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The Variance of the Electron Density for Non-centrosymmetric Space Groups

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An estimate of the variance in the electron density for $P1$ has been derived by consideration of the errors in the observed and calculated structure factors for accurate diffractometer experiments. It is concluded that the variance in the electron density is substantially dependent on the errors in the form-factor curves for the better quality instruments available.

Introduction

The electron density for the space group $P1$ is given by

$$\varrho(\mathbf{r}) = (2/v) \Sigma |F_o(\mathbf{h})| \cos [\theta(\mathbf{h}) - \alpha(\mathbf{h})] \quad (1)$$

where, $\theta(\mathbf{h}) = 2\pi\mathbf{h} \cdot \mathbf{r}$ and $\alpha(\mathbf{h})$ is the phase angle. The usual treatment of errors in the electron density assumes (*a*) that there are no errors in the phase angles and (*b*) that the variance of $|F_o(\mathbf{h})|$ can be represented by $|\Delta(\mathbf{h})|^2$ where $|\Delta(\mathbf{h})| = ||F_o(\mathbf{h})| - |F_c(\mathbf{h})||$. These assumptions lead to an expression for the variance of the electron density

$$\sigma^2[\varrho(\mathbf{r})] = (2/v)^2 \Sigma |\Delta(\mathbf{h})|^2 \cos^2 [\theta(\mathbf{h}) - \alpha(\mathbf{h})] \quad (2)$$

and the apparent paradox that the error in $\varrho(\mathbf{r})$ increases indefinitely with the number of observations.

It has recently been shown by Killean & Lawrence (1969) that a set of variances for the $|\Delta(\mathbf{h})|$ can be obtained on an absolute scale for use in least-squares refinement, and this paper is concerned with applying these variances of the observed and calculated structure factors to the determination of a new expression for the standard deviation of the electron density.

The variance of the observed structure factor

An analysis of the variance of the observed structure factor gives an expression

$$\sigma_o^2(\mathbf{h}) = \frac{K}{4\,\mathrm{Lp}} \cdot \frac{(I+B)}{(I-B)} + c^2|F_o(\mathbf{h})|^2 \quad (3)$$

where $\sigma_o^2(\mathbf{h})$ is the variance in $|F_o(\mathbf{h})|$ and the other quantities have been defined in the previous paper. The first term on the right-hand side of this equation arises from counting statistics and the second term is due to random instrumental setting errors. It is advisable for accurate experimental work to make the first term negligibly small compared with the second term and it is not difficult to show (Killean, 1967) that to do this only relatively low counts are required to produce a very low R index based on counting statistics alone. Consequently (2) reduces, still assuming no error in the phase angles, to

$$\sigma^2[\varrho(\mathbf{r})] = (2/v)^2 c^2 \Sigma |F_o(\mathbf{h})|^2 \cos^2 [\theta(\mathbf{h}) - \alpha(\mathbf{h})] < (2/v)^2 c^2 \Sigma |F_o(\mathbf{h})|^2 .$$

It is well known that $\Sigma |F_o(\mathbf{h})|^2$ summed over an infinite number of planes is related to the height of the origin peak of the Patterson synthesis and is therefore finite. The apparent paradox indicated in the introduction is resolved.

The variance of the calculated structure factor

Consider the expression for the calculated structure factor,

$$F_c(\mathbf{h}) = \sum_j [f(\mathbf{h}) + \delta(\mathbf{h})] \exp 2\pi i \mathbf{h} \cdot \mathbf{r}_j$$

where $\delta(\mathbf{h})$ is the asymmetric correction which has to be applied to the scattering factor, $f(\mathbf{h})$, due to bonding of the atom. It has been shown (Killean & Lawrence, 1969) that a consideration of the error vector polygon arising from the $\delta(\mathbf{h})$, gives a variance in the calculated structure factor

$$\sigma_c^2(\mathbf{h}) = k^2[\Sigma f(\mathbf{h})^2] = k^2\langle |F(\mathbf{h})|^2 \rangle . \quad (4)$$

Since the calculated structure factors are used to compute the phase angles this variance will give rise to a variance in the phase angle. Because

$$F_c(\mathbf{h}) = A_c(\mathbf{h}) + iB_c(\mathbf{h}) ,$$

it follows from (4) that

$$\sigma_c^2[A(\mathbf{h})] = \sigma_c^2[B(\mathbf{h})] = \tfrac{1}{2}\sigma_c^2(\mathbf{h}) . \quad (5)$$

Care should be taken in applying this expression to other non-centrosymmetric space groups which have centrosymmetric projections where all $B(\mathbf{h})$ are zero.

The variance of the electron density

The variance of the electron density given by (1) can now be expressed as

$$\sigma^2[\varrho(\mathbf{r})] = (2/v)^2 \Sigma \sigma^2\{|F_o(\mathbf{h})| \cos [\theta(\mathbf{h}) - \alpha(\mathbf{h})]\} .$$

Now

$$\sigma\{|F_o(\mathbf{h})| \cos[\theta(\mathbf{h})-\alpha(\mathbf{h})]\} = |F_o(\mathbf{h})|\sigma\{\cos[\theta(\mathbf{h})-\alpha(\mathbf{h})]\} + |\cos[\theta(\mathbf{h})-\alpha(\mathbf{h})]|\sigma_o(\mathbf{h}) = |F_o(\mathbf{h})|\,|\sin[\theta(\mathbf{h})-\alpha(\mathbf{h})]|\sigma[\alpha(\mathbf{h})] + |\cos[\theta(\mathbf{h})-\alpha(\mathbf{h})]|\sigma_o(\mathbf{h}) .$$

Let

$$\varphi(\mathbf{h}) = \theta(\mathbf{h}) - \alpha(\mathbf{h}) .$$

$$\sigma[|F_o(\mathbf{h})| \cos\varphi(\mathbf{h})] = |F_o(\mathbf{h})|\,|\sin\varphi(\mathbf{h})|\sigma[\alpha(\mathbf{h})] + |\cos\varphi(\mathbf{h})|\sigma_o(\mathbf{h})$$

and hence

$$\sigma^2[\varrho(\mathbf{r})] = (2/v)^2 \Sigma\,[|F_o(\mathbf{h})|^2 \sin^2\varphi(\mathbf{h})\sigma^2[\alpha(\mathbf{h})] + \cos^2\varphi(\mathbf{h})\sigma_o^2(\mathbf{h})| + 2|F_o(\mathbf{h})|\,|\sin\varphi(\mathbf{h})\cos\varphi(\mathbf{h})|\sigma[\alpha(\mathbf{h})]\sigma_o(\mathbf{h})] . \quad (6)$$

A reasonable estimate of $\sigma[\alpha(\mathbf{h})]$ can be obtained from

$$\cos\{\alpha(\mathbf{h})+\sigma[\alpha(\mathbf{h})]\} = \frac{A_c(\mathbf{h})-\sigma_c[A(\mathbf{h})]}{|F_c(\mathbf{h})|+\sigma_c(\mathbf{h})}$$

$$\sigma[\alpha(\mathbf{h})] = \cos^{-1}\left[\frac{A_c(\mathbf{h})-\sigma_c[A(\mathbf{h})]}{|F_c(\mathbf{h})|+\sigma_c(\mathbf{h})}\right] - \cos^{-1}\left[\frac{A_c(\mathbf{h})}{|F_c(\mathbf{h})|}\right] = \cos^{-1}\left[\frac{A_c(\mathbf{h})-(1/\sqrt{2})\sigma_c(\mathbf{h})}{|F_c(\mathbf{h})|+\sigma_c(\mathbf{h})}\right] - \cos^{-1}\left[\frac{A_c(\mathbf{h})}{|F_c(\mathbf{h})|}\right], \quad (7)$$

and consequently all the terms on the right-hand side of (6) are known numerically and the variance of the electron density may be computed at any point.

The average value of the variance of the electron density at general positions may be obtained in the usual way (Cruickshank, 1965) by replacing the trigonometric functions by their averages.

$$\sigma^2[\varrho(\mathbf{r})] = (2/v)^2 \Sigma\,[\tfrac{1}{2}|F_o(\mathbf{h})|^2\sigma^2[\alpha(\mathbf{h})] + \tfrac{1}{2}\sigma_o^2(\mathbf{h}) + (2/\pi)\,|F_o(\mathbf{h})|\sigma[\alpha(\mathbf{h})]\sigma_o(\mathbf{h})]$$

and assuming a negligible variance due to counting statistics

$$\sigma^2[\varrho(\mathbf{r})] = (2/v)^2 \Sigma\left[|F_o(\mathbf{h})|^2\left(\frac{\sigma^2[\alpha(\mathbf{h})]}{2} + \frac{c^2}{2} + \frac{2c\sigma[\alpha(\mathbf{h})]}{\pi}\right)\right]. \quad (8)$$

The value of c, the fractional error in the structure factor, varies from diffractometer to diffractometer for the same crystal and may be considered as a figure of merit for a particular instrument. Extreme values that have been found for an all light-atom organic crystal are 0·070 and 0·022 and it is clearly desirable to have an instrument manufactured to sufficiently high tolerances that the 'c^2-term' in (8) is negligible compared with the term due to errors in the scattering-factor curves. From analysis of a limited amount of data obtained from the best available instrument – that giving c of 0·022 – the average error in the scattering factor curves for an all light-atom structure appears to be about 3%. Substitution of this value in (7) gives $\langle\sigma[\alpha(\mathbf{h})]\rangle$ of 0·05 radian. Consequently

$$\frac{\sigma^2[\alpha(\mathbf{h})]}{2} = 0{\cdot}00125$$

$$\frac{c^2}{2} = 0{\cdot}00024 \text{ (best) or } 0{\cdot}00245 \text{ (worst)}$$

$$\frac{2c\sigma[\alpha(\mathbf{h})]}{\pi} = 0{\cdot}00070 \text{ (best) or } 0{\cdot}00223 \text{ (worst)}$$

and clearly for any diffractometer the contribution to the variance in the electron density from the errors in the phases is by no means negligible and predominates for better quality instruments.

The errors in the positional parameters may be derived in the usual way (Cruickshank, 1965), but it is essential to allow for the errors in the phase angles when computing the standard deviations of the various derivatives of the electron-density function. This can be done in a derivation similar to that of equation (6).

References

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