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The signs of products of structure factors.

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Numerous authors have discussed the probability that the product of structure factors $F_{\mathbf{H}}.F_{\mathbf{K}}$ has the same sign as the structure factor $F_{\mathbf{H+K}}$ (Cochran, 1952; Zachariasen, 1952). Cochran's somewhat involved demonstration uses a relationship (Sayre, 1952) which was established for crystals containing but one kind of atoms, all of which are resolved, and is therefore not generally applicable to projections. Zachariasen's derivation has been questioned by Lavine (1952).

The relationship can be established quite simply for crystals of the kind considered by Sayre by calculating directly the average value of $U_{\mathbf{H}}.U_{\mathbf{K}}$, subject to the restriction that $\mathbf{H}+\mathbf{K}$ be held constant.

Using the usual symbols, we have by definition

$$U_{\mathbf{H}} = 2\sum_{j}^{N/2} q_j \cos 2\pi\mathbf{H}.\mathbf{r}_j$$

for a centrosymmetrical crystal. Accordingly,

$$U_{\mathbf{H}}.U_{\mathbf{K}} = 4\sum_{i}^{N/2}\sum_{j}^{N/2} q_i q_j \cos 2\pi\mathbf{H}.\mathbf{r}_i \cos 2\pi\mathbf{K}.\mathbf{r}_j$$

and by simple trigonometric manipulation

$$U_{\mathbf{H}}.U_{\mathbf{K}} = 2\sum_{i}^{N/2}\sum_{j}^{N/2} q_i q_j [\cos 2\pi(\mathbf{H}.\mathbf{r}_i+\mathbf{K}.\mathbf{r}_j)+\cos 2\pi(\mathbf{H}.\mathbf{r}_i-\mathbf{K}.\mathbf{r}_j)] .$$

Separating the terms with $i = j$ yields

$$U_{\mathbf{H}}.U_{\mathbf{K}} = 2\sum_{i}^{N/2} q_i^2[\cos 2\pi(\mathbf{H}+\mathbf{K}).\mathbf{r}_i+\cos 2\pi(\mathbf{H}-\mathbf{K}).\mathbf{r}_i]$$
$$+2\sum_{i\neq j}^{N/2}\sum^{N/2} q_i q_j [\cos 2\pi(\mathbf{H}.\mathbf{r}_i+\mathbf{K}.\mathbf{r}_j)+\cos 2\pi(\mathbf{H}.\mathbf{r}_i-\mathbf{K}.\mathbf{r}_j)] .$$

If we now take averages, keeping $\mathbf{H}+\mathbf{K}$ constant, the double sum and the term of the single sum involving $\mathbf{H}-\mathbf{K}$ will average zero, under the conditions discussed by Wilson (1949), and we obtain

$$\overline{U_{\mathbf{H}}.U_{\mathbf{K}}}^{\mathbf{H+K}} = 2\sum_{i}^{N/2} q_i^2 \cos 2\pi(\mathbf{H}+\mathbf{K}).\mathbf{r}_i .$$

Then, if all atoms are the same, $q_i = 1/N$ and may be factored out of the sum, with the result

$$\overline{U_{\mathbf{H}}.U_{\mathbf{K}}}^{\mathbf{H+K}} = U_{\mathbf{H+K}}/N .$$

Since the average of $U_{\mathbf{H}}.U_{\mathbf{K}}$ has the same sign as $U_{\mathbf{H+K}}$ one concludes that, at least for large values of the product, the product has the same sign as $U_{\mathbf{H+K}}$ more often than not. By keeping $\mathbf{H}-\mathbf{K}$ constant during averaging the same result follows with respect to $U_{\mathbf{H-K}}$. It is also clear that the relationship will be true even when all atoms are not exactly the same, particularly when $U_{\mathbf{H+K}}$ is not small. For if the atoms are nearly the same we may set $q_i = q+\Delta q_i$, where q is an average value and $\Delta q_i \ll q$. If we then ignore $\Delta^2 q_i$ we find that

$$2\sum_{i}^{N/2} q_i^2 \cos 2\pi(\mathbf{H}+\mathbf{K}).\mathbf{r}_i = q[U_{\mathbf{H+K}}+2\sum_{i}^{N/2} \Delta q_i \cos 2\pi(\mathbf{H}+\mathbf{K}).\mathbf{r}_i]$$

and $U_{\mathbf{H+K}}$, unless small, will almost always determine the sign of the quantity in the brackets. Moreover, $q = 1/N$ as before.

The quantitative relationship has been tested with some data from the $h0l$ zone of dicyandiamide (Hughes, 1940), a crystal containing only carbon, nitrogen and hydrogen, of which the latter is ignored. $N = 12$ for the zone and for three different reflections, 800, 400 and $\bar{1}0$,0,12, one observes U/N to be $-0{\cdot}014$, $-0{\cdot}042$, and $+0{\cdot}084$ respectively. The corresponding values for the averages of products are $-0{\cdot}013$, $-0{\cdot}059$, and $+0{\cdot}080$. To obtain appropriate values for the averages one must include products where one or both of the factors are unobservably small. Such factors were taken to be one-half of their estimated maximum possible value. The signs were taken from the final structure. The low observed value for 400 is undoubtedly due largely to extinction; it corresponds to the largest intensity in the zone, and $F_{\text{obs.}}$ is considerably smaller than $F_{\text{calc.}}$. The agreement is accordingly within the limits of error in estimating intensities, even for 800 which is included as a sample of a moderately weak reflection ($U_{800} = 0{\cdot}17$, $\sigma = 0{\cdot}29$).

In the above examples the sign relationship held to the following extent:

	800	400	$\bar{1}0$,0,12
Held	45	62	47
Failed	30	30	8

These numbers represent *all* products within the limiting circle for Cu $K\alpha$ radiation, including those with one or both factors unobservably small. Thus for $\bar{1}0$,0,12, four of the eight 'failures' and eighteen of the 'successes' are in the latter category.

If the above computation is made for an asymmetric crystal one obtains the same result, namely that

$$\overline{U_{\mathbf{H}}.U_{\mathbf{K}}}^{\mathbf{H+K}} = U_{\mathbf{H+K}}/N ,$$

thus indicating that in this case the complex products have phase angles differing from the phase of $U_{\mathbf{H+K}}$ by less than $\frac{1}{2}\pi$ more often than not.

The sign relationship has been demonstrated for any centrosymmetric crystal by computing the joint probability of the three quantities $U_{\mathbf{H}}$, $U_{\mathbf{K}}$ and $U_{\mathbf{H+K}}$, but this calculation is beyond the scope of a Short Communication.

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