$$\begin{cases}\varphi_{i_1}=3x\\ \varphi_{i_2}=4x\\ \varphi_{i_3}=5x\end{cases}\qquad\begin{cases}\varphi_{j_1}=3y\\ \varphi_{j_2}=4y\\ \varphi_{j_3}=5y\end{cases}\qquad\begin{cases}\varphi_{p_1}=3z\\ \varphi_{p_2}=4z\\ \varphi_{p_3}=5z.\end{cases}$$

Phases in (*a*) and (*b*) consistitute the *primary set.*

(*c*) The phases in the *secondary set* are those defined through $\sum_2$ relationships involving pairs of phases from the primary set: they, too, can be expressed in magic-integer form.

(*d*) All the triplets that link together the phases in the combined primary and secondary set are now found, other than triplets used to obtain secondary reflections from the primary ones. The general algebraic form of these triplets will be

$$m_1x+m_2y+m_3z+b\equiv 0\ (\mathrm{mod}\ 1),$$

where b is a phase constant which arises from symmetry translation. It may be expected that the 'best' value of the unknown x, y, z corresponds to a maximum of the function

$$\psi(x,y,z)=\sum|E_1E_2E_3|\cos 2\pi(m_1x+m_2y+m_3z+b),$$

with $0\le x,y,z<1$. It should be noticed that ψ is a Fourier summation which can easily be evaluated. In fact, ψ is essentially a figure of merit for a large number of phases evaluated in terms of a small number of magic-integer variables and gives a measure of the internal consistency of $\sum_2$ relationships. The ψ map generally presents several peaks and therefore can provide several solutions for the variables.

(2) *The random-start method*

These are procedures which try to solve crystal structures by starting from random initial phases (Baggio *et al.*, 1978; Yao, 1981). They may be so described:

(*a*) A number of reflections (say NUM $\sim$ 100 or larger) at the bottom of the CONVERGE map are selected. These, and the relationships which link them, form the system for which trial phases will be found.

(*b*) A pseudo-random number generator is used to generate M sets of NUM random phases. Each of the M sets is refined and extended by the tangent formula or similar methods.

(3) *Accurate calculation of s.i.'s and s.s.'s with* 1, 2, 3, 4, . . ., *n phases*

Having a large set of good phase relationships allows one to overcome difficulties in the early stages and in the refinement process of the phasing procedure. Accurate estimates of s.i.'s and s.s.'s may be achieved by the application of techniques such as the representation method or the neighbourhood principle (Hauptman, 1975; Giacovazzo, 1977*a*, 1980*b*). So far, second-representation formulae are available for triplets and one-phase seminvariants; in particular, reliably estimated negative triplets can be recognized, which is of great help in the phasing process (Cascarano, Giacovazzo, Camalli *et al.*, 1984). Estimation of higher-order s.s.'s with upper representations or upper neighbourhoods is rather difficult, both because the procedures are time consuming and because the efficiency of the present joint probability distribution techniques deteriorates with complexity. However, further progress can be expected in the field.

Table 2.2.8.1. *Magic-integer sequences for small numbers of phases (n) together with the number of sets produced and the root-mean-square error in the phases*

n	Sequence								No. of sets	R.m.s. error (°)
1	1								4	26
2	2	3							12	29
3	3	4	5						20	37
4	5	7	8	9					32	42
5	8	11	13	14	15				50	45
6	13	18	21	23	24	25			80	47
7	21	29	34	37	39	40	41		128	48
8	34	47	55	60	63	65	66	67	206	49

(4) *Modified tangent formulae and least-squares determination and refinement of phases*

The problem of deriving the individual phase angles from triplet relationships is greatly overdetermined: indeed the number of triplets, in fact, greatly exceeds the number of phases so that any $\varphi_{\mathbf{h}}$ may be determined by a least-squares approach (Hauptman *et al.*, 1969). The function to be minimized may be

$$M=\frac{\sum_{\mathbf{k}}w_{\mathbf{k}}[\cos(\varphi_{\mathbf{h}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}-\mathbf{k}})-C_{\mathbf{k}}]^2}{\sum w_{\mathbf{k}}},$$

where $C_{\mathbf{k}}$ is the estimate of the cosine obtained by probabilistic or other methods.

Effective least-squares procedures based on linear equations (Debaerdemaeker & Woolfson, 1983; Woolfson, 1977) can also be used. A triplet relationship is usually represented by

$$(\varphi_p\pm\varphi_q\pm\varphi_r+b)\approx 0\ (\mathrm{mod}\ 2\pi),\qquad(2.2.8.2)$$

where b is a factor arising from translational symmetry. If (2.2.8.2) is expressed in cycles and suitably weighted, then it may be written as

$$w(\varphi_p\pm\varphi_q\pm\varphi_r+b)=wn,$$

where n is some integer. If the integers were known then the equation would appear (in matrix notation) as

$$\boldsymbol{A\Phi}=\boldsymbol{C},\qquad(2.2.8.3)$$

giving the least-squares solution

$$\boldsymbol{\Phi}=(\boldsymbol{A}^T\boldsymbol{A})^{-1}\boldsymbol{A}^T\boldsymbol{C}.\qquad(2.2.8.4)$$

When approximate phases are available, the nearest integers may be found and equations (2.2.8.3) and (2.2.8.4) constitute the basis for further refinement.

Modified tangent procedures are also used, such as (Sint & Schenk, 1975; Busetta, 1976)

$$\tan\varphi_{\mathbf{h}}\simeq\frac{\sum_j G_{\mathbf{h},\mathbf{k}_j}\sin(\varphi_{\mathbf{k}_j}+\varphi_{\mathbf{h}-\mathbf{k}_j}-\Delta_j)}{\sum G_{\mathbf{h},\mathbf{k}_j}\cos(\varphi_{\mathbf{k}_j}+\varphi_{\mathbf{h}-\mathbf{k}_j}-\Delta_j)},$$

where Δ_j is an estimate for the triplet phase sum $(\varphi_{\mathbf{h}}-\varphi_{\mathbf{k}_j}-\varphi_{\mathbf{h}-\mathbf{k}_j})$.

(5) *Techniques based on the positivity of Karle–Hauptman determinants*

(The main formulae have been briefly described in Section 2.2.5.7.) The maximum determinant rule has been applied to solve small structures (de Rango, 1969; Vermin & de Graaff, 1978) *via* determinants of small order. It has, however, been found that their use (Taylor *et al.*, 1978) is not of sufficient power to justify the

references