

above, in which only the single inelastic scattering of electrons is taken into account, is successful at least qualitatively in explaining the experimental features observed for the H.K. lines. This is probably because any inelastic process of the electron scattering contributing to formation of the H.K. lines can take place only at a small depth beneath the crystal surface as a result of the small extinction distance in the Bragg case, which is estimated to be of the order of ten Ångströms at most for lower-order H.K. lines from MgO.

Other simplifications assumed in the theory, such as those due to the two-wave approximation and the approximate forms of the structure factors for Kikuchi patterns, should be more refined for quantitative discussion. In this respect, however, more quantitative experimental data should be accumulated.

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## Discrepancy Factors for use in Crystal Structure Analysis. II. Normalized Index $\bar{R}_2$ for Crystals with a Few Heavy Atoms in the Asymmetric Unit Belonging to the Triclinic, Monoclinic and Orthorhombic Systems\*

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Theoretical expressions for the normalized form of the discrepancy index  $R_2$  of Wilson have been obtained for crystals containing heavy atoms of similar scattering power, with the heavy-atom part of the structure taken as the trial model. The results obtained are applicable for crystals belonging to 72 space groups of the triclinic, monoclinic and orthorhombic systems. Expressions for two limiting situations, namely complete relatedness and complete unrelatedness, have been tabulated for the commonly occurring cases corresponding to the number of heavy atoms in the asymmetric unit being one or two. Theoretical curves for this index as a function of the fractional heavy-atom contribution are also given for the various cases.

#### Introduction

Wilson (1969) suggested the discrepancy index  $R_2$  (which is the ratio of the sum of the squares of the differences in the observed and calculated intensities over the various observed reflexions to the sum of the squares of the observed intensities) for use in crystal structure analysis, since it is the simplest index to manipulate theoretically. He has also considered the effect of a badly misplaced atom on this index.

Parthasarathy & Parthasarathi (1972) (hereafter abbreviated as PP, 1972) have worked out theoretical expressions of this index for crystals containing a few (*i.e.* 1 or 2) or many heavy atoms in the unit cell, and their final expressions (Table 1 of PP, 1972) are valid for triclinic space groups only. Since organic molecules crystallize more frequently in monoclinic or orthorhombic than in triclinic space groups, it would be useful to work out the values of this index\* for these space groups corresponding to the commonly occur-

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\* The theoretical evaluation of other possible types of discrepancy indices for space groups of higher symmetry seems to be too complicated to be carried out at present.

ring case of a crystal containing a few (1 or 2) heavy atoms in the *asymmetric unit* (besides a large number of light atoms) taking the trial model to consist of the heavy atoms alone. In this paper we shall therefore obtain the theoretical expressions of this  $R$  index as a function of  $\sigma_1^2$ , which is the fractional heavy-atom contribution to the local mean intensity. We shall however consider the index in the normalized form (see next section for the definition of the normalized index) since Srinivasan & Ramachandran (1965) have shown that the normalization procedure has certain advantages. Owing to theoretical difficulties we shall not consider the general case of an imperfectly related trial model. We shall consider here two limiting situations, namely, when the model (consisting of the heavy atoms alone) is completely correct (*i.e.* the related case, referred to as the  $R$  case) and when the model is completely wrong (*i.e.* the unrelated case, referred to as the  $UR$  case). We shall neglect errors in the observed data, since at this stage of structure analysis, the contribution to the  $R$  index due to the incompleteness of the trial model is much greater than that arising from the random errors in the observed intensities.

The notation in this paper closely follows that in PP (1972). Thus the heavy atoms constituting the model are denoted by the symbol  $P$  and the true structure by  $N$ .

### Derivation of the theoretical expressions

Consider a crystal containing  $N$  atoms in general positions, of which  $P$  are heavy atoms and the remaining  $Q (= N - P)$  are light atoms of similar scattering power. Let  $s$  be the symmetry number of the space group, so that  $P/s (= p, \text{ say})$  and  $Q/s (= q, \text{ say})$  respectively represent the number of heavy and light atoms in the asymmetric unit. Following the normalization procedure of Srinivasan & Ramachandran (1965), we define the normalized  $R_2$  index, denoted by  $\bar{R}_2$ , as

$$\bar{R}_2 = \frac{\sum_{hkl} (I_N - I_P^c/\sigma_1^2)^2}{\sum_{hkl} I_N^2}, \quad (1)$$

which may be compared with equation (2) of PP (1972). Equation (1) can be rewritten in terms of the normalized intensity variables  $z_N$  and  $z_P^c$  as

$$\bar{R}_2 = \frac{\langle (z_N - z_P^c)^2 \rangle}{\langle z_N^2 \rangle}. \quad (2)$$

On simplification (2) yields

$$\bar{R}_2 = [\langle z_N^2 \rangle + \langle z_P^{c2} \rangle - 2\langle z_N z_P^c \rangle] / \langle z_N^2 \rangle. \quad (3)$$

Since  $F_N = F_P + F_Q$ , it follows that

$$z_N = \sigma_1^2 z_P + \sigma_2^2 z_Q + 2\sigma_1\sigma_2 \sqrt{z_P z_Q} \varepsilon_{PQ} \quad (4)$$

where

$$\begin{aligned} \varepsilon_{PQ} &= \cos(\alpha_P - \alpha_Q) \quad \text{for } NC \\ &= s_P s_Q \quad \text{for } C. \end{aligned} \quad (5)$$

Here the symbols  $C$  and  $NC$  denote centrosymmetric and non-centrosymmetric space groups respectively.

Since  $F_P$  and  $F_Q$  are independent contributions to the structure factor  $F_N$ , it follows from (5) that

$$\langle \varepsilon_{PQ} \rangle = 0 \quad \text{for } C \text{ and } NC \quad (6)$$

$$\begin{aligned} \langle \varepsilon_{PQ}^2 \rangle &= \frac{1}{2} \quad \text{for } NC \\ &= 1 \quad \text{for } C. \end{aligned} \quad (7)$$

Making use of (4) and (6) and the known property that  $\langle z_P \rangle = \langle z_Q \rangle = 1$  it can be shown that

$$\langle z_N^2 \rangle = \sigma_1^4 \langle z_P^2 \rangle + \sigma_2^4 \langle z_Q^2 \rangle + 2\sigma_1^2 \sigma_2^2 [1 + 2\langle \varepsilon_{PQ}^2 \rangle]. \quad (8)$$

Since the  $Q$  atoms are taken to be of similar scattering power and sufficiently large in number,  $F_Q$  follows the acentric or centric distribution of Wilson (1949) according as the crystal is non-centrosymmetric or centrosymmetric. Hence we have

$$\begin{aligned} \langle z_Q^2 \rangle &= 2 \quad \text{for } NC \\ &= 3 \quad \text{for } C. \end{aligned} \quad (9)$$

Making use of (7) and (9) in (8) we obtain

$$\begin{aligned} \langle z_N^2 \rangle &= \sigma_1^4 \langle z_P^2 \rangle + 2\sigma_2^4 + 4\sigma_1^2 \sigma_2^2 \quad \text{for } NC \\ &= \sigma_1^4 \langle z_P^2 \rangle + 3\sigma_2^4 + 6\sigma_1^2 \sigma_2^2 \quad \text{for } C. \end{aligned} \quad (10)$$

For a model of the related type  $F_P^c = F_P$  so that  $z_P^c = z_P$ . Hence by making use of (4) and (6) we obtain

$$\langle z_N z_P^c \rangle = \langle z_N z_P \rangle = \sigma_1^2 \langle z_P^2 \rangle + \sigma_2^2. \quad (11)$$

However, if the model is of the unrelated type  $z_N$  and  $z_P^c$  will be independent random variables so that

$$\langle z_N z_P^c \rangle = \langle z_N \rangle \langle z_P^c \rangle = 1. \quad (12)$$

Since the model contains the same number and types of  $P$  atoms as the given structure, it follows that even for an unrelated model

$$\langle z_P^2 \rangle = \langle z_P^{c2} \rangle. \quad (13)$$

Making use of (10)–(13) in (3) and simplifying, we obtain the following results.

#### Related case

$$\begin{aligned} \bar{R}_2 &= \frac{(1 + \sigma_1^4 - 2\sigma_1^2) \langle z_P^2 \rangle - 2\sigma_1^4 + 2\sigma_1^2}{\sigma_1^4 \langle z_P^2 \rangle + 2 - 2\sigma_1^4} \quad \text{for } NC \\ &= \frac{(1 + \sigma_1^4 - 2\sigma_1^2) \langle z_P^2 \rangle + 1 - 3\sigma_1^4 + 2\sigma_1^2}{\sigma_1^4 \langle z_P^2 \rangle + 3 - 3\sigma_1^4} \quad \text{for } C. \end{aligned} \quad (14)$$

#### Unrelated case

$$\begin{aligned} \bar{R}_2 &= \frac{(1 + \sigma_1^4) \langle z_P^2 \rangle - 2\sigma_1^4}{\sigma_1^4 \langle z_P^2 \rangle + 2 - 2\sigma_1^4} \quad \text{for } NC \\ &= \frac{(1 + \sigma_1^4) \langle z_P^2 \rangle + 1 - 3\sigma_1^4}{\sigma_1^4 \langle z_P^2 \rangle + 3 - 3\sigma_1^4} \quad \text{for } C. \end{aligned} \quad (15)$$

The expressions (14) and (15) involve the quantity  $\langle z_P^2 \rangle$  which is determined by the space-group symmetry, number ( $p$ ) of heavy atoms in the asymmetric unit and their scattering powers. Assuming the  $P$  atoms to occupy general positions, subject to the space-group

symmetry, the values of  $\langle z_p^2 \rangle$  could be obtained from the results in Table 1 of Foster & Hargreaves (1963b) or those in Table 2 of Parthasarathy (1973). When all the  $P$  atoms are of the same type, it can thus be shown that  $\langle z_p^2 \rangle = (2-1/p), (3-3/2p), (2-1/2p), (3-3/4p), (2-1/4p), (2+1/4p)$  and  $(3+3/8p)$  for the space-group categories\* 1, 2, ..., 7 respectively. Substituting these in (14) and (15) we can obtain the final expressions for the index  $\bar{R}_2$  for the various categories of space groups. The results thus obtained for the cases with  $p=1$  or 2 are summarized in Table 1.

### Discussion of the theoretical results

The expressions in Table 1 are applicable for crystals belonging to 72 space groups of the triclinic, monoclinic and orthorhombic systems which can conveniently be grouped into seven categories based on the form of the trigonometric part of the geometrical structure factors (Foster & Hargreaves, 1963a, b). Of these the categories 1, 3, 5 and 6 correspond to non-centrosymmetric space groups while the rest correspond to centrosymmetric space groups. It is seen that for the category 1, if  $p=1$ , the expressions for the  $\bar{R}_2$  index for the related and unrelated cases become identical. This is to be expected since in space group  $P1$  with one heavy atom in the unit cell, the origin can be chosen on the heavy atom itself both in the structure and the model. The variation of the  $\bar{R}_2$  index with  $\sigma_1^2$  is shown in Fig. 1 for the various categories of space groups (except category 1 which is a trivial case) for the case  $p=1$ . The corresponding curves for the case  $p=2$  are shown in Fig. 2. A study of these figures shows that in

\* These numbers correspond to the serial numbers in column 1 of Table 1 of Foster & Hargreaves (1963b).

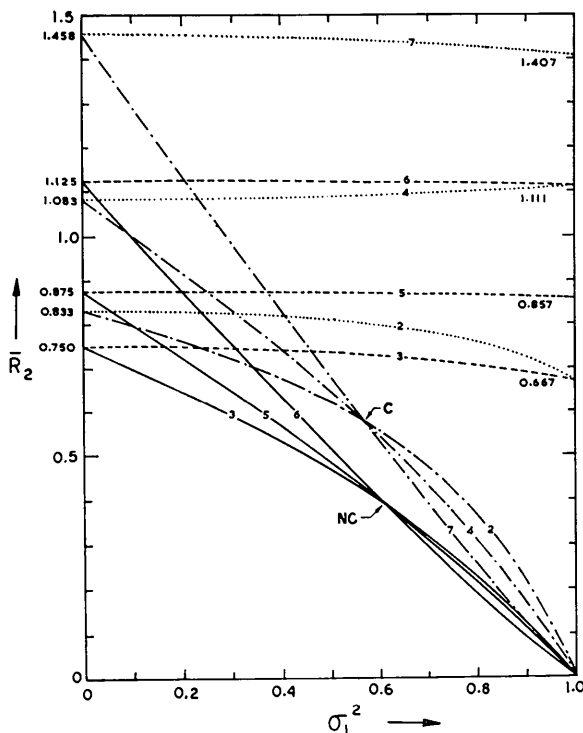


Fig. 1. The variation of the  $\bar{R}_2$  index as a function of the heavy-atom contribution  $\sigma_1^2$  for the six categories of space group belonging to the triclinic, monoclinic and orthorhombic systems for the case with  $p=1$ . The numbers 2 to 7 on the curves represent the space-group category numbers. The values of  $\bar{R}_2$  for  $\sigma_1^2=0$  and 1 are also entered in the figure. The representation of the curves is as follows: Related model belonging to non-centrosymmetric space groups ———; Unrelated model belonging to non-centrosymmetric space groups - - - -; Related model belonging to centrosymmetric space groups - · - · - ·; Unrelated model belonging to centrosymmetric space groups · · · · ·.

Table 1. Final expression for the  $\bar{R}_2$  index for the related and unrelated cases corresponding to the seven categories of space group belonging to the triclinic, monoclinic and orthorhombic systems when the number ( $p$ ) of heavy atoms in the asymmetric units is 1 or 2

Space-group category number	$p=1$		$p=2$	
	R case	UR case	R case	UR case
1	$\frac{1-\sigma_1^4}{2-\sigma_1^4}$	$\frac{1-\sigma_1^4}{2-\sigma_1^4}$	$\frac{3-2\sigma_1^2-\sigma_1^4}{4-\sigma_1^4}$	$\frac{3-\sigma_1^4}{4-\sigma_1^4}$
2	$\frac{5-2\sigma_1^2-3\sigma_1^4}{3(2-\sigma_1^4)}$	$\frac{5-3\sigma_1^4}{3(2-\sigma_1^4)}$	$\frac{13-10\sigma_1^2-3\sigma_1^4}{3(4-\sigma_1^4)}$	$\frac{13-3\sigma_1^4}{3(4-\sigma_1^4)}$
3	$\frac{3-2\sigma_1^2-\sigma_1^4}{4-\sigma_1^4}$	$\frac{3-\sigma_1^4}{4-\sigma_1^4}$	$\frac{7-6\sigma_1^2-\sigma_1^4}{8-\sigma_1^4}$	$\frac{7-\sigma_1^4}{8-\sigma_1^4}$
4	$\frac{13-10\sigma_1^2-3\sigma_1^4}{3(4-\sigma_1^4)}$	$\frac{13-3\sigma_1^4}{3(4-\sigma_1^4)}$	$\frac{29-26\sigma_1^2-3\sigma_1^4}{3(8-\sigma_1^4)}$	$\frac{29-3\sigma_1^4}{3(8-\sigma_1^4)}$
5	$\frac{7-6\sigma_1^2-\sigma_1^4}{8-\sigma_1^4}$	$\frac{7-\sigma_1^4}{8-\sigma_1^4}$	$\frac{15-14\sigma_1^2-\sigma_1^4}{16-\sigma_1^4}$	$\frac{15-\sigma_1^4}{16-\sigma_1^4}$
6	$\frac{9-10\sigma_1^2+\sigma_1^4}{8+\sigma_1^4}$	$\frac{9+\sigma_1^4}{8+\sigma_1^4}$	$\frac{17-18\sigma_1^2+\sigma_1^4}{16+\sigma_1^4}$	$\frac{17+\sigma_1^4}{16+\sigma_1^4}$
7	$\frac{35-38\sigma_1^2+3\sigma_1^4}{3(8+\sigma_1^4)}$	$\frac{35+3\sigma_1^4}{3(8+\sigma_1^4)}$	$\frac{67-70\sigma_1^2+3\sigma_1^4}{3(16+\sigma_1^4)}$	$\frac{67+3\sigma_1^4}{3(16+\sigma_1^4)}$

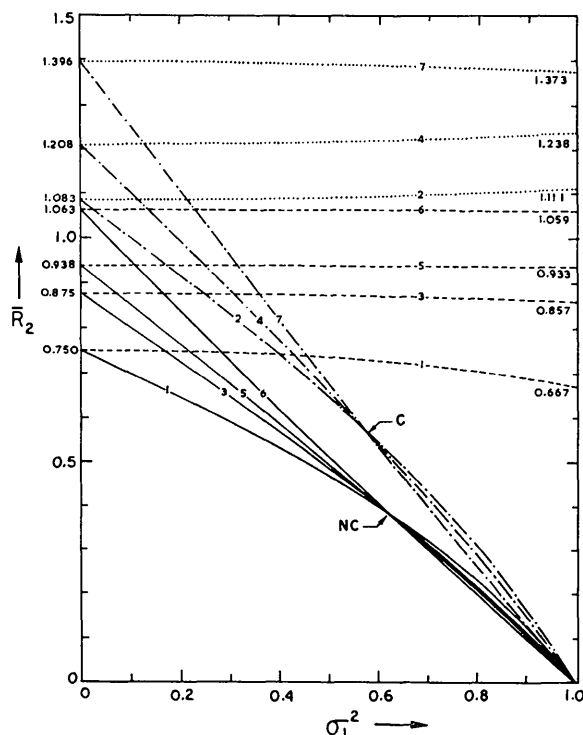


Fig. 2. The value of the  $\bar{R}_2$  index as a function of  $\sigma_1^2$  for the seven categories of space group for the case with  $p=2$ . For other details see the caption to Fig. 1.

the normal range  $0 \leq \sigma_1^2 \leq 0.5$ , the curves for the various categories differ significantly. This points to the need for calculating the value of the  $R$  index for the given crystal, taking into account the space-group symmetry in order to improve the effectiveness of the  $R$  index in the test for the correctness of the positions of the heavy atoms.

The situations considered for obtaining the curves marked 2 in Figs. 1 and 2 of PP (1972) for the unnormalized index  $R_2$  correspond respectively to those for curves marked 2 and 1 in Figs. 1 and 2 of the present paper. A comparison of the relevant curves in this paper and in PP (1972) shows that, for the unrelated case, the normalized index  $\bar{R}_2$  (unlike the unnormalized index  $R_2$ ) remains practically flat throughout the range 0 to 1 of  $\sigma_1^2$ . Thus particularly when  $\sigma_1^2$  is not large, say  $\sigma_1^2 < 0.5$ , the curves for the  $R$  and  $UR$  cases for a given situation (*i.e.*  $\sigma_1^2$  and  $p$  being fixed) are closer in the case of the unnormalized than in the normalized index. Hence when  $\sigma_1^2$  is not large, which is generally the case, the normalized index  $\bar{R}_2$  seems to be preferable to the unnormalized index  $R_2$ . Such a conclusion has in fact been reached in the case of the normalized and un-

normalized forms of the conventional  $R$  index by Srinivasan & Ramachandran (1965). It may incidentally be noted that when  $\sigma_1^2 \rightarrow 1$ ,  $\bar{R}_2 \rightarrow R_2$ .

A study of Figs. 1 and 2 also reveals that in crystals of a given type (*i.e.*  $C$  or  $NC$ ) the distinction between the curves for the  $R$  and  $UR$  cases for any given values of  $p$  and  $\sigma_1^2$  is more marked for categories of space groups of higher symmetry. For example, for non-centrosymmetric crystals when  $\sigma_1^{2*} = 0.3$  and  $p=1$ , the differences in the values of the  $\bar{R}_2$  index for  $R$  and  $UR$  cases are respectively 0.154, 0.228 and 0.371 for the categories 3, 5 and 6. Similarly these values for centrosymmetric crystals are respectively 0.105, 0.256 and 0.470 for the categories 2, 4 and 7. It is seen from Fig. 2 that, for  $p=2$ , the value of  $\bar{R}_2$  for the  $R$  case for a given value of  $\sigma_1^2$  is always greater for centrosymmetric than for non-centrosymmetric space groups. A similar statement holds good for the  $UR$  case also. This property has in fact been observed by Wilson (1950) in the case of the conventional  $R$  index for a completely wrong structure (*i.e.*  $UR$  case). It is however seen from Fig. 1 that such a property is not universal for the case  $p=1$ . For example, for the  $UR$  case, the curve for category 2 (*i.e.* the crystal is of the  $C$  type) is below that of category 5 or 6 (*i.e.* the crystal is of  $NC$  type). Similarly for the  $R$  case, the curve for category 2 is below that for category 6 when  $\sigma_1^2 < 0.3$  (Fig. 1). This shows that for crystals having asymmetric units of the same complexity and with one heavy atom per asymmetric unit, the value of the  $\bar{R}_2$  index for a non-centrosymmetric crystal belonging to category 5 or 6 could be greater than that for a centrosymmetric crystal belonging to category 2.

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\* For crystals containing atoms in general positions the value of  $\sigma_1^2$  is determined by the asymmetric unit.

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