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A simple rule for the electron-density error at special positions.

By P.M. DE WOLFF, *Laboratorium voor Technische Natuurkunde, Technische Hogeschool, Delft, The Netherlands*

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At special positions, the errors in the electron density can be several times those at general positions. This was shown by Cruickshank & Rollett (1953), whose formula, however, does not readily yield an estimation of the factor by which the r.m.s. error $\sigma(\varrho)$ is increased. We shall show that, to an approximation sufficient for most purposes, this factor is $g^{\frac{1}{2}}$, g being the order of the point group of the special position.

Consider the deviation $\Delta\varrho$ caused by deviations ΔF (complex in the acentric case) of the structure factors from their true values:

$$V\,.\,\Delta\varrho=\sum_{-h\,-k\,-l}^{+h\,+k\,+l}\Delta F_{hkl}\exp\{2\pi i(hx+ky+lz)\}$$
$$=\sum_{\text{all}\mathbf{H}}\Delta F_H\exp 2\pi i\mathbf{H}\,.\,\mathbf{r}\,. \quad (1)$$

Now one may write:

$$V\,.\,\Delta\varrho=q_1+\ldots+q_G+q_0\,, \quad (2)$$

q_j being defined by

$$q_j=\sum_j\Delta F_H\exp 2\pi i\mathbf{H}\,.\,\mathbf{r}\,, \quad (3)$$

where G is the order of the point group P of the crystal; $\sum$ is a sum over **H**-vectors only from non-degenerate forms, and from each form only one, whereas $\sum_j$ is obtained from $\sum_1$ by transforming **H** by the jth element P_j of P. The sum $\sum_0$ is over all reflexions in degenerate forms. Thus in orthorhombic centric space groups, $\sum_1$ might contain all reflexions with all-positive indices; whereas $\sum_0$ contains those with at least one index zero.

Now if S_j is a space group operation of which P_j is the translation-free component,

$$q_j(\mathbf{r})=q_1(\mathbf{r}_j), \quad (4)$$

where $\mathbf{r}_j=S_j^{-1}\mathbf{r}$.

This follows from the phase relation between symmetry-related F's, which obtains for the ΔF's as well:

$$\Delta F_{H_j}\exp 2\pi i\mathbf{H}_j\,.\,\mathbf{r}=\Delta F_H\exp 2\pi i\mathbf{H}\cdot\mathbf{r}_j\,,$$

where $\mathbf{H}_j=P_j\cdot\mathbf{H}$.

On account of (4), (2) can be rewritten:

$$V\,.\,\Delta\varrho(\mathbf{r})=q_0(\mathbf{r})+\sum_{j=1}^{G}q_1(\mathbf{r}_j)\,. \quad (5)$$

Since q_0 is real and independent of the other q's, upon squaring and averaging we obtain:

$$V^2\,.\,\sigma^2\{\varrho(\mathbf{r})\}=\langle q_0^2(\mathbf{r})\rangle+\sum_{j=1}^{G}\sum_{k=1}^{G}\langle q_1(\mathbf{r}_j)q_1^*(\mathbf{r}_k)\rangle\,. \quad (6)$$

After substitution of (3) the products in the double sum can be written (note that $\langle\Delta F_H\Delta F_{H'}^*\rangle=0$ for $\mathbf{H}\neq\mathbf{H}'$):

$$\langle q_1(\mathbf{r}_j)q_1^*(\mathbf{r}_k)\rangle=\sum_1\sigma^2(F_H)\{\exp 2\pi i\mathbf{H}\,.\,(\mathbf{r}_j-\mathbf{r}_k)\}$$
$$=\varphi(\mathbf{r}_j-\mathbf{r}_k)\,, \quad (7)$$

with the definitions

$$\sigma^2(F_H)=\langle|\Delta F_H|^2\rangle\,;$$
$$\varphi(\mathbf{u})=\sum_1\sigma^2(F_H)\exp 2\pi i\mathbf{H}\,.\,\mathbf{u}\,. \quad (8)$$

Hence (6) becomes:

$$V^2\sigma^2\{\varrho(\mathbf{r})\}=\langle q_0^2(\mathbf{r})\rangle+\sum_{j=1}^{G}\sum_{k=1}^{G}\varphi(\mathbf{r}_j-\mathbf{r}_k)\,. \quad (9)$$

Now the real part of φ has a peak at the origin, the extent of which is determined by series termination broadening. Outside this peak, φ will be vanishingly small (see end of paper). Hence in (9), only the terms with $\mathbf{r}_k=\mathbf{r}_j$ need be considered; their number is Gg if the order of the point group of position **r** is g.

Denoting the error for this position by σ_g, we find

$$V^2\sigma_g^2(\varrho)=\langle q_0^2\rangle+Gg\sum_1\sigma^2(F_H)\,. \quad (10)$$

The first term can be treated by a subdivision of q_0 in mutually dependent sums similar to (2). For a general position ($g=1$), the result is $\langle q_0^2\rangle=\sum_0\sigma^2(F_H)$ and (10) reduces to the well-known formula (Cruickshank, 1949)

$$V^2\sigma_1^2(\varrho)=\sum_{\text{all}\,H}\sigma^2(F_H)\,.$$

For a special position ($g>1$), it follows from (10) that

$$\sigma_g^2(\varrho)=g\sigma_1^2(\varrho) \quad (11)$$

provided $\langle q_0^2\rangle$ is affected by the special position in the same way as the second term. Special values of $\langle q_0^2\rangle$ can be calculated by Cruickshank & Rollett's more explicit method. Alternatively, they can be computed by applying the present method to projections. For instance, the contribution of a zone ($hk0$) will be enhanced in a special position A according to the plane point group of A in the c projection; this group may have an order different from g.

However, the number of reflexions involved in q_0 is in general relatively small, so (11) will often be a sufficiently accurate estimate for the enhancement. This is illustrated by Table 1 giving the errors σ_{CR} calculated from unpublished estimates ΔF by Cruickshank & Rollett for a structure with space group $R\bar{3}m$, compared with $\sigma_1\,.\,g^{\frac{1}{2}}$. Their value 0·018 for (x, y, z) is taken as σ_1. It is evident that no significant enhancement is to be expected for positions like (x, o, z), which are not special in the usual sense.

Table 1. $\sigma(\varrho)$ *for dimethyltriacetylene*

Position	g	$\sigma_1\,.\,g^{\frac{1}{2}}$	σ_{CR}
x, 0, z	1	0·018	0·018
x, $\bar{x}$, z	2	0·025	0·030
0, 0, z	6	0·044	0·042
0, 0, 0	12	0·062	0·053

If $\sigma(F_H)$ depends strongly on F_H, it follows from (8) that φ will more or less resemble the structure's Patterson function. Then according to (9) the error at atomic positions, too, will be enhanced; but this effect is much smaller than at special positions.

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References

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