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Overall Values of Conventional Discrepancy Indices in the Presence of Random Positional Errors: Crystal with Similar Atoms

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Abstract

The overall values of the conventional discrepancy indices based on structure amplitudes [*i.e.* $R(F)$] and intensities [*i.e.* $R(I)$] are evaluated as functions of the mean positional error $\langle|\Delta\mathbf{r}|\rangle$ and the fractional contribution of the known atoms to the local mean intensity (*i.e.* σ_1^2) for crystals containing a large number of similar atoms. The results are tabulated for both the centrosymmetric and non-centrosymmetric cases.

1. Introduction

The use of discrepancy indices in the various stages of crystal structure analysis is well known. Of the various indices that have been proposed (Srinivasan & Parthasarathy, 1976; hereafter SP, 1976), the conventional discrepancy indices [denoted by $R(F)$ and $R(I)$] are the ones normally computed in crystallographic programs. Wilson (1950) worked out the maximum probable values of $R(F)$ for centrosymmetric and non-centrosymmetric (hereafter *C* and *NC*) cases when the trial structure is of the unrelated *complete* (*i.e.* $\sigma_1^2 = 1$)† type. He also considered the effect of a single badly misplaced atom on $R(F)$ and $R(I)$ when the trial structure is of the complete type (Wilson, 1969). Luzzati (1952) considered the effect of random positional errors on $R(F)$ and obtained $R(F)$ as a function of sin θ for different fixed values of the mean positional error $\langle|\Delta\mathbf{r}|\rangle$. His results, however, apply only for a complete model (*i.e.* $\sigma_1^2 = 1$). Srinivasan, Raghupathy Sarma & Ramachandran (1963) worked out the values of $R(F)$ for two limiting situations, namely, the related (*i.e.* $\langle|\Delta\mathbf{r}|\rangle = 0$) and the unrelated (*i.e.* $\langle|\Delta\mathbf{r}|\rangle$ very large) cases and their results apply to a complete as well as an incomplete type of trial structure (*i.e.* $0 < \sigma_1^2 \leq 1$). Thus the *overall values* of $R(F)$ and $R(I)$ [denoted by $\bar{R}(F)$ and $\bar{R}(I)$, respectively] applicable for the general case of an *imperfectly related* (*i.e.* $\langle|\Delta\mathbf{r}|\rangle$ finite) *incomplete* (*i.e.* $0 < \sigma_1^2 \leq 1$) type are not available. These overall values are important because: (1) crystallographers judge the correctness of trial structures generally from the overall values of the conventional R indices computed with all the observed independent reflections as a single group; (2) the trial structures met with in practice are such that they often account for only part of the structure (*i.e.* $\sigma_1^2 < 1$) and, further, they involve atoms with random positional errors. In the presence of random positional errors the R indices are expected to be monotonically increasing functions of $(\sin\theta)/\lambda$ (hereafter *S*). In this paper we shall therefore obtain the theoretical overall values of $R(F)$ and $R(I)$ as functions of σ_1^2 and $\langle|\Delta\mathbf{r}|\rangle$ for the general case of an imperfectly related incomplete model. The results obtained here are applicable only for crystals containing similar atoms.

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* Contribution No. 485.

† See § 2 for a definition of σ_1^2.

2. Theoretical considerations

Consider a crystal (C or NC) consisting of N atoms in the unit cell of which P are known. Let $\langle|\Delta\mathbf{r}|\rangle$ be the mean positional error of the P atoms of the trial structure. Let $|F_N|$ and $|F_P^c|$ be the structure factor magnitudes of a reflection $\mathbf{H}$ for the crystal and trial structures respectively. Let I_N $(=|F_N|^2)$ and I_P^c $(=|F_P^c|^2)$ be the corresponding intensities. σ_1^2, denoting the fractional contribution to the local mean intensity from the P atoms of the trial structure, is defined by

$$\sigma_1^2=\sigma_P^2/\sigma_N^2, \tag{1}$$

where

$$\sigma_\alpha^2=\sum_{k=1}^{\alpha} f_{\alpha k}^2,\quad \alpha=N \text{ or } P. \tag{2}$$

Since for a structure with equal atoms $\sigma_\alpha^2=\alpha f^2$ ($\alpha=N$ or P), we can write

$$\sigma_1^2=P/N, \tag{3}$$

which is independent of S. The normalized structure amplitudes y_N and y_P^c and the corresponding intensities z_N and z_P^c are defined by

$$\begin{aligned} z_N&=y_N^2=|F_N|^2/\sigma_N^2,\\ z_P^c&=[y_P^c]^2=|F_P^c|^2/\sigma_P^2. \end{aligned} \tag{4}$$

We shall presently derive the theoretical expression required for the evaluation of $\bar{R}(F)$. Since the corresponding expression for $\bar{R}(I)$ can be derived by a similar method we shall give only the final result for this case.

The overall value of the conventional discrepancy index based on structure amplitudes is defined by

$$\bar{R}(F)=\frac{\sum\left||F_N|-|F_P^c|\right|}{\sum|F_N|}, \tag{5}$$

where the summations are over all the independent observed reflections. If the reflections are divided into groups based on the values of S, we can rewrite (5) as

$$\bar{R}(F)=\frac{\sum_j\sum_i\left||F_N|-|F_P^c|\right|_{ij}}{\sum_j\sum_i|F_N|_{ij}}, \tag{6}$$

where the summation over i is carried out over reflections in a given range of S and that over j is carried out over the various ranges of S. Making use of the variables y_N and y_P^c [see (4)], we can rewrite (6) as

$$\bar{R}(F)=\frac{\sum_j\sigma_{Nj}\sum_i|y_N-\sigma_1y_P^c|_{ij}}{\sum_j\sigma_{Nj}\sum_i y_{Nij}}, \tag{7}$$

where σ_{Nj} denotes the value of σ_N in the jth range of S. In writing (7) we have taken the value of σ_N for all reflections in a given range of S to be constant and this would be practically true when the range of S is sufficiently small. If n_j denotes the number of reflections in the jth range of S, we can rewrite (7) as

$$\bar{R}(F)=\frac{\sum_j\sigma_{Nj}n_j\langle|y_N-\sigma_1y_P^c|\rangle_j}{\sum_j\sigma_{Nj}n_j\langle y_N\rangle_j}. \tag{8}$$

For a crystal with similar atoms $\langle y_N\rangle$ can be obtained from the Wilson (1949) distributions as

$$\begin{aligned} \langle y_N\rangle&=(2/\pi)^{1/2}\quad \text{for } C,\\ &=(\pi/2)^{1/2}\quad \text{for } NC, \end{aligned} \tag{9}$$

and thus $\langle y_N\rangle$ is independent of S. For equal atom structures we can take σ_N^2 to be Nf^2. We can therefore rewrite (8) as

$$\bar{R}(F)=\frac{\sum_j f_jn_jR_j(y)}{\sum_j f_jn_j}, \tag{10}$$

where $R_j(y)$ is the value of $R(y)$ in the jth interval of S and $R(y)$ is defined by

$$R(y)=\frac{\langle|y_N-\sigma_1y_P^c|\rangle}{\langle y_N\rangle}. \tag{11}$$

If we make the partitioning of the whole range of S into infinitesimally small intervals, then the summation can be replaced by an integration. The number of reflections in the range between S and $S+\mathrm{d}S$ will be proportional to the volume $4\pi H^2\mathrm{d}H$ of reciprocal space between shells of radii H and $H+\mathrm{d}H$ where $H=2S$. This volume is evidently $32\pi S^2\mathrm{d}S$. If the data consist of reflections in the range $0<S\le S_{\max}$ we can rewrite (10) as

$$\bar{R}(F)=\frac{\int_0^{S_{\max}} f(S)S^2R(y)\,\mathrm{d}S}{\int_0^{S_{\max}} f(S)S^2\,\mathrm{d}S}. \tag{12}$$

From the results of Srinivasan & Ramachandran (1965), $R(y)$ defined in (11) can be interpreted as an R index for a point atom structure taking into account the incompleteness of the trial structure. From (11) it is clear that $R(y)$ can be evaluated from a knowledge of the joint *probability density function* (hereafter pdf) of y_N and y_P^c as

$$R(y)=\frac{1}{\beta}\int_0^\infty\int_0^\infty|y_N-\sigma_1y_P^c|\,P(y_N,y_P^c)\,\mathrm{d}y_N\,\mathrm{d}y_P^c, \tag{13}$$

where β is the value of $\langle y_N \rangle$ as given in (9). The function $P(y_N, y_P^c)$ for the C case is known to be (SP, 1976)

$$P(y_N, y_P^c) = \frac{2}{\pi\sigma_B} \exp\left[-\frac{1}{2\sigma_B^2}(y_N^2 + y_P^{c^2})\right] \times \cosh\left[\frac{\sigma_A y_N y_P^c}{\sigma_B^2}\right], \qquad (14)$$

where

$$\sigma_A = \sigma_1 D, \quad \sigma_B = (1 - \sigma_A^2)^{\frac{1}{2}}, \qquad (15)$$

and

$$D = \exp(-\pi^3 S^2 \langle |\Delta \mathbf{r}| \rangle^2). \qquad (16)$$

The function $P(y_N, y_P^c)$ for the NC case is (SP, 1976)

$$P(y_N, y_P^c) = \frac{4 y_N y_P^c}{\sigma_B^2} \exp\left[-\frac{(y_N^2 + y_P^{c^2})}{\sigma_B^2}\right] I_0\left[\frac{2\sigma_A y_N y_P^c}{\sigma_B^2}\right], \qquad (17)$$

where I_0 is the modified Bessel function of the first kind of order zero. Substituting (14) [or (17) for the NC case] in (13) and carrying out the resulting integrations we can obtain the value of $R(y)$. However, it is not possible to evaluate the integrals in (13) in a closed form. Numerical evaluation of (13) can be facilitated by changing the variables to

$$u = y_N/(1 + y_N), \quad v = y_P^c/(1 + y_P^c). \qquad (18)$$

We can then rewrite (13) as

$$R(y) = \frac{1}{\beta} \int_0^1 \int_0^1 \left| \frac{u}{1-u} - \sigma_1 \frac{v}{1-v} \right| P\left[\frac{u}{1-u}, \frac{v}{1-v}\right] \times \frac{\mathrm{d}u\,\mathrm{d}v}{(1-u)^2(1-v)^2}, \qquad (19)$$

where we have to use (14) or (17) according as the crystal is C or NC, respectively. From (19) and (14) it is clear that $R(y)$ depends on σ_1 and D. For a given trial structure, σ_1^2 is a fixed quantity. Hence, for a fixed value of σ_1^2 the integrals in (19) can be evaluated numerically for different fixed values of D, say $D = 0$, 0·01, 0·02,..., 1·0. From the values of $R(y)$ thus obtained, the overall value $\bar{R}(F)$ for a given trial structure (*i.e.* $\langle |\Delta \mathbf{r}| \rangle$ fixed) can be worked out as explained below.

Table 1. *Value of $\bar{R}(F)$ as a function of σ_1^2 and $\langle |\Delta \mathbf{r}| \rangle$: centrosymmetric case*

σ_1^2 ⟨ Δr ⟩	0.20	0.30	0.40	0.50	0.55	0.60	0.65	0.70	0.75	0.80	0.85	0.90	0.95	1.00
0.00	71.2	66.7	62.6	58.1	55.7	53.1	50.3	47.1	43.7	39.8	35.0	29.2	20.8	0.0
0.01	71.2	66.8	62.6	58.1	55.8	53.2	50.3	47.1	43.8	39.9	35.2	29.4	21.1	1.2
0.02	71.2	66.8	62.6	58.2	55.9	53.3	50.5	47.3	44.0	40.2	35.5	29.8	21.9	4.4
0.03	71.3	66.8	62.7	58.3	56.0	53.5	50.7	47.6	44.4	40.6	36.1	30.6	23.1	8.3
0.04	71.3	66.9	62.8	58.5	56.3	53.8	51.1	48.0	44.9	41.2	36.9	31.6	24.6	12.0
0.05	71.3	67.0	63.0	58.7	56.5	54.1	51.5	48.5	45.5	42.0	37.8	32.9	26.3	15.5
0.06	71.3	67.1	63.2	59.0	56.9	54.5	52.0	49.1	46.2	42.9	38.9	34.3	28.2	18.8
0.07	71.3	67.2	63.4	59.3	57.3	55.0	52.6	49.8	47.0	43.8	40.1	35.8	30.3	22.0
0.08	71.5	67.3	63.6	59.7	57.7	55.5	53.2	50.6	47.9	44.9	41.4	37.4	32.3	25.1
0.09	71.6	67.5	63.8	60.1	58.2	56.1	53.9	51.4	48.9	46.1	42.8	39.1	34.5	28.0
0.10	71.6	67.6	64.1	60.5	58.7	56.7	54.6	52.2	49.9	47.3	44.2	40.8	36.6	30.8
0.11	71.7	67.8	64.4	60.9	59.2	57.3	55.3	53.1	50.9	48.5	45.7	42.5	38.7	33.5
0.12	71.8	68.0	64.7	61.4	59.7	58.0	56.1	54.0	52.0	49.7	47.1	44.2	40.7	36.1
0.13	71.9	68.2	65.0	61.8	60.3	58.6	56.9	54.9	53.1	51.0	48.6	45.9	42.7	38.6
0.14	72.0	68.3	65.3	62.3	60.9	59.3	57.7	55.9	54.1	52.2	50.0	47.6	44.7	41.0
0.15	72.1	68.5	65.6	62.8	61.5	60.0	58.5	56.8	55.2	53.4	51.5	49.3	46.6	43.3
0.16	72.2	68.7	65.9	63.3	62.0	60.7	59.3	57.7	56.3	54.7	52.8	50.9	48.5	45.5
0.17	72.2	68.9	66.3	63.7	62.6	61.4	60.1	58.6	57.3	55.9	54.2	52.4	50.3	47.5
0.18	72.3	69.1	66.6	64.2	63.2	62.0	60.8	59.5	58.3	57.0	55.5	53.9	52.0	49.5
0.19	72.4	69.3	66.9	64.7	63.7	62.7	61.6	60.4	59.3	58.1	56.8	55.4	53.4	51.4
0.20	72.5	69.5	67.2	65.2	64.3	63.3	62.3	61.2	60.3	59.2	58.0	56.7	55.2	53.2
0.22	72.7	69.8	67.8	66.0	65.3	64.5	63.7	62.9	62.1	61.3	60.4	59.3	58.1	56.5
0.24	72.9	70.2	68.4	66.9	66.3	65.7	65.0	64.3	63.8	63.2	62.5	61.7	60.7	59.5
0.26	73.0	70.5	68.9	67.6	67.2	66.7	66.2	65.7	65.3	64.9	64.4	63.8	63.1	62.1
0.28	73.2	70.8	69.4	68.3	68.0	67.7	67.3	66.9	66.7	66.4	66.1	65.7	65.2	64.5
0.30	73.3	71.0	69.8	69.0	68.7	68.5	68.3	68.0	67.9	67.8	67.6	67.4	67.1	66.5
0.35	73.5	71.6	70.7	70.2	70.2	70.2	70.3	70.3	70.4	70.6	70.7	70.8	70.8	70.7
0.40	73.7	72.0	71.3	71.2	71.3	71.5	71.7	71.9	72.3	72.6	72.9	73.2	73.5	73.6
0.45	73.9	72.3	71.8	71.9	72.1	72.4	72.8	73.1	73.6	74.0	74.5	75.0	75.4	75.7
0.50	74.0	72.5	72.1	72.4	72.7	73.1	73.5	73.9	74.5	75.1	75.6	76.2	76.7	77.2
0.55	74.1	72.6	72.4	72.7	73.1	73.6	74.1	74.5	75.2	75.8	76.5	77.1	77.7	78.3
0.60	74.1	72.8	72.6	73.0	73.5	73.9	74.5	75.0	75.7	76.4	77.1	77.8	78.5	79.1

Table 2. *Value of $\bar{R}(I)$ as a function of σ_1^2 and $\langle |\Delta \mathbf{r}| \rangle$: centrosymmetric case*

σ_1^2 ⟨ Δr ⟩	0.20	0.30	0.40	0.50	0.55	0.60	0.65	0.70	0.75	0.80	0.85	0.90	0.95	1.00
0.00	90.9	87.4	83.8	78.3	75.6	72.3	68.5	64.2	59.7	54.3	47.9	39.4	27.7	0.0
0.01	90.9	87.4	83.9	78.4	75.6	72.3	68.6	64.2	59.8	54.4	48.0	39.6	28.0	1.1
0.02	91.0	87.5	83.9	78.5	75.7	72.5	68.8	64.4	60.1	54.7	48.4	40.2	28.8	4.0
0.03	91.0	87.5	84.0	78.6	75.9	72.7	69.0	64.8	60.5	55.3	49.1	41.1	30.2	8.0
0.04	91.0	87.6	84.1	78.8	76.2	73.0	69.4	65.3	61.1	56.0	50.0	42.4	32.1	12.3
0.05	91.0	87.7	84.3	79.1	76.5	73.4	69.9	65.9	61.8	56.9	51.2	43.8	34.2	16.6
0.06	91.1	87.8	84.4	79.4	76.9	73.9	70.5	66.6	62.7	58.0	52.5	45.5	36.5	20.8
0.07	91.1	87.9	84.7	79.7	77.3	74.4	71.2	67.4	63.7	59.2	54.0	47.4	39.0	25.0
0.08	91.2	88.0	84.9	80.1	77.8	75.0	71.9	68.3	64.8	60.5	55.6	49.4	41.7	29.0
0.09	91.2	88.1	85.1	80.5	78.3	75.7	72.7	69.3	65.9	61.9	57.3	51.6	44.4	32.9
0.10	91.3	88.3	85.4	81.0	78.9	76.4	73.6	70.3	67.2	63.4	59.1	53.7	47.1	36.8
0.11	91.3	88.4	85.7	81.5	79.5	77.2	74.5	71.4	68.5	65.0	61.0	56.0	49.9	40.5
0.12	91.4	88.6	86.0	82.0	80.1	77.9	75.4	72.6	69.8	66.6	62.8	58.2	52.6	44.1
0.13	91.5	88.8	86.4	82.6	80.8	78.7	76.4	73.7	71.2	68.2	64.8	60.5	55.4	47.6
0.14	91.6	89.0	86.7	83.1	81.5	79.6	77.4	74.9	72.6	69.8	66.7	62.8	58.1	51.0
0.15	91.6	89.1	87.0	83.7	82.2	80.4	78.4	76.1	74.0	71.5	68.6	65.0	60.7	54.3
0.16	91.7	89.3	87.4	84.2	82.9	81.3	79.4	77.3	75.4	73.1	70.5	67.2	63.3	57.5
0.17	91.8	89.5	87.7	84.8	83.6	82.1	80.4	78.5	76.8	74.7	72.4	69.4	65.9	60.6
0.18	91.9	89.7	88.1	85.4	84.3	83.0	81.4	79.7	78.2	76.3	74.2	71.5	68.4	63.5
0.19	91.9	89.9	88.4	85.9	85.0	83.8	82.4	80.9	79.5	77.9	76.0	73.6	70.7	66.4
0.20	92.0	90.1	88.8	86.5	85.7	84.6	83.4	82.0	80.9	79.4	77.8	75.6	73.1	69.1
0.22	92.2	90.5	89.5	87.6	87.0	86.2	85.3	84.2	83.4	82.3	81.1	79.5	77.5	74.2
0.24	92.3	90.8	90.1	88.6	88.3	87.7	87.1	86.3	85.8	85.1	84.2	83.0	81.5	78.9
0.26	92.5	91.2	90.7	89.6	89.4	89.1	88.8	88.3	88.0	87.6	87.1	86.3	85.2	83.2
0.28	92.6	91.5	91.3	90.5	90.5	90.5	90.3	90.1	90.1	90.0	89.8	89.3	88.6	87.1
0.30	92.7	91.8	91.8	91.4	91.6	91.7	91.7	91.7	92.0	92.1	92.2	92.0	91.7	90.6
0.35	93.0	92.4	93.0	93.2	93.7	94.2	94.7	95.2	96.0	96.6	97.3	97.7	98.1	97.9
0.40	93.2	92.9	93.8	94.5	95.4	96.2	97.1	97.9	99.0	100.1	101.2	102.1	103.0	103.4
0.45	93.3	93.3	94.5	95.6	96.7	97.7	98.9	100.0	101.4	102.8	104.2	105.5	106.7	107.6
0.50	93.5	93.6	95.1	96.5	97.7	98.9	100.3	101.6	103.2	104.8	106.5	108.1	109.6	110.9
0.55	93.6	93.8	95.5	97.1	98.5	99.9	101.4	102.8	104.6	106.5	108.3	110.1	111.9	113.4
0.60	93.6	94.0	95.8	97.6	99.1	100.6	102.2	103.9	105.8	107.8	109.8	111.7	113.7	115.5

Table 3. *Value of $\bar{R}(F)$ as a function of σ_1^2 and $\langle |\Delta \mathbf{r}| \rangle$: non-centrosymmetric case*

σ_1^2 ⟨ Δr ⟩	0.20	0.30	0.40	0.50	0.55	0.60	0.65	0.70	0.75	0.80	0.85	0.90	0.95	1.00
0.00	61.4	54.7	49.2	44.1	41.7	39.2	36.6	33.7	31.0	27.9	24.2	19.9	13.8	0.0
0.01	61.4	54.7	49.3	44.1	41.8	39.3	36.7	33.8	31.0	27.9	24.3	20.0	14.0	0.7
0.02	61.4	54.7	49.3	44.2	41.8	39.3	36.8	33.9	31.2	28.1	24.5	20.3	14.5	2.5
0.03	61.4	54.8	49.3	44.3	41.9	39.5	36.9	34.1	31.4	28.5	24.9	20.9	15.3	4.8
0.04	61.4	54.8	49.4	44.4	42.1	39.7	37.2	34.4	31.8	28.9	25.5	21.6	16.4	7.3
0.05	61.4	54.9	49.5	44.5	42.3	39.9	37.4	34.7	32.2	29.4	26.1	22.4	17.6	9.7
0.06	61.5	54.9	49.6	44.7	42.5	40.2	37.8	35.1	32.7	30.0	26.9	23.4	18.9	12.0
0.07	61.5	55.0	49.7	44.9	42.8	40.5	38.2	35.6	33.3	30.7	27.8	24.5	20.3	14.3
0.08	61.5	55.1	49.9	45.2	43.1	40.9	38.6	36.1	33.9	31.5	28.7	25.6	21.8	16.4
0.09	61.5	55.1	50.1	45.4	43.4	41.2	39.1	36.7	34.6	32.3	29.7	26.8	23.3	18.5
0.10	61.6	55.2	50.2	45.7	43.7	41.7	39.6	37.3	35.3	33.1	30.7	28.0	24.8	20.5
0.11	61.6	55.3	50.4	46.0	44.1	42.1	40.1	37.9	36.0	34.0	31.7	29.2	26.3	22.4
0.12	61.7	55.4	50.6	46.3	44.5	42.5	40.6	38.6	36.8	34.9	32.7	30.5	27.8	24.3
0.13	61.7	55.6	50.8	46.6	44.8	43.0	41.2	39.2	37.5	35.8	33.8	31.7	29.2	26.1
0.14	61.8	55.7	51.0	46.9	45.2	43.5	41.7	39.9	38.3	36.7	34.8	32.9	30.6	27.8
0.15	61.8	55.8	51.2	47.3	45.6	44.0	42.3	40.6	39.1	37.5	35.8	34.1	32.0	29.4
0.16	61.9	55.9	51.4	47.6	46.0	44.4	42.9	41.2	39.8	38.4	36.8	35.2	33.4	31.0
0.17	61.9	56.0	51.6	47.9	46.4	44.9	43.4	41.9	40.6	39.3	37.8	36.4	34.6	32.5
0.18	62.0	56.1	51.8	48.2	46.8	45.4	44.0	42.5	41.3	40.1	38.8	37.4	35.9	34.0
0.19	62.0	56.2	52.0	48.6	47.2	45.8	44.5	43.1	42.0	40.9	39.7	38.5	37.1	35.3
0.20	62.1	56.4	52.2	48.9	47.6	46.3	45.0	43.7	42.7	41.7	40.6	39.5	38.2	36.6
0.22	62.2	56.6	52.6	49.5	48.3	47.1	46.1	44.9	44.1	43.2	42.3	41.4	40.4	39.1
0.24	62.2	56.8	53.0	50.1	49.0	47.9	47.0	46.0	45.3	44.6	43.8	43.1	42.3	41.2
0.26	62.3	57.0	53.3	50.6	49.6	48.7	47.8	47.0	46.4	45.8	45.2	44.7	44.0	43.2
0.28	62.4	57.2	53.7	51.1	50.2	49.4	48.6	47.9	47.4	47.0	46.5	46.1	45.6	44.9
0.30	62.5	57.3	53.9	51.5	50.7	50.0	49.3	48.7	48.1	48.0	47.6	47.3	46.9	46.4
0.35	62.6	57.7	54.5	52.4	51.8	51.2	50.8	50.3	50.1	50.0	49.9	49.8	49.7	49.5
0.40	62.7	57.9	55.0	53.1	52.6	52.1	51.8	51.5	51.5	51.5	51.5	51.6	51.7	51.6
0.45	62.8	58.1	55.3	53.5	53.1	52.8	52.6	52.3	52.4	52.6	52.7	52.9	53.1	53.2
0.50	62.9	58.2	55.5	53.9	53.5	53.2	53.1	52.9	53.1	53.3	53.5	53.8	54.1	54.3
0.55	62.9	58.3	55.7	54.1	53.8	53.6	53.5	53.4	53.6	53.9	54.1	54.5	54.8	55.1
0.60	62.9	58.4	55.9	54.3	54.1	53.8	53.8	53.7	54.0	54.3	54.6	55.0	55.4	55.7

Table 4. *Value of $\bar{R}(I)$ as a function of σ_1^2 and $\langle |\Delta \mathbf{r}| \rangle$: non-centrosymmetric case*

σ_1^2 ⟨ Δr ⟩	0.20	0.30	0.40	0.50	0.55	0.60	0.65	0.70	0.75	0.80	0.85	0.90	0.95	1.00
0.00	84.9	80.8	75.3	66.9	63.9	60.5	56.9	52.6	48.6	44.0	38.3	31.5	21.5	0.0
0.01	84.9	80.8	75.3	67.0	64.0	60.6	56.9	52.6	48.7	44.0	38.4	31.6	21.8	0.7
0.02	84.9	80.8	75.4	67.0	64.0	60.7	57.0	52.8	48.9	44.3	38.7	32.1	22.5	2.8
0.03	84.9	80.8	75.4	67.1	64.2	60.8	57.2	53.0	49.2	44.7	39.2	32.8	23.6	5.6
0.04	84.9	80.8	75.5	67.3	64.4	61.1	57.5	53.4	49.6	45.3	39.9	33.7	25.0	8.9
0.05	84.9	80.9	75.6	67.5	64.6	61.4	57.9	53.9	50.2	45.9	40.8	34.9	26.7	12.3
0.06	84.9	80.9	75.7	67.7	64.9	61.7	58.3	54.4	50.8	46.8	41.8	36.2	28.5	15.7
0.07	85.0	81.0	75.8	67.9	65.2	62.1	58.8	55.0	51.6	47.7	43.0	37.7	30.5	19.0
0.08	85.0	81.1	75.9	68.2	65.5	62.5	59.4	55.7	52.4	48.7	44.2	39.2	32.6	22.2
0.09	85.0	81.1	76.1	68.5	65.9	63.0	60.0	56.4	53.3	49.8	45.6	40.9	34.7	25.3
0.10	85.1	81.2	76.2	68.8	66.3	63.5	60.6	57.2	54.3	50.9	47.0	42.6	36.9	28.3
0.11	85.1	81.3	76.4	69.2	66.8	64.1	61.3	58.0	55.3	52.1	48.4	44.3	39.1	31.3
0.12	85.1	81.4	76.6	69.4	67.2	64.7	62.0	58.9	56.3	53.3	49.9	46.1	41.2	34.2
0.13	85.2	81.5	76.8	69.9	67.7	65.3	62.7	59.8	57.3	54.6	51.4	47.9	43.4	37.0
0.14	85.2	81.6	77.0	70.3	68.2	65.9	63.5	60.7	58.4	55.9	52.9	49.6	45.5	39.7
0.15	85.3	81.7	77.2	70.7	68.7	66.5	64.2	61.6	59.5	57.1	54.4	51.4	47.6	42.3
0.16	85.3	81.8	77.4	71.1	69.2	67.1	65.0	62.5	60.6	58.4	55.8	53.1	49.7	44.8
0.17	85.3	81.9	77.7	71.6	69.7	67.8	65.8	63.4	61.6	59.6	57.3	54.8	51.7	47.2
0.18	85.4	82.0	77.9	72.0	70.3	68.4	66.5	64.3	62.7	60.9	58.7	56.5	53.6	49.6
0.19	85.4	82.1	78.1	72.4	70.8	69.0	67.3	65.2	63.7	62.1	60.1	58.1	55.5	51.8
0.20	85.5	82.2	78.3	72.8	71.3	69.6	68.0	66.1	64.8	63.3	61.5	59.7	57.7	54.0
0.22	85.6	82.4	78.8	73.6	72.3	70.8	69.4	67.8	66.7	65.5	64.1	62.7	60.8	58.0
0.24	85.6	82.5	79.2	74.3	73.2	72.0	70.8	69.4	68.6	67.7	66.6	65.5	63.9	61.7
0.26	85.7	82.8	79.6	75.0	74.1	73.0	72.0	70.9	70.3	69.7	68.8	68.0	66.9	65.1
0.28	85.8	83.0	79.9	75.7	74.9	74.0	73.2	72.3	71.9	71.5	70.9	70.4	69.5	68.2
0.30	85.9	83.2	80.3	76.3	75.6	74.9	74.3	73.5	73.3	73.1	72.8	72.5	71.9	70.9
0.35	86.0	83.6	81.0	77.6	77.2	76.8	76.6	76.2	76.4	76.6	76.7	77.0	77.0	76.7
0.40	86.1	83.8	81.6	78.6	78.5	78.3	78.4	78.3	78.8	79.3	79.8	80.4	80.8	81.0
0.45	86.2	84.1	82.0	79.4	79.4	79.5	79.7	79.9	80.6	81.4	82.1	83.0	83.8	84.4
0.50	86.3	84.3	82.4	80.0	80.2	80.4	80.8	81.1	82.0	83.0	84.0	85.1	86.1	86.9
0.55	86.4	84.4	82.7	80.5	80.8	81.1	81.6	82.1	83.1	84.3	85.4	86.7	87.8	88.9
0.60	86.4	84.5	82.9	80.9	81.3	81.7	82.3	82.9	84.0	85.3	86.5	87.9	89.3	90.5

Since a given trial structure of a crystal is characterized by fixed values of σ_1 and $\langle|\Delta\mathbf{r}|\rangle$, for the evaluation of $\bar{R}(F)$ from (12), σ_1 and $\langle|\Delta\mathbf{r}|\rangle$ are to be treated as fixed quantities. The integral on the right-hand side of (12) is to be evaluated numerically. For this the values of $R(y)$ are needed at discrete values of S. This can in turn be obtained by first calculating the relevant values of D from (16) and then by interpolation.

The overall value of the conventional R index based on intensities is defined by

$$\bar{R}(I)=\frac{\sum|I_N-I_P^c|}{\sum I_N}. \tag{20}$$

By following a procedure similar to that employed for $R(F)$ and using the known result that $\langle y_N^2\rangle=1$ it can be shown that

$$\bar{R}(I)=\frac{\int_0^{S_{\max}} f^2(S)\,S^2R(z)\,\mathrm{d}S}{\int_0^{S_{\max}} f^2(S)\,S^2\,\mathrm{d}S}, \tag{21}$$

where

$$R(z)=\langle|y_N^2-\sigma_1^2y_P^{c^2}|\rangle=\int_0^1\int_0^1\left|\left(\frac{u}{1-u}\right)^2-\sigma_1^2\left(\frac{v}{1-v}\right)^2\right| \times P\left(\frac{u}{1-u},\frac{v}{1-v}\right)\frac{\mathrm{d}u\,\mathrm{d}v}{(1-u)^2(1-v)^2}. \tag{22}$$

The procedure for the evaluation of $\bar{R}(I)$ for any given trial structure is similar to that discussed earlier for $\bar{R}(F)$.

3. Discussion of the theoretical results

The overall values of $R(F)$ and $R(I)$ as functions of σ_1^2 and $\langle|\Delta\mathbf{r}|\rangle$ (in Å) were evaluated by the procedure discussed in § 2 by taking f in (12) and (21) to be the scattering factor of the C atom. $S_{\max}$ in (12) and (21) is taken to be 0·6485 which is the maximum value of $(\sin\theta)/\lambda$ corresponding to Cu $K\alpha$ radiation. The results thus obtained for $\bar{R}(F)$ and $\bar{R}(I)$ are given in Tables 1 and 2 respectively for the centrosymmetric case, and in Tables 3 and 4 for the non-centrosymmetric case. Since a major portion of an organic or a biomolecule is composed of C atoms and since the scattering powers of O and N are comparable with C, these results could be expected to hold good for organic crystal structures. A study of these tables shows that $\bar{R}(I)$ would be preferable to $\bar{R}(F)$ particularly in the conventional refinement stage.

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Thermal Diffuse Scattering for Molecular Crystals: Errors in X-ray Diffraction Intensities and Atomic Parameters

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Abstract

First-order TDS calculations have been made for naphthalene at 100 K to judge the suitability of different models for calculating TDS corrections used in practice. It appears that a long-wave model which takes account of the non-linearity of the frequency dispersion, gives about the same corrections for structural parameters as the lattice dynamical model for rigid body molecules and harmonic vibrations. Long-

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