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Comments on probability distributions for interatomic vectors and atomic coordinates.

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Recent papers by Hauptman and Karle (Hauptman & Karle, 1952; Karle & Hauptman, 1954; hereafter referred to as I, II respectively) have described a probability approach to the determination of interatomic vectors and atomic coordinates. The purpose of the present note is to point out that the principal results of I and II are essentially equivalent to familiar Patterson and Fourier methods.

By I(58), the probability distribution of interatomic vectors between atoms of the ith and jth kinds is

$$P(x,y,z) = K_3 \prod_{h,k,l} \frac{\exp\left(\frac{R^2_{hkl}}{\sigma_2}\frac{B_{ij}\cos 2\pi(hx+ky+lz)}{1+B_{ij}\cos 2\pi(hx+ky+lz)}\right)}{1+B_{ij}\cos 2\pi(hx+ky+lz)}.$$

In any practical case $B_{ij} = 2f_if_j/\sigma_2 < 1$ (e.g. for 20 like atoms in the unit cell $B_{ij} = \frac{1}{10}$). It is thus possible to expand $\log P(x,y,z)$ in powers of B_{ij}, whence

$$\log P(x,y,z) = \log K_3 + \sum_{n=1}^{\infty}(-1)^{n-1}\sum_{h,k,l}\left(\frac{R^2_{hkl}}{\sigma_2}-\frac{1}{n}\right)B^n_{ij}\cos^n 2\pi\mathbf{h}\cdot\mathbf{x}\,, \quad (1)$$

where $\mathbf{h}\cdot\mathbf{x} = hx+ky+lz$. When the scattering factors f_i can be written $f_i = Z_i\hat{f}$, for all i, where Z_i is independent of h, k, l, B_{ij} is independent of h, k, l; in the general case, B_{ij}, in its dependence on h, k, l, acts much as a small temperature factor. Treating the former case, for simplicity,

$$\log P(x,y,z) - \log K_3 = \sum_{n=1}^{\infty}(-1)^{n-1}B^n_{ij}\sum_{h,k,l}\left(\frac{R^2_{hkl}}{\sigma_2}-\frac{1}{n}\right)\cos^n 2\pi\mathbf{h}\cdot\mathbf{x}\,. \quad (2)$$

When $n = 1$ the term in the r.h.s. is

$$B_{ij}\sum_{h,k,l}\left(\frac{R^2_{h,k,l}}{\sigma_2}-1\right)\cos 2\pi\mathbf{h}\cdot\mathbf{x}\,, \quad (3)$$

a 'sharpened' Patterson function with origin peak removed and scaled by the factor B_{ij}. The Patterson in (3) is then 'corrected' by other distributions scaled by factors B^2_{ij}, B^3_{ij}, etc. For $B_{ij} \sim \frac{1}{10}$ only the first two corrections need be considered. That for $n = 2$ is

$$-B^2_{ij}\sum_{h,k,l}\left(\frac{R^2_{h,k,l}}{\sigma_2}-\frac{1}{2}\right)\cos^2 2\pi\mathbf{h}\cdot\mathbf{x}\,. \quad (4)$$

The expression (4) can be written

$$-\tfrac{1}{2}B^2_{ij}\sum_{h,k,l}\left(\frac{R^2_{h,k,l}}{\sigma_2}-\frac{1}{2}\right)(1+\cos 2\pi\mathbf{h}\cdot 2\mathbf{x})\,, \quad (5)$$

and (4) is thus a sharpened Patterson on half the scale (in x, y, z) of (3), with an origin peak halved in height, together with a constant term

$$-\tfrac{1}{2}B^2_{ij}\sum_{h,k,l}\left(\frac{R^2_{h,k,l}}{\sigma_2}-\frac{1}{2}\right). \quad (6)$$

The Patterson in (4) is of order $B_{ij}/2$ and negative with respect to that in (3). Similarly the term for $n = 3$ yields a Patterson on one-third the scale (in x, y, z) with an origin peak of two-thirds height, a constant term and a correction

$$\tfrac{3}{4}B^3_{ij}\sum_{h,k,l}\left(\frac{R^2_{h,k,l}}{\sigma_2}-\frac{1}{3}\right)\cos 2\pi\mathbf{h}\cdot\mathbf{x} \quad (7)$$

to be added to (3). The nature and size of these corrections to (3) show that $\log P(x,y,z)$ is simply a sharpened Patterson with origin peak almost absent, together with minor peaks not ordinarily coinciding with those for interatomic vectors. Since the maxima of $\exp\{f(x)\}$ coincide with those of $f(x)$, the maxima of $P(x,y,z)$ coincide with the maxima of a sharpened Patterson. For a finite set of (h, k, l) a sharpened Patterson peak has finite width, the width for convenience being taken between first zeros on either side. Defining peak width in $P(x,y,z)$ as the width between first values of $P(x,y,z)$, on either side of a peak, equal to unity, $P(x,y,z)$ has peak widths identical with those of a sharpened Patterson of like terms, except in so far as the widths in $P(x,y,z)$ are modified by a slight dependence of B_{ij} on h, k, l or by chance coincidences between the Pattersons on scales (in x, y, z) 1, $\frac{1}{2}$, $\frac{1}{3}$, etc. Thus $P(x,y,z)$ shows no improvement in resolving power over the sharpened Patterson.*

Paper I suggests, however, that the choice of B_{ij} determines I(58) as a distribution for vectors between atoms of the kind i and the kind j only, so that only a few of the whole set of interatomic vectors appear in any particular distribution. That this is not the case is apparent, once the relationship between I(58) and the Patterson is realized. Even when B_{ij} is very different from B_{pq}, say, all Patterson peaks appear in either distribution. The methods suggested in the 'Additional procedures for analysis' of I are then simply the superposition of two or more Pattersons relatively displaced by vector distances. The resulting distributions have many maxima of which the most prominent result from peak coincidences. For example, the suggested method for resolving the ambiguity between (x, y, z) and $(1-x, 1-y, 1-z)$ to obtain a consistent point set, appears to correspond closely to the superposition method of Clastre & Gay (1950*a*, *b*).

II(5) gives the probability distribution for the magnitudes of structure factors, given the coordinates of atom 1, for a centrosymmetric crystal,

$$P(A_{\mathbf{h}_1},\ldots,A_{\mathbf{h}_m}) = K\exp\left(-\sum_{\mu=1}^{m}\frac{(A_{\mathbf{h}_\mu}-f_{1\mathbf{h}_\mu}\xi_{1\mathbf{h}_\mu})^2}{2m_2\sum_{j=2}^{N/n}f^2_{j\mathbf{h}_\mu}}\right). \quad (8)$$

Reference to II(2) then yields the distribution of the

* An attempt to improve on the resolution by including terms other than the first in the probability distribution, I(10), merely gave further terms of order B^2_{ij}, B^3_{ij}, etc.

$\xi_{1\mathbf{h}_\mu}$ as II(5). Let this distribution be Q. Q may be interpreted as a function of x, y, z giving the most probable coordinates of atom 1, and

$$\log Q = \log K - \sum_{\mu=1}^{m} \frac{(A_{\mathbf{h}_\mu} - f_{1\mathbf{h}_\mu}\xi_{1\mathbf{h}_\mu})^2}{2m_2 \sum_{j=2}^{N/n} f_{j\mathbf{h}_\mu}^2} . \quad (9)$$

Put

$$m_2 \sum_{j=2}^{N/n} f_{j\mathbf{h}_\mu}^2 = \tau_{\mathbf{h}_\mu} ,$$

then

$$\log \frac{Q}{K} = -\sum_{\mu=1}^{m} \left[\frac{A_{\mathbf{h}_\mu}^2}{2\tau_{\mathbf{h}_\mu}} - \frac{2f_{1\mathbf{h}_\mu} A_{\mathbf{h}_\mu} \xi_{1\mathbf{h}_\mu}}{2\tau_{\mathbf{h}_\mu}} + \frac{f_{1\mathbf{h}_\mu}^2 \xi_{1\mathbf{h}_\mu}^2}{2\tau_{\mathbf{h}_\mu}} \right] . \quad (10)$$

The first term on the r.h.s. is a constant; in the space group $P\bar{1}$, the third becomes

$$-\sum_{\mu=1}^{m} \frac{f_{1\mathbf{h}_\mu}^2}{2\tau_{\mathbf{h}_\mu}} (2 + \xi_{1,2\mathbf{h}_\mu}) ,$$

which has large negative peaks at 0 or $\frac{1}{2}$; and the second term is a Fourier series sharpened by the factors $f_{1\mathbf{h}_\mu}/\tau_{\mathbf{h}_\mu}$. The distribution obtained by a probability approach when the phases of the structure factors are known is thus very similar to a sharpened Fourier series.

When the signs of the $A_{\mathbf{h}_\mu}$ are not known, Karle & Hauptman suggest the use of II(8),

$$\frac{Q}{K} = \prod_{\mu=1}^{m} \left\{ \exp\left(\frac{-(|A_{\mathbf{h}_\mu}| - f_{1\mathbf{h}_\mu}\xi_{1\mathbf{h}_\mu})^2}{2\tau_{\mathbf{h}_\mu}} \right) + \exp\left(\frac{-(|A_{\mathbf{h}_\mu}| + f_{1\mathbf{h}_\mu}\xi_{1\mathbf{h}_\mu})^2}{2\tau_{\mathbf{h}_\mu}} \right) \right\}$$

$$= \prod_{\mu=1}^{m} 2 \exp\left(\frac{-(|A_{\mathbf{h}_\mu}|^2 + f_{1\mathbf{h}_\mu}^2 \xi_{1\mathbf{h}_\mu}^2)}{2\tau_{\mathbf{h}_\mu}} \right) \times \cosh\left(\frac{f_{1\mathbf{h}_\mu} |A_{\mathbf{h}_\mu}| \xi_{1\mathbf{h}_\mu}}{\tau_{\mathbf{h}_\mu}} \right) . \quad (11)$$

Reference above shows that only terms in $A_{\mathbf{h}_\mu}\xi_{1\mathbf{h}_\mu}$ are important, so that the structure-dependent part of $\log(Q/K)$ is

$$\sum_{\mu=1}^{m} \log\cosh\left(\frac{f_{1\mathbf{h}_\mu} |A_{\mathbf{h}_\mu}| \xi_{1\mathbf{h}_\mu}}{\tau_{\mathbf{h}_\mu}} \right) . \quad (12)$$

Using the series expansion of $\log\cosh x$ and interchanging the order of summations, this term becomes

$$\sum_{s=1}^{\infty} \frac{2^{2s}}{2s} \frac{(2^{2s}-1)}{(2s)!} B_{2s} \sum_{\mu=1}^{m} \left(\frac{f_{1\mathbf{h}_\mu} |A_{\mathbf{h}_\mu}| \xi_{1\mathbf{h}_\mu}}{\tau_{\mathbf{h}_\mu}} \right)^{2s} , \quad (13)$$

where the B_{2s} are Bernouilli numbers. Since (13) contains only even powers of $|A_{\mathbf{h}_\mu}|$ it must be of the Patterson type. Indeed the corrections obtained for $s = 2, 3$, etc., to the Patterson obtained by taking $s = 1$, are even less significant than those made by (4) and (7) to (3), since with all like atoms (13) becomes, in $P\bar{1}$,

$$\sum_{s=1}^{\infty} \frac{2^{2s}}{2s} \frac{(2^{2s}-1)}{(2s)!} \frac{B_{2s}}{(N-2)^s} \sum_{\mu=1}^{m} \frac{|A_{\mathbf{h}_\mu}|^2}{\tau_{\mathbf{h}_\mu}} (2 + \xi_{1,2\mathbf{h}_\mu}) \Big\}^s , \quad (14)$$

the successive coefficients for the summations over μ being approximately $1/(2N)$, $-1/(12N^2)$, $1/(45N^3)$, etc. for $s = 1, 2, 3$ etc. Thus the probability distribution for coordinates when the structure-factor signs are not known is essentially a sharpened Patterson, which is on half scale in x, y, z, and thus has some peaks coincident with atomic positions.

Similar discussions can be given for the distributions in II for non-centrosymmetric crystals. If the position of one atom is arbitrarily fixed and the phase angles are assumed unknown, the resulting Patterson-like distribution is of normal scale in x, y, z with the fixed atom as origin; thus again some peaks coincide with the atomic positions.

It may be remarked that II(5) can be written down directly by appealing to the central limit theorem (Cramér, 1946) on the assumption of the independence of the $\xi_{i\mathbf{h}_\mu}$, $\mu = 1, \ldots, m$, for each set i. The assumption of independence is clearly equivalent to taking the first term alone in the series referred to in II. It does not seem possible, however, to obtain better than the sharpened Patterson if this assumption is made.

References

Clastre, J. & Gay, R. (1950*a*). *C. R. Acad. Sci., Paris*, **230**, 1976.

Clastre, J. & Gay, R. (1950*b*). *J. Phys. Radium*, **11**, 75.

Cramér, H. (1946). *Mathematical Methods of Statistics*. Princeton: University Press.

Hauptman, H. & Karle, J. (1952). *Acta Cryst.* **5**, 48.

Karle, J. & Hauptman, H. (1954). *Acta Cryst.* **7**, 375.

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Conversion of Norelco fluorescent spectrograph to an X-ray diffractometer.

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The North American Philips Fluorescent Attachment consists of an OEG-50-Machlett tungsten tube, which is run at 50 kV., 50 mA. and sprays X-rays on to a sample. An elemental analysis of the sample is made by analyzing the characteristic K and L fluorescent lines by means of a single crystal and a goniometer.

By utilizing a pure element such as cobalt one obtains the characteristic $K\alpha$ and $K\beta$ lines practically free of continuous background. A filter will essentially eliminate the $K\beta$. To make use of this plane source of monochromatic radiation for powder diffraction one must create a focal spot so as to utilize the geometrical focusing conditions necessary for high resolution. This is done by use of a slit between the plane source of fluorescent radiation and the powder specimen. In addition, the plane source of Co radiation is tilted upward so as to obtain