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Overall values of conventional discrepancy indices for crystals with heavy atoms. Part I—Results for a triclinic crystal when the model consists of the heavy atoms and a part of light atoms*

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Abstract. The joint probability density functions of the normalized structure amplitudes of the structure and the model (*i.e.*, y_N and y_p^c) are derived for triclinic crystals containing heavy atoms (1, 2 and many) by taking the model to consist of the heavy atoms and a part of the light atoms in the unit cell. These functions are derived for the two cases where the model is completely correct (*i.e.*, the related case) and where the model is completely wrong (*i.e.*, the unrelated case) in terms of the fractional contributions to the local mean intensity from the heavy atoms and all known atoms (*i.e.*, σ_{1h}^2 and σ_1^2) as parameters. These functions are then used to obtain the theoretical local values of $\langle y_N \rangle$ and $\langle | y_N^n - \sigma_1^n (y_p^c)^n | \rangle$, $n = 1, 2$. A method of using these results to compute the theoretical overall values of $R(F)$ and $R(I)$ for the related and unrelated cases is briefly described. A comparison of the observed values of these indices with their theoretical values for the related and unrelated cases would help in determining the correctness of the proposed trial structure.

Keywords. Conventional R-indices; triclinic crystals; heavy atoms; light atoms.

1. Introduction

The conventional discrepancy indices denoted by $R(F)$ and $R(I)$ are the ones generally used by crystallographers to judge the correctness of models (*i.e.*, trial structures). These indices have been evaluated for different types of models of structures with *similar atoms* obeying Wilson distributions (Wilson 1949) and the investigations of different workers are summarized by Parthasarathy and Ponnuswamy (1979). The largest likely value of $R(F)$ for a wrong complete model corresponding to the hypercentric case has been obtained by Douglas and Woolfson (1954) (see also Rogers and Wilson, 1953 for their comments on the behaviour of $R(F)$ for hypersymmetric structures). Parthasarathy *et al* (1973) worked out the value of $R(F)$ for a triclinic crystal with two heavy atoms in the unit cell by taking the heavy-atom part alone as the model. The overall values of $R(F)$ and $R(I)$ have not been considered for an incomplete model consisting of both the heavy atoms and a part of the light atoms. In this paper we derive results which lead to the overall values† of $R(F)$ and $R(I)$

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†The value of R computed using reflections in a narrow region of $\sin\theta/\lambda$ is called a *local value* of R while its value computed using all the independent measured data as a single group is called the *overall value* of R. The latter is denoted by $\bar{R}$. Thus one must distinguish between the local and the overall values of R-indices.

for such models of triclinic crystals (space groups $P1$ and $P\bar{1}$). We shall consider the one-atom, two-atom and many-atom ($P = MN$ and $P = MC$) cases (for the nomenclature see Srinivasan and Parthasarathy 1976; SP 1976 hereafter).

Here we shall make the following simplifying assumptions: (i) we assume all the heavy atoms in the cell to be of the same type (*e.g.*, all chlorines or all bromines, etc.) and the light atoms to be of similar scattering power (*e.g.*, C, N and O). (ii) we derive the results only for two limiting situations, namely, the related case (*i.e.*, the model is completely correct) and unrelated case (*i.e.*, the model is completely wrong).

2. Derivation of the theoretical results required for obtaining the overall values of *R*-indices

2.1 *Notation and preliminary results*

Consider a triclinic crystal (C or NC)* containing N atoms in the unit cell of which P_h are heavy atoms** (all of one kind) and the remaining ($N-P_h$) are light atoms (of similar scattering power). At a given stage in structure determination suppose the trial structure consists of these P_h heavy atoms and a set of P_l light atoms and let Q denote the number of light atoms yet to be located in the unit cell. If we denote the total number of atoms in the trial structure by P, then we can write,

$$P = P_h + P_l,\ N = P + Q. \tag{1}$$

The structure factor of a reflection $H(=hkl)$ can be written in terms of the contributions from the individual groups of atoms as

$$F_N = F_P + F_Q, \tag{2}$$

where F_P can be written as

$$F_P = F_{P_h} + F_{P_l}. \tag{3}$$

Let F_P^c denote the calculated structure factor for the reflection H due to the contributions from the P atoms of the model. The contributions to the local mean intensity from the various groups of atoms can be written as

$$\langle |F_\alpha|^2 \rangle = \sum_{i=1}^{\alpha} f_{\alpha i}^2 = \sigma_\alpha^2, \text{ say } (\alpha = N, P, Q, P_h \text{ or } P_l), \tag{4a}$$

and

$$\langle |F_P^c|^2 \rangle = \sum_{j=1}^{P} f_{P_j}^2 = \sigma_P^2. \tag{4b}$$

*We shall use the abbreviations C and NC to denote the centrosymmetric and non-centrosymmetric cases respectively.

**In Part I we shall denote the *heavy atoms* by the symbol P_h instead of the usual symbol P, since we shall use P to denote the total number of *known* (*i.e.*, both heavy and light) atoms in the unit cell.

Let the fractional contribution to the local mean intensity from the P—, Q—, P_h— and P_l-groups be denoted by σ_1^2, σ_2^2, σ_{1h}^2 and σ_{1l}^2 respectively. From (4a) and (4b) it follows that

$$\sigma_1^2 = \sigma_P^2/\sigma_N^2,\ \sigma_2^2 = \sigma_Q^2/\sigma_N^2,$$

$$\sigma_{1h}^2 = \sigma_{Ph}^2/\sigma_N^2,\ \sigma_{1l}^2 = \sigma_{Pl}^2/\sigma_N^2. \tag{5}$$

From (5) we obtain

$$\sigma_1^2 + \sigma_2^2 = 1, \tag{6}$$

$$\sigma_{1h}^2 + \sigma_{1l}^2 = \sigma_1^2, \tag{7}$$

$$\sigma_{1h}^2 + \sigma_{1l}^2 + \sigma_2^2 = 1. \tag{8}$$

The normalized variables y_N and y_P^c are defined in the usual way, namely,

$$y_N = |F_N|/\langle|F_N|^2\rangle^{1/2},\ y_P^c = |F_P^c|/\langle|F_P^c|^2\rangle^{1/2}. \tag{9}$$

Let $P(y_N, y_P^c)$ denote the joint probability density function (PDF hereafter) of y_N and y_P^c. It may be noted that for the related case $F_P^c = F_P$ and $y_P^c = y_P$ while for the unrelated case y_P and y_P^c are independent random variables.

2.2 *General expression for the overall value of $R(F)$*

Following the arguments of Parthasarathy and Ponnuswamy (1979) (hereafter PP 1979) the overall value of $R(F)$ [*i.e.* $\bar{R}(F)$] for an incomplete model can be written as [see equation (8) of PP 1979]

$$\bar{R}(F) = \frac{\sum_{hkl} ||F_N| - |F_P^c||}{\sum_{hkl} |F_N|}, \tag{10a}$$

$$= \frac{\sum_j \sigma_{Nj}\, n_j \langle|y_N - \sigma_1 y_P^c|\rangle_j}{\sum_j \sigma_{Nj}\, n_j \langle y_N\rangle_j}. \tag{10b}$$

The derivation of (10b) from (10a) involves the partitioning of the reciprocal space into thin shells. The subscript j to a quantity denotes that the quantity pertains to the jth shell. n_j denotes the number of independent reflections in the jth shell. Thus it is clear from (10b) that if the local values of $\langle|y_N - \sigma_1 y_P^c|\rangle$ and $\langle y_N\rangle$ are known in the different ranges of $\sin\theta/\lambda$, then the summation in (10b) can be carried out and

the overall value $\bar{R}(F)$ for a given model of a crystal can be obtained. The local value of $\langle | y_N - \sigma_1 y_P^c | \rangle$ can be obtained from the joint PDF of y_N and y_P^c as

$$\langle | y_N - \sigma_1 y_P^c | \rangle = \int_0^\infty \int_0^\infty | y_N - \sigma_1 y_P^c | P(y_N, y_P^c)\, dy_N\, dy_P^c \tag{11}$$

Since the joint PDF $P(y_N, y_P^c)$ for the various cases that are considered in this paper turn out to be complicated functions, the double integral in (11) cannot be evaluated in closed form. To facilitate evaluation by numerical methods, the variables of integrations in (11) are changed by using the transformation

$$y_N = u/(1-u),\ y_P^c = v/(1-v). \tag{12}$$

Now we can rewrite (11) as

$$\langle | y_N - \sigma_1 y_P^c | \rangle = \int_0^1 \int_0^1 \left| \left(\frac{u}{1-u}\right) - \sigma_1 \left(\frac{v}{1-v}\right) \right| P\left(\frac{u}{1-u}, \frac{v}{1-v}\right) \times \frac{du\, dv}{(1-u)^2 (1-v)^2}. \tag{13}$$

The theoretical expression for $\langle y_N \rangle$ for the cases of our interest is given by Parthasarathy (1966). Making use of the values of $\langle | y - \sigma_1 y_P^c | \rangle$ and $\langle y_N \rangle$ thus obtained in (10b) we can evaluate $R(F)$ for a given trial structure.

2.3 *General expression for the overall value of R(I)*

Following the procedure that has been used for obtaining (10b) from (10a) and using the result $\langle y_N^2 \rangle = 1$, the theoretical expression for the overall value of $R(I)$ for an incomplete model can be shown to be

$$\bar{R}(I) = \frac{\sum_{hkl} | I_N - I_P^c |}{\sum_{hkl} I_N} = \frac{\sum_j \sigma_{Nj}^2 n_j \langle | y_N^2 - \sigma_1^2 (y_P^c)^2 | \rangle_j}{\sum_j \sigma_{Nj}^2 n_j}. \tag{14}$$

The local value of $\langle | y_N^2 - \sigma_1^2 (y_P^c)^2 | \rangle$ can be obtained from

$$\langle | y_N^2 - \sigma_1^2 (y_P^c)^2 | \rangle = \int_0^\infty \int_0^\infty | y_N^2 - \sigma_1^2 (y_P^c)^2 | P(y_N, y_P^c)\, dy_N\, dy_P^c \tag{15a}$$

$$= \int_0^1 \int_0^1 \left| \left(\frac{u}{1-u}\right)^2 - \sigma_1^2 \left(\frac{v}{1-v}\right)^2 \right| P\left(\frac{u}{1-u}, \frac{v}{1-v}\right) \frac{du\, dv}{(1-u)^2 (1-v)^2}. \tag{15b}$$

We have used the transformation (12) for obtaining (15b) from (15a).

The following points should be noted regarding the evaluation of

$$\langle | y_N^n - \sigma_1^n (y_P^c)^n | \rangle, \ (n=1, 2)$$

for the related case. Here $F_P^c = F_P$ and $y_P^c = y_P$ so that the relevant results can be obtained by simply replacing y_P^c by y_P in equations (10b) to (15b) which are valid for the general case of an imperfectly related model. Thus, in particular

$$\langle | y_N^n - \sigma_1^n (y_P^c)^n | \rangle, \ (n=1, 2)$$

for the related case can be obtained from (13) and (15b) as

$$\langle | y_N - \sigma_1 y_P | \rangle = \int_0^1 \int_0^1 \left| \left(\frac{u}{1-u}\right) - \sigma_1 \left(\frac{v}{1-v}\right) \right| P\left(\frac{u}{1-u}, \frac{v}{1-v}\right) \times \frac{du\, dv}{(1-u)^2 (1-v)^2} \tag{16}$$

$$\langle | y_N^2 - \sigma_1^2 y_P^2 | \rangle = \int_0^1 \int_0^1 \left| \left(\frac{u}{1-u}\right)^2 - \sigma_1^2 \left(\frac{v}{1-v}\right)^2 \right| P\left(\frac{u}{1-u}, \frac{v}{1-v}\right) \times \frac{du\, dv}{(1-u)^2 (1-v)^2} \tag{17}$$

From the above considerations [see (10), (13) to (17)] it is clear that for the evaluation of the theoretical overall values of $R(F)$ and $R(I)$ we must first obtain $P(y_N, y_P)$ for the related case, $P(y_N, y_P^c)$ for the unrelated case and the expression for $\langle y_N \rangle$*. Since we are considering the one-atom, two-atom and many-atom ($P_h = M$, MN and MC) cases we shall work out the expressions for $P(y_N, y_P)$, $P(y_N, y_P^c)$ and $\langle y_N \rangle$ for these cases individually.

2.4 *Theoretical results for the non-centrosymmetric case*

2.4a *Derivation of $P(y_N, y_P)$ for the related case:* $P(y_N, y_P)$ for the related case can be obtained from the conditional PDF $P(y_N; y_P)$ and the PDF $P(y_P)$ by using the formula

$$P(y_N, y_P) = P(y_N; y_P)\ P(y_P). \tag{18}$$

Now assuming the Q-group to consist of a sufficiently large number of similar atoms so as to obey the acentric Wilson distribution (Wilson 1949), the conditional

*Since $\langle y_N \rangle$ is a property of the crystals but not of the model, the theoretical expression for $\langle y_N \rangle$ will be independent of the type of model (*e.g.*, related and unrelated models).

PDF of y_N for a given y_P (whatever be the nature of the P-group) has been shown to be [see (3·24) on p.37 of SP 1976]

$$P(y_N; y_P) = \frac{2y_N}{\sigma_2^2}\exp\left[-\frac{(y_N^2+\sigma_1^2 y_P^2)}{\sigma_2^2}\right] I_0\left(\frac{2\sigma_1 y_N y_P}{\sigma_2^2}\right). \tag{19}$$

Since $P(y_P)$ is different for the one-atom, two-atom and many-atom cases, we shall derive $P(y_P)$ for these cases.

(i) *One-atom case:* $P(y_P)$ required for the present case (*i.e.* $P_h=1$) can be readily obtained from the expression for $P(y_N)$ in equation (3·26) of SP (1976) by replacing the set $(y_N, \sigma_1^2 = \sigma_P^2/\sigma_N^2, \sigma_2^2 = \sigma_Q^2/\sigma_N^2)$ by the set $(y_P, \sigma_{P_h}^2/\sigma_P^2, \sigma_{P_l}^2/\sigma_P^2)$.

Making use of (5) we can rewrite σ_{Ph}^2/σ_P^2 and σ_{Pl}^2/σ_P^2 as

$$\sigma_{P_h}^2/\sigma_P^2 = \sigma_{1h}^2/\sigma_1^2,\ \sigma_{P_l}^2/\sigma_P^2 = \sigma_{1l}^2/\sigma_1^2. \tag{20}$$

We thus obtain $P(y_P)$ for the present case to be

$$P(y_P) = \frac{2\sigma_1^2}{\sigma_{1l}^2}\exp\left(-\frac{\sigma_{1h}^2}{\sigma_{1l}^2}\right) y_P \exp\left(-\frac{\sigma_1^2}{\sigma_{1l}^2}y_P^2\right) I_0\left(\frac{2\sigma_1\sigma_{1h}}{\sigma_{1l}^2}y_P\right) \tag{21}$$

(ii) *Two-atom case:* $P(y_P)$ required for the present case (*i.e.*, $P_h=2$) is obtained from the expression for $P(y_N)$ given in equation (15) of Srikrishnan and Parthasarathy (1970) by replacing the set $(y_N, \sigma_1^2, \sigma_2^2)$ by the set $(y_P, \sigma_{1h}^2/\sigma_1^2, \sigma_{1l}^2/\sigma_1^2)$ as*

$$P(y_P) = \frac{2\sigma_1}{\sigma_{1l}^2} y_P \exp\left(-\frac{\sigma_1^2 y_P^2}{\sigma_{1l}^2}\right) \int_0^1 \exp\left[-\frac{2\sigma_{1h}^2}{\sigma_{1l}^2}\sin^2\left(\frac{\pi x}{2}\right)\right]$$

$$\times I_0\left[\frac{2\sqrt{2}\,\sigma_1\,\sigma_{1h}\,y_P}{\sigma_{1l}^2}\sin\left(\frac{\pi x}{2}\right)\right] dx. \tag{22}$$

(iii) *Many-atom* ($P_h = MN$) *case:* $P(y_P)$ for this case will evidently be the acentric Wilson distribution, namely,

$$P(y_P) = 2y_P \exp(-y_P^2). \tag{23}$$

*We have also made the substitution $\theta = (\pi/2)\,x$ for convenience.

(iv) *Many-atom* ($P_h = MC$) *case:* $P(y_P)$ for the present case is obtained from the expression for $P(y_N)$ in equation (8) of Parthasarathy (1966) by replacing the set $(y, \sigma_1^2, \sigma_2^2)$ by the set $(y_P, \sigma_{1h}^2/\sigma_1^2, \sigma_{1l}^2/\sigma_1^2)$ as

$$P(y_P) = \frac{2\sigma_1^2\, y_P}{[\sigma_{1l}^2\,(\sigma_1^2 + \sigma_{1h}^2)]^{1/2}} \exp\left[-\frac{\sigma_1^4\, y_P^2}{\sigma_{1l}^2\,(\sigma_1^2 + \sigma_{1h}^2)}\right] I_0\left[\frac{\sigma_1\,\sigma_{1h}^2\, y_P^2}{\sigma_{1l}^2\,(\sigma_1^2 + \sigma^2{}_h)}\right]. \quad (24)$$

Substituting (9) and the appropriate $P(y_P)$ from (21)–(24) in (18) we can obtain the required $P(y_N, y_P)$. The results obtained for the cases P_h=1, 2, *MN* and *MC* are given in table 1.

2.4b *Derivation of* $P(y_N, y_P^c)$ *for the unrelated case:* In this case y_N and y_P^c are independent random variables. Hence if $P(y_N)$ and $P(y_P^c)$ are the PDF's of y_N and y_P^c respectively, the joint PDF of y_N and y_P^c will be given by the formula

$$P(y_N, y_P^c) = P(y_N)\, P(y_P^c)\,. \quad (25)$$

Table 1. The joint PDF of y_N and y_P for a related model consisting of P_h (=1, 2, *MN* or *MC*) heavy and P_l light atoms per unit cell: A non-centrosymmetric crystal.

P_h	$P(y_N, y_P)$
1	$\left(\frac{\sigma_1}{\sigma_{1l}}\right)^2 E_1\, E_1'\, B \exp(-r^2)\, I_0(2a)$
2	$\left(\frac{\sigma_1}{\sigma_{1l}}\right)^2 E_1\, E_1'\, B \int_0^1 \exp(-2r^2 S_x^2)\, I_0(2\sqrt{2}\, a\, S_x)\, dx$
MN	$E_1\, B \exp(-y_P^2/\sigma_2^2)$
MC	$(\sigma_1^2/g)\, E_1\, B \exp[-s^2(g^2 + \sigma_1^2\,\sigma_2^2)\, y_P^2/g^2]\, I_0\,[(\sigma_1\,\sigma_{1h}\, y_P/g)^2]$

Note 1: $E_1 = (4\, y_N\, y_P/\sigma_2^2) \exp(-y_N^2/\sigma_2^2)$, $E_1' = \exp\left[-\frac{\sigma_1^2(1 - \sigma_{1h}^2)\, y_P^2}{\sigma_2^2\, \sigma_{1l}^2}\right]$

Note 2: Symbols used in tables (1)–(8) and their definition:

$B = I_0(2\,\sigma_1 y_N y_P/\sigma_2^2)$; $C = \cosh(\sigma_1 y_N y_P/\sigma_2^2)$

$S_x = \sin(\pi x/2)$, $S_z = \sin(\pi z/2)$, $a = \sigma_1\,\sigma_{1h}\, y_P/\sigma_{1l}^2$, $b = \sigma_1\,\sigma_{1h}\, y_P^c/\sigma_{1l}^2$

$k = \sigma_1\, y_N/\sigma_2^2$; $r = \sigma_{1h}/\sigma_{1l}$, $s = \sigma_1/\sigma_2$, $t = 1 - \sigma_{1h}^2$,

$g = \sigma_{1l}^2\,[\sigma_1^2 + \sigma_{1h}^2]^{1/2}$

It is obvious that $P(y_P^c)$ needed in (25) corresponding to the cases $P_h=1$, 2, MN and MC can be obtained from (21) to (24) respectively by replacing y_P by y_P^c in these expressions. $P(y_N)$ needed in (25) for these cases can be obtained as follows.

(i) *One-atom case:* $P(y_N)$ for this case is obtained from the expression for $P(y_N)$ in equation (3·26) of SP (1976) by replacing the set $[\sigma_1^2=\sigma_P^2/\sigma_N^2,\ \sigma_2^2=\sigma_Q^2/\sigma_N^2]$ by the set $[\sigma_{P_h}^2/\sigma_N^2,\ (\sigma_{P_l}^2+\sigma_Q^2)/\sigma_N^2]$. Making use of (5) we can rewrite $\sigma_{P_h}^2/\sigma_N^2$ and $(\sigma_{P_l}^2+\sigma_Q^2)/\sigma_N^2$ as

$$\sigma_{P_h}^2/\sigma_N^2=\sigma_{1h}^2,\quad (\sigma_{P_l}^2+\sigma_Q^2)/\sigma_N^2=\sigma_{1l}^2+\sigma_2^2=1-\sigma_{1h}^2 \tag{26}$$

Thus $P(y_N)$ for this case is

$$P(y_N)=\frac{2y_N}{1-\sigma_{1h}^2}\exp\left[-\frac{(\sigma_{1h}^2+y_N^2)}{(1-\sigma_{1h}^2)}\right]I_0\left[\frac{2\sigma_{1h}\,y_N}{1-\sigma_{1h}^2}\right]. \tag{27}$$

(ii) *Two-atom case :* $P(y_N)$ for the present case can be similarly obtained from the expression for $P(y_N)$ in equation (15) of Srikrishnan and Parthasarathy (1970) by replacing the set $(\sigma_1^2,\ \sigma_2^2)$ by the set $(\sigma_{1h}^2,\ 1-\sigma_{1h}^2)$ as

$$P(y_N)=\frac{2y_N}{1-\sigma_{1h}^2}\exp\left[-\frac{y_N^2}{(1-\sigma_{1h}^2)}\right]\int_0^1\exp\left[-\frac{2\sigma_{1h}^2}{(1-\sigma_{1h}^2)}\sin^2\left(\frac{\pi z}{2}\right)\right]$$

$$\times\, I_0\left[\frac{2\sqrt{2}\,\sigma_{1h}\,y_N}{(1-\sigma_{1h}^2)}\sin\left(\frac{\pi z}{2}\right)\right]dz. \tag{28}$$

(iii) *Many-atom* ($P_h=MN$) *case:* $P(y_N)$ for the present case will be given by the acentric Wilson distribution, namely,

$$P(y_N)=2\,y_N\exp(-y_N^2). \tag{29}$$

(iv) *Many-atom* ($P_h=MC$) *case:* $P(y_N)$ for the present case can be obtained from the expression for $P(y_N)$ in equation (8) of Parthasarathy (1966) by replacing the set $(y,\ \sigma_1^2,\ \sigma_2^2)$ by the set $(y_N,\ \sigma_{1h}^2,\ 1-\sigma_{1h}^2)$ as

$$P(y_N)=\frac{2\,y_N}{(1-\sigma_{1h}^2)^{1/2}}\exp\left(-\frac{y_N^2}{(1-\sigma_{1h}^4)}\right)I_0\left(\frac{\sigma_{1h}^2\,y_N^2}{1-\sigma_{1h}^4}\right). \tag{30}$$

Substituting for the appropriate $P(y_N)$ from (27) to (30) and the appropriate $P(y_P^c)$ from (21) to (24) in (25) we can obtain the joint PDF of y_N and y_P^c for the cases $P_h=1$, 2, MN and MC. The results thus obtained are summarized in table 2.

Table 2. The joint PDF of y_N and y_P^c for an unrelated model consisting of $P_h(=1, 2, MN \text{ or } MC)$ heavy and P_l light atoms per unit cell: A non-centrosymmetric crystal.

P_h	$P(y_N, y_P^c)$
1	$E_2 \exp\,[-r^2(t+\sigma_{1l}^2)/t]\quad I_0(2\sigma_{1h}\,y_N/t)\quad I_0(2b)$
2	$E_2 \int_0^1\int_0^1 \exp\,[-2(r^2 S_z^2 + \sigma_{1h}^2 S_x^2/t)]\quad I_0[2\sqrt{2}\,\sigma_{1h}\,y_N\,S_x/t]\quad I_0[2\sqrt{2}\,b\,S_z]\,dx\,dz$
MN	$4\,y_N\,y_P^c \exp\,[-y_N^2 - y_P^{c\,2}]$
MC	$\dfrac{4\,\sigma_1^2\,y_N\,y_P^c}{g\,(1-\sigma_{1h}^4)^{1/2}} \exp\left[-\dfrac{y_N^2}{(1-\sigma_{1h}^4)} - \dfrac{\sigma_1^4\,y_P^{c\,2}}{g^2}\right] I_0\,[(\sigma_1\,\sigma_{1h}\,y_P^c/g)^2]\quad I_0\left[\dfrac{\sigma_{1h}^2\,y_N^2}{1-\sigma_{1h}^4}\right]$

Note: $E_2 = \dfrac{4\,\sigma_1^2\,y_N\,y_P^c}{\sigma_{1l}^2(1-\sigma_{1h}^2)} \exp\left[-\dfrac{y_N^2}{(1-\sigma_{1h}^2)} - \dfrac{\sigma_1^2\,y_P^{c\,2}}{\sigma_{1l}^2}\right]$.

For the definition of the symbols used, see footnote 2 of table 1.

2.4c *Theoretical expressions for* $\langle y_N \rangle$ *for the various cases:* The theoretical expressions of $\langle y_N \rangle$ for the cases $P_h=1$ and 2 can be obtained from table 3·6 of SP (1976) by replacing the set (σ_1^2, σ_2^2) by the set $(\sigma_{1h}^2, 1-\sigma_{1h}^2)$. For the case $P_h=MN$, y_N follows the acentric Wilson distribution so that $\langle y_N \rangle = \sqrt{\pi}/2$. For the case $P_h = MC$, $\langle y_N \rangle$ can be obtained from (3·86) of SP (1976) by replacing σ_c^2 by σ_{1h}^2. Thus we obtain

$$\langle y_N \rangle = \begin{cases} \dfrac{1}{2}\left(\dfrac{\pi}{1-\sigma_{1h}^2}\right)^{1/2} \exp\left[-\dfrac{\sigma_{1h}^2}{2(1-\sigma_{1h}^2)}\right]\left\{I_0\left[\dfrac{\sigma_{1h}^2}{2(1-\sigma_{1h}^2)}\right]\right. \\ \qquad \left. + \sigma_{1h}^2\, I_1\left[\dfrac{\sigma_{1h}^2}{2(1-\sigma_{1h}^2)}\right]\right\} \text{ for } P_h = 1 \\ \dfrac{[\pi\,(1-\sigma_{1h}^2)]^{1/2}}{2}\,{}_2F_2\left[-\tfrac{1}{2}, \tfrac{1}{2};\ 1,\ 1;\ -\dfrac{2\sigma_{1h}^2}{(1-\sigma_{1h}^2)}\right] \text{ for } P_h = 2 \\ \dfrac{\sqrt{\pi}}{2} \text{ for } P_h = MN \\ \left(\dfrac{1+\sigma_{1h}^2}{\pi}\right)^{1/2} E\left[\left(\dfrac{2\sigma_{1h}^2}{1+\sigma_{1h}^2}\right)^{1/2}\right] \text{ for } P_h = MC\,. \end{cases} \tag{31}$$

2.5 *Theoretical results for the centrosymmetric case*

The procedure to be followed for deriving the theoretical results for the C case is quite analogous to that employed in § 2.4 for the NC case. We shall therefore present only the essential steps.

2.5a *Derivation of $P(y_N, y_P)$ for the related case:* Assuming the Q-group to consist of a sufficiently large number of similar atoms so as to obey the centric Wilson distribution, the conditional PDF of y_N for a given y_P (whatever be the nature of the P-group) has been shown to be [see (3·32) of SP (1976)]

$$P(y_N; y_P) = \left(\frac{2}{\pi\sigma_2^2}\right)^{1/2} \exp\left[-\frac{(y_N^2 + \sigma_1^2 y_P^2)}{2\sigma_2^2}\right] \cos h\left(\frac{\sigma_1 y_N y_P}{\sigma_2^2}\right). \qquad (32)$$

$P(y_P)$ for the one-atom and two-atom cases can be obtained from the respective expressions for $P(y_N)$ in equations (3·33) and (3·34) of SP (1976) by replacing the set $(y_N, \sigma_1^2, \sigma_2^2)$ by the set $(y_P, \sigma_{1h}^2/\sigma_1^2, \sigma_{1l}^2/\sigma_1^2)$. $P(y_P)$ for the many-atom case (*i.e.*, $P_h = M$) will be given by the centric-Wilson distribution. $P(y_P)$ thus obtained for the various cases are summarised in table 3. We can obtain $P(y_N, y_P)$ for the cases $P_h = 1$, 2 and M by substituting for $P(y_N; y_P)$ from (32) and for the appropriate $P(y_P)$ from table 3 in (18). The results thus obtained are summarised in table 4.

2.5b *Derivation of $P(y_N, y_P^c)$ for the unrelated case:* Since y_N and y_P^c are now independent random variables the joint PDF of y_N and y_P^c will be given by (16). $P(y_P^c)$ fro the cases P_h=1, 2 and M are available in table 3. $P(y_N)$ for the one-atom and two-atom cases can be obtained by replacing the set (σ_1^2, σ_2^2) by the set $(\sigma_{1h}^2, 1-\sigma_{1h}^2)$ respec-

Table 3. The PDF's of y_P for the cases $P_h = 1$, 2 and M: A centrosymmetric crystal.

P_h	$P(y_P)$
1	$E_3 \exp(-r^2/2) \cosh(a)$
2	$E_3 \int_0^1 \exp[-r^2 S_z^2] \cosh(\sqrt{2}\, a\, S_z)\, dz$
M	$(2/\pi)^{1/2} \exp(-y_P^2/2)$

Note: $E_3 = (2/\pi)^{1/2} (\sigma_1/\sigma_{1l}) \exp\left[-\dfrac{\sigma_1^2\, y_P^2}{2\,\sigma_{1l}^2}\right]$

$P(y_P^c)$ for the cases $P_h = 1$, 2 and M of a C crystal can be obtained by simply replacing y_P by y_P^c in the above expressions. See also the footnote 2 of table 1.

tively in equations (3.33) and (3.34) of SP (1976). $P(y_N)$ for the many-atom case will be given by the centric Wilson distribution. The expressions for $P(y_N)$ for the cases $P_h = 1$, 2 and M thus obtained are summarised in table 5. Substituting the appropriate $P(y_N)$ from table 5 and the appropriate $P(y_P^c)$ from table 3 in (25) we can obtain the joint PDF of y_N and y_P^c for the cases $P_h = 1$, 2, and M. The results thus obtained are summarised in table 6.

2.5c. *Theoretical expressions for* $\langle y_N \rangle$ *for the various cases:* The theoretical expressions of $\langle y_N \rangle$ for the cases $P_h = 1$ and 2 can be obtained from the results in table

Table 4. The joint PDF of y_N and y_P for a related model consisting of P_h (=1, 2 or M) heavy and P_l light atoms per unit cell: A centrosymmetric crystal.

P_h	$P(y_N, y_P)$
1	$E_4\, C \exp(-r^2/2) \cosh(a)$
2	$E_4\, C \int_0^1 \exp[-r^2 S_z^2] \cosh(\sqrt{2}\, a\, S_z)\, dz$
M	$\frac{2C}{\pi\sigma_2} \exp[-(y_N^2 + y_P^2)/2\,\sigma_2^2]$

Note: $E_4 = \dfrac{2\,\sigma_1}{\pi\,\sigma_2\,\sigma_{1l}} \exp\left[-\dfrac{y_N^2}{2\,\sigma_2^2} - \dfrac{\sigma_1^2(1-\sigma_{1h}^2)\,y_P^2}{2\,\sigma_2^2\,\sigma_{1l}^2}\right]$

See also the footnote 2 to table 1.

Table 5. The PDF's of y_N for the cases $P_h = 1$, 2 and M: A centrosymmetric crystal.

P_h	$P(y_N)$
1	$E_5 \exp[-\sigma_{1h/2t}^2] \cosh(\sigma_{1h}\, y_N/t)$
2	$E_5 \int_0^1 \exp[-\sigma_{1h}^2 S_x^2/t] \cosh[\sqrt{2}\,\sigma_{1h}\, y_N\, S_x/t] dx$
3	$(2/\pi)^{\frac{1}{2}} \exp(-y_N^2/2)$

Note: $E_5 = [2/\pi(1-\sigma_{1h}^2)]^{\frac{1}{2}} \exp[-y_N^2/2\,(1-\sigma_{1h}^2)]$

See also the footnote 2 to table 1.

Table 6. The joint PDF of y_N and y_P^c for an unrelated model consisting of $P_h(=1, 2$ or $M)$ heavy and P_l light atoms per unit cell: A centrosymmetric crystal.

P_h	$P(y_N, y_P^c)$
1	$E_6 \exp[-r^2(t+\sigma_{1l}^2)/2t] \cosh(b) \cosh(\sigma_{1h} y_N/t)$
2	$E_6 \int_0^1\int_0^1 \exp[-r^2 S_z^2 - \sigma_{1h}^2 S_x^2/t] \cosh[\sqrt{2}\,\sigma_{1h} y_N S_x/t] \cosh[\sqrt{2}\,b\,S_z]\,dx dz$
M	$(2/\pi) \exp[-(y_N^2 + y_P^{c\,2})/2]$

Note: $E_6 = \dfrac{2\sigma_1}{\pi\sigma_{1l}(1-\sigma_{1h}^2)^{1/2}} \exp\left[-\dfrac{y_N^2}{2(1-\sigma_{1h}^2)} - \dfrac{\sigma_1^2 y_P^{c\,2}}{2\sigma_{1l}^2}\right]$

See also the footnote 2 to table 1.

(3.6) of SP (1976) by replacing the set (σ_1^2, σ_2^2) by the set $(\sigma_{1h}^2, 1-\sigma_{1h}^2)$. Since for the case $P_h=M$, y_N follows the centric-Wilson distribution, $\langle y_N\rangle=\sqrt{2/\pi}$. We thus have

$$\langle y_N\rangle = \begin{cases} \left[\dfrac{2}{\pi}(1-\sigma_{1h}^2)\right]^{1/2} \exp\left[-\dfrac{\sigma_{1h}^2}{2(1-\sigma_{1h}^2)}\right] \\ \qquad + \sigma_{1h}\,\mathrm{erf}\left[\dfrac{\sigma_{1h}}{\sqrt{2(1-\sigma_{1h}^2)}}\right] \text{ for } P_h = 1 \\ \left[\dfrac{2}{\pi(1-\sigma_{1h}^2)}\right]^{1/2} \exp\left[-\dfrac{\sigma_{1h}^2}{2(1-\sigma_{1h}^2)}\right]\left\{I_0\left[\dfrac{\sigma_{1h}^2}{2(1-\sigma_{1h}^2)}\right]\right. \\ \qquad \left. + \sigma_{1h}^2 I_1\left[\dfrac{\sigma_{1h}^2}{2(1-\sigma_{1h}^2)}\right]\right\} \text{ for } P_h = 2 \\ \sqrt{\dfrac{2}{\pi}} \text{ for } P = M \end{cases} \tag{33}$$

2.6. *Evaluation of R(F) and R(I) corresponding to the limiting situation* $\sigma_{1l}^2 = 0$

$R(F)$ and $R(I)$ for the limiting case corresponding to $\sigma_{1l}^2=0$ (*i.e.*, the case where the P-group contains only the heavy atoms) can be obtained by following the same method as that outlined in the earlier sections and involves the use of the appropriate joint PDF of y_N and y_P^c. It is easier to obtain $P(y_N, y_P^c)$ required for the present situation (*i.e.* $\sigma_{1l}^2=0$) directly than by a limiting process from the distributions derived in the previous sections for the general situation (*i.e.* $\sigma_{1l}^2 \neq 0$). Hence we

shall presently derive $P(y_N, y_P^c)$ valid for the situation $\sigma_{1l}^2=0$. In this connection it should be noted that $\sigma_{1h}^2=\sigma_1^2$ if $\sigma_{1l}^2=0$ and that $P(y_N; y_P^c)$ and $P(y_N)$ obtained in the previous sections are valid for the present case as well.

2.6a *Derivation of* $P(y_N, y_P)$ *and* $P(y_N, y_P^c)$ *for the various cases corresponding to the limiting situation* $\sigma_{1l}^2=0$: If the P-group is assumed to consist only of the heavy atoms (*i.e.*, $P=P_h$ and $P_l=0$) then $P(y_P)$ for the cases $P(=P_h)=1$ and 2 will be given respectively by (3.1) and (3.3) of SP (1976). $P(y_P)$ for the many-atom case will be given by the appropriate Wilson distribution. Substituting the appropriate expression for $P(y_N; y_P)$ from (19) or (32) we can obtain $P(y_N, y_P)$ for the various cases. The results are given in tables 7 and 8 for the *NC* and *C* cases respectively. Substituting the appropriate expression for $P(y_N)$ from (27) to (30) or table 5 and the appropriate expression* for $P(y_P^c)$ in (25) and simplifying we can obtain the expression for $P(y_N, y_P^c)$ for the various cases. These results are also summarised in tables 7 and 8 for the *NC* and *C* cases respectively. The expressions for $\langle y_N \rangle$ obtained in (31) and (33) are valid for the corresponding cases of the present situation (*i.e.*, the situation in which $\sigma_{1l}^2=0$). The method of evaluation of $\langle | y_N^n - \sigma_1^n (y_P^c)^n | \rangle$, $(n=1, 2)$, for the various cases corresponding to $\sigma_{1l}^2=0$ is exactly similar to that described in the previous sections.

Table 7. Expressions for $P(y_N, y_P)$ and $P(y_N, y_P^c)$ for the cases $P_h(=P)=1$, 2, *MN* and *MC* when $\sigma_{1l}^2=0$: A non-centrosymmetric crystal.

P_h	$P(y_N, y_P)$	$P(y_N, y_P^c)$
1	$E_7\, B \exp(-s^2 y_P^2)\, \delta(y_P-1)$	$E_7 \exp(-s^2)\, I_0(2k)\, \delta(y_P^c-1)$
2	$(\sqrt{2}/\pi) E_7 B \exp(-s^2 y_P^2)(1-y_P^2/2)^{-1/2}$	$(\sqrt{2}/\pi) E_7 (1-y_P^{c2}/2)^{-1/2} \int_0^1 \exp[-2s^2 S_z^2]\, I_0[2\sqrt{2k}\, S_z]\, dz$
MN	$2 E_7 B\, y_P \exp(-y_P^2/\sigma_2^2)$	$4\, y_N\, y_P^c \exp[-y_N^2 - y_P^{c2}]$
MC	$(2/\pi)^{1/2} E_7\, B \exp[-(1+\sigma_1^2)\, y_P^2/2\,\sigma_2^2]$	$(8/\pi)\, y_N (1-\sigma_1^4)^{-1/2} \exp\left[-\frac{y_N^2}{1-\sigma_1^4} - \frac{y_P^{c2}}{2}\right] I_0\left[\frac{\sigma_1^2 y_N^2}{1-\sigma_1^4}\right]$

Note: $E_7 = (2y_N/\sigma_2^2) \exp(-y_N^2/\sigma_2^2)$.

If $\sigma_{1l}^2=0$, then $\sigma_{1h}^2=\sigma_1^2$ and $1-\sigma_{1h}^2=\sigma_2^2$. For the case $P=2$, the domain of definition is $0 \leqslant y_N < \infty$, $0 \leqslant y_P,\ y_P^c \leqslant \sqrt{2}$. For the others it is $0 \leqslant y_N, y_P, y_P^c < \infty$. $P(y_N, y_P)$ corresponds to the related case and $P(y_N, y_P^c)$ to the unrelated case. This footnote also applies to table 8. See also the footnote 2 to table 1.

*This can be obtained from the expression for $P(y_P)$ for the corresponding case by replacing y_P by y_P^c.

Table 8. Expressions for $P(y_N, y_P)$ and $P(y_N, y_P^c)$ for the cases $P_h\,(=P) = 1, 2$ and M when $\sigma_{1l}^2 = 0$: A centrosymmetric crystal.

P_h	$P(y_N, y_P)$	$P(y_N, y_P^c)$
1	$(2/\pi)^{1/2}\, E_8\, C\, \delta\,(y_P - 1)$	$(2/\pi)^{1/2}\, E_8'\cosh(k) \exp(-s^2/2)\, \delta\,(y_P^c - 1)$
2	$2\,\pi^{-3/2} E_8\, C(1 - y_P^2/2)^{-1/2}$	$2\pi^{-3/2}\, E_8'(1 - y_P^{c2}/2)^{-1/2} \int_0^1 \exp[-s^2 S_x^2] \cosh[\sqrt{2}kS_x]\, dx$
M	$(2C/\pi\sigma_2) \exp[-(y_N^2+y_P^2)/2\,\sigma_2^2]$	$(2/\pi) \exp[-(y_N^2+y_P^{c2})/2]$

Note: $E_8 = (1/\sigma_2) \exp[-(y_N^2 + \sigma_1^2 y_P^2)/2\,\sigma_2^2]$ $E_8' = (1/\sigma_2) \exp(-y_N^2/2\,\sigma_2^2)$.

See also the footnote 2 to table 1.

3. Discussion of the theoretical results

3.1 *General remarks*

From tables 1, 2, 4 and 6 it is seen that $P(y_N, y_P^c)$ for each of the cases $P=1$ and 2 is a function of σ_1^2 and σ_{1h}^2 (for both the related and unrelated cases). However for the cases $P=MN$ (*i.e.*, *NC* crystal) and $P=M$ (*i.e.*, *C* crystal), $P(y_N, y_P)$ depends only on σ_1^2 and $P(y_N, y_P^c)$ is independent of both σ_1^2 and σ_{1h}^2. $\langle y_N \rangle$ for all the cases is a function of only σ_{1h}^2 (see (31) and (33)). Hence it follows that $\langle\,|\, y_N^n - \sigma_1^n\,(y_P^c)\,|\,\rangle$, $(n=1, 2)$ and consequently $\bar{R}(F)$ and $\bar{R}(I)$ see (10b) and (14) are expected to be functions of both σ_1^2 and σ_{1h}^2 for all the cases except $P=MN$ and $P=M$. For the latter two cases, these quantities are functions of only σ_1^2.

In order to facilitate the theoretical evaluation of the overall values of $R(F)$ and $R(I)$ by using (10b) and (14) respectively the values of* $\langle\,|\, y_N^n - \sigma_1^n\,(y_P^c)^n\,|\,\rangle$, $(n=1, 2)$ and $\langle y_N \rangle$ have been tabulated for the various cases as functions of σ_{1h}^2 and σ_1^2 (see tables (9)–(19)†). It may be noted here that quantities $\langle\,|\, y_N^n - \sigma_1^n\,(y_P^c)^n\,|\,\rangle$, $n=1, 2$, are to be evaluated by substituting the appropriate function $P(y_N, y_P^c)$ derived in § 2 into equations (13) and (15b) and calculating the resulting integrations numerically. The quantity $\langle y_N \rangle$ can be evaluated from the results in (31) for the *NC* case and those in (33) for the *C* case.

*In the subsequent sections we shall use y_P^c in the general sense. That is, y_P^c is to be interpreted as y_P when the related case is implied. We shall also use the term *R*-index to denote any one of the indices considered in this paper. However, when the discussion is specific with respect to a given type of *R*-index the exact symbol will be used.

†These tables can be had from the authors on request.

3.2 *Procedure for computing the overall values of R-indices*

The procedure for calculating the overall values of the R-indices for the related and unrelated cases corresponding to a given situation consists of the following steps: (a) Divide the interval $0 \leqslant \sin\theta/\lambda \leqslant S^0_{\max}$ (where $S^0_{\max}$ is the largest value of $\sin\theta/\lambda$ for the reflections in the data of the given crystal) into m narrow intervals* such that in each interval the values of σ_1^2 and σ_{1h}^2 remain practically constant. (b) Determine the values of σ_1^2, σ_{1h}^2 and σ_N^2 corresponding to these m intervals (or ranges) of $\sin\theta/\lambda$. Let $(\sigma_1^2)_i$, $(\sigma_{1h}^2)_i$ and $(\sigma_N^2)_i$ respectively denote the values of σ_1^2, σ_{1h}^2 and σ_N^2 in the ith range. (c) Using the values of σ_1^2 and σ_{1h}^2 thus obtained and making use of the appropriate tables *i.e.* tables (9)–(19) for $\langle | y_N^n - \sigma_1^n (y_P^c)^n | \rangle$, $n=1, 2$, obtain the values of these quantities by interpolation (see Abramowitz, 1965). (d) Determine the values of $\langle y_N \rangle_i$ from the appropriate tables by interpolation (*Note:* $\langle y_N \rangle$ is a function of σ_{1h}^2 only). (e) Determine the number of reflections in the various ranges. Let these be denoted by n_i, $i=1$ to m. (f) Make use of the values of n_i, $(\sigma_N^2)_i$, $\langle | y_N^n - \sigma_1^n (y_P^c)^n | \rangle_i$ and $\langle y_N \rangle_i$ thus obtained in (10b) and (14) and compute the overall values of $R(F)$ and $R(I)$. (g) Compare the observed overall values of $R(F)$ and $R(I)$ for the trial structure with the corresponding theoretical values thus obtained for the related and unrelated cases in order to judge the correctness of the model.

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*It would be sufficient to divide the reflections with range $0 \leqslant S \leqslant S^0_{\max}$ such that there are about hundred reflections per interval. A Fortran subroutine for obtaining the boundaries of the various intervals is available with the authors.