ 2\Sigma^2 + (k-1)S^2 - \sum I [(1+k)p_i^2 - q_i f_i] \}$$

from (17). If only a few atoms are misplaced the im-
portant terms are those containing $\Sigma$, $S$, and $S'$; the residual is then

$$R_2 = \{ 2\Sigma_0^*(\Sigma_1 + \Sigma_2) + (k-1) [(S_0^* + S_0^* + S_1^* + S_2^*)S_0]$$
$$+ 2\Sigma_0^*(\Sigma_1 + \Sigma_2) \}$$
$$- \sum_{t+2} [(1+k)p_i^2 - q_i f_i]$$

which reduces to (1) and (2) when dispersion is negl-
gated.

3. Special cases

The general expression for $R_2$ can be simplified in
various ways, depending on the assumptions that can
plausibly be made about the atomic positions and about
the way in which the calculations are handled if, for
example, $I_1$ relates to the observed intensities and $I_2$ to
the calculated. Those considered worth special mention
are:
(i) All the atoms occupy the same Wyckoff position.
(ii) There is no appreciable dispersion.
(iii) The structures 1 and 2 are different arrangements
of the same atoms.
(iv) The structures have no common part, so that
$\Sigma_0$ and $T_0$ are zero.
(v) No assumption is made about the positions of
the atoms peculiar to structure 2, and $S_2$ and $T_2$
are put equal to zero.

It is, of course, possible for two or more of these
possibilities to occur together; there is, for example,
nothing incompatible in any combination of the first
four.

3.1 All atoms in the same Wyckoff position

If all atoms are in the general position, or in the same
special position with different parameters, $p$ and $q$
have the same value for all atoms, and can be taken
outside the summation signs. Equation (20) then then

$$R_2 = \{ 2\Sigma (\Sigma_1 + \Sigma_2) - 2\Sigma_0^*(\Sigma_1 - \Sigma_2) + (k-1) [S_1^2 + S_2^2]$$
$$+ (k-1) [(S_1 + S_2)S_0^* + (S_1^* + S_2^*)S_0]$$
$$- (S_1^2 + S_2^2 + S_1S_2 + S_1S_2^*) - [(1+k)p - q/p] (T_1 + T_2)$$
$$+ (2\Sigma^2 + (k-1)S^2 - [1+(k)p - q/p]T^2).$$

The situation of having all atoms in the general posi-
tion is very common among organic structures, but
much less common among inorganic and metallic
structures.

3.2 Dispersion negligible

If there is no appreciable dispersion it is unnecessary
to distinguish between $S$, $S^*$, and $S'$, so that (20) be-
comes

$$R_2 = \{ 2k\Sigma (\Sigma_1 + \Sigma_2) - (k-1)\Sigma_0^* - 2(k+1)\Sigma_1^*$$
$$+ (k+1)\Sigma_2^* - \sum_{t+2} [(1+k)p_i^2 - q_i f_i]$$
$$+ \{ (1+k)\Sigma^2 - \sum I [(1+k)p_i^2 - q_i f_i] \},$$

or, if all the atoms have the same Wyckoff position,

$$R_2 = \{ 2k\Sigma (\Sigma_1 + \Sigma_2) - (k-1)\Sigma_0^* - 2(k+1)\Sigma_1^*$$
$$+ (k+1)\Sigma_2^* - [(1+k)p - q/p] (T_1 + T_2)$$
$$+ [(1+k)\Sigma^2 - [(1+k)p - q/p]T^2].$$

3.3 Different arrangements of the same atoms

If structures 1 and 2 consist of the same numbers and
kinds of atoms in different arrangements the values of
$\Sigma_1$ and $\Sigma_2$; $S_1$ and $S_2$; and $T_1$ and $T_2$ are equal, so that
(20) becomes

$$R_2 = \{ 4\Sigma_1 - 2\Sigma_0^* + 2(k-1) (S_1S_0^* + S_1^* S_0 - S_2^*)$$
$$- \sum_{t+2} [(1+k)p_i^2 - q_i f_i]$$
$$+ (2\Sigma^2 + (k-1)S^2 - \sum I [(1+k)p_i^2 - q_i f_i] \}.$$
If, in addition, the atoms all occupy the same Wyckoff position,

\[ R_2 = \{4\Sigma_1 - 2\Sigma_1^2 + 2(k-1)(\Sigma_S^* + S_S^* - S_1^2) \]

\[ - 2[(1+k)p-q/p]T \}

\[ + \{2\Sigma^2 + (k-1)S^2 -[(1+k)p-q/p]T \} , \]

with a further obvious simplification if dispersion can be neglected.

3.4 No common part

If the structures have no common part \( \Sigma_0, S_0 \) and \( S_0 \) are zero and \( \Sigma, S \) and \( S \) are equal to \( \Sigma_1, S_1 \) and \( S_1 \). The expression for \( R_2 \) is then given by \( (19) \) with the terms in \( \Sigma_0, S_0 \) and \( S_0 \) omitted and subscripts \( i \) added in the denominator. If, in addition, the structures are different arrangements of the same atoms, the expression reduces to

\[ R_2 = \{2\Sigma_1^2 + 2(k-1)S_1^2 - 2 \Sigma \Sigma \}

\[ + \{2\Sigma^2 + (k-1)S^2 -[(1+k)p-q/p]T \} . \]

If, further, all atoms are in the same Wyckoff position,

\[ R_2 = \{2\Sigma_1^2 + 2(k-1)S_1^2 - 2 \Sigma \Sigma \}

\[ - 2[(1+k)p-q/p]T \}

\[ + \{2\Sigma^2 + (k-1)S^2 -[(1+k)p-q/p]T \} . \]

Wilson (1974, 1975a) has given the values of \( R_2 \) for this case for the space groups \( P1 \) and \( PT \) (for which \( p, q \) and \( k \) are 1, 1, 1 and 2, 6, 2 respectively), not taking dispersion into account. Equation \( (28) \) correctly reduces to his equations \( (12) \) and \( (14) \) after the appropriate substitutions.

3.5 Atoms peculiar to second structure omitted

It may be thought advisable to leave the atoms peculiar to one structure out of consideration if, for example, \( I_1 \) relates to the observed intensities, and at the current stage of refinement the positions of the atoms are unknown. The calculated intensities \( I_2 \) will then relate to only the common part of the two structures, and \( \Sigma_2, S_2, S_2 \) and \( T_2 \) will be zero. Equation \( (20) \) becomes

\[ R_2 = \{2\Sigma_2^2 + 2(k-1)S_2^2 - 2 \Sigma \Sigma \}

\[ - 2[(1+k)p-q/p]T \}

\[ + \{2\Sigma^2 + (k-1)S^2 -[(1+k)p-q/p]T \} . \]

This is approximately half the value of \( R_2 \) given by \( (25) \), in which the atoms peculiar to the second structure are put in the wrong positions. From the point of view of reducing the residual it is better to omit than to misplace – a conclusion in accordance with common sense.

4. Problems of scaling

In the preceding discussions it has been assumed that \( G, H_1 \) and \( H_2 \) and the corresponding intensities are all on the same 'absolute' scale. In practice this will not always be the case. If \( I_1 \) is the observed intensity and \( I_2 \) the calculated, the scaling factor implicit in \( I_2 \) should be adjusted at each stage of refinement so that the average values are equal – this has been discussed in more detail elsewhere (Wilson, 1974a; Lomer & Wilson, 1975). In the type of problem discussed here, however, for which some atoms may not be included in the calculation of \( I_2 \), the best procedure will probably be to adjust the scaling so that

\[ \langle I_1 \rangle = \langle I_2 \rangle + \Sigma_2 ; \]

one thus takes into account the actual average of the calculated intensity for the atoms whose positions are supposed known, and the average to be expected on statistical grounds for the atoms whose positions are unknown. The procedure of Parthasarathi & Parthasarathy (1975), following Srinivasan & Ramachandran (1965), goes some way towards this, but is not identical with it. Refining the scaling factor by least squares would seem to be unjustifiable, since the value obtained is known to be biased by 'defects in the model', which missing or misplaced atoms certainly are. It would be easy, but tedious, to elaborate on the consequences of doing so. Some extreme examples are given by Wilson (1974b).

References