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Discrepancy Indices for use in Crystal Structure Analysis. III. A Theoretical Comparison of the Normalized Indices

BY S. PARTHASARATHY AND V. PARTHASARATHI

Centre of Advanced Study in Physics, University of Madras, Guindy Campus, Madras-600025, India*

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Theoretical expressions relating six kinds of normalized R indices and the parameter $\sigma_A(=\sigma_1 D)$ are derived and used to make a comparative study of the relative efficiency of these R indices in different crystallographic situations. It is found that the various R indices exhibit different properties in the various stages of structure analysis. In all stages the index based on intensity seems to be preferable to the corresponding index based on structure-factor magnitude. For structure completion and refinement of an incomplete model, the index ${}_B R_1(I)$ seems to be the best. The indices $R_1(I)$ and $R_1^*(I)$ are found to be best for the initial and final refinement stages respectively.

1. Introduction

The use of discrepancy indices (R indices) in crystal-structure analysis in the structure-completion stage as an index of the correctness of the trial model, and in the refinement stage as an index indicating the extent of the refinement process is well known. Different types of R indices such as the conventional R indices (*International Tables for X-ray Crystallography*, 1959), Booth-type R indices (Booth, 1945; Wilson, 1969) and the fractional-type R indices (Srinivasan & Srikrishnan, 1966) have been suggested for this purpose. The following questions naturally arise. Are the different R indices equally powerful at various stages of structure determination? If they are not, which of the R indices are to be recommended for use in the various stages? In the present paper we attempt to answer these questions with reference to crystals and models satisfying the requirements of the basic Wilson distributions (Wilson, 1949). Since the study of Srinivasan & Ramachandran (1965*a*) of such crystals has shown that the conventional R index in the normalized form (see § 2 for the definitions of the normalized indices) has certain desirable properties compared with the unnormalized form, we shall deal with the R indices in their normalized forms. One advantage of dealing with R indices in the normalized form is that they are a function of a single parameter† $\sigma_A(=\sigma_1 D)$, which takes care of the incompleteness of the model *via* the quantity σ_1 and the coordinate errors of the atoms in the model *via* the quantity D simultaneously.

The factors that contribute to the value of any type of R index are (i) random errors in the observed intensities and (ii) deficiencies in the model arising from its incompleteness (*i.e.* non-inclusion of all the atoms in the crystal), errors in the atomic parameters, errors due to non-inclusion of bonding electrons *etc.* Since it is difficult to derive general theoretical expressions for any given type of R index taking into account all the different sources of error, it becomes essential to make the following simplifying assumptions. (i) The observed intensities are assumed to be known with perfect accuracy. (ii) We shall consider only two important types of deficiency of the model, namely incompleteness due to non-inclusion of *all* the atoms, and imperfection due to random coordinate errors. In spite of these simplifying assumptions the conclusions reached regarding the relative efficiency of the different indices at various stages could be expected to hold good in practice.

Since different workers have used different notations for the various R indices (see Table 1), it is essential to use a uniform symbolism to avoid confusion. In § 2 we shall describe the symbolism that has been arrived at during a discussion with Professor R. Srinivasan. In § 3 we shall describe the method of obtaining expressions for the R indices in terms of the parameter σ_A. After a general discussion of the results in § 4, a comparative study of the indices in the structure-completion stage (*i.e.* σ_1^2 increased) and the refinement stage (*i.e.* $\langle|\Delta\mathbf{r}|\rangle$ decreased) is made in § 5. In this paper we shall use C and NC for the terms 'centrosymmetric' and 'non-centrosymmetric' respectively and the abbreviation p.d.f. for 'probability density function'. The other notation and nomenclature follow that in Parthasarathy & Parthasarathi (1972).

2. Notation for the discrepancy indices

Let $|F_N|$ denote the true structure-factor magnitude of reflexion $\mathbf{H}(=hkl)$ for the given crystal structure with N atoms in the unit cell and let $|F_P^c|$ be that calculated for the imperfectly related model structure containing $P(<N)$ atoms. Let σ_1^2 denote the fractional contribution to the local mean intensity from the

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† See Srinivasan & Ramachandran (1966) for the physical significance of the quantity σ_A. See equations (1) and (10) for the definitions of σ_1 and D respectively.

atoms in the model relative to that in the true structure, so that

$$\sigma_1^2=\langle|F_P^c|^2\rangle/\langle|F_N|^2\rangle=\sigma_P^2/\sigma_N^2\,. \quad (1)$$

The discrepancy of the model with respect to the true structure can be measured in terms of either one of the absolute discrepancies Δ_F and Δ_I, namely

$$\Delta_F=\big||F_N|-|F_P^c|\big|,\quad \Delta_I=|I_N-I_P^c| \quad (2)$$

or either one of the fractional discrepancies δ_F and δ_I (Srinivasan & Srikrishnan, 1966),

$$\delta_F=\left|\frac{|F_N|-|F_P^c|}{|F_N| \text{ or } |F_P^c|}\right|,\quad \delta_I=\left|\frac{I_N-I_P^c}{I_N \text{ or } I_P^c}\right| \quad (3)$$

where 'or' in the denominator of (3) denotes that whichever is greater is to be used. We shall define the R indices based on any one of the above discrepancies to be in the unnormalized form. Srinivasan & Ramachandran (1965*b*, hereafter SR) considered a modified form of the conventional R index based on the discrepancy Δ_F', namely

$$\Delta_F'=\big||F_N|-|F_P^c|/\sigma_1\big|\,. \quad (4)$$

An R index based on such a type of discrepancy is said to be in the normalized form, since the variables of interest, namely $|F_N|$ and $|F_P^c|$ satisfy the 'normalization' relation,

$$\langle|F_N|^2\rangle=k\langle|F_P^c|^2\rangle \quad (5)$$

where $k=1/\sigma_1^2$ is the normalization constant needed to make the mean-square values of the structure-factor magnitudes of the structure and model equal. Srinivasan & Srikrishnan (1966) later extended this concept to the fractional type R indices. Thus we say that an R index is in the normalized form if it is based on any one of the following discrepancies:

$$\Delta_F'=\big||F_N|-|F_P^c|/\sigma_1\big|\,,\quad \Delta_I'=|I_N-I_P^c|/\sigma_1^2| \quad (6)$$

$$\delta_F'=\left|\frac{|F_N|-|F_P^c|/\sigma_1}{|F_N| \text{ or } |F_P^c|/\sigma_1}\right|,\quad \delta_I'=\left|\frac{I_N-I_P^c/\sigma_1^2}{I_N \text{ or } I_P^c/\sigma_1^2}\right|. \quad (7)$$

It is possible to define R indices based on the squares of each one of the discrepancies defined in (6) and (7) Since Booth (1945) was the first to suggest an R index based on the squares of the discrepancy of the type $(|F_N|-|F_P^c|)^2$, we shall refer to such indices as Booth-type indices. Making use of the discrepancies in (6) and (7) and the concept of squaring, eight possible types of normalized R indices could be defined and six* of these are given in Table 1 with their symbols.

We have used post-subscript 1 to the R-index symbol to denote that the index is in the normalized form

* Since a study of the other two possible indices ${}_BR_1^*(F)$ and ${}_BR_1^*(I)$ has shown that they are inferior to the six indices dealt with in this paper in several aspects, these two will not be considered.

Table 1. *Definition of different types of normalized R indices and their theoretical expressions for crystals and models satisfying Wilson statistics*

To define the indices in the unnormalized form, set $\sigma_1=1$ in the defining relations occurring in column 2. The results in the other columns do not apply to unnormalized indices. It may however be noted that the final expressions in columns 4 and 5 apply to unnormalized indices corresponding to a complete model since $\sigma_1=1$ for such a situation. Note that for denoting unnormalized indices the post-subscript 1 is to be dropped [*e.g.* ${}_BR(F)$ *etc.*]. The index $R_1(F)$ has been denoted by R_1 in SR and the index $R_1(I)$ by R_Z in PS. Index ${}_BR(F)$ is denoted by R_B in Parthasarathy & Parthasarathi (1972) and by R_2 in Booth (1945). Indices $R(F)$, $R(I)$ and ${}_BR(I)$ are denoted respectively by R, R_1 and R_2 by Wilson (1969). Indices $R_1^*(F)$ and $R_1^*(I)$ have been denoted by R_1' and R_1'' respectively in Srikrishnan & Srinivasan (1968). Note also that v is defined by $v=y_q$ if $y_q\le 1$ and $1/y_q$ if $y_q>1$. Further $\sigma_A^2+\sigma_B^2=1$ and $\sigma_A=\sigma_1 D$. The summation $\sum$ is over the n observed reflexions.

Notation	Definition	Relation to normalized variables	Theoretical expressions: *C* case	Theoretical expressions: *NC* case
$R_1(F)$	$\dfrac{\sum\big\|\|F_N\|-\|F_P^c\|/\sigma_1\big\|}{\sum\|F_N\|}$	$\dfrac{\langle\|y_N-y_P^c\|\rangle}{\langle y_N\rangle}=\dfrac{\langle\|y_d\|\rangle}{\langle y_N\rangle}$	$\sqrt{2(1+\sigma_A)}+\sqrt{2(1-\sigma_A)}-2$	$\dfrac{3\sigma_B^3}{2}\displaystyle\int_0^1 \dfrac{{}_2F_1(-\frac{1}{4},-\frac{3}{4};1;\sigma_A^2x^2)x\,dx}{\sqrt{(1+x)}\ (1-\sigma_A^2x^2)^2}$
${}_BR_1(F)$	$\dfrac{\sum(\|F_N\|-\|F_P^c\|/\sigma_1)^2}{\sum\|F_N\|^2}$	$\langle(y_N-y_P^c)^2\rangle=\langle y_d^2\rangle$ $=2-2\langle y_p\rangle$ $=2-2\langle z_p^{1/2}\rangle$	$2-\dfrac{4}{\pi}[\sigma_B+\sigma_A\sin^{-1}(\sigma_A)]$	$2-2\left[E(\sigma_A)-\dfrac{\sigma_B^2}{2}K(\sigma_A)\right]$
$R_1^*(F)$	$\dfrac{1}{n}\sum\left\|\dfrac{\|F_N\|-\|F_P^c\|/\sigma_1}{\|F_N\| \text{ or } \|F_P^c\|/\sigma_1}\right\|$	$\left\langle\left\|\dfrac{y_N-y_P^c}{y_N \text{ or } y_P^c}\right\|\right\rangle$ $=1-\langle v\rangle$	$1-\dfrac{2}{\pi}[\sigma_B\log_e(2\sigma_B)+\sigma_A\sin^{-1}(\sigma_A)]$	$1-4\sigma_B^2\displaystyle\int_0^1\dfrac{y_q^2(1+y_q^2)\,dy_q}{[(1+y_q^2)^2-4\sigma_A^2y_q^2]^{3/2}}$
$R_1(I)$	$\dfrac{\sum\|I_N-I_P^c/\sigma_1^2\|}{\sum I_N}$	$\langle\|z_N-z_P^c\|\rangle=\langle\|z_d^2\|\rangle$	$\dfrac{4\sigma_B}{\pi}$	σ_B
${}_BR_1(I)$	$\dfrac{\sum(I_N-I_P^c/\sigma_1^2)^2}{\sum I_N^2}$	$\dfrac{\langle(z_N-z_P^c)^2\rangle}{\langle z_P^2\rangle}=\dfrac{\langle z_d^2\rangle}{\langle z_N^2\rangle}$	$\dfrac{4\sigma_B^2}{3}$	σ_B^2
$R_1^*(I)$	$\dfrac{1}{n}\sum\left\|\dfrac{I_N-I_P^c/\sigma_1^2}{I_N \text{ or } I_P^c/\sigma_1^2}\right\|$	$\left\langle\left\|\dfrac{z_N-z_P^c}{z_N \text{ or } z_P^c}\right\|\right\rangle$ $=1-\langle v^2\rangle$	$2\sigma_B^2-\dfrac{4\sigma_B}{\pi}\left[1+\dfrac{\sigma_A}{2}\log_e\left(\dfrac{1-\sigma_A}{1+\sigma_A}\right)\right]$	$2\sigma_B\left[1-\sigma_B\log_e\left(\dfrac{1+\sigma_B}{\sigma_B}\right)\right]$

(*e.g.* R_1). The fractional type index is denoted by using an asterisk as a post-superscript to the R-index symbol (*e.g.* R^*). The Booth-type indices are denoted by B pre-subscript to the R-index symbol (*e.g.* ${}_BR$). The R index could be defined with either the structure amplitude $|F|$ or the intensity I and this is indicated by either F or I in parentheses [*e.g.* $R(F)$ or $R(I)$].

3. Theoretical expressions for the R indices in terms of σ_A

Expressions for the R indices in terms of the parameter $\sigma_A(=\sigma_1 D)$ are useful since they could be used to study, from a theoretical point of view, the influence of both structure completion and structure refinement on the R indices independently. For obtaining such a relationship, it is found to be convenient to relate first the R indices to the normalized structure amplitudes $y_N(=|F_N|/\sigma_N)$ and $y_P^c(=|F_P^c|/\sigma_P)$ and the normalized intensities $z_N(=y_N^2)$ and $z_P^c(=y_P^{c2})$. These relations are also summarized in Table 1. Making use of these relationships, the various R indices are also directly expressed in terms of the difference, product and quotient variables† y_d, y_p and y_q (or z_d, z_p and z_q), namely

$$y_d=y_N-y_P^c\,,\quad y_p=y_Ny_P^c\,,\quad y_q=y_N/y_P^c\,. \tag{8}$$

$$z_d=z_N-z_P^c\,,\quad z_p=z_Nz_P^c=y_p^2\,,\quad z_q=(z_N/z_P^c)=y_q^2\,. \tag{9}$$

The p.d.f. of the latter variables obtained in the earlier papers (SR and PS) could therefore be used to obtain the relation of the R indices to σ_A.

The values of $R_1(F)$ as a function of σ_A were obtained in SR from the p.d.f. of y_d. An explicit expression has, however, been derived only for the C case (SR). Luzzati (1952) has evaluated $R(F)$ for C and NC cases and his result, which is applicable only in the refinement stage (*i.e.*, $\sigma_1^2=1$), is covered by the more general treatment in SR. Chandrasekharan & Srinivasan (1969) have obtained graphs for $R_1(F)$ as a function of $\langle|\Delta\mathbf{r}|\rangle$ for different values of σ_1^2 and their results are valid for the two-dimensional case. Explicit expressions for $R_1(I)$ in terms of σ_A for both C and NC cases have been derived in PS. Srikrishnan & Srinivasan (1968) have derived by numerical methods the values of $R_1^*(F)$ and $R_1^*(I)$ as a function of σ_A for both C and NC cases, though no explicit expressions are available. They have also obtained graphs of $R_1^*(F)$ *vs.* $\langle|\Delta\mathbf{r}|\rangle$ and $R_1^*(I)$ *vs.* $\langle|\Delta\mathbf{r}|\rangle$ for different values of σ_1^2 and these curves are applicable for the two-dimensional case only. Parthasarathy & Parthasarathi (1972) have derived the expressions for the unnormalized indices ${}_BR(I)$ and ${}_BR(F)$ but not for the normalized ones ${}_BR_1(I)$ and ${}_BR_1(F)$. Thus, since explicit expressions for the normalized R indices as a function of σ_A are available only for $R_1(F)$ for the C case and $R_1(I)$ for the C and NC cases, the expressions for the other cases are derived in the Appendix. The final expressions thus derived are summarized in Table 1.

4. Discussion of the theoretical results

From Table 1 it is clear that all the R indices† depend on the quantities σ_1 and D. For an incomplete model containing only P out of N atoms of the structure, the quantity σ_1 [see (1)] will be less than unity and this is generally the case during the initial stages of structure analysis. For structures containing atoms of similar scattering power (*e.g.* most organic crystals) σ_1 will be given by $\sqrt{P/N}$, which is practically independent of $(\sin\theta)/\lambda$. During the structure-completion stage as more and more atoms are added to the model, $P\to N$ so that $\sigma_1\to 1$. Thus, for the refinement stage, when usually all the non-hydrogen atoms have been located (with random positional errors) we can set $\sigma_1\simeq 1$ and such a model is referred to as an imperfectly related *complete* model (Parthasarathy & Parthasarathi, 1972). During refinement of a complete model, the normalized index of a given type therefore becomes identical with the corresponding unnormalized index.

The dependence of the R indices on the coordinate errors of the model is *via* the parameter D, which for the three-dimensional case is given by (Luzzati, 1952)

$$D=\exp\left[-\frac{\pi^3}{4}\langle|\Delta\mathbf{r}|\rangle^2H^2\right] \tag{10}$$

where $H=(2\sin\theta)/\lambda$ $(=2s$, say). As the model is refined, *i.e.* as $\langle|\Delta\mathbf{r}|\rangle$ decreases, $D\to 1$. Thus while $D=0$ for a completely wrong model, $D=1$ for a completely correct one.

From the above discussion it is clear that the R indices are functions of the three quantities σ_1, $\langle|\Delta\mathbf{r}|\rangle$ and $(\sin\theta)/\lambda$. Thus to obtain the value of $\langle|\Delta\mathbf{r}|\rangle$ for a model structure of any given crystal it is necessary to take into account the variation of R index with $(\sin\theta)/\lambda$. For this the following two procedures could be adopted (i) The experimental values of a given type of R index are first calculated by dividing reflexions into narrow regions of $(\sin\theta)/\lambda$. From a comparative study of the plot of the experimental R values *vs.* $(\sin\theta)/\lambda$ with the theoretical curves obtained for different $\langle|\Delta\mathbf{r}|\rangle$ values, the value of $\langle|\Delta\mathbf{r}|\rangle$ for the model could be deduced (Luzzati, 1952). (ii) A more convenient method however is to obtain $\langle|\Delta\mathbf{r}|\rangle$ directly from the overall value of the R index calculated from all the observed reflexions as a single group (see Srikrishnan & Srinivasan, 1968). If $H_{\max}$ $(=2s_{\max})$ denotes the maximum value of the reciprocal-lattice vector for the reflexions included

† These variables have been denoted by different symbols in the earlier papers (SR; Parthasarathy & Srinivasan, 1967, hereafter PS). The present notation is the one arrived at during a discussion with Professor R. Srinivasan. Such a change has been necessary to unify symbols used in different papers.

† In the rest of our discussion the general term R index is used to denote any one of the R indices considered in this paper. However, when the discussion is specific with respect to a given type of R index, the exact symbol is used.

in the calculation of the R index, then the overall (or weighted) value of the R index, denoted by $\bar{R}$, will be given by

$$\bar{R}=\frac{3}{H_{\max}^3}\int_0^{H_{\max}} R(\sigma_1^2,\langle|\Delta\mathbf{r}|\rangle,H)H^2\mathrm{d}H \qquad (11)$$

$$=\frac{3}{s_{\max}^3}\int_0^{s_{\max}} R(\sigma_1^2,\langle|\Delta\mathbf{r}|\rangle,s)s^2\mathrm{d}s \qquad (12)$$

where the weight for a given H is taken to be the fractional number of reciprocal-lattice points in a thin shell of radius H and thickness $\mathrm{d}H$. In all cases except ${}_BR_1(I)$ the values of $\bar{R}$ for various values of σ_1^2 and $\langle|\Delta\mathbf{r}|\rangle$ are to be obtained by numerical integration of (12). Since at any stage of a crystal-structure analysis the values† of $\bar{R}$ and σ_1 will be known, it is always possible to arrive at the possible inaccuracies ($\langle|\Delta\mathbf{r}|\rangle$) in the coordinates of the atoms in the model.

Since it is possible to obtain an explicit expression for ${}_B\bar{R}_1(I)$, we shall derive it presently. For a NC crystal and model satisfying the requirements of Wilson's acentric distribution, $\sigma_1^2(=P/N)$ will be independent of H, so that from Table 1 we see that

$${}_B\bar{R}_1(I)=\langle\sigma_B^2\rangle_H=1-\sigma_1^2\langle D^2\rangle_H\,. \qquad (13)$$

Making use of (10) and (12) in (13) we obtain

$${}_B\bar{R}_1(I)=1-\frac{3\sigma_1^2}{s_{\max}^3}\int_0^{s_{\max}}\exp\left[-2\pi^3\langle|\Delta\mathbf{r}|\rangle^2s^2\right]s^2\mathrm{d}s \qquad (14)$$

which on simplification yields

$${}_B\bar{R}_1(I)=1-\frac{3\sigma_1^2}{2s_{\max}^3(2\pi^3)^{3/2}\langle|\Delta\mathbf{r}|\rangle^3}\times\left[\frac{\sqrt{\pi}}{2}\,\mathrm{erf}\,(\sqrt{2\pi^3}\langle|\Delta\mathbf{r}|\rangle s_{\max})-\sqrt{2\pi^3}\langle|\Delta\mathbf{r}|\rangle s_{\max}\times\exp\{-2\pi^3\langle|\Delta\mathbf{r}|\rangle^2s_{\max}^2\}\right]. \qquad (15)$$

Since for the C case ${}_BR_1(I)=4\sigma_B^2/3$ the expression for ${}_B\bar{R}_1(I)$ will be $\frac{4}{3}$ times the quantity on the right-hand side of (15).

5. Comparative study of the normalized R indices

We shall presently make a comparative study of the relative efficiency of the various normalized R indices for the following three situations: (i) structure completion stage; (ii) refinement of an incomplete model; and (iii) refinement of a complete model. To facilitate such a study the theoretical curves of the overall R indices‡ for the following three situations have been obtained*:(i) $\bar{R}$ *vs* σ_1^2 when $\langle|\Delta\mathbf{r}|\rangle=0{\cdot}1$ Å; (ii) $\bar{R}$ *vs* $\langle|\Delta\mathbf{r}|\rangle$ when $\sigma_1^2=0{\cdot}5$; and (iii) $\bar{R}$ *vs* $\langle|\Delta\mathbf{r}|\rangle$ when $\sigma_1^2=1$. It may be noted here that for situation (i) we have chosen a value of 0·1 Å for $\langle|\Delta\mathbf{r}|\rangle$, since during the structure-completion stage the positions of the atoms in the model suffer coordinate errors with $\langle|\Delta\mathbf{r}|\rangle\simeq0{\cdot}1$ Å, and that for situation (ii) we have set $\sigma_1^2=0{\cdot}5$, since it corresponds to a typical model containing 50% of the atoms of the true structure. It is obvious that situation (iii) corresponds to the usual stage of refinement of a complete model. The curves obtained for these three situations are shown in Fig. 1(*a*)–(*c*) for the C case and in Fig. 1(*d*)–(*f*) for the NC case.

In order to make a comparative study of the various indices under different situations, we have to adopt a criterion for their relative efficiency. Since for a given situation the R index which decreases systematically as the relevant parameter is varied in the proper direction (*e.g.* for structure completion σ_1^2 is to be increased and for refinement $\langle|\Delta\mathbf{r}|\rangle$ is to be decreased) is to be preferred, we shall adopt the criterion that the R index for which the curve has the largest slope (as the relevant parameter is varied) is the best for use under that situation. If two indices appear to be equally good from this criterion then we shall adopt the additional criterion that the index which shows a greater fractional fall† is to be preferred. A study of Fig. 1 with this in view reveals the general feature that, for any given type of R index, the one based on I is preferable to the one based on F, during any stage of structure analysis. The following two points regarding the values of the R indices may also be noted. (i) For any given situation, the value of an R index based on intensity is always greater than that of the corresponding type of R index based on structure-factor magnitudes, and (ii) the value of any given R index is always larger‡ for the C than for the NC case, provided the aspects for the two cases such as the value of σ_1^2, $\langle|\Delta\mathbf{r}|\rangle$ and $s_{\max}$ are the same.

(i) *Structure-completion stage*

The relevant curves are shown in Fig. 1(*a*) for the C case and those in Fig. 1(*d*) for the NC case. From these curves it is seen that, of all the indices, the index ${}_BR_1(I)$ has the largest slope and hence is the best during this stage of structure analysis. It is also seen that both the

† The quantity σ_1 could be evaluated at any stage of structure determination from a knowledge of the known contents of the unit cell of the structure and the model.

‡ From (12) and (15) it is seen that the evaluation of $\bar{R}$ requires the value of λ. The curves in Fig. 1 are for Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å).

* Relationship with the quantity σ_1^2 is used in Fig. 1 instead of σ_1 since only the former is a direct measure of the fractional contribution to the local mean intensity. Also for crystals with similar atoms, $\sigma_1^2(=P/N)$ is a measure of the fractional number of atoms in the model structure.

† If R_{I} and R_{II} represent the values of an R index for two subsequent situations, then we define the fractional fall in the R index by $|R_{\mathrm{II}}-R_{\mathrm{I}}|/\frac{1}{2}[R_{\mathrm{II}}+R_{\mathrm{I}}]$.

‡ A recent study of the ${}_BR_1(I)$ index for structures with heavy atoms has shown that this R index could have a larger value for the NC case than for the C case under certain circumstances (for details see the last paragraph in Parthasarathi & Parthasarathy, 1975).

Booth-type indices show a systematic and *linear* fall with increasing value of σ_1^2. Though the index $R_1(I)$ is seen to have a *slightly* larger slope than ${}_BR_1(F)$, the latter shows a much greater fractional decrease for a given increase of σ_1^2. Thus, though from the criterion of slope alone, $R_1(I)$ has a slight advantage over ${}_BR_1(F)$, the latter may be preferred owing to its larger fractional decrease with increasing value of σ_1^2. It is inter-

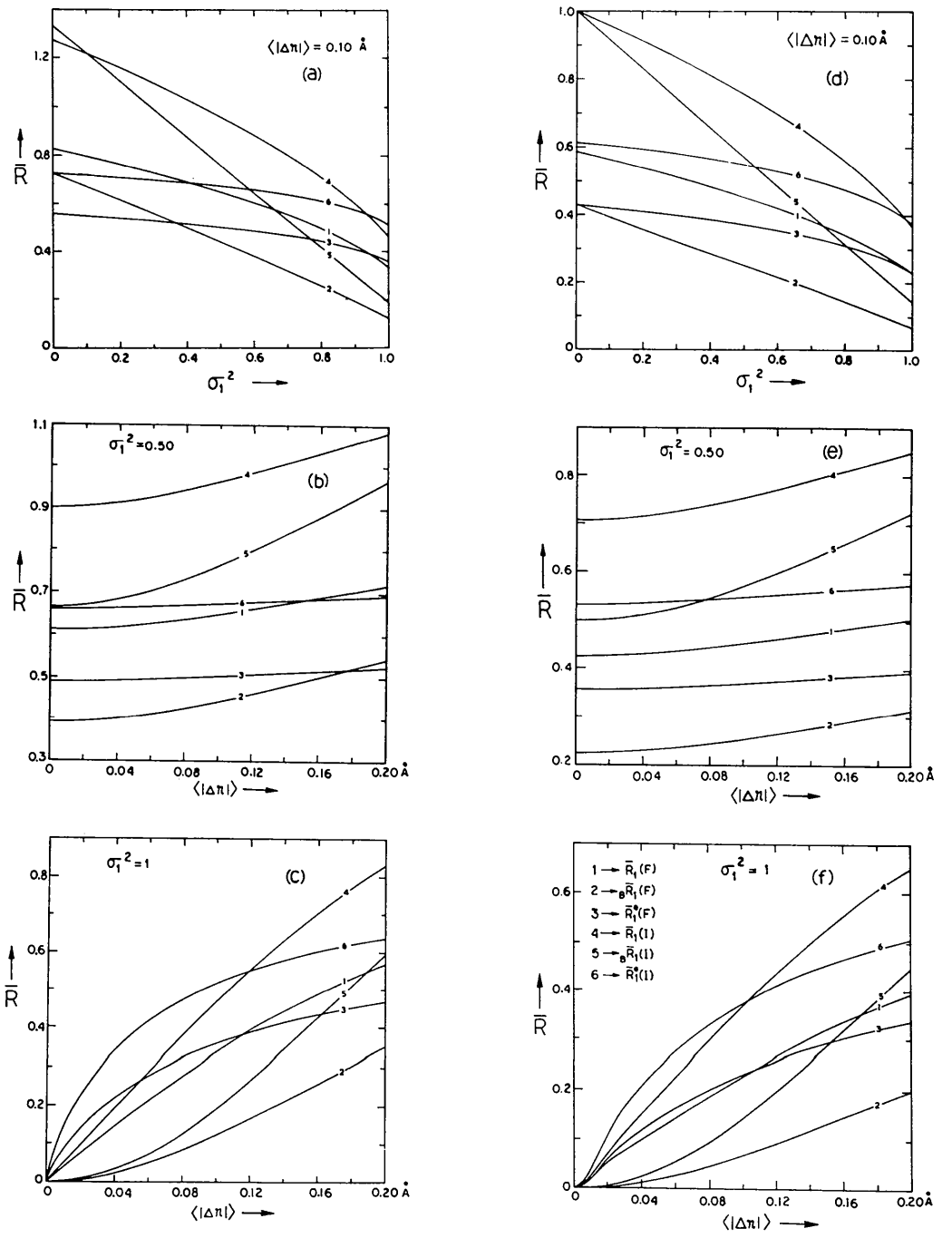

Fig. 1. Representation of the overall values of the different R indices as functions of σ_1^2 and $\langle|\Delta\mathbf{r}|\rangle$ respectively. Curves in (*a*) (*b*) and (*c*) correspond to the *C* case while those in (*d*), (*e*) and (*f*) correspond to the *NC* case. Curves in (*a*) and (*d*) show $\bar{R}$ *vs.* σ_1^2 when $\langle|\Delta\mathbf{r}|\rangle = 0{\cdot}1$ Å (structure-completion stage). Curves in (*b*) and (*e*) show $\bar{R}$ *vs.* $\langle|\Delta\mathbf{r}|\rangle$ when $\sigma_1^2 = 0{\cdot}5$ (refinement of an incomplete model) while curves in (*c*) and (*f*) show $\bar{R}$ *vs.* $\langle|\Delta\mathbf{r}|\rangle$ for $\sigma_1^2 = 1{\cdot}0$ (refinement of a complete imperfect model.) The numbers 1 to 6 against the various curves are used to denote the R indices such that $1 = \bar{R}_1\,(F)$, $2 = {}_B\bar{R}_1\,(F)$, $3 = \bar{R}_1^*(F)$, $4 = \bar{R}_1\,(I)$, $5 = {}_B\bar{R}_1\,(I)$ and $6 = \bar{R}_1^*\,(I)$.

esting to see that the conventional index $R_1(F)$ is inferior to the index ${}_BR_1(F)$. It is also obvious that fractional-type indices $R_1^*(I)$ and $R_1^*(F)$ are the least suitable during this stage.

(ii) *Refinement of an incomplete model*

The relevant curves are shown in Fig. 1(*b*) for the *C* case and in Fig. 1(*e*) for the *NC* case. A study of these figures shows that while $R_1^*(I)$ and $R_1^*(F)$ are practically insensitive to variation of $\langle|\Delta\mathbf{r}|\rangle$, the others show some decrease with decreasing value of $\langle|\Delta\mathbf{r}|\rangle$ in the region $\langle|\Delta\mathbf{r}|\rangle > 0{\cdot}06$ Å. The rate of decrease, however, is most marked for the index ${}_BR_1(I)$. Thus during the refinement of an incomplete model also the index ${}_BR_1(I)$ seems to be the best. However, it is seen that all the *R* indices become insensitive in the region $\langle|\Delta\mathbf{r}|\rangle < 0{\cdot}06$ Å. Thus it appears that refinement of an incomplete model to high order could not be judged by the use of *R* indices. In this connexion it is relevant to note that the study of phase-angle distribution has also shown that the refinement of an incomplete model could not be rapid (Parthasarathy & Parthasarathi, 1974).

(iii) *Refinement of a complete model*

It may be noted that for such a model, since $\sigma_1^2 = 1$, the normalized *R* index of any type becomes identical with the corresponding unnormalized form. The relevant curves are those in Fig. 1(*c*) for the *C* case and in Fig. 1(*f*) for the *NC* case. It is seen that for $0{\cdot}05 \leq \langle|\Delta\mathbf{r}|\rangle \leq 0{\cdot}13$ Å† (which we shall refer to as the initial refinement stage for convenience) the index $R_1(I)$ has the greatest slope and hence is the best. It may be noted here that for $\langle|\Delta\mathbf{r}|\rangle > 0{\cdot}13$ Å the index ${}_BR_1(I)$ has a larger slope and a greater fractional fall with decreasing $\langle|\Delta\mathbf{r}|\rangle$ than $R_1(I)$ and hence is to be preferred. It is also interesting to note that from the point of view of both the slope and fractional fall the index ${}_BR_1(I)$ is better than the conventional *R* index $R_1(F)$ for $\langle|\Delta\mathbf{r}|\rangle > 0{\cdot}08$ Å. In the range $\langle|\Delta\mathbf{r}|\rangle < 0{\cdot}05$ Å (called the final refinement stage for convenience), $R_1^*(I)$ has the greatest rate of fall with decreasing value of $\langle|\Delta\mathbf{r}|\rangle$ and hence seems to be preferable.

To conclude we may state the following. (i) The properties of the various indices are found to be different in the structure-completion and refinement stages. In all stages of structure analysis the index based on intensity seems to be preferable to the corresponding index based on structure-factor magnitude. In the early stages of structure analysis (*i.e.* structure completion or refinement of an incomplete model) the index ${}_BR_1(I)$ seems to be the best. For the initial refinement stage (*i.e.* $\langle|\Delta\mathbf{r}|\rangle > 0{\cdot}05$ Å) the index $R_1(I)$ seems to be the best while for the final refinement stage (*i.e.* $\langle|\Delta\mathbf{r}|\rangle < 0{\cdot}05$ Å) the index $R_1^*(I)$ appears to be the best.

† These values, 0·05 and 0·13 Å, were arrived at from a study of the actual values of the slopes of these curves computed by numerical methods.

Since the above study has shown that the Booth-type index based on intensity is the best during the structure completion stage it is useful to obtain expressions for this index for structures and models of any complexity. It will also be useful to make a comparative study on the relative efficiency of the normalized and unnormalized forms of this index for different types of structures during the structure completion stage. Such a study has been undertaken and the results will be reported in a separate paper.

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APPENDIX

Derivation of expressions for the *R* indices as a function of σ_A

(i) $R_1(F)$*and* $R_1(I)$ *indices*

Explicit expressions for $R_1(F)$ for the *C* case and $R_1(I)$ for both *C* and *NC* cases are available (see SR and PS). A convenient expression for $R_1(F)$ for the *NC* case can be derived as follows. From equation (24) of PS the joint p.d.f. of y_N and y_P^c for the *NC* case can be shown to be

$$P(y_N, y_P^c) = \frac{4y_N y_P^c}{\sigma_B^2} \exp\{-(y_N^2 + y_P^{c2})/\sigma_B^2\} \times I_o[2\sigma_A y_N y_P^c/\sigma_B^2]\,. \quad \text{(A-1)}$$

Following the variable transformation method employed in PS we obtain the joint p.d.f. of $y_s(=y_N+y_P^c)$ and $|y_d|(=|y_N-y_P^c|)$ to be

$$P(y_s, |y_d|) = \frac{(y_s^2 - y_d^2)}{\sigma_B^2} I_o[\sigma_A(y_s^2 - y_d^2)/2\sigma_B^2] \times \exp[-(y_s^2 + y_d^2)/2\sigma_B^2],\ y_d \leq y_s < \infty\,,\quad 0 \leq y_d < \infty \quad \text{(A-2)}$$

so that

$$P(|y_d|) = \int_{y_d}^{\infty} P(y_s, |y_d|)\mathrm{d}y_d \quad \text{(A-3)}$$

$$= \frac{|y_d|^3}{\sigma_B^2} \int_0^1 I_o\left[\frac{\sigma_A y_d^2(1-t^2)}{2\sigma_B^2 t^2}\right] \times \exp\left[-\frac{y_d^2(1+t^2)}{2\sigma_B^2 t^2}\right] \frac{(1-t^2)}{t^4}\,\mathrm{d}t\,. \quad \text{(A-4)}$$

The expectation value of $|y_d|$ will therefore be given by

$$\langle|y_d|\rangle = \int_0^{\infty} |y_d| P(|y_d|)\mathrm{d}y_d\,. \quad \text{(A-5)}$$

Substituting (A-4) in (A-5), interchanging the order of integrations and carrying out the integration with

respect to y_d by using equation (23) on p. 330 of Erdelyi (1954) and then using equation (vii) on p. 11 of Sneddon (1961), we obtain

$$\langle|y_d|\rangle=\frac{3\sqrt{\pi}}{4}\sigma_B^3\int_0^1\frac{{}_2F_1(-\frac{1}{4},-\frac{3}{4};1;\sigma_A^2x^2)x\mathrm{d}x}{\sqrt{(1+x)}(1-\sigma_A^2x^2)^2}. \tag{A-6}$$

Since $R_1(F)=\langle|y_d|\rangle/\langle y_N\rangle$ and $\langle y_N\rangle=\sqrt{\pi}/2$ for the *NC* case, we obtain from (A-6)

$$R_1(F)=\frac{3\sigma_B^3}{2}\int_0^1\frac{{}_2F_1(-\frac{1}{4},-\frac{3}{4};1;\sigma_A^2x^2)x\mathrm{d}x}{\sqrt{(1+x)}\,(1-\sigma_A^2x^2)^2} \tag{A-7}$$

which is to be evaluated by a numerical procedure. The calculation in SR for this case involves a double integral.

(ii) ${}_BR_1(F)$ *and* ${}_BR_1(I)$ *indices*

From Table 1 it is seen that

$${}_BR_1(F)=2-2\langle z_p^{1/2}\rangle. \tag{A-8}$$

Putting $n=\frac{1}{2}$ in equation (A-13) of PS we have for the *C* case

$$\langle z_p^{1/2}\rangle=\frac{2}{\pi}{}_2F_1(-\tfrac{1}{2},-\tfrac{1}{2};\tfrac{1}{2};\sigma_A^2), \tag{A-9}$$

Making use of equation 3(v) on p. 43 and equations 1(i) and 1(vi) on p. 42 of Sneddon (1961) in (A-9) we obtain

$$\langle z_p^{1/2}\rangle=\frac{2}{\pi}[\sigma_B+\sigma_A\sin^{-1}(\sigma_A)]. \tag{A-10}$$

From (A-8) and (A-10) it is seen that

$${}_BR_1(F)=2-\frac{4}{\pi}[\sigma_B+\sigma_A\sin^{-1}(\sigma_A)]. \tag{A-11}$$

Putting $n=\frac{1}{2}$ in equation (A-20) of PS we obtain for the NC case

$$\langle z_p^{1/2}\rangle=\frac{\pi}{4}{}_2F_1(-\tfrac{1}{2},-\tfrac{1}{2};1;\sigma_A^2). \tag{A-12}$$

Making use of equation 3(ii) on p. 43 and equations 1(viii) and 1(ix) on p. 42 of Sneddon (1961) it can be shown that

$${}_2F_1(-\tfrac{1}{2},-\tfrac{1}{2};1;\sigma_A^2)=\frac{4}{\pi}\left[E(\sigma_A)-\frac{\sigma_B^2}{2}K(\sigma_A)\right]. \tag{A-13}$$

Making use of (A-12) and (A-13) in (A-8) we obtain

$${}_BR_1(F)=2-2\left[E(\sigma_A)-\frac{\sigma_B^2}{2}K(\sigma_A)\right]. \tag{A-14}$$

We know that (see Table 1)

$${}_BR_1(I)=\langle z_d^2\rangle/\langle z_N^2\rangle. \tag{A-15}$$

Since for the *C* case $\langle z_d^2\rangle=4\sigma_B^2$ [see equation (40-*b*) of PS] and $\langle z_N^2\rangle=3$ and for the *NC* case $\langle z_d^2\rangle=2\sigma_B^2$ [see equation (43-*b*) of PS] and $\langle z_N^2\rangle=2$, we obtain from (A-15)

$${}_BR_1(I)=\tfrac{4}{3}\sigma_B^2 \quad \text{for } C, \tag{A-16}$$

$$=\sigma_B^2 \quad \text{for } NC. \tag{A-17}$$

(iii) $R_1^*(F)$ *and* $R_1^*(I)$ *indices*

We know that (see Table 1)

$$R_1^*(F)=1-\langle v\rangle \tag{A-18}$$

where

$$\langle v\rangle=\int_0^1 y_qP(y_q)\mathrm{d}y_q+\int_1^\infty P(y_q)\mathrm{d}y_q/y_q. \tag{A-19}$$

Since y_q and $1/y_q$ obey the same probability distribution law (Srinivasan, Subramanian & Ramachandran, 1964; SR) the two integrals in (A-19) have equal values. Equation (A-18) can therefore be rewritten as

$$R_1^*(F)=1-2\int_0^1 y_qP(y_q)\mathrm{d}y_q. \tag{A-20}$$

From Table 1(*b*) of SR we obtain for the *C* case:

$$P(y_q)=\frac{2\sigma_B}{\pi}\frac{(1+y_q^2)}{[(1+y_q^2)^2-4\sigma_A^2y_q^2]}. \tag{A-21}$$

Substituting (A-21) in (A-20) we can rewrite it as

$$R_1^*(F)=1-\frac{2\sigma_B}{\pi}\left[\int_0^1\frac{y_q\mathrm{d}y_q}{(y_q^2+2\sigma_Ay_q+1)}+\int_0^1\frac{y_q\mathrm{d}y_q}{(y_q^2-2\sigma_Ay_q+1)}\right]. \tag{A-22}$$

Making use of equations (70) and (75) of Peirce & Foster (1966) in (A-22) and simplifying the resulting expression by using equations (672) and (669) of Peirce & Foster (1966), we obtain

$$R_1^*(F)=1-\frac{2}{\pi}[\sigma_B\log_e(2\sigma_B)+\sigma_A\sin^{-1}(\sigma_A)]. \tag{A-23}$$

For the *NC* case, $R_1^*(F)$ is to be evaluated numerically by using the result given in Table 1 (see Srikrishnan & Srinivasan, 1968).

We know that (see Table 1)

$$R_1^*(I)=1-\langle v^2\rangle \tag{A-24}$$

where

$$\langle v^2\rangle=\int_0^1 y_q^2P(y_q)\mathrm{d}y_q+\int_1^\infty P(y_q)\mathrm{d}y_q/y_q^2=2\int_0^1 y_q^2P(y_q)\mathrm{d}y_q. \tag{A-25}$$

It may be noted that to obtain the above result we have used the property that y_q and $1/y_q$ obey the same probability distribution as before. Making use of (A-21) and (A-25) in (A-24) we obtain for the *C* case

$$R_1^*(I)=1-\frac{4\sigma_B}{\pi}\int_0^1\frac{y_q^2(1+y_q^2)\mathrm{d}y_q}{[(1+y_q^2)^2-4\sigma_A^2y_q^2]}$$
$$=1-\frac{4\sigma_B}{\pi}\int_0^1\left[1+\sigma_A\left\{\frac{y_q}{(y_q^2-2\sigma_Ay_q+1)}-\frac{y_q}{(y_q^2+2\sigma_Ay_q+1)}\right\}-\tfrac{1}{2}\left\{\frac{1}{(y_q^2-2\sigma_Ay_q+1)}+\frac{1}{(y_q^2+2\sigma_Ay_q+1)}\right\}\right]\times\mathrm{d}y_q\,. \quad \text{(A-26)}$$

Making use of equations (70), (75) and (672) of Peirce & Foster (1966) in (A-26) and simplifying, we obtain

$$R_1^*(I)=2\sigma_B^2-\frac{4\sigma_B}{\pi}\left[1+\frac{\sigma_A}{2}\log_e\left(\frac{1-\sigma_A}{1+\sigma_A}\right)\right]. \quad \text{(A-27)}$$

Substituting for the p.d.f. of y_q as obtained from Table (1*b*) of SR in (A-25), changing the variable of integration to $x=y_q^2$ and using the result in (A-24) we can show for the *NC* case that

$$R_1^*(I)=1-2\sigma_B^2\int_0^1\frac{(x^2+x)\mathrm{d}x}{[1+2(1-2\sigma_A^2)x+x^2]^{3/2}}\,. \quad \text{(A-28)}$$

Making use of equations (2.264-6) and (2.264-7) on p. 83 and equation (2.261) on p. 81 of Gradshteyn & Ryzhik (1965) we can show that (A-28) reduces to

$$R_1^*(I)=2\sigma_B\left[1-\sigma_B\log_e\left(\frac{1+\sigma_B}{\sigma_B}\right)\right]. \quad \text{(A-29)}$$

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Debye Temperatures of KI and RbI and the Anharmonic Parameters of their Potential Functions

BY P. D. PATHAK AND N. M. PANDYA

Physics Department, University School of Sciences, Ahmedabad-9, India

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Debye temperatures of potassium iodide and rubidium iodide have been determined by X-ray diffraction from room temperature up to about 800 K with methods due to Paskin [*Acta Cryst.* (1957), **10**, 667–669] and Chipman [*J. Appl. Phys.* (1960), **31**, 2012–2015]. The anharmonic contribution to the Debye θ up to about 650 K is shown to arise essentially from thermal expansion. The plot of the reduced thermal expansion $\alpha/\alpha_{m/2}$ *versus* $T/Aa^2\theta^2$ is a common curve. Here $\alpha_{m/2}$ is the value of α at $T=\frac{1}{2}T_m$, T_m being the melting point. A is the mean atomic weight and a is the lattice constant. The values of the anharmonic parameters γ_0 in the potential energy function of Willis [*Acta Cryst.* (1969), A**25**, 277–300] are found to be $-0{\cdot}065\times10^{-12}$ erg Å^{-4} for KI and $-0{\cdot}116\times10^{-12}$ erg Å^{-4} for RbI.

Introduction

Variation of Debye temperature θ_M with temperature for KI up to about 700 K has been investigated by Pearman & Tompson (1967), by Vadets, Giller, Kovich & Fedyshin (1970) and by Geshka & Mikhalchenko (1971). A similar study for RbI from 6 K to 370 K has been made by Hovi & Pirinen (1972). However, a high-