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REGULAR PAPERS**Computer Program TRIO-FIT for Third Order
Calculation of Ion Trajectory with Help
of Automatic Fitting Function**

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Computer program TRIO FIT was constructed in order to calculate ion trajectory up to third order approximation with the help of automatic fitting function (simplex method). The way how to use TRIO-FIT is explained by using a model mass spectrometer system.

1. Introduction

The principle of ion optics for a mass spectrometer had been already developed since the Aston's mass spectrograph was constructed. The first order ion optics was completed by the paper of Mattauch and Herzog in 1934. In 1950, the second order ion optics was established and large mass spectrometers were designed and constructed. In 1970, we have calculated the ion trajectory in an electric and a magnetic field up to third order approximation and made a computer program TRIO¹⁾ using these results. This program TRIO has often been used effectively for two purposes: the design of a new mass

spectrometer²⁾ and the improvement of an existing mass spectrometer.

Since 1980, field desorption (FD), fast atom bombardment (FAB) and secondary ion (SI) ionization techniques have been introduced, and it becomes possible to produce molecular ions of labile compounds of several thousand daltons. The demand for new ion optics of a high performance mass spectrometer has arisen. High mass range and high transmission efficiency become important as well as the mass resolution. In order to allow high transmission keeping still high resolution, the second and third order image aberrations should be corrected by giving the special curvature at the boundary of electrode

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and/or magnet or by introducing quadrupole, hexapole and/or octupole lenses. Then, the ion optical system becomes complicate and we must optimize more than ten parameters of a mass spectrometer system. It is very difficult to find the best solution by trial and error method. We have introduced one of the automatic fitting function (simplex method) and made computer program TRIO-FIT. There is already a computer code of ion optical calculation by means of the fitting function.^{3,4)} The advantageous feature of TRIO-FIT is the capability of calculating the trajectory in an electric field and the flexibility of choosing any constraint equation. In the present paper, we explain the way how to use TRIO-FIT for a model mass spectrometer.

2. Automatic Fitting Routine: Simplex Method

Several mathematical methods have been proposed for the purpose of optimization.⁵⁾ Simplex code⁶⁾ was adopted in TRIO-FIT because it converges quickly from a set of rough initial values. The problem is how to define the constraint equation. In other computer codes, constraints are given in the form of a transfer matrix element. The merit of such a method is that all input data are given as "data format" and the source program need not be modified. The demerit is that we can not choose an arbitrary constraint. Then, in TRIO-FIT we adopt the method that we will write the arbitrary constraint equation explicitly in the subroutine FCN. The details will

Fig. 1. The ion optical block diagram of a modified Nier-Johnson type mass spectrometer. Indication A means the original position of the source and detector slits (the field strength of an electric Q-lens equals to zero). Indication B means the calculated position of source and detector slits (the field strength of an electric Q-lens equals to -1.67).

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be explained in the following example.

3. Construction of Program

Several modifications of the original TRIO were made in TRIO-FIT. The main program was changed and three subroutines MATRIX, FCN, SIMPLX were added. We will explain this new function by using a model system. We intend to modify a Nier-Johnson-type mass spectrometer by introducing a quadrupole lens between an electrode and a magnet in order to improve ion optical character in the axial direction. The ion optical block diagram is shown in Fig. 1. Two drift length DE1, DM2 and the field strength QK of the electric quadrupole lens are chosen as the parameters which should be determined by TRIO-FIT so as to satisfy the triple focusing condition (radial angle, axial angle and energy focusing).

3.1. Main Program

The main program (source program) should be prepared by the user. The preparation is quite simple as shown in appendix. The way how to write the main program for a model system is explained following to the statement number.

30— 60: Labelled COMMON statements which can never be omitted.
70— 80: DIMENSION and EXTERNAL statements for subroutine SIMPLX
90—280: Arguments for the subroutine SIMPLX.
300—340: Print out of ion optical informations before fitting.
350—360: Call the subroutine SIMPLX.
370—390: Print out of ion optical informa-

tions after fitting.

3.2. Subroutines

3.2.1. SIMPLX (FCN, N, X, EPSF, EPSX, ICONT, NCUT, JXD, XD, JOKEN, XMAX, XMIN, IPRINT, NMOD, FMIN, KAISU, W, NW)

The meanings of arguments are as follows.

FCN: The constraint equation. (subroutine is given in Appendix I)

N: Number of variables.

X: Components of vector x on N dimensional space. Initial values are given ($X(J)=V_J$, $J=1, 2\cdots N$) and optimized values are given as output data.

EPSF } : When the value or the change
EPSX } of constraint equation becomes less than these numbers, the search stops.

ICONT: As input parameters. ICONT=1 requests to search till the shape of constraint to be conede type. ICONT $\neq$ 1 does not request such a condition. As output parameters. ICONT = 1 means that the search finished after convergence. ICONT = -1 means that it finished without convergence.

NCUT: Maximum number of calculating the values of constraint equation. The program stops when the calculating number is bigger than this number.

JXD } : The program changes the J component of X by $\pm[XD(J)*X(J)]$.
XD } If JXD = 1, XD(J) can be arbitrary given. If JXD $\neq$ 1, XD(J) = 0.1 is always used.

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JOKEN	If JOKEN $\neq$ 0, the variables	IPRINT	IPRINT indicates the style of
XMAX	X(J) is searched between maxi-	NMOD	intermediate output.
XMIN	mum value XMAX(J) and mini-		IPRINT $\geq$ 4 No output.
	mum value XMIN(J). If JOKEN		IPRINT=1, 2 short informations
	=0, X(J) has no limitation.		are printed out.

Appendix I.

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10C   TRIC-FIT PROGRAM
20C   MAIN   PROGRAM
3C    COMMON /BLOCK1/A(2,59)
40    COMMON /BLOCK2/B(2,59)
50    COMMON /BLOCK3/NGROUP,NORDER
60    COMMON /BLOCK4/APRINT,BPRINT,TPRINT
70    DIMENSION X(3),XD(3),XMAX(3),XMIN(3),W(50)
80    EXTERNAL FCN
9C    N=3
100   X(1)= 1.0
110   X(2)= 1.0
120   X(3)= 0.0
130   EPSF = 1.0E-8
140   EPSX = 2.0E-7
150   ICONT = 0
160   NCUT =1000
170   JXD = 0
180   JOKEN = 1
190   XMAX(1) = 100.0
200   XMAX(2) = 100.0
210   XMAX(3) = 100.0
220   XMIN(1) = 0.0
230   XMIN(2) = 0.0
240   XMIN(3) =-100.0
250   IPRINT= 2
260   NMOD = 5
270   NW = N*N + 8*N +5
280   KAISU = 0
290C
300   WRITE(6,680)
310 680 FORMAT(/1H , 'BEFORE FIT SIMPLEX'/)
320   CALL MATRIX(N,X,3)
330   WRITE(6,690)
340 690 FORMAT(1H0,/)
350   CALL SIMPLX(FCN,N,X,EPSF,EPSX,ICONT,NCUT,JXD,XD,JOKEN,XMAX,
360   & XMIN,IPRINT,NMOD,FMIN,KAISU,W,EW)
370   WRITE(6,681)
380 681 FORMAT(/1H , 'AFTER FIT SIMPLEX'/)
390   CALL MATRIX(N,X,3)
400   STOP
410   END
420   SUBROUTINE FCN(N,X,F)
430   COMMON/BLOCK1/ A(2,59)
440   DIMENSION X(N)
450   M = N
460   CALL MATRIX(M,X,1)
470   F = A(1,2)*A(1,2) +A(1,4)*A(1,4) +A(1,51)*A(1,51)
480   RETURN
490   END

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500     SUBROUTINE MATRIX(N,X,IFIT)
510     COMMON/BLOCK1/ A(2,59)
520     COMMON/BLOCK2/ B(2,59)
530     COMMON/BLOCK3/ NGROUP,NORDER
540     COMMON/BLOCK4/ APRINT,BPRINT,TPRINT
550     DIMENSION X(N)
560     REAL      N1
570     NGROUP = 3
580     TPRINT = 0.0
590     NORDER = 1
600     IF(IFIT.EQ.1) GO TO 199
610     NORDER = 2
620     IF(IFIT.EQ.2) GO TO 199
630     NORDER = 2
640     TPRINT = 1.0
650     CALL START
660 199 CONTINUE
670     DE1 = X(1)
680     DM2 = X(2)
690     DQM = 1.0
700     DEQ = 0.525
710     AE= 1.25
720     WE = 70.0
730     C1 = 0.0
740     C2 = 0.0
750     C3= 0.0
760     RO1E= 0.0
770     RO2E=0.0
780     GAPE=0.025
790     NE1 = 2
800     NE2 = 2
810     AM = 1.0
820     WM = 70.0
830     N1 = 0.0
840     EP1M = 0.0
850     EP2M = 0.0
860     FO1M= 0.0
870     RO2M= 0.0
880     GAPM=0.025
890     NM1 = 2
900     NM2 = 2
910     QK = X(3)
920     QL = 0.2
930     QR = 0.07
940     NQ1 = 1
950     NQ2 = 1
960     CALL UNITA
970     CALL DRIFT(DE1)
980     CALL ELECT(AE,WE,C1,C2,C3,RO1E,RO2E,GAPE,NE1,NE2)
990     CALL DRIFT(DEQ)
1000    CALL QUAD(QK,QL,QR,NQ1,NQ2)
1010    CALL DRIFT(DQM)
1020    CALL MAGNET(AM,WM,N1,EP1M,EP2M,FO1M,RO2M,GAPM,NM1,NM2)
1030    CALL DRIFT(DM2)
1040    IF( IFIT .EQ. 1) RETURN
1050    IF(IFIT .EQ. 2) GO TO 2999
1060    CALL PRINTA
1070 2999 CONTINUE
1080    RETURN
1090    END

```

IPRINT=1 standard form of output. FMIN and X(J) are printed out every tenth repetition.

IPRINT = -1, -2 Detailed information are printed out after every [NMOD] repetition.

KAISU: Number of calling the function.

FMIN: Value of optimized constraint equation.

$W\}$: working area. $NW \geq N^2 + 8N + 1$,
 $NW\}$: $W(K)$, $K \geq NW$.

the source LIST of subroutine SIMPLX is omitted because it is too lengthy and the modification by user is unnecessary.

3.2.2. FCN (N, X, F)

The meanings of arguments are as follows:

F: The constraint equation. F must be defined in this subroutine in the explicit formula like as

$$F = A(1, 2) \times A(1, 2) + A(1, 4) \times A(1, 4) + A(1, 51) \times A(1, 51)$$

$N\}$: These arguments are the same
 $X\}$: as defined in SIMPLX.

The way how to write the subroutine FCN for a model system is explained following to the statement number.

420-450: Name of SUBROUTINE, COMMON and DIMENSION. User need not to modify these statement.

460: Calculation of transfer matrix of a system under the current variables.

470: Definition of constraint equation.

3.2.3. MATRIX (N, X, IFIT)

The meanings of arguments are as follows:

IFIT: This arguments defines the condition of print out format.

= 1 NO printout of transfer matrix. IFIT must be 1 in subroutine FCN.

= 2 Only transfer matrix is printed out.

= 3 All ion optical parameters and the total transfer matrix elements are printed out.

$N\}$: These arguments are the same
 $X\}$: as defined in SIMPLX

The total transfer matrix of a system is calculated by this program. The arrangement of statement is almost the same as those of main program of original TRIO. The meaning of arguments of subroutines used in MATRIX are the same as original TRIO. MATRIX is usually called in FCN just before defining the constraint equation F.

The way how to write the subroutine MATRIX for a model system is explained following to the statement number.

500-550: Name of SUBROUTINE and COMMON, DIMENSION, area. User need not modify these statements.

560: REAL statement for N1.

570-660: Definition of NORDER and print out style.

670-950: Definition of element parameters of a model mass spectrometer system. It should be noted that $DE1 = X(1)$, $DM2 = X(2)$ and $QK = X(3)$ are the variables which should be determined by TRIO-FIT in this example.

960-1030: Arrangement of a mass spectrometer is defined and the total

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transfer matrix is calculated.
1040-1090: Print out the total transfer matrix if requested.

4. Conclusion

We have made the computer program TRIO-FIT and explained how to use this program for a model system. The result of calculation is given in Table I and II showing that the triple focusing conditions

$$(x|A) = (x|D) = (y|B) = 0$$

are satisfied. In this paper we have used

TRIO-FIT only in the first order approximation.

It was shown in other paper⁷⁾ that TRIO-FIT was very useful for the second and third order aberration correction of a high performance mass spectrometer. We are sure that TRIO-FIT is helpful for everyone who wants to design a high performance mass spectrometer. The program is written in FORTRAN IV and is available in the form of a magnetic tape.

Table I. OUTPUT of TRIO-FIT of a model mass spectrometer before fitting. Initial values of drift lengths (DE1, DM2) and Q-lens strength (QK) are 1.0, 1.0 and 0.0, respectively

BEFORE FIT SIMPLEX

ION TRAJECTORY CALCULATION BY "TRIO"										
SECOND ORDER										
MASS AND ENERGY DISPERSION										
DRIFT SPACE			DL=	1.0000						
FRINGING FIELD ELECTRIC SECTOR ENTRANCE			RO1=	0.	GAP=	0.0250	NE1=	2		
CYLINDRICAL ELECTRIC SECTOR MAIN			AE=	1.2500	WE=	70.0000				
FRINGING FIELD ELECTRIC SECTOR EXIT			RO2=	0.	GAP=	0.0250	NE2=	2		
DRIFT SPACE			DL=	0.5250						
FRINGING FIELD ELECTRIC QUAD ENTRANCE			QR=	0.0700	NQ1=	1				
MAIN ELECTRIC QUAD			QK=	0.0000	CL=	0.2000				
FRINGING FIELD ELECTRIC QUAD EXIT			QR=	0.0700	NQ2=	1				
DRIFT SPACE			DL=	1.0000						
FRINGING FIELD MAGNETIC SECTOR ENTRANCE			EP1=	0.	RO1=	0.	GAP=	0.0250	NM1=	2
HOMOGENEOUS MAGNETIC SECTOR MAIN			AM=	1.0000	WM=	70.0000				
FRINGING FIELD MAGNETIC SECTOR EXIT			EP2=	0.	RO2=	0.	GAP=	0.0250	NM2=	2
DRIFT SPACE			DL=	1.0000						
A-MATRIX										
	X	A	C	D	XX	XA	XC	XD	AA	AC
X	-0.19245	-0.75144	0.79807	0.54224	-1.04586	-0.77034	-2.24132	0.00565	0.13625	-1.72399
A	1.57157	0.94015	0.46940	-1.11170	1.02043	4.04006	-0.97734	-2.23990	4.89231	-0.68692
	AD	CC	CD	DD	YY	YB	BD			
X	-0.67702	-0.54438	1.69397	0.26579	-0.82918	-8.34020	-21.75550			
A	-3.18968	-0.35205	0.67645	0.95355	-0.47012	-4.01635	-7.46644			
	Y	B	YX	YA	YC	YD	BX	BA	BC	BD
Y	1.07837	6.83159	4.07302	3.76787	0.48671	-2.67213	17.98551	17.97203	2.78568	-9.51915
B	0.04892	1.23724	2.76940	2.27192	0.48330	-1.86904	13.68741	10.88525	2.62973	-9.20666

START SIMPLEX MINIMIZATION										
INITIAL FMIN = 47.530										

***** START REINVESTIGATION(NO. 1.) *****										
***** START REINVESTIGATION(NO. 2.) *****										
***** START REINVESTIGATION(NO. 3.) *****										
***** START REINVESTIGATION(NO. 4.) *****										
***** SIMPLEX MINIMIZATION HAS CONVERGED *****										

LAST FMIN = 0.85683E-11										
SIMPLEX METHOD ENDS *****										

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Table II. OUTPUT of TRIO-FIT of a model mass spectrometer after fitting

AFTER FIT SIMPLEX

ION TRAJECTORY CALCULATION BY "TRIO"											
SECOND ORDER											
MASS AND ENERGY DISPERSION											

DRIFT SPACE				DL=	1.2782						
FRINGING FIELD ELECTRIC SECTOR ENTRANCE				RO1=	0.	GAP=	0.0250	NE1=	2		
CYLINDRICAL ELECTRIC SECTOR MAIN				AE=	1.2500	WE=	70.0000				
FRINGING FIELD ELECTRIC SECTOR EXIT				RO2=	0.	GAP=	0.0250	NE2=	2		
DRIFT SPACE				DL=	0.5250						
FRINGING FIELD ELECTRIC QUAD ENTRANCE				QR=	0.0700	NQ1=	1				
MAIN ELECTRIC QUAD				QK=	-1.6961	QL=	0.2000				
FRINGING FIELD ELECTRIC QUAD EXIT				QR=	0.0700	NQ2=	1				
DRIFT SPACE				DL=	1.0000						
FRINGING FIELD MAGNETIC SECTOR ENTRANCE				EP1=	0.	RO1=	0.	GAP=	0.0250	NM1=	2
HOMOGENEOUS MAGNETIC SECTOR MAIN				AM=	1.0000	WM=	70.0000				
FRINGING FIELD MAGNETIC SECTOR EXIT				EP2=	0.	RO2=	0.	GAP=	0.0250	NM2=	2
DRIFT SPACE				DL=	1.6148						
A-MATRIX											
	X	A	C	D	XX	XA	XC	XD	AA	AC	
X	0.66906	0.00000	1.08666	0.00000	-1.98193	-1.1 0075	-3.64932	1.29368	2.39830	-3.21887	
A	1.91225	1.49461	0.46940	-1.58235	0.94439	5.7 0905	-1.23299	-2.17777	8.08434	-1.04773	
	AD	CC	CD	DD	YY	YB	BD				
X	-0.41933	-0.76083	3.22201	0.05490	-0.46013	-1.7 2890	-4.06165				
A	-4.08837	-0.35205	1.02897	1.33472	-0.21164	-1.3 1509	-1.03392				
	Y	B	YX	YA	YC	YD	BX	BA	EC	ED	
Y	-1.19614	0.00000	2.90215	3.09092	-0.30331	-0.5 9087	16.92619	14.52299	0.89563	-9.42634	
B	-0.55923	-0.83601	0.17742	0.79523	-0.13945	0.4 6244	5.88509	-4.62955	0.63072	-3.99413	

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