Discrepancy Indices for Use in Crystal Structure Analysis. IV. Theoretical Expressions for the Indices $_BR_1(I)$ and $_BR(I)$ for any Incomplete Model of a Complex Structure*

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General expressions for the discrepancy indices $_BR_1(I_N)$ and $_BR(I_N)$, which are needed to test the correctness of any type of incomplete model of a complex structure containing any number and species of atoms in the unit cell, are derived for the related and unrelated cases. Explicit expressions for these indices for crystals containing all atoms in general positions are also tabulated for the seven categories of space group in the triclinic, monoclinic and orthorhombic systems. Expressions needed for handling crystals containing atoms in both general and special positions and those needed for taking into account random errors of observation in the intensities are also derived.

Introduction

A comparative study of six types of discrepancy indices in their normalized form for crystals and models satisfying the requirements of the basic Wilson distributions (Wilson, 1949) in the different stages of structure analysis carried out in Part III of this series (Parthasarathy & Parthasarathi, 1975) has shown that of all the indices, the Booth-type index based on intensity, *i.e.* $_BR_1(I)$, is the best during the structure completion stage. It is therefore useful to obtain general expressions for this index which can be used to test the correctness of any type of incomplete model of a complex structure.† Explicit expressions for the indices $_BR_1(I)$ and $_BR(I)$ for the related and unrelated cases have been derived earlier for a few special cases (Parthasarathy & Parthasarathi, 1972; Parthasarathi & Parthasarathy, 1975; – the former is hereafter briefly referred to as PP). Wilson (1969) has studied the effect of a single wrong atom in an otherwise correct and complete model structure on the index $_BR(I)$ and Lenstra (1974) has recently carried out similar studies for incomplete models. In this paper we shall derive general expressions for the indices $_BR_1(I)$ and $_BR(I)$ corresponding to the related and unrelated cases when the trial model as well as the crystal contain any *number* and *type* of atoms in the unit cell in both general and special positions; these results hold good for crystals belonging to the triclinic, monoclinic and orthorhombic systems. The case of crystals with pseudosymmetry is however not considered since individual treatments are needed for specific types of pseudosymmetry. In the theory it is found to be convenient to treat first the case of crystals with all atoms in general positions and this is dealt with in §2. Expressions

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† It is fortunate that of the various *R* indices suggested so far, this is the simplest to manipulate theoretically for any complex situation.

applicable to crystals and models with atoms in both general and special positions are derived in §3. Expressions which take into account random errors in the observed intensities are obtained in §4. §5 contains a discussion of the results.

In this paper we shall generally follow the notation and nomenclature used in PP. A few changes are however found to be necessary. Some of these will be explained here and the others at the appropriate places in the text. We shall consider a crystal containing N atoms in the unit cell and an incomplete model containing P atoms. The unknown atoms are denoted by $Q(=N-P)$ as in PP. In a model of the semi-related type, the correct atoms and the wrong atoms will be denoted by the symbols R and W respectively (instead of Pr and Pw used in the paper PP), and the group of atoms designated as Pr' in PP by the symbol R'. The fractional contribution to the local mean intensity from the P, Q, R and W groups of atoms will be denoted by the symbols σ_{1P}^2, σ_{1Q}^2, σ_{1R}^2 and σ_{1W}^2 respectively (these were denoted by σ_1^2, σ_2^2, σ_{1r}^2 and σ_{1w}^2 in PP). We shall use I_{obs} to denote the observed intensity for a given reflection and I_N for its true value. That is, $I_N = I_{obs}$ when there are no errors of observation. As in PP we shall denote the calculated intensity for the model by I_P^c. We shall use the symbols $_BR_1(I_N)$ and $_BR(I_N)$ when we deal with the ideal situation in which the intensities are assumed to be known with perfect accuracy and the symbols $_BR_1(I_{obs})$ and $_BR(I_{obs})$ when dealing with the actual situation in which observed intensities with random errors are involved. That is

$$_BR_1(I_N) = \langle (I_N - I_P^c/\sigma_{1P}^2)^2 \rangle / \langle I_N^2 \rangle \tag{1}$$

$$_BR(I_N) = \langle (I_N - I_P^c)^2 \rangle / \langle I_N^2 \rangle \tag{2}$$

$$_BR_1(I_{obs}) = \langle (I_{obs} - I_P^c/\sigma_{1P}^2)^2 \rangle / \langle I_{obs}^2 \rangle \tag{3}$$

$$_BR(I_{obs}) = \langle (I_{obs} - I_P^c)^2 \rangle / \langle I_{obs}^2 \rangle . \tag{4}$$

We shall define a quantity α to be

$\alpha = 2$ for the non-centrosymmetric case

$\quad = 3$ for the centrosymmetric case. $\tag{5}$

2. Derivation of expressions for $_BR_1(I_N)$ and $_BR(I_N)$: all atoms in general positions

Notation

Let s_g be the symmetry number (*i.e.* the number of equivalent general positions in the unit cell) of the space group. Lower-case letters (*e.g.*, n, p, r and w) are used to denote the number of atoms in the asymmetric unit. Thus

$$n = N/s_g, \quad p = P/s_g . \tag{6}$$

The quantities pertaining to the whole unit cell are characterized by N, P, *etc.* as subscripts to the relevant quantities and those pertaining to the asymmetric unit by n, p, *etc.*, as subscripts. Following Foster & Hargreaves (1963a; 1963b; these two papers are hereafter briefly referred to as FH, 1963a and FH, 1963b respectively), the sum of the mth powers of the scattering factors of the atoms in group j ($j = n$, p or r) of the asymmetric unit is denoted by $S_j(m)$. That is

$$S_j(m) = \sum_{k=1}^{j} f_{jk}^m, \quad j = n, p \text{ or } r . \tag{7}$$

The meaning of the quantities $S_p(2)$, $S_p(4)$, $S_n(2)$ and $S_n(4)$ which occur in the final expressions for the R indices is now obvious. Following Parthasarathy (1973), the quantities* $C_p(4)$, $C_r(4)$ and $C_n(4)$ are defined to be

$$C_j(4) = S_j(4)/[S_j(2)]^2, \quad j = n, p \text{ or } r . \tag{8}$$

We shall first obtain the expressions for $_BR_1(I_N)$ and $_BR(I_N)$ for the semi-related case and then deduce the expressions for the related and unrelated cases by taking suitable limits.

Index $_BR_1(I_N)$

Semi-related case: In the present notation the structure factor relations in equations (3), (4) and (A1) of PP can be rewritten as

$$F_N = F_P + F_Q, \quad F_P^c = F_R + F_W, \quad F_P = F_R + F_{R'} . \tag{9}$$

From (1) it can be shown that

$$_BR_1(I_N) = 1 + \frac{\dfrac{1}{\sigma_{1P}^4} \langle I_P^{c2} \rangle - \dfrac{2}{\sigma_{1P}^2} \langle I_N I_P^c \rangle}{\langle I_N^2 \rangle} . \tag{10}$$

Since the atoms in the model correspond in number and scattering power to the P atoms of the true structure, it follows that

$$\langle (I_P^c)^m \rangle = \langle I_P^m \rangle, \quad m = 1, 2, \ldots . \tag{11}$$

A convenient expression for the quantity $\langle I_N I_P^c \rangle$ occurring in (10) can be obtained from PP. Thus, rewriting equation (A7) of PP in terms of the intensity variables, we obtain

$$\langle I_N I_P^c \rangle = \langle I_R^2 \rangle + \langle I_R \rangle [\langle I_W \rangle + \langle I_Q \rangle] + \langle I_N \rangle \langle I_W \rangle . \tag{12}$$

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* In the rest of the paper these quantities are briefly denoted by C_p, C_r and C_n respectively for convenience.

Making use of the results in (9) and (11), we can show that

$$\langle I_W \rangle = \langle I_{R'} \rangle = \langle I_P \rangle - \langle I_R \rangle, \quad \langle I_Q \rangle = \langle I_N \rangle - \langle I_P \rangle. \tag{13}$$

In view of (13), we can rewrite (12) to obtain

$$\langle I_N I_P^c \rangle = \langle I_R^2 \rangle - \langle I_R \rangle^2 + \langle I_N \rangle \langle I_P \rangle . \tag{14}$$

Making use of (11) and (14) in (10), we obtain

$$_BR_1(I_N) = 1 + \frac{\dfrac{1}{\sigma_{1P}^4} \langle I_P^2 \rangle - \dfrac{2}{\sigma_{1P}^2} [\langle I_R^2 \rangle - \langle I_R \rangle^2 + \langle I_N \rangle \langle I_P \rangle]}{\langle I_N^2 \rangle} . \tag{15}$$

In terms of the normalized variables z_N, z_P and z_R of PP, we can rewrite (15) as

$$_BR_1(I_N) = 1 + \frac{\langle z_P^2 \rangle - \dfrac{2}{\sigma_{1P}^2} [\sigma_{1R}^4 \langle z_R^2 \rangle - \sigma_{1R}^4 + \sigma_{1P}^2]}{\langle z_N^2 \rangle} . \tag{16}$$

For the seven categories of space group in the triclinic, monoclinic and orthorhombic systems (for details of classification into seven categories see FH, 1963b) the second-order moments of z_N, z_P and z_R can be shown to take the general form (see Parthasarathy, 1973)

$$\langle z_N^2 \rangle = \alpha - \beta C_n, \quad \langle z_P^2 \rangle = \alpha - \beta C_p, \quad \langle z_R^2 \rangle = \alpha - \beta C_r, \tag{17}$$

provided the quantity α is defined as in (5) and β as in Table 1. Substituting (17) in (16) we obtain

$$_BR_1(I_N) = 1 + \frac{\left[\alpha - 2 + 2(1-\alpha) \dfrac{\sigma_{1R}^4}{\sigma_{1P}^2} - \beta C_p + 2\beta C_r \dfrac{\sigma_{1R}^4}{\sigma_{1P}^2} \right]}{\alpha - \beta C_n} . \tag{18}$$

Table 1. *Values of the constants β, τ_g, μ_g and ν_g for the seven categories of space group belonging to the triclinic, monoclinic and orthorhombic systems*

	Space-group category number						
Constants	1	2	3	4	5	6	7
β	1	$\frac{3}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	$\frac{1}{4}$	$-\frac{1}{4}$	$-\frac{3}{8}$
τ_g	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{8}$
μ_g	2	$\frac{3}{4}$	$\frac{1}{2}$	$\frac{3}{16}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{3}{64}$
ν_g	1	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{64}$	$\frac{1}{64}$	$-\frac{1}{64}$	$-\frac{3}{512}$

Note: The values of τ_i, μ_i and ν_i ($i = 1, 2$) can also be read from the above table (against τ_g, μ_g and ν_g respectively), provided the category number appropriate to the special positions of interest is known. This can be determined from a study of Table 1 of FH (1963b) keeping in view the form of the geometrical structure-factor formulae for these special positions.

Related case: If all the atoms in the model are correct, then $\sigma_{1R} \to \sigma_{1P}$ and $C_r \to C_p$. Equation (18) therefore yields

$$_BR_1(I_N) = 1 + \frac{\alpha - 2 + 2(1-\alpha)\sigma_{1P}^2 + \beta(2\sigma_{1P}^2 - 1)C_p}{\alpha - \beta C_n} . \tag{19}$$

Unrelated case: If all the atoms in the model are wrong then $\sigma_{1R} \to 0$ and hence (18) yields

$$_B R_1(I_N) = 1 + \frac{\alpha - 2 - \beta C_p}{\alpha - \beta C_n} . \tag{20}$$

For the present case, for atoms in general positions only, the quantity σ_{1P}^2 in (19) can be shown to be

$$\sigma_{1P}^2 = S_p(2)/S_n(2) . \tag{21}$$

Index $_B R(I_N)$

The results for the unnormalized index $_B R(I_N)$ can be obtained by following exactly the same procedure and hence only the equations are given.

Semi-related case:

$$_B R(I_N) = 1 + \frac{\langle I_P^2 \rangle - 2[\langle I_R^2 \rangle - \langle I_R \rangle^2 + \langle I_N \rangle \langle I_P \rangle]}{\langle I_N^2 \rangle}$$

$$= 1 + \frac{\sigma_{1P}^4 \langle z_P^2 \rangle - 2[\sigma_{1R}^4 \langle z_R^2 \rangle - \sigma_{1R}^4 + \sigma_{1P}^2]}{\langle z_N^2 \rangle}$$

$$= 1 + \frac{\alpha \sigma_{1P}^4 + 2(1-\alpha)\sigma_{1R}^4 - 2\sigma_{1P}^2 - \beta C_p \sigma_{1P}^4 + 2\beta C_r \sigma_{1R}^4}{\alpha - \beta C_n}$$

$$. \tag{22a,b,c}$$

Related case:

$$_B R(I_N) = 1 + \frac{\sigma_{1P}^2 [(2-\alpha)\sigma_{1P}^2 - 2 + \beta C_p \sigma_{1P}^2]}{\alpha - \beta C_n} . \tag{23}$$

Unrelated case:

$$_B R(I_N) = 1 + \frac{\sigma_{1P}^2 [\alpha \sigma_{1P}^2 - 2 - \beta C_p \sigma_{1P}^2]}{\alpha - \beta C_n} . \tag{24}$$

3. Derivation of expressions for $_B R_1(I_N)$ and $_B R(I_N)$: atoms in both general and special positions

We can think of three possible types of special position, namely, special positions with 1, 2 and 3 fixed parameters respectively (or equivalently, with 2, 1 and 0 variable parameters; see FH, 1963b) and for brevity we shall refer to the special position with i fixed parameters as special position of type i ($i = 1, 2, 3$).* We shall use the letter g as subscript to any quantity pertaining to general position and the numbers 1, 2 and 3 as subscripts to quantities pertaining to special positions of types 1, 2 and 3 respectively. Thus while s_g is used to denote the number of equivalent general positions in the unit cell, the symbol s_i is used to denote the number of equivalent special positions of type i ($i = 1, 2, 3$). Following Foster & Hargreaves (1963b) we shall define the quantity λ_i by

$$\lambda_i = s_i/s_g, \quad i = 1, 2, 3 . \tag{25}$$

Of the N atoms in the unit cell, let N_g occur in general positions and N_1, N_2 and N_3 in special positions of types 1, 2 and 3 respectively. Of the P atoms of the

incomplete model let P_g occur in general positions and P_1, P_2 and P_3 in the three types of special positions. Thus

$$N = N_g + \sum_{i=1}^{3} N_i, \quad P = P_g + \sum_{i=1}^{3} P_i . \tag{26}$$

We shall define the quantities† n_g, p_g, n_i and p_i to be

$$n_g = N_g/s_g, \quad p_g = P_g/s_g,$$
$$n_i = N_i/s_i, \quad p_i = P_i/s_i, \quad i = 1, 2, 3 . \tag{27}$$

In an obvious notation, the following structure factor equations hold good

$$F_N = F_{Ng} + \sum_{i=1}^{3} F_{Ni}, \quad F_P^c = F_{Pg} + \sum_{i=1}^{3} F_{Pi} . \tag{28}$$

For the treatment of cases involving atoms in both general and special positions, it is convenient to handle structure factors F_n and F_p^c for the asymmetric unit instead of the absolute structure factors F_N and F_p^c (see FH, 1963a). We shall therefore define the quantities F_n and F_p^c to be

$$F_n = F_N/s_g = F_{ng} + \sum_{i=1}^{3} \lambda_i F_{ni} \tag{29}$$

$$F_p^c = F_P^c/s_g = F_{pg}^c + \sum_{i=1}^{3} \lambda_i F_{pi}^c , \tag{30}$$

where

$$F_{ng} = F_{Ng}/s_g, \quad F_{pg}^c = F_{Pg}^c/s_g,$$
$$F_{ni} = F_{Ni}/s_i, \quad F_{pi}^c = F_{Pi}^c/s_i, \quad i = 1, 2, 3 . \tag{31}$$

We shall denote the intensity variables associated with F_n and F_p^c by I_n and I_p^c respectively. That is

$$I_n = |F_n|^2 = I_N/s_g^2, \quad I_p^c = |F_p^c|^2 = I_p^c/s_g^2 . \tag{32}$$

Related case: For this case we have to set $\langle I_R^m \rangle = \langle I_P^m \rangle$, $m = 1, 2$ in (15) and (22a). Since $I_p^c = I_P$ for a related model, we obtain

$$_B R_1(I_N) = 1 + \frac{\left(\frac{1}{\sigma_{1P}^4} - \frac{2}{\sigma_{1P}^2} \right) \langle I_p^2 \rangle + \frac{2}{\sigma_{1P}^2} [\langle I_p \rangle^2 - \langle I_n \rangle \langle I_p \rangle]}{\langle I_n^2 \rangle}$$

$$\tag{33}$$

$$_B R(I_N) = 1 + \frac{2\langle I_p \rangle^2 - \langle I_p^2 \rangle - 2\langle I_n \rangle \langle I_p \rangle}{\langle I_n^2 \rangle} \tag{34}$$

where we have made use of (32). In crystals containing atoms in both general and fixed positions (*i.e.*, special positions of type 3), since the atoms in the fixed positions make different but specific (*i.e.* constant) contributions to different categories of hkl reflexions (see FH, 1963b), the values of the R index for a given model of such a crystal would be different for the different categories of reflexion. This aspect is to be remembered in the evaluation of R indices.

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* For convenience we shall also refer to special position of type 3 as fixed position.

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† If N_g, N_i, n_g, n_i *etc.*, occur as subscripts to other quantities, then they will be written as Ng, Ni, ng, ni, *etc.*, for convenience.

Semi-related case: In crystals containing atoms in both general and special positions, the correct locations of all the atoms in fixed positions would usually be known even at the beginning of a structure analysis (*i.e.* after the space group has been determined). It is therefore more appropriate to derive expressions for the R indices corresponding to the semi-related case by assuming that all atoms in fixed positions in the crystal are included in the model as correct atoms (*i.e.* $R = P_3 = N_3$ and $F_R = F_{P3} = F_{N3}$) while all the other atoms of the model are wrong. We shall also assume that the wrong atoms of the semi-related model correspond in number and *type* of location to the corresponding P atoms of the true structure. That is, if an atom is known to lie at some point on a mirror plane in a given crystal (the exact location $\mathbf{r}$ of the atom being unknown) then in the semi-related model also the atom is taken to lie on the same mirror plane but at an entirely different point $\mathbf{r}'$. With these assumptions, it is obvious that (11) holds good for the present case as well. Further, since (14) was derived by assuming that only the R group of atoms is common to the model and true structure, it also applies to the present case provided we replace I_R by $I_{P3}(= |F_{P3}|^2)$. That is

$$\langle I_N I_P^c \rangle = \langle I_{P3}^2 \rangle - \langle I_{P3} \rangle^2 + \langle I_N \rangle \langle I_P \rangle . \tag{35}$$

For a given category of hkl reflexions, since the contribution I_{P3} from the atoms in the fixed positions is a constant quantity [see equation (46)], it is obvious that

$$\langle I_{P3}^2 \rangle = \langle I_{P3} \rangle^2 = I_{p3}^2 . \tag{36}$$

In view of (36), we obtain from (35)

$$\langle I_N I_P^c \rangle = \langle I_N \rangle \langle I_P \rangle . \tag{37}$$

Making use of (11) and (37) in (12), we thus obtain

$$_B R_1(I_N) = 1 + \cfrac{\cfrac{1}{\sigma_{1P}^4} \langle I_P^2 \rangle - \cfrac{2}{\sigma_{1P}^2} \langle I_N \rangle \langle I_P \rangle}{\langle I_N^2 \rangle} , \tag{38}$$

which in terms of the intensity variables I_n and I_p becomes

$$_B R_1(I_N) = 1 + \cfrac{\cfrac{1}{\sigma_{1P}^4} \langle I_p^2 \rangle - \cfrac{2}{\sigma_{1P}^2} \langle I_n \rangle \langle I_p \rangle}{\langle I_n^2 \rangle} . \tag{39}$$

By following a similar procedure, we can show from (22a) that

$$_B R(I_N) = 1 + \frac{\langle I_p^2 \rangle - 2 \langle I_n \rangle \langle I_p \rangle}{\langle I_n^2 \rangle} . \tag{40}$$

For further simplifications of (33), (34), (39) and (40) it is necessary to obtain expressions for $\langle I_n^m \rangle$ and $\langle I_p^m \rangle$, $m = 1, 2$, by assuming that all the atoms in fixed positions in the structure are included as correct atoms in the model (*i.e.* $I_{P3} = I_{N3}$) and we shall now consider this aspect.

From Table 3 of FH(1963b) it is seen that

$$\langle I_n \rangle = \langle I_{ng} \rangle + \sum_{i=1}^{3} \lambda_i^2 \langle I_{ni} \rangle \tag{41}$$

and

$$\langle I_n^2 \rangle = \langle I_{ng}^2 \rangle + \sum_{i=1}^{3} \lambda_i^4 \langle I_{ni}^2 \rangle + K_1 \langle I_{ng} \rangle [\sum_{i=1}^{3} \lambda_i^2 \langle I_{ni} \rangle]$$
$$+ K_1 [\lambda_1^2 \lambda_2^2 \langle I_{n1} \rangle \langle I_{n2} \rangle + \lambda_2^2 \lambda_3^2 \langle I_{n2} \rangle \langle I_{n3} \rangle$$
$$+ \lambda_3^2 \lambda_1^2 \langle I_{n3} \rangle \langle I_{n1} \rangle] \tag{42}$$

where the quantity K_1 is defined to be

$K_1 = 6$ for the centrosymmetric case

$\quad\; = 4$ for the non-centrosymmetric case. $\tag{43}$

From Table 1 of FH (1963b) it is seen that for any of the seven categories of space group, the expressions for $\langle I_{ng} \rangle$ and $\langle I_{ng}^2 \rangle$ can be written in the form

$$\langle I_{ng} \rangle = \tau_g S_{ng}(2), \quad \langle I_{ng}^2 \rangle = \mu_g [S_{ng}(2)]^2 - \nu_g S_{ng}(4) \tag{44}$$

provided the quantities τ_g, μ_g and ν_g are defined as in Table 1. Similarly it is readily seen that $\langle I_{ni} \rangle$ and $\langle I_{ni}^2 \rangle$ ($i = 1$ and 2) can be written as

$$\langle I_{ni} \rangle = \tau_i S_{ni}(2), \quad \langle I_{ni}^2 \rangle = \mu_i [S_{ni}(2)]^2 - \nu_i S_{ni}(4),$$
$$i = 1, 2 . \tag{45}$$

The quantities τ_i, μ_i and ν_i ($i = 1, 2$) have specific values for a given space group and can be evaluated by the method described in §5. If $f_1, f_2, \ldots, f_{n3}$ are the scattering powers of atoms at the non-equivalent fixed points $1, 2, \ldots, n_3$, we can show that (see FH, 1963b)

$$\langle I_{n3}^m \rangle = [\sum_{j=1}^{n_3} l_j f_j]^{2m} \tag{46}$$

where $l_j = 0$, $+1$ or -1. The appropriate values of l_j are to be obtained from the geometrical structure factor by substituting the coordinates of the fixed points. It is obvious from (46) that for a given category of hkl reflexions, I_{n3} has a constant value.

Substituting (44) and (45) in (41) and (42) we thus obtain

$$\langle I_n \rangle = \tau_g S_{ng}(2) + \sum_{i=1}^{2} \lambda_i^2 \tau_i S_{ni}(2) + \lambda_3^2 \langle I_{n3} \rangle \tag{47}$$

$$\langle I_n^2 \rangle = \mu_g [S_{ng}(2)]^2 - \nu_g S_{ng}(4) + \sum_{i=1}^{2} \lambda_i^4 [\mu_i \{S_{ni}(2)\}^2$$
$$- \nu_i S_{ni}(4)] + \lambda_3^4 \langle I_{n3}^2 \rangle + K_1 \tau_g S_{ng}(2) [\sum_{i=1}^{2} \lambda_i^2 \tau_i S_{ni}(2)$$
$$+ \lambda_3^2 \langle I_{n3} \rangle] + K_1 [\lambda_1^2 \lambda_2^2 \tau_1 \tau_2 S_{n1}(2) S_{n2}(2)$$
$$+ \lambda_2^2 \lambda_3^2 \tau_2 S_{n2}(2) \langle I_{n3} \rangle + \lambda_3^2 \lambda_1^2 \tau_1 S_{n1}(2) \langle I_{n3} \rangle] . \tag{48}$$

Following a similar procedure and remembering the assumption that $F_{P3} = F_{N3}$ we can similarly show that

$$\langle I_p \rangle = \tau_g S_{pg}(2) + \sum_{i=1}^{2} \lambda_i^2 \tau_i S_{pi}(2) + \lambda_3^2 \langle I_{n3} \rangle \qquad (49)$$

$$\langle I_p^2 \rangle = \mu_g [S_{pg}(2)]^2 - \nu_g S_{pg}(4) + \sum_{i=1}^{2} \lambda_i^4 [\mu_i \{S_{pi}(2)\}^2$$

$$- \nu_i S_{pi}(4)] + \lambda_3^4 \langle I_{n3}^2 \rangle + K_1 \tau_g S_{pg}(2) [\sum_{i=1}^{2} \lambda_i^2 \tau_i S_{pi}(2)$$

$$+ \lambda_3^2 \langle I_{n3} \rangle] + K_1 [\lambda_1^2 \lambda_2^2 \tau_1 \tau_2 S_{p1}(2) S_{p2}(2)$$

$$+ \lambda_2^2 \lambda_3^2 \tau_2 S_{p2}(2) \langle I_{n3} \rangle + \lambda_3^2 \lambda_1^2 \tau_1 S_{p1}(2) \langle I_{n3} \rangle] . \qquad (50)$$

Since the expressions for $\langle I_p^m \rangle$ and $\langle I_n^m \rangle$, $m = 1, 2$, are complicated, it is not convenient to substitute (47) – (50) in (33), (34), (39) and (40) and simplify the resulting expressions. However for any actual situation, it would be easier first to evaluate these quantities numerically from a knowledge of the unit-cell contents of the crystal and the model and then substitute these numbers in the latter equations for obtaining the relevant numerical values of the R indices. From (47) and (49) it is seen that the quantity σ_{1P}^2 for the present case takes the form

$$\sigma_{1P}^2 = \frac{\tau_g S_{pg}(2) + \sum_{i=1}^{2} \lambda_i^2 \tau_i S_{pi}(2) + \lambda_3^2 \langle I_{n3} \rangle}{\tau_g S_{ng}(2) + \sum_{i=1}^{2} \lambda_i^2 \tau_i S_{ni}(2) + \lambda_3^2 \langle I_{n3} \rangle} . \qquad (51)$$

4. Theoretical expressions for $_B R_1(I_{obs})$ and $_B R(I_{obs})$

The indices $_B R_1(I_{obs})$ and $_B R(I_{obs})$ can be related to the indices $_B R_1(I_N)$ and $_B R(I_N)$ respectively and the latter can be evaluated from the theoretical results in §§2 and 3. If we define

$$\varepsilon = I_{obs} - I_N, \quad \delta = I_N - I_P^c, \quad \delta_1 = I_N - I_P^c / \sigma_{1P}^2$$

and assume that (i) the errors in the observed intensities are normally distributed with parameters $(0, \sigma_\varepsilon)$ and (ii) there is no correlation between the error and the magnitude of the intensity (Wilson, 1969), then following the treatment in PP, it can be readily shown that

$$_B R_1(I_{obs}) = \frac{\sigma_\varepsilon^2 + \langle \delta_1^2 \rangle}{\langle I_N^2 \rangle + \sigma_\varepsilon^2}$$

$$= \left[\frac{\sigma_\varepsilon^2}{\langle I_N^2 \rangle} + {}_B R_1(I_N) \right] \bigg/ \left[1 + \frac{\sigma_\varepsilon^2}{\langle I_N^2 \rangle} \right] \qquad (52)$$

$$_B R(I_{obs}) = \frac{\sigma_\varepsilon^2 + \langle \delta^2 \rangle}{\langle I_N^2 \rangle + \sigma_\varepsilon^2}$$

$$= \left[\frac{\sigma_\varepsilon^2}{\langle I_N^2 \rangle} + {}_B R(I_N) \right] \bigg/ \left[1 + \frac{\sigma_\varepsilon^2}{\langle I_N^2 \rangle} \right] . \qquad (53)$$

When the intensities are sufficiently accurate, we can neglect the term σ_ε^2 in the denominator in comparison with $\langle I_N^2 \rangle$ and obtain the following more compact expressions from (52) and (53),

$$_B R_1(I_{obs}) \simeq {}_B R_1(I_N) + \sigma_\varepsilon^2 / \langle I_N^2 \rangle \qquad (54)$$

$$_B R(I_{obs}) \simeq {}_B R(I_N) + \sigma_\varepsilon^2 / \langle I_N^2 \rangle . \qquad (55)$$

5. Discussion of results

All atoms in general positions

Explicit expressions for $_B R_1(I_N)$ and $_B R(I_N)$ for the related and unrelated cases for the seven categories of space group of the triclinic, monoclinic and orthorhombic systems are to be obtained by substituting the appropriate values of α and β in the general expressions obtained in (19), (20), (23) and (24) and the final results thus obtained are summarized in Table 2. It is seen that these expressions depend on the quantities σ_{1P}^2, C_n and C_p. For any given model of a structure under investigation, these quantities can be evaluated from a knowledge of the contents (i.e. the species of atom, their scattering powers and the number of atoms in each species) of the asymmetric units of the true structure and the trial model. In structures containing atoms of widely different scattering power, these quantities in general vary with $(\sin \theta)/\lambda$ and therefore, so will the theoretical values of the R indices. Furthermore, in space groups of higher symmetry these theoretical values may differ for different classes of reflexion. The overall values of the R index (taking into account these two factors) for the related and unrelated cases which are needed in practice can be obtained by the following procedure: Divide the reflexions into r regions of $(\sin \theta)/\lambda$. Suppose there are c distinct categories of reflexion in each range, the category being determined by the form of the geometrical structure factor. Making use of the known values of the scattering factors of the atoms corresponding to the middle of the range and the known contents of the asymmetric units of true and trial structures and employing the theoretical expressions appropriate to the various categories of reflexions, calculate the theoretical values of the R index for the c categories of reflexion. For reflexions of category j in range i let the value of the R index be denoted by R_{ij} and let f_{ij} be the fractional number of such reflexions. The theoretical overall value of the R index, denoted by $\bar{R}$, would then be given by

$$\bar{R} = \sum_{i=1}^{r} \sum_{j=1}^{c} f_{ij} R_{ij} .$$

Atoms in both general and special positions

When atoms occur in both general and special positions, the change in the geometrical structure-factor formula and the different multiplicities of equivalent positions for atoms in special positions must be taken into account for determining the quantities $\langle I_n^m \rangle$ and $\langle I_p^m \rangle$, $m = 1, 2$, from (47)–(50). Given the space group of the crystal, the possible types of special position and the quantities (whichever is relevant for the given space group), $s_g, \tau_g, \mu_g, \nu_g, s_i, \lambda_i$ $(i = 1, 2, 3), \tau_j, \mu_j$ and ν_j $(j = 1, 2)$, are uniquely determined. The numerical values of the quantities τ_g, μ_g and ν_g for any of the seven categories of space group can be read from Table 1. The values of the quantities τ_j, μ_j and ν_j $(j = 1, 2)$ can be obtained

Table 2. *Theoretical expressions for $_BR_1(I_N)$ and $_BR(I_N)$ for the related and unrelated cases for any model of a complex crystal belonging to triclinic, monoclinic and orthorhombic systems: all atoms in general positions*

Space-group category number	$_BR_1(I_n)$		$_BR(I_N)$	
	Related	Unrelated	Related	Unrelated
1	$\dfrac{2t_1+t_6}{2-C_n}$	$\dfrac{2-t_5}{2-C_n}$	$\dfrac{2t_1+t_7}{2-C_n}$	$\dfrac{2t_2-t_8}{2-C_n}$
2	$\dfrac{8t_1+3t_6}{6-3C_n}$	$\dfrac{8-3t_5}{6-3C_n}$	$\dfrac{2t_3+3t_7}{6-3C_n}$	$\dfrac{2t_4-3t_8}{6-3C_n}$
3	$\dfrac{4t_1+t_6}{4-C_n}$	$\dfrac{4-t_5}{4-C_n}$	$\dfrac{4t_1+t_7}{4-C_n}$	$\dfrac{4t_2-t_8}{4-C_n}$
4	$\dfrac{16t_1+3t_6}{12-3C_n}$	$\dfrac{16-3t_5}{12-3C_n}$	$\dfrac{4t_3+3t_7}{12-3C_n}$	$\dfrac{4t_4-3t_8}{12-3C_n}$
5	$\dfrac{8t_1+t_6}{8-C_n}$	$\dfrac{8-t_5}{8-C_n}$	$\dfrac{8t_1+t_7}{8-C_n}$	$\dfrac{8t_2-t_8}{8-C_n}$
6	$\dfrac{8t_1-t_6}{8+C_n}$	$\dfrac{8+t_5}{8+C_n}$	$\dfrac{8t_1-t_7}{8+C_n}$	$\dfrac{8t_2+t_8}{8+C_n}$
7	$\dfrac{32t_1-3t_6}{24+3C_n}$	$\dfrac{32+3t_5}{24+3C_n}$	$\dfrac{8t_3-3t_7}{24+3C_n}$	$\dfrac{8t_4+3t_8}{24+3C_n}$

$t_1 = 1 - \sigma_{1P}^2$ $t_5 = C_p + C_n$

$t_2 = 1 - \sigma_{1P}^2 + \sigma_{1P}^4$ $t_6 = (2\sigma_{1P}^2 - 1)C_p - C_n$

$t_3 = 3 - 2\sigma_{1P}^2 - \sigma_{1P}^4$ $t_7 = \sigma_{1P}^4 C_p - C_n$

$t_4 = 3 - 2\sigma_{1P}^2 + 3\sigma_{1P}^4$ $t_8 = \sigma_{1P}^4 C_p + C_n$

by studying Table 1 of FH (1963b) keeping in view (i) the forms of the geometrical structure factors for these special positions and (ii) the form of the expressions in (45). It is useful to note here that in crystals containing atoms in fixed positions, it is in general necessary to classify the reflexions into different categories and evaluate the theoretical and experimental values of the R indices for the various categories separately. The method of classifying the reflexions into categories can be understood from the illustrative examples given in FH (1963b) in connexion with the moments test for space-group determination.

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Derivation of Carbon–Nitrogen, Hydrogen–Nitrogen and Nitrogen–Nitrogen Non-Bonded Potential Parameters in Molecular Crystals*

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Potential function parameters for CN, HN, and NN non-bonded atom–atom pair interactions were derived from the heats of sublimation of cyanogen and dicyanoacetylene and from the crystal structures of cyanogen, dicyanoacetylene, tetracyanoethylene, *s*-tetrazine, pteridine and pyridazino[4,5-*d*]pyridazine. Procedure and CC, CH, and HH parameters used were those of Williams [*J. Chem. Phys.* (1967). **47**, 4680–4684]. The exponents of CN, HN, and NN repulsion terms were taken equal to those of CC, CH, and CC repulsion terms, respectively. The lattice summation was cut off at 6, 5·5 and 6 Å for the CN, HN, and NN terms, respectively. The coefficients of the attractive and repulsive terms were fitted by weighted least-squares calculations to 45 observational equations. It proved to be necessary to estimate externally the parameters of the HN attractive term. The derived parameters show rough agreement with the values found by other investigators. The experimental values of the heats of sublimation of cyanogen and dicyanoacetylene are reproduced within 4% with the calculated parameters. The parameters predict reasonable values for the heats of sublimation of tetracyanoethylene, *s*-tetrazine, pteridine and pyridazino[4,5-*d*]pyridazine. A difference of about 6 kcal mole⁻¹ between the heats of sublimation of the latter two isomers was calculated.

Introduction

In order to calculate the lattice energy of molecular crystals the atom–atom approximation has proved to

be a valuable tool (Williams, 1966, 1967, 1974; Kitaigorodskii, 1973). In all these calculations lattice energy is treated, completely or for the greater part, as a limited summation of interatomic potentials between the atoms of a molecule chosen as central and the atoms of a limited number of neighbouring molecules. Pair-

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* This work forms part of a thesis by Govers (1974).