

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

A variant of (2.2.5.2) valid for cs. space groups is

$$(U_{\mathbf{h}} \pm U_{\mathbf{h}'})^2 \leq (1 \pm U_{\mathbf{h}+\mathbf{h}'})(1 \pm U_{\mathbf{h}-\mathbf{h}'}).$$

After Harker & Kasper's contributions, several other inequalities were discovered (Gillis, 1948; Goedkoop, 1950; Okaya & Nitta, 1952; de Wolff & Bouman, 1954; Bouman, 1956; Oda *et al.*, 1961). The most general are the Karle–Hauptman inequalities (Karle & Hauptman, 1950):

$$D_m = \begin{vmatrix} U_0 & U_{-\mathbf{h}_1} & U_{-\mathbf{h}_2} & \dots & U_{-\mathbf{h}_n} \\ U_{\mathbf{h}_1} & U_0 & U_{\mathbf{h}_1-\mathbf{h}_2} & \dots & U_{\mathbf{h}_1-\mathbf{h}_n} \\ U_{\mathbf{h}_2} & U_{\mathbf{h}_2-\mathbf{h}_1} & U_0 & \dots & U_{\mathbf{h}_2-\mathbf{h}_n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ U_{\mathbf{h}_n} & U_{\mathbf{h}_n-\mathbf{h}_1} & U_{\mathbf{h}_n-\mathbf{h}_2} & \dots & U_0 \end{vmatrix} \geq 0. \quad (2.2.5.3)$$

The determinant can be of any order but the leading column (or row) must consist of U 's with different indices, although, within the column, symmetry-related U 's may occur. For $n = 2$ and $\mathbf{h}_2 = 2\mathbf{h}_1 = 2\mathbf{h}$, equation (2.2.5.3) reduces to

$$D_3 = \begin{vmatrix} U_0 & U_{-\mathbf{h}} & U_{-2\mathbf{h}} \\ U_{\mathbf{h}} & U_0 & U_{-\mathbf{h}} \\ U_{2\mathbf{h}} & U_{\mathbf{h}} & U_0 \end{vmatrix} \geq 0,$$

which, for cs. structures, gives the Harker & Kasper inequality

$$U_{\mathbf{h}}^2 \leq 0.5 + 0.5U_{2\mathbf{h}}.$$

For $m = 3$, equation (2.2.5.3) becomes

$$D_3 = \begin{vmatrix} U_0 & U_{-\mathbf{h}} & U_{-\mathbf{k}} \\ U_{\mathbf{h}} & U_0 & U_{\mathbf{h}-\mathbf{k}} \\ U_{\mathbf{k}} & U_{\mathbf{k}-\mathbf{h}} & U_0 \end{vmatrix} \geq 0,$$

from which

$$1 - |U_{\mathbf{h}}|^2 - |U_{\mathbf{k}}|^2 - |U_{\mathbf{h}-\mathbf{k}}|^2 + 2|U_{\mathbf{h}}U_{\mathbf{k}}U_{\mathbf{h}-\mathbf{k}}| \cos \alpha_{\mathbf{h}, \mathbf{k}} \geq 0, \quad (2.2.5.4)$$

where

$$\alpha_{\mathbf{h}, \mathbf{k}} = \varphi_{\mathbf{h}} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}-\mathbf{k}}.$$

If the moduli $|U_{\mathbf{h}}|$, $|U_{\mathbf{k}}|$, $|U_{\mathbf{h}-\mathbf{k}}|$ are large enough, (2.2.5.4) is not satisfied for all values of $\alpha_{\mathbf{h}, \mathbf{k}}$. In cs. structures the eventual check that one of the two values of $\alpha_{\mathbf{h}, \mathbf{k}}$ does not satisfy (2.2.5.4) brings about the unambiguous identification of the sign of the product $U_{\mathbf{h}}U_{\mathbf{k}}U_{\mathbf{h}-\mathbf{k}}$.

It was observed (Gillis, 1948) that 'there was a number of cases in which both signs satisfied the inequality, one of them by a comfortable margin and the other by only a relatively small margin. In almost all such cases it was the former sign which was the correct one. That suggests that the method may have some power in reserve in the sense that there are still fundamentally stronger inequalities to be discovered'. Today we identify this power in reserve in the use of probability theory.

2.2.5.2. Probabilistic phase relationships for structure invariants

For any space group (see Section 2.2.3) there are linear combinations of phases with cosines that are, in principle, fixed by the $|E|$ magnitudes alone (s.i.'s) or by the $|E|$ values and the trigonometric form of the structure factor (s.s.'s). This result greatly stimulated the calculation of conditional distribution functions

$$P(\Phi|\{R\}), \quad (2.2.5.5)$$

where $R_{\mathbf{h}} = |E_{\mathbf{h}}|$, $\Phi = \sum A_i \varphi_{\mathbf{h}_i}$ is an s.i. or an s.s. and $\{R\}$ is a

suitable set of diffraction magnitudes. The method was first proposed by Hauptman & Karle (1953) and was developed further by several authors (Bertaut, 1955*a,b*, 1960; Klug, 1958; Naya *et al.*, 1964, 1965; Giacovazzo, 1980*a*). From a probabilistic point of view the crystallographic problem is clear: the joint distribution $P(E_{\mathbf{h}_1}, \dots, E_{\mathbf{h}_n})$, from which the conditional distributions (2.2.5.5) can be derived, involves a number of normalized structure factors each of which is a linear sum of random variables (the atomic contributions to the structure factors). So, for the probabilistic interpretation of the phase problem, the atomic positions and the reciprocal vectors may be considered as random variables. A further problem is that of identifying, for a given Φ , a suitable set of magnitudes $|E|$ on which Φ primarily depends. The formulation of the *nested neighbourhood principle* first (Hauptman, 1975) fixed the idea of defining a sequence of sets of reflections each contained in the succeeding one and having the property that any s.i. or s.s. may be estimated *via* the magnitudes constituting the various neighbourhoods. A subsequent more general theory, the *representation method* (Giacovazzo, 1977*a*, 1980*b*), arranges for any Φ the set of intensities in a sequence of subsets in order of their expected effectiveness (in the statistical sense) for the estimation of Φ .

In the following sections the main formulae estimating low-order invariants and seminvariants or relating phases to other phases and diffraction magnitudes are given.

2.2.5.3. Triplet relationships

The basic formula for the estimation of the triplet phase $\Phi = \varphi_{\mathbf{h}} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}-\mathbf{k}}$ given the parameter $G = 2\sigma_3\sigma_2^{-3/2} \times R_{\mathbf{h}}R_{\mathbf{k}}R_{\mathbf{h}-\mathbf{k}}$ is Cochran's (1955) formula

$$P(\Phi) = [2\pi I_0(G)]^{-1} \exp(G \cos \Phi), \quad (2.2.5.6)$$

where $\sigma_n = \sum_{j=1}^N Z_j^n$, Z_j is the atomic number of the j th atom and I_n is the modified Bessel function of order n . In Fig. 2.2.5.1 the distribution $P(\Phi)$ is shown for different values of G .

The conditional probability distribution for $\varphi_{\mathbf{h}}$, given a set of $(\varphi_{\mathbf{k}_j} + \varphi_{\mathbf{h}-\mathbf{k}_j})$ and $G_j = 2\sigma_3\sigma_2^{-3/2} R_{\mathbf{h}}R_{\mathbf{k}_j}R_{\mathbf{h}-\mathbf{k}_j}$, is given (Karle & Hauptman, 1956; Karle & Karle, 1966) by

$$P(\varphi_{\mathbf{h}}) = [2\pi I_0(\alpha)]^{-1} \exp[\alpha \cos(\varphi_{\mathbf{h}} - \beta_{\mathbf{h}})], \quad (2.2.5.7)$$

where

$$\alpha^2 = \left[\sum_{j=1}^r G_{\mathbf{h}, \mathbf{k}_j} \cos(\varphi_{\mathbf{k}_j} + \varphi_{\mathbf{h}-\mathbf{k}_j}) \right]^2 + \left[\sum_{j=1}^r G_{\mathbf{h}, \mathbf{k}_j} \sin(\varphi_{\mathbf{k}_j} + \varphi_{\mathbf{h}-\mathbf{k}_j}) \right]^2 \quad (2.2.5.8)$$

$$\tan \beta_{\mathbf{h}} = \frac{\sum_j G_{\mathbf{h}, \mathbf{k}_j} \sin(\varphi_{\mathbf{k}_j} + \varphi_{\mathbf{h}-\mathbf{k}_j})}{\sum_j G_{\mathbf{h}, \mathbf{k}_j} \cos(\varphi_{\mathbf{k}_j} + \varphi_{\mathbf{h}-\mathbf{k}_j})}. \quad (2.2.5.9)$$

$\beta_{\mathbf{h}}$ is the most probable value for $\varphi_{\mathbf{h}}$. The variance of $\varphi_{\mathbf{h}}$ may be obtained from (2.2.5.7) and is given by

$$V_{\mathbf{h}} = \frac{\pi^2}{3} + [I_0(\alpha)]^{-1} \sum_{n=1}^{\infty} \frac{I_{2n}(\alpha)}{n^2} - 4[I_0(\alpha)]^{-1} \sum_{n=0}^{\infty} \frac{I_{2n+1}(\alpha)}{(2n+1)^2}, \quad (2.2.5.10)$$

which is plotted in Fig. 2.2.5.2.

Equation (2.2.5.9) is the so-called *tangent formula*. According to (2.2.5.10), the larger is α the more reliable is the relation $\varphi_{\mathbf{h}} = \beta_{\mathbf{h}}$.

For an equal-atom structure $\sigma_3\sigma_2^{-3/2} = N^{-1/2}$.

2.2. DIRECT METHODS

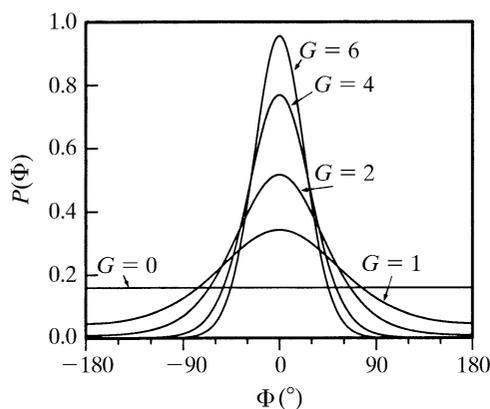


Fig. 2.2.5.1. Curves of (2.2.5.6) for some values of $G = 2\sigma_3\sigma_2^{-3/2}|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|$.

The basic conditional formula for sign determination of $E_{\mathbf{h}}$ in cs. crystals is Cochran & Woolfson's (1955) formula

$$P^+ = \frac{1}{2} + \frac{1}{2} \tanh \left(\sigma_3 \sigma_2^{-3/2} |E_{\mathbf{h}}| \sum_{j=1}^r E_{\mathbf{k}_j} E_{\mathbf{h}-\mathbf{k}_j} \right), \quad (2.2.5.11)$$

where P^+ is the probability that $E_{\mathbf{h}}$ is positive and \mathbf{k} ranges over the set of known values $E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}$. The larger the absolute value of the argument of \tanh , the more reliable is the phase indication.

An auxiliary formula exploiting all the $|E|$'s in reciprocal space in order to estimate a single Φ is the $B_{3,0}$ formula (Hauptman & Karle, 1958; Karle & Hauptman, 1958) given by

$$\begin{aligned} & |E_{\mathbf{h}_1} E_{\mathbf{h}_2} E_{-\mathbf{h}_1-\mathbf{h}_2}| \cos(\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} - \varphi_{\mathbf{h}_1+\mathbf{h}_2}) \\ & \simeq C \langle (|E_{\mathbf{k}}|^p - \overline{|E|^p}) (|E_{\mathbf{h}_1+\mathbf{k}}|^p - \overline{|E|^p}) (|E_{\mathbf{h}_1+\mathbf{h}_2+\mathbf{k}}|^p - \overline{|E|^p}) \rangle_{\mathbf{k}} \\ & - \frac{2\sigma_6}{\sigma_4^{3/2}} + \frac{\sigma_8^{1/2}}{\sigma_4} (|E_{\mathbf{h}_1}|^2 + |E_{\mathbf{h}_2}|^2 + |E_{\mathbf{h}_1+\mathbf{h}_2}|^2) \dots, \quad (2.2.5.12) \end{aligned}$$

where C is a constant which differs for cs. and ncs. crystals, $\overline{|E|^p}$ is the average value of $|E|^p$ and p is normally chosen to be some small number. Several modifications of (2.2.5.12) have been proposed (Hauptman, 1964, 1970; Karle, 1970a; Giacovazzo, 1977b).

A recent formula (Cascarano, Giacovazzo, Camalli *et al.*, 1984) exploits information contained within the second representation of Φ , that is to say, within the collection of special quintets (see Section 2.2.5.6):

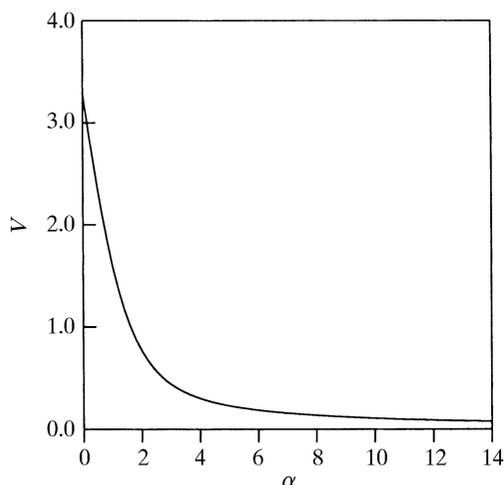


Fig. 2.2.5.2. Variance (in square radians) as a function of α .

$$\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} - \varphi_{\mathbf{h}_1+\mathbf{h}_2} + \varphi_{\mathbf{k}} - \varphi_{-\mathbf{k}},$$

where \mathbf{k} is a free vector. The formula retains the same algebraic form as (2.2.5.6), but

$$G = \frac{2R_{\mathbf{h}_1} R_{\mathbf{h}_2} R_{\mathbf{h}_3}}{\sqrt{N}} (1 + Q), \quad (2.2.5.13)$$

where $[\mathbf{h}_3 = -(\mathbf{h}_1 + \mathbf{h}_2)]$,

$$Q = \sum_{\mathbf{k}} \frac{\sum_{i=1}^m A_{\mathbf{k},i} / N}{1 + (\varepsilon_{\mathbf{h}_1} \varepsilon_{\mathbf{h}_2} \varepsilon_{\mathbf{h}_3} + \sum_{i=1}^m B_{\mathbf{k},i}) / 2N},$$

$$\begin{aligned} A_{\mathbf{k},i} &= \varepsilon_{\mathbf{k}} [\varepsilon_{\mathbf{h}_1+\mathbf{k}\mathbf{R}_i} (\varepsilon_{\mathbf{h}_2-\mathbf{k}\mathbf{R}_i} + \varepsilon_{\mathbf{h}_3-\mathbf{k}\mathbf{R}_i}) \\ &+ \varepsilon_{\mathbf{h}_2+\mathbf{k}\mathbf{R}_i} (\varepsilon_{\mathbf{h}_1-\mathbf{k}\mathbf{R}_i} + \varepsilon_{\mathbf{h}_3-\mathbf{k}\mathbf{R}_i}) \\ &+ \varepsilon_{\mathbf{h}_3+\mathbf{k}\mathbf{R}_i} (\varepsilon_{\mathbf{h}_1-\mathbf{k}\mathbf{R}_i} + \varepsilon_{\mathbf{h}_2-\mathbf{k}\mathbf{R}_i})], \\ B_{\mathbf{k},i} &= \varepsilon_{\mathbf{h}_1} [\varepsilon_{\mathbf{k}} (\varepsilon_{\mathbf{h}_1+\mathbf{k}\mathbf{R}_i} + \varepsilon_{\mathbf{h}_1-\mathbf{k}\mathbf{R}_i}) \\ &+ \varepsilon_{\mathbf{h}_2+\mathbf{k}\mathbf{R}_i} \varepsilon_{\mathbf{h}_3-\mathbf{k}\mathbf{R}_i} + \varepsilon_{\mathbf{h}_2-\mathbf{k}\mathbf{R}_i} \varepsilon_{\mathbf{h}_3+\mathbf{k}\mathbf{R}_i}] \\ &+ \varepsilon_{\mathbf{h}_2} [\varepsilon_{\mathbf{k}} (\varepsilon_{\mathbf{h}_2+\mathbf{k}\mathbf{R}_i} + \varepsilon_{\mathbf{h}_2-\mathbf{k}\mathbf{R}_i}) \\ &+ \varepsilon_{\mathbf{h}_1+\mathbf{k}\mathbf{R}_i} \varepsilon_{\mathbf{h}_3-\mathbf{k}\mathbf{R}_i} + \varepsilon_{\mathbf{h}_1-\mathbf{k}\mathbf{R}_i} \varepsilon_{\mathbf{h}_3+\mathbf{k}\mathbf{R}_i}] \\ &+ \varepsilon_{\mathbf{h}_3} [\varepsilon_{\mathbf{k}} (\varepsilon_{\mathbf{h}_3+\mathbf{k}\mathbf{R}_i} + \varepsilon_{\mathbf{h}_3-\mathbf{k}\mathbf{R}_i}) \\ &+ \varepsilon_{\mathbf{h}_1+\mathbf{k}\mathbf{R}_i} \varepsilon_{\mathbf{h}_2-\mathbf{k}\mathbf{R}_i} + \varepsilon_{\mathbf{h}_1-\mathbf{k}\mathbf{R}_i} \varepsilon_{\mathbf{h}_2+\mathbf{k}\mathbf{R}_i}]; \end{aligned}$$

$\varepsilon = |E|^2 - 1$, $(\varepsilon_{\mathbf{h}_1} \varepsilon_{\mathbf{h}_2} \varepsilon_{\mathbf{h}_3} + \sum_{i=1}^m B_{\mathbf{k},i})$ is assumed to be zero if it is experimentally negative. The prime to the summation warns the reader that precautions have to be taken in order to avoid duplications in the contributions.

G may be positive or negative. In particular, if $G < 0$ the triplet is estimated negative.

The accuracy with which the value of Φ is estimated strongly depends on $\varepsilon_{\mathbf{k}}$. Thus, in practice, only a subset of reciprocal space (the reflections \mathbf{k} with large values of ε) may be used for estimating Φ .

(2.2.5.13) proved to be quite useful in practice. Positive triplet cosines are ranked in order of reliability by (2.2.5.13) markedly better than by Cochran's parameters. Negative estimated triplet cosines may be excluded from the phasing process and may be used as a figure of merit for finding the correct solution in a multisolution procedure.

2.2.5.4. Triplet relationships using structural information

A strength of direct methods is that no knowledge of structure is required for their application. However, when some *a priori* information is available, it should certainly be a weakness of the methods not to make use of this knowledge. The conditional distribution of Φ given $R_{\mathbf{h}} R_{\mathbf{k}} R_{\mathbf{h}-\mathbf{k}}$ and the first three of the five kinds of *a priori* information described in Section 2.2.4.1 is (Main, 1976; Heinemann, 1977a)

$$P(\Phi) \simeq \frac{\exp\{2QR_1 R_2 R_3 \cos(\Phi - q)\}}{2\pi I_0(2QR_1 R_2 R_3)}, \quad (2.2.5.14)$$

where

$$Q \exp(iq) = \frac{\sum_{i=1}^p g_i(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3)}{\langle |F_{\mathbf{h}_1}|^2 \rangle^{1/2} \langle |F_{\mathbf{h}_2}|^2 \rangle^{1/2} \langle |F_{\mathbf{h}_3}|^2 \rangle^{1/2}}.$$

$\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3$ stand for $\mathbf{h}, -\mathbf{k}, -\mathbf{h} + \mathbf{k}$, and R_1, R_2, R_3 for $R_{\mathbf{h}}, R_{\mathbf{k}}, R_{\mathbf{h}-\mathbf{k}}$. The quantities $\langle |F_{\mathbf{h}_i}|^2 \rangle$ have been calculated in Section 2.2.4.1 according to different categories: $g_i(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3)$ is a suitable average of the product of three scattering factors for the i th atomic group, p is the number of atomic groups in the cell including those related by symmetry elements. We have the following categories.