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Response to Olczak's comment on *Probability density functions of the average and difference intensities of Friedel opposites*

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The recently published article by Shmueli & Flack (2010) deals with average and difference reduced intensities of $|F(\mathbf{h})|^2$ and $|F(-\mathbf{h})|^2$, known as Friedel opposites. First, well established trigonometric series of these quantities are re-derived and normalized and their probability density functions (hereafter: p.d.f.s), admitting any chemical composition and not relying in any way on the central limit theorem, are derived for the space group $P1$. This derivation rests on an assumption which is the basis of major grievances of Olczak (2011), to which we shall respond.

Consider the expressions for the structure factor and for its squared magnitude:

$$F(\mathbf{h}) = \sum_{j=1}^{N} f_j \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j) \qquad (1)$$

and

$$|F(\mathbf{h})|^2 = \sum_{j=1}^{N} \sum_{k=1}^{N} f_j f_k^* \exp(2\pi i \mathbf{h} \cdot \mathbf{R}_{jk}), \qquad (2)$$

where $\mathbf{R}_{jk} = \mathbf{r}_j - \mathbf{r}_k$ and the (complex) atomic scattering factor contains the displacement parameters and those of resonant scattering. Obviously, the argument of the exponential in equation (2) will also appear in the expressions for the average and difference reduced intensities, normalized or not.

The fractional part of the scalar product $\mathbf{h} \cdot \mathbf{r}_j$ in equation (1) is assumed in various applications to direct methods and intensity statistics to be uniformly distributed in the [0, 1] interval. This assumption has a number-theoretical justification (*e.g.* Weyl, 1916) and can be used if all the atoms (and especially the heavy atoms) are in general positions. Olczak (2011) calls it assumption B.

In our derivations of the p.d.f.s of the normalized average and difference reduced intensities we naturally came across the scalar product $\mathbf{h} \cdot \mathbf{R}_{jk}$ shown in equation (2). We assumed that the interatomic vectors $\mathbf{R}_{jk} = \mathbf{r}_j - \mathbf{r}_k$ are in the general positions of the Patterson unit cell and hence that the fractional part of the scalar product $\mathbf{h} \cdot \mathbf{R}_{jk} = \mathbf{h} \cdot (\mathbf{r}_j - \mathbf{r}_k)$ is uniformly distributed in the [0, 1] interval. The overriding advantage of this approach is that it allows p.d.f.s to be obtained in analytical form, but of course they needed to be subjected to several tests to establish their usefulness (see Shmueli & Flack, 2010). The text of Shmueli & Flack (2010) makes it clear that it is being used as an assumption (approximation) in need of further verification.

According to Olczak (2011), the use of this assumption (i) is inconsistent with the 'commonly used' assumption B, (ii) the result obtained from our calculation 'loses its physical sense' and (iii) our results 'are interesting from the mathematical point of view but not related to any crystal structure'.

Having derived the p.d.f.s, we performed two runs of tests: First, we compared the p.d.f.s with simulated histograms recalculated from a hypothetical structure. The results, shown in Figs. 1 and 2 of Shmueli & Flack (2010), display very good to good agreement of the histograms with the p.d.f.s. This mainly confirmed the correctness of the expressions.

However, a p.d.f. is physically meaningful if it agrees with a distribution related to experimental data, and a crucial test was indicated. We therefore compared the p.d.f.s with histograms recalculated from the parameters of a solved $P1$ structure (CSD: YIDYIF). The results, shown in Figs. 3 and 4 of Shmueli & Flack (2010), display qualitatative agreement and it is concluded that the p.d.f.s are useful.

Objection (i) of Olczak (2011) would preclude assuming anything during one's scientific work, and is therefore not reasonable. Objection (ii) referring to results that lose physical sense is taken care of by Figs. 3 and 4 of Shmueli & Flack (2010) and his comment (iii) is flattering but incorrect, as shown above. We have not been able to derive analytical forms of the p.d.f.s without assuming a uniform distribution of the fractional parts of the scalar products $\mathbf{h} \cdot \mathbf{R}_{jk}$. On the other hand, it is possible to undertake simulations similar to those described in Shmueli & Flack (2010) in which, instead of $\frac{1}{2}N(N-1)$ independent vectors, one takes $N-1$ independent vectors and evaluates the others from these. This concludes our response.

References

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