between these two atoms is over 5 Å. The iodine atom, however, is closely associated with five oxygen atoms, two of which belong to the water molecules. They were all found at distances varying from 3·52 to 3·62 Å, and are shown by dotted lines in Fig. 1.

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# Remarks on a Non-Statistical Approach to the *F* Phase Problem

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The non-negativity criterion is that the volume $\Lambda(\varrho).d\varrho$, for which the expected $\varrho$ lies in the interval $(\varrho, \varrho+d\varrho)$, shall vanish for $\varrho<0$. However, providing the overlap is negligible, the expected volume $\Lambda(\varrho)$ within one cell is known for all $\varrho$ values. It is possible to set up general $\Lambda$ criteria, since $\Lambda$ can be studied for arbitrary phase angles. Some preliminary examples of the use of the $\Lambda$ concept are given and the results compared with known results.

The first attempts to solve the phase problem—among which the Harker & Kasper (1948) and Sayre (1952) methods are outstanding—were non-statistical in nature. Since then, starting with Zachariasen (1952), interest has been focused more and more upon statistical methods (e.g., Klug (1958)).

A disadvantage of the statistical approach is that it often lacks physical perspicuity, and it is often difficult to visualize how much of the experimental and general information has really been used to advantage. The hypotheses are often difficult to assess and sometimes even to accept. For instance, of fundamental interest in most statistical attempts to solve the sign problem is the probability distribution $\mathscr{P}(E)$ (and analogous joint probability distributions). The functions $\mathscr{P}$ are usually derived on the assumption that the atomic parameters are random variables subject only to symmetry relations. However, the *a priori* probability of a certain value $\mathbf{r}_{(n)}$ may range from zero to unity; in fact, the probability of any one atomic-coordinate value is a function of all other coordinates (cf. e.g., Bertaut (1955)). However elaborate the assumptions made about interatomic vectors, *some* sort of *a priori* assumption must be made. In the following paper (Löfgren, 1961) it will be shown that these assumptions critically influence certain expressions that are therefore unpredictable.

Instead of *statistically* deriving the properties of reciprocal-space functions ($E$, $|E|^2$ etc.), one may start with direct-space functions, such as ${}_g\varrho$ (for notations, see Löfgren (1960)), the Patterson function, etc. From this starting point, relations which have either been arrived at *statistically* or are original can be derived *exactly*. (Several such examples do exist, furnished notably by Cochran, e. g. (1958).) We shall restrict ourselves here to a certain property of the ${}_g\varrho$ function and give examples of its use.

A direct space equivalent of $\mathscr{P}(E)$ is $V^{-1}\Lambda({}_g\varrho)$. $\Lambda({}_g\varrho)d_g\varrho$ is defined as the volume (within one cell) for which ${}_g\varrho$ (which is assumed to be real) falls in the interval $({}_g\varrho, {}_g\varrho+d_g\varrho)$. The $\Lambda$ expected for *correct* phases is evidently not a function of atomic positions, providing that overlap is negligible, and it is then predictable if the cell contents are known. In fact, one then has

$$\Lambda=\sum_{n=1}^{N}\Lambda_{(n)}\,, \tag{1}$$

where $\Lambda_{(n)}$ is the atomic contribution.

In order to study $\Lambda(\alpha)$ for *arbitrary* phases, it can be transformed, e.g., according to:

$$\Psi_\nu(\alpha)=\int_{-\infty}^{\infty}\Lambda\,.\,{}_g\varrho^\nu d_g\varrho=\oint {}_g\varrho^\nu dv(\mathbf{r})={}_gF^{(\nu)}(0)\;, \tag{2}$$

where

$${}_gF^{(\nu)}(\mathbf{h})=\frac{1}{V^{\nu-1}}\sum_{\mathbf{h}_1+\mathbf{h}_2+\ldots+\mathbf{h}_\nu=\mathbf{h}}{}_gF(\mathbf{h}_1){}_gF(\mathbf{h}_2)\ldots{}_gF(\mathbf{h}_\nu)\;.$$

For *correct* phases and a completely resolved ${}_g\varrho^\nu(\mathbf{r})$, one can postulate the value (use (1)):

$$\begin{aligned}\Psi_{\nu.\,\mathrm{post.}}&=\int_{-\infty}^{\infty}\Lambda\,.\,{}_g\varrho^\nu d_g\varrho=\sum_{n=1}^{N}\int_{-\infty}^{\infty}\Lambda_{(n)}{}_g\varrho^\nu d_g\varrho\\&=\sum_{n=1}^{N}\oint {}_g\varrho^\nu_{(n)}(\mathbf{r})dv(\mathbf{r})=\sum_{n=1}^{N}{}_gf^{(\nu)}_{(n)}(0)\;,\end{aligned} \tag{3}$$

where ${}_gf^{(\nu)}_{(n)}(0)$ is analogous to ${}_gF^{(\nu)}(0)$.

Of special practical interest is $\nu=3$ (cf. Cochran (1952), Cochran & Douglas (1955), (1957), and Löfgren (1960)).

Equations (2) and (3) are easily generalized by substituting a polynomial in ${}_g\varrho$ for ${}_g\varrho^\nu$ (cf. Woolfson (1958*a*, *b*)). For reasons to be made clear elsewhere, the following function is of fundamental interest:

$$\begin{aligned}\Psi(\alpha)&=\oint\left\{\sum_{\nu=1}^{m}A_\nu * {}_g\varrho^\nu\right\}^2 dv(\mathbf{r})\\&=(1/V)\sum_{\mathbf{h}}\left|\sum_{\nu=1}^{m}a_\nu(\mathbf{h})\,.\,{}_gF^{(\nu)}(\mathbf{h})\right|^2,\end{aligned} \tag{4}$$

where, by definition,

$$A_\nu(\mathbf{r})=(1/V)\sum_{\mathbf{h}}a_\nu(\mathbf{h})\,.\exp\left[-2\pi i\mathbf{h}\,.\,\mathbf{r}\right]\,,$$

($a_\nu(\mathbf{h})$ being arbitrary real functions of $\mathbf{h}$ or constants) and $*$ indicates convolution. Specifically for constant $a_\nu$'s, the operation $A_\nu *$ is equivalent to $a_\nu\times$ and (4) is a straightforward generalization of (2). (The integral

$$\int_{-\infty}^{\infty}\Lambda\left\{\sum_{\nu=1}^{m}A_\nu * {}_g\varrho^\nu\right\}^2 d_g\varrho\;,$$

analogous to the second member of (2) can be interpreted as an alternative representation of $\Psi(\alpha)$—equation (4)—even for $a_\nu$'s dependent on $\mathbf{h}$, but this interpretation is not essential to the present context.)

For correct phases and negligible overlap, (4) can be evaluated according to:

$$\begin{aligned}\Psi_{\mathrm{post.}}&=\oint\left\{\sum_{\nu=1}^{m}A_\nu * {}_g\varrho^\nu\right\}^2 dv(\mathbf{r})\\&=\sum_{n=1}^{N}\oint\left\{\sum_{\nu=1}^{m}A_\nu * {}_g\varrho^\nu_{(n)}\right\}^2 dv(\mathbf{r})\\&=(1/V)\sum_{n=1}^{N}\sum_{\mathbf{h}}\left\{\sum_{\nu=1}^{m}a_\nu\,.\,{}_gf^{(\nu)}_{(n)}(\mathbf{h})\right\}^2.\end{aligned} \tag{5}$$

It can be proved that $\Psi_{\mathrm{post.}}(a_1, a_2, \ldots, a_m)$ has a non-trivial ($\Sigma a_\nu^2 \neq 0$) minimum if, and only if, the system

$$\sum_{\nu=1}^{m}a_\nu\,.\,{}_gf^{(\nu)}_{(n)}(\mathbf{h})=0 \quad (n=1, 2, \ldots, N) \tag{6}$$

has a non-trivial solution. This system is solvable if the number of kinds of atoms, $M\leq m-1$. The resulting minimum must be zero, cf. (5) and (6). $\Psi(\alpha)$ then assumes an absolute minimum in $\alpha$ space, for correct $\alpha$'s.

If $M>m-1$ it is still possible to minimize $\Psi_{\mathrm{post.}}$ for each $\mathbf{h}$, e.g., after fixing any one $a_\nu$. If we allow $m=2$, and fix $a_1$ and assume the atoms of Cochran & Woolfson (1955), we find the following, partly using their symbols:

$$\left\{\begin{aligned}&\Psi(\alpha)=(1/V)\sum_{\mathbf{h}}\left|U(\mathbf{h})-(\varepsilon_3/\varepsilon_4)\overline{U(\mathbf{h}')U(\mathbf{h}-\mathbf{h}')}^{\mathbf{h}'}\right|^2\\&\Psi_{\mathrm{post.}}=(1/V)\{[\varepsilon_2\varepsilon_4-\varepsilon_3^2]/\varepsilon_4\}\sum_{\mathbf{h}}1\;,\end{aligned}\right. \tag{7}$$

where $\sum_{\mathbf{h}}1$ is the number of $\mathbf{h}$'s summed over. Similarly fixing $a_2$:

$$\left\{\begin{aligned}&\Psi(\alpha)=(1/V)\sum_{\mathbf{h}}\left|-(\varepsilon_3/\varepsilon_2)U(\mathbf{h})+\overline{U(\mathbf{h}')U(\mathbf{h}-\mathbf{h}')}^{\mathbf{h}'}\right|^2\\&\Psi_{\mathrm{post.}}=(1/V)\{[\varepsilon_2\varepsilon_4-\varepsilon_3^2]/\varepsilon_2\}\sum_{\mathbf{h}}1\;.\end{aligned}\right. \tag{8}$$

Equations (7) and (8) should be compared with the results of Cochran (1955), § 4. These results ((7) and (8)) are not valid if, e.g., $\mathbf{h}$'s with large $|U|$'s are selected which would imply an unresolved structure. It is easily realized (apply Wilson's (1949) statistics to the 'intensities' $|\Sigma a_\nu\,.\,{}_gF^{(\nu)}(\mathbf{h})|^2$) that they might be approximately true, e.g., for $\mathbf{h}$'s in an $|\mathbf{h}|$ interval.

Equations (2) and (3), (4) and (5) are susceptible to systematic development (especially for partial series) and simplification to be given elsewhere. The $\Lambda$ concept will make it clear under which circumstances the $\Psi(\alpha)$ minimum is unique and occurring for $\Lambda=\Sigma\Lambda_{(n)}$.

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# A Non-Statistical Derivation of some Intensity Laws. The Unpredictability of $\mathscr{P}(E)$, $N(z)$ etc.

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The variance criterion, $\langle (I-\Sigma)^2\rangle$, is reconsidered in a slightly modified and generalized form. The approach is in terms of the Patterson function and permits a physical visualization of the criterion. The result is in agreement with standard statistical results in certain space groups only and with special assumptions.

It is maintained that because fundamental statistical quantities like $\mathscr{P}(E)$ critically depend on the unpredictable overlap in high order $\varrho$ self-convolutes, they are quite generally useless.

(A summary of conclusions is given at the end of this article.)

As was stressed by Löfgren (1961), there is an advantage of avoiding probability distributions such as $\mathscr{P}(|{}_gF|)$ in deriving laws for reciprocal-space functions (for ${}_gF(\mathbf{h})$ see Löfgren (1960). We assume that ${}_gf(\mathbf{h})$, corresponding to ${}_gF(\mathbf{h})$ for correct phases, is such that ${}_gf(\mathbf{h})={}_gf(-\mathbf{h})$). Direct-space functions should be taken, instead, as a starting-point. We shall thus study some aspects of the Patterson function, ${}_gP$.

We start with:

$$\oint \{{}_gP(\mathbf{r})-C\,{}_gP_{\text{origin}}(\mathbf{r})\}^2 dv(\mathbf{r}) = (1/V)\sum_{\mathbf{h}}\{|{}_gF(\mathbf{h})|^2 - C.\sum_{n=1}^{N}{}_gf^2_{(n)}(\mathbf{h})\}^2, \qquad (1)$$

where (cf. Lipson & Cochran (1953), p. 152)

$${}_gP(\mathbf{r}) = \sum_{n,m=1}^{N} {}_gP_{(n,m)}(\mathbf{r}-(\mathbf{r}_{(n)}-\mathbf{r}_{(m)}))\,, \qquad (2)$$

with:

$${}_gP_{(n,m)}(\mathbf{r}) = (1/V)\sum_{\mathbf{h}} {}_gf_{(n)}(\mathbf{h})\,.\,{}_gf_{(m)}(\mathbf{h})\,.\exp\,[-2\pi i\mathbf{h}.\mathbf{r}]\,, \qquad (3)$$

and, further:

$${}_gP_{\text{origin}}(\mathbf{r}) = \sum_{n=1}^{N} {}_gP_{(n,n)}(\mathbf{r})\,, \qquad (4)$$

and $C$ is an arbitrary constant.

Let us suppose that for certain $n-m$ pairs,

$$\mathbf{r}_{(n)}-\mathbf{r}_{(m)} = \text{constant vector} = \mathbf{r}^{(\lambda)}; \qquad (5)$$

i.e., $\mathbf{r}^{(\lambda)}$ are the different Patterson peak positions.

If we further suppose that the sums

$$\sum_{\substack{n,m\\ \mathbf{r}^{(\lambda)}=\text{constant}\neq 0}} {}_gP_{(n,m)}(\mathbf{r}-\mathbf{r}^{(\lambda)})$$

are completely resolved for different $\lambda$ and completely resolved from $(1-C)\,.\,{}_gP_{\text{origin}}(\mathbf{r})$, we have, in the same manner as in Löfgren (1961):

$$\begin{aligned}\oint \{{}_gP(\mathbf{r})-C\,.\,{}_gP_{\text{origin}}(\mathbf{r})\}^2 dv(\mathbf{r}) &= \oint (1-C)^2\,{}_gP^2_{\text{origin}}(\mathbf{r})\,dv(\mathbf{r}) \\ &\quad + \sum_{\lambda}\oint \{\sum_{\substack{n,m\\ \mathbf{r}^{(\lambda)}=\text{constant}\neq 0}} {}_gP_{(n,m)}(\mathbf{r})\}^2 dv(\mathbf{r}) \\ &= (1-C)^2(1/V)\sum_{\mathbf{h}}\{\sum_{n}{}_gf^2_{(n)}(\mathbf{h})\}^2 \\ &\quad + (1/V)\sum_{\lambda}\sum_{\mathbf{h}}\{\sum_{\substack{n,m\\ \mathbf{r}^{(\lambda)}=\text{constant}\neq 0}} {}_gf_{(n)}(\mathbf{h})\,.\,{}_gf_{(m)}(\mathbf{h})\}^2. \end{aligned} \qquad (6)$$

If we assume for example that the only causes of