$$+R_{12}R_{13}R_{23}R_{45}^2 \cos(\Phi_{12}+\Phi_{13}+\Phi_{23}+2\Phi_{45})\left(\frac{\sigma_5}{\sigma_2^{5/2}}-\frac{6\sigma_3\sigma_4}{\sigma_2^{7/2}}+\frac{6\sigma_3^3}{\sigma_2^{9/2}}\right)+\ldots \text{ 9 terms}$$

$$+R_1R_2R_{34}R_{13}R_{24}\cos(\Phi_1+\Phi_2+\Phi_{34}-\Phi_{13}-\Phi_{24})\left(\frac{2\sigma_5}{\sigma_2^{5/2}}-\frac{12\sigma_3\sigma_4}{\sigma_2^{7/2}}+\frac{12\sigma_3^3}{\sigma_2^{9/2}}\right)+\ldots \text{ 59 terms}$$

$$+R_1^2R_{12}R_{13}R_{23}\cos(2\Phi_1+\Phi_{23}-\Phi_{12}-\Phi_{13})\left(\frac{\sigma_5}{\sigma_2^{5/2}}-\frac{6\sigma_3\sigma_4}{\sigma_2^{7/2}}+\frac{6\sigma_3^3}{\sigma_2^{9/2}}\right)+\ldots \text{ 29 terms}$$

$$+R_1R_{12}R_{13}R_{24}R_{25}\cos(\Phi_1+\Phi_{13}+\Phi_{24}+\Phi_{25}-\Phi_{12})\left(\frac{2\sigma_5}{\sigma_2^{5/2}}-\frac{10\sigma_3\sigma_4}{\sigma_2^{7/2}}+\frac{8\sigma_3^3}{\sigma_2^{9/2}}\right)+\ldots \text{ 59 terms.}$$

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Quintets: the Probabilistic Theory of the Structure Invariant $\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}+\varphi_{\mathbf{n}}$*

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(*Received* 23 *June* 1976; *accepted* 21 *January* 1977)

It is assumed that a crystal structure in $P1$ is fixed and that the 15 non-negative numbers $R_1, R_2, R_3, R_4, R_5; R_{12}, R_{13}, R_{14}, R_{15}, R_{23}, R_{24}, R_{25}, R_{34}, R_{35}, R_{45}$ are also specified. The random variables (vectors) **h**, **k**, **l**, **m**, **n** are assumed to be uniformly and independently distributed in the regions of reciprocal space defined by

$$|E_{\mathbf{h}}|=R_1,\ |E_{\mathbf{k}}|=R_2,\ |E_{\mathbf{l}}|=R_3,\ |E_{\mathbf{m}}|=R_4,\ |E_{\mathbf{n}}|=R_5; \tag{1}$$

$$|E_{\mathbf{h+k}}|=R_{12},\ |E_{\mathbf{h+l}}|=R_{13},\ |E_{\mathbf{h+m}}|=R_{14},\ |E_{\mathbf{h+n}}|=R_{15},\ |E_{\mathbf{k+l}}|=R_{23},$$
$$|E_{\mathbf{k+m}}|=R_{24},\ |E_{\mathbf{k+n}}|=R_{25},\ |E_{\mathbf{l+m}}|=R_{34},\ |E_{\mathbf{l+n}}|=R_{35},\ |E_{\mathbf{m+n}}|=R_{45}: \tag{2}$$

and

$$\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}+\mathbf{n}=0\,. \tag{3}$$

Then the structure invariant $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}+\varphi_{\mathbf{n}}$, as a function of the primitive random variables **h**, **k**, **l**, **m**, **n**, is itself a random variable, and its conditional probability distribution, given (1) and (2), is derived. The distribution leads to estimates for $\cos\varphi$ in terms of the 15 magnitudes (1) and (2).

1. The probabilistic background

Suppose that a crystal structure consisting of N atoms (not necessarily identical) per unit cell in $P1$ is fixed and that the 15 non-negative numbers $R_1, R_2, R_3, R_4, R_5; R_{12}, R_{13}, R_{14}, R_{15}, R_{23}, R_{24}, R_{25}, R_{34}, R_{35}, R_{45}$ are also specified. Define the fivefold Cartesian product $W\times W\times W\times W\times W$ of reciprocal space W to be the collection of all ordered quintuples (**h**, **k**, **l**, **m**, **n**) where **h**, **k**, **l**, **m**, **n** are reciprocal vectors. Suppose next that the ordered quintuple of reciprocal vectors (**h**, **k**, **l**, **m**, **n**) is a random variable which is uniformly distributed over the subset of $W\times W\times W\times W\times W$ defined by

$$|E_{\mathbf{h}}|=R_1,\ |E_{\mathbf{k}}|=R_2,\ |E_{\mathbf{l}}|=R_3,\ |E_{\mathbf{m}}|=R_4,\ |E_{\mathbf{n}}|=R_5; \tag{1.1}$$

$$|E_{\mathbf{h+k}}|=R_{12},\ |E_{\mathbf{h+l}}|=R_{13},\ |E_{\mathbf{h+m}}|=R_{14},\ |E_{\mathbf{h+n}}|=R_{15},$$
$$|E_{\mathbf{k+l}}|=R_{23},\ |E_{\mathbf{k+m}}|=R_{24},\ |E_{\mathbf{k+n}}|=R_{25},\ |E_{\mathbf{l+m}}|=R_{34},$$
$$|E_{\mathbf{l+n}}|=R_{35},\ |E_{\mathbf{m+n}}|=R_{45}; \tag{1.2}$$

and

$$\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}+\mathbf{n}=0\,. \tag{1.3}$$

* Presented at the Intercongress Symposium: Direct Methods in Crystallography, August 3–6, 1976, Buffalo, New York, Abstract PB13; and at the ACA Meeting, August 9–12, 1976, Evanston, Ill., Abstract SD3.

It follows that the random variables **h**, **k**, **l**, **m**, **n**, the components of the ordered quintuple (**h**, **k**, **l**, **m**, **n**), are not independently distributed in reciprocal space. In order to ensure that the domain of the random variable (**h**, **k**, **l**, **m**, **n**) be non-vacuous, it is necessary to interpret the exact equality $|E_{\mathbf{h}}|=R_1$ of (1.1), for example, as an inequality, $R_1\le|E_{\mathbf{h}}|\le R_1+dR_1$, where dR_1 is a small positive quantity, *etc.* Then the structure invariant

$$\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}+\varphi_{\mathbf{n}}\,, \tag{1.4}$$

as a function of the primitive random variables **h**, **k**, **l**, **m**, **n**, is itself a random variable, and its conditional probability distribution, given the 15 magnitudes (1.1) and (1.2), the major result of this paper, is derived. To this end it is necessary first to obtain the joint conditional probability distribution of the five phases $\varphi_{\mathbf{h}}$, $\varphi_{\mathbf{k}}$, $\varphi_{\mathbf{l}}$, $\varphi_{\mathbf{m}}$, $\varphi_{\mathbf{n}}$, given the 15 magnitudes (1.1) and (1.2).

Finally, the following usual definition is made

$$\sigma_n=\sum_{j=1}^{N} f_j^n\,, \tag{1.5}$$

where f_j is the zero-angle atomic scattering factor for the atom labeled j. In the X-ray diffraction case the f_j are equal to the atomic numbers Z_j and are therefore all positive; in the neutron diffraction case some of the f_j may be negative.

2. The joint conditional probability distribution of the five phases $\varphi_{\mathbf{h}}$, $\varphi_{\mathbf{k}}$, $\varphi_{\mathbf{l}}$, $\varphi_{\mathbf{m}}$, $\varphi_{\mathbf{n}}$, given the 15 magnitudes $|E_{\mathbf{h}}|$, $|E_{\mathbf{k}}|$, $|E_{\mathbf{l}}|$, $|E_{\mathbf{m}}|$, $|E_{\mathbf{n}}|$; $|E_{\mathbf{h+k}}|$, $|E_{\mathbf{h+l}}|$, $|E_{\mathbf{h+m}}|$, $|E_{\mathbf{h+n}}|$, $|E_{\mathbf{k+l}}|$, $|E_{\mathbf{k+m}}|$, $|E_{\mathbf{k+n}}|$, $|E_{\mathbf{l+m}}|$, $|E_{\mathbf{l+n}}|$, $|E_{\mathbf{m+n}}|$

Under the hypotheses of § 1, denote by

$$P_{5|15}=P(\Phi_1,\Phi_2,\Phi_3,\Phi_4,\Phi_5|R_1,R_2,R_3,R_4,R_5;\; R_{12},R_{13},R_{14},R_{15},R_{23},R_{24},R_{25},R_{34},R_{35},R_{45}) \tag{2.1}$$

the joint conditional probability distribution of the five phases $\varphi_{\mathbf{h}}$, $\varphi_{\mathbf{k}}$, $\varphi_{\mathbf{l}}$, $\varphi_{\mathbf{m}}$, $\varphi_{\mathbf{n}}$, given the 15 magnitudes (1.1) and (1.2). Then $P_{5|15}$ is obtained from P_{15} [equation (3.3) of the previous paper, Fortier & Hauptman (1977)] by fixing the 15 magnitude variables R_1, R_2, ..., R_{45} of the latter in accordance with the scheme defined by (1.1) and (1.2), integrating P_{15} with respect to the ten phase variables Φ_{12}, Φ_{13}, ..., Φ_{45} from 0 to 2π, and multiplying the result by a suitable normalizing parameter:

$$P_{5|15}=\frac{1}{K}\int_0^{2\pi}\cdots\int_0^{2\pi}P_{15}d\Phi_{12}d\Phi_{13}d\Phi_{14}\ldots d\Phi_{45}\,. \tag{2.2}$$

As of now it has not been possible to carry out the tenfold integration (2.2) exactly. Furthermore, even if these integrations could be performed, it seems very likely that the resulting expression would be too intractable to be useful in the applications. For these reasons an approximation technique has been devised as follows: first the Taylor expansion of P_{15} is found. The tenfold integration (2.2) is then readily performed. Finally, by analogy with an earlier formula for the quartet structure invariant (Hauptman, 1975, 1976), a functional form for $P_{1|15}$ is assumed the Taylor expansion of which, correct to terms up to and including those of order $1/N^{3/2}$, agrees with that of (2.2). Thus, substituting the Taylor expansion of P_{15} [equation (3.3), Fortier & Hauptman (1977)] into (2.1) and carrying out the tenfold integration, one readily finds

$$\begin{aligned}P_{5|15}\simeq{}&\frac{1}{K}\exp\left[\frac{2}{\sigma_2^{9/2}}(15\sigma_3^3-10\sigma_2\sigma_3\sigma_4\right.\\&+\sigma_2^2\sigma_5)R_1R_2R_3R_4R_5\\&\left.\times\cos(\Phi_1+\Phi_2+\Phi_3+\Phi_4+\Phi_5)\right]\\&\times\left[1+\frac{\sigma_3^2}{\sigma_2^3}(R_1^2R_2^2R_{12}^2+9\text{ similar terms})\right.\\&+\frac{\sigma_3^2}{\sigma_2^3}(R_1^2R_{23}^2R_{45}^2+14\text{ similar terms})\\&-\frac{2\sigma_3}{\sigma_2^{9/2}}(3\sigma_3^2-\sigma_2\sigma_4)R_1R_2R_3R_4R_5(R_{12}^2+R_{13}^2\\&+R_{14}^2+R_{15}^2+R_{23}^2+R_{24}^2+R_{25}^2+R_{34}^2+R_{35}^2+R_{45}^2)\\&\times\cos(\Phi_1+\Phi_2+\Phi_3+\Phi_4+\Phi_5)\\&+\frac{2\sigma_3^3}{\sigma_2^{9/2}}R_1R_2R_3R_4R_5(R_{12}^2R_{34}^2+R_{12}^2R_{35}^2\\&+R_{12}^2R_{45}^2+R_{13}^2R_{24}^2+R_{13}^2R_{25}^2+R_{13}^2R_{45}^2\\&+R_{14}^2R_{23}^2+R_{14}^2R_{25}^2+R_{14}^2R_{35}^2+R_{15}^2R_{23}^2\\&+R_{15}^2R_{24}^2+R_{15}^2R_{34}^2+R_{23}^2R_{45}^2+R_{24}^2R_{35}^2\\&\left.+R_{25}^2R_{34}^2)\cos(\Phi_1+\Phi_2+\Phi_3+\Phi_4+\Phi_5)\right]\end{aligned} \tag{2.3}$$

which is the Taylor expansion of $P_{5|15}$ correct up to and including terms of order $1/N^{3/2}$, and K is a suitable normalizing parameter independent of Φ_1, ..., Φ_5. Although (2.3) is a good approximation to $P_{5|15}$ when the values of the ten parameters R_{12}, R_{13},... are small, this approximation is clearly not satisfactory when some of R_{12}, R_{13}, ... are large because (2.3) may then become substantially negative, which no well-behaved probability distribution can do. Employing the formula

$$x=\exp(\log x) \tag{2.4}$$

and expanding the logarithm of the right hand side of (2.3), one readily transforms (2.3) into pure exponential form

$$P_{5|15} \simeq \frac{1}{K} \exp\left\{\left[\frac{2\sigma_3^3}{\sigma_2^{9/2}} \sum_{15} R_{12}^2 R_{34}^2 - \frac{2\sigma_3}{\sigma_2^{9/2}}(3\sigma_3^2-\sigma_2\sigma_4)\sum_{10} R_{12}^2 + \frac{2}{\sigma_2^{9/2}}(15\sigma_3^3-10\sigma_2\sigma_3\sigma_4+\sigma_2^2\sigma_5)\right] \times R_1R_2R_3R_4R_5 \cos(\Phi_1+\Phi_2+\Phi_3+\Phi_4+\Phi_5)\right\} \quad (2.5)$$

correct to order $1/N^{3/2}$, where

$$\sum_{15} R_{12}^2R_{34}^2 = R_{12}^2R_{34}^2 + R_{12}^2R_{35}^2 + R_{12}^2R_{45}^2 + R_{13}^2R_{24}^2 + R_{13}^2R_{25}^2 + R_{13}^2R_{45}^2 + R_{14}^2R_{23}^2 + R_{14}^2R_{25}^2 + R_{14}^2R_{35}^2 + R_{15}^2R_{23}^2 + R_{15}^2R_{24}^2 + R_{15}^2R_{34}^2 + R_{23}^2R_{45}^2 + R_{24}^2R_{35}^2 + R_{25}^2R_{34}^2, \quad (2.6)$$

$$\sum_{10} R_{12}^2 = R_{12}^2 + R_{13}^2 + R_{14}^2 + R_{15}^2 + R_{23}^2 + R_{24}^2 + R_{25}^2 + R_{34}^2 + R_{35}^2 + R_{45}^2, \quad (2.7)$$

and K is a suitable normalizing parameter independent of $\Phi_1, \ldots, \Phi_5$. Although (2.5) is always positive and is therefore almost surely a better approximation to $P_{5|15}$ than is (2.3) for all values of the 15 parameters $R_1, R_2, \ldots R_{45}$, presumably a still better approximation is available as reference to the analogous distribution for quartets [Hauptman (1975) equation (2.5)] suggests. The earlier (quartet) distribution is in the exponential–Bessel-function form. It is therefore plausible to assume that the correct functional form for $P_{5|15}$ is an exponential multiplied by ten Bessel functions. Under this assumption, and with the employment of the relation,

$$I_0(z) \simeq \exp\left(\frac{z^2}{4}\right) \text{ if } z \text{ is small}, \quad (2.8)$$

the pure exponential form (2.5) for $P_{5|15}$ is readily transformed into the exponential–Bessel-function form:

$$P_{5|15} \simeq \frac{1}{K} \exp\left\{\left[\frac{2\sigma_3^3}{\sigma_2^{9/2}}(R_{12}^2R_{34}^2 + R_{12}^2R_{35}^2 + R_{12}^2R_{45}^2 + R_{13}^2R_{24}^2 + R_{13}^2R_{25}^2 + R_{13}^2R_{45}^2 + R_{14}^2R_{23}^2 + R_{14}^2R_{25}^2 + R_{14}^2R_{35}^2 + R_{15}^2R_{23}^2 + R_{15}^2R_{24}^2 + R_{15}^2R_{34}^2 + R_{23}^2R_{45}^2 + R_{24}^2R_{35}^2 + R_{25}^2R_{34}^2) + \frac{2}{\sigma_2^{9/2}}(15\sigma_3^3-10\sigma_2\sigma_3\sigma_4+\sigma_2^2\sigma_5)\right] \times R_1R_2R_3R_4R_5\cos(\Phi_1+\Phi_2+\Phi_3+\Phi_4+\Phi_5)\right\} \times \prod_{10} I_0(2R_{12}U_{12}) \quad (2.9)$$

where K is a suitable normalizing parameter,

$$U_{12} = \left[\frac{\sigma_3^2}{\sigma_2^3}R_1^2R_2^2 - \frac{2\sigma_3(3\sigma_3^2-\sigma_2\sigma_4)}{\sigma_2^{9/2}}R_1R_2R_3R_4R_5 \times \cos(\Phi_1+\Phi_2+\Phi_3+\Phi_4+\Phi_5) + \left(\frac{3\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}\right)^2 R_3^2R_4^2R_5^2\right]^{1/2}, \quad (2.10)$$

etc., and I_0 is the modified Bessel function. In a similar way the following alternative exponential–Bessel-function form for $P_{5|15}$ is derived.

$$P_{5|15} \simeq \frac{1}{K} \exp\left\{\frac{2}{\sigma_2^{9/2}}(15\sigma_3^3-10\sigma_2\sigma_3\sigma_4+\sigma_2^2\sigma_5) \times R_1R_2R_3R_4R_5\cos(\Phi_1+\Phi_2+\Phi_3+\Phi_4+\Phi_5)\right\} \times \prod_{10} I_0(2R_{12}V_{12}) \quad (2.11)$$

where again K is a suitable normalizing parameter and

$$V_{12} = \left\{\frac{\sigma_3^2}{\sigma_2^3}R_1^2R_2^2 + \frac{\sigma_3}{\sigma_2^{9/2}} \times [\sigma_3^2(R_{34}^2+R_{35}^2+R_{45}^2) - 2(3\sigma_3^2-\sigma_2\sigma_4)] \times R_1R_2R_3R_4R_5\cos(\Phi_1+\Phi_2+\Phi_3+\Phi_4+\Phi_5) + \frac{1}{4\sigma_2^6}[\sigma_3^2(R_{34}^2+R_{35}^2+R_{45}^2) - 2(3\sigma_3^2-\sigma_2\sigma_4)]^2R_3^2R_4^2R_5^2\right\}^{1/2}, \quad (2.12)$$

etc. Since $P_{5|15}$ is a function of the sum $\Phi=\Phi_1+\Phi_2+\Phi_3+\Phi_4+\Phi_5$, the conditional probability distribution of the structure invariant $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}+\varphi_{\mathbf{n}}$, given the 15 magnitudes (1.1) and (1.2) in its second neighborhood, is immediately obtained, as shown next.

3. The conditional probability distribution of the structure invariant $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}+\varphi_{\mathbf{n}}$, given the 15 magnitudes $|E_{\mathbf{h}}|, |E_{\mathbf{k}}|, |E_{\mathbf{l}}|, |E_{\mathbf{m}}|, |E_{\mathbf{n}}|, |E_{\mathbf{h+k}}|, |E_{\mathbf{h+l}}|, |E_{\mathbf{h+m}}|, |E_{\mathbf{h+n}}|, |E_{\mathbf{k+l}}|, |E_{\mathbf{k+m}}|, |E_{\mathbf{k+n}}|, |E_{\mathbf{l+m}}|, |E_{\mathbf{l+n}}|, |E_{\mathbf{m+n}}|$

Under the hypotheses of § 1, denote by

$$P_{1|15} = P(\Phi|R_1, R_2, R_3, R_4, R_5; R_{12}, R_{13}, R_{14}, R_{15}, R_{23}, R_{24}, R_{25}, R_{34}, R_{35}, R_{45}) \quad (3.1)$$

the conditional probability distribution of the structure invariant

$$\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}+\varphi_{\mathbf{n}}, \quad (3.2)$$

given the 15 magnitudes (1.1) and (1.2) in the second neighborhood of φ. Then $P_{1|15}$ is immediately obtainable from (2.9) and (2.11) respectively. Thus, correct up to and including terms of order $1/N^{3/2}$, the major results of this paper are given by

$$P_{1|15}\simeq\frac{1}{K}\exp\left\{\left[\frac{2\sigma_3^3}{\sigma_2^{9/2}}(R_{12}^2R_{34}^2+R_{12}^2R_{35}^2+R_{12}^2R_{45}^2 +R_{13}^2R_{24}^2+R_{13}^2R_{25}^2+R_{13}^2R_{45}^2+R_{14}^2R_{23}^2 +R_{14}^2R_{25}^2+R_{14}^2R_{35}^2+R_{15}^2R_{23}^2+R_{15}^2R_{24}^2 +R_{15}^2R_{34}^2+R_{23}^2R_{45}^2+R_{24}^2R_{35}^2+R_{25}^2R_{34}^2) +\frac{2}{\sigma_2^{9/2}}(15\sigma_3^3-10\sigma_2\sigma_3\sigma_4+\sigma_2^2\sigma_5)\right]\times R_1R_2R_3R_4R_5\cos\Phi\right\} \times I_0(2R_{12}X_{12})I_0(2R_{13}X_{13})I_0(2R_{14}X_{14}) \times I_0(2R_{15}X_{15})I_0(2R_{23}X_{23})I_0(2R_{24}X_{24}) \times I_0(2R_{25}X_{25})I_0(2R_{34}X_{34})I_0(2R_{35}X_{35}) \times I_0(2R_{45}X_{45})\,, \tag{3.3}$$

where K is a suitable normalizing parameter,

$$X_{12}=\left[\frac{\sigma_3^2}{\sigma_2^3}R_1^2R_2^2-\frac{2\sigma_3(3\sigma_3^2-\sigma_2\sigma_4)}{\sigma_2^{9/2}}R_1R_2R_3R_4R_5 \times\cos\Phi+\left(\frac{3\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}\right)^2R_3^2R_4^2R_5^2\right]^{1/2}, \tag{3.4}$$

etc., and, by the alternative exponential–Bessel form for $P_{1|15}$,

$$P_{1|15}\simeq\frac{1}{K}\exp\left\{\frac{2}{\sigma_2^{9/2}}(15\sigma_3^3-10\sigma_2\sigma_3\sigma_4 +\sigma_4^2\sigma_5)R_1R_2R_3R_4R_5\cos\Phi\right\} \times I_0(2R_{12}Y_{12})I_0(2R_{13}Y_{13})I_0(2R_{14}Y_{14}) \times I_0(2R_{15}Y_{15})I_0(2R_{23}Y_{23})I_0(2R_{24}Y_{24}) \times I_0(2R_{25}Y_{25})I_0(2R_{34}Y_{34})I_0(2R_{35}Y_{35}) \times I_0(2R_{45}Y_{45})\,, \tag{3.5}$$

where again K is a suitable normalizing parameter and

$$Y_{12}=\left\{\frac{\sigma_3^2}{\sigma_2^3}R_1^2R_2^2+\frac{\sigma_3}{\sigma_2^{9/2}}\left[\sigma_3^2(R_{34}^2+R_{35}^2+R_{45}^2) -2(3\sigma_3^2-\sigma_2\sigma_4)\right]R_1R_2R_3R_4R_5\cos\Phi +\frac{1}{4\sigma_2^6}[\sigma_3^2(R_{34}^2+R_{35}^2+R_{45}^2) -2(3\sigma_3^2-\sigma_2\sigma_4)]^2R_3^2R_4^2R_5^2\right\}^{1/2}, \tag{3.6}$$

etc.

3.1. *Exponential form of the distribution*

Although, as described earlier, the pure exponential form of the distribution is not expected to be as accurate as either of the exponential–Bessel-function forms (3.3), (3.5), because of its simplicity, ease of calculation, and ability to yield results which are at least qualitatively correct, it appears worthwhile to give the exponential form as derived from (2.5):

$$P_{1|15}\simeq\frac{1}{K}\exp(\Delta R_1R_2R_3R_4R_5\cos\Phi) \tag{3.7}$$

where Δ, the 'discriminant' of φ, is the fourth-degree polynomial in the ten R's, R_{12}, R_{13}, ...,

$$\Delta=\frac{2\sigma_3^3}{\sigma_2^{9/2}}\sum_{15}R_{12}^2R_{34}^2-\frac{2\sigma_3}{\sigma_2^{9/2}}(3\sigma_3^2-\sigma_2\sigma_4)\sum_{10}R_{12}^2 +\frac{2}{\sigma_2^{9/2}}(15\sigma_3^3-10\sigma_2\sigma_3\sigma_4+\sigma_2^2\sigma_5)\,, \tag{3.8}$$

and K $[=2\pi I_0(\Delta R_1R_2R_3R_4R_5)]$ is a suitable normalizing parameter independent of Φ. Clearly (3.7) has a unique maximum at $\Phi=0$ or $\Phi=\pi$ according as $\Delta>0$ or $\Delta<0$ respectively. A disadvantage of (3.7) is that it is incapable of giving a maximum between 0 and π whereas (3.3) or (3.5) may have a maximum anywhere in the interval $(0,\pi)$. It is worth noting that if the ten 'cross-terms' R_{12}, R_{13}, ..., R_{45} are mostly large then $P_{1|15}$, whether given by (3.3), (3.5) or (3.7) has a unique maximum at $\Phi=0$, in accordance with the prediction of the first row of Table 2 of a previous paper (Hauptman, 1977). If, on the other hand, certain of the cross-terms R_{12}, R_{13}, ..., R_{45} are large and others are small, then φ may well be equal to π, as shown next.

3.2. *First special case*

The special case that

$$R_{12}, R_{13}, R_{14}, R_{15}\text{ are all large,} \tag{3.9}$$

but

$$R_{23}\simeq R_{24}\simeq R_{25}\simeq R_{34}\simeq R_{35}\simeq R_{45}\simeq 0\,. \tag{3.10}$$

In this special case (3.3) and (3.5) both reduce to [since $I_0(0)=1$]

$$P_{1|15}\simeq\frac{1}{K}\exp\left\{\frac{2}{\sigma_2^{9/2}}(15\sigma_3^3-10\sigma_2\sigma_3\sigma_4 +\sigma_2^2\sigma_5)R_1R_2R_3R_4R_5\cos\Phi\right\} \times I_0(2R_{12}X_{12})I_0(2R_{13}X_{13})I_0(2R_{14}X_{14}) \times I_0(2R_{15}X_{15})\,, \tag{3.11}$$

where X_{12} is given by (3.4), *etc.*

Hence (3.11) has a unique maximum at $\Phi=\pi$ provided that R_{12}, R_{13}, R_{14} and R_{15} are sufficiently large so that, in this special case, $\varphi\simeq\pi$, in agreement with the prediction of the second row of Table 2 of Hauptman (1977). It is noteworthy that, in this special case, Δ (3.8) reduces to

$$\Delta = -\frac{2\sigma_3}{\sigma_2^{9/2}}(3\sigma_3^2-\sigma_2\sigma_4)(R_{12}^2+R_{13}^2+R_{14}^2+R_{15}^2) + \frac{2}{\sigma_2^{9/2}}(15\sigma_3^3-10\sigma_2\sigma_3\sigma_4+\sigma_2^2\sigma_5)<0 \qquad (3.12)$$

so that (3.7) also has a maximum at $\Phi=\pi$, implying again that $\varphi\simeq\pi$.

Clearly there are four other special cases analogous to (3.9) and (3.10), obtained by symmetry, for which $\varphi\simeq\pi$, in agreement with rows 3–6 of Table 2 of Hauptman (1977).

3.3. *Second special case*

The special case that

$$R_{12},\ R_{13},\ R_{23} \text{ are all large} \qquad (3.13)$$

but

$$R_{14}\simeq R_{15}\simeq R_{24}\simeq R_{25}\simeq R_{34}\simeq R_{35}\simeq R_{45}\simeq 0\,. \qquad (3.14)$$

In this special case (3.3) and (3.5) both reduce to

$$P_{1|15}\simeq \frac{1}{K}\exp\left\{\frac{2}{\sigma_2^{9/2}}(15\sigma_3^3-10\sigma_2\sigma_3\sigma_4+\sigma_2^2\sigma_5) \times R_1R_2R_3R_4R_5\cos\Phi\right\} \times I_0(2R_{12}X_{12})I_0(2R_{13}X_{13})I_0(2R_{23}X_{23}) \qquad (3.15)$$

where X_{12} is given by (3.4) *etc.*

Hence (3.15) has a unique maximum at $\Phi=\pi$ provided that R_{12}, R_{13} and R_{23} are sufficiently large so that, in this special case, $\varphi\simeq\pi$, in agreement with the prediction of the seventh row of Table 2 of Hauptman (1977). Again, in this special case, Δ (3.8) reduces to

$$\Delta = -\frac{2\sigma_3}{\sigma_2^{9/2}}(3\sigma_3^2-\sigma_2\sigma_4)(R_{12}^2+R_{13}^2+R_{23}^2) + \frac{2}{\sigma_2^{9/2}}(15\sigma_3^3-10\sigma_2\sigma_3\sigma_4+\sigma_2^2\sigma_5)<0 \qquad (3.16)$$

so that (3.7) also has a maximum at $\Phi=\pi$, implying again that $\varphi\simeq\pi$.

Clearly there are nine other special cases analogous to (3.13) and (3.14), obtained by symmetry, for which $\varphi\simeq\pi$, in agreement with rows 8–16 of Table 2 of Hauptman (1977).

Finally, in the special case that all cross-terms R_{12}, R_{13}, ..., R_{45} are very small, (3.5) and (3.7) both reduce to

$$P_{1|15}\simeq \frac{1}{K}\exp\left\{\frac{2}{\sigma_2^{9/2}}(15\sigma_3^3-10\sigma_2\sigma_3\sigma_4+\sigma_2^2\sigma_5) \times R_1R_2R_3R_4R_5\cos\Phi\right\}, \qquad (3.17)$$

so that, in this very special case, φ is probably equal to zero.

3.4. *Expected values*

Although the conditional expected value of cos φ may be obtained from (3.3) or (3.5), the result is complicated and does not lend itself readily to numerical calculation. It seems better to use the exponential form (3.7) which leads to a simple formula having at least approximate validity:

$$\varepsilon(\cos\varphi\,|\,R_1, R_2, R_3, R_4, R_5; R_{12},R_{13},R_{14},R_{15},R_{23},R_{24},R_{25},R_{34},R_{35},R_{45}) \simeq \frac{I_1(\Delta R_1R_2R_3R_4R_5)}{I_0(\Delta R_1R_2R_3R_4R_5)}, \qquad (3.18)$$

which is positive or negative according as $\Delta>0$ or $\Delta<0$. In the special case that all ten cross-terms R_{12}, ..., R_{45} are large then $\Delta>0$ and (3.18) is positive; in the special case that (3.9) and (3.10) hold, or that (3.13) and (3.14) hold, then the discriminant Δ is negative and (3.18) is negative too.

3.5. *A conjecture*

It has been seen that, according as

$$\Delta \gg 0 \qquad (3.19)$$

or

$$\Delta \ll 0\,, \qquad (3.20)$$

then

$$\varphi\simeq 0 \qquad (3.21)$$

or

$$\varphi\simeq\pi \qquad (3.22)$$

respectively. It is plausible to conjecture that if

$$\Delta\simeq 0 \qquad (3.23)$$

then

$$\varphi\simeq\pm\frac{\pi}{2}, \qquad (3.24)$$

although the reliability of the estimate (3.24) is clearly not as high as that of (3.21) or (3.22).

4. Concluding remarks

The conditional probability distribution of the structure invariant (3.2), given the 15 magnitudes (1.1) and (1.2) in its second neighborhood, has been found. Just as the analogous distributions for quartets have already proven to be useful in the applications, it is likely that the distribution derived here, in particular (3.3) and (3.5), will have an important role to play in devising improved techniques of phase determination, especially for very complex structures.

It should be observed finally that in the presence of one or a few heavy atoms the distributions derived here are sharpened, thus leading to more reliable estimates of φ, as anticipated. In the extreme case that $\sigma_3=0$ (possible only in the neutron diffraction case when some of the f_j may be negative), a situation which appears rarely, if ever, to occur in practice, the distributions (3.3) and (3.5) reduce to the conditional distribution of φ when only the five magnitudes (1.1) of the first neighborhood are given, so that nothing is gained by going to the second neighborhood of φ. Since the same phenomenon has already been observed for quartets (Hauptman, 1976), it is beginning to appear that the condition $\sigma_3 \neq 0$ may be a necessary one for a solution of the phase problem to exist; but a final resolution of this question will have to await further developments. (There is some evidence which suggests that the more stringent requirement $(3\sigma_3^2-\sigma_2\sigma_4)/\sigma_2^3>0$ may in fact be necessary.) In the X-ray diffraction case there is no problem since then every f_j is positive, and σ_3 is therefore also positive. Furthermore, in the applications to neutron diffraction the condition $\sigma_3^2/\sigma_2^3=0$ appears rarely, if ever, to be fulfilled, so that the results derived here are almost sure to be useful for neutron diffraction as well.

Finally, the initial applications of quintets have been made (Fortier, Fronckowiak & Hauptman, 1977; Fronckowiak, Fortier, De Titta & Hauptman, 1977). These show that quintets will be at least as important in the applications as quartets or triples, and strongly suggest that the use of all available invariants and seminvariants will be more useful still.

This research was supported in part by Grant No. MPS73-04992 from the National Science Foundation, DHEW Grant Nos. HL15378 and RR05716, and Ministère de l'Education, Gouvernement du Québec.

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Experimental Charge Density Distribution in Potassium Azide by Diffraction Methods

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(*Received* 5 *October* 1976; *accepted* 20 *December* 1976)

The electron density distribution of potassium azide is determined from high-resolution X-ray intensity measurements. The calculated distributions of errors in the experimental densities are included. Refinement of high-order X-ray data yields parameters in good agreement with neutron diffraction results. The inclusion of high-order data in calculating the deformation density is found to be necessary to obtain a quantitative distribution. Densities calculated with only low-order data are qualitatively similar but lack detail in the shape as well as in the height of the bonding features.

Introduction

In recent years, methods have been developed for direct experimental determination of the electron distribution in solids using accurate X-ray and neutron diffraction measurements (Coppens, 1975). An obvious objective is the comparison of experimental results with theoretical calculations of the electron density distribution. For several reasons, most previous comparisons have been unsatisfactory (Coppens & Stevens, 1976). The electron density distribution has been found to be a very sensitive function of the quality of the wavefunction, but because of computational limitations, the sophisticated calculations necessary are at present available only for very small molecules. On the other hand, small-molecule systems are experimentally difficult since they are often gases or liquids at room temperature.

Experimental studies of the electron density distribution in the azide ion have been undertaken for comparison with *ab initio* molecular-orbital calculations (Stevens, Rys & Coppens, 1977*a*,*b*). The present study of potassium azide complements a recent experimental study of the azide ion in the structure of NaN_3 (Stevens & Hope, 1977). The studies of the azide ion in two different crystal forms provide additional information on the effects of the crystal field and thermal smearing.

A detailed analysis of the experimental error distribution has been included so that the significance of features in the experimental density maps can be assessed.

Experimental methods

X-ray data collection and processing

A small single crystal with dimensions 0·22 × 0·20 ×