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Comments on a method of structure determination. By J. D. DUNITZ, *The Royal Institution*, 21, Albe-marle Street, London W. 1, England and L. E. ORGEL, *University Chemical Laboratory, Cambridge, England*

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Björnhaug & Krogh-Moe (1955) have recently suggested that the directly calculable function

$$R(\mathbf{x}) = \sum_{\mathbf{h}} |F(\mathbf{h}) \cos 2\pi\mathbf{h} \cdot \mathbf{x}|$$

may be useful as providing a direct method of determining atomic positions in centrosymmetric crystals. The justification for such a suggestion may be stated somewhat as follows: in so far as the low value of the electron-density function between atoms arises from the occurrence of low absolute values of the trigonometric part, $\cos 2\pi h x$, and not from cancellation of terms of opposite sign, the value of $R(\mathbf{x})$ is expected to be significantly lower in regions between atoms than in the vicinity of atoms. Atomic positions may thus be recognized by a higher-than-average value of $R(\mathbf{x})$. This is an interesting idea but more detailed examination shows that it does not, fortunately, provide a useful method of structure analysis.

We first note that $|\cos 2\pi h x|$ behaves rather like a cosine wave of twice the frequency, plus a constant term. By expansion as a Fourier series, we have

$$\begin{aligned} |\cos 2\pi h x| &= \frac{2}{\pi} + \sum_{n=1}^{\infty} (-1)^{n+1} \frac{4}{\pi(4n^2-1)} \cos 2\pi \cdot 2hn x \\ &= \frac{4}{\pi} \left(\frac{1}{2} + \frac{1}{3} \cos 2\pi \cdot 2hx - \frac{1}{15} \cos 2\pi \cdot 4hx \right. \\ &\quad \left. + \frac{1}{35} \cos 2\pi \cdot 6hx \dots \right). \end{aligned}$$

The principal fluctuating contribution to $R(\mathbf{x})$ is thus the modified Patterson function with coefficients weighted as $1/F$ and drawn on half the correct scale. In a half-scale Patterson, peaks arising from interaction of atoms related

by the symmetry centre occur at the actual atomic positions, and only if the Patterson function is dominated by such peaks will $R(\mathbf{x})$ lead to a correct assignment of atomic positions. The condition under which this will occur is that the unit cell contains only two atoms related by the centre: in any more complex structure the general interactions, occurring with doubled weight, will dominate. Under these circumstances it would seem preferable to compute the Patterson function itself rather than $R(\mathbf{x})$.

The failure of $R(\mathbf{x})$ to distinguish atomic positions can also be understood from a simple statistical argument. For $2N$ point atoms of unit weight in the centrosymmetric cell, we have

$$R(\mathbf{x}) = 2 \sum_n \left| \sum_{i=1}^N \cos 2\pi\mathbf{h} \cdot \mathbf{x}_i \cos 2\pi\mathbf{h} \cdot \mathbf{x} \right|.$$

We now consider the root-mean-square value of each term in the \mathbf{h} summation for various values of \mathbf{x} . This is $N^{\frac{1}{2}}$ for arbitrary \mathbf{x} , $(N + \frac{1}{2})^{\frac{1}{2}}$ when $\mathbf{x} = \pm \mathbf{x}_i$, and $(N + 1)^{\frac{1}{2}}$ when $\mathbf{x} = \pm (\mathbf{x}_i \pm \mathbf{x}_j)/2$. The distinction between 'peaks' and fluctuations of the background is thus quite small and likely to be unreliable. The relationship with the Patterson function is seen by subtracting the background value, $N^{\frac{1}{2}}$, from that at special positions related to the atomic coordinates. The difference at $(\mathbf{x}_i \pm \mathbf{x}_j)/2$ is approximately twice that at \mathbf{x}_i .

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The crystal structure of solid chlorine: correction. By ROBERT L. COLLIN, *Cancer Research Institute, New England Deaconess Hospital, 194 Pilgrim Road, Boston 15, Massachusetts, U.S.A.*

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The unit cell dimensions quoted in the above paper (Collin, 1952) are slightly in error. The correct dimensions are

$$a = 6.24, b = 4.48, c = 8.26 \text{ \AA}.$$

The interatomic distances were calculated with the above dimensions and hence are correct as quoted.

Reference

- COLLIN, R. L. (1952). *Acta Cryst.* **5**, 431.