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A generalization of the Patterson function.

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In a recent communication Sayre (1953) has described a 'double Patterson' function which can be evaluated approximately because of the known fact that for centrosymmetric crystals $U_{\mathbf{H}} . U_{\mathbf{K}} . U_{\mathbf{H}+\mathbf{K}}$ tends to be positive. I have been considering for some time the possible usefulness of another generalized Patterson function which can be evaluated approximately for the same reason.

If we rewrite the sign relationship by saying that $U_{\mathbf{K}/2+\mathbf{H}} . U_{\mathbf{K}/2-\mathbf{H}}$ tends to have the same sign as $U_{\mathbf{K}}$, we can define a generalized 'sharpened up' Patterson function:

$$P_{\mathbf{K}} = \exp\left[-i\alpha_{\mathbf{K}}\right] \sum_{\mathbf{H}} U_{\mathbf{K}/2+\mathbf{H}} . U_{\mathbf{K}/2-\mathbf{H}} C(|\mathbf{H}|) \exp\left[-2\pi i \mathbf{H} . \mathbf{r}\right] ,$$

where $\exp[-i\alpha_{\mathbf{K}}]$ is the sign of $U_{\mathbf{K}}$ when there is a center of symmetry, $C(|\mathbf{H}|)$ is a convergence factor of the type $\exp[-B|\mathbf{H}|^2]$ designed to prevent series-termination difficulties, and the other symbols have their usual significance. When $U_{\mathbf{K}}$ is large, $P_{\mathbf{K}}$ can be computed approximately without knowing any signs because the product sign-relationship guarantees that the sign of the product will usually match $\exp[-i\alpha_{\mathbf{K}}]$ for the larger products which are most important in determining $P_{\mathbf{K}}$. Even for asymmetric structures $P_{\mathbf{K}}$ can probably be evaluated approximately, for it has been shown (Hughes, 1953) that the phases of the products tend to be that of $U_{\mathbf{K}}$ so that $\exp[-i\alpha_{\mathbf{K}}] . U_{\mathbf{K}/2+\mathbf{H}} . U_{\mathbf{K}/2-\mathbf{H}}$ tends to be real and positive.

To interpret $P_{\mathbf{K}}$ we note from the definition of $U_{\mathbf{K}}$ that

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

If this is inserted in the expression for $P_{\mathbf{K}}$ and the order of summation is reversed one obtains

$$\begin{aligned} P_{\mathbf{K}} &= \exp\{-i\alpha_{\mathbf{K}}\} \sum_{i}^{N} \sum_{j}^{N} \sum_{\mathbf{H}} q_i q_j C(|\mathbf{H}|) \exp\{2\pi i[\mathbf{K}/2 . (\mathbf{r}_i+\mathbf{r}_j) \\ &\qquad + \mathbf{H} . (\mathbf{r}_i-\mathbf{r}_j-\mathbf{r})]\} \\ &= \exp\{-i\alpha_{\mathbf{K}}\} \sum_{i}^{N} \sum_{j}^{N} \exp\{2\pi i \mathbf{K} . (\mathbf{r}_i+\mathbf{r}_j)/2\} \mathrm{P}_{ij} , \end{aligned}$$

where

$$P_{ij} = \sum_{\mathbf{H}} q_i q_j C(|\mathbf{H}|) \exp\{-2\pi i \mathbf{H} . [\mathbf{r}-(\mathbf{r}_i-\mathbf{r}_j)]\}$$

is the usual expression for the peak arising from the ith and the jth atoms. Setting $\mathbf{K} = 0$ we find that P_0 is the ordinary 'sharpened up' Patterson function.

When $\mathbf{K} \neq 0$, $P_{\mathbf{K}}$ differs from P_0 in two respects: one is the sign (or phase) $\exp[-i\alpha_{\mathbf{K}}]$ multiplying the entire function and the other is the factor $\exp[2\pi i \mathbf{K} . (\mathbf{r}_i+\mathbf{r}_j)/2]$ multiplying the ijth peak which is located at $\mathbf{r}_i-\mathbf{r}_j$. This latter factor can be of any phase, depending upon $\mathbf{K} . (\mathbf{r}_i+\mathbf{r}_j)/2$, *except* that if i and j are atoms related by a center $\mathbf{r}_i = -\mathbf{r}_j$, $\mathbf{r}_i+\mathbf{r}_j = 0$ and the factor is always unity. The peaks in question are at $\mathbf{r}_i-\mathbf{r}_j = \pm 2\mathbf{r}_i$ and are just the peaks we need to identify in order to determine the structure. If we add $P_{\mathbf{K}}$ to $P_{-\mathbf{K}}$ in order to get rid of the imaginary part of the factor we see that all peaks, including the origin peak, are multiplied by *cosines* generally different from unity except for the interesting case of peaks between atoms related by centers.

Accordingly, if one knew the signs of some large U's so that the $\exp[-i\alpha_{\mathbf{K}}]$ factors could be allowed for, one could add together the corresponding $P_{\mathbf{K}}$'s and expect that all the peaks would tend to cancel out except those showing the positions of atoms related by centers. This would not require the separate summation of a $P_{\mathbf{K}}$ for each value of $\mathbf{K}$ used; the sum over $\mathbf{K}$'s can be carried out before making the more tedious sum over $\mathbf{H}$'s.

In the above, if $\mathbf{K}$ is not an even-order vector, $\mathbf{K}/2$ and the $\mathbf{H}$'s cannot be ordinary reciprocal-lattice vectors, but will be 'half-odd-order' vectors. But it can be shown that if one uses $\mathbf{K}$'s some of which are even and some odd, the sums of the $P_{\mathbf{K}}$'s will produce a unit cell doubled in all directions, containing one double-sized centrosymmetric unit and which will be just the Fourier synthesis of the crystal with atoms replaced by their corresponding Patterson peaks. This involvement of half-odd-order vectors is a matter of interest in connection with another recent note by Sayre (1952) regarding such vectors and a theorem due to Shannon.

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References

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