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Overall values of conventional discrepancy indices for crystals with heavy atoms. Part II. Results for monoclinic and orthorhombic crystals when the heavy-atom part alone constitutes the model

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Abstract. Theoretical expressions of $\langle y_N \rangle$, $\langle | y_N - \sigma_1 y_P^c | \rangle$ and $\langle | y_N^2 - \sigma_1^2 (y_P^c)^2 | \rangle$ (where y_N and y_P^c are the normalized structure amplitudes of the structure and the model respectively) are derived in terms of the heavy atom contribution σ_1^2 for monoclinic and orthorhombic crystals containing a few (*i.e.*, 1 or 2) heavy atoms of the same kind per asymmetric unit by taking the heavy atom part alone as the model. Results are obtained for both the related and unrelated cases. The local values of $\langle y_N \rangle$ and $\langle | y_N^n - \sigma_1^n (y_P^c)^n | \rangle$, $(n=1, 2)$ calculated from these expressions can be used to calculate the overall values of the conventional R-indices $R(F)$ and $R(I)$ for the related and unrelated cases. These overall values could be used to check the correctness of heavy atoms located in the structure.

Keywords. Theoretical evaluation; conventional R-indices; monoclinic crystal; orthorhombic crystal; heavy atoms.

1. Introduction

In Part I (Parthasarathy and Ponnuswamy 1981) we have derived the overall values of the discrepancy indices $R(F)$ and $R(I)$ for triclinic crystals when the model consists of the heavy atoms and a part of the light atoms in the unit cell. Here we shall derive the theoretical overall values of $R(F)$ and $R(I)$ for monoclinic and orthorhombic crystals containing a few (*i.e.*, 1 or 2) heavy atoms in the asymmetric unit (besides a large number of light atoms) by taking the heavy-atom part alone† as the model. Since the overall values of $R(F)$ and $R(I)$ can be calculated from the values of $\langle | y_N - \sigma_1 y_P^c | \rangle$, $\langle | y_N^2 - \sigma_1^2 (y_P^c)^2 | \rangle$ and $\langle y_N \rangle$ [see (10b) and (14) of Part I for details] we shall obtain these three quantities as a function of the heavy atom contribution σ_1^2.

In Part I the results were obtained by first deriving the theoretical expressions for the joint PDF of y_N and y_P^c. Since the joint PDF's for the situations considered in this part cannot be obtained in a closed form, it becomes essential to tackle the present

Contribution No. 550

†Since the theoretical treatment for models containing both heavy and a part of light atoms becomes complicated when space group symmetry is to be taken into account we shall consider here models consisting of heavy atoms alone.

problem by a different method. The procedure used in this part consists of expressing y_N in terms of the normalized structure amplitudes y_Q and y_P and further expressing y_P and y_P^c in terms of contributions from the independent groups of equivalent atoms (for details see § 2).

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

2.1 *Notation and preliminary results*

Consider a crystal containing q light atoms of similar scattering power (*e.g.*, C, N and O) and p heavy atoms (of the same type) per asymmetric unit occupying general positions. Let s be the symmetry number of the space group (*i.e.*, the number of equivalent general positions in the unit cell). The structure factor of a reflection **H** can be written in terms of the contributions from the P- and Q-groups of atoms as*

$$F_N = F_P + F_Q. \tag{1}$$

We shall assume the crystal to belong to one of the categories of space groups of the monoclinic or orthorhombic system under the Foster-Hargreaves classification scheme [see Foster and Hargreaves 1963a, 1963b]. We shall assume q to be sufficiently large so that F_Q follows the centric or acentric Wilson distribution (Wilson 1949) according as the crystal is centrosymmetric or non-centrosymmetric**. We can obtain from (1) that

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

where ω is defined to be

$$\begin{aligned} \omega &= \cos\psi_0 \text{ for the } NC \text{ case,} \\ &= s_P\, s_Q \text{ for the } C \text{ case,} \end{aligned} \tag{3}$$

where $\psi_0 = \alpha_P - \alpha_Q$ (for the NC case) and s_P and s_Q are the signs of the structure factors F_P and F_Q (for the C case). In terms of the normalized structure amplitudes y_N, y_P and y_Q and the quantities σ_1^2 and σ_2^2 namely,

$$y_a = |F_a| / \langle |F_a|^2\rangle^{1/2},\ a = N, P \text{ or } Q, \tag{4}$$

$$\sigma_1^2 = \langle |F_P|^2\rangle / \langle |F_N|^2\rangle,\ \sigma_2^2 = \langle |F_Q|^2\rangle / \langle |F_N|^2\rangle, \tag{5}$$

*$Q(=sq)$ and $P(=sp)$ respectively denote the number of light atoms and heavy atoms per unit cell. $N(=P+Q)$ is the total number of atoms in the unit cell.

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

we can rewrite (2) as

$$y_N^2 = \sigma_1^2\ y_P^2 + \sigma_2^2\ y_Q^2 + 2\ \sigma_1\ \sigma_2\ y_P\ y_Q\ \omega. \tag{6}$$

Suppose the model structure is made up of only the P heavy atoms in the unit cell. The calculated structure factor F_P^c of the reflection **H** due to contributions from these heavy atoms is related to the normalized structure amplitude y_P^c by

$$y_P^c = |F_P^c|/\langle |F_P^c|^2\rangle^{1/2}. \tag{7}$$

We rewrite F_P^c as

$$F_P^c = sf_P\Big[\sum_{j=1}^{p} \xi_{pj}^c + i\sum_{j=1}^{p} \eta_{pj}^c\Big] = sf_P\,(\xi_P^c + i\eta_P^c), \tag{8}$$

where ξ_{pj}^c and η_{pj}^c are the trigonometric factors of the geometrical structure factor of the jth atom in the asymmetric unit and the other $(s-1)$ atoms equivalent to it. From (8) we have

$$|F_P^c| = sf_P\,[(\xi_P^c)^2 + (\eta_P^c)^2]^{1/2} = sf_P\,E_P^c, \text{ say} \tag{9}$$

where
$$E_P^c = [(\xi_P^c)^2 + (\eta_P^c)^2]^{1/2}. \tag{10}$$

For the C case $\eta_P^c \equiv 0$ so that (10) can be written as

$$E_P^c = |\xi_P^c|. \tag{11}$$

Using table 1 of Foster and Hargreaves (1963b), $\langle |F_P^c|^2\rangle$ can be written as

$$\langle |F_P^c|^2\rangle = \epsilon s^2\, p\, f_P^2, \tag{12}$$

where ϵ is a constant whose value depends on the space-group category. From Foster and Hargreaves (1963b) it can be shown that $\epsilon = 1, \frac{1}{2}, \frac{1}{2}, \frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{1}{8}$ for the categories 1, 2, 3, 4, 5, 6 and 7 respectively. Making use of (9) and (12) in (7) we obtain

$$y_P^c = E_P^c/(\epsilon p)^{1/2}. \tag{13}$$

It can be similarly shown that

$$y_P = E_P/(\epsilon p)^{1/2}, \tag{14}$$

where
$$E_P = (\xi_P^2 + \eta_P^2)^{1/2}, \tag{15}$$

for *NC* case and

$$E_P = |\, \xi_P \,|, \tag{16}$$

for *C* case.

Making use of (6), (13) and (14) we write $\langle |\, y_N - \sigma_1 y_P^c \,| \rangle$, $\langle y_N \rangle$ and $\langle |\, y_N^2 - \sigma_1^2 (y_P^c)^2 \,| \rangle$ as,

$$\langle |\, y_N - \sigma_1 y_P^c \,| \rangle = \langle |\, [\sigma_2^2 y_Q^2 + k_1 \sigma_1 \sigma_2 E_P y_Q \omega + k_2 \sigma_1^2 E_P^2]^{1/2} - k_3 \sigma_1 E_P^c \,| \rangle, \tag{17}$$

$$\langle y_N \rangle = \langle [\sigma_2^2 y_Q^2 + k_1 \sigma_1 \sigma_2 E_P y_Q \omega + k_2 \sigma_1^2 E_P^2]^{1/2} \rangle, \tag{18}$$

$$\langle |\, y_N^2 - \sigma_1^2 (y_P^c)^2 \,| \rangle = \langle |\, \sigma_2^2 y_Q^2 + k_1 \sigma_1 \sigma_2 E_P y_Q \omega + k_2 \sigma_1^2 \{E_P^2 - (E_P^c)^2\} \,| \rangle, \tag{19}$$

where k_i ($i = 1, 2, 3$) are defined to be

$$k_1 = \frac{2}{(\epsilon p)^{1/2}}, \quad k_2 = \frac{1}{\epsilon p}, \quad k_3 = \frac{1}{(\epsilon p)^{1/2}}. \tag{20}$$

The expressions for $\langle |\, y_N - \sigma_1 y_P^c \,| \rangle$, $\langle y_N \rangle$ and $\langle |\, y_N^2 - \sigma_1^2 (y_P^c)^2 \,| \rangle$ for the *C* and *NC* cases are obtained separately since the quantity ω in (17)–(19) obey different distribution laws for the *C* and *NC* cases. For the related case $y_P^c = y_P$ so that $E_P^c = E_P$. For the unrelated case E_P and E_P^c are independent random variables. Hence it is clear that the theory for related and unrelated cases for a given type of crystal (*i.e.*, *C* or *NC*) is also to be considered separately. Consider the following four cases individually; (i) Related model of a *C* crystal, (ii) Related model of an *NC* crystal, (iii) Unrelated model of a *C* crystal and (iv) Unrelated model of an *NC* crystal.

2.2 *Theoretical expressions for* $\langle |\, y_N - \sigma_1 y_P \,| \rangle$, $\langle y_N \rangle$ *and* $\langle |\, y_N^2 - \sigma_1^2 y_P^2 \,| \rangle$ *for the related case*

By setting $E_P^c = E_P$ we obtain from (17) and (19)

$$\langle |\, y_N - \sigma_1 y_P \,| \rangle = \langle |\, [\sigma_2^2 y_Q^2 + k_1 \sigma_1 \sigma_2 E_P y_Q \omega + k_2 \sigma_1^2 E_P^2]^{1/2} - k_3 \sigma_1 E_P \,| \rangle, \tag{21}$$

$$\langle |\, y_N^2 - \sigma_1^2 y_P^2 \,| \rangle = \langle |\sigma_2^2 y_Q^2 + k_1 \sigma_1 \sigma_2 E_P y_Q \omega \,| \rangle. \tag{22}$$

Since $\langle y_N \rangle$ is a property of the crystal but not of the model, (18) will be valid for both the related and unrelated cases.

2.2*a Centrosymmetric crystal:* Since s_P and s_Q are independent quantities and since each of s_P and s_Q is equally likely to be $+1$ and -1, it follows that $\omega\ (=s_P\, s_Q)$ is equally likely to be $+1$ and -1. We can hence write the probability density function (abbreviated *as* PDF) of ω to be

$$P(\omega) = \tfrac{1}{2}\,\delta\,(\omega-1) + \tfrac{1}{2}\,\delta(\omega+1) \tag{23}$$

The PDF of y_Q will be the centric Wilson distribution (Wilson 1949)

$$P(y_Q) = \sqrt{\frac{2}{\pi}}\,\exp\,(-y_Q^2/2). \tag{24}$$

We shall presently give the theory for the space-group category 7 since the results for the other categories can be written by analogy. By definition (Foster and Hargreaves 1963a)

$$E_P = E_P\,(\theta, \phi, \psi)\,, \tag{25}$$

where (θ, ϕ, ψ) is an abbreviation for the set $(\theta_i, \phi_i, \psi_i;\ i=1$ to $p)$ with $3p$ elements. The quantities θ_i, ϕ_i, ψ_i $(i=1$ to $p)$ are mutually independent random variables distributed uniformly in the interval 0 to 2π (Foster and Hargreaves 1963a). It is convenient to define the random variables θ_i', ϕ_i', ψ_i' by

$$\theta_i' = \theta_i/(2\pi),\ \ \phi_i' = \phi_i/(2\pi),\ \ \psi_i' = \psi_i/(2\pi),\ \ i = 1 \text{ to } p.$$

We can hence write (25) equivalently as

$$E_P = E_P\,(\theta', \phi', \psi'). \tag{26}$$

The quantities θ_i', ϕ_i', ψ_i' $(i=1$ to $p)$ are mutually independent random variables uniformly distributed in the interval 0 to 1. Since the quantities ω, y_Q and θ_i', ϕ_i', ψ_i' $(i=1$ to $p)$ are mutually independent, the joint PDF of these random variables will be the product of their PDF's. That is

$$P(y_Q, \omega, \theta_1', \phi_1', \psi_1', \ldots, \theta_p', \phi_p', \psi_p') = P(y_Q)\,P(\omega) \prod_{i=1}^{p} [P(\theta_i')\,P(\phi_i')\,P(\psi_i')]. \tag{27}$$

Since each random variable of the set $(\theta_i', \phi_i', \psi_i';\ i=1$ to $p)$ is uniformly distributed in the interval 0 to 1, it follows that

$$P(\theta_i') = P(\phi_i') = P(\psi_i') = 1,\ \ i=1 \text{ to } p. \tag{28}$$

Substituting (23), (24) and (28) in (27) we obtain

$$P(y_Q, \omega, \theta'_1, \phi'_1, \psi'_1, \ldots, \theta'_p \phi'_p \psi'_p) = \frac{1}{\sqrt{2\pi}} \exp(-y_Q^2/2) \times [\delta(\omega-1)+\delta(\omega+1)]. \tag{29}$$

Making use of (29) in (21) we obtain

$$\langle | y_N - \sigma_1 y_P | \rangle = \frac{1}{\sqrt{2\pi}} \int_{y_Q=0}^{\infty} \int_{\omega=-\infty}^{\infty} \int_0^1 \cdots \int_0^1 | (\sigma_2^2 y_Q^2 + k_1 \sigma_1 \sigma_2 E_P y_Q \omega + k_2 \sigma_1^2 E_P^2)^{1/2} - k_3 \sigma_1 E_P | \exp(-y_Q^2/2) [\delta(\omega-1)+\delta(\omega+1)] \, dy_Q \, d\omega \prod_{i=1}^{p} (d\theta'_i \, d\phi'_i \, d\psi'_i), \tag{30}$$

which involves a $(3p+2)$-tuple integral. Carrying out the integration over ω first by using the property of Dirac delta function we can rewrite (30) as

$$\langle | y_N - \sigma_1 y_P | \rangle = \frac{1}{\sqrt{2\pi}} \int_{y_Q=0}^{\infty} \int_0^1 \cdots \int_0^1 \{ | (\sigma_2^2 y_Q^2 + k_1 \sigma_1 \sigma_2 E_P y_Q + k_2 \sigma_1^2 E_P^2)^{1/2} - k_3 \sigma_1 E_P | + | (\sigma_2^2 y_Q^2 - k_1 \sigma_1 \sigma_2 E_P y_Q + k_2 \sigma_1^2 E_P^2)^{1/2} - k_3 \sigma_1 E_P | \} \times \exp -(y_Q^2/2) \, dy_Q \prod_{i=1}^{p} (d\theta'_i \, d\phi'_i \, d\psi'_i). \tag{31}$$

For facilitating numerical integration of (31) the variable of integration is changed by the substitution,

$$y_Q = u/(1-u). \tag{32}$$

We obtain from (31)

$$\langle | y_N - \sigma_1 y_P | \rangle = \frac{1}{\sqrt{2\pi}} \int_0^1 \int_0^1 \cdots \int_0^1 [\{ | (\sigma_2^2 y_Q^2 + k_1 \sigma_1 \sigma_2 E_P y_Q + k_2 \sigma_1^2 E_P^2)^{1/2} - k_3 \sigma_1 E_P | + | (\sigma_2^2 y_Q^2 - k_1 \sigma_1 \sigma_2 E_P y_Q + k_2 \sigma_1^2 E_P^2)^{1/2} - k_3 \sigma_1 E_P | \} \exp(-y_Q^2/2)]_u \times \frac{du}{(1-u)^2} \prod_{i=1}^{p} (d\theta'_i \, d\phi'_i \, d\psi'_i), \tag{33}$$

which involves a $(3p+1)$-tuple integral. In (33) we have used the notation $[-]_u$ to mean that in the expression within the square parentheses, the quantity y_Q is to be replaced by $u/(1-u)$ while carrying out the numerical integration. We shall use this symbolic notation in the subsequent derivations as well.

Making use of (29) in (18) and following the above procedure used for obtaining (33) we can show that

$$\langle y_N \rangle = \frac{1}{\sqrt{2\pi}} \int_{y_Q=0}^{\infty} \int_{\omega=-\infty}^{\infty} \int_0^1 \cdots \int_0^1 (\sigma_2^2 y_Q^2 + k_1 \sigma_1 \sigma_2 E_P y_Q \omega$$

$$+ k_2 \sigma_1^2 E_P^2)^{1/2} \exp(-y_Q^2/2) [\delta(\omega - 1) + \delta(\omega + 1)]$$

$$\times dy_Q \, d\omega \prod_{i=1}^{p} (d\theta_i' \, d\phi_i' \, d\psi_i') = \frac{1}{\sqrt{2\pi}} \int_0^1 \int_0^1 \cdots \int_0^1 [\{(\sigma_2^2 y_Q^2$$

$$+ k_1 \sigma_1 \sigma_2 E_P y_Q + k_2 \sigma_1^2 E_P^2)^{1/2} + (\sigma_2^2 y_Q^2 - k_1 \sigma_1 \sigma_2 E_P y_Q$$

$$+ k_2 \sigma_1^2 E_P^2)^{1/2}\} \exp(-y_Q^2/2)]_u \frac{du}{(1-u)^2} \prod_{i=1}^{p} (d\theta_i' \, d\phi_i' \, d\psi_i'). \quad (34)$$

Making use of (29) in (22) and the procedure used for obtaining (33) we obtain

$$\langle | y_N^2 - \sigma_1^2 y_P^2 | \rangle = \frac{1}{\sqrt{2\pi}} \int_{y_Q=0}^{\infty} \int_{\omega=-\infty}^{\infty} \int_0^1 \cdots \int_0^1 | \sigma_2^2 y_Q^2$$

$$+ k_1 \sigma_1 \sigma_2 E_P y_Q \omega | \exp(-y_Q^2/2) [\delta(\omega - 1)$$

$$+ \delta(\omega + 1)] \, dy_Q \, d\omega \prod_{i=1}^{p} (d\theta_i' \, d\phi_i' \, d\psi_i')$$

$$= \frac{1}{\sqrt{2\pi}} \int_0^1 \int_0^1 \cdots \int_0^1 [\{| \sigma_2^2 y_Q^2 + k_1 \sigma_1 \sigma_2 E_P y_Q |$$

$$+ | \sigma_2^2 y_Q^2 - k_1 \sigma_1 \sigma_2 E_P y_Q |\} \exp(-y_Q^2/2)]_u \frac{du}{(1-u)^2}$$

$$\times \prod_{i=1}^{p} (d\theta_i' \, d\phi_i' \, d\psi_i'). \quad (35)$$

The multiple integrals in (33)–(35) are to be evaluated numerically.

2.2*b Non-centrosymmetric crystal:* Since the P and Q groups are independent of each other, ψ_0 $(=\alpha_P - \alpha_Q)$ will be uniformly distributed in the interval 0 to 2π (Parthasarathy and Srinivasan 1964). Let

$$\psi_0' = \psi_0/(2\pi). \tag{36}$$

Now ψ_0' will be uniformly distributed in the interval 0 to 1. The PDF of y_Q will be given by the acentric Wilson distribution (Wilson 1949)

$$P(y_Q) = 2\, y_Q \exp(-y_Q^2). \tag{37}$$

The random variables θ_i', ϕ_i', ψ_i' ($i=1$ to p) occurring in E_P are mutually independent and each follows the uniform distribution in the interval 0 to 1. Hence we can write the joint PDF of y_Q, ψ_0', θ_i', ϕ_i', ψ_i' ($i=1$ to p) as

$$P(y_Q, \psi_0', \theta_1', \phi_1', \psi_1', \ldots, \theta_p', \phi_p', \psi_p') = P(y_Q)\, P(\psi_0')$$

$$\times \prod_{i=1}^{p} [P(\theta_i')\, P(\phi_i')\, P(\psi_i')] = 2\, y_Q \exp(-y_Q^2) \tag{38}$$

Making use of (38) we obtain from (21) that

$$\langle |y_N - \sigma_1\, y_P| \rangle = 2 \int_0^\infty \int_0^1 \int_0^1 \cdots \int_0^1 |\{\sigma_2^2\, y_Q^2 + k_1\, \sigma_1\, \sigma_2\, E_P\, y_Q \cos(2\pi\psi_0')$$

$$+ k_2\, \sigma_1^2\, E_P^2\}^{1/2} - k_3\, \sigma_1\, E_P|\, y_Q \exp(-y_Q^2)\, dy_Q\, d\psi_0' \prod_{i=1}^{p} (d\theta_i'\, d\phi_i'\, d\psi_i'). \tag{39}$$

Making use of the substitution (32), we can rewrite (39) as

$$\langle |y_N - \sigma_1\, y_P| \rangle = 2 \int_0^1 \int_0^1 \int_0^1 \cdots \int_0^1 [|\{\sigma_2^2\, y_Q^2 + k_1\, \sigma_1\, \sigma_2\, E_P\, y_Q \cos(2\pi\psi_0')$$

$$+ k_2\, \sigma_1^2\, E_P^2\}^{1/2} - k_3\, \sigma_1\, E_P|\, y_Q \exp(-y_Q^2)] \frac{du\, d\psi_0'}{(1-u)^2} \prod_{i=1}^{p} (d\theta_i'\, d\phi_i'\, d\psi_i'). \tag{40}$$

Making use of (38) in (18) and following the procedure that was used for obtaining (40) we obtain

$$\langle y_N \rangle = 2 \int_0^\infty \int_0^1 \int_0^1 \cdots \int_0^1 \{\sigma_2^2\, y_Q^2 + k_1\, \sigma_1\, \sigma_2\, E_P\, y_Q \cos(2\pi\psi_0') + k_2\, \sigma_1^2\, E_P^2\}^{1/2}$$

$$\times y_Q \exp(-y_Q^2)\, dy_Q\, d\psi_0' \prod_{i=1}^{p} (d\theta_i'\, d\phi_i'\, d\psi_i')$$

$$= 2 \int_0^1 \int_0^1 \int_0^1 \cdots \int_0^1 [\{\sigma_2^2 y_Q^2 + k_1 \sigma_1 \sigma_2 E_P y_Q \cos(2\pi\psi_0') + k_2 \sigma_1^2 E_P^2\}^{1/2}$$

$$y_Q \exp(-y_Q^2)]_u \frac{du\, d\psi_0'}{(1-u)^2} \prod_{i=1}^{p} (d\theta_i'\, d\phi_i'\, d\psi_i'). \tag{41}$$

Making use of (38) in (22) and following the procedure that was used for obtaining (40) we obtain

$$\langle | y_N^2 - \sigma_1^2 y_P^2 | \rangle = \langle | \sigma_2^2 y_Q^2 + k_1 \sigma_1 \sigma_2 E_P y_Q \cos(2\pi\psi_0') | \rangle$$

$$= 2 \int_0^1 \int_0^1 \int_0^1 \cdots \int_0^1 [| \sigma_2^2 y_Q^2 + k_1 \sigma_1 \sigma_2 E_P y_Q \cos(2\pi\psi_0') |\, y_Q \exp(-y_Q^2)]_u$$

$$\times \frac{du\, d\psi_0^i}{(1-u)^2} \prod_{i=1}^{p} (d\theta_i'\, d\phi_i'\, d\psi_i'). \tag{42}$$

2.3 *Theoretical expressions for* $\langle | y_N - \sigma_1 y_P^c | \rangle$ and $\langle | y_N^2 - \sigma_1^2 (y_P^c)^2 | \rangle$ *for the unrelated case*

Since the procedure to be followed for this case is analogous to that for the related case we give here only the essential steps. Here $E_P \neq E_P^c$ and E_P and E_P^c are independent random variables We shall write

$$E_P = E_P(\theta', \phi', \psi'), \quad E_P^c = E_P^c(\theta'', \phi'', \psi''), \tag{43}$$

where (θ', ϕ', ψ') stands for the set $(\theta_i', \phi_i', \psi_i';\ i=1 \text{ to } p)$ and $(\theta'', \phi'', \psi'')$ for $(\theta_i'', \phi_i'', \psi_i'';\ i=1 \text{ to } p)$. The random variables $\theta_i', \phi_i', \psi_i', \theta_i'', \phi_i'', \psi_i''$ $(i=1 \text{ to } p)$ are all mutually independent and each follows the uniform distribution in the interval 0 to 1.

2.3*a Centrosymmetric case:* In this case the joint PDF of $y_Q, \omega, \theta_i', \phi_i', \psi_i', \theta_i'', \phi'', \psi_i''$ $(i=1 \text{ to } p)$ is given by

$$P(y_Q, \omega, \theta_1', \phi_1', \psi_1', \ldots, \theta_p', \phi_p', \psi_p', \theta_1'', \phi_1'', \psi_1'', \ldots, \theta_p'', \phi_p'', \psi_p'')$$

$$= P(y_Q)\, P(\omega) \prod_{i=1}^{p} [P(\theta_i')\, P(\phi_i')\, P(\psi_i')\, P(\theta_i'')\, P(\phi_i'')\, P(\psi_i'')]$$

$$= \frac{1}{\sqrt{2\pi}} \exp(-y_Q^2/^2). \tag{44}$$

Following the procedure used in § 2.2a and using (44) in (17) we obtain

$$\langle | y_N - \sigma_1 y_P^c | \rangle = \frac{1}{\sqrt{2\pi}} \int_0^1 \int_0^1 \cdots \int_0^1 [\{ | (\sigma_2^2 y_Q^2 + k_1 \sigma_1 \sigma_2 E_P y_Q + k_2 \sigma_1^2 E_P^2)^{1/2} - k_3 \sigma_1 E_P^c | + | (\sigma_2^2 y_Q^2 - k_1 \sigma_1 \sigma_2 E_P y_Q + k_2 \sigma_1^2 E_P^2)^{1/2} - k_3 \sigma_1 E_P^c | \} \exp(-y_Q^2/2)]_u \times \frac{du}{(1-u)^2} \prod_{i=1}^{p} (d\theta_i' \, d\phi_i' \, d\psi_i' \, d\theta_i'' \, d\phi_i'' \, d\psi_i''). \tag{45}$$

Similarly we obtain from (44) and (19)

$$\langle | y_N^2 - \sigma_1^2 (y_P^c)^2 | \rangle = \frac{1}{\sqrt{2\pi}} \int_0^1 \int_0^1 \cdots \int_0^1 [\{ | \sigma_2^2 y_Q^2 + k_1 \sigma_1 \sigma_2 E_P y_Q + k_2 \sigma_1^2 (E_P^2 - E_P^{c^2}) | + | \sigma_2^2 y_Q^2 - k_1 \sigma_1 \sigma_2 E_P y_Q + k_2 \sigma_1^2 (E_P^2 - E_P^{c^2}) | \} \times \exp(-y_Q^2/2)]_u \frac{du}{(1-u)^2} \prod_{i=1}^{p} (d\theta_i' \, d\phi_i' \, d\psi_i' \, d\theta_i'' \, d\phi_i'' \, d\psi_i''). \tag{46}$$

Here $\langle y_N \rangle$ will be the same as that obtained in (34) for the related case.

2.3b Non-centrosymmetric case: Here the joint PDF of y_Q, ψ_0', θ_i', ϕ_i', ψ_i', θ_i'', ϕ_i'', ψ_i'' ($i=1$ to p) is

$$\begin{aligned} P(y_Q, \psi_0', \theta_1', \phi_1', \psi_1', \ldots, \theta_p', \phi_p', \psi_p', \theta_1'', \phi_1'', \psi_1'', \ldots, \theta_p'', \phi_p'', \psi_p'') \\ = P(y_Q) P(\psi_0') \prod_{i=1}^{p} [P(\theta_i') P(\phi_i') P(\psi_i') \; P(\theta_i'') P(\phi'') P(\psi_i'')] \\ = 2 y_Q \exp(-y_Q^2). \end{aligned} \tag{47}$$

Making use of (47) in (17) and following the procedure used in § 2.2b we obtain

$$\langle | y_N - \sigma_1 y_P^c | \rangle = 2 \int_0^1 \int_0^1 \int_0^1 \cdots \int_0^1 [| \{\sigma_2^2 y_Q^2 + k_1 \sigma_1 \sigma_2 E_P y_Q \cos(2\pi \psi_0') + k_2 \sigma_1^2 E_P^2\}^{1/2} - k_3 \sigma_1 E_P^c | y_Q \exp(-y_Q^2)]_u \frac{du}{(1-u)^2} d\psi_0' \times \prod_{i=1}^{p} (d\theta_i' \, d\phi_i' \, d\psi_i' \; d\theta_i'' \, d\phi_i'' \, d\psi_i'') \tag{48}$$

Making use of (47) in (19) we can similarly show that

$$\langle |y_N^2 - \sigma_1^2 (y_P^c)^2| \rangle = \langle |\sigma_2^2 y_Q^2 + k_1 \sigma_1 \sigma_2 E_P y_Q \cos(2\pi\psi_0') + k_2 \sigma_1^2 (E_P^2 - E_P^{c2})| \rangle$$

$$= 2 \int_0^1 \int_0^1 \int_0^1 \cdots \int_0^1 [|\sigma_2^2 y_Q^2 + k_1 \sigma_1 \sigma_2 E_P y_Q \cos(2\pi\psi_0')$$

$$+ k_2 \sigma_1^2 (E_P^2 - E_P^{c2})| y_Q \exp(-y_Q^2)] \int_u \frac{du}{(1-u)^2} d\psi_0'$$

$$\times \prod_{i=1}^{p} (d\theta_i' \, d\phi_i' \, d\psi_i' \, d\theta_i'' \, d\phi_i'' \, d\psi''), \tag{49}$$

$\langle y_N \rangle$ for the unrelated case will be the same as that obtained in (41) for the related case.

3. Discussion of the theoretical results

The theoretical values of $\langle | y_N^n - (\sigma_1 y_P^c)^n | \rangle$, $n=1$, 2 and $\langle y_N \rangle$ for the various cases are evaluated by making use of the results derived in § 2. The calculation of these quantities involve the substitution of the appropriate expressions for $E(\theta', \phi', \psi')$ and E^c $(\theta'', \phi'', \psi'')$ corresponding to the various categories and then evaluating the resulting multiple integrals by the Monte Carlo Method (Demidovich and Mason 1973). The expressions for E_P and E_P^c required for this purpose can be readily obtained from table 1 of Foster and Hargreaves (1963b). The values of $\langle | y_N^n - (\sigma_1 y_P^c)^n | \rangle$, $n=1$, 2 and $\langle y_N \rangle$ thus obtained are summarized in tables 1 to 4 for the various cases*. The local values of $R(F)$ and $R(I)$, namely,

$$R(F) = \langle | y_N - \sigma_1 y_P^c | \rangle / \langle y_N \rangle \text{ and } R(I) = \langle | y_N^2 - \sigma_1^2 (y_P^c)^2 | \rangle$$

can be calculated by making use of tables 1 to 4. These are represented in figure 1 for $p=1$ and in figure 2 for $p=2$. From a study of these figures it is seen that in crystals of a given type (*i.e.*, *C* or *NC*) the distinction between the curves for the related and unrelated cases for any given value of p and σ_1^2 is more marked for categories of space groups of higher symmetry. This would imply that for an asymmetric unit of a given complexity the efficiency of the *R*-indices for indicating the correctness of a trial structure is larger for the space groups of the orthorhombic system than for the tricline system.

The numerical results obtained in tables 1 to 4 could be used to test the correctness of the positions of heavy atoms by following procedure described in § 3.2 in Part I.

*These tables can be had from the authors on request. For the present case $\sigma_1^2 = \sigma_{1h}^2$.

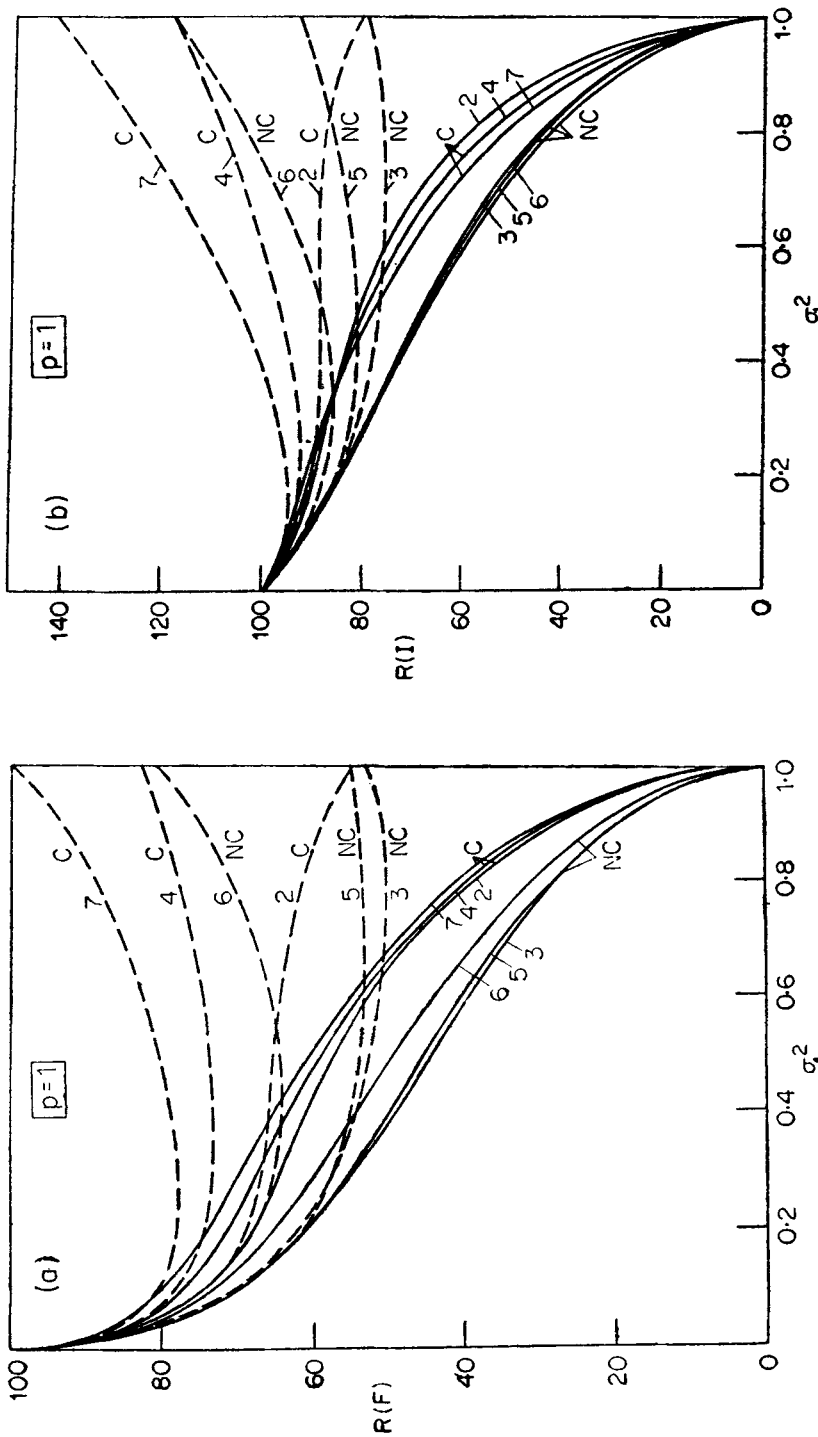

Figure 1. Variation of $R(F)$ and $R(I)$ as a function of the heavy-atom contribution σ_1^2 for the related and unrelated cases of a crystal with one heavy-atom (i.e. p=1) in the asymmetric unit when the heavy-atom part is chosen as the model. The numbers near curves are the space-group category numbers. The solid lines are four the related case and the broken lines are for the unrelated case. The curves pertaining to the centrosymmetric space groups are indicated by C and to the non-centrosymmetric case by NC.

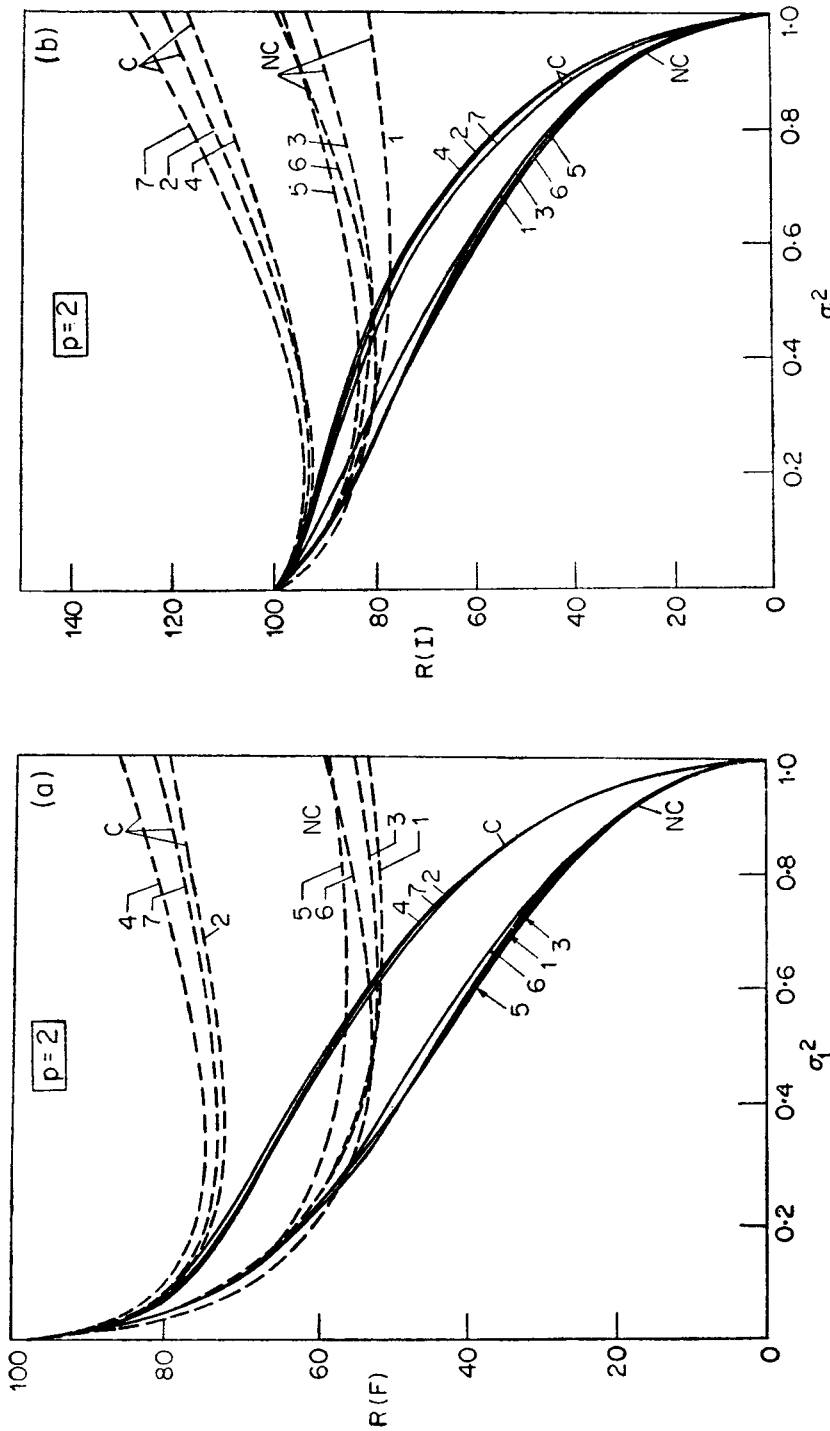

Figure 2. Variation of $R(F)$ and $R(I)$ as a function of the heavy-atom contribution σ_1^2 for the related and unrelated cases of a crystal with two heavy atoms (i.e. $p=2$) in the asymmetric unit when the heavy-atom part is chosen as the model. See the legend to Figure 1 for further details.

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Wilson A J C 1949 *Acta Crystallogr.* **2** 318