

DLS-76

A PROGRAM FOR THE SIMULATION OF CRYSTAL STRUCTURES

BY GEOMETRIC REFINEMENT

by

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Preface

DLS-76 is the successor of the original distance least squares program DLS by VILLIGER (1969). It is a much extended and revised version of DLS-74, a preliminary program set up by GUIGAS (1975) at the University of Karlsruhe, BRD. DLS-76 incorporates all the features (such as linear constraints etc.) which have been developed and used in various modified versions since 1969. The present program is written in FORTRAN IV and has been extensively tested on the CDC 6400/6500 at ETH Zuerich. This program is distributed with the disclaimer that it is to be used at your own risk. Comments will be much appreciated.

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1. INTRODUCTION

For a great many crystal structures interatomic distances and bond angles can be predicted within fairly narrow limits. For the present purpose, bond angles are conveniently expressed in terms of bonded and non-bonded distances. Especially for framework type structures the total number of predictable interatomic distances as a rule exceeds the number of adjustable atom coordinates or positional parameters. In the 2-dimensional (hypothetical) example shown in Fig. 1 a total of at least 10 crystallographically non-equivalent distances¹ would presumably be predictable and could then be used to determine the 6 positional parameters of the structure since interatomic distances are a function only of the atom coordinates and the unit cell constants².

It is evident that in such a case the positional parameters can be computed from prescribed interatomic distances D_j^0 by a least-squares procedure minimizing the residual function

$$\rho_w = \sum_{\substack{j \\ (m,n)}} w_j^2 [D_j^0 - D_j^{(m,n)}]^2$$

in which $D_j^{m,n}$ is the calculated distance of type j between atoms m and n , and w_j is the weight ascribed to the interatomic distance of type j . This method of geometric or DLS refinement, first described in detail by MEIER and VILLIGER (1969), produces optimized model structures with respect to prescribed interatomic distances (or ratios of interatomic distances) and unit cell constants for a given space group. Only very approximate starting coordinates are needed. Possible variables are atom coordinates and/or unit cell constants (or functions thereof). The weight w_j of each error equation is normally based on bonding considerations (cf. BAUR, 1977) or observed variations in bond length values.

Applications of DLS include

- (i) Evaluation of hypothetical structures and preliminary refinement of trial structures. This is of particular use in structure determinations based on powder data (cf. BARRER and VILLIGER, 1969).
- (ii) Study of geometrical constraints in framework type structures and determination of probable space group symmetry (cf. MEIER and VILLIGER, 1969).
- (iii) Analysis and refinement of pseudosymmetric crystal structures (GRAMLICH and MEIER, 1971; TILLMANN, GEBERT and BAUR, 1973; DOLLASE and BAUR, 1976).

¹ 5 M-X and 5 X-X distances

² The distance $D^{m,n}$ between a pair of atoms m and n is

$$D^{m,n} = [a^2(x_m - x_n)^2 + b^2(y_m - y_n)^2 + c^2(z_m - z_n)^2 + 2ab \cos \gamma (x_m - x_n)(y_m - y_n) + 2ac \cos \beta (x_m - x_n)(z_m - z_n) + 2bc \cos \alpha (y_m - y_n)(z_m - z_n)]^{1/2}$$

- (iv) Interpretation of symmetrized and of superimposed structures (MEIER, 1973).
- (v) Simulation of the response of complex crystal structures to changes in pressure and/or temperature, as well as estimation of likely changes in cell dimensions on isostructural substitution (DEMPSEY and STRENS, 1976; KHAN, 1976).

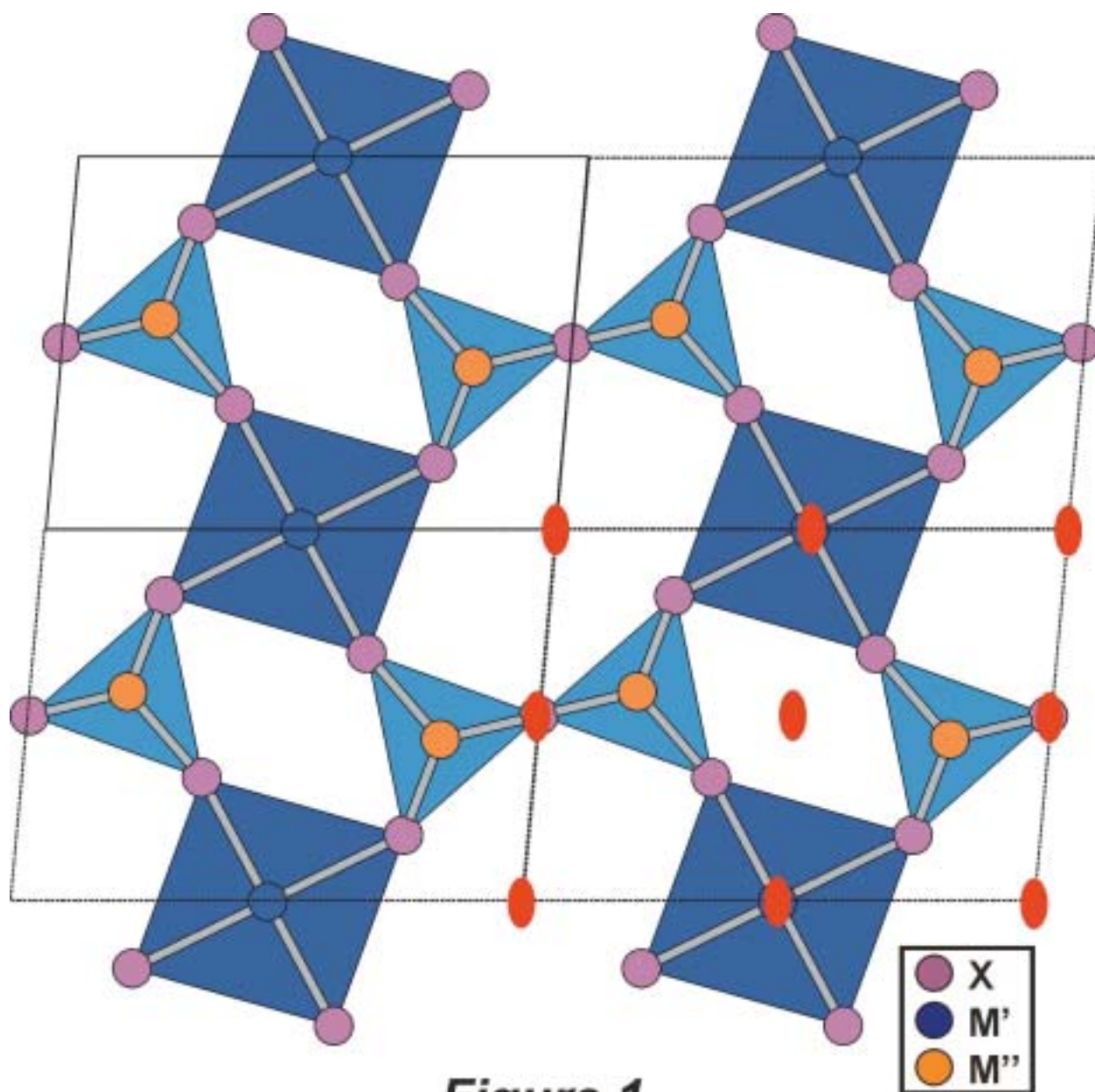


Figure 1

Hard constraints are imposed upon the error equations by crystallographic

symmetry elements. Other subsidiary conditions are encountered (e.g.) in analysis of pseudosymmetric structures. To ensure that a DLS model structure with reduced symmetry (hettotype or H-type structure) remains compatible with an experimentally determined structure of idealized high symmetry (aristotype or A-type structure) subsidiary conditions of the form

$$\sum_{i=1}^n d(i)^{-1} \Delta x_i = 0$$

are applied where Δx_i are the displacements which generate the H-type structure from the A-type, $d(i)$ the pseudosymmetry operations and n is the index of the subgroup relation (MEIER and VILLIGER, 1969). The weights of these soft constraints (which are treated like observational equations according to WASER, 1963) are based on the standard deviations of the coordinates of the A-type structure.

2. PROGRAM DESCRIPTION

In the first part of this chapter a general description of the features of the program is given. In the second part the more specific operation and program flow is described together with information which may be helpful when installing the program on another computer.

2.1 Program features and applications

The basic features of the present program as compared to previous versions are:

- Simplified and flexible data input

The input data are kept to a minimum and are checked as far as possible. In case an error is detected detailed error messages are printed. However, the program is stopped only after all input cards have been processed. Prescribed distances which happen to be symmetrically equivalent are eliminated by the program. For tetrahedral framework structures only the connectivity of the atoms must be specified and the program generates all error equations (T-O, O-O, and T-T distances) itself. (See description of TETCON card).

- Random atom coordinates

To further simplify the data input atom coordinates obtained from a random number generator can be used instead of punched coordinates. As shown by GUIGAS (1975) DLS computations converge in most instances even when random coordinates are used as starting parameters, in which case some 10 to 40 cycles are usually required.

Random coordinates have two further advantages:

(1) By testing around 5 to 10 different random parameter sets it is possible that the program may find two or more non-equivalent solutions which otherwise would remain undetected.

(2) Estimated starting parameters frequently tend to correspond to a higher symmetry than the one actually desired. This results in some very high correlations and the refinement can be inhibited or a solution will only be found in the higher symmetry. The same situation arises when a symmetry reduction is performed. In this case random coordinates should be used or the trick used in Example 2 (with NATOM cards) may be applied.

- Refinement procedures

Basically the program uses the least squares method. However, there is a choice of two different modes, the Newton-Raphson and the Gauss-Newton procedures. GUIGAS (1975) investigated the convergence behavior of these two procedures and his recommendations are as follows:

In the Newton-Raphson procedure the first and the second derivatives of the distances are calculated. Normally this leads to a faster convergence. It

is recommended for runs with invariant cell parameters, when using random starting coordinates, and when the other procedure does not converge. The Gauss-Newton procedure is the classical one, in which only the first derivatives are calculated. It is employed with advantage when cell parameters are also refined, when linear constraints are used, and when the Newton-Raphson method fails.

- Refinement of cell parameters and of prescribed distances (constant ratio or R refinement)

In addition to the atom coordinates the cell parameters can also be varied. This is useful for the determination of ideal cell parameters. In the constant ratio refinement the prescribed distances are also refined but their ratios are kept constant. In this way a model with ideal polyhedra will result. Normally these refinements should only be tried using coordinates which have already been partially refined.

- Linear restrictions

The program also allows for linear restrictions on the coordinates which arise when the symmetry for the DLS refinement has been reduced. These restrictions can be included as soft and/or hard constraints and are simply punched on cards as equations. This application is illustrated in Example 2.

- Adjustment of prescribed interatomic distances (APID)

It has been shown (cf. BROWN, GIBBS and RIBBE, 1969) that in framework silicates e.g. T-O distances depend to some extent on the T-O-T angle. Such relationships can be included as polynomial functions. The program will adjust the prescribed interatomic distances after each set of refinement cycles according to this function.

- Calculation of approximate eigenvalues of the matrix

If the refinement has converged, the approximate eigenvalues of the matrix are printed for the last cycle. In the case of the Newton-Raphson procedure they are to be interpreted as follows:

- All eigenvalues are positive: A minimum has been found.
- All eigenvalues are negative: This corresponds to a maximum in the function and the parameters do not represent a proper solution of the least squares problem.
- Positive and negative eigenvalues are present: This indicates a saddle point of the function and is again not an actual solution.
 - Some eigenvalues are extremely small (approaching zero): In this case no statement about the nature of the solution can be made.

- Difference vectors of reference structure and DLS model

Frequently, one may wish to compare the DLS model with the coordinates obtained by X-ray analysis (reference structure). If the coordinates of the latter are supplied as starting values DLS-76 will calculate the difference vectors between the two structures and their magnitudes (in Å). In space groups with no fixed origin one or more coordinates of an arbitrarily chosen atom have to be fixed in the DLS-refinement. In these cases the deviations between the DLS model and the reference structure are minimized by translating the DLS model along the respective axes.

- Parameter file

In order to divide a large job into several smaller jobs, the refined parameters of each cycle can be written on a parameter file. This file can also be used to select "prerefined" sets of coordinates which have resulted from a run with different sets of random starting coordinates.

- Additional features

There are a number of additional features in the program for special applications (e.g. variable and fixed damping factors, convergence test, tests whether distances lie within specified limits etc.). Information on these can be found in the description of the data input.

2.2 Program flow and operations

This part is intended for users who would like to understand the detailed operation of the program and who may want to modify some parts of it. The general outlay of the program and the function of some of the more important subroutines will be described here. Numerous comment cards are included in the source deck which describe in detail the specific operations performed.

General

The standard version is dimensioned for

100 atoms (independent and dependent)
200 distances
150 variables

The approximate memory requirements are therefore as follows

program code, including system routines	ca. 16K without I/O buffers
arrays (labeled common)	ca. 13K
matrix array (blank common)	11.5K

adding up to a total of about 40K without I/O buffers.

The program uses 3 machine specific functions, namely

DATE(DA)	in the main program for the current date. The date is printed in subroutine KOPF
SECOND(CP)	in the main program which gives the CP time since start of job
RANF(Y)	in subroutine DATIN which returns a random number between 0 and 1 (see comment cards in DATIN)

(CA, CP and Y are all dummy arguments)

A simplified flow chart giving an overview of the program is shown in Fig. 2 on the next page. The calling sequence of the subroutines can be readily seen in this chart. The main program, described below in more detail, is marked with heavy lines. The subroutine calls are indicated by dotted lines. The subroutine names are given and their function is briefly explained. For simplicity only the more important subroutine calls are included.

Main program

As indicated in the flow chart this routine controls the program flow by calls to different subroutines according to the control flags set by the user. The parameter file is also written by this program but only minor calculations (such as R-values) are performed.

Subroutine DATIN

All input data is handled by this routine. The cards are read twice, first to determine their function and a second time to read the parameters. In the CDC version this is done by means of the DECODE statement. The input parameters and the dimension bounds are checked, error messages printed, index tables built up and some preliminary calculations performed. DATIN also contains the random coordinate generator and for this reason it is called each time a new set of coordinates is generated. The program is stopped by this routine when a FINISH card is encountered.

Subroutine SYMOP

The coded symmetry information on the ATOM cards (special positions) and the SYMEQ cards are decoded by this routine. The homogeneous, non-translational part is then stored in arrays $B(K,K,N)$ and $SIGN(K,K,NEQU)$ for the ATOM card number N and SYMEQ card number $NEQU$, respectively. Similarly $BI(K,N)$ contains the invariant part of the restriction and $SI(K,NEQU)$ the translational part of the symmetry transformation. SYMOP also calculates all dependent coordinates from the independent ones according to these symmetry transformations.

Subroutine SETUP

SETUP is called only in case of tetrahedral structures when TETCON cards are supplied. Internally the connectivity of each tetrahedron is stored in $ICON(NZA,11)$. The routine generates all distances around the central atom NZA (i.e. T-O, O-O and T-T distances), evaluates their prescribed values using the information of the BONDIS cards and eliminates equivalent distances. It sets up the array $MD(NZA,18)$ which contains the internal number of each distance around atom NZA in the order described in the Glossary of Symbols. This array is used in subroutine APID.

Subroutine EQUI

This routine is called to test if two distances are symmetrically equivalent. The test is done in the following way. First the calculated values of the two distances are compared. If the difference is larger than 10^{-8} , the distances are considered as not equivalent. If they do agree within this limit, artificial shifts are applied to the atom parameters and the resulting distances are compared once more. If they still agree the distances are considered equivalent.

Subroutine DATOUT

The checked input data, i.e. the program control flags and the initial parameters (cell constants, atom coordinates, linear restrictions etc.) are printed by this routine. It has also a second entry (PAREX) which is called at the end of a run to print the final atom parameters in a special format.

Subroutine DISDER

The matrix and vector of the equations to be solved in each iteration cycle

(the normal equations in the Gauss-Newton procedure) are set up by this routine. This involves mainly the calculation of the distances and their derivatives. The more important equations on which the calculations are based are derived in chapter 6.

Subroutine MATOUT

This routine may be called to print the matrix and vector set up by subroutine DISDER. It is also used to calculate and print the correlation matrix, the estimated standard deviations (in the case of the Gauss-Newton procedure) and to print the approximate eigenvalues.

Subroutine INVERT and INCH

These two routines are used to calculate the inverse matrix. They are based on the procedure for inverting large symmetric matrices described by BUSING and LEVY (1962). As a further option a diagonal matrix approximation is also available.

Subroutine APID

Subroutine APID adjusts in an iterative manner the prescribed interatomic distances in tetrahedral structures according to a function supplied on the BONDIS card. This function expresses the dependence of the T-O distances on the observed T-O-T angle. Prescribed O-O distances are calculated using an ideal tetrahedral angle and the adjusted prescribed T-O distances. For calculating the T-T distances the T-O-T angle supplied on the BONDIS card is used. The routine also checks whether the observed distances are within prescribed ranges and it can adjust the weight of "out of bound distances" in order to force them back. The calculations are mainly controlled by the array ICON(NZ,11) which contains the connectivity around each tetrahedral atom and the array MD(NZA,18) which contains the number of all distances of each tetrahedron (see also Glossary of Symbols). At the end a table is printed of all old and new prescribed D^o 's and of the distances and angles in the model which are of likely interest.

3. DATA INPUT

The data input for DLS-76 is similar to that of the well-known X-RAY-SYSTEM. Each data card has a name consisting of up to six characters which determines its function. Currently the following cards are accepted:

- 1) TITLE
- 2) DLS-76
- 3) FACTOR
- 4) RANGES
- 5) CELL
- 6) ATOM
- 7) SYMEQ
- 8) NOREF
- 9) BONDIS
- 10) TETCON
- 11) DISTAN
- 12) LINRES
- 13) FILES
- 14) END
- 15) FINISH

With the exception of the FILES card, which can appear anywhere in the deck, the data cards should be in the above order. Generally not all these data cards will be used depending on the specific problem.

3.1 Function and Format of Data Cards

- TITLE card (optional)

FORMAT (A6,18A4)

Cols. Specified punching or function of the field

1 - 5 TITLE
7 - 78 Alphanumeric text which will be printed as
 heading on each page.

- DLS-76 card

FORMAT (A6,1X,I3,14I2,2X,5I2)

Cols. Specified punching or function of the field

1 - 6 DLS-76

8 - 10 0/1/-N: use Gauss-Newton/use Newton-Raphson
 procedure/do first N cycles Gauss-Newton and
 finish with Newton-Raphson.

11 - 12 0/1: full matrix/diagonal matrix approximation.

13 - 14 0/N: do not/generate N sets of coordinates.
 Coordinates which are invariant are not gene-
 rated and the value supplied on the ATOM card
 is used.

15 - 16 0/N: do not/do make N cycles of distance
 refinement.

17 - 18 0/N: do not/do make N cycles of prescribed
 distance refinement (constant ratio refinement).

19 - 20 0/N: do not/do make N "APID" cycles (adjusted
 prescribed interatomic distances; see BONDIS
 and TETCON cards).

21 - 22 0/1: do not/do refine cell parameters

23 - 24 NC}
 } select parameters of cycle NC of APID cycle
 } NA of set number NS (if random coordinates
 } have been used), when reading from file

25 - 26 NA}
 } NFILEA (see FILES card).

27 - 28 NS}

29 - 30 0/1: do/do not make a convergence test (see
 FACTOR card).

31 - 32 0/N: do not/use variable damping factor for
 parameter shifts. (If in a particular cycle the
 agreement factor increases, all calculated
 parameter shifts will be halved N times or at
 least until the new agreement factor is smaller
 than the old one).

33 - 34 0/1: do not/translate refined DLS model along
x to minimise average deviations from initial
coordinates. (This can only be used when the
space group requires the x coordinate of an
atom to be arbitrarily fixed.)
35 - 36 0/1: do not/translate refined DLS model along y.
37 - 38 0/1: do not/translate refined DLS model along z.
39 - 40 not used.

Output control:

41 - 42 0/1: print parameters after first and final
cycle/after each cycle.
43 - 44 0/1: print distances after first and final
cycle/after each cycle.
45 - 46 0/1/2: do not/print matrix and vector of final
cycle/of each cycle.
47 - 48 0/1/2/-1/-2: do not/print elements of corre-
lation matrix of magnitude greater than the
value specified on the FACTOR card after final
cycle/after each cycle/print complete corre-
lation matrix after final cycle/after each
cycle.

Note: when using Newton-Raphson procedure,
the correlation matrix will only be calculated
after the final cycle (using Newton-Gauss
procedure). Each time the correlation matrix
is calculated the estimated standard deviation
of the atom coordinates will also be printed.

49 - 50 0/1/2: do not/write parameters of final cycle/
write parameters of every cycle in card format
on file NFILEA (see FILES card).

- FACTOR card (optional)

FORMAT (A6,4X,3F5.2,I5,4E10.4)

<u>Cols.</u>	<u>Specified punching or function of the field</u>
1 - 6	FACTOR
11 - 15	Damping factor to be applied to coordinate changes (default 1.0).
16 - 20	Damping factor for cell parameter changes (default 1.0).
21 - 25	Damping factor for changes of prescribed distances (default 1.0).
26 - 30	Starting number for random number generator (integer, default 0).
31 - 40	Factor for convergence test (default 0.0001). Refinement stops when all parameter changes are smaller than this value (see col. 30 on DLS-76 card).
41 - 50	Multiply all weights of linear restrictions (see LINRES card) with this factor (default 1.0).
51 - 60	Multiply all weights of distances which are outside a given range with this factor (see RANGES card). The distances are only checked and this factor applied during an APID cycle (default 1.0).
61 - 70	Minimum absolute value for correlation matrix printout (default 0.5). Only the elements with an absolute value greater than this one will be printed if requested on column 48 of DLS-76 card.

Note: If the card is not supplied or a field is left blank, the default values are used.

- RANGES card (optional)

FORMAT (A6,4X,5F5.2)

With this card the range for each type of distance in a tetrahedral framework can be defined. In an APID run the program will mark with an asterisk those distances which fall outside this range and will multiply the appropriate weight by the factor supplied on the FACTOR card (col. 51-60). When this factor is not equal to 1.0, the adjustment of the corresponding prescribed distance will be suppressed.

Cols. Specified punching or function of the field

1 - 6	RANGES
11 - 15	Relative deviation of the T-O distance (default: 0.03)
16 - 20	Lower limit of O-T-O angle (default: 104.5)
21 - 25	Upper limit of O-T-O angle (default: 114.5)
26 - 30	Lower limit of T-O-T angle (default: 115.5)
31 - 35	Upper limit of T-O-T angle (default: 175.5)

Note: If the card is not supplied or the field is left blank, the default values are used.

- ATOM card

FORMAT (A6,1X,A6,3F8.5,2X,A3,1X,30A1)

Cols. Specified punching or function of the field

1 - 4	ATOM
8 - 13	Atom label
14 - 21	x coordinate
22 - 29	y coordinate
30 - 37	z coordinate
40 - 42	Atom type (used in connection with BONDIS card)
44 - 73	If the atom is in a special position this field contains in free format the relation between the coordinates and/or the values of the fixed coordinate in a form similar to that commonly used (see below).

Note: For each symmetrically independent atom an ATOM card must be supplied. The atom type must be stated when the distances are specified by BONDIS and TETCON cards. Atoms which are symmetrically equivalent to these-atoms must be listed on SYMEQ cards.

Special positions:

Special positions are written in the form commonly used, e.g. X,2X,Z whereby the following special rules must be observed:

- 1) Coordinates considered as independent may not have a sign, a coefficient or an additional constant.
- 2) An independent coordinate must appear at its correct place, e.g. if Y is considered to be the independent coordinate, it must appear in the second position, after the first comma.
- 3) Coordinates fixed by symmetry are punched in the form 0,1/2,-3/4 etc. (and not as floating point numbers).

The following symbols may be used to describe a special position:

0 1 2 3 4 5 6 7 8 9 + - / , X Y Z

Blanks may be included anywhere, the comma is used as separator.

Examples:

X,2X-1,1/2	correct
-X,1-2X,1/2	not allowed (violates rule 1)
Y,2Y-1,1/2	not allowed (violates rule 2)
X, -X,Z	correct
2X, X,Z	not allowed (must be written

	as 2Y,Y,Z)
X,1/2X,Z	not allowed (no fractional coefficients allowed)
1/4, 1/4, 1/4	correct
-Y, Y, 0	correct

The coordinate fields (cols. 14 - 37) of dependent or fixed coordinates can be left blank.

- SYMEQ card

FORMAT (A6,1X,A6,1X,A6,1X,40A1)

This card is used to specify symmetrically equivalent atoms to the atoms supplied on ATOM cards.

Cols. Specified punching or function of the field

1 - 5 SYMEQ
 8 - 13 Atom label of independent atom (must appear on an ATOM card).
 15 - 20 Atom label of the symmetrically equivalent atom to the atom in cols. 8-13. This label should not appear on an atom card.
 22 - 61 Symmetry operation which transforms the independent atom (cols. 8-13) into the dependent atom (cols. 15-20).

The symmetry operation can be punched in free format in the same manner as the special position on the ATOM card. The transformations of the "general positions" in the International Tables are used throughout (also for atoms in special positions). For atoms in neighbouring cells additional translations must be added.

The following symbols may be used to state the symmetry operation:

1 2 3 4 5 6 7 8 9 + - / , X Y Z

Blanks may be included anywhere, the comma is used as separator. If a translation is a fraction of a cell edge, it must be given as a quotient n/m, where n and m are integers. The order of the terms is free, but additions of translations are not performed, i.e. 1 + 1/4 must be punched as 5/4 (see examples 2 and 3).

Examples: (all acceptable)

-Z, X, -Y
 1/4+Z, 3/4+Y, 3/4-X
 Z+5/4, 3/4+Y, -X+3/4
 X-Y, -Y, 1/2+Z
 -X+1, -X+Y-1, Z-1/2

- NOREF card

Using this card parameters (atom coordinates, cell parameters) which are not already invariant or dependent due to symmetry restrictions (special positions) can be set constant. There are two formats for this card, one for atom coordinates and one for cell parameters.

a) Atom coordinates

FORMAT (A6,1X,A6,3(A1,2X))

Cols. Specified punching or function of the field

1 - 5	NOREF
8 - 13	Atom label
14	X, Y and/or Z, depending which coordinate
17	should be kept invariant. X, Y and Z may be
20	in any order.

If the cols. 14, 17 and 20 are left blank, all three coordinates are set invariant. The card NOREF ATOMS, where ATOMS is punched in columns 8-12 forces all coordinates invariant. In this case only cell parameters and prescribed distances can be refined.

b) Cell parameters

FORMAT (A6,1X,A6,6A4)

Cols. Specified punching or function of the field

1 - 5	NOREF
8 - 11	CELL
14 - 17	These fields may contain any of the following
18 - 21	words in any order:
22 - 25	Abbb, Bbbb, Cbbb, ALFA, BETA, GAMA (b=blank)
26 - 29	
30 - 33	The parameters of the words appearing are set
34 - 37	invariant.

Note: A NOREF CELL card is only necessary in case of cell refinement when parameters not already invariant or dependent due to crystal system requirements are to be fixed.

- BONDIS card

FORMAT (A6,1X,3(A3,1X),1X,4E10.4,3F5.0)

This card can be used in conjunction with the TETCON card to specify the prescribed interatomic distances of tetrahedral atoms and their weights. Additionally it is used to specify the dependence of the T-O distance as a function of the T-O-T angle. If an APID run (adjusted prescribed interatomic distances) is requested (Col. 20 on DLS-76 card) this function is used to calculate new prescribed distances according to the T-O-T angles in the model.

The card contains the bond type, the distance function for this bond type and the weights for the various types of distances. The function has the form

$$DO = A + B(TOT - _) + C(TOT - _)^2$$

where DO : prescribed interatomic distance
 TOT : actual angle at bridging atom
 _ : standard T-O-T angle (e.g. 145°)
 A,B,C : constants

Cols. Specified punching or function of the field

1 - 5	BONDIS
8 - 10	Atom type of tetrahedral atom (central atom)
12 - 14	Atom type of bridging atom
16 - 18	Atom type of outer T-atom
21 - 30	Parameter A of distance function
31 - 40	B
41 - 50	C
51 - 60	Angle _ in degrees (default 145°)
61 - 65	Weight for T-O bond of this bond type
66 - 70	Weight for O-O bond
71 - 75	Weight for T-T bond

Note: This card must be supplied if the error equations (DISTAN-cards) are generated by the program from the connectivity specifications and of course always when an APID run is to be performed.

- TETCON card

FORMAT (A6,7X,9(A6,1X))

This card serves to specify the connectivity of tetrahedral atoms, i.e. the way these atoms are connected in the tetrahedral framework. On one card the central atom and the atoms of its first and second coordination are stated.

Together with the information from the BONDIS card, the program generates all independent T-O, O-O and T-T distances and assigns the proper prescribed distances and weights. This saves punching all these DISTAN cards. However, distances generated in this way can always be overwritten by supplying a DISTAN card, and, of course, other distances can be added with DISTAN cards.

In an APID run the TETCON card supplies all the necessary information for the calculation of the adjusted prescribed interatomic distances of tetrahedral framework structures.

<u>Cols.</u>	<u>Specified punching or function of the field</u>
1 - 6	TETCON
14 - 19	Label of the T-atom
21 - 26	Label of first bridging atom (O-atom)
28 - 33	Label of second,
35 - 40	third,
42 - 47	and fourth bridging atom
49 - 54	Label of outer T-atom bonded to first,
56 - 61	second,
63 - 68	third,
70 - 75	and fourth bridging atom.

Note: All labels of atoms considered must appear either on an ATOM or a SYMEQ card.

Special positions:

Only those T-O bonds which are symmetrically independent must be specified. However, make sure that all O-atoms are punched which are necessary for the specification of all independent O-O distances. For each independent T-O bond the outer T-atom must also be given (for the determination of bond type). Bonds or distances which are symmetrically equivalent are eliminated by the program.

- DISTAN card

FORMAT (A6,1X,2(A6,1X),2F10.5,A1,F10.5)

This is the standard card to specify an error equation. Each card contains the label of two atoms, their prescribed distances and the weight assigned to these distances. In addition a reference distance can also be supplied in case a constant (distance) ratio refinement is to be performed.

Cols. Specified punching or function of the field

1 - 6	DISTAN
8 - 13	Atom label of first atom
15 - 20	Atom label of second atom
22 - 31	Prescribed interatomic distance between the two atoms. If the field is left blank, the value of the previous card is used.
32 - 41	Weight assigned to this distance. If the field is left blank, the weight will be taken as 1.0. However, if the distance field is also blank, the weight of the previous card will be used.
42	Blank/any alphanumeric character: This prescribed distance is invariant/this prescribed distance will be refined in a constant ratio refinement. All prescribed distances having the same character in this field depend on the same reference distance. Their ratio to the reference distance will be kept constant during the refinement (see example).
43 - 52	Reference distance. If this field is left blank (and column 42 is not blank) the prescribed distance for this card will be taken as reference distance, i.e. the distance ratio will be 1.0.

Example (with constant ratio refinement)

```

DISTAN A1    A2    2.0    1.0    R 2.0
DISTAN A1    A3    3.0    1.0    R 2.0
DISTAN A1    A4
DISTAN A1    A5    2.5    1.0    R 2.0

```

All four prescribed distances will be varied, but not independently because all cards have the same character R in column 42 (the third card has the same values as the second card). According to these specifications the ratio of distance 2 to distance 1 and distance 3 to distance 1 is always 3:2 and the ratio of distance 4 to distance 1 is 2.5:2. As a consequence of this, distance 4 and 3 will have a ratio of 2.5:3.

Note: Constant ratio refinement and APID refinement can not be combined. In the latter case a prescribed distance can be held constant (not adjusted by the APID function) by supplying a DISTAN card for this distance and punching a C in column 42.

- LINRES card

FORMAT (A6,1X,F8.1,1X,5(F4.0,2A1,A6,1X,A1,A6),1X,A1,1X)

This card allows to impose linear restrictions on the shifts of the atom coordinates in the form of hard and/or soft constraints. These restrictions take the form

$2.0 * _X (ATOM1) - 1.0 * _Z (ATOM3) = 0$
as an example.

Cols. Specified punching or function of the field

1 - 6 LINRES
8 - 15 Weight or sigma of this restriction for soft constraints. If this field is left blank, the restriction will be taken as a hard constraint and the variable of the last term of this restriction is eliminated. Values preceded by a minus sign are interpreted as weights, otherwise they are taken as sigmas and the weight for the restriction is calculated as follows:

Weight = 1/(sigma * nr. of terms in restriction)

17 - 20 First coefficient of the restriction. If the coefficient is +1.0, the field can be left blank.

21 Multiplication sign * (optional)

22 X, Y or Z

23 - 28 Atom label

Further terms of the restriction are punched in the same manner in the columns

29-32, 41-44, 53-56, 65-68 coefficients

33, 45, 57, 69 multiplication sign (optional)

34, 46, 58, 70 X, Y or Z

35-40, 47-52, 59-64, 71-76 atom label

In this way up to 5 terms can be punched per card. The restriction can be continued on further cards using the same format (the weight can be omitted). On the last card of the restriction the two characters "=0" must be punched in columns 78-79. A restriction may contain up to 20 terms. Blank fields may be left on cards, i.e. one can use as many cards as are desired.

Note: A hard constraint on a single coordinate (e.g. $_X (ATOM1) = 0$) must be put in using a NOREF card.

- FILES card

FORMAT (A6,I3,3X,I3)

The FILES card is used to change at any time the logical number of the input file and the parameter output file (not the printing file). In this way, the input or part of it can be read from a mass storage file and not from the card reader, and the parameter output can be diverted either to the card. punch or a disk file.

Although the FILES card can be placed anywhere in the data deck it will mainly be used in connection with the transfer of parameters from one job to another. In this case, it has to be inserted after the ATOM cards to read the new parameters from the file (which are on NATOM cards) and also after the TETCON card (if used) in place of or before the DISTAN cards.

Please note that when a refinement is divided into several jobs, the card deck is not changed except for the insertion of the FILES cards. Only the DISTAN cards are removed if in the previous job the prescribed distances were altered, either by a constant ratio refinement or an APID cycle. (For further details see section on the format of the parameter file.)

Cols. Specified punching or function of the field

1 - 5	FILES
7 - 9	logical number NTIN of the input file
13 - 15	logical number NFILEA of the parameter file (output file) or card punch

The default values set by the program (in subroutine DATIN) are

NTIN	= 5	Input file (normally card reader)
NFILEA	= 8	Parameter output file
NTOUT	= 6	Output file (printer)

If a field is left blank, the file number is not changed. In the present version, the file numbers 7, 8, 9 and 10 can be used. If number 8 is chosen as input file the file will be rewound each time the FILES 8 card is encountered. The file number 7 is assigned to the card punch.

- END card

FORMAT (A6)

The END card signals the end of a data deck and starts the computation. After this card another complete job may follow.

Cols. Specified punching

1 - 3 END

FINISH card

FORMAT (A5)

After reading this card, the program is immediately stopped. It must occur at the very end of a data deck.

Cols. Specified punching

1 - 6 FINISH

3.2 Parameter File

When requested in column 50 of the DLS-76 card the refined parameters (atom coordinates and also cell constants and distances if their values have been changed in the run) are written on a separate file which can be used as input of a subsequent run. The file consists of coded card records and the card format is similar or identical to the normal input cards. Currently the following card types will be written:

Name	Content
(Col. 1-6)	
TITLE	title as supplied on input card
CYCLE	FORMAT (A6,I4,2I5) NC, NA, NS (see DLS-76 card, cols. 23-28) All parameter sets are identified by such a card. When reading the file the program can thus select the requested set.
CELL	Format like normal input card(1
NATOM	new atom parameters, format as on ATOM card (coordinates only)
DISTAN	Format like normal input card(1
FILES N	Here N is the logical number of the card reader. This card appears at the end of a set of parameter cards and switches the input back to the normal input device.

(1 These cards are only written when the values of the respective parameters have been changed.

- BOUND card (CDC-version only)

FORMAT (A6,4X,4E10.4)

With this card limits or bounds can be specified for the weighted deviations of linear restrictions and/or distances. If the residual of a particular restriction or distance exceeds these limits the corresponding weight will be multiplied by the absolute value of the residual divided by the "modified bound". The "modified bound" has to be smaller than the specified limit and is calculated according to the following equation:

$$\text{"modified bound"} = 3.0 * \text{bound} / (3.0 + t)$$

where t is supplied on the card.

Cols. Specified punching or function of the field

1 - 5	BOUND
11 - 20	Bound for linear restrictions defined in multiples of sigmas (see LINRES card). (default: 3.0)
21 - 30	Term t for the calculation of the "modified bound" in linear restrictions, a suitable value

is 1.0. If left blank no bound checks for linear restrictions are made.

31 - 40 Bounds for weighted deviations in distances. (default: 0.05)

41 - 50 Term t for the calculation of the "modified bound" for the distances. Blank: no bound check.

Note: The correction factors will also be written on the parameter file on WEIMOD cards and can thus be applied in a subsequent run.

- GENER card (optional) (CDC-version only)

FORMAT (A6,4X,3I5)

When this card is encountered the symmetry information for the specified space group is read from the file and all required atoms outside the asymmetric unit (i.e. atoms on the SYMEQ-cards) are generated and their connectivity determined (i.e. the information contained on the TETCON cards). Thus SYMEQ cards and TETCON cards are not required in this case. The program assumes the four shortest T-O and T-T bonds to be the correct connections and therefore the atom coordinates should already be sufficient accurate.

<u>Cols.</u>	<u>Specified punching or function of the field</u>
1 - 5	GENER
11 - 15	Space group number as in International Tables of X-Ray Crystallography, Vol. I. If two orientations are listed (e.g. space group 125, P4/nbm) the first listed is positive (+) and the second is negative (-). The symmetry cards are read from the master data file of program POWD (Smith Plot Program).
16 - 20	File number of the symmetry data file (default 8)
21 - 21	0/1: Do not/print all information used to set up the connectivity tables. This may be used as a debugging aid in case the automatic setting up has failed (e.g. because of inaccurate starting coordinates).

Note: The GENER card should appear after the ATOM cards in place of the SYMEQ cards. The TETCON cards must also be omitted. However, DISTAN cards may still be added.

4. EXAMPLES

Two test examples are provided to illustrate the operation and output of DLS-76. The first example is a straight-forward DLS-refinement and can be used to check the basic operations of the program. The second example is somewhat more elaborate and makes use of a number of special features of DLS-76. Some background information and a description of the two examples is given below.

Example 1: Low-quartz-type structure of AlPO_4

AlPO_4 has a quartz-type structure which was refined in space group $P3_121$ by D. SCHWARZENBACH (1966). The following data are required to set up the basic DLS job:

Unit cell parameters: hexagonal system
a = 4.9429 \AA , c = 10.9476 \AA

Atomic positions: There are 4 atoms in the asymmetric unit, i.e.

Al in 3a	x, 0, 1/3
P in 3b	x, x, 1/2
O1 in 6c	x, y, z
O2 in 6c	x, y, z

For each of these atoms an ATOM card has to be punched, containing the atom label, approximate coordinates and, in case of Al and P, a specification of those parameters which are fixed by symmetry. Further atoms supplied on SYMEQ cards have to be included in order to be able to specify all independent distances. Besides a new atom label each of these cards contains the label of the symmetrically related atom on the respective ATOM card and the transformation (including translational components where applicable) which generates the coordinates of this additional atom.

Interatomic distances: In the present example the interatomic distances are supplied by DISTAN cards¹. For each independent distance (T-O and O-O distances, T = Al, P) one DISTAN card is punched. Each such card contains the atom labels of two atoms, the prescribed value of their distance and the weight associated with this distance. The values for the T-O distances used here are those given by LOUISNATHAN and GIBBS (1972) and the O-O distances are calculated assuming an ideal tetrahedral angle.

The input and output for this example using the Newton-Raphson procedure is reproduced below. The refinement converges after 6 cycles. The parameters, the shifts and the resulting interatomic distances are printed for the first and the last cycle only, as specified on the DLS-76 input card. For the intermediate cycles only the R-values are printed which serve as an indication of the progress of the refinement.

(1 Alternatively, TETCON and BONDIS cards could be used in this case.

Input for Example 1:

```
TITLE *** EXAMPLE 1 : ALPO4 *** SPACE GROUP P3(1)21
DLS-76 1 10
CELL HEX 4.9429 10.9476
ATOM AL .4 X,0,1/3
ATOM P .6 X,X,1/2
ATOM O1 .5 .4 .3
ATOM O2 .8 .7 .6
SYMEQ O1 O1* X-Y,-Y,2/3-Z
SYMEQ O1 O1** Y,X,1-Z
SYMEQ O2 O2* Y-X+1,1-X,Z-1/3
SYMEQ O2 O2** Y,X-1,1-Z
SYMEQ O2 O2*** Y,X,1-Z
DISTAN AL O1 1.748 2.
DISTAN AL O2* 1.748 2.
DISTAN O1 O1* 2.8545 1.
DISTAN O1 O2* 2.8545 1.
DISTAN O1 O2** 2.8545 1.
DISTAN O2* O2** 2.8545 1.
DISTAN P O1 1.538 2.
DISTAN P O2 1.538 2.
DISTAN O1 O1** 2.5115 1.
DISTAN O1 O2 2.5115 1.
DISTAN O1 O2*** 2.5115 1.
DISTAN O2 O2*** 2.5115 1.
END
FINISH
```

Output from this example file is provided in the file DLSexample1.out

Example 2: Desymmetrization of the crystal structure of analcime

Analcime is a framework silicate and is normally described as cubic with space group Ia3d and $a = 13.73 \text{ \AA}$. It has a remarkably constant unit cell composition of $\text{Na}_{16}\text{Al}_{16}\text{Si}_{32}\text{O}_{96} \cdot 16 \text{ H}_2\text{O}$, which, if fully ordered, is incompatible with cubic symmetry. MEIER (1973) therefore proposed on the basis of DLS calculations that the symmetry should at least be reduced to $I4_1/acd$ which would allow for Si, Al ordering assuming a likely distribution scheme.

A recent neutron-diffraction study (FERRARIS et al., 1972) based on space group Ia3d led to the following atomic coordinates of the framework atoms (estimated standard deviation in parentheses):

T(Si,Al)	in 48g	.16208(15)	.08792(15)	.125	(x,1/4-x,1/8)
O	in 96h	.10428(14)	.13440(16)	.21932(12)	(x,y,z)

On reducing the symmetry to $I4_1/acd$ these two positions would split up into the following 5 independent positions¹ (origin in 1):

T1(Al)	in 16f	.16208	.08792	.125	(x,1/4-x,1/8)
T2(Si)	in 32g	.08792	.12500	.33792	(x,y,z)
O1	in 32g	.10428	.13440	.21932	
O2	in 32g	.14572	.03068	.38440	
O3	in 32g	.13440	.21932	.39572	

These parameters are punched on ATOM cards and could be used as starting parameters. However, they still possess cubic symmetry and are unlikely to refine in the tetragonal space group. Instead, somewhat desymmetrized or random coordinates are needed for starting the refinement. The values on the atom cards are then used as reference coordinates only in the calculation of the linear restrictions and in the calculation of the total parameter shifts. To enable actual checking in this test example "pseudo-random" coordinates supplied by NATOM cards are used here. Such cards are usually only read from the parameter file and overwrite the starting coordinates but not the reference coordinates.

As pointed out in Section 1 the symmetrized DLS coordinates should still agree (say within 3#) with the experimentally determined coordinates of the high-symmetry reference structure. Therefore, restrictions have to be placed on the total coordinate shifts. These restrictions are applied as weighted constraints. In this example the 3-fold axes are removed and the constraints are accordingly:

¹Compared to the setting in the Int. Tables (Vol. I, page 142) the origin has been shifted to 0,0,1/2.

$$\begin{aligned}
_x(T1) - _z(T2) - _x(T2) &= 0 \\
_x(O1) - _x(O2) - _z(O3) &= 0 \\
_y(O1) + _z(O2) + _x(O3) &= 0 \\
_z(O1) - _y(O2) + _y(O3) &= 0
\end{aligned}$$

These equations are punched on LINRES cards. The weights used here are the reciprocal values of the estimated standard deviations of the respective coordinates as obtained by FERRARIS et al. (1972). These weights are all multiplied by a factor of .012 (punched on the FACTOR card) to scale them to the weights of the distance error equations.

The distance error equations for this example are generated from two TETCON cards (one for each tetrahedron). For the prescribed interatomic distances a function is supplied (on a BONDIS card) for each bond type giving the relationship between T-O bond distance and T-O-T angle which is taken into account in an APID cycle after a maximum of 15 cycles of DLS refinement using standard distance values.

The input and complete output is reproduced below. The linear restrictions, bond distance functions and (as a check) the bonding scheme for each tetrahedron as stated on the TETCON card are also printed. Despite the near-random starting coordinates used in this example, the Newton-Gauss refinement converges in 12 cycles, i.e. the shifts in the coordinates become all less than 0.0001 after 12 cycles.

The parameter shifts, the interatomic distances, the difference vectors relative to the initial (reference) coordinates and the residuals of the linear restrictions are again only printed for the first and final cycle. For the intermediate cycles only the R-values are printed and in addition the sum RHO over all squared residuals resulting from the distances and the linear restrictions. Once the convergence test becomes positive (after 12 cycles), the prescribed distances are adjusted according to the function supplied and the T-O-T angles in the model. A list of all the actual distances in the refined model, the original distances as well as the new prescribed distances are printed, and another refinement with the new set of prescribed distances is started. Convergence is reached after 3 cycles and all final parameters and values are then printed. The differences in the coordinates of the refined DLS model and the reference structure are given in the last table of the output.

Input for Example 2:

```

TITLE *** EXAMPLE 2 : ANALCIME *** I4(1)/ACD (WITH LINEAR
RESTRICIONS)
DLS-76      15      1
FACTOR                                .012
CELL      TET      13.73              13.73
ATOM      T1      .16208              AL  X,1/4-X,1/8
ATOM      T2      .08792      .125      .33792      SI
ATOM      O1      .10428      .1344      .21932      O
ATOM      O2      .14572      .03068      .3844      O
ATOM      O3      .1344      .21932      .39572      O
NATOM     T1      .11      .14      .125
NATOM     T2      .21      .22      .23
NATOM     O1      .31      .32      .33
NATOM     O2      .41      .42      .43
NATOM     O3      .51      .52      .53
SYMEQ     T1      T1*      X,-Y,1/2-Z
SYMEQ     T2      T2*      1/4-Y,1/4+X,3/4-Z
SYMEQ     T2      T2**     Y-1/4,1/4-X,3/4-Z
SYMEQ     T2      T2***    1/4+Y,1/4-X,Z-1/4
SYMEQ     O1      O1*      1/4-Y,1/4-X,1/4-Z
SYMEQ     O2      O2*      1/4+Y,1/4-X,Z-1/4
SYMEQ     O2      O2**     X,-Y,1/2-Z
SYMEQ     O3      O3*      Y-1/4,1/4-X,3/4-Z
BONDIS    SI  O  SI  1.620      -.0004      0.      145.      2.      1.      .1
BONDIS    SI  O  AL  1.593      -.0004
BONDIS    AL  O  SI  1.740      -.0004
TETCON    T1      O1      O2*      O1*      O2**     T2      T2***
TETCON    T2      O1      O2      O3      O3*      T1      T1*      T2*      T2**
LINRES    2223.    1.      *XT1      -1.      *ZT2      -1.      *XT2
=0
LINRES    2380.    1.      *XO1      -1.      *XO2      -1.      *ZO3
=0
LINRES    2083.    1.      *YO1      1.      *ZO2      1.      *XO3
=0
LINRES    2776.    1.      *ZO1      -1.      *YO2      1.      *YO3
=0
END
FINISH

```

5. GLOSSARY OF SYMBOLS

The dimensions of the arrays are given in the description of their index variables. The index limits are defined in the subroutine DATIN. Symbols marked with an asterisk are read as input data.

5.1 Control integers and single variables

The control integers on the DLS-76 card are explained in Section 3.

* CORR	see FACTOR card cols. 61 - 70
* CVGTST	see FACTOR card cols. 31 - 40
IA	Number of BONDIS cards (maximum value is IDIMAP = 15)
* ICAL	DLS-76 card col. 30
* ICOR	DLS-76 card col. 48
* IDIS	DLS-76 card col. 44
* IDOB	DLS-76 card col. 18
* IGIT	DLS-76 card col. 22
* IMAT	DLS-76 card col. 46
* INEW	DLS-76 card col. 10
* IORT	DLS-76 card col. 42
* IPCH	DLS-76 card col. 50
* IRNG	DLS-76 card col. 14
* IRNG1	Starting number of random generator (FACTOR card cols. 26 - 30)
ISYS	Internal crystal system indicator (see DATIN)
* IVF	DLS-76 card cols. 32
* LSYS	Crystal system indicator as on CELL card
M	Number of distances (maximum value is IDIMM = 200)
N	Number of atoms (N1 + N2)
N1	Number of atoms in asymmetric unit
N2	Number of atoms outside asymmetric unit

* NA	DLS-76 card col. 26
* NAPID	DLS-76 card col. 20
* NC	DLS-76 card col. 24
* NCYCLE	DLS-76 card col. 16
* NDIAG	DLS-76 card col. 12
NDO	Number of different prescribed ratios of interatomic distances (maximum number of ratios is IDIMRT = 40)
NEQU	Number of SYMEQ cards (maximum value is IDNEQU = 60)
* NFILEA	Logical number of parameter file
NRE	Number of linear restrictions (maximum value is IDIMLI = 35)
NRH	Number of hard constraints
* NS	DLS-76 card col. 28
* NTIN	Logical number of card reader
NTOUT	Logical number of line printer
NV	Total number of variables (NVO + NVG + NVD) (maximum value is IDIMNV = 150)
NV1	NVO + NVG
NVD	Number of distance variables
NVG	Number of lattice constant variables
NVO	Number of coordinate variables
NZA	Number of TETCON cards (maximum value is IDIMNZ = 40)
RDATE	Date
* RDD	RANGES card cols. 11 - 15
* ROTOL	RANGES card cols. 16 - 20
* ROTOU	RANGES card cols. 21 - 25
* RTOTL	RANGES card cols. 26 - 30
* RTOTU	RANGES card cols. 31 - 35
* WFAC	See FACTOR card cols. 51 - 60

* WRF See FACTOR card cols. 41 - 50

5.2 Arrays

* A(6) Lattice constants

* AOLD(6) Lattice constants (of previous cycle)

B(K,K,N) (K = 1,3) homogeneous part of the restrictions resulting from special positions (for atoms in the asymmetric unit only)

BEDING(NRE) Residual of the linear restriction NRE

BI(K,N) (K = 1,3) invariant part of restrictions given by a special position (see B(K,K,N))

BT(IA) Bond type. Its value is calculated from the atom type numbers of the 3 atoms defining the bond type of a T-O bond. (see subroutine DATIN)

* CAPID(IA,4) Parameters of distance function (see BONDIS card)

D(M) Calculated interatomic distances

DELTAD(M) DOB(M) - D(M)

DELV(NV) Vector of parameter shifts of current refinement cycle

DGEL(NV) Approximate eigenvalues of matrix

* DOB(M) Prescribed interatomic distances

* DOBIN(M) Initial values of prescribed interatomic distances

DOBOLD(M) Prescribed interatomic distances of previous APID cycle

* FUDGE(3) Damping factors as stated on FACTOR card

G(3,3) Metric tensor

GABL1(3,3,6) First derivatives of metric tensor

GABL2A(3,6,6) }

}

GABL2B(3,6,6) }	Second derivatives of metric tensor
}	
GABL2C(3,6,6) }	
IBT(NZA,4)	Bond types of the four T-O distances of central atom NZA
ICON(NZA,11)	Tetrahedral connectivity of central atom NZA
	ICON(NZA,1 to 9) : internal representation of TETCON card
	ICON(NZA,10) : number of non-equivalent T-O distances
	ICON(NZA,11) : number of non-equivalent O-O distances
* ID(N)	Label of atom N
IFAK(K,N)	Can have values D,I,L,R indicating whether the coordinate K of atom number N is dependent, invariant, dependent by a linear restriction! or to be refined, respectively
IFELD(6)	Number of cell parameters which are to be refined (up to 6)
IGIN(6)	Can have values D,I,R indicating whether the corresponding cell parameter is dependent, invariant, or to be refined, respectively
* IMOV(3)	See DLS-76 card cols. 34 - 38
* ISYMB(M)	Symbol on DISTAN card which identifies the reference distance in a constant ratio refinement
* ITYPE(N)	Number of atom type of atom number N
IV(NV)	Can have values of 1,2,3 indicating whether the variable NV is an X, Y or Z coordinate, respectively
IV1(NV)	Contains the number of the atom to which the variable NV belongs
IZ1(NRE)	Number of terms in the linear restriction NRE
KA(K,NEQU)	(K = 1,2) Atom number of both atoms on SYMEQ card NEQU
KARI(NRE,IZ1)	Variable number corresponding to term IZ1 of the linear restriction NRE

KATOR(M) Flag for the calculation of derivatives of distance M (determined by subroutine DATIN)

0 if both atoms are in the asymmetric unit and not on a special position

-1 if atoms are not related and at least one of them is not in the asymmetric unit, or else at least one of them is in a special position

MYS>0 if both atoms are symmetrically related (see SYMSIG(K,K,40))

KVAR(K,I1) (K = 1,3). Contains the variable number of coordinate K of atom N. If KVAR is zero the coordinate is not to be refined.

KTYPE(NT) Atom type symbol

LDR(NDO) Variable number of prescribed distance NDO in a constant ratio refinement

LIND(NRE) Term number of the variable which is eliminated in the hard constraint NRE

LINH(NRE) If the linear restriction NRE is a hard constraint, LINH(NRE) is 1, otherwise it is 0.

LJ(M) DOB(LJ(M)) is the prescribed distance for distance D(M)

MD(NZA, 18) Index to the D and DOB arrays of all distances around central tetrahedral atom NZA (inclusive outer O-T and T-T distances)

MD(NZA, 1 to 4): T-01, T-02, T-03, T-04

MD(NZA, 5 to 10): 01-02, 01-03, 01-04
02-03, 02-04, 03-04

MD(NZA,11 to 14): 01-T1, 02-T2, 03-T3,
04-T4

MD(NZA,15 to 18): T-T1, T-T2, T-T3, T-T4

MSYMAB(N) Number of atom in asymmetric unit, symmetrically equivalent to atom N

MTR(N) MTR(N) = N indicates that the atom N is

in a special position or outside the asymmetric unit (otherwise $MTR(N) = 0$)

MW(M) MW(M) = 2 if distance M is outside specified ranges, otherwise MW(M) = 1

NN(M,K) (K = 1,2). Number of the first or second atom on DISTAN card number M

NN11(M,K) (K = 1,2). Number of the atom in the asymmetric unit to which atom K on DISTAN card M is symmetrically related

OTO(NZA, 6) O-T-O angles at central atom NZA (in same order as O-O distances in MD(NZA,18) array)

RAT(NDO) Prescribed distance ratio (prescribed distance/reference distance on DISTAN card)

* RESKO(NRE, IZ1) Coefficient of term IZ1 of the linear restriction NRE, (IZ1 IDIMIZ = 20)

S(NV*(NV+3)/2) Matrix array. Only upper triangle is stored as one-dimensional array

SI(K,NEQU) (K = 1,3). Translational part of symmetry transformation of SYMEQ card number NEQU

SIGN(K,K,NEQU) (K = 1,3). Non-translational (homogeneous) part of symmetry transformation of SYMEQ card number NEQU

* SYMOPS(10,N) Symmetry transformation (coded) as punched on ATOM and SYMEQ cards

SYMSIG(K,K,40) (K = 1,3). This variable is only defined when both atoms on a DISTAN card are symmetrically equivalent, in which case

$$SYMSIG(K,K,MYS) = B1 - B2$$

where B1 and B2 are the non-translational parts of the symmetry transformations (including restrictions due to special positions) leading to ATOM1 and ATOM2, respectively

T(NV) Normal vector (gradient)

TOT(NZA, 4) T-O-T angles observed at central atom NZA (in same order as T-T distances in MD(NZA,18) array)

* W(M) Weight of DOB (M)

* WEIGHT(IA,K) (K = 1,3). Weights assigned to T-O, O-O and T-T distances, respectively (see BONDIS card)

WR(NRE) Weight of linear restriction NRE

* X(K,N) X, Y, Z coordinate (K = 1,3) of atom N
* XINI (K,N) X, Y, Z coordinate (input values)
XOLD(K,N) X, Y, Z coordinate of previous cycle

6. FORMULAE

In the following the more important formulae which form the mathematical basis of DLS-76 are briefly surveyed. The symbols used here and their names in the program are listed in Table 1 at the end of this section.

Given a set of m weighted distance error equations and q weighted linear restrictions or soft constraints (treated as additional equations; cf. WASER, 1963) the following function $\underline{S}(\underline{v})$ must be minimized.

$$\underline{S}(\underline{v}) = \sum_{j=1}^m w_j^2 (D_j^o - D_j)^2 + \sum_{l=1}^q u_l^2 c_l^2$$

where

$$D_j^o = d_{ji} D_i^o \quad D_j(z_1, \dots, z_x, a_1, \dots, a_\lambda) \quad c_l = \sum_{r=1}^v h_{l,r} (z_r - z_r^o)$$

\underline{v} shall represent a vector consisting of the variable atomic coordinates z_r , cell parameters as and (in a constant ratio refinement) of variable prescribed distances D_j . If in addition to the q soft constraints some coordinates are also subject to hard constraints (i.e. restrictions which must be exactly fulfilled), then an interatomic distance D_j may depend on additional coordinates other than those of the two atoms directly involved.

The equation for the shift \underline{v} towards a minimum of \underline{S} may be given as

$$\underline{S}'(\underline{v} + \underline{v}) = 0$$

This can be approximated by

$$\underline{S}'(\underline{v}) + \underline{S}''(\underline{v}) \underline{v} = 0$$

or, if we set

$$\underline{S} = \underline{f}^T \underline{f} + \underline{c}^T \underline{c}$$

($f_j = w_j (D_j^o - D_j)$, $j = 1, \dots, m$; $c_l = u_l c_l$, $l = 1, \dots, q$)
by

$$2 \underline{f}^T(\underline{v}) (\underline{f}(\underline{v}) + \underline{f}'(\underline{v}) \underline{v}) + 2 \underline{c}^T(\underline{v}) (\underline{c}(\underline{v}) + \underline{c}'(\underline{v}) \underline{v}) = 0$$

The iteration

$$S \underline{v} = \underline{T}$$

then takes the form

$$\underline{S}'' \underline{v} = -\underline{S}'$$

in the Newton-Raphson procedure

and

$$(2\underline{f}^T \underline{f}' + 2\underline{z}^T \underline{z}') \underline{v} = -\underline{z}'$$

in the Gauss-Newton procedure.

In both procedures the vector \underline{T} contains in general the partial derivatives of ρ with respect to the coordinates z_r , the cell parameters a_r and the variable prescribed distances D_r^0 :

$$\underline{T} = -\left(\frac{\partial \rho}{\partial z}, \dots, \frac{\partial \rho}{\partial a_1}, \dots, \frac{\partial \rho}{\partial D_1^0}\right)^T$$

where

$$\begin{aligned} \frac{\partial \rho}{\partial z_r} &= -2 \sum_{j=1}^m w_j^2 (D_j^0 - D_j) \frac{\partial D_j}{\partial z_r} + 2 \sum_{l=1}^q u_l^2 c_l h_{l,r} \\ \frac{\partial \rho}{\partial a_r} &= -2 \sum_{j=1}^m w_j^2 (D_j^0 - D_j) \frac{\partial D_j}{\partial a_r} \\ \frac{\partial \rho}{\partial D_r^0} &= -2 \sum_{j=1}^m w_j^2 (D_j^0 - D_j) h_{j,r} \end{aligned}$$

An element S_{rs} of the matrix S is given by

$$S_{rs} = \frac{\partial^2 \rho}{\partial \zeta_r \partial \zeta_s}$$

in the Newton-Raphson procedure and as

$$S_{rs} = 2 \sum_{j=1}^m \frac{\partial f_j}{\partial \zeta_r} \frac{\partial f_j}{\partial \zeta_s} + 2 \sum_{l=1}^q \frac{\partial \varphi_l}{\partial \zeta_r} \frac{\partial \varphi_l}{\partial \zeta_s}$$

in the Gauss-Newton procedure where \underline{z} and \underline{a} are variables of the above

three types.

The following is a summary of all possible S_{rs} .

Types of variables	Newton-Raphson	Gauss-Newton
z_r, z_s	$2 \sum_{j=1}^m w_j^2 \left[\frac{\partial D_j}{\partial D_r} \frac{\partial D_j}{\partial D_s} - (D_j^o - D_j) \frac{\partial^2 D_j}{\partial z_r \partial z_s} \right]$ $+ 2 \sum_{l=1}^q u_l^2 h_{l,r} h_{l,s}$	$2 \sum_{j=1}^m w_j^2 \frac{\partial D_j}{\partial z_r} \frac{\partial D_j}{\partial z_s} + 2 \sum_{l=1}^q u_l^2 h_{l,r} h_{l,s}$
z_r, a_s	$2 \sum_{j=1}^m w_j^2 \left[\frac{\partial D_j}{\partial z_r} \frac{\partial D_j}{\partial a_s} - (D_j^o - D_j) \frac{\partial^2 D_j}{\partial z_r \partial a_s} \right]$	$2 \sum_{j=1}^m w_j^2 \frac{\partial D_j}{\partial z_r} \frac{\partial D_j}{\partial a_s}$
z_r, D_s^o	$- 2 \sum_{j=1}^m w_j^2 \frac{\partial D_j}{\partial z_r} d_{j,s}$	
a_r, a_s	$2 \sum_{j=1}^m w_j^2 \left[\frac{\partial D_j}{\partial a_r} \frac{\partial D_j}{\partial a_s} - (D_j^o - D_j) \frac{\partial^2 D_j}{\partial a_r \partial a_s} \right]$	$2 \sum_{j=1}^m w_j^2 \frac{\partial D_j}{\partial a_r} \frac{\partial D_j}{\partial a_s}$
a_r, D_s^o	$- 2 \sum_{j=1}^m w_j^2 \frac{\partial D_j}{\partial a_r} d_{j,s}$	
D_r^o, D_s^o	$2 \sum_{j=1}^m w_j^2 d_{j,r} d_{j,s} \quad (\text{only for } r=s)$	

The distance $D(P,Q)$ between the two atoms P and Q having coordinates \underline{x} and \underline{x}' can be expressed by

$$D(P,Q) = \left[\sum_{i=1}^3 \sum_{k=1}^3 g_{ik} \Delta x_i \Delta x_k \right]^{\frac{1}{2}} \quad (\underline{x} = \underline{x} - \underline{x}')$$

Generally P and Q are outside the asymmetric unit and \underline{x} and \underline{x}' can be given as

$$\underline{x} = B\underline{y} + \underline{b} \quad \underline{x}' = B'\underline{y}' + \underline{b}'$$

If P or Q occupy a special position, then B, \underline{b} or B', \underline{b}' contain the information of the symmetry transformation leading to P or Q as well as the relations describing the special positions. (Symmetry information on SYMEQ-card and on corresponding ATOM-card).

If a component y_i of \underline{y} is not set invariant then $y_i = z_k$ for a given k, or

$$y_i = y_i^o - \frac{\lambda}{h_{ii}} \sum_{r \neq i} h_{lr} (z_r - z_r^o)$$

for a hard linear constraint 1.

Hence, $\underline{x} = \underline{x} - \underline{x}'$ may be understood as dependent on a vector $\underline{z} =$

$(z_1, \dots, z_n)^T$ of n variable coordinates.

If we define

$$R_{kr} = \frac{\partial y_k}{\partial \Delta z_r}$$

and

$$A_{ir} = \frac{\partial \Delta x_i}{\partial z_r}$$

we may write

$$\frac{\partial \Delta x}{\partial z} = A = BR = B'R'$$

where A is a (3 x n)-matrix.

Hence, we obtain the following derivatives of D with respect to coordinates and cell parameters.

$$\begin{aligned} \frac{\partial D}{\partial z_r} &= \frac{\lambda}{D} \sum_{i=1}^3 \sum_{k=1}^3 g_{ik} A_{ir} \Delta x_k \\ \frac{\partial D}{\partial a_r} &= \frac{\lambda}{2D} \sum_{i=1}^3 \sum_{k=1}^3 \frac{\partial g_{ik}}{\partial a_r} \Delta x_i \Delta x_k \\ \frac{\partial^2 D}{\partial z_r \partial z_s} &= \frac{\lambda}{D} \left[\sum_{i=1}^3 \sum_{k=1}^3 g_{ik} A_{ir} A_{ks} - \frac{\partial D}{\partial z_r} \frac{\partial D}{\partial z_s} \right] \\ \frac{\partial^2 D}{\partial z_r \partial a_s} &= \frac{\lambda}{D} \left[\sum_{i=1}^3 \sum_{k=1}^3 \frac{\partial g_{ik}}{\partial a_s} A_{ir} \Delta x_k - \frac{\partial D}{\partial z_r} \frac{\partial D}{\partial a_s} \right] \\ \frac{\partial^2 D}{\partial a_r \partial a_s} &= \frac{\lambda}{2D} \left[\sum_{i=1}^3 \sum_{k=1}^3 \frac{\partial^2 g_{ik}}{\partial a_r \partial a_s} \Delta x_i \Delta x_k - 2 \frac{\partial D}{\partial a_r} \frac{\partial D}{\partial a_s} \right] \end{aligned}$$

In the calculation of A the program distinguishes three cases

(i) P and Q are both in the asymmetric unit and in general position indicated

by KATOR(J) = 0)0 Then A has the form

$$A = \begin{pmatrix} 1 & 0 & 0 & -1 & 0 & 0 \\ 0 & 1 & 0 & 0 & -1 & 0 \\ 0 & 0 & 1 & 0 & 0 & -1 \end{pmatrix}$$

(ii) P and Q are symmetrically equivalent (KATOR(J)>0) Then $\underline{y} = \underline{y}'$ and $R = R'$

and A can be written as

$$A = (B - B')R$$

(B - B' corresponds to SYMSIG(I,K,KATOR(J))

(iii) P and/or Q are not in the asymmetric unit and/or in special positions
(KATOR(J)<0):

$$A = BR - B'R'$$

TABLE 1

Symbol in text	Meaning	Designation in program
A	matrix containing the derivatives of \underline{x} with respect to all variable coordinates on which \underline{x} depends	ALIN(I,K)
a_r	variable cell parameter number r	A(I)
B	matrix containing the homogeneous part of the symmetry information on a SYMEQ card and the corresponding ATOM card	B(I,K,N) (includes SIGN(I,K,NEQU))
\underline{b}	vector representing the inhomogeneous part of the symmetry information	SIGN(I,K,NEQU)*BI(K,N) + SI(I,NEQU)
c_l	linear constraint number l	BEDING(L)
D_j	calculated interatomic distance	D(J)
D_j^0	prescribed distance	DOB(J)
D_r^0	variable prescribed distance	DOB(LJ(J))
d_{jr}	ratio of D_j^0 to D_r^0	RAT(LJ(J))
$\underline{f}, _$	auxiliary quantities in the representation of #p as a sum of two scalar products	
g_{ik}	metric tensor	G(I,K)
h_{lr}	coefficient of term r in constraint l	RESKO(L,I)
m	number of distance equations	M
n	number of variable coordinates on which a particular distance depends	KK
$_$	number of terms in constraint l	IZ1(L)
q	number of weighted (soft) constraints	NRE-NRH
R	auxiliary quantity: matrix containing the derivatives of the y_k with respect to all variable coordinates on which	

the y_k depend

<u>—</u>	function to be minimized	ROV
S	normal matrix/Jacobian matrix of <u>—</u> '	S (KLM)
<u>T</u>	vector of constants in system represented by S	T (I)
u_1^2	squared weight of soft constraint 1	WR (L)
<u>v</u>	vector composed of variables z_r, a_s, D_t^0	
<u>v</u>	shift of <u>v</u> to be calculated in an iteration cycle	DELV (I)
wj2	squared weight of distance j	W (J)
<u>x</u>	coordinates of an atom	X (K, N)
<u>x</u>	difference of the coordinates of two atoms belonging to a particular distance	DELTA (K)
<u>y</u>	auxiliary quantity: vector composed of the free parameters ¹ which describe the position of a particular atom	
<u>z</u>	vector containing all variable coordinates on which a particular distance depends	
z_r	variable coordinate number r	
z_r^0	initial value of z_r	

¹ In the sense that a dependence due to a linear restriction is allowed.

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