On the Application of Phase Relationships to Complex Structures. XII. The Use of Magic Integers in Phase Determination

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The use of magic integers in phase determination is examined in the light of the theory of Main [*Acta Cryst.* (1977). A**33**, 750–757]. The integers may be used in the economical search of an n-dimensional function of the phases. An interpolation procedure in the n-dimensional phase space allows the use of integer sequences of quite high error, with a consequent reduction in the magnitudes of the integers used. The number of variables to be associated with the magic-integer sequences is also examined. It is found that this number has virtually no effect on either accuracy of phase representation or on computing time. The range of one of the variables can be restricted, where necessary, in order to define the enantiomorph, thus using several phases simultaneously to give a strong enantiomorph definition. A convergence procedure is described for choosing the phases to be represented by magic integers. Magic integers may also be used to choose sets of phase values for the reflexions used in *MULTAN* to start phase determination. This replaces the more usual quadrant permutation method and results in large savings in the number of starting sets to be explored. *MULTAN* is thus made more powerful for the same computing time as before.

Introduction

After the initial successes of the use of magic integers by White & Woolfson (1975) and Declercq, Germain & Woolfson (1975) for phase determination, Main (1977) in paper XI of this series examined the nature of the phase errors involved in the magic-integer representation and gave a recipe for generating efficient magic-integer sequences. This paper examines some of the techniques used in the application of magic integers in the light of the theory in paper XI.

Exploring phase space

One of the uses of magic integers is to represent a large number of phases in terms for a small number of variables and then to compute a figure of merit for the phases. The figure of merit is plotted as a function of the variables used, called a ψ map by White & Woolfson (1975), and the peaks in the ψ map indicate the best phases to use in subsequent calculations. The economy of variables in such a calculation is very large, with consequent enormous savings in computer time, and it becomes possible to test thousands of different phase combinations by a single Fourier transformation.

To investigate the characteristics of this process, it is convenient to regard it as follows. If there are n phases in the calculation, the figure of merit evaluated is essentially an n-dimensional function. We are therefore looking for the point in this n-dimensional space which corresponds to the global maximum (or minimum) of the function. Instead of evaluating the complete function, this n-dimensional space is explored along a family of parallel straight lines by the use of magic integers as explained by Main (1977). These lines will not necessarily go through the function maximum, but at least one of them should go near enough to the maximum to detect its presence. It is possible that several lines pass close to the maximum. In this case, several maxima will appear in the ψ map, each one corresponding to a point on one of the lines close to the single maximum in n-dimensional space. These peaks in the ψ map will usually be in apparently unrelated positions and yet will lead to very similar sets of phases, especially after phase refinement. This effect is commonly observed (P. S. White & S. E. Hull, 1975, private communication) and it would be an advantage if such related solutions could be recognized at the outset.

In order to illustrate this behaviour, let us take an order-4 Karle–Hauptman determinant (Karle & Hauptman, 1950) as a simple function of the phases which we can evaluate. The magnitudes of the reflexions in the determinant are taken to be all the same and equal to U, and the phases are expressed in terms of the magic-integer sequence 4 6 7 as shown in Table 1. The three phases in the body of the determinant are represented by a single variable, x, and s_1, s_2, s_3 are the signs (+ or −) of the magic integers used. The symbols α and β represent phases which can be set at particular values for each calculation. In the expansion of the determinant there are four terms of the kind $\cos(m_1 x + m_2 x + m_3 x)$ and three involving the sum of four phases as $\cos(m_1 x + m_2 x + m_3 x + m_4 x)$, where the m_i are

Table 1. *Karle–Hauptman determinant used to investigate the behaviour of magic integer sequences*

Magnitudes

$$\begin{vmatrix} 1 & U & U & U \\ U & 1 & U & U \\ U & U & 1 & U \\ U & U & U & 1 \end{vmatrix}$$

Phases

$$\begin{vmatrix} 0 & 0 & \alpha & \beta \\ 0 & 0 & \varphi_3\,(=s_3 7x) & \varphi_2\,(=s_2 6x) \\ -\alpha & -\varphi_3\,(=-s_3 7x) & 0 & \varphi_1\,(=s_1 4x) \\ -\beta & -\varphi_2\,(=-s_2 6x) & -\varphi_1\,(=-s_1 4x) & 0 \end{vmatrix}$$

Table 2. *Indices of the terms in the expansion of the determinant shown in Table 1*

$s_1\ s_2\ s_3$	Indices of triples	Indices of quartets
+ − +	4 6 7 17	10 11 13
+ + −	4 6 7 9	2 3 13
+ + +	4 6 7 5	2 11 1
− + +	4 6 7 3	10 3 1

integers. After collecting like terms, these are both of the form cos(mx) where the size of m depends upon the signs s_1, s_2, s_3 in the determinant. Table 2 shows the values of the indices m which may be obtained from different sign combinations.

If $\alpha = \beta = 0$, the value of the determinant is a maximum when all other phases are zero, *i.e.* when $x = 0$. With $U = 0.35$ and the signs s_1, s_2, s_3 as − + +, which minimizes the highest index in the expansion, the value of the determinant is plotted as a function of x in Fig. 1. The map is centrosymmetric; so only half of it is shown. As predicted, the absolute maximum is at $x = 0$, but subsidiary maxima appear at $x = 0.17, 0.30$ and 0.47 cycles. These can be explained using the construction described by Main (1977) in which the three equations $\varphi_1 = 4x$, $\varphi_2 = 6x$, $\varphi_3 = 7x$ [all values of φ reduced modulo (1)], represent a family of parallel straight lines in three-dimensional phase space. A section through the origin perpendicular to the lines is shown in Fig. 2, giving the point where each line cuts the section. The value of x at each unique point and its distance from the origin can be calculated from simple geometry and these are given in Table 3. The remaining points in Fig. 2 are centrosymmetrically related to those in Table 3. The maximum of the determinant occurs at the origin ($x = 0$). The points, A, B and C are the closest points on adjacent lines to this maximum and these give rise to the three subsidiary maxima seen in Fig. 1. The actual values of x at A, B and C are marked on the figure and it can be seen that the maxima occur very close to the marked values. Moreover, the heights of the maxima correlate with the distances of A, B and C in phase space from the absolute maximum at $x = 0$.

This calculation was repeated with the signs s_1, s_2, s_3 in the determinant as + − +, thus maximizing the highest index in the expansion of the determinant. The resultant plot of determinant value as a function of x is shown in Fig. 3. Because of the higher maximum index (now 17 instead of 7), the 'resolution' of the map

has been increased over that in Fig. 1. The x values of all the points in Fig. 2 are marked on the map and it can be seen that they correspond to the maxima of the function. In effect, we can see the next-nearest neighbours to the origin point O. The two points G and I have similar x values and are not resolved in Fig. 3; otherwise all other points correspond to discrete maxima.

In this simple case, the phases represented by any of the maxima in Fig. 3 should be capable of refinement to their values at the absolute maxima at $x = 0$. Clearly, this is the source of the closely related phase sets from
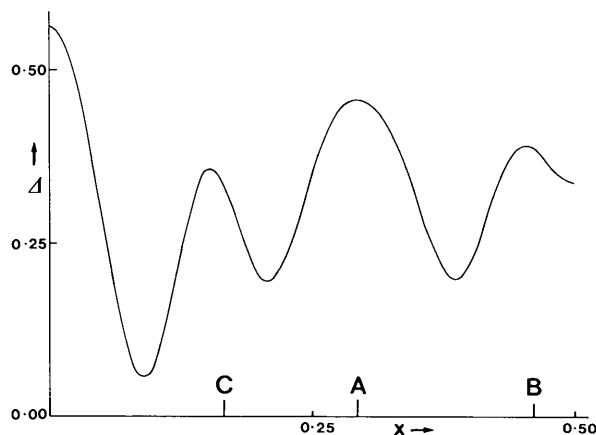

Fig. 1. Plot of value of determinant, Δ, as a function of magic-integer parameter x. The determinant is that defined in Table 1 with $U = 0.35$, $\alpha = \beta = 0$, $s_1 s_2 s_3 = - + +$.
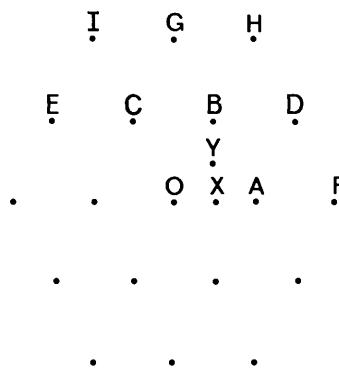

Fig. 2. Section perpendicular to the family of lines created by $\varphi_1 = 4x$, $\varphi_2 = 6x$, $\varphi_3 = 7x$, mod (1), in phase space.

Table 3. *The value of x and distance from the origin of each point in Fig. 2*

Point	Value of x ($\times$ 101 cycles)	Distance from origin (cycles)
O	0	0·000
A	30	0·299
B	47	0·359
C	17	0·372
D	24	0·545
E	13	0·572
F	41	0·597
G	37	0·666
H	7	0·717
I	34	0·744

the ψ map. If the maximum in phase space is not at the origin as assumed in this example, the section in Fig. 2 can be moved parallel to itself so that it once more contains the maximum. This has the effect of changing the x values of all the lattice points in the section by a constant so that the relative x values are the same as before. Instead of looking for a single peak in the ψ map, it is now possible to search for a group of related peaks whose relative x values can be predicted from the particular magic-integer sequence in use. It is merely an exercise in n-dimensional geometry to calculate these relative values of x for any magic-integer sequence and thus to predict which peaks in the ψ map correspond to closely related phase sets.

Interpolation in phase space

Now that the determinant value as a function of the magic-integer parameter x can be explained in all its detail, it is interesting to see the effect of moving the determinant maximum to different points in phase
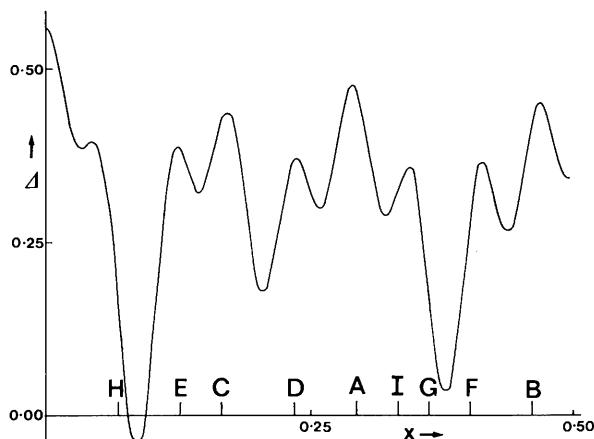
Table 4. *Phases (°) corresponding to points in phase space shown in Fig. 2 when O is at $x = -5/3434$*

Point	O	A	X
x	−0·001	0·296	
φ_1	−2·1	65·6	31·7
φ_2	−3·1	−81·5	−42·3
φ_3	−3·7	24·9	10·6

space. The phases which maximize the determinant are those which give all the triple phase products in the expansion of a phase of zero. For example, if the values of α and β (defined in Table 1) are set at 10·6° and 42·3° respectively, the determinant will have a maximum value when $\varphi_1 = 31\cdot7°$, $\varphi_2 = 42\cdot3°$ and $\varphi_3 = 10\cdot7°$. If the origin, O, in Fig. 2 is at $x = -0\cdot001$, then the determinant maximum is at the point X and is exactly midway between the lattice points O and A. This means the required phases are represented equally as well by $x = -0\cdot001$ (corresponding to the point O) and $x = 0\cdot296$ (corresponding to A). This should give rise to two principal maxima in a plot of determinant value as a function of x. With the sign combination + − + (defined in Table 2) for the signs of the magic integers, this plot is shown in Fig. 4. It can be seen that there are, indeed, two principal maxima at the predicted values of x. Also, all the subsidiary maxima can be explained in terms of the nearest neighbours of the points O and A in Fig. 2, as described in the previous section.

This result gives rise to the possibility of interpolation in phase space between the points corresponding to maxima in the magic-integer map. In the example just given, the phases corresponding to the principle maxima in Fig. 4 are shown in Table 4. Since the maxima are of equal height, it is reasonable to assume the maximum in phase space is midway
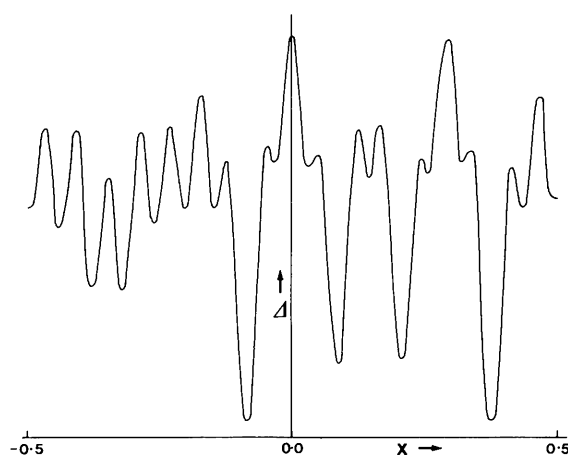

Fig. 3. Plot of value of determinant, Δ, as a function of magic-integer parameter x. The determinant is that defined in Table 1 with $U = 0\cdot35$, $\alpha = \beta = 0$, $s_1 s_2 s_3 = + - +$. The x values of the points in Fig. 2 are marked.

Fig. 4. Plot of value of determinant, Δ, as a function of magic-integer parameter x. The determinant is that defined in Table 1 with $U = 0\cdot35$, $\alpha = 10\cdot6°$, $\beta = 42\cdot3°$, $s_1 s_2 s_3 = + - +$.

between these points and this leads directly to the phase values shown in the final column in Table 4. These are precisely the values of φ_1, φ_2 and φ_3 which maximize the determinant. Note that these phases cannot be represented exactly in terms of the magic integers, but have been obtained by interpolation in phase space between two points which *are* represented by magic integers.

A second example to illustrate interpolation is obtained by taking $\alpha = 42 \cdot 3°$ and $\beta = 49 \cdot 4°$. The determinant is now maximized by $\varphi_1 = 7 \cdot 1°$, $\varphi_2 = 49 \cdot 4°$ and $\varphi_3 = 42 \cdot 3°$. This is the point Y in Fig. 2 when the origin, O, is at $x = 0 \cdot 001$. Y is equidistant from the three points O, A and B which can be represented by magic integers. The plot of determinant value against x should therefore show three equal maxima at the x values of O, A and B, i.e. $0 \cdot 001$, $0 \cdot 298$ and $0 \cdot 466$ respectively. Fig. 5 shows this plot and confirms the prediction. As before, all the subsidiary maxima can be explained in terms of the nearest neighbours of the points O, A and B in the section in Fig. 2. Clearly, the point in phase space which is equidistant from the phases represented by the three principal maxima yields precise values for the phases which maximize the determinant. These are shown in Table 5.

These examples are very contrived but, in principle, interpolation in phase space is possible in the general case of any magic-integer sequence of arbitrary length. However, it remains to be shown that this can be made a practical extension to the magic-integer technique. Such a development would be very valuable since it would be possible to derive phases which are more accurate than those given directly by the magic integers. In effect, the multiple solutions from the ψ map would be combined to yield a single set of phases which is more accurate than any of the sets obtained directly from the map. For long sequences this has a dramatic effect on the magnitudes of the integers which must be used. For example, if 100 phases are represented with an r.m.s. error of about $62°$, the theory in paper XI shows that the integers must be of the order of 10^{14}. This is clearly impractical. On the other hand, if the r.m.s. error of the sequence can be allowed to rise to $82°$, the integers need only be of the order of 10^2.

The ψ map

The ψ map as used by White & Woolfson (1975) is essentially a figure of merit for a large number of phases evaluated as a function of a small number of magic-integer variables. The form they used was

$$\psi(x,y,z) = \sum_r |E_{1r} E_{2r} E_{3r}|$$
$$\times \cos \{2\pi(H_r x + K_r y + L_r z + b_r)\}, \qquad (1)$$

which is a measure of the internal consistency of Σ_2 relationships as a function of three variables. Clearly,

Table 5. *Phases ($°$) corresponding to points in phase space shown in Fig. 2 when O is at $x = 4/5151$*

Point	O	A	B	Y
x	0·001	0·298	0·466	
φ_1	1·1	68·9	−48·8	7·1
φ_2	1·7	−76·7	−73·1	−49·4
φ_3	2·0	30·5	94·5	42·3

any kind of phase relationship which can be expressed in terms of trigonometric functions can easily be incorporated into the ψ map. It is not limited to Σ_2 relationships only. However, the ψ map can be expressed as a function of any number of magic-integer variables and it is of interest to determine the optimum number.

Paper XI gives the lower bound of the r.m.s. error of a magic-integer sequence as

$$\Delta\varphi_{lb} =$$

$$2 \left\{ \frac{\pi(n-1)}{n(n+1)} \right\}^{1/2} \left\{ \frac{\Gamma[(n+1)/2]}{\left(\sum_{i=1}^{n} m_i^2 \right)^{1/2}} \right\}^{1/(n-1)} \text{radians.} \quad (2)$$

As an efficient sequence has an actual r.m.s. error only slightly greater than this, equation (2) can safely be used to estimate actual phase errors.

Let there be M points in the ψ map in N dimensions. This gives a map with $M^{1/N}$ points in each direction. The actual number of points chosen in each direction will normally be a simple function of the corresponding indices of the Fourier coefficients. In this case, a convenient function to take is

$$M^{1/N} = a \times \text{r.m.s. index} \qquad (3)$$

where a is a small integer.

It will be expected that

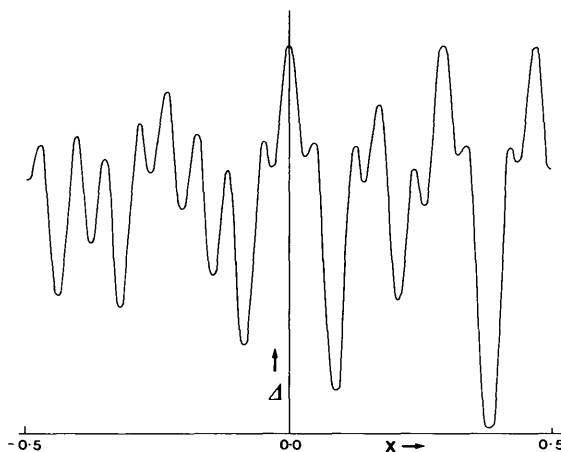$$\text{r.m.s. index} = p \times \text{r.m.s. magic integer,} \qquad (4)$$

Fig. 5. Plot of value of determinant, Δ, as a function of magic-integer parameter x. The determinant is that defined in Table 1 with $U = 0 \cdot 35$, $\alpha = 42 \cdot 3°$, $\beta = 49 \cdot 4°$, $s_1 s_2 s_3 = + - +$.

where p is a function of the average number of phases represented by magic integers in each Fourier coefficient and the number of dimensions, N, of the map.

The r.m.s. magic integer is obviously given by

$$\frac{1}{n}\left(\sum_{i=1}^{n} m_i^2\right)^{1/2};\qquad(5)$$

so from (2), (3), (4) and (5) we obtain

$$\Delta\varphi_{1b} = 2\left\{\frac{\pi(n-1)}{n(n+1)}\right\}^{1/2}\left\{\frac{ap\,\Gamma[(n+1)/2]}{n^{1/2}M^{1/N}}\right\}^{1/(n-1)}.\qquad(6)$$

The expression can now be evaluated for realistic values of the parameters involved to see which kind of ψ map will lead to the smallest r.m.s. errors in the phases. Values of p depend upon the particular problem but, for Σ_2 relationships, we may take $p = 1\cdot5$ for $N = 1$, $p = 1$ for $N = 2$ and $p = 0\cdot8$ for $N = 3$. The value of p decreases as N increases because the more variables that are used to express the phases in each relationship, the easier it is to avoid the addition of integers to produce high values of the indices. Table 6 shows $\Delta\varphi_{1b}$ calculated from (6) with $M = 4096$, $a = 5$, $Nn = 18$ and different combinations of p and N. Clearly, $\Delta\varphi_{1b}$ is quite insensitive to variations in the parameters and it matters little whether the ψ map is evaluated in terms of one, two or three variables. Separation of variables becomes more important as the number of phases in each relationship increases but, on the other hand, $\Delta\varphi_{1b}$ becomes even more insensitive as n increases. It appears therefore that the number of dimensions of the ψ map is merely a matter of programming convenience and personal taste.

Choosing reflexions for the ψ map

Declercq, Germain & Woolfson (1975) described an algorithm for choosing the reflexions which contribute to the ψ map. These were divided into two groups – the primary set and the secondary set. Phases in the secondary set are defined through Σ_2 relationships containing two phases from the primary set and primary-set phases are expressed in terms of the magic integers. An improved algorithm has been used successfully and will be described here. It is similar to the convergence procedure used by *MULTAN* and attempts to maximize the weighted sum of phase relationships which contribute to the ψ map.

Table 6. *Values of $\Delta\varphi_{1b}$ (°) obtained from equation (6) with $M = 4096$, $a = 5$, $Nn = 18$*

p	N	1	2	3
0·8				56·5
1·0		55·8	57·1	59·0
1·5		57·1		

Initially, all reflexions are put in the primary set. The effect of removing each reflexion in turn from the primary set is then examined. If the phase of the reflexion can be defined through phase relationships in terms of primaries it can become a secondary; otherwise it will be eliminated. In either case other reflexions may have to be eliminated because they can no longer be defined as secondaries. The elimination of reflexions results in the elimination of all phase relationships to which the reflexions contribute and the weighted sum of all eliminated relationships is recorded. At the end of examining each primary reflexion in this way, that reflexion which results in the smallest loss of phase relationships is taken out of the primary set. If no phase relationships are eliminated by removing any reflexion from the primary set, that reflexion with the lowest weight of relationships associated with it becomes a secondary. Reflexions are removed from the primary set in this way until the required number of primaries is reached. The usual checks are made to ensure that the origin can be uniquely defined by the remaining primary reflexions. The weight of a Σ_2 relationship is taken as $\kappa I_1(\kappa)/I_0(\kappa)$ where $\kappa = 2N^{-1/2}|E_1E_2E_3|$ and similar expressions pertain for other types of relationship.

It has been found (Declercq & Germain, 1976, private communication) that this algorithm usually results in the same number of primary and secondary reflexions as before, but increases the number of phase relationships with which they are associated. This means the phases should be better defined by the ψ map.

If the enantiomorph is not already fixed by the space group or other means, only cosine functions will appear in the expression for the ψ map, making the map centrosymmetric. Enantiomorph definition can then be achieved by computing only the asymmetric unit of the map instead of the more usual practice of restricting the possible values of a single, properly chosen phase. This means that many phases will be used simultaneously to give a strong enantiomorph definition. The importance of this has been pointed out by Hauptman & Duax (1972), but the method they describe is only easily applicable to a limited number of space groups. The technique described here is quite general, although the reflexions used are not so carefully chosen as in the Hauptman & Duax method.

Magic-integer phase permutation

A further use of magic integers which has already proved to be very valuable is in the generation of starting sets of phases for *MULTAN*. Until now, the unknown phases among the reflexions chosen to start the phase determination have been given all combinations of the values $\pm\pi/4$, $\pm3\pi/4$. For n unknown phases, quadrant permutation can give rise to 4^n sets

of phases. This number increases rapidly with n and so severely limits the number of unknown phases which can be included.

Instead of the n unknown phases being given values by quadrant permutation, let them be represented by a magic-integer sequence of length n, i.e. let the phases be given by

$$\varphi_i = m_i x \bmod (1). \qquad (7)$$

It is now possible to choose any number of sets of phase values by assigning the appropriate number of values to the magic-integer variable, x, at equally spaced intervals in the range $0 < x < 1$.

The question now arises as to how many sets of phases should be generated. Each set of phase values can be plotted as a point in n-dimensional·phase space and these points will lie on the lines represented by the equations (7). A sensible interval of x will give rise to points which have about the same separation in the direction of the lines as the separation of the lines themselves. This should result in an even distribution of points over the whole of the phase space. The average separation of the lines may be taken as the diameter of the hypersphere of equivalent volume to the Voronoi polyhedron which was fully described in paper XI. The radius of the hypersphere is given as

$$a = \frac{1}{\sqrt{\pi}} \left\{ \frac{\Gamma[(n + 1)/2]}{\left[\sum\limits_{i=1}^{n} m_i^2 \right]^{1/2}} \right\}^{1/(n-1)}. \qquad (8)$$

Now, when x changes by a small amount δx, the phase φ_i changes by a corresponding amount $\delta\varphi_i$ given by

$$\delta\varphi_i = m_i \, \delta x. \qquad (9)$$

The distance moved in phase space is therefore

$$\delta s = \left(\sum_{i=1}^{n} \delta\varphi_i^2 \right)^{1/2} = \left(\sum_{i=1}^{n} m_i^2 \right)^{1/2} \delta x. \qquad (10)$$

It follows that, in the interval $0 < x < 1$, the total length of the lines generated is given by

$$s = \left(\sum_{i=1}^{n} m_i^2 \right)^{1/2}. \qquad (11)$$

From (8) and (11), the interval of x which will give an even distribution of points in phase space will be

$$\Delta x = \frac{2a}{s} = \frac{2}{\sqrt{\pi}} \left\{ \frac{\Gamma[(n + 1)/2]}{[\sum m_i^2]^{n/2}} \right\}^{1/(n-1)}. \qquad (12)$$

For the magic-integer sequences and values of n of practical interest, the interval of x given by (12) leads to approximately the same number of phase sets as the following simple algorithm. Let the phase φ_n, associated with the largest integer m_n, take on values from $\pi/4$ to $2\pi m_n - \pi/4$ radians at intervals of $\pi/2$, i.e. it takes on the four values $\pm\pi/4$, $\pm3\pi/4$ repeatedly, for x in the range 0 to 2π radians. Each of these phase values leads

to a unique value of x which, in turn, is used to generate the remaining phases in the set. Clearly, this will always generate $4m_n$ sets of phases. In *MULTAN*, the phase φ_n is chosen as the phase which is restricted in value to fix the enantiomorph (where necessary), in which case only the appropriate values of φ_n are used.

It is now necessary to examine the errors in the phases when they are generated in this way. If the correct starting phases are represented by a point in phase space, at least one of the points generated by the above algorithm must be acceptably close to this. The expected distance between the correct point and the nearest generated point gives the expected sum of the squares of the errors in the starting phases. This, in turn, leads to the r.m.s. error in the phases. The value of this clearly depends upon the actual magic-integer sequence used but, employing the same ideas as set out in paper XI, the lower bound of the r.m.s. error can be obtained as follows.

The number of phase sets generated is $4m_n$. The volume of phase space associated with each set is therefore

$$V = \frac{1}{4m_n}, \qquad (13)$$

where the dimensions of the space are measured in cycles. The lower bound of the r.m.s. error will be obtained when this volume is assumed to be an n-dimensional hypersphere. The volume of such a hypersphere of radius a is given by

$$V = \frac{2a^n}{n} \frac{\pi^{n/2}}{\Gamma(n/2)}. \qquad (14)$$

Paper XI gives the mean square distance of a point in the hypersphere from its geometric centre as

$$\overline{d^2} = \frac{na^2}{n + 2}. \qquad (15)$$

This gives the sum of the squares of the expected errors in n phases. The lower bound of the r.m.s. error of a typical phase is therefore given by

$$\Delta\varphi_{lb} = 2\pi \left(\frac{\overline{d^2}}{n} \right)^{1/2} \text{radians.} \qquad (16)$$

From (13), (14), (15) and (16), the lower bound of the r.m.s. phase error is given by

$$\Delta\varphi_{lb} = 2 \left\{ \frac{\pi}{n + 2} \right\}^{1/2} \left\{ \frac{\Gamma[(n + 2)/2]}{4m_n} \right\}^{1/n} \text{radians.} \qquad (17)$$

Provided the magic-integer sequences used are set up as described in paper XI, the actual r.m.s. errors in the starting phases should be only very little more than the lower bound given by equation (17). In the case where $n = 1$, m_n will be taken as 1 and (17) gives the exact r.m.s. error of 26·0°.

A simple illustration of magic-integer phase permutation is given in Fig. 6. The 16 phase combinations produced by quadrant permutation on two unknown phases are plotted in Fig. 6(a). A convenient magic-integer sequence of length two is 2 3 and the set of lines generated by the equations (7) using these integers is shown in Fig. 6 (b). If φ_2 now takes only the four values $\pm\pi/4$, $\pm 3\pi/4$, the corresponding values of φ_1 are shown plotted in the diagram. Clearly, there are now only 12 phase combinations instead of the 16 in Fig. 6(a). There are two reasons for this reduction in number. The first is that the r.m.s. error of the magic-integer phases is slightly higher than the error of the phases produced by quadrant permutation. Equation (17) shows that for $n = 2$ and $m_n = 3$, the lower bound of the r.m.s. error is 29·3°. This is to be compared with an r.m.s. error of 26·0° for quadrant permutation. There is ample evidence that the r.m.s. error of the starting phases can be allowed to rise, because MULTAN often produces more than one set of phases from which the structure can be obtained. These multiple solutions will be less frequent when the starting phase values are spaced more widely apart. The second reason for a saving in the number of phase sets by magic integers can be seen from Fig. 6. The 12 sets generated by magic integers obviously produce a much more closely packed lattice in phase space than the 16 sets in Fig. 6(a). Phase space is therefore covered in a more efficient manner and this will be true of any magic-integer sequence set up as described in paper XI.

The reduction in the number of phase sets becomes very large as n increases. Table 7 compares the number of sets produced by quadrant permutation with those produced by two different sets of magic integer sequences. The sequences chosen are those based on the geometric progression 1 2 4 8 16 ... of common ratio $r = 2$ and the Fibonacci series 1 1 2 3 5 8 ... of limiting ratio $r = 1·618$. These are given in Tables 2 and 3 of paper XI respectively. Also shown in Table 7 is the lower bound of the r.m.s. error of the starting phases as calculated from equation (17).

The magic-integer sequences actually used in MULTAN are those for which $r = 2$. The saving in computing time for the larger values of n is quite dramatic, making the program much more efficient. Alternatively, for the same computing time as before, additional reflexions can be included in the starting set thus making MULTAN more powerful. It is not yet known how high an error can be tolerated in the starting phases, but all the tests carried out to date indicate that the errors produced by the $r = 2$ sequences are acceptably low. No structure has been found which the new MULTAN will not solve that could be solved before. On the other hand, a number of structures have been determined with the new version which could not be solved in a reasonable amount of computer time with the older program. As an example, Margulis & Lessinger (1977) solved N-acetyl colchinol, $C_{20}H_{23}NO_5$, $P2_1$, $Z = 4$ using magic-integer permutation after many trials with quadrant permutation had failed. Using 260 E's and the complete set of Σ_2 relationships, they generated 504 sets of phases. The most likely of these, as indicated by the combined figure of merit, gave a map which contained 46 out of the 52 non-hydrogen atoms in the asymmetric unit. The highest false peak was 26th in order of height. The same starting set of phases would have given rise to 8192 sets by quadrant permutation. Of the known structures that have been used as tests, two are of interest because previous tests of MULTAN on them have already been reported (Lessinger, 1976). They are 3,3-dimethyl-4,5,9,10,11,12-hexacarboxymethyltetra-cyclo[7,2,1,0²·⁴,0²·⁸]dodeca-5,7,10-triene, referred to as RR (Declercq, Germain & Henke, 1973), and tetra-phenylhydrazine, referred to as TPH (Hoekstra, Vos, Braun & Hornstra, 1975). The previous version of MULTAN solved these only with difficulty, whereas they are now solved with ease with a wide range of parameters used for the programs. For example, with 250 E's for RR and the complete set of Σ_2's, 56 sets of phases were generated. The 'best' (according to combined figure of merit) map showed 36 out of the 38
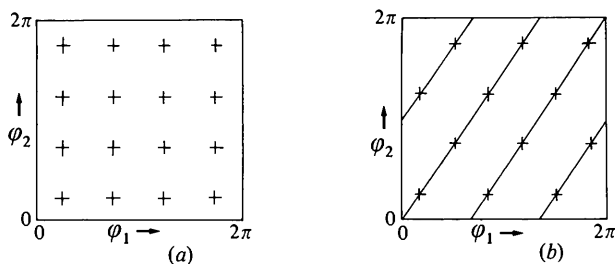

Fig. 6. (a) The 16 phase sets generated for two unknown phases by quadrant permutation. (b) The 12 phase sets generated for two unknown phases by magic-integer permutation (magic-integer sequence is 2 3).

Table 7. *Number of phase sets generated by quadrant permutation and magic integer permutation as a function of the number, n, of unknown phases*

Also given is the lower bound of the r.m.s. error of the phases in degrees.

n	QP	$\Delta\varphi_{rms}$	$r = 2$	$\Delta\varphi_{1b}$	$r = 1·618$	$\Delta\varphi_{1b}$
			Magic-integer permutation			
1	4	26·0	4	26·0	4	26·0
2	16	26·0	12	29·3	12	29·3
3	64	26·0	28	32·5	20	36·8
4	256	26·0	60	35·2	36	40·3
5	1024	26·0	124	37·0	60	43·0
6	4096	26·0	252	38·4	100	44·9
7	16384	26·0	508	39·4	164	46·4
8	65536	26·0	1020	40·1	268	47·5
9	262144	26·0	2044	40·7	436	48·4
10	1048576	26·0	4092	41·1	708	49·1

independent non-hydrogen atoms and the highest spurious peak was 35th in order of height. Similarly, for TPH, with 270 E's and all the Σ_2's, the 'best' map from the 56 sets of phases generated gave all 39 atoms of the structure. In this case, the highest spurious peak was 39th. The performance of the individual figures of merit for both of these structures is worth reporting. For RR, the best set of phases was first in ranking order on residual, second on ψ_0 and 15th on $\Sigma\alpha$, while the best set for TPH was first on residual, first on ψ_0 and 18th on $\Sigma\alpha$ (out of 56). Since $\Sigma\alpha$ is a measure of the internal consistency of the Σ_2 relationships, it is clear that the correct phases do not correspond to the most consistent set of Σ_2's and, in fact, are a long way from this situation. As the phase-determination process relies initially upon the assumption that $\varphi_{\bar{h}} + \varphi_{h-k} + \varphi_k = 0$ for all h and k, this could be the reason why these two structures were previously rather difficult to solve. Copies of this latest version of MULTAN are available from the author upon request.

Only the starting phases which are not restricted by space-group symmetry are given values by magic-integer permutation. Phases which can take on only two values because of symmetry are still given those two values in different phase combinations as before. For n phases assigned to magic integers, the number of sets produced is

$$N_1 = 2^{n+2} - 4. \qquad (18)$$

This number is obviously modified by the requirements of enantiomorph and origin fixing in the usual way. If the Fibonacci sequences were used, the number of phase sets produced would be

$$N_2 = \frac{8}{\sqrt{5}} \left\{ \left[\frac{1 + \sqrt{5}}{2} \right]^{(n+1)} - \left[\frac{1 - \sqrt{5}}{2} \right]^{(n+1)} \right\} - 4. \qquad (19)$$

It is clearly of interest to determine how large an error can be tolerated in the starting phases in MULTAN, since any permitted increase in error results in a large decrease in the number of phase sets which must be generated. In general, when the phase sets are generated from a magic integer sequence based on an integer-geometric progression of limiting ratio r, the number of sets produced for n phases will be a function of r^n.

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On the Application of Phase Relationships to Complex Structures.
XIII.* The Choice of Reflexions

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Alternative methods of choosing the reflexions for use in direct methods are discussed. The original CONVERGE method, as implemented in the MULTAN system of computer programs, is compared with several variants and an iterative procedure for maximizing the ratio of triple-phase invariants to reflexions is described.

Introduction

Woolfson (1977) has outlined a computer program package for direct phase determination which, in time,

may replace tangent-formula-based programs such as MULTAN (Main, Woolfson, Lessinger, Germain & Declercq, 1974). At the heart of MULTAN is the CONVERGE procedure (Germain, Main & Woolfson, 1970) which determines the reflexions to be used in the starting set (origin and enantiomorph-defining

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* Part XII: Main (1978).