2.2. DIRECT METHODS

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

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

$$\{\psi\} = \{\varphi_{\mathbf{H}} - \varphi_{\mathbf{h}} + \varphi_{\mathbf{h}R_n} + \varphi_{\mathbf{k}R_j} - \varphi_{\mathbf{k}R_j}\} \qquad (2.2.5.40)$$

provided that $\mathbf{h}$ and 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 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

$$E_1 = E_{\mathbf{H}}, \; E_2 = E_{\mathbf{h}}, \; E_3 = E_{\mathbf{k}},$$
$$E_{4,j} = E_{\mathbf{h}+\mathbf{k}R_j}, \; E_{5,j} = E_{\mathbf{H}+\mathbf{k}R_j},$$

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

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

$$B_{\mathbf{h},\mathbf{k},n} = \left[\varepsilon_1 \varepsilon_3 \sum_{j=1}^{m} \varepsilon_{5,j} + \varepsilon_1 \sum_{\substack{R_j = R_i R_n \\ R_i = R_j R_n}} \varepsilon_{4,i}\varepsilon_{4j} + \varepsilon_2 \varepsilon_3 \sum_{j=1}^{m} \varepsilon_{4,j} \right. \\ \left. + \varepsilon_2 \sum_{\substack{R_j = R_i \\ R_j + R_i R_n = 0}} \varepsilon_{4,i}\varepsilon_{5,j} + \frac{1}{4}\varepsilon_1 H_4(E_2) \right] \Big/ (2N).$$

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

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

which, subtracted from one another, give

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

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

Probability distributions valid in $P2_1$ according to the neighbour-hood 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 R_α and R_β can be compatible with (2.2.5.34), and for each pair (R_α, R_β) 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

225

the condition of resolved atoms but changes the shape of each atom. Let

$$\rho(\mathbf{r}) = \sum_{j=1}^{N} \rho_j(\mathbf{r} - \mathbf{r}_j),$$

where $\rho_j(\mathbf{r})$ is an atomic function and $\mathbf{r}_j$ is the coordinate of the 'centre' of the atom. Then the Fourier transform of the electron density can be written as

$$F_{\mathbf{h}} = \sum_{j=1}^{N} \int_V \rho_j(\mathbf{r} - \mathbf{r}_j) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}) \, dV$$

$$= \sum_{j=1}^{N} f_j \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j). \qquad (2.2.6.1)$$

If the atoms do not overlap

$$\rho^n(\mathbf{r}) = \left[\sum_{j=1}^{N} \rho_j(\mathbf{r} - \mathbf{r}_j) \right]^n \simeq \sum_{j=1}^{N} \rho_j^n(\mathbf{r} - \mathbf{r}_j)$$

and its Fourier transform gives

$$_nF_{\mathbf{h}} = \int_V \rho^n(\mathbf{r}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}) \, dV$$

$$= \sum_{j=1}^{N} {_n}f_j \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j). \qquad (2.2.6.2)$$

$_nf_j$ is the scattering factor for the jth peak of $\rho^n(\mathbf{r})$:

$$_nf_j(\mathbf{h}) = \int_V \rho_j^n(\mathbf{r}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}) \, d\mathbf{r}.$$

We now introduce the condition that all atoms are equal, so that $f_j \equiv f$ and $_nf_j \equiv {_n}f$ for any j. From (2.2.6.1) and (2.2.6.2) we may write

$$F_{\mathbf{h}} = \frac{f}{{_n}f} {_n}F_{\mathbf{h}} = \theta_n \, {_n}F_{\mathbf{h}}, \qquad (2.2.6.3)$$

where θ_n is a function which corrects for the difference of shape of the atoms with electron distributions $\rho(\mathbf{r})$ and $\rho^n(\mathbf{r})$. Since

$$\rho^n(\mathbf{r}) = \rho(\mathbf{r}) \ldots \rho(\mathbf{r})$$

$$= \frac{1}{V^n} \sum_{\substack{\mathbf{h}_1, \ldots, \mathbf{h}_n \\ -\infty}}^{+\infty} F_{\mathbf{h}_1} \ldots F_{\mathbf{h}_n} \exp[-2\pi i(\mathbf{h}_1 + \ldots + \mathbf{h}_n) \cdot \mathbf{r}],$$

the Fourier transform of both sides gives

$$_nF_{\mathbf{h}} = \frac{1}{V^n} \sum_{\substack{\mathbf{h}_1, \ldots, \mathbf{h}_n \\ -\infty}}^{+\infty} F_{\mathbf{h}_1} \ldots F_{\mathbf{h}_n} \int_V \exp[2\pi i(\mathbf{h} - \mathbf{h}_1 - \ldots - \mathbf{h}_n) \cdot \mathbf{r}] \, dV$$

$$= \frac{1}{V^{n-1}} \sum_{\substack{\mathbf{h}_1, \ldots, \mathbf{h}_{n-1} \\ -\infty}}^{+\infty} F_{\mathbf{h}_1} F_{\mathbf{h}_2} \ldots F_{\mathbf{h} - \mathbf{h}_1 - \mathbf{h}_2 - \ldots - \mathbf{h}_{n-1}},$$

from which the following relation arises:

$$F_{\mathbf{h}} = \theta_n \frac{1}{V^{n-1}} \sum_{\substack{\mathbf{h}_1, \ldots, \mathbf{h}_{n-1} \\ -\infty}}^{+\infty} F_{\mathbf{h}_1} F_{\mathbf{h}_2} \ldots F_{\mathbf{h} - \mathbf{h}_1 - \mathbf{h}_2 - \ldots - \mathbf{h}_{n-1}}. \qquad (2.2.6.4)$$

For $n = 2$, equation (2.2.6.4) reduces to Sayre's (1952) equation [but see also Hughes (1953)]

$$F_{\mathbf{h}} = \theta_2 \frac{1}{V} \sum_{\mathbf{k}} F_{\mathbf{k}} F_{\mathbf{h} - \mathbf{k}}. \qquad (2.2.6.5)$$

If the structure contains resolved isotropic atoms of two types, P and

Q, it is impossible to find a factor θ_2 such that the relation $F_{\mathbf{h}} = \theta_2 \, {_2}F_{\mathbf{h}}$ holds, since this would imply values of θ_2 such that $(_2f)_P = \theta_2(f)_P$ and $(_2f)_Q = \theta_2(f)_Q$ simultaneously. However, the following relationship can be stated (Woolfson, 1958):

$$F_{\mathbf{h}} = \frac{A_s}{V} \sum_{\mathbf{k}} F_{\mathbf{k}} F_{\mathbf{h} - \mathbf{k}} + \frac{B_s}{V^2} \sum_{\mathbf{k}, \mathbf{l}} F_{\mathbf{k}} F_{\mathbf{l}} F_{\mathbf{h} - \mathbf{k} - \mathbf{l}}, \qquad (2.2.6.6)$$

where A_s and B_s are adjustable parameters of $(\sin \theta)/\lambda$. Equation (2.2.6.6) can easily be generalized to the case of structures containing resolved atoms of more than two types (von Eller, 1973).

Besides the algebraic properties of the electron density, Patterson methods also can be developed so that they provide phase indications. For example, it is possible to find the reciprocal counterpart of the function

$$P_n(\mathbf{u}_1, \mathbf{u}_2, \ldots, \mathbf{u}_n) = \int_V \rho(\mathbf{r})\rho(\mathbf{r} + \mathbf{u}_1) \ldots \rho(\mathbf{r} + \mathbf{u}_n) \, dV. \qquad (2.2.6.7)$$

For $n = 1$ the function (2.2.6.7) coincides with the usual Patterson function $P(\mathbf{u})$; for $n = 2$, (2.2.6.7) reduces to the double Patterson function $P_2(\mathbf{u}_1, \mathbf{u}_2)$ introduced by Sayre (1953). Expansion of $P_2(\mathbf{u}_1, \mathbf{u}_2)$ as a Fourier series yields

$$P_2(\mathbf{u}_1, \mathbf{u}_2) = \frac{1}{V^2} \sum_{\mathbf{h}_1, \mathbf{h}_2} E_{\mathbf{h}_1} E_{\mathbf{h}_2} E_{\mathbf{h}_3} \exp[-2\pi i(\mathbf{h}_1 \cdot \mathbf{u}_1 + \mathbf{h}_2 \cdot \mathbf{u}_2)]. \qquad (2.2.6.8)$$

Vice versa, the value of a triplet invariant may be considered as the Fourier transform of the double Patterson.

Among the main results relating direct- and reciprocal-space properties it may be remembered:

(a) from the properties of $P_2(\mathbf{u}_1, \mathbf{u}_2)$ the following relationship may be obtained (Vaughan, 1958)

$$E_{\mathbf{h}_1} E_{\mathbf{h}_2} E_{\mathbf{h}_1 + \mathbf{h}_2} - N^{-3/2}$$

$$\simeq A_1 \langle (|E_{\mathbf{k}}|^2 - 1)(|E_{\mathbf{h}_1 + \mathbf{k}}|^2 - 1)(|E_{-\mathbf{h}_2 + \mathbf{k}}|^2 - 1) \rangle_{\mathbf{k}} - B_1,$$

which is clearly related to (2.2.5.12);

(b) the zero points in the Patterson function provide information about the value of a triplet invariant (Anzenhofer & Hoppe, 1962; Allegra, 1979);

(c) the Hoppe sections (Hoppe, 1963) of the double Patterson provide useful information for determining the triplet signs (Krabbendam & Kroon, 1971; Simonov & Weissberg, 1970);

(d) one phase s.s.'s of the first rank can be estimated *via* the Fourier transform of single Harker sections of the Patterson (Ardito et al., 1985), i.e.

$$F_{\mathbf{H}} \sim \frac{1}{L} \exp(2\pi i \mathbf{h} \cdot \mathbf{T}_n) \int_{HS(\mathbf{I}, \mathbf{C}_n)} P(\mathbf{u}) \exp(2\pi i \mathbf{h} \cdot \mathbf{u}) \, d\mathbf{u}, \qquad (2.2.6.9)$$

where (see Section 2.2.5.9) $\mathbf{H} = \mathbf{h}(\mathbf{I} - \mathbf{R}_n)$ is the s.s., $\mathbf{u}$ varies over the complete Harker section corresponding to the operator $\mathbf{C}_n$ [in symbols $HS(\mathbf{I}, \mathbf{C}_n)$] and L is a constant which takes into account the dimensionality of the Harker section.

If no spurious peak is on the Harker section, then (2.2.6.9) is an exact relationship. Owing to the finiteness of experimental data and to the presence of spurious peaks, (2.2.6.9) cannot be considered in practice an exact relation: it works better when heavy atoms are in the chemical formula.

More recently (Cascarano, Giacovazzo, Luić *et al.*, 1987), a special least-squares procedure has been proposed for discriminating spurious peaks among those lying on Harker sections and for improving positional and thermal parameters of heavy atoms.

(*e*) translation and rotation functions (see Chapter 2.3), when defined in direct space, always have their counterpart in reciprocal space.

2.2.7. Scheme of procedure for phase determination

A traditional procedure for phase assignment may be schematically presented as follows:

Stage 1: *Normalization of s.f.'s.* See Section 2.2.4.

Stage 2: *(Possible) estimation of one-phase s.s.'s.* The computing program recognizes the one-phase s.s.'s and applies the proper formulae (see Section 2.2.5.9).

Each phase is associated with a reliability value, to allow the user to regard as known only those phases with reliability higher than a given threshold.

Stage 3: *Search of the triplets.* The reflections are listed for decreasing $|E|$ values and, related to each $|E|$ value, all possible triplets are reported (this is the so-called $\sum_2$ list). The value $G = 2|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h-k}}|/\sqrt{N}$ is associated with every triplet for an evaluation of its efficiency. Usually reflections with $|E| < E_s$ (E_s may range from 1.2 to 1.6) are omitted from this stage onward.

Stage 4: *Definition of the origin and enantiomorph.* This stage is carried out according to the theory developed in Section 2.2.3. Phases chosen for defining the origin and enantiomorph, one-phase seminvariants estimated at stage 2, and symbolic phases described at stage 5 are the only phases known at the beginning of the phasing procedure. This set of phases is conventionally referred to as the *starting set*, from which iterative application of the tangent formula will derive new phase estimates.

Stage 5: *Assignment of one or more (symbolic or numerical) phases.* In complex structures the number of phases assigned for fixing the origin and the enantiomorph may be inadequate as a basis for further phase determination. Furthermore, only a few one-phase s.s.'s can be determined with sufficient reliability to make them qualify as members of the starting set. Symbolic phases may then be associated with some (generally from 1 to 6) high-modulus reflections (symbolic addition procedures). Iterative application of triplet relations leads to the determination of other phases which, in part, will remain expressed by symbols (Karle & Karle, 1966).

In other procedures (multisolution procedures) each symbol is assigned four phase values in turn: $\pi/4, 3\pi/4, 5\pi/4, 7\pi/4$. If p symbols are used, in at least one of the possible 4^p solutions each symbolic phase has unit probability of being within 45° of its true value, with a mean error of 22.5°.

To find a good starting set a *convergence method* (Germain *et al.*, 1970) is used according to which: (*a*)

$$\langle\alpha_{\mathbf{h}}\rangle = \sum_j G_j I_1(G_j)/I_0(G_j)$$

is calculated for all reflections (*j* runs over the set of triplets containing **h**); (*b*) the reflection is found with smallest $\langle\alpha\rangle$ not already in the starting set; it is retained to define the origin if the origin cannot be defined without it; (*c*) the reflection is eliminated if it is not used for origin definition. Its $\langle\alpha\rangle$ is recorded and $\langle\alpha\rangle$ values for other reflections are updated; (*d*) the cycle is repeated from (*b*) until all reflections are eliminated; (*e*) the reflections with the smallest $\langle\alpha\rangle$ at the time of elimination go into the starting set; (*f*) the cycle from (*a*) is repeated until all reflections have been chosen.

Stage 6: *Application of tangent formula.* Phases are determined in reverse order of elimination in the convergence procedure. In order to ensure that poorly determined phases $\varphi_{\mathbf{k}_j}$ and $\varphi_{\mathbf{h-k}_j}$ have little effect in the determination of other phases a weighted tangent formula is normally used (Germain *et al.*, 1971):

$$\tan\varphi_{\mathbf{h}} = \frac{\sum_j w_{\mathbf{k}_j} w_{\mathbf{h-k}_j} |E_{\mathbf{k}_j}E_{\mathbf{h-k}_j}|\sin(\varphi_{\mathbf{k}_j} + \varphi_{\mathbf{h-k}_j})}{\sum_j w_{\mathbf{k}_j} w_{\mathbf{h-k}_j} |E_{\mathbf{k}_j}E_{\mathbf{h-k}_j}|\cos(\varphi_{\mathbf{k}_j} + \varphi_{\mathbf{h-k}_j})}, \quad (2.2.7.1)$$

where

$$w_{\mathbf{h}} = \min\,(0.2\alpha, 1).$$

Once a large number of contributions are available in (2.2.7.1) for a given $\varphi_{\mathbf{h}}$, then the value of $\alpha_{\mathbf{h}}$ quickly becomes greater than 5, and so assigns an unrealistic unitary weight to $\varphi_{\mathbf{h}}$. In this respect a different weighting scheme may be proposed (Hull & Irwin, 1978) according to which

$$w = \psi\exp(-x^2)\int_0^x \exp(t^2)\,\mathrm{d}t, \quad (2.2.7.2)$$

where $x = \alpha/\langle\alpha\rangle$ and $\psi = 1.8585$ is a constant chosen so that $w = 1$ when $x = 1$. Except for ψ, the right-hand side of (2.2.7.2) is the Dawson integral which assumes its maximum value at $x = 1$ (see Fig. 2.2.7.1): when $\alpha > \langle\alpha\rangle$ or $\alpha < \langle\alpha\rangle$ then $w < 1$ and so the agreement between α and $\langle\alpha\rangle$ is promoted.

Alternative weighting schemes for the tangent formula are frequently used [for example, see Debaerdemaeker *et al.* (1985)]. In one (Giacovazzo, 1979*b*), the values $\alpha_{\mathbf{k}_j}$ and $\alpha_{\mathbf{h-k}_j}$ (which are usually available in direct procedures) are considered as additional *a priori* information so that (2.2.7.1) may be replaced by

$$\tan\varphi_{\mathbf{h}} \simeq \frac{\sum_j\beta_j \sin(\varphi_{\mathbf{k}_j} + \varphi_{\mathbf{h-k}_j})}{\sum_j\beta_j \cos(\varphi_{\mathbf{k}_j} + \varphi_{\mathbf{h-k}_j})}, \quad (2.2.7.3)$$

where β_j is the solution of the equation

$$D_1(\beta_j) = D_1(G_j)D_1(\alpha_{\mathbf{k}_j})D_1(\alpha_{\mathbf{h-k}_j}). \quad (2.2.7.4)$$

In (2.2.7.4),

$$G_j = 2|E_{\mathbf{h}}E_{\mathbf{k}_j}E_{\mathbf{h-k}_j}|/\sqrt{N}$$

or the corresponding second representation parameter, and $D_1(x) = I_1(x)/I_0(x)$ is the ratio of two modified Bessel functions.

In order to promote (in accordance with the aims of Hull and Irwin) the agreement between α and $\langle\alpha\rangle$, the distribution of α may be used (Cascarano, Giacovazzo, Burla *et al.*, 1984; Burla *et al.*, 1987); in particular, the first two moments of the distribution: accordingly,

$$w = \left\{\exp\left[\frac{-(\alpha - \langle\alpha\rangle)^2}{2\sigma_\alpha^2}\right]\right\}^{1/3}$$

may be used, where σ_α^2 is the estimated variance of α.

Stage 7: *Figures of merit.* The correct solution is found among several by means of figures of merit (FOMs) which are expected to be extreme for the correct solution. Largely used are (Germain *et al.*, 1970)
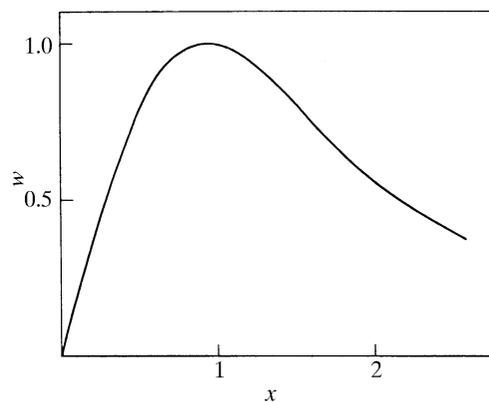

Fig. 2.2.7.1. The form of w as given by (2.2.7.2).

227

references