The Application of Phase Relationships to Complex Structures. VII. Magic Integers

By Peter S. White* and M. M. Woolfson

Department of Physics, University of York, England

With phases expressed in cycles so that $0 \leq \varphi < 1$ it is possible with a single symbol x, in the range 0 to 1, to represent several phases, say m, by

$$\varphi_i = n_i x \bmod (1)$$

where i runs from 1 to m and the integers, n_i, are referred to as 'magic integers'. A starting set of phases may consist of some which fix the origin and enantiomorph, some known by $\sum_1$ relationships for example and others given magic-integer representation in terms of x, y and z. Relationships between the starting-set phases then appear in the form

$$Hx + Ky + Lz + b \simeq 0,$$

and maxima of the function,

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

lead to sets of possible values of the unknown phases in the starting set of reflexions. By means of the magic-integer process complex structures requiring very large starting sets may be tackled. Examples of the application of the method are given.

Introduction

The phase-permutation method as incorporated in the computer program *MULTAN* (Germain, Main & Woolfson, 1971) depends fairly critically on the precision with which the first few phases are developed. The process is a stepwise one, and one or two bad phase relationships early on can lead to a completely wrong answer. This problem can normally be overcome by increasing the number of reflexions in the starting set and thereby bypassing the bad relationship. However, as the number of sets of phases developed is exponentially related to the size of the starting set, the number of phases that can be permuted is severely limited. If, for example, there were n variable reflexions in the starting set then 4^n sets of phases would be developed. Four variable phases, requiring 256 permutations, is the limit of what could normally be contemplated.

The present work is aimed at developing a method by which phases can be allocated to a significantly larger set of starting reflexions than is feasible in the permutation method. While the method involves the use of the same relationships as does the permutation method it is not a 'stepwise' one and so should not be so sensitive to the occasional bad relationship.

Magic integers – the basic concept

In a normal application of the symbolic-addition process a number of phases may be expressed explicitly,

other phases are represented by symbols and further phases are generated in terms of these symbols. However, if the number of symbols is too large, difficulties may arise and, for this reason, the number of symbols is usually kept to a minimum.

For a general phase a symbol may turn out to have any value between 0 and 2π, and one usually hopes to get an indication for the phase through the symbolic-addition process. We have evolved a mathematical device, which we call 'magic integers', by which a single symbol may be made to represent several phases and this is now described.

We take three phases $\varphi_1, \varphi_2, \varphi_3$ expressed in cycles so that

$$0 \leq \varphi < 1 \qquad (1)$$

and set up the following equations

$$\varphi_1 = 3x \bmod (1)$$
$$\varphi_2 = 4x \bmod (1)$$
$$\varphi_3 = 5x \bmod (1). \qquad (2)$$

The proposition we now examine is that, no matter what the values of φ, for some value of x in the range $0 \leq x < 1$ the three equations can be approximately satisfied. That this is so is best seen by considering some examples:

(i) $\varphi_1 = 0 \cdot 3$, $\varphi_2 = 0 \cdot 2$, $\varphi_3 = 0 \cdot 7$ with $x = 0 \cdot 766$

$3x = 2 \cdot 298$ and $3x \bmod (1) = 0 \cdot 298$

$4x = 3 \cdot 064$ and $4x \bmod (1) = 0 \cdot 064$

$5x = 3 \cdot 830$ and $5x \bmod (1) = 0 \cdot 830$.

The errors, 0·002, 0·136 and 0·130 cycles respectively, correspond to 1, 49 and 47°.

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* Present address: Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada.

(ii) $\varphi_1 = 0.8$, $\varphi_2 = 0.6$, $\varphi_3 = 0.0$ with $x = 0.622$

$$3x = 1.866 \text{ and } 3x \bmod (1) = 0.866$$
$$4x = 2.488 \text{ and } 4x \bmod (1) = 0.488$$
$$5x = 3.110 \text{ and } 5x \bmod (1) = 0.110 .$$

The errors in this case correspond to 24, 40 and 40°.

These two examples are illustrated graphically in Fig. 1 which shows the three functions $\varphi = 3x \bmod (1)$, $\varphi = 4x \bmod (1)$ and $\varphi = 5x \bmod (1)$; the values of x for the two examples are also shown.

Magic-integer representation of phases has thus far been described in terms of the three integers 3, 4 and 5. It is possible, however, to use other sets of integers or, indeed, to have more than three integers. The accuracy with which phases can be represented by magic integers tends to increase with the magnitude of the integers. On the other hand, we shall show that the use of magic-integer representation of phases is most economical if the integers are small and, in practice, a compromise is sought between these conflicting requirements.

Table 1 shows the characteristics of various sets of magic integers. For sets of three integers it was possible to consider the phases φ_i at intervals of 0·01. All possible permutations of $\varphi_1, \varphi_2, \varphi_3$ were generated and the values of x giving the best fits found. It was then possible to obtain a mean error and a maximum possible error for the integer set. For sets containing more than three integers such a procedure was found to be too time-consuming and a less rigorous approach had to be adopted. In these cases 1000 random sets of φ's were generated and the x's giving the best fits found. Whilst this probably gave a good approximation to the mean error, the maximum error found by this method must be treated with some suspicion. Table 1 gives the mean and maximum errors for a selection of the best sets found.
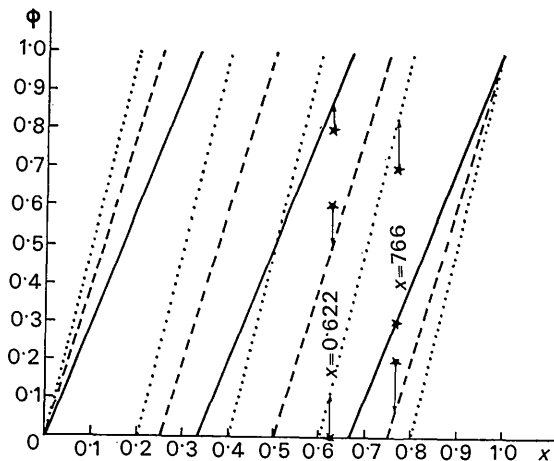
Table 1. *A comparison of possible sets of magic integers*

Integer set								R.m.s. error	Maximum error
1	2	3						47	90
1	3	4						42	79
1	3	6						35	65
1	4	16						23	43
2	3	4						38	72
2	3	7						33	65
3	4	5						33	65
3	4	6						34	65
3	4	13						25	50
3	5	6						33	65
3	5	7						30	68
4	5	6						31	65
4	5	7						29	54
4	5	21						23	43
5	6	7						30	61
5	6	31						23	54
2	3	7	13					39	75
3	4	5	6					46	83
3	4	5	7					45	83
3	4	5	13					40	72
3	4	13	25					33	65
4	5	7	10					38	75
4	5	7	13					37	69
4	5	21	41					28	56
3	4	5	8	13				49	102
3	4	5	9	12				51	93
3	4	5	9	20				46	88
3	4	5	21	28				42	83
3	5	7	14	21				46	88
4	5	6	11	17				48	93
5	7	9	11	13				45	92
5	7	9	11	20				45	90
6	7	8	13	21				48	89
13	15	17	19	21				45	85
3	4	5	11	16	27			50	98
3	4	5	12	15	19			53	98
3	4	5	15	20	25			50	100
3	4	5	30	40	50			44	87
4	5	6	7	8	9			56	106
5	7	9	11	13	15			53	99
7	9	11	13	17	30			49	91
7	10	13	16	19	22			52	98
7	9	11	13	17	23	43		52	100
17	23	29	33	37	63	100		44	87
9	11	13	15	17	19	21	23	61	111
13	17	19	23	25	27	34	61	54	106
21	23	24	25	26	27	33	60	53	100

The use of magic integers

Consider a situation where a number of phases are represented in the following manner:

$$\varphi_1 = 3x \bmod (1) \quad \varphi_4 = 3y \bmod (1) \quad \varphi_7 = 3z \bmod (1)$$
$$\varphi_2 = 4x \bmod (1) \quad \varphi_5 = 4y \bmod (1) \quad \varphi_8 = 4z \bmod (1)$$
$$\varphi_3 = 5x \bmod (1) \quad \varphi_6 = 5y \bmod (1) \quad \varphi_9 = 5z \bmod (1) . \quad (3)$$

If there is a phase relationship

$$\varphi_1 + \varphi_3 + \varphi_6 + \pi \simeq 0 \bmod (1) , \quad (4)$$

this can be represented by

$$3x + 5x + 5y + \pi \simeq 0 \bmod (1) \quad (5)$$

or

$$8x + 5y + \pi \simeq 0 \bmod (1) . \quad (6)$$

Fig. 1. The graph shows the functions $\varphi = 3x \bmod(1)$ (full line), $\varphi = 4x \bmod(1)$ (dashed line) and $\varphi = 5x \bmod(1)$ (dotted line). The values of x giving matches with the sets of φ's given in the text are indicated.

In general, any relationship involving the phases represented by magic integers and fixed phases can be expressed as an equation of the type

$$Hx + Ky + Lz + b \simeq 0 \bmod (1) . \qquad (7)$$

The π in equation (6) and the b in equation (7) arise because of translational symmetry in the space group and because the φ's are considered only in one asymmetric unit of reciprocal space.

At the beginning of the phase-determining process several phases will be known as a result of origin and enantiomorph definition and possibly of $\sum_1$ relationships. If the phases of a number of reflexions can be represented by magic integers then there will be a number of $\sum_2$ relationships between these phases, which may be written in the cosine form

$$\cos \{2\pi(Hx + Ky + Lz + b)\} \underset{\sim}{\lessgtr} 1 . \qquad (8)$$

Where the symbol $\underset{\sim}{\lessgtr}$ means 'tends to be close to but must be less than'. We can express the condition that the relationships of type (8) should be satisfied as well as possible, and also take account of the strength of the relationships by looking for maxima of the function

$$\psi(x,y,z) = \sum_r |E_{1r}E_{2r}E_{3r}| \cos \{2\pi(H_r x + K_r y + L_r z + b_r)\} . \qquad (9)$$

These maxima may be sought by evaluating $\psi(x,y,z)$ over the range 0 to 1 for each of the variables and, since this is a straightforward Fourier summation, it presents no difficulty. Adequate resolution can be obtained by evaluating the function at about four times the maximum-index points along each axis; hence the requirement to keep the magnitude of the magic integers as low as possible. A high peak in the map can be translated into phases, and these phases should satisfy the phase relationships linking the phases in the initial set.

In a test of this idea with a trial structure [the photolysis product of Karle, Karle & Estlin, (1967)], the largest peak was at $x = 0.59$, $y = 0.83$ and $z = 0.78$. This gave the results in Table 2. These calculated phases, together with those which fix the origin and enantiomorph, led directly to a solution of the structure.

Table 2. *Results for the trial structure*

			Calculated phase	Published phase
3x	1·77	0·77	277	295
4x	2·36	0·36	129	151
5x	2·95	0·95	⌐342	307
3y	2·49	0·49	176	238
4y	3·32	0·32	115	170
5y	4·15	0·15	54	50
3z	2·34	0·34	122	126
4z	3·12	0·12	43	47
5z	3·90	0·90	324	331

A more demanding test of the method was made on hexahelicene ($C_{26}H_{16}$, space group $P2_12_12_1$) for which *MULTAN* found only half the molecule, the rest being obtained by a recycling process (Declercq, Germain, Main & Woolfson, 1973). Four reflexions were used to define the origin and enantiomorph and the phases of the eight general reflexions at the bottom of the *MULTAN* convergence map were represented by magic integers. In this case four phases were represented by each variable with the integer set 2, 3, 7, 13, only two variables being used. The twelve relationships between the eight phases were expressed in terms of magic integers and a map computed of the function

$$\psi(x,y) = \sum_i \omega_i \cos \{2\pi(H_i x + K_i y + b_i)\} , \qquad (10)$$

where ω_i is the product of three normalized structure factors, as in (9). There were 47 maxima for which $\psi/12 \geq 0.4$. Of these the twelve highest peaks were examined and two were found to give sets of phases that were similar to those published. However, when these sets of phases were used as starting sets for the phase development section of *MULTAN*, they failed to give the structure.

When the value of the invariant

$$s = \varphi_1 \pm \varphi_2 \pm \varphi_3 + b \qquad (11)$$

is represented in terms of magic integers there are four influences which cause it to deviate from 0 mod (2π). These are the value of s itself, and the errors in the representations of the three phases. It seems probable that, if we represent the phases φ precisely, the value of ψ would be greater than that found from the Fourier map. In fact, it is possible to improve the accuracy of determination of the phases φ by starting with the magic-integer value for each phase and refining it *independently* using the maximization of ψ as a refinement criterion. The method which has been found to be quite effective and very rapid in refining the φ values is that of parameter shift. This consists of taking the φ's one at a time, changing their values in steps over a small range and shifting them to that value within the range which gives the maximum value of ψ. Three or four cycles of this process lead to a convergence to a maximum of $\psi'(\varphi_1, \varphi_2, \ldots \varphi_n)$ which is now considered to be

$$\psi'(\varphi_1, \varphi_2, \ldots \varphi_n) = \sum_r \omega_r \cos \{2\pi(\varphi_{1r} \pm \varphi_{2r} \pm \varphi_{3r} + b_r)\} . \qquad (12)$$

When this refinement was applied to the phase estimates for hexahelicene the value of $\psi/12$ increased from 0·7 to 0·99. Details of these results are given in Table 3, which shows that, although the mean deviation from the published phases was not greatly improved, a more even distribution of deviations was obtained. When the refined phases were used as a starting set for phase determination an E map resulted which showed the whole structure.

Table 3. *Summary of the results of magic integers for hexahelicene*

		Set A $x=0\cdot103$ $y=0\cdot887$	Set B $x=0\cdot085$ $y=0\cdot904$	Refined phases Set A	Set B	Published phases
φ_1	$2x$	74	60	44	50	75
φ_2	$3x$	111	91	71	81	57
φ_3	$7x$	259	213	249	223	274
φ_4	$13x$	122	36	132	126	155
φ_5	$2y$	278	290	298	310	323
φ_6	$3y$	238	255	258	265	198
φ_7	$7y$	75	116	115	126	184
φ_8	$13y$	193	268	182	188	119
ψ/n		0·72	0·64	0·99	0·99	
Mean deviation from published phases		46°	67°	40°	42°	

Conclusions

We have shown that by the application of magic integers it is possible to allocate phases to a starting set of reflexions in a less arbitrary manner than by the phase-permutation method. The resulting saving in the number of sets of phases to be developed may well be significant for structures that require a large starting set to obtain a solution. As a rough estimate, the time required for the magic-integer and refinement procedures is about the same as that required for the development of one or two complete sets of phases. Normally the number of peaks in the ψ map is not too great and different peaks sometimes give virtually the same values for the individual φ's. For structures for which

MULTAN gives a solution by the permutation of phases then the use of magic integers can give a saving of computer time of between 50 to 75%. In those cases where the convergence map gives poor phase development the phase-permutation method may be quite impossible and the magic-integer approach is then extremely valuable.

The method is currently being developed by trying to accept a limited number of $\sum_2$ relationships before the allocation of magic integers. This is aimed at including more $\sum_2$ relationships in the map and enabling about 30 or 40 reflexions to be phased. At present the procedure is handled by a separate computer program which is run between the CONVERGE and FASTAN procedures in MULTAN. A magic-integer routine will eventually be incorporated as an option in the MULTAN package.

References

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The Effect of Coulombic Interactions on the Calculated Crystal Structures of Benzene at Atmospheric and 25 kbar Pressure

By David Hall

Department of Chemistry, University of Auckland, Auckland, New Zealand

and Donald E. Williams

Department of Chemistry, University of Louisville, Louisville, Kentucky 40208, U. S. A.

The crystal structures of benzene I (orthorhombic) and high-pressure benzene II (monoclinic) were calculated at atmospheric pressure and 25 kbar pressure by minimization of the intermolecular lattice energy subject to the pressure constraint. The first set of calculations used an atom–atom (exp-6) potential with no net coulombic charges on the atoms. The second set of calculations used an (exp-6–1) potential which placed charges of $\pm0\cdot18$ electron on each atom of the benzene molecule. The no-charge calculation incorrectly predicted that benzene should be monoclinic at both atmospheric and 25 kbar pressure. The coulombic charge calculation correctly predicted the observed crystal transition, favoring the orthorhombic structure at atmospheric pressure but favoring the monoclinic structure at 25 kbar. In the latter calculations there were substantial coulombic contributions to the lattice energy.

Introduction

The crystal structure of benzene I has been determined by X-ray diffraction at $-3°$ (Cox, Cruickshank &

Smith, 1958) and by neutron diffraction at $-55°$ and $-135°$ (Bacon, Curry & Wilson, 1964). Since our calculated model does not include vibrational effects, we will compare our results with the observed structure