Acta Cryst. (1976). A**32**, 144

Probability Distribution of the Difference in Intensities of Two Unrelated Structures

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(*Received* 22 *May* 1975; *accepted* 20 *August* 1975)

This note deals with the probability distribution of the difference in intensities of two unrelated structures, having the same symmetry and containing p and q atoms respectively ($p>q$). Both centrosymmetric and non-centrosymmetric cases are discussed. The corresponding residual $R_I=\sum|I_1-I_2|/\sum I_1$, where I_1 and I_2 are the intensities for two unrelated structures having the same symmetry and the same atoms, has the value $4/\pi\simeq 1{\cdot}273$ for centrosymmetric structures and 1 for non-centrosymmetric structures.

1. Introduction

Wilson (1950) has considered the probable values of the residual

$$R=\sum|F_1-F_2|/\sum F_1 \qquad (1)$$

where F_1 represents the magnitude of the structure amplitudes from a correct structure and F_2 represents the corresponding values for an unrelated structure with the same symmetry and the same atoms. The largest likely values of R have been used thereafter in discussing the correctness of a structure proposal in case of single-crystal data.

An analogous residual

$$R_I=\sum|I_1-I_2|/\sum I_1 \qquad (2)$$

with intensities I instead of structure amplitudes proved to be more convenient for structure analyses based on powder data both for X-rays (Thöni, 1973) and neutrons (Rietveld, 1968). This residual has briefly been mentioned by Wilson (1969) when discussing the effect of a badly misplaced atom on different types of residuals. It was therefore thought worthwhile to work out more generally the corresponding probability distribution of the intensity difference $|I_1-I_2|$, both in the centrosymmetric and non-centrosymmetric case. The largest likely values of R_I can easily be deduced therefrom.

2. The probability distribution $P(w)$

Consider a first structure containing p atoms and a second unrelated structure with the same symmetry, containing q atoms, where $p>q$. We assume that the group q contains a sufficiently large number of atoms so that the intensities I_q (and therefore I_p also) will follow the ideal centric or acentric probability distribution $P(I)$ given by (Howells, Phillips & Rogers, 1950)

$$_{\bar{1}}P(I)=(2\pi\sigma^2)^{-1/2}I^{-1/2}\exp(-I/2\sigma^2) \qquad (3)$$

$$_{1}P(I)=(\sigma^2)^{-1}\exp(-I/\sigma^2)\,, \qquad (4)$$

where σ^2 is the mean-square value of the distribution which equals the sum of the square of the atomic scattering factors. Alternatively one can take I_p to represent the observed intensities and I_q the calculated intensities for one and the same structure, in the case of a completely wrong structure proposal.

Denoting for convenience I_p-I_q by D, the distribution for D can be worked out using a general theorem in probability theory,

$$P(D)=\int_{0\text{ or }|D|}^{\infty}P(I_q)P(D+I_q)\mathrm{d}I_q\,, \qquad (5)$$

where I_q and $I_p=D+I_q$ are assumed to be completely independent of each other. While D can have any value between $-\infty$ and $+\infty$, the distributions $P(I_q)$ and $P(I_p)$ exist only in the range 0 to ∞. The lower limit of integration in (5) therefore becomes 0 for $D>0$ and $|D|$ for $D<0$.

It is convenient to work out the results in terms of the following normalized variables

$$w=D/\sigma_p^2;\quad s=\sigma_q^2/\sigma_p^2;\quad M=I_q/\sigma_p^2\,, \qquad (6)$$

since the final expressions take simple forms in terms of these quantities.

(*a*) *Centrosymmetric case*

If (3) and (6) are substituted into (5), the distribution for w takes the form

$$P(w)=(2\pi)^{-1}s^{-1/2}\exp(-w/2)\int_{0\text{ or }|w|}^{\infty}[M(M+w)]^{-1/2}\times\exp[-M(1+s)/2s]\mathrm{d}M \qquad (7)$$

or

$$P(w)=(2\pi)^{-1}s^{-1/2}\exp(-w/2)\times\exp(-|w|(1+s)/2s)\,.\,L(w)\qquad w<0 \qquad (8a)$$

$$P(w)=(2\pi)^{-1}s^{-1/2}\exp(-w/2)\,.\,L(w)\qquad w>0\,, \qquad (8b)$$

where

$$L(w)=\int_0^{\infty}[M(M+|w|)]^{-1/2}\exp[-M(1+s)/2s]\mathrm{d}M\,. \qquad (9)$$

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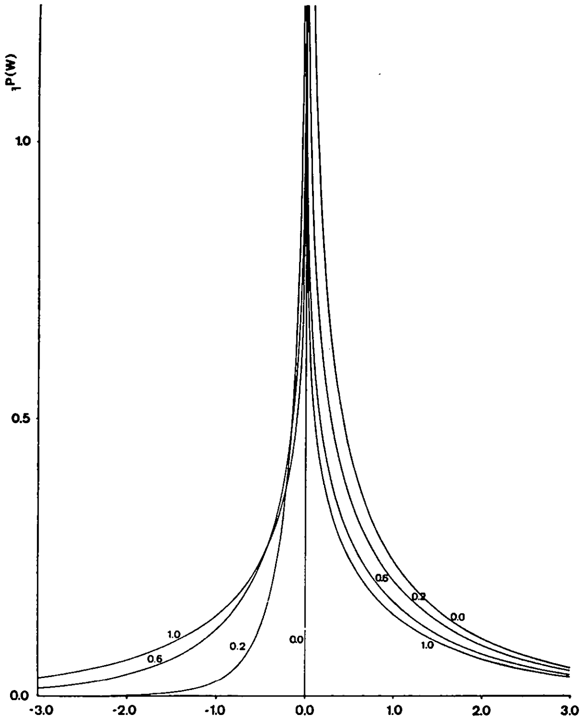

Fig. 1. Probability distribution $P(w)$ for the centrosymmetric case corresponding to $s=0{\cdot}0$, $0{\cdot}2$, $0{\cdot}6$, $1{\cdot}0$.

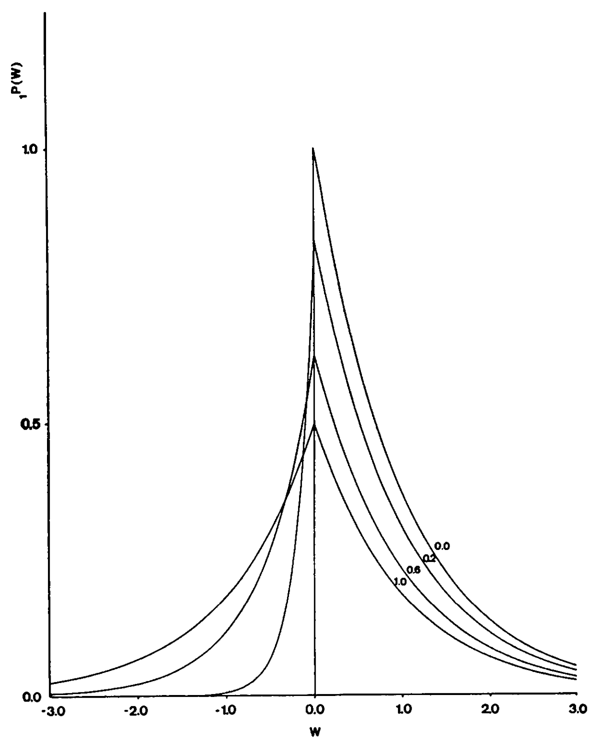

Fig. 2. Probability distribution $P(w)$ for the non-centrosymmetric case corresponding to $s=0{\cdot}0$, $0{\cdot}2$, $0{\cdot}6$, $1{\cdot}0$.

With the result (Erdelyi, 1954, p. 138)

$$\int_0^\infty (t^2+2at)^{\gamma-1/2}\exp(-pt)\mathrm{d}t$$
$$=\pi^{-1/2}\Gamma(\gamma+\tfrac{1}{2})\,.\,(2a/p)^\gamma\exp(ap)\,.\,K_\gamma(ap)$$
$$|\mathrm{Arg}\,a|<\pi;\quad \mathrm{Re}\,\gamma>-\tfrac{1}{2};\quad \mathrm{Re}\,p>0\,,$$

where $\Gamma(x)$ is the gamma function, and $K_\gamma(x)$ the Bessel function of order γ, (9) reduces to

$$L(w)=\exp[|w|(1+s)/4s]\,.\,K_0[|w|(1+s)/4s]\,.$$

The distribution for w then takes the form:

$$P(w)=(2\pi)^{-1}s^{-1/2}\exp(-w/2)\exp[-|w|(1+s)/4s]\times K_0[|w|(1+s)/4s] \quad (10a)$$
$$w<0$$

$$P(w)=(2\pi)^{-1}s^{-1/2}\exp(-w/2)\exp[+|w|(1+s)/4s]\times K_0[|w|(1+s)/4s] \quad (10b)$$
$$w>0\,.$$

The nature of the function $P(w)$ in the centrosymmetric case is shown in Fig. 1 for different values of s.

(b) Non-centrosymmetric case

If (4) and (6) are substituted into (5), we get

$$P(w)=s^{-1}\exp(-w)\int_{0\text{ or }|w|}^\infty \exp[-M(1+s)/s]\mathrm{d}M\,. \quad (11)$$

Integration leads to the simple result

$$P(w)=(1+s)^{-1}\exp(-|w|/s)\quad w<0 \quad (12a)$$
$$P(w)=(1+s)^{-1}\exp(-|w|)\quad w>0\,. \quad (12b)$$

The distribution function $P(w)$ for this non-centrosymmetric case is given for different values of s in Fig. 2.

(c) Properties of $P(w)$

Figs. 1 and 2 show the probability distribution $P(w)$ for the difference in intensities of two unrelated structures for different values of s. In the limit $s\to 0$ we get as expected the original normalized intensity distributions, as shown easily by an expansion. As s increases, the function $P(w)$ develops more and more on the negative side and for $s=1$ becomes completely symmetric about $w=0$. This general behaviour is similar for both centrosymmetric and non-centrosymmetric structures. A comparison of Figs. 1 and 2 shows that, for a particular value of s, the curve is sharper for the centrosymmetric than for the non-centrosymmetric case. A comparison with the corresponding probability distributions for the difference in structure amplitudes (Ramachandran, Srinivasan & Raghupathy Sarma, 1963) shows an increased sensitivity with respect to a centre of symmetry.

3. Largest likely values for the residual R_I

The residual R_I defined in (2) can easily be worked out in terms of the available distribution $P(w)$. From its definition, it is readily seen that

$$R_I=\langle|D|\rangle/\langle I_p\rangle=\langle|w|\rangle=\int_{-\infty}^{+\infty}|w|P(w)\mathrm{d}w\,. \quad (13)$$

Using (10*a*), (10*b*) and (13), we have for the centrosymmetric case

$$R_I=\pi^{-1}s^{-1/2}\int_0^\infty |w| \cosh\,[|w|(1-s)/4s] \times K_0[|w|(1+s)/4s]\mathrm{d}w\,. \quad (14)$$

In general this integral can only be evaluated numerically. However it reduces considerably in the limit $s\rightarrow 1$ to

$$R_I=\pi^{-1}\int_0^\infty |w|K_0(|w|/2)\mathrm{d}w\,. \quad (15)$$

With the result (Erdelyi, 1954, p. 331)

$$\int_0^\infty K_\gamma(ax)x^{s-1}\mathrm{d}x=a^{-s}2^{s-2}\Gamma(\tfrac{1}{2}s-\tfrac{1}{2}\gamma)\Gamma(\tfrac{1}{2}s+\tfrac{1}{2}\gamma)$$
$$\mathrm{Re}\,s>|\mathrm{Re}\,\gamma|\,,\ \mathrm{Re}\,\alpha>0\,,$$

the residual becomes

$$R_I=\pi^{-1}(\tfrac{1}{2})^{-2}\Gamma^2(1)=4/\pi\simeq 1{\cdot}273\,. \quad (16)$$

Using (12*a*), (12*b*) and (13), we get for the non-centrosymmetric case the following simple result

$$R_I=(1+s^2)/(1+s)\,. \quad (17)$$

The residual R_I as a function of s is shown in Fig. 3 for both the centrosymmetric (C) and non-centrosymmetric (A) cases.

The values of R_I for the centrosymmetric and non-centrosymmetric cases for $s=1$ ($4/\pi\simeq 1{\cdot}273$ and 1 respectively) can directly be compared with the corresponding values of the residual R for structure amplitudes defined in (1) (0·828 and 0·586 respectively), first deduced by Wilson (1950), for a proposed structure which is completely wrong.

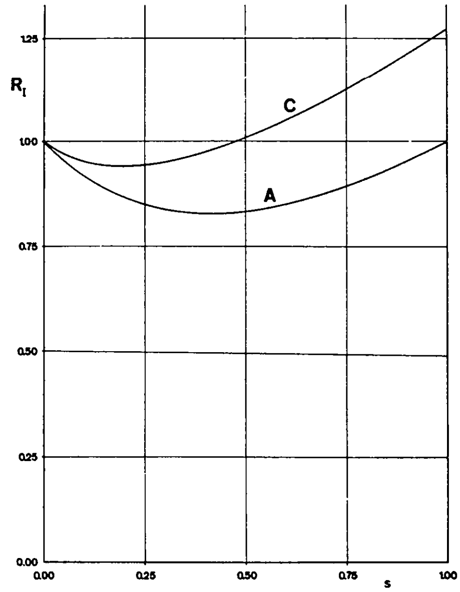

Fig. 3. Residual R_I as a function of s. C and A denote centrosymmetric and acentric (non-centrosymmetric) cases respectively.

Thus R_I for an entirely wrong centrosymmetric structure is $4/\pi$ times as big as for a wrong non-centrosymmetric structure, which has to be compared with a factor of $\sqrt{2}$ in case of the residual R. The residual R_I for intensities is therefore less sensitive with respect to a centre of symmetry than the residual R in the case of the structure amplitudes.

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