

# Direct Determination of Crystal Structure

## IV. Starting sets

By

Hidewo TAKAHASHI

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Faculty of Education  
Kagoshima University  
Kagoshima, Japan

### Abstract

Electronic computer program to obtain starting sets satisfying tangent formula in the phases was formed. The number of the initial sets obtained from the 20 sets of 14 random phases was 6. The phases of the 5 sets satisfy the tangent formula. The number of triplets  $h$ ,  $k$ ,  $h-k$  in the set are 30. The phases of the 4 sets satisfy the sums of phases,  $\psi(h) = \psi(k) + \psi(h-k)$ . The phases of the sets of 200 phases obtained by the tangent formula from the starting sets did not agree with the true phases.

### 1. Introduction

Recently, there appeared the Lead Article for direct determination of crystal structures by Woolfson (1987) in *Acta Crystallographica*. This paper showed clearly the outline of the development of the phase determination methods. We can study at glance the trunk of the recent phase determination without useless boughs and branches growing luxuriantly in this field. His discussion was mainly concentrated on the development of the equations indicating the relation between correct phases, especially on so-called tangent formula. However, even though the tangent formula is valid for the correct phases, the correct phases can be only obtained from the other correct phases. Hence, we must start to determine correctly the starting set of phases, at first. Therefore, the most important task in the investigation of the methods for the phase determination is not to make higher the accuracy of tangent formula but to cultivate the method determining the phases of the starting set. So far as we judge by the description of Woolfson, any numbers, magic numbers or random

numbers, can be allowed for the phases of the starting set.

Furusaki (1979) showed that correct phases could be obtained through the method of trial and error, giving the random phases to the phases of the starting sets. Furusaki (1982) suggested that the reason why the random phases of the starting sets converged to the correct phases might be that there was power of amending correctly phases in the tangent formula. The present author (1987) pointed out that the power was due to the power effect of absolute values of structure factors, since the phases of the starting set were fixed for initial 10 cycles calculation in Furusaki's method. The power effect should be exact if the sum rule of the phases,

$$\psi(\mathbf{h}) = \psi(\mathbf{k}) + \psi(\mathbf{h}-\mathbf{k}),$$

is valid for any 3 reflections  $\mathbf{h}$ ,  $\mathbf{k}$  and  $\mathbf{h}-\mathbf{k}$ . That is to say, the power effect is valid if the weights of the any phases in the tangent formula are equal to one another. But, the sum rule is not satisfied for reflections with small absolute values of structure factors. Owing to this, to determine correctly the phases of the stronger reflections in the starting set becomes important.

If we must initially guess correct phases in order to satisfy the sum rule or the tangent formula, the number of the phases to be given correct values should be limited to be very small, since the number of stronger reflections making pairs of  $\mathbf{k}$  and  $\mathbf{h}-\mathbf{k}$  is small. Then, the problem whether or not we can determine correctly the remaining phases by using the sum rule or the tangent formula should arise. To estimate the size of starting set and the proportion of the correct phases in the set in order to determine correctly the phases necessary for crystal structure analysis is a very difficult task. This problem should theoretically be solved by taking account of the power effect and the weights of the phases in the tangent formula in future. But, we can show tentatively by simulations that a number of phases can be determined suitably by a certain initial set. The present author (1987) already showed that the phases could be determined if 20 phases of stronger reflections were correctly given among the set of 30 reflections of which absolute values of structure factors lie in from the first until the 30th in our set of the structure factors. However, we can not determine correctly the 20 phases by the use of the tangent formula, since the 20 reflections are not related with one another with respect to the tangent formula by pairing  $\mathbf{k}$  and  $\mathbf{h}-\mathbf{k}$  reflections.

The present author's method is to make converge normalized structure factors with the random phases of considerably large starting set to the observed normalized structure

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factors. Hence, the problem on the starting set of phases does not occur. The phase relation used in the method is only the equation (3, 8) of Karle and Karle (1966) (equivalent to the equation (18) of Woolfson, and called the equation of K and K hereafter). By changing the control parameter of the convergence from the absolute values of the structure factors to the difference between phases before and after one cycle calculation, we can obtain phases satisfying self-consistently the equation of K and K. This idea is equivalent to the essential idea of Symbolic Addition method. The computer program for this idea is easily formed. The difference between Symbolic Addition method and this method is that the phase relation in the Symbolic Addition method is the sum rule but the phase relation in our method is the equation of K and K. Hence, a phase is calculated by some pairs of phases in our method, in general.

The starting set of 14 reflections with true phases was chosen from 50 strong reflections. The phases of the starting set were converged to satisfy with one another the phase relation of the equation of K and K. It is natural that the results of calculation satisfy also the sum rule. That is, the sum of phases of each pair of reflections  $k$  and  $h-k$  is nearly equal to the phase of reflection  $h$ . The results of the application of the method to the sets of the 200 reflections were bad for the phase determination. This means that even though we can determine a few number of phases to satisfy the sum rule, we can not determine all the correct phases necessary for crystal structure analysis. In this paper, the author demonstrates the difficulty of phase determination from a few number of strong reflections through the simulation calculations.

The simulations described in this paper were carried out by using the same material in the previous paper (1987). The number of independent atoms is 30 and the space group is P 2.

## 2. Starting sets

The largest group of the reflections related with one another through the equation K and K in the 50 strong reflections was chosen as the starting set of the reflections. As stated in the previous paper, the reflections are numbered according to the magnitude of structure factors, of which reflection indices are limited within  $0 \leq h \leq 14$ ,  $0 \leq k \leq 14$  and  $0 \leq l \leq 14$ . The number of the reflections belonging the starting set decreased to 14 by further examination, which was reported as 18 in the previous paper. The indices of the 14 reflections are listed in the Table 1.

Table 1. Indices of the initial set.

<b>h</b>	<b>h</b>	<b>k</b>	<b>l</b>	<b>h</b>	<b>h</b>	<b>k</b>	<b>l</b>
1	-12	0	6	8	-3	0	12
2	9	0	5	9	10	0	7
3	-13	0	5	10	2	9	14
4	-7	9	9	11	-7	5	1
5	-5	1	11	12	3	5	8
6	-3	0	11	13	-8	6	3
7	-6	5	4	14	-4	0	10

At first, the starting set of the true 14 phases was fixed constantly to obtain 200 phases in the 30 cycles calculation. The result was analyzed by the method described in the previous paper (1987). The number of phases equal to the true phases was only 66 in this case. Hence, we can not determine this crystal structure, even though the 14 phases are determined correctly.

If the symmetry of crystal structure becomes higher, the number of the phases in the starting set becomes larger, when the number of the reflections of basic set from which the starting set is to be chosen is the same. The space group of the testing material is P2, hence, the number of the phases in the starting set is comparatively small. This smallness of the starting set might give rise the indetermination of the phases. Hence, we can not deduce the impossibility of the phase determination from this simple fact, but this suggests the difficulty of the phase determination by deriving the new phases from the starting set through the tangent formula.

The author's convergence method was applied to the result. The convergence speed can be adjusted suitably as described in the previous paper (1987). In this case, only the case (B) with the number of the reflections being 150, very high speed convergence, was tested. The number of equal phases to the true phases became 151. This fact suggests that the phases can not be determined simply by the 14 true phases, but if we can determine correctly the phases of the starting sets, we may be able to save computer CPU time by applying the author's convergence method to the results derived by using the equation of K and K to the fixed phases of starting sets.

In order to obtain the phases of the starting set, the electronic computer program was formed. The program is the modified one from the given in Appendix in the previous paper (1987). The outline of the program is as follows. The starting set of phases is given by randomly as described in the previous papers. The control parameter is the difference of the

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phases between one cycle calculation. That is, when the difference of the phase of a reflection  $h$  before and after one cycle calculation is larger than  $\pi/8$ , the contribution of the reflection and of the related reflections forming  $k$  and  $h-k$  pairs is nullified, and the phase of the reflection  $h$  is calculated by the structure factors of the remaining pairs of the reflections. In this case, when the number of the reflections with zero contribution becomes large, it happens that some calculated structure factors become zero in one cycle calculation, and finally all the calculated structure factors become zero. Hence, the contributions of the one reflections with the largest absolute value of the structure factor among the reflections which have different values of phases in a cycle calculation and those of the reflections forming  $k$  and  $h-k$  pairs are put to be zero. When all phases can not have definite values by 5 cycles calculation, the set of phases is abandoned. The list of the program is given in Appendix.

It is necessary to estimate the validity of the program. At first, we must notice that all the true phases do not satisfy the equation of K and K at once. Hence, the new phases were obtained by 10 cycles calculation from the starting set of true phases. The number of the new phases equal to the true phases by this adjustment became 11. Therefore, the number of phases to be determined by the equation of K and K in any way is limited within 11 at most. The 6 set of phases were obtained from the 20 sets of random phases. The phases of the 6 sets are listed in Table 2. The numbers of the correct phases for the 6 sets were 7, 10, 10, 7, 9, 6.

Table 2. The phases of the initial sets.

$h$	No.1	No.2	No.3	No.4	No.5	No.6
1	0.00000	0.00000	3.14159	3.14159	3.14159	3.14159
2	3.14159	0.00000	0.00000	3.14159	3.14159	0.00000
3	3.14159	3.14159	0.00000	3.14159	3.14159	3.14159
4	0.23339	3.13886	4.94839	3.34362	2.57387	4.86417
5	2.46228	1.39306	1.81400	0.05731	3.91269	3.69131
6	3.14159	0.00000	3.14159	0.00000	0.00000	3.14159
7	3.22793	3.72735	0.24738	4.78884	1.28510	2.70324
8	3.14159	3.14159	0.00000	3.14159	0.00000	0.00000
9	0.00000	0.00000	0.00000	0.00000	3.14159	3.14159
10	3.14159	3.14159	4.71239	0.73641	5.49779	5.56065
11	3.22607	3.72771	3.38809	4.78789	1.28610	2.70439
12	3.23149	3.72666	3.39066	4.79066	4.42478	5.84264
13	2.55218	1.97812	2.06306	1.70638	5.19588	0.10917
14	0.00000	3.14159	0.00000	0.00000	0.00000	3.14159

To examine the degree of satisfaction of the phases of the starting sets for the equation of  $K$  and  $K$ , the differences between the phases of the sets and the phases obtained by the equation  $K$  and  $K$  with substituting the phases of the sets were calculated and listed in Table 3. We can see that the phases satisfy very good the equation of  $K$  and  $K$ , except the set of No. 6. Although the phases are not necessary to satisfy the sumrule  $\psi(h) = \psi(k) + \psi(h-k)$ , the differences of the phases  $\psi(h) - \psi(k) - \psi(h-k)$  were calculated and listed in Table 4. By examining the Table 3, the results of the sets of No. 1, 2, 3 and 5 were fairly good in satisfying the sum rule for each of 3 phases.

Table 3. The differences between the determined phases  $\psi(h)$  and the phases satisfying the tangent formula in the initial sets.

$h$	No.1	No.2	No.3	No.4	No.5	No.6
1	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
2	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
3	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
4	0.16214	-0.00189	0.16395	-0.37298	0.15120	-0.48814
5	0.00000	0.00001	0.00001	0.00000	0.00000	0.00000
6	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
7	-0.01200	0.00024	-0.01184	0.02565	-0.01040	0.03377
8	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
9	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
10	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
11	-0.02352	0.00078	-0.02232	0.04565	-0.01793	0.06236
12	-0.01685	-0.00005	-0.01777	0.04193	-0.01773	0.05233
13	-0.01685	-0.00005	-0.01777	0.04193	-0.01773	0.05233
14	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

It is natural that the 200 phases derived by the equation of  $K$  and  $K$  from the starting sets with the 14 phases do not coincide with the true phases, since the 200 phases obtained from the starting set of the true 14 phases did not coincide with the true phases. The convergence method with the rapid convergence described above was applied to the results, the R-value of only one set became small ( $R=0.13770$ ), the R-values of the other sets were nearly 0.2. The analysis of the sets showed that the maximum numbers of the coincided phases were 57, 54, 68, 61, 53 and 51. These number could be obtained from the random phases.

We can conclude that the true solution of phases problems may be difficult only by means of the sum rule and for the small number of strong reflections in the starting sets.

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Table 4. The differences between the phases  $\psi(\mathbf{h})$  and  $\psi(\mathbf{k}) + \psi(\mathbf{h}-\mathbf{k})$  in the initial sets.

$\mathbf{h}$	$\mathbf{k}$	$\mathbf{h}-\mathbf{k}$	No.1	No.2	No.3	No.4	No.5	No.6
1	6	2	-6.28318	0.00000	0.00000	0.00000	0.00000	0.00000
2	6	1	0.00000	0.00000	-6.28318	0.00000	0.00000	-6.28318
2	10	4	-6.04979	-6.28591	-6.04718	-0.53438	-6.06551	-6.97966
2	14	3	0.00000	-6.28318	0.00000	0.00000	0.00000	-6.28318
3	7	11	-6.28505	-6.28283	-6.28407	-6.28414	0.00100	0.00115
3	8	9	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
3	11	7	-6.28133	-6.28355	-6.28230	-6.28224	-0.00100	-0.00115
3	14	2	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
4	10	2	-6.04979	-0.00273	0.23600	-0.53438	-6.06551	-0.69648
5	13	12	-6.28319	-6.28318	-6.28318	-6.28319	-6.28319	0.00000
6	1	2	0.00000	0.00000	0.00000	-6.28318	-6.28318	0.00000
6	2	1	0.00000	0.00000	0.00000	-6.28318	-6.28318	0.00000
7	3	11	0.00186	-0.00036	0.00088	0.00095	-6.28418	-6.28433
7	8	12	-0.00356	0.00069	-0.00169	-0.00182	0.00191	0.00219
8	3	9	0.00000	0.00000	0.00000	0.00000	-6.28318	-6.28318
8	7	12	-6.27963	-6.28388	-6.28150	-6.28137	-6.28510	-6.28538
8	9	3	0.00000	0.00000	0.00000	0.00000	-6.28318	-6.28318
8	12	7	-6.28675	-6.28250	-6.28487	-6.28501	-6.28127	-6.28099
9	8	3	-6.28318	-6.28318	0.00000	-6.28318	0.00000	0.00000
9	12	11	-6.28860	-6.28213	-6.28575	-6.28595	-6.28028	-6.27984
10	2	4	-0.23339	0.00273	-0.23600	-5.74880	-0.21767	0.69648
10	4	2	-0.23339	0.00273	-0.23600	-5.74880	-0.21767	0.69648
11	3	7	-0.00186	0.00036	-0.00088	-0.00095	-6.28218	-6.28203
11	12	9	-0.00542	0.00105	-0.00257	-0.00277	-6.28027	-6.27984
12	8	7	0.00356	-0.00069	0.00169	0.00182	-0.00191	-0.00219
12	9	11	0.00542	-0.00105	0.00257	0.00277	-0.00291	-0.00334
12	11	9	0.00542	-0.00105	0.00257	0.00277	-0.00291	-0.00334
13	5	12	0.00000	-0.00001	-0.00001	0.00000	0.00000	-6.28319
14	2	3	-6.28318	0.00000	0.00000	-6.28318	-6.28318	0.00000
14	3	2	-6.28318	0.00000	0.00000	-6.28318	-6.28318	0.00000

### 3. Remarks

The author wishes to correct the description in the previous papers in this series. The author wrote that the convergence speed was slowed if the number of zero contribution of the phases increased. This was the author's misjudge for the relations with the number of the zero contribution and CPU time. Probably, this may be due to the ambiguity of the relation between the numbers of zero contribution and the number LNREF in the previous paper (1985). When the number of the zero contribution in (B) in the paper (1987) increased, the convergence speed was accelerated. Hence, it becomes doubtful whether or not the (A) are necessary.

The present author had been doubtful for the reports of the successes of phase determination, since he did not believe that all phases could be determined from very small

number of correct phases of strong reflections. In the previous papers, the present author noticed that it was not necessarily impossible to determine all the phases from the small number of correct phases of the strong reflections. The present author pointed out that this was due to the power effect of amplitudes of structure factors in the case of fixing the strong correct phases for several cycles of calculation. Hence, the next problem to be solved is to determine correctly the phases of small number of strong reflection. But, this is very difficult, since strong reflections do not make triplets  $h$ ,  $k$  and  $h-k$  in many cases. We must determine correctly the phases of the isolated reflections. The initial sets obtained in this paper are satisfying the condition required for Symbolic Addition method. The phases derived from the initial sets did not agree with the correct phases. This indicates that there are many sets of small numbers of phases satisfying the tangent formula, but that the correct phases can not be determined from the sets of phases.

### References

- Furusaki, A. (1979). *Acta Cryst.* **A35**, 220-224.  
Furusaki, A. Abe, K. and Matsumoto, T. (1982). *Bull. Chem. Soc. Japan.* **55**, 611-612  
Furusaki, A. (1982). *J. Crystallogr. Soc. Japan (in Japanese)*. **24**, 149-164.  
Karle, J. and Karle, L. L. (1966). *Acta Cryst.* **21**, 849-859.  
Woolfson M. M. (1987). *Acta Cryst.* **A43**, 593-612  
Takahashi, H. (1985). *Bull. Kagoshima Univ. Fac. Educ. (Nat. Sci.)*, **37**, 5-9.  
Takahashi, H. (1987). *Bull. Kagoshima Univ. Fac. Educ. (Nat. Sci.)*. **39**, 11-26.



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COMPLEX EPHS
DIMENSION IH(3,15),EPHS(15),MRL(15,20,2),
1AF(15),ANGM(15),AFC(15),NRM(15)
PAIT=6.283185307179586
PAI=PAIT/2.0
500 FORMAT(8I10)
IX=8735
NREF=14
READ(1,510)((IH(J,I),J=1,3),I=1,NREF)
510 FORMAT(4(3I5,2X))
READ(1,530)(AF(I),I=1,NREF)
530 FORMAT(4F15.5)
DO 10 I=1,NREF
READ(1,500)NRM(I)
IF(NRM(I).EQ.0) GO TO 10
READ(1,540)(MRL(I,J,1),MRL(I,J,2),J=1,NRM(I))
10 CONTINUE
540 FORMAT(4(2I5,5X))
EPS=PAIT/16
NCAL=20
NTR=0
NCC=0
100 CONTINUE
NTR=NTR+1
IF(NTR.GT.NCAL) STOP
DO 20 I=1,NREF
ANGM(I)=10.0
EPHS(I)=0.0
CALL RANPHS(I,IH,EPHS(I),IX)
20 CONTINUE
DO 30 I=1,NREF
IED=NRM(I)
IF(IED.EQ.0)GO TO 30
CALL DETPHS(I,IED,IH,AF,EPHS,MRL,EPHS(I),AFC(I),ANGM(I),PAIT)
30 CONTINUE
IR=0
CALL FACCOM(NREF,IH,AF,MRL,NRM,EPHS,ANGM,AFC,PAIT,IX,EPS,IR)
IF(IR.NE.0)GO TO 40
NCC=NCC+1
* GO TO 50
DO 60 J=1,10
DO 70 I=1,NREF
IED=NRM(I)
IF(IED.EQ.0)GO TO 70
CALL DETPHS(I,IED,IH,AF,EPHS,MRL,EPHS(I),AFC(I),ANGM(I),PAIT)
70 CONTINUE
60 CONTINUE
50 CONTINUE
WRITE(7,500)NCC
WRITE(7,530)(ANGM(I),I=1,NREF)

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40  CONTINUE
    GO TO 100
    END
    SUBROUTINE DETPHS(IJ, IED, IH, AF, EPHS, MRL, EPH, AC, ANG, PAIT)
    COMPLEX EPHS, EPH, SUMEH, SM, REPS
    DIMENSION IH(3,15), AF(15), EPHS(15), MRL(15,20,2), IK(3)
    SUMEH=0.0
    NSM=0
    DO 10 I=1, IED
    J=MRL(IJ, I, 1)
    K=MRL(IJ, I, 2)
    DO 20 KA=1, 3
    IK(KA)=IH(KA, IJ)-IH(KA, J)
20  CONTINUE
    CALL REPHS(K, IH, IK, EPHS(K), REPS)
    SM=EPHS(J)*REPS
    IF(SM.NE.0.0)NSM=NSM+1
    SUMEH=SUMEH+SM*AF(J)*AF(K)
10  CONTINUE
    IF(NSM.EQ.0)ANG=10.0
    IF(NSM.EQ.0)EPH=0.0
    IF(NSM.EQ.0)RETURN
    SUMEH=SUMEH/NSM
    AA=CONJG(SUMEH)*SUMEH
    AC=SQRT(AA)
    CALL UNICMP(SUMEH, AC, EPH, ANG, PAIT)
    IF(IH(2, IJ).EQ.0.AND.REAL(EPH).GE.0.0)ANG=0.0
    IF(IH(2, IJ).EQ.0.AND.REAL(EPH).LT.0.0)ANG=PAIT/2.0
    RETURN
    END
    SUBROUTINE UNICMP(FC, ABF, UNTV, ANG, PAIT)
    COMPLEX FC, UNTV
    IF(ABF.EQ.0.0)UNTV=0.0
    IF(ABF.EQ.0.0)RETURN
    A=REAL(FC)/ABF
    B=AIMAG(FC)/ABF
    UNTV=CMPLX(A, B)
    CALL ARG(PAIT, UNTV, ANG)
    RETURN
    END
    SUBROUTINE REPHS(K, IH, IK, EPH, REPS)
    COMPLEX EPH, REPS
    DIMENSION IK(3), IH(3,15)
    IJK=0
    NN=0
    NA=0
    DO 10 I=1, 3
    IF(IK(I).NE.IH(I, K))IJK=1
    IF(IK(I)*IH(I, K).LT.0)NN=NN+1
    IF(IK(I).NE.0)NA=NA+1

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10  CONTINUE
    IF(IJK.EQ.0)REPS=EPH
    IF(IJK.EQ.0)RETURN
    IF(NN.EQ.NA)REPS=CONJG(EPH)
    IF(NN.EQ.NA)RETURN
    AKO=0.5*IK(2)
    CKO=AKO-AINT(AKO)
    EPS=0.001
    IF(ABS(CKO).LT.EPS) GO TO 30
    IF(ABS(CKO).GE.EPS) GO TO 40
30  CONTINUE
    IF(IK(2).LT.0)REPS=CONJG(EPH)
    IF(IK(2).LT.0)RETURN
    REPS=EPH
    RETURN
40  CONTINUE
    A=REAL(EPH)
    B=AIMAG(EPH)
    IF(IH(1,K).LT.0) GO TO 50
    IF(IK(2).LT.0)REPS=CMPLX(-A,B)
    IF(IK(2).LT.0)RETURN
    IF(IK(2).GT.0)REPS=CMPLX(-A,-B)
    IF(IK(2).GT.0)RETURN
50  CONTINUE
    IF(IK(2).GT.0)REPS=CMPLX(-A,-B)
    IF(IK(2).GT.0)RETURN
    IF(IK(2).LT.0)REPS=CMPLX(-A,B)
    IF(IK(2).LT.0)RETURN
    END
    SUBROUTINE FACCOM(NREF, IH, AF, MRL, NRM, EPHS,
1  ANGM, AFC, PAIT, IX, EPS, IR)
    COMPLEX EPHS, EP
    DIMENSION IH(3,15), AF(15), MRL(15,20,2), NRM(15),
1  EPHS(15), AFC(15), ANGM(15), IAM(15), HANGM(15), IBM(15),
2  PM(15), NPM(15), NPO(15)
    DO 10 I=1, NREF
    IAM(I)=0
10  CONTINUE
20  CONTINUE
    NC=0
    DO 30 I=1, NREF
    IBM(I)=0
    IF(IAM(I).EQ.1)NC=NC+1
    IF(NC.GT.1)IAM(I)=0
30  CONTINUE
    DO 40 I=1, NREF
    IED=NRM(I)
    IF(IAM(I).EQ.0) GO TO 40
    IBM(I)=1
    DO 50 J=1, IED

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JA=MRL(I,J,1)
JB=MRL(I,J,2)
IBM(JA)=1
IBM(JB)=1
50 CONTINUE
40 CONTINUE
DO 60 I=1,NREF
IF(IBM(I).EQ.1)EPHS(I)=0.0
60 CONTINUE
NCC=0
NA=0
80 CONTINUE
NC=1
DO 71 I=1,NREF
CALL RANDOM(IX,RAN)
PM(I)=RAN*NREF
71 CONTINUE
CALL NUMBR(NREF,PM,NPM,NPO)
DO 70 I=1,NREF
IA=NPO(I)
IED=NRM(IA)
CALL DETPHS(IA,IED,IH,AF,EPHS,MRL,EP,AFF,
1HANGM(IA),PAIT)
IF(HANGM(IA).EQ.10.0)NC=0
IF(HANGM(IA).EQ.10.0)GO TO 70
EPHS(IA)=EP
70 CONTINUE
IF(NC.EQ.0)NCC=NCC+1
IF(NCC.EQ.5)IR=1
IF(IR.EQ.1)RETURN
IF(NC.EQ.0)GO TO 80
NCC=0
NA=NA+1
IF(MOD(NA,5).NE.0)GO TO 80
DO 90 J=1,5
DO 100 I=1,NREF
IED=NRM(I)
CALL DETPHS(I,IED,IH,AF,EPHS,MRL,EP,AFF,
1HANGM(I),PAIT)
EPHS(I)=EP
100 CONTINUE
90 CONTINUE
CALL CRITLM(NREF,ANGM,HANGM,IAM,NN,PAIT,EPS)
DO 110 I=1,NREF
ANGM(I)=HANGM(I)
110 CONTINUE
IF(NN.GT.0)GO TO 20
RETURN
END
SUBROUTINE ARG(PAIT,UNTV,ANG)

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COMPLEX UNTV
AA=REAL(UNTV)
BB=AIMAG(UNTV)
IF(AA.EQ.0.0.AND.BB.EQ.0.0)ANG=10.0
IF(AA.EQ.0.0.AND.BB.EQ.0.0) RETURN
IF(AA.EQ.0.0.AND.BB.EQ.1.0)ANG=PAIT/4.0
IF(AA.EQ.0.0.AND.BB.EQ.-1.0)ANG=PAIT*3.0/4.0
IF(AA.EQ.0.0)RETURN
D=BB/AA
C=ATAN(D)
IF(AA.GT.0.0.AND.BB.GE.0.0)ANG=C
IF(AA.GT.0.0.AND.BB.GE.0.0)RETURN
IF(AA.GT.0.0.AND.BB.LT.0.0)ANG=PAIT+C
IF(AA.GT.0.0)RETURN
ANG=PAIT/2.0+C
RETURN
END
SUBROUTINE RANPHS(I,IH,EPH,IX)
COMPLEX EPH
DIMENSION IH(3,500)
A=0.707107
CALL RANDOM(IX,RAN)
IF(RAN.LT.0.125)EPH=CMLPX(1.0,0.0)
IF(RAN.GE.0.125.AND.RAN.LT.0.25)EPH=CMLPX(A,A)
IF(RAN.GE.0.25.AND.RAN.LT.0.375)EPH=CMLPX(0.0,1.0)
IF(RAN.GE.0.375.AND.RAN.LT.0.5)EPH=CMLPX(-A,A)
IF(RAN.GE.0.5.AND.RAN.LT.0.625)EPH=CMLPX(-1.0,0.0)
IF(RAN.GE.0.625.AND.RAN.LT.0.75)EPH=CMLPX(-A,-A)
IF(RAN.GE.0.75.AND.RAN.LT.0.875)EPH=CMLPX(0.0,-1.0)
IF(RAN.GE.0.875.AND.RAN.LT.1.0)EPH=CMLPX(A,-A)
IF(IH(2,I).EQ.0.AND.RAN.LT.0.5)EPH=CMLPX(1.0,0.0)
IF(IH(2,I).EQ.0.AND.RAN.GE.0.5)EPH=CMLPX(-1.0,0.0)
RETURN
END
SUBROUTINE CRITLM(NR,ANGM,HANGM,IAM,NN,
1 PAIT,EPS)
DIMENSION ANGM(15),HANGM(15),IAM(15)
PAI=PAIT/2.0
DO 10 I=1,NR
IAM(I)=0
CONTINUE
NN=0
DO 20 I=1,NR
DA=ANGM(I)-HANGM(I)
IF(DA.GE.0.0)DA=DA-PAIT*AIN(T(DA/PAIT))
IF(DA.LT.0.0)DA=DA-PAIT*(AIN(T(DA/PAIT))-1.0)
IF(DA.GE.PAI)DA=DA-PAIT
ADA=ABS(DA)
IF(ADA.GT.EPS)IAM(I)=1
IF(ADA.GT.EPS)NN=NN+1

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```

20  CONTINUE
    RETURN
    END
    SUBROUTINE RANDOM(IR,RAN)
    REAL*8  A,B,C,C1,W
*  A=23  B=11317  C=32749  C1=1/32749
    DATA A,B/23.D0,11317.D0/
*  DATA C,C1/32749.D0,0.30535283520107484D-4/

    W=IABS(IR)
    W=DMOD(A*W+B,C)
    IR=W
    IF(W.EQ.0) W=1.0
    RAN=W*C1
    RETURN
    END
    SUBROUTINE NUMBR(NREF,RH,MRH,MHR)
    DIMENSION RH(200),MRH(200),RHH(200),MHR(200),IM(200)
    DO 10 I=1,NREF
    RHH(I)=RH(I)
10  CONTINUE
    IA=NREF-1
    DO 20 I=1,IA
    JA=I+1
    DO 30 J=JA,NREF
    IF(RHH(I).GE.RHH(J)) GO TO 40
    SRS=RHH(I)
    RHH(I)=RHH(J)
    RHH(J)=SRS
40  CONTINUE
30  CONTINUE
20  CONTINUE
    DO 50 I=1,NREF
    IM(I)=0
50  CONTINUE
    DO 60 I=1,NREF
    IJK=0
    DO 70 J=1,NREF
    IF(IJK.EQ.1) GO TO 70
    IF(IM(J).EQ.1) GO TO 70
    IF(RHH(I).NE.RH(J)) GO TO 70
    MRH(J)=I
    IJK=1
    IM(J)=1
70  CONTINUE
60  CONTINUE
    DO 80 I=1,NREF
    IM(I)=0
80  CONTINUE
    DO 90 I=1,NREF

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```
IJK=0
DO 100 J=1,NREF
IF(IJK.EQ.1) GO TO 100
IF(IM(J).EQ.1) GO TO 100
IF(RH(I).NE.RHH(J)) GO TO 100
MHR(J)=I
IJK=1
IM(J)=1
100 CONTINUE
90 CONTINUE
RETURN
END
```