$$\tan\theta_{\mathbf{H}} = \frac{\left(\sum_{\mathbf{h},\,n} G_{\mathbf{h},\,n} \sin 2\pi\mathbf{h}\cdot\mathbf{T}_n\right)}{\left(\sum_{\mathbf{h},\,n} G_{\mathbf{h},\,n} \cos 2\pi\mathbf{h}\cdot\mathbf{T}_n\right)} \qquad (2.2.5.39)$$

with a reliability measured by

$$\alpha = \left\{\left(\sum_{\mathbf{h},\,n} G_{\mathbf{h},\,n} \sin 2\pi\mathbf{h}\cdot\mathbf{T}_n\right)^2 + \left(\sum_{\mathbf{h},\,n} G_{\mathbf{h},\,n} \cos 2\pi\mathbf{h}\cdot\mathbf{T}_n\right)^2\right\}^{1/2}.$$

The second representation of $\varphi_{\mathbf{H}}$ is the set of special quintets

$$\{\psi\} = \{\varphi_{\mathbf{H}} - \varphi_{\mathbf{h}} + \varphi_{\mathbf{h}\boldsymbol{R}_n} + \varphi_{\mathbf{k}\boldsymbol{R}_j} - \varphi_{\mathbf{k}\boldsymbol{R}_j}\} \qquad (2.2.5.40)$$

provided that $\mathbf{h}$ and $\boldsymbol{R}_n$ vary over the vectors and matrices for which (2.2.5.36) is compatible, $\mathbf{k}$ over the asymmetric region of the reciprocal space, and $\boldsymbol{R}_j$ over the rotation matrices in the space group. Formulae estimating $\varphi_{\mathbf{H}}$ *via* the second representation in all the space groups [all the base and cross magnitudes of the quintets (2.2.5.40) now constitute the *a priori* information] have recently been secured (Giacovazzo, 1978; Cascarano & Giacovazzo, 1983; Cascarano, Giacovazzo, Calabrese *et al.*, 1984). Such formulae contain, besides the contribution of order $N^{-1/2}$ provided by the first representation, a supplementary (not negligible) contribution of order $N^{-3/2}$ arising from quintets.

Denoting

$$E_1 = E_{\mathbf{H}},\ E_2 = E_{\mathbf{h}},\ E_3 = E_{\mathbf{k}},$$
$$E_{4,\,j} = E_{\mathbf{h}+\mathbf{k}\boldsymbol{R}_j},\ E_{5,\,j} = E_{\mathbf{H}+\mathbf{k}\boldsymbol{R}_j},$$

formulae (2.2.5.37), (2.2.5.38), (2.2.5.39) still hold provided that $\sum_{\mathbf{h},\,n} G_{\mathbf{h},\,n}$ is replaced by

$$\sum_{\mathbf{h},\,n} G_{\mathbf{h},\,n} + \sum_{\mathbf{h},\,\mathbf{k},\,n}{}' \frac{|E_{\mathbf{H}}|}{2N^{3/2}} \frac{A_{\mathbf{h},\,\mathbf{k},\,n}}{1 + B_{\mathbf{h},\,\mathbf{k},\,n}},$$

where

$$A_{\mathbf{h},\,\mathbf{k},\,n} = \left[(2|E_2|^2 - 1)\varepsilon_3\left(\sum_{\substack{\boldsymbol{R}_i=\boldsymbol{R}_j\\ \boldsymbol{R}_j+\boldsymbol{R}_i\boldsymbol{R}_n=0}} \varepsilon_{4,\,i}\varepsilon_{5,\,j} + \sum_{\substack{\boldsymbol{R}_j=\boldsymbol{R}_i\boldsymbol{R}_n\\ \boldsymbol{R}_i=\boldsymbol{R}_j\boldsymbol{R}_n}} \varepsilon_{4,\,i}\varepsilon_{4,\,j}\right) - \frac{\varepsilon_3}{2}\sum_{j=1}^{m}\varepsilon_{4,\,j} - \frac{1}{2}\sum_{\substack{\boldsymbol{R}_j=\boldsymbol{R}_i\\ \boldsymbol{R}_j+\boldsymbol{R}_i\boldsymbol{R}_n=0}} \varepsilon_{4,\,i}\varepsilon_{5,\,j}\right] \Big/ N,$$

$$B_{\mathbf{h},\,\mathbf{k},\,n} = \left[\varepsilon_1\varepsilon_3\sum_{j=1}^{m}\varepsilon_{5,\,j} + \varepsilon_1\sum_{\substack{\boldsymbol{R}_j=\boldsymbol{R}_i\boldsymbol{R}_n\\ \boldsymbol{R}_i=\boldsymbol{R}_j\boldsymbol{R}_n}} \varepsilon_{4,\,i}\varepsilon_{4j} + \varepsilon_2\varepsilon_3\sum_{j=1}^{m}\varepsilon_{4,\,j} + \varepsilon_2\sum_{\substack{\boldsymbol{R}_j=\boldsymbol{R}_i\\ \boldsymbol{R}_j+\boldsymbol{R}_i\boldsymbol{R}_n=0}} \varepsilon_{4,\,i}\varepsilon_{5,\,j} + \tfrac{1}{4}\varepsilon_1 H_4(E_2)\right] \Big/ (2N).$$

m is the number of symmetry operators and $H_4(E) = E^4 - 6E^2 + 3$ is the Hermite polynomial of order four.

$B_{\mathbf{h},\,\mathbf{k},\,n}$ is assumed to be zero if it is computed negative. The prime to the summation warns the reader that precautions have to be taken in order to avoid duplication in the contributions.

2.2.5.10. *Formulae estimating two-phase structure seminvariants of the first rank*

Two-phase s.s.'s of the first rank were first evaluated in some cs. space groups by the method of coincidence by Grant *et al.* (1957); the idea was extended to ncs. space groups by Debaerdemaeker & Woolfson (1972), and in a more general way by Giacovazzo (1977*e*, *f*).

The technique was based on the combination of the two triplets

$$\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} \simeq \varphi_{\mathbf{h}_1+\mathbf{h}_2}$$
$$\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2\boldsymbol{R}} \simeq \varphi_{\mathbf{h}_1+\mathbf{h}_2\boldsymbol{R}},$$

which, subtracted from one another, give

$$\varphi_{\mathbf{h}_1+\mathbf{h}_2\boldsymbol{R}} - \varphi_{\mathbf{h}_1+\mathbf{h}_2} \simeq \varphi_{\mathbf{h}_2\boldsymbol{R}} - \varphi_{\mathbf{h}_2} \simeq -2\pi\mathbf{h}\cdot\mathbf{T}.$$

If all four $|E|$'s are sufficiently large, an estimate of the two-phase seminvariant $\varphi_{\mathbf{h}_1+\mathbf{h}_2\boldsymbol{R}} - \varphi_{\mathbf{h}_1+\mathbf{h}_2}$ is available.

Probability distributions valid in $P2_1$ according to the neighbourhood principle have been given by Hauptman & Green (1978). Finally, the theory of representations was combined by Giacovazzo (1979*a*) with the joint probability distribution method in order to estimate two-phase s.s.'s in all the space groups.

According to representation theory, the problem is that of evaluating $\Phi = \varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2}$ *via* the special quartets (2.2.5.35*a*) and (2.2.5.35*b*). Thus, contributions of order N^{-1} will appear in the probabilistic formulae, which will be functions of the basis and of the cross magnitudes of the quartets (2.2.5.35) . Since more pairs of matrices $\boldsymbol{R}_\alpha$ and $\boldsymbol{R}_\beta$ can be compatible with (2.2.5.34), and for each pair $(\boldsymbol{R}_\alpha, \boldsymbol{R}_\beta)$ more pairs of vectors $\mathbf{h}_1$ and $\mathbf{h}_2$ may satisfy (2.2.5.34), several quartets can in general be exploited for estimating Φ. The simplest case occurs in $P\bar{1}$ where the two quartets (2.2.5.35) suggest the calculation of the six-variate distribution function ($\mathbf{u}_1 = \mathbf{h}_1 + \mathbf{h}_2, \mathbf{u}_2 = \mathbf{h}_1 - \mathbf{h}_2$)

$$P(E_{\mathbf{h}_1}, E_{\mathbf{h}_2}, E_{\mathbf{h}_1+\mathbf{h}_2}, E_{\mathbf{h}_1-\mathbf{h}_2}, E_{2\mathbf{h}_1}, E_{2\mathbf{h}_2})$$

which leads to the probability formula

$$P^+ \simeq 0.5 + 0.5\tanh\left(\frac{|E_{\mathbf{h}_1+\mathbf{h}_2}E_{\mathbf{h}_1-\mathbf{h}_2}|}{2N}\cdot\frac{A}{1+B}\right),$$

where P^+ is the probability that the product $E_{\mathbf{h}_1+\mathbf{h}_2}E_{\mathbf{h}_1-\mathbf{h}_2}$ is positive, and

$$A = \varepsilon_{\mathbf{h}_1} + \varepsilon_{\mathbf{h}_2} + 2\varepsilon_{\mathbf{h}_1}\varepsilon_{\mathbf{h}_2} + \varepsilon_{\mathbf{h}_1}\varepsilon_{2\mathbf{h}_1} + \varepsilon_{\mathbf{h}_2}\varepsilon_{2\mathbf{h}_2}$$
$$B = (\varepsilon_{\mathbf{h}_1}\varepsilon_{\mathbf{h}_2}\varepsilon_{\mathbf{u}_1} + \varepsilon_{\mathbf{h}_1}\varepsilon_{\mathbf{h}_2}\varepsilon_{\mathbf{u}_2} + \varepsilon_{\mathbf{u}_1}\varepsilon_{\mathbf{u}_2}\varepsilon_{2\mathbf{h}_1} + \varepsilon_{\mathbf{u}_1}\varepsilon_{\mathbf{u}_2}\varepsilon_{2\mathbf{h}_2})/(2N).$$

It may be seen that in favourable cases $P^+ < 0.5$.

For the sake of brevity, the probabilistic formulae for the general case are not given and the reader is referred to the original papers.

2.2.6. Direct methods in real and reciprocal space: Sayre's equation

The statistical treatment suggested by Wilson for scaling observed intensities corresponds, in direct space, to the origin peak of the Patterson function, so it is not surprising that a general correspondence exists between probabilistic formulation in reciprocal space and algebraic properties in direct space.

For a structure containing atoms which are fully resolved from one another, the operation of raising $\rho(\mathbf{r})$ to the nth power retains

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references