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COMPUTER PROGRAM FOR THE CALCULATION OF FORCE CONSTANTS USING THE GENERALIZED INVERSE MATRIX

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ABSTRACT

A FORTRAN program for the calculation of force constants using the generalized inverse of the Jacobian matrix is described. The method can be applied with success to solve "ill-conditioned" problems since it effectively removes the singularity difficulties in the least squares problems. Detailed instructions for the use of the program together with test results are given also.

KIVONAT

A molekulák erőállandóinak számitására szolgáló FORTRAN programot ismertetünk. A módszer a Jacobi matrix általánositott inverzének kiszámitásával hatékony módon eltávolitja a legkisebb négyzetek elvén alapuló paraméter-finomitás során fellépő mátrix-szingularitási nehézségeket és igy sikeresen alkalmazható rosszul kondicionált feladatok megoldására. A program használatával kapcsolatos információkat és próbafuttatások eredményeit is közöljük.

РЕЗЮМЕ

Для вычисления постоянных силы разработана программа на языке FORTRAN, употребляющая псевдообратную матрицу. Метод успешно применяется для решения задач с особенной матрицей, так как учитывает ранг матрицы Якоби, находящейся в методе наименьших квадратов. В работе даются подробные указания применения программы, а также результаты отлаживания программы.

C O N T E N T S

I. INTRODUCTION

The method of least squares for force constant calculations has been in general use for a considerable time and the principles of the procedure are well known [1-3].

The force constants are determined so that they minimize the weighted sum of squared deviations /S/ between ν_i^{obs} /or λ_i^{obs}/ [1], the i-th observed frequency /or frequency parameter/ and ν_i^{calc} /or λ_i^{calc}/, the i-th calculated frequency /or frequency parameter/

$$S = \sum_{i=1}^{m} W_i /\nu_i^{obs} - \nu_i^{calc}/^2 \qquad /1/$$

$$S = \sum_{i=1}^{m} W_i /\lambda_i^{obs} - \lambda_i^{calc}/^2 = \tilde{\underline{\varepsilon}}\underline{\underline{W}}\underline{\varepsilon} \qquad /1a/$$

where W_i is the i-th element of a weight matrix, m is the number of observed frequencies an $\sim$ denotes the transpose of a matrix or a vector.

In the end a linearized set of normal equations is obtained [2]

$$/\tilde{\underline{\underline{J}}}\underline{\underline{W}}\underline{\underline{J}}/\Delta\underline{f} = \tilde{\underline{\underline{J}}}\underline{\underline{W}}\Delta\underline{\lambda} \qquad /2/$$

with the solution

$$\Delta\underline{f} = /\tilde{\underline{\underline{J}}}\underline{\underline{W}}\underline{\underline{J}}/^{-1}\ \tilde{\underline{\underline{J}}}\underline{\underline{W}}\Delta\underline{\lambda} \qquad /3/$$

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[1] If the force constants are expressed in mdyne/Å and the G elements calculated using a.m.u. then $\lambda/sec^{-1}/ = 4\pi^2c^2\nu^2\ N^{-1} = 5.89141\cdot10^{-7}\nu^2$ $/cm^{-1}/$, where c is the velocity of light and N is the Avogadro number.

[2] Similar equations can be obtained when S is a function of frequencies /1/.

where, if we have m observations and n unknown force constants, J_{mxn} is an m x n Jacobian matrix with the elements $\partial\lambda_m/\partial f_n$, in which λ_m is the m-th frequency parameter and f_n is the n-th force constant. $\Delta\underline{f}$ is a vector of adjustments to the trial set of force constants and $\Delta\underline{\lambda}$ is a deviation vector whose elements are the differences between the observed and calculated frequency parameters. The adjustments of force constants has to be repeated until a converged set is reached according to some sort of criterion. If the $\underline{\underline{\tilde{J}WJ}}$ matrix is nearly singular which implies that the problem is ill-conditioned the calculation either diverges or oscillates.

Several authors [4-14] have investigated this problem and modified the original method to improve convergence, while others [15-21] have suggested methods for computing force constants which avoid the necessity for solving /2/. In a short communication [22] we described a method which effectively removes the singularity difficulties by applying the generalized inverse of the Jacobian matrix $\underline{\underline{J}}$ and taking into account the rank of the matrix $\underline{\underline{J}}$.

A program has been written in FORTRAN and it adjusts the force constants to give a weighted least-squares fit of calculated frequencies of isotopic molecules /maximum 5 molecules/ to the observed frequencies. However, other input data /Coriolis coefficients, centrifugal-stretching constants etc./ can also be included with some minor modifications.

The program in the present form can be applied with greatest advantage to vibrational problems in symmetry coordinate representation and the maximum dimension of the $\underline{\underline{F}}$ matrix is 6x6. The dimensions, of course, can be extended for a computer of larger memory, if required. We have run the program on an ICL 1900 computer and it occupies approximately 24 K storage when compiled. [1/] This report provides the necessary information for using the force constant calculation program followed by test results and complete listing.

[1/] The program can, of course, be improved with respect to storage and speed of computation.

II. MATHEMATICAL BACKGROUND

II.1. Mathematical method

In the refinement calculation of the force constants based on the least--squares method one of the main problems is that in many cases the matrix $\underline{\underline{\tilde{J}WJ}}$ in /2/ is nearly singular /or singular/ which implies that a stable solution for the equation cannot be expected.

It has been shown [22] that the application of the generalized inverse of the matrix $\underline{\underline{J}}_w = \underline{\underline{W}}^{1/2}\,\underline{\underline{J}}$ enables one to find a solution of the weighted squares of residuals $/\underline{\tilde{r}}\,\underline{\underline{W}}\underline{r}/$ [1] directly even if the matrix $\underline{\underline{\tilde{J}WJ}}$ is nearly singular or singular, i.e. if the problem is ill-conditioned. In this case the least-squares solution can be written as

$$\Delta\underline{f} = \underline{\underline{J}}_w^{+}\Delta\underline{\lambda}_w \qquad /4/$$

where $\underline{\underline{J}}_w^{+}$ is the generalized inverse of the matrix $\underline{\underline{J}}_w$ and $\Delta\underline{\lambda}_w = \underline{\underline{W}}^{1/2}\Delta\underline{\lambda}$.

The solution /4/ is the minimum norm solution of the normal equations /2/, i.e. the Euclidean norm $\|\Delta\underline{f}\| = \left(\Sigma|\Delta f_i|^2\right)^{1/2} = \text{min.}$, and therefore the solution is unique [23].

It should be noted that the following relation is valid:

$$\underline{\underline{J}}_w^{+} = /\underline{\underline{\tilde{J}}}_w\,\underline{\underline{J}}_w/^{+}\underline{\underline{\tilde{J}}}_w \quad . \qquad /5/$$

The numerical computation of the generalized inverse matrix $\underline{\underline{J}}_w^{+}$ represents a significant mathematical problem. However, the singular value decomposition [24] seems to be a numerically stable and fairly fast method for the computation of the matrix $\underline{\underline{J}}_w^{+}$.

The decomposition of $\underline{\underline{J}}_w$ can be written in the form

$$\underline{\underline{J}}_w = \underline{\underline{U}}\;\underline{\underline{\Sigma}}_n\;\underline{\underline{\tilde{V}}} \qquad /6/$$

where $\underline{\underline{\Sigma}}_n$ is an n x n diagonal matrix the elements σ_i of which are the non-negative square roots of the eigenvalues of $\underline{\underline{\tilde{J}}}_w\,\underline{\underline{J}}_w = \underline{\underline{\tilde{J}WJ}}$ and are called the singular values of $\underline{\underline{J}}_w$. The columns of $\underline{\underline{U}}$ are the orthonormalized eigenvectors associated with the n largest eigenvalues of $\underline{\underline{J}}_w\,\underline{\underline{\tilde{J}}}_w$ and the columns of $\underline{\underline{V}}$ are the orthonormalized eigenvectors of $\underline{\underline{\tilde{J}}}_w\,\underline{\underline{J}}_w$. Both matrices

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1/ $\underline{r} = \Delta\underline{\lambda} - \underline{\underline{J}}\Delta\underline{f}$

$\underline{\underline{U}}$ and $\underline{\underline{V}}$ satisfy the equation

$$\tilde{\underline{\underline{U}}}\underline{\underline{U}} = \tilde{\underline{\underline{V}}}\underline{\underline{V}} = \underline{\underline{V}}\tilde{\underline{\underline{V}}} = \underline{\underline{E}}_n \qquad /7/$$

and can be obtained without solving the eigenvalue problems of $\underline{\underline{J}}_w \tilde{\underline{\underline{J}}}_w$ and $\tilde{\underline{\underline{J}}}_w \underline{\underline{J}}_w$ by applying the method described in [24]. /See the procedure MINFIT in the program. This procedure is a FORTRAN version of the ALGOL procedure of the same name written by Golub and Reinsch [25]./ Once the decomposition has been obtained the generalized inverse of $\underline{\underline{J}}_w$ can be written as

$$\underline{\underline{J}}_w^+ = \underline{\underline{V}}\ \underline{\underline{\Sigma}}_n^+\ \tilde{\underline{\underline{U}}} \quad . \qquad /8/$$

The elements σ_i^+ on the diagonal of $\underline{\underline{\Sigma}}_n^+$ are $1/\sigma_i$ or zero depending on whether $\sigma_i \neq 0$ or $\sigma_i = 0$, respectively [26].

If r, the rank of $\underline{\underline{J}}_w$, is less than n, /8/ can be rewritten as

$$\hat{\underline{\underline{J}}}_w^+ = \underline{\underline{V}}\ \underline{\underline{\Sigma}}_r^+\ \tilde{\underline{\underline{U}}} \qquad /9/$$

with

$$\tilde{\underline{\underline{U}}}\underline{\underline{U}} = \tilde{\underline{\underline{V}}}\underline{\underline{V}} = \underline{\underline{E}}_r \qquad /10/$$

and

$$\Sigma_r^+ = \mathrm{diag}/\sigma_1^{-1}, \ \ldots\ , \sigma_r^{-1}/\ , \qquad /11/$$

where $\sigma_1 \geq \sigma_2 \geq \ldots \geq \sigma_r > 0$ and $\sigma_{r+1} = \sigma_{r+2} = \ldots = \sigma_n = 0$. If the matrix $\underline{\underline{J}}_w$ is of rank n then the equations /6/ and /8/ give

$$/\tilde{\underline{\underline{J}}}_w\ \underline{\underline{J}}_w/^+ = /\tilde{\underline{\underline{J}}}_w\ \underline{\underline{J}}_w/^{-1} \qquad /12/$$

and by taking into account equation /5/ one obtains

$$\underline{\underline{J}}_w^+ = /\tilde{\underline{\underline{J}}}_w\ \underline{\underline{J}}_w/^{-1}\ \tilde{\underline{\underline{J}}}_w \qquad /13/$$

that is in the case of maximum rank the generalized inverse method is equivalent to the "classical " method.

II.2. Numerical properties

It is known [27] that the condition number of a matrix is σ_1/σ_n, where σ_1 and σ_n are the largest and smallest singular values of the matrix,

respectively, and this plays an important role with respect to the matrix inversion. In most cases none of the singular values is exactly zero but there are one or more singular values which are very small in comparison with the others, consequently the condition number is large /it may be of order of 10^3 or larger/, therefore the matrix is ill-conditioned. In these cases the practical procedure is that the relatively small σ_i elements are replaced by zero, in such a way that the ill-conditioned matrix $\underline{\underline{J}}_w$ is approximated by a matrix $\hat{\underline{\underline{J}}}_w$ of lower rank with an essentially better condition number.

If it is assumed that the singular values $\sigma_{r+1}, \sigma_{r+2}, \ldots, \sigma_n$ of $\underline{\underline{J}}_w$ matrix are negligibly small in comparison with the others it can be shown [24] that the approximation is such that

$$\| \underline{\underline{J}}_w - \hat{\underline{\underline{J}}}_w \|_F = /\sigma_{r+1}^2 + \ldots + \sigma_n^2/^{1/2} \qquad /14/$$

where the matrix $\hat{\underline{\underline{J}}}_w$ of rank r is an approximation to $\underline{\underline{J}}_w$ with a condition number

$$\mathrm{cond}/\hat{\underline{\underline{J}}}_w/ = \frac{\sigma_1}{\sigma_r} \qquad /15/$$

and $\| \ \|_F$ denotes the Frobenius matrix norm /the Frobenius matrix norm of $\underline{\underline{A}}$ is $\| \underline{\underline{A}} \|_F^2 = \mathrm{trace}\, \tilde{\underline{\underline{A}}}\, \underline{\underline{A}}$/.

Equation /14/ represents essentially a perturbation of the $\underline{\underline{J}}_w$ by a matrix $\delta \underline{\underline{J}}_w$ whose norm is [1]

$$\| \delta \underline{\underline{J}}_w \|_F = \left(\sum_{r+1}^{n} \sigma_i^2 \right)^{1/2} . \qquad /16/$$

Then instead of /4/ one obtains

$$\Delta \underline{f} = \hat{\underline{\underline{J}}}_w^{+} \Delta \underline{\lambda}_w \ , \qquad /17/$$

where $\hat{\underline{\underline{J}}}_w^{+}$ is an approximation to the generalized inverse /8/. In an ideal case there is a difference of several orders of magnitude between the singular values $\sigma_1, \ldots, \sigma_r$ and $\sigma_{r+1}, \ldots, \sigma_n$ i.e. the rank of $\underline{\underline{J}}_w$ can be determined easily. Then the condition number of $\hat{\underline{\underline{J}}}_w$ /15/ is small and at the same time the matrix perturbation /16/ is small, too, or may be of no significance at all if one takes into account that the elements of the Jacobian matrix are not exact because of errors in the input data. In less favourable cases the difference mentioned above

[1] It should be noted that the Frobenius matrix norm is orthogonally invariant.

is smaller /see the example of dichloromethane molecule in IV.2./ and the determination of the rank of the matrix $\underline{\underline{J}}_w$, i.e. the selection of the condition number of the approximating matrix $\hat{\underline{\underline{J}}}_w$, is a somewhat arbitrary procedure and it must be performed carefully. /See Comment 1 in III.3./

II.3. The iteration cycle

The iteration cycle of the force constant refinement starts with the computation of the eigenvalues and eigenvectors of the matrix $\underline{\underline{GF}}_o$, where $\underline{\underline{F}}_o$ is a set of trial force constants, and the construction of the Jacobian matrix then follows from the matrix of eigenvectors. /For solving the vibrational problem the method of Schachtschneider and Snyder [33] was used./

In each step the corrections to the force constants are obtained in the form of /17/ and the norm of this correction vector is minimum, which means, in other words, that in the i-th step among all the possible vectors $\underline{f}$, the vector $\underline{f}_i$ obtained by correcting the vector $\underline{f}_{i-1}$ of the /i-1/-th step by the correction vector /17/ is the closest /in norm/ to the vector $\underline{f}_{i-1}$. It may occur, that even the minimum norm solution is too large to ensure convergence. In this case it is suggested that the correction vector /17/ be multiplied by a suitable scaling factor, in particular at the beginning of the iteration cycle when the difference between the values $\tilde{\underline{r}}\underline{\underline{W}}\underline{r}$ and $\tilde{\underline{\varepsilon}}\underline{\underline{W}}\underline{\varepsilon}$ is large.

The refinement will be terminated when the largest element of the correction vector $\Delta\underline{f}$ will become smaller than a given tolerance. /See TOLF in the input data in III.1./ The dispersions of the force constants and the correlation coefficients, d_i and c_{ij}, respectively, can also be given in the generalized inverse method as[1/]

$$d_i = \frac{\tilde{\underline{r}}\underline{\underline{W}}\underline{r}}{m-\rho} A_{ii} \qquad /18/$$

and

$$c_{ij} = \frac{A_{ij}}{/A_{ii}\ A_{jj}/^{1/2}} \quad , \qquad /19/$$

where $\tilde{\underline{r}}\underline{\underline{W}}\underline{r}$ is the weighted square of residuals computed with the final set of force constants, m is the number of observed data, $\rho = \mathrm{rank}/\underline{\underline{J}}_w/$, i.e. ρ is equal to n less the number of singular values set to zero, and $\underline{\underline{A}} = /\tilde{\hat{\underline{\underline{J}}}}_w\ \hat{\underline{\underline{J}}}_w/^+$ with the approximation $\hat{\underline{\underline{J}}}_w$ of the Jacobian matrix computed in the last iteration step.

1/ For statistical analysis in the determination of force constants by the "classical" method of least squares see e.g. [3].

The small values of the dispersions of the force constants in the dichloromethane molecule test results are probably surprising since the original problem is ill-conditioned. However, this can be understood if one takes into consideration that in each iteration step the computation of the correction vector $\Delta\underline{f}$ is performed with a Jacobian matrix of good condition and the correction of the force constants by a vector of minimum norm corresponds to a very strong constraint during the iteration. Since the least squares method is essentially a statistical method, the precise meaning and the validity of the dispersions and correlation coefficients obtained by /18/ and /19/ need further detailed statistical discussion. /See e.g. [28, 29]./

III. THE USE OF THE PROGRAM

III.1. Preparation of input data and input formats

Card	Column	Variable	Description	Format
1	1-2	IND	IND = 10, an index indicating the start of a problem.	I2
2	1-9	TOL	A machine dependent constant which should be set equal to B/EPS1 where B is the smallest positive number representable in the computer; for EPS1 see the next variable.	D9.1
2	10-18	EPS1	The smallest number for which 1 + EPS1 > 1 in computer arithmetic.	D9.1
3	1-10	CN	The condition number chosen, see Comment 1.	F10.4
3	11-20	TOLF	The iteration cycle is terminated if the largest element of the force constant correction vector is smaller than TOLF /e.g. TOLF = 0.001/.	F10.4
3	21-30	SC	The number by which the elements of the force constant correction vector are multiplied. See Comment 2.	F10.4
3	31-32	NWF	Code number for weighting the input data. If NWF = 0 W/I/ = $1/\lambda_i$, NWF = 1 W/I/ = $1/\lambda_i^2$, NWF = 2 W/I/ = 1.0 See Comment 3.	I2
3	33-34	NS	The maximum number of iteration steps /e.g. NS = 20/.	I2
4	1-3	NQ	The order of the G matrix. The maximum value of NQ is 6, but the dimensions can be extended.	I3
4	4-6	NF	The number of independent force constants to be refined /which is equal to the number of columns of the Jacobian matrix /See Comment 4 /.	I3

4	7-9	NOZ	The number of all nonzero $\underline{Z}$ matrix elements. See Comment 4.	I3
4	10-12	INUMB	The number of all frequencies. INUMB = NQ x NUMBG.	I3
4	13-15	NUMBG	The number of isotopic molecules. The maximum value of NUMBG is 5.	I3
4	16-18	NFC	The number of all nonzero force constants to be constrained. See Comment 4.	I3
5	1-56	RECORD/I/	This card contains information about the problem, e.g. the name of molecule.	7A8
6-...[1]	1-18,..., 55-72	NRO/I/, NCO/I/, NFO/I/, Z/I/	The information about the initial force constants to be refined is punched onto cards in 18 column fields, 4 fields per card. The first 3 columns of each field give the row number of the $\underline{F}$ matrix element, columns 4 to 6 give the column number of the element, columns 7 to 9 give the number of the force constant in the $\underline{\Phi}$/ FI/K,1/ [2] vector and columns 10 up to and including 18 give the element of $\underline{Z}$ vector by which the force constant in the $\underline{\Phi}$ vector will be multiplied. I runs from 1 to NOZ. If the card is not full the remainder is left blank. See Comment 4.	4/3I3,F9.6/
7-...	1-12,..., 61-72	FI/K,1/[2]	The initial values of independent force constants to be refined are punched onto cards in 12 column fields, 6 fields per card. Only the upper triangle elements should be punched. Zero initial values must be entered also. K runs from 1 to NF. If the card is not full the remainder is left blank. See Comment 4.	6F12.6

1/ -... denotes that the information may be punched onto more than one card of the same type depending on the actual problem.

2/ It should be noted that FI/K,1/ is actually a vector and it is treated as a two dimensional array only because of the present form of subroutine MINFIT.

8-...	1-18,..., 55-72	NRO/NOZ+I/, NCO/NOZ+I/, FIC/I/	If there are force constants to be constrained /NFC≠0/ then they are punched onto cards in 18 column fields, 4 fields per card. The first 3 columns of each field give the row number of the $\underline{\underline{F}}$ matrix element, columns 4 to 6 give the column number of the element and columns 7 up to and including 18 give the value of the constrained $\underline{\underline{F}}$ matrix element. Only the upper triangle elements should be punched. I runs from 1 to NFC, the number of fixed force constants. If the card is not full the remainder is left blank. See Comment 5.	4/2I3,F12.6/
9-...	1-20	RECORD1/I,J/	The cards contain information about the isotope molecules /e.g. the name of molecule/. I runs from 1 to NUMBG. NUMBG cards must be included, even if blank.	5A4
10-...	1-12,..., 61-72	D/I/	The vector of all observed frequencies /in cm^{-1}/ the elements of which are arranged in the order of symmetry co-ordinates within each symmetry block. The frequencies of isotopic molecules are entered in the order of the $\underline{\underline{G}}$ matrices. The frequencies are punched onto cards in 12 column fields, 6 fields per card. I runs from 1 to INUMB. If a frequency has not been observed the corresponding element of D/I/ is set equal to zero.	6F12.6

11-...	1-24,..., 49-72	NROWG/L/, NCOLG/L/, DATING/L/	The $\underline{\underline{G}}$ matrix elements are punched onto cards in 24 column fields, 3 fields per card. The first 3 columns of each field give the row number of the $\underline{\underline{G}}$ matrix element, columns 4 to 6 give the column number of the element and columns 7 up to and including 24 give the value of the $\underline{\underline{G}}$ matrix element. The row number following the last element of each $\underline{\underline{G}}$ matrix is set equal to -1. If the card is not full the remainder is left blank. Only the upper triangle elements of the $\underline{\underline{G}}$ matrix should be punched. Zero elements need not be entered. The $\underline{\underline{G}}$ matrices should be entered in the order of isotopic molecules. See Comment 6.	3/2I3,E18.9/
12			The last card is a blank card if there is no other problem, otherwise the next problem should follow with card 1.	

III.2. Presentation of the output

First the input data are printed out:

1. the title of the problem
2. the weighting of the input frequencies
3. the scaling factor of the force constant correction vector
4. the condition number chosen
5. the condition of terminating the iteration cycle
6. observed frequencies for each isotopic molecule
7. the $\underline{\underline{G}}$ matrix for each isotopic molecule
8. initial $\underline{\underline{F}}$ matrix
9. the observed and calculated frequencies and frequency parameters for each isotopic molecule
10. $\underline{\underline{\varepsilon W \varepsilon}}$ /See equation /1a//

After each iteration step the following are printed out:

1. the singular values /σ_i/
2. the elements of the $\underline{\underline{\Sigma}}_r^+$ matrix /See equation /11//
3. the condition number /See equation /15//
4. the solution vector $\Delta\underline{f}$ /See equation /17//
5. the norm of the solution vector $\Delta\underline{f}$
6. the force constant correction vector /solution vector multiplied by scaling number/
7. the adjusted $\underline{\underline{F}}$ matrix
8. the observed and calculated frequencies and frequency parameters for each isotopic molecule
9. $\underline{\underline{\tilde{r}Wr}}$
10. $\underline{\underline{\tilde{\varepsilon}W\varepsilon}}$

After the final step the following are printed out:

1-6. see above
7. the final set of force constants
8. the standard errors of the force constants /See equation /18//
9. the correlation matrix /See equation /19//
10. the observed and calculated frequencies and frequency parameters for each isotopic molecule
11. $\underline{\underline{\tilde{r}Wr}}$
12. $\underline{\underline{\tilde{\varepsilon}W\varepsilon}}$
13. the Jacobian matrix for each isotopic molecule
14. the eigenvector matrix $\underline{\underline{L}}$ for each isotopic molecule
15. the inverse of the eigenvector matrix $\underline{\underline{L}}^{-1}$ for each isotopic molecule

III.3 Comments

1/ Condition number /CN/: According to our experience if a condition number between 100.0 - 200.0 is chosen convergence readily occurs. Therefore it is suggested that in the first run of the program CN be set equal to 100.0 and NS to 5. If the question were to be posed as to whether or not the choide is unsatisfactory in that the force constant calculation does not converge, a look at the singular values would help in selecting a more suitable value for CN. /See also II.2./

2/ The scaling factor /SC/ is a number by which all elements of the force constant correction vector are multiplied. In the early stages of convergence it may happen that the linear approximation /$\Delta\underline{\lambda} = \underline{\underline{J}}\Delta\underline{f}$/ does

not hold true and some elements of the solution vector are too large. In this case the application of a scaling factor <1 is recommended. In the first run SC can be set equal to 1.0. If "overshooting" has occured, it is then suggested that a smaller value for SC be used /e.g. 0.5/. /See also II.2./

3/ For a percentage fit the entries in W/I/ are $1/\lambda_i^2$ /NWF = 1/ and $1/\lambda_i$ /NWF = 0/ for an absolute fit. It is also possible to give all the frequencies unit weight /NWF = 2/.

4/ The initial values of the NF force constants to be adjusted will be read into the $\underline{\Phi}$ /FI/K,1// vector. Then by multiplying the $\underline{\Phi}$ vector by the Z matrix[1/] the $\underline{f}$ vector is obtained which contains the $\underline{\underline{F}}$ matrix elements which will be refined:

$$\underline{f} = \underline{\underline{Z}}\,\underline{\Phi} \ .$$

If k is the dimension of the $\underline{\underline{F}}$ matrix then the $\underline{\underline{Z}}$ matrix is a k(k+1)/2 by NF matrix [2/] and its elements are uniquely determined by 3 numbers: the row and column number of the $\underline{\underline{F}}$ matrix element and the number of the force constant in $\underline{\Phi}$. Therefore the nonzero elements of $\underline{\underline{Z}}$ can be stored as four one-dimensional arrays:

NRO/I/: the row number of the $\underline{\underline{F}}$ element
NCO/I/: the column number of the $\underline{\underline{F}}$ element
NFO/I/: the number of the force constant in $\underline{\Phi}$
Z/I/: the value of the $\underline{\underline{Z}}$ matrix element.

I runs from 1 to NOZ, the number of non-zero elements. The elements of the $\underline{f}$ vector are rearranged into the $\underline{\underline{F}}$ matrix by the program using the information given by the elements of the arrays NRO/I/ and NCO/I/.

5/ If some elements of the $\underline{\underline{F}}$ matrix will be fixed then their values will be read into the FIC/I/ vector and NRO/I/ and NCO/I/ give the row and column number, respectively, of the $\underline{\underline{F}}$ element constrained. The initial $\underline{\underline{F}}$ matrix is constructed by the program from the force constants to be refined and to be constrained, respectively.

6/ The $\underline{\underline{G}}$ matrix elements can be calculated by hand using the formulae given in the textbook of Wilson, Decius and Cross [31]. There are programs available in the literature /e.g. [32]/ which evaluate the $\underline{\underline{G}}$ matrix elements in internal valence coordinates and in symmetry coordinates. If the $\underline{\underline{G}}$ matrix is set up in symmetry coordinates one should make use of the known assignment of the vibration frequencies to their different symmetry species, i.e., the order of frequencies should correspond to the order or symmetry coordinates. If the $\underline{\underline{G}}$ matrix is calculated by a separate program its elements can be transferred onto a magnetic tape or punched onto cards suitable for input to this program.

1/ The transformation matrix $\underline{\underline{Z}}$ was introduced in [2] and we used the method described in [30] for the storage of the $\underline{\underline{Z}}$ matrix.

2/ If not all the elements of the $\underline{\underline{F}}$ matrix are subjected to refinement the dimension of the $\underline{\underline{Z}}$ matrix will be accordingly smaller.

IV. TEST RUNS

Water /H_2O, D_2O, HDO/[1] and dichloromethane /CH_2Cl_2, CD_2Cl_2, $CHDCl_2$/ were choosen as test molecules. The computations have been carried out by using symmetry coordinates.

IV.1. Water molecule

Input data:

G matrices:

$$\underline{\underline{G}}_{H_2O} : \begin{pmatrix} 1.03908 & -0.085594 & 0.0 \\ & 2.14085 & 0.0 \\ & & 1.07043 \end{pmatrix}$$

$$\underline{\underline{G}}_{D_2O} : \begin{pmatrix} 0.543348 & -0.085594 & 0.0 \\ & 1.14938 & 0.0 \\ & & 0.574690 \end{pmatrix}$$

$$\underline{\underline{G}}_{HDO} : \begin{pmatrix} 0.791217 & -0.085594 & 0.247868 \\ & 1.64512 & 0.0 \\ & & 0.822558 \end{pmatrix}$$

Initial F matrix:[2]

$$\underline{\underline{F}}_{o} : \begin{pmatrix} 8.3562 & 0.1084 & 0.0 \\ & 0.7536 & 0.0 \\ & & 8.5475 \end{pmatrix}$$

Observed frequencies /in cm^{-1}/[3]

	H_2O	D_2O	HDO
ω_1	3832.2	2763.8	3889.8
ω_2	1648.5	1206.4	2824.3
ω_3	3942.5	2888.8	1440.2

1/ The water molecule does not represent an ill-conditioned problem and it was selected to illustrate how the present method works in a "classical" case.

2/ See first column of Table VII in [16]. The force constants are given in mdyne/Å.

3/ See first column of Table VI in [16]. The frequencies are harmonic frequencies.

The values of the other input parameters can be seen on the list of input cards /each row represents one card/:

LIST OF INPUT CARDS:

```
 10
   1.0E-75  1.0E-11
  1000.0000    0.0010    1.0000 010
   3  4  4  9  3  0
 FORCE CONSTANT CALCULATION FOR WATER MOLECULE
   1  1  1 1.000000  1  2  2 1.000000  2  2  3 1.000000  3  3  4 1.000000
    8.3562       0.1084       0.7536       8.5475
  H2O MOLECULE
  D2O MOLECULE
  HDO MOLECULE
    3832.2       1648.5       3942.5       2763.8       1206.4       2888.8
    3889.8       2824.3       1440.2
   1  1   0.103908489E 01  1  2  -0.855939564E-01  2  2   0.214085272E 01
   3  3   0.107042636E 01 -1
   1  1   0.543348324E 00  1  2  -0.855939564E-01  2  2   0.114937958E 01
   3  3   0.574689792E 00 -1
   1  1   0.791216609E 00  1  2  -0.855939564E-01  1  3   0.247868285E 00
   2  2   0.164511615E 01  3  3   0.822558077E 00 -1
 00
```

The singular values of the matrix $\underline{\underline{J}}_w$: 0.2557740×10^{1}, 0.5411786×10^{0}, 0.4429977×10^{0}, 0.4472247×10^{-1}. The condition number $\sigma_1/\sigma_4 = 57.191$ is smaller than the input condition number 100.0 and thus ensures the convergence.

Final results:

After 4 iteration steps the refinement procedure converged.

Final F matrix /with dispersions/:

$$\begin{pmatrix} 8.3544\pm0.0064 & 0.332\pm0.060 & 0.0 \\ & 0.7596\pm0.0045 & 0.0 \\ & & 8.5550\pm0.0051 \end{pmatrix}$$

Correlation matrix:

F_{11}	F_{12}	F_{22}	F_{33}
1.00	0.60	0.58	-0.16
	1.00	0.98	-0.005
		1.00	-0.005
			1.00

Observed and calculated frequencies:

	H_2O		D_2O		HDO	
	ω_{obs}	ω_{calc}	ω_{obs}	ω_{calc}	ω_{obs}	ω_{calc}
ω_1	3832.2	3832.273	2763.8	2763.855	3889.8	3889.870
ω_2	1648.5	1646.896	1206.4	1204.795	2824.3	2823.946
ω_3	3942.5	3942.572	2888.8	2888.803	1440.2	1443.354

$\tilde{\underline{\underline{r}}}\underline{\underline{W}}\underline{r} = 0.301538 \times 10^{-4}$

$\tilde{\underline{\underline{\varepsilon}}}\underline{\underline{W}}\varepsilon = 0.301553 \times 10^{-4}$

The output includes the $\underline{\underline{J}}$, $\underline{\underline{L}}$ and $\underline{\underline{L}}^{-1}$ matrices too.

IV.2. Dichloromethane molecule /A' symmetry block/

Input data:

G matrices:

$\underline{\underline{G}}_{CH_2Cl_2}$:

1.10679	-0.145451	0.0	0.0	0.0	0.0
	0.598272	0.0	0.0	0.0	0.0
		1.04435	-0.052221	-0.101907	0.061204
			0.080923	0.102112	-0.061327
				2.17025	-0.017753
					0.098276

$\underline{\underline{G}}_{CD_2Cl_2}$:

0.611050	-0.145451	0.0	0.0	0.0	0.0
	0.398595	0.0	0.0	0.0	0.0
		0.548615	-0.052221	-0.101907	0.061204
			0.080923	0.102112	-0.061327
				1.18563	-0.067558
					0.095757

$\underline{\underline{G}}_{CHDCl_2}$:

0.858918	-0.145451	0.247868	0.0	0.0	0.0
	0.498433	0.0	0.0	-0.221701	-0.011214
		0.796484	-0.052221	-0.101907	0.061204
			0.080923	0.102112	-0.061327
				1.67794	-0.042656
					0.097016

Initial F matrix:[1]

$$\underline{\underline{F}}_o : \begin{pmatrix} 4.7595 & -0.4746 & 0.0 & 0.0 & 0.0 & 0.0 \\ & 0.9202 & 0.0 & 0.0 & 0.0 & 0.0 \\ & & 4.9092 & -0.1029 & 0.0308 & 0.7387 \\ & & & 3.8082 & -0.2639 & 0.2082 \\ & & & & 0.5680 & 0.3515 \\ & & & & & 1.3212 \end{pmatrix}$$

Observed frequencies /in cm^{-1}/:[2]

CH_2Cl_2	CD_2Cl_2	$CHDCl_2$
3045	2304	3019
897	...[3]	2248
2990	2198	1283
1424	1052[4]	778
706	679.0	684
286	282.0	283

The values of the other input parameters can be seen on the list of input cards /each row represents one card/:

---

[1] See first column of Table XII in [16]. The force constants are given in mdyne/Å.

[2] See first column of Table XI in [16]. The order of the frequencies is somewhat different from that in [16].

[3] This frequency is missing; however, a zero must be punched onto the proper field of the input card.

[4] 1052 cm^{-1} was used instead of 995 cm^{-1}

LIST OF INPUT CARDS:

```
10
 1.0E-75  1.0E-11
 100.0000     0.0010     1.0000 010
 6 13 13 18  3  0
 FORCE CONSTANT CALCULATION FOR CH2CL2 MOLECULE
 1  1  1 1.000000  1  2  2 1.000000  2  2  3 1.000000  3  3  4 1.000000
 3  4  5 1.000000  3  5  6 1.000000  3  6  7 1.000000  4  4  8 1.000000
 4  5  9 1.000000  4  6 10 1.000000  5  5 11 1.000000  5  6 12 1.000000
 6  6 13 1.000000
  4.7595      -0.4746       0.9202       4.9092      -0.1029       0.0308
  0.7387       3.8082      -0.2639       0.2082       0.5680       0.3515
  1.3212
 CH2CL2 MOLECULE
 CD2CL2 MOLECULE
 CHDCL2 MOLECULE
  3045.0        897.0       2990.0       1424.0        706.0        286.0
  2304.0          0.0       2198.0       1052.0        679.0        282.0
  3019.0       2248.0       1283.0        778.0        684.0        283.0
 1  1   0.110678626E 01  1  2  -0.145451276E 00  2  2   0.598271578E 00
 3  3   0.104435192E 01  3  4  -0.522212077E-01  3  5  -0.101906786E 00
 3  6   0.612037414E-01  4  4   0.809233427E-01  4  5   0.102112191E 00
 4  6  -0.613271044E-01  5  5   0.217025385E 01  5  6  -0.177527984E-01
 6  6   0.982761123E-01 -1
 1  1   0.611049689E 00  1  2  -0.145451276E 00  2  2   0.398595128E 00
 3  3   0.548615346E 00  3  4  -0.522212077E-01  3  5  -0.101906786E 00
 3  6   0.612037414E-01  4  4   0.809233427E-01  4  5   0.102112191E 00
 4  6  -0.613271044E-01  5  5   0.118563446E 01  5  6  -0.675582619E-01
 6  6   0.957567792E-01 -1
 1  1   0.858917975E 00  1  2  -0.145451276E 00  1  3   0.247868285E 00
 2  2   0.498433353E 00  2  5  -0.221700983E 00  2  6  -0.112144046E-01
 3  3   0.796483631E 00  3  4  -0.522212077E-01  3  5  -0.101906786E 00
 3  6   0.612037414E-01  4  4   0.809233427E-01  4  5   0.102112191E 00
 4  6  -0.613271044E-01  5  5   0.167794415E 01  5  6  -0.426555301E-01
 6  6   0.970164457E-01 -1
00
```

The singular values of the matrix $\underline{\underline{J}}_w$: 0.2829452×10^{1}, 0.1041755×10^{1}, 0.7687411×10^{0}, 0.7420551×10^{0}, 0.6176945×10^{0}, 0.4520438×10^{0}, 0.1087264×10^{0}, 0.7168403×10^{-1}, 0.6102980×10^{-1}, 0.1789531×10^{-1}, 0.3984935×10^{-2}, 0.1205883×10^{-2}, $0.1275912 \times 10^{-10}$.

The condition number of $\underline{\underline{J}}_w$: 2.218×10^{11}.

Since a value of 100.0 was selected for CN the last four elements of the matrix have been set equal to zero i.e. the condition number of $\underline{\underline{J}}_w \sigma_1/\sigma_9$ is equal to 46.4 at the start of the iteration cycle. The value of the condition number in each step is smaller than the input condition number and the calculation converges. If CN = 200.0 then the last three elements will be set equal to zero and the refinement converges to a force field which is somewhat different from that obtained with CN = 100.0.

Final results:

After 5 iteration steps the refinement procedure converged.

Final F matrix /with dispersions/:

$$\begin{pmatrix} 4.724\pm0.067 & -0.547\pm0.12 & & & & & \\ & 0.919\pm0.041 & 4.942\pm0.034 & -0.113\pm0.033 & 0.149\pm0.086 & 0.751\pm0.035 \\ & & & 3.773\pm0.012 & -0.079_6\pm0.041 & 0.249\pm0.025 \\ & & & & 0.5611\pm0.0074 & 0.215\pm0.033 \\ & & & & & 1.264\pm0.027 \end{pmatrix}$$

Correlation matrix:

F_{11}	F_{12}	F_{22}	F_{33}	F_{34}	F_{35}	F_{36}	F_{44}	F_{45}	F_{46}	F_{55}	F_{56}	F_{66}
1.00	0.97	-0.93	-0.29	-0.43	-0.25	0.43	0.13	0.06	-0.14	-0.18	-0.13	0.18
	1.00	-0.96	-0.27	-0.44	-0.25	0.44	0.13	0.06	-0.14	-0.18	-0.13	0.18
		1.00	0.28	0.44	0.25	-0.45	-0.17	-0.12	0.19	0.21	0.18	-0.16
			1.00	0.83	0.86	-0.81	-0.32	-0.27	0.33	0.55	0.46	-0.31
				1.00	0.95	-0.97	-0.27	-0.29	0.26	0.61	0.56	-0.38
					1.00	-0.92	-0.39	-0.17	0.35	0.54	0.43	-0.44
						1.00	0.32	0.45	-0.41	-0.70	-0.56	0.16
							1.00	0.25	-0.91	-0.35	-0.28	0.29
								1.00	-0.50	-0.76	-0.78	-0.45
									1.00	0.48	0.28	0.11
										1.00	0.75	0.09
											1.00	-0.17
												1.00

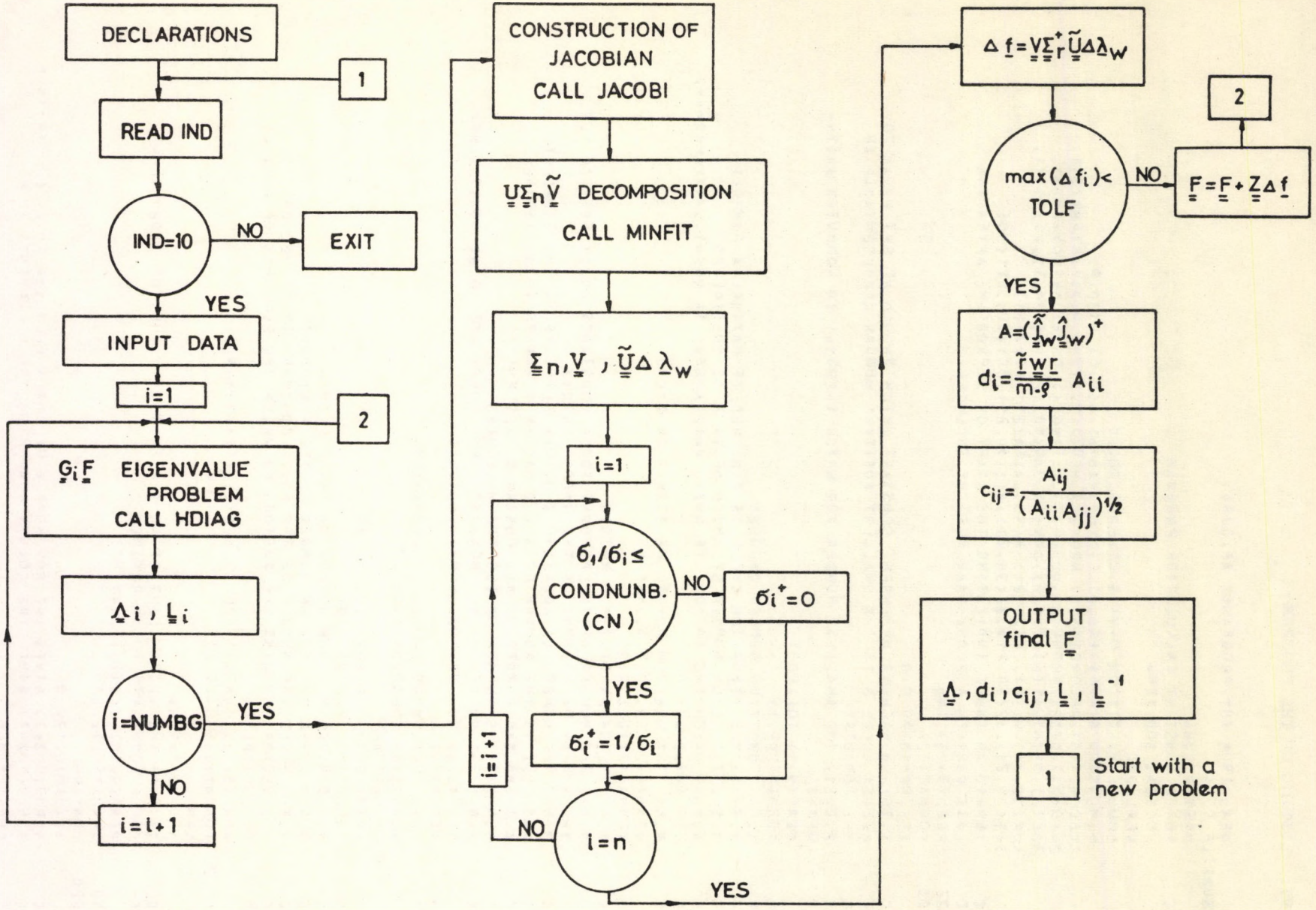
Observed and calculated frequencies:

CH_2Cl_2		CD_2Cl_2		$CHDCl_2$	
ν_{obs}	ν_{calc}	ν_{obs}	ν_{calc}	ν_{obs}	ν_{calc}
3045	3045.173	2304	2302.842	3019	3020.044
897	897.314	...	698.932	2248	2248.421
2990	2992.066	2198	2194.268	1283	1276.339
1424	1431.565	1052	1049.138	778	778.963
706	711.902	679.0	675.194	684	680.488
286	284.607	282.0	282.712	283	283.642

$\tilde{\underline{\underline{r}}}\underline{\underline{W}}\underline{\underline{r}} = 0.924465 \times 10^{-3}$

$\tilde{\underline{\underline{\varepsilon}}}\underline{\underline{W}}\underline{\underline{\varepsilon}} = 0.924479 \times 10^{-3}$

The output includes the $\underline{\underline{J}}$, $\underline{\underline{L}}$ and $\underline{\underline{L}}^{-1}$ matrices too.


DECLARATIONS
1
READ IND
IND=10
NO
EXIT
YES
INPUT DATA
i=1
2
$G_i F$ EIGENVALUE PROBLEM CALL HDIAG
Λ_i , L_i
i=NUMBG
YES
NO
i=i+1
CONSTRUCTION OF JACOBIAN CALL JACOBI
$U\Sigma_n\tilde{V}$ DECOMPOSITION CALL MINFIT
Σ_n, V , $\tilde{U}\Delta\lambda_w$
i=1
$\sigma_1/\sigma_i \leq$ CONDNUNB. (CN)
NO
$\sigma_i^+=0$
YES
$\sigma_i^+=1/\sigma_i$
i=i+1
NO
i=n
YES
$\Delta f = V\Sigma_r^+\tilde{U}\Delta\lambda_w$
2
max(Δf_i)< TOLF
NO
$F=F+Z\Delta f$
YES
$A=(\tilde{J}_w\hat{J}_w)^+$
$d_i=\frac{\tilde{r}_w r_w}{m-\varrho} A_{ii}$
$c_{ij}=\frac{A_{ij}}{(A_{ii}A_{jj})^{1/2}}$
OUTPUT final F
Λ, d_i, c_{ij}, L, L^{-1}
1
Start with a new problem

VI. LISTING OF THE PROGRAM

```
      READ FROM (MT,PROGRAMOK AF.CJB4)
SUBFILE CJB4
      MASTER CJB4
C     FORCE CONSTANT CALCULATION PROGRAM
      LOGICAL BOO,SING
      REAL JAC
      DOUBLE PRECISION U,V1,S,U1,EPS1,TOL,Q
      DIMENSION G(6,6),F(6,6),C(6,6),H(6,6),A(6,6),V(30,6),
     1RECORD(15),RECORD1(5,5),NRO(21),NCO(21),Z(21),Q(21),SIGMA(21),
     2NFO(21),D(30),NROWG(4),NCOLG(4),DATING(4),DG(6),DX(30),DD(6),
     3DC(6),DV(6),D1(6),DX1(6),DDV(6),JAC(30,22),EPS(30,1),FI(21,1),
     4QR(30,21),W(30),CR(21,21),R(30),ALFA(21),FIC(10),
     5A1(21,21),A2(30,21),AL(30,21),ALI(30,21),DC1(30),DV1(30)
C     IND=10 AN INDEX INDICATING THE START OF A PROBLEM. AFTER THE
C     LAST PROBLEM A BLANK CARD MUST BE INCLUDED.
22    READ(5,23) IND
23    FORMAT(I2)
      IF(IND-10)90,0,0
C     1.TOL, A MACHINE DEPENDENT CONSTANT WHICH SHOULD BE SET EQUAL TO
C     B/EPS1 WHERE B IS THE SMALLEST POSITIVE NUMBER REPRESENTABLE IN
C     THE COMPUTER
C     2.EPS1, THE SMALLEST NUMBER FOR WHICH 1+EPS1>1 IN COMPUTER ARITH-
C     METIC
      READ(5,1) TOL,EPS1
1     FORMAT(2D9.1)
C     1.CN, CONDITION NUMBER CHOOSEN
C     2.TOLF, THE ITERATION CYCLE IS FINISHED IF MAX(DELTA F)<TOLF
C     3.SC, THE SCALE NUMBER BY WHICH DELTA F IS MULTIPLIED
C     4.NWF, WEIGHTING FACTOR, IF NWF=0 W=1/LAMBDA, IF NWF=1 W=1/LAMBDA**2
C     ,IF NWF=2 W=1.0
C     5.NS, THE MAXIMUM NUMBER OF ITERATION STEPS
      READ(5,2) CN,TOLF,SC,NWF,NS
2     FORMAT(3F10.4,2I2)
C     1.NQ THE ORDER OF THE G MATRIX
C     2.NF, THE NUMBER OF INDEPENDENT FORCE CONSTANTS TO BE REFINED I.E.
C     THE NUMBER OF COLUMNS OF THE JACOBI MATRIX
C     3.NOZ THE NUMBER OF NON-ZERO Z MATRIX ELEMENTS.IN THE SIMPLEST
C     CASE NOZ IS THE NUMBER OF ALL F MATRIX ELEMENTS TO BE REFINED.
C     4.INUMB THE NUMBER OF ALL OBSERVED FREQUENCIES
C     5.NUMBG THE NUMBER OF ISOTOPE MOLECULES
C     6.NFC THE NUMBER OF ALL NONZERO FORCE CONSTANTS TO BE CONSTRAINED
      READ(5,4) NQ, NF,NOZ,INUMB,NUMBG,NFC
4     FORMAT(6I3)
C     CARD CONTAINING PROBLEM INFORMATION
      READ(5,6) (RECORD(I),I=1,7)
    6 FORMAT(7A8)
      WRITE(6,50) (RECORD(I),I=1,7)
50    FORMAT(1H1,////2X,7A8)
C     1.NRO GIVES THE ROW NUMBER OF THE F ELEMENT
C     2.NCO GIVES THE COLUMN NUMBER OF THE F ELEMENT
C     3.NFO GIVES THE NUMBER OF THE FORCE CONSTANT IN FI VECTOR
C     4.Z VECTOR CONTAINS THE FACTORS BY WHICH THE ELEMENTS OF FI WILL
C     BE MULTIPLIED
      READ(5,20) (NRO(I),NCO(I),NFO(I),Z(I),I=1,NOZ)
   20 FORMAT(4(3I3,F9.6))
      NP=1
      DO 820 I=1,NP
C     FI(K,1) THE VECTOR CONTAINING THE INITIAL VALUES OF INDEPENDENT
C     FORCE CONSTANTS TO BE REFINED
      READ(5,10) (FI(K,I),K=1,NF)
10    FORMAT(6F12.6)
820   CONTINUE
      IF(NFC)0,129,0
C     1.NRO(NOZ+I) GIVES THE ROW NUMBER OF THE F ELEMENTS TO BE CONSTRAINED
C     2.NCO(NOZ+I) GIVES THE COLUMN NUMBER OF THE F ELEMENTS TO BE
C     CONSTRAINED
C     3.FIC(I) VECTOR CONTAINING THE VALUES OF CONSTRAINED F ELEMENTS
      READ(5,21) (NRO(NOZ+I),NCO(NOZ+I),FIC(I),I=1,NFC)
21    FORMAT(4(2I3,F12.6))
```

```
129   DO 131 I=1,NUMBG
C     CARD CONTAINING INFORMATION ON ISOTOPE MOLECULES
  131 READ(5,5) (RECORD1(I,J),J=1,5)
    5 FORMAT(5A4)
C     D(I) ALL THE OBSERVED FREQUENCIES IN CM-1,THEY SHOULD FOLLOW THE
C     ORDER OF ISOTOPE MOLECULES. IF AN OBSERVED FREQUENCY IS MISSING
C     THE CORRESPONDING ELEMENT OF D(I) IS SET EQUAL TO ZERO
      READ(5,10) (D(I),I=1,INUMB)
      INUMB1=0
      DO 628 I=1,INUMB
      IF(D(I))629,0,629
      INUMB1=INUMB1+1
      W(I)=0.0
      GO TO 628
629   IF(NWF-1)0,630,631
      W(I)=1./(5.89141E-7*D(I)*D(I))
      GO TO 628
630   W(I)=1./(5.89141E-7*D(I)*D(I)**2)
      GO TO 628
631   W(I)=1.0
628   CONTINUE
      IF(NWF-1)0,635,636
      WRITE(6,3)
3     FORMAT(/2X,19HWEIGHTING: 1/LAMBDA)
      GO TO 1637
635   WRITE(6,12)
12    FORMAT(/2X,22HWEIGHTING: 1/LAMBDA**2)
      GO TO 1637
636   WRITE(6,13)
13    FORMAT(/2X,14HWEIGHTING: 1.0)
1637  WRITE(6,14) SC
14    FORMAT(/2X,6HSCALE:,F6.1)
      WRITE(6,15) CN
15    FORMAT(/2X,18HCONDITION NUMBER: ,F8.1)
      WRITE(6,16) TOLF
16    FORMAT(/2X,47HTHE ITERATION CYCLE IS FINISHED IF MAX(DELTA F)
     12H< ,F7.4)
      WRITE(6,8)
8     FORMAT(///2X,17HINPUT FREQUENCIES)
      DO 141 K=1,NUMBG
      WRITE(6,7) (RECORD1(K,J),J=1,4)
      WRITE(6,142)
142   FORMAT(/)
      WRITE(6,24) (D(I+(K-1)*NQ),I=1,NQ)
24    FORMAT(6E14.6)
141   CONTINUE
      WRITE(6,3000)
      DO 133 K=1,NUMBG
      DO 132 I=1,NQ
      DO 132 J=1,NQ
  132 G(I,J)=0.0
C     READ G MATRICES FOR ALL ISOTOPE MOLECULES
C     1.NROWG GIVES THE ROW NUMBER OF THE G MATRIX ELEMENT
C     2.NCOLG GIVES THE COLUMN NUMBER OF THE G MATRIX ELEMENT
C     3.DATING IS THE G MATRIX ELEMENT. 3 GROUPS(NROWG,NCOLG,DATING)
C     ARE PUNCHED ONTO EACH CARD. THE ROW NUMBER FOLLOWING THE LAST
C     ELEMENT IS SET EQUAL TO -1. ZERO G MATRIX ELEMENTS NEED NOT BE ENTERED
  124 READ(5,9) (NROWG(L),NCOLG(L),DATING(L),L=1,3)
9     FORMAT(3(2I3,E18.9))
      DO 134 L=1,3
      IF(NROWG(L))135,610,136
  136 IF(NCOLG(L)-NROWG(L))610,137,137
  137 IF(NQ-NCOLG(L))610,138,138
  138 I=NROWG(L)
      J=NCOLG(L)
      G(J,I)=DATING(L)
  134 G(I,J)=DATING(L)
      GO TO 124
  135 WRITE(6,7) (RECORD1(K,J),J=1,4)
```

```
    7 FORMAT(//5A4)
      WRITE(6,11)
   11 FORMAT(10HO G MATRIX)
      DO 1004 I=1,NQ
 1004 WRITE(6,56) I,(G(I,J),J=1,NQ)
      IF(1+NROWG(L))610,139,610
  139 NR1=0
      IEGEN=0
      CALL OVERFL(JZZ)
      CALL HDIAG(G,NQ,IEGEN,A,NR1)
      CALL OVERFL(JZZ)
      IF(JZZ.NE.2) WRITE(6,1237)
 1237 FORMAT(33H UNDERFLOWS OR OVERFLOWS IN HDIAG)
      DO 140 J=1,NQ
      IF(0.0005-G(J,J))147,145,145
  145 DG(J)=0.0
      GO TO 149
  147 DG(J)=G(J,J)
  149 DO 140 I=1,NQ
      L=(K-1)*NQ+I
      V(L,J)=A(I,J)*SQRT(DG(J))
  140 A2(L,J)=A(I,J)*1./SQRT(DG(J))
  133 CONTINUE
      NUMB3=0
      DO 254 I=1,INUMB
  254 DX(I)=5.89141E-7*D(I)*D(I)
      DO 162 I=1,NQ
      DO 162 J=1,NQ
  162 F(I,J)=0.0
      IF(NFC)0,151,0
      DO 150 K=1,NFC
      I=NRO(NQZ+K)
      J=NCO(NQZ+K)
      F(I,J)=FIC(K)
  150 F(J,I)=F(I,J)
  151 DO 171 L=1,NP
      DO 170 K=1,NQZ
      IF(NQ-NCO(K))615,166,166
  166 IF(NCO(K)-NRO(K))615,167,167
  167 IF(NF-NFO(K))615,168,168
  168 I=NRO(K)
      J=NCO(K)
      M=NFO(K)
      F(I,J)=F(I,J)+Z(K)*FI(M,L)
  170 F(J,I)=F(I,J)
  171 CONTINUE
      WRITE(6,54)
   54 FORMAT(1H1////53X,16HINITIAL F MATRIX)
      DO 179 I=1,NQ
  179 WRITE(6,56) I,(F(I,J),J=1,NQ)
   56 FORMAT(5HO ROWI4/(10E14.6))
      FIMAX=100.0
C     SOLVING THE EIGENVALUE PROBLEM FOR ALL ISOTOPE MOLECULES
  165 DO 210 N=1,NUMBG
      DO 200 J=1,NQ
      DO 195 L=1,NQ
      DD(L)=0.0
      S=0.0
      DO 194 K=1,NQ
      M=(J-1)*NQ+K
  194 S=S+F(L,K)*V(M,J)
  195 DD(L)=S
      DO 200 I=1,NQ
      H(I,J)=0.0
      S=0.0
      DO 199 M=1,NQ
      K=(N-1)*NQ+M
  199 S=S+V(K,I)*DD(M)
  200 H(I,J)=S
```

```
      NR=0
      IEGEN=0
      CALL OVERFL(JZZ)
      CALL HDIAG(H,NQ,IEGEN,C,NR)
      CALL OVERFL(JZZ)
      IF(JZZ.NE.2) WRITE(6,1237)
      DO 208 I=1,NQ
      M=(N-1)*NQ+I
      DC(I)=H(I,I)
      DV(I)=SIGN(SQRT(ABS(H(I,I))/5.89141E-7),H(I,I))
      DC1(M)=DC(I)
      DV1(M)=DV(I)
      DO 275 K=1,NQ
      L=(N-1)*NQ+K
      S=0.0
      U=0.0
      DO 274 J=1,NQ
      S=S+V(L,J)*C(J,I)
274   U=U+A2(L,J)*C(J,I)
      AL(M,K)=S
275   ALI(M,K)=U
208   CONTINUE
      IF(FIMAX-TOLF)210,0,0
      IF(NUMB3-NS)0,210,210
      DO 216 J=1,NP
      DO 215 I=1,NQ
      M=(N-1)*NQ+I
      IF(DX(M))680,0,680
      DD(I)=0.0
      DDV(I)=0.0
      GO TO 681
680   DD(I)=DX(M)-DC(I)
      DDV(I)=D(M)-DV(I)
681   EPS(M,J)=DD(I)
      D1(I)=D(M)
  215 DX1(I)=DX(M)
216   CONTINUE
      WRITE(6,7) (RECORD1(N,J),J=1,5)
      WRITE(6,25) (I,D1(I),DV(I),DDV(I),DX1(I),DC(I),DD(I),I=1,NQ)
   25 FORMAT(63HO  OBSERVED AND CALCULATED FREQUENCIES AND FREQUENCY PAR
     1AMETERS/(I5,3F10.3,F20.6,F10.6,F12.6))
  210 CONTINUE
      IF(FIMAX-TOLF)3012,0,0
      IF(NUMB3-NS)0,3012,0
C     CONSTRUCTION OF THE JACOBI MATRIX
      CALL JACOBI(NQ,NOZ,NUMBG,NFO,NRO,NCO,AL,JAC)
3012  DO 900 I=1,NP
      ORMF0=0.0
      DO 901 J=1,INUMB
      U=EPS(J,I)
901   ORMF0=ORMF0+U*W(J)*U
900   CONTINUE
      IF(NUMB3)0,957,0
      ORMR=0.0
      DO 711 I=1,INUMB
      S=-EPS(I,1)
      DO 712 J=1,NF
      U1=JR(I,J)
      V1=FI(J,1)
712   S=S+U1*V1
      R(I)=-S
711   ORMR=ORMR+R(I)*W(I)*R(I)
      IF(FIMAX-TOLF)400,0,0
      IF(NUMB3-NS)0,400,400
      WRITE(6,31) ORMR
31    FORMAT(////4X,8HR'WR    =,D18.10)
957   WRITE(6,902) ORMF0
902   FORMAT(//4X,8HNORMEPS=,D18.10,/)
```

```
      DO 801 I=1,INUMB
      DO 801 J=1,NF
801   QR(I,J)=JAC(I,J)
852   FORMAT(8E14.6)
      DO 632 I=1,INUMB
      U=SQRT(W(I))
      DO 633 J=1,NF
      S=JAC(I,J)
633   JAC(I,J)=U*S
      DO 634 K=1,NP
      S=EPS(I,K)
634   EPS(I,K)=U*S
632   CONTINUE
      DO 702 I=1,INUMB
      DO 702 J=NF+1,NF+NP
702   JAC(I,J)=EPS(I,J-NF)
C     SINGULAR VALUE DECOMPOSITION OF THE JACOBI MATRIX
      CALL MINFIT(INUMB,NF,NP,JAC,Q,EPS1,TOL)
      NUMB3=NUMB3+1
      WRITE(6,660) NUMB3
660   FORMAT(1H1/54X,I3,6H. STEP,//)
      QMAX=0.0
      DO 1010 I=1,NF-1
      DO 1011 K=1,I
      IF(Q(K)-Q(I+1))1012,1012,1011
1011  CONTINUE
      GO TO 1010
1012  IND1=K
      IND2=I+1
      QMAX=Q(I+1)
      QMAX1=JAC(I+1,NF+1)
      DO 1015 J=1,NF
1015  ALFA(J)=JAC(J,I+1)
      DO 1013 K=IND1,IND2
      L=IND2-(K-IND1)
      IF(L-IND1)1014,0,1014
      JAC(L,NF+1)=QMAX1
      DO 1016 J=1,NF
1016  JAC(J,L)=ALFA(J)
      Q(L)=QMAX
      GO TO 1013
1014  Q(L)=Q(L-1)
      DO 1026 J=1,NF
1026  JAC(J,L)=JAC(J,L-1)
      JAC(L,NF+1)=JAC(L-1,NF+1)
1013  CONTINUE
1010  CONTINUE
      WRITE(6,703)
703   FORMAT(1HO///,54X,15HSINGULAR VALUES,//)
      WRITE(6,704) (Q(I),I=1,NF)
704   FORMAT(1HO,8D15.7)
      NR6=0
      DO 1022 I=1,NF
      IF(Q(1)/Q(I)-CN)0,0,1023
      SIGMA(I)=1./Q(I)
      GO TO 1022
1023  SIGMA(I)=0.0
      NR6=NR6+1
1022  CONTINUE
      COND=Q(1)/Q(NF-NR6)
      WRITE(6,1024)
1024  FORMAT(1HO///,49X,21HSIGMA MATRIX ELEMENTS,//)
      WRITE(6,1025) (SIGMA(I),I=1,NF)
1025  FORMAT(1HO,8F15.7)
      WRITE(6,661) COND
661   FORMAT(//5X,10HCONDNUMB.=,E12.5,//)
C     CALCULATION OF THE FORCE CONSTANT CORRECTION VECTOR
      DO 707 I=1,NF
      DO 708 J=1,NF
```

```
708   ALFA(J)=JAC(I,J)*SIGMA(J)
      DO 709 K=1,NP
      S=0.0
      DO 710 J=1,NF
710   S=S+ALFA(J)*JAC(J,NF+K)
709   FI(I,K)=S
707   CONTINUE
      WRITE(6,77)
77    FORMAT(/50X,15HSOLUTION VECTOR,/)
      DO 79 J=1,NP
      WRITE(6,78) (FI(I,J),I=1,NF)
78    FORMAT(6F14.10)
79    CONTINUE
      DO 2012 I=1,NP
      FNORM=0.0
      DO 2013 J=1,NF
2013  FNORM=FNORM+FI(J,I)**2
2012  CONTINUE
      WRITE(6,2014) FNORM
2014  FORMAT(///5X,6HFNORM=,E14.6,/)
676   FORMAT(1H0,8E15.6)
      IF(FNORM-5.0E-2)603,0,0
      DO 601 J=1,NP
      DO 602 I=1,NF
602   FI(I,J)=FI(I,J)*SC
601   CONTINUE
603   WRITE(6,604)
604   FORMAT(//50X,17HCORRECTION VECTOR,/)
      DO 605 J=1,NP
      WRITE(6,606) (FI(I,J),I=1,NF)
606   FORMAT(6F14.10)
605   CONTINUE
C     REFINEMENT OF THE F MATRIX, TEST OF CONVERGENCE
      DO 607 J=1,NP
      FIMAX=0.0
      DO 608 I=1,NF
      IF(FIMAX-ABS(FI(I,J)))0,608,608
      FIMAX=ABS(FI(I,J))
608   CONTINUE
607   CONTINUE
722   DO 328 L=1,NP
      DO 329 K=1,NOZ
      I=NRO(K)
      J=NCO(K)
      M=NFO(K)
      F(I,J)=F(I,J)+Z(K)*FI(M,L)
  329 F(J,I)=F(I,J)
328   CONTINUE
      IF(FIMAX-TOLF)165,0,0
      IF(NUMB3-NS)0,165,165
      WRITE(6,1635)
1635  FORMAT(///53X,17HADJUSTED F MATRIX,/)
      DO 1636 I=1,NQ
1636  WRITE(6,56) I,(F(I,J),J=1,NQ)
      GO TO 165
400   WRITE(6,60)
60    FORMAT(/////49X,28HFINAL SET OF FORCE CONSTANTS,/)
      DO 331 I=1,NQ
331   WRITE(6,676) (F(I,J),J=1,NQ)
2015  DO 714 I=1,NF
      DO 715 J=1,NF
715   ALFA(J)=JAC(I,J)*(SIGMA(J)**2)
      DO 716 K=1,NF
      S=0.0
      DO 717 J=1,NF
717   S=S+ALFA(J)*JAC(K,J)
716   A1(I,K)=S
714   CONTINUE
      DO 621 I=1,NF
```

```
      DO 622 J=I,NF
      IF(I-J)623,0,623
      U=ABS(A1(I,I))
      S=U*ORMR/(INUMB-INUMB1-(NF-NR6))
      SIGMA(I)=DSQRT(S)
623   U=A1(I,J)
      V1=A1(I,I)
      U1=A1(J,J)
      CR(I,J)=U/DSQRT(DABS(V1*U1))
      CR(J,I)=CR(I,J)
622   CONTINUE
621   CONTINUE
      DO 651 I=1,NQ
      DO 651 J=1,NQ
651   JAC(I,J)=0.0
      DO 650 K=1,NOZ
      I=NRO(K)
      J=NCO(K)
      M=NFO(K)
      JAC(I,J)=Z(K)*SIGMA(M)
650   JAC(J,I)=JAC(I,J)
      WRITE(6,637)
637   FORMAT(///48X,30HDISPERSIONS OF FORCE CONSTANTS,/)
      DO 652 I=1,NQ
652   WRITE(6,676) (JAC(I,J),J=1,NQ)
      WRITE(6,624)
624   FORMAT(///53X,18HCORRELATION MATRIX,/)
      DO 625 I=1,NF
625   WRITE(6,676) (CR(I,J),J=1,NF)
      DO 958 N=1,NUMBG
      WRITE(6,7) (RECORD1(N,J),J=1,5)
      DO 1017 I=1,NQ
      M=(N-1)*NQ+I
      DC(I)=DC1(M)
      DV(I)=DV1(M)
      IF(DX(M))1018,0,1018
      DD(I)=0.0
      DDV(I)=0.0
      GO TO 1019
1018  DD(I)=DX(M)-DC(I)
      DDV(I)=D(M)-DV(I)
1019  D1(I)=D(M)
1017  DX1(I)=DX(M)
      WRITE(6,25) (I,D1(I),DV(I),DDV(I),DX1(I),DC(I),DD(I),I=1,NQ)
958   CONTINUE
      WRITE(6,31) ORMR
      WRITE(6,902) ORMF0
      WRITE(6,626)
626   FORMAT(///55X,13HJACOBI MATRIX,/)
      DO 627 I=1,NUMBG
      DO 1021 J=1,NQ
      M=(I-1)*NQ+J
1021  WRITE(6,676) (QR(M,K),K=1,NF)
      WRITE(6,3000)
3000  FORMAT(//)
627   CONTINUE
      WRITE(6,2010)
2010  FORMAT(//52X,18HEIGENVECTOR MATRIX,/)
      DO 4150 K=1,NUMBG
      WRITE(6,7) (RECORD1(K,J),J=1,4)
      DO 2011 I=1,NQ
      WRITE(6,676) (AL(L,I),L=(K-1)*NQ+1,K*NQ)
2011  CONTINUE
4150  CONTINUE
      WRITE(6,2020)
2020  FORMAT(//45X,33HINVERSE OF THE EIGENVECTOR MATRIX,/)
      DO 2022 K=1,NUMBG
      WRITE(6,7) (RECORD1(K,J),J=1,4)
      DO 2021 I=1,NQ
```

```
      L=(K-1)*NQ+I
      WRITE(6,676) (ALI(L,J),J=1,NQ)
2021  CONTINUE
2022  CONTINUE
      GO TO 22
610   WRITE(6,80) L,NROWG(L),NCOLG(L),DATING(L)
80    FORMAT(23HOG MATRIX ERROR PROBLEM,6H FIELDI3,6H READSI3,I3,F12.6)
      GO TO 90
615   WRITE(6,82) K,NRO(K),NCO(K),NFO(K),Z(K)
82    FORMAT(15HOF MATRIX ERROR,6H FIELDI3,6H READSI4,I4,F12.6)
90    CALL EXIT
      END

END OF SEGMENT, LENGTH  4185, NAME  CJB4
```

```
      SUBROUTINE JACOBI(M,N,NI,NFI,NR,NC,A,B)
      DIMENSION NFI(21),NR(21),NC(21),A(30,21),B(30,22)
      DO 1 I=1,NI
      DO 2 J=1,M
      M1=(I-1)*M+J
      DO 2 K=1,N
      NFOM=NFI(K)
      IF(K-1)3,4,3
3     NUMB=K-1
      DO 5 L=1,NUMB
      IF(NFI(L)-NFOM)5,2,5
5     CONTINUE
4     L=NR(K)
      K1=NC(K)
      IF(K1-L)8,7,6
7     B(M1,NFOM)=A(M1,K1)*A(M1,K1)
      GO TO 2
6     B(M1,NFOM)=2*A(M1,K1)*A(M1,L)
2     CONTINUE
1     CONTINUE
8     RETURN
      END

END OF SEGMENT, LENGTH   216, NAME  JACOBI
```

```
      SUBROUTINE MINFIT(M,N,NP,AB,Q,EPS,TOL)
      DOUBLE PRECISION U,S,G,F,V,H,EPS,E,C,XM,Y,Z,D4,TOL,Q
      DIMENSION AB(30,22),Q(21),E(21)
C     HOUSHOLDER S REDUCTION TO BIDIAGONAL FORM
      G=0.0
      XM=0.0
      NPM=N+NP
      DO 1 I=1,N
      E(I)=G
      S=0.0
      L=I+1
      DO 2 J=I,M
      U=AB(J,I)
2     S=S+U**2
      IF(S-TOL)0,3,3
      G=0.0
      GO TO 4
3     F=AB(I,I)
      IF(F)0,5,5
      G=DSQRT(S)
      GO TO 6
5     G=-DSQRT(S)
6     H=F*G-S
      AB(I,I)=F-G
      DO 7 J=L,NPM
      S=0.0
      DO 8 K=I,M
      U=AB(K,I)
      V=AB(K,J)
8     S=S+U*V
      F=S/H
      DO 9 K=I,M
      U=AB(K,J)
      V=AB(K,I)
9     AB(K,J)=U+F*V
7     CONTINUE
4     Q(I)=G
      S=0.0
      IF(I-M)0,0,10
      IF(L-N)0,0,10
      DO 11 J=L,N
      U=AB(I,J)
11    S=S+U**2
10    IF(S-TOL)0,12,12
      G=0.0
      GO TO 13
12    F=AB(I,I+1)
      IF(F)0,14,14
      G=DSQRT(S)
      GO TO 15
14    G=-DSQRT(S)
15    H=F*G-S
      AB(I,I+1)=F-G
      IF(L-N)0,0,13
      DO 16 J=L,N
      U=AB(I,J)
16    E(J)=U/H
      DO 17 J=L,M
      S=0.0
      DO 18 K=L,N
      U=AB(J,K)
      V=AB(I,K)
18    S=S+U*V
      DO 19 K=L,N
      U=AB(J,K)
19    AB(J,K)=U+S*E(K)
17    CONTINUE
13    U=Q(I)
      V=DABS(U)+DABS(E(I))
```

```
      IF(XM-Y)0,1,1
      XM=Y
1     CONTINUE
C     ACCUMULATION OF RIGHT HAND TRANSFORMATION
      DO 20 I=1,N
      M1=N-(I-1)
      IF(G)0,21,0
      U=AB(M1,M1+1)
      H=U*G
      DO 22 J=L,N
      U=AB(M1,J)
22    AB(J,M1)=U/H
      DO 23 J=L,N
      S=0.0
      DO 24 K=L,N
      U=AB(M1,K)
      V=AB(K,J)
24    S=S+U*V
      DO 25 K=L,N
      U=AB(K,J)
      V=AB(K,M1)
25    AB(K,J)=U+S*V
23    CONTINUE
21    IF(L-N)0,0,50
      DO 26 J=L,N
      AB(M1,J)=0.0
26    AB(J,M1)=0.0
50    AB(M1,M1)=1.0
      G=E(M1)
20    L=M1
      EPS=EPS*XM
      N1=N+1
      IF(M-N)0,51,51
      DO 27 I=M+1,N
      DO 28 J=N1,NPM
28    AB(I,J)=0.0
27    CONTINUE
C     DIAGONALIZATION OF THE BIDIAGONAL FORM
51    DO 29 K=1,N
      M1=N-(K-1)
C     TEST F SPLITTING
42    DO 30 L=1,M1
      M2=M1-(L-1)
      IF(DABS(E(M2))-EPS)34,34,0
      IF(DABS(Q(M2-1))-EPS)31,31,30
30    CONTINUE
C     CANCELLATION OF E(L) IF L GREATER THAN 1
31    C=0.0
      S=1.0
      L1=M2-1
      DO 33 I=M2,M1
      F=S*E(I)
      E(I)=C*E(I)
      IF(DABS(F)-EPS)34,34,0
      G=Q(I)
      Q(I)=DSQRT(F*F+G*G)
      H=Q(I)
      C=G/H
      S=-F/H
      DO 35 J=N1,NPM
      Y=AB(L1,J)
      Z=AB(I,J)
      AB(L1,J)=C*Y+S*Z
      AB(I,J)=-(S*Y)+C*Z
35    CONTINUE
33    CONTINUE
34    Z=Q(M1)
      IF(M2-M1)0,36,0
C     SHIFT FROM BOTTOM 2*2 MINOR
```

```
      XM=Q(M2)
      Y=Q(M1-1)
      G=E(M1-1)
      H=E(M1)
      F=((Y-Z)*(Y+Z)+(G-H)*(G+H))/(2*H*Y)
      G=DSQRT(F*F+1)
      D4=(XM-Z)*(XM+Z)
      IF(F)0,37,37
      F=(D4+H*(Y/(F-G)-H))/XM
      GO TO 38
37    F=(D4+H*(Y/(F+G)-H))/XM
C     NEXT QR TRANSFORMATION
38    C=1.0
      S=1.0
      DO 39 I=M2+1,M1
      G=E(I)
      Y=Q(I)
      H=S*G
      G=C*G
      E(I-1)=DSQRT(F*F+H*H)
      Z=E(I-1)
      C=F/Z
      S=H/Z
      F=XM*C+G*S
      G=-XM*S+G*C
      H=Y*S
      Y=Y*C
      DO 40 J=1,N
      XM=AB(J,I-1)
      Z=AB(J,I)
      AB(J,I-1)=XM*C+Z*S
40    AB(J,I)=-XM*S+Z*C
      Q(I-1)=DSQRT(F*F+H*H)
      Z=Q(I-1)
      C=F/Z
      S=H/Z
      F=C*G+S*Y
      XM=-S*G+C*Y
      DO 41 J=N1,NPM
      Y=AB(I-1,J)
      Z=AB(I,J)
      AB(I-1,J)=C*Y+S*Z
41    AB(I,J)=-S*Y+C*Z
39    CONTINUE
      E(M2)=0.0
      E(M1)=F
      Q(M1)=XM
      GO TO 42
C     CONVERGENCE
36    IF(Z)0,29,29
C     Q(K) IS MADE NON NEGATIV
      Q(M1)=-Z
      DO 43 J=1,N
43    AB(J,M1)=-AB(J,M1)
29    CONTINUE
      RETURN
      END

END OF SEGMENT, LENGTH  2187, NAME  MINFIT
```

```
      SUBROUTINE  HDIAG (H,N,IEGEN,U,NR)
      DOUBLE PRECISION HTEMP,TANG,SINE,COSINE,RAP,HDTEST,HDIMIN,XMAX
      DIMENSION H(6,6),U(6,6),X(6),IQ(6)
      IF (IEGEN) 15,10,15
   10 DO 14 I=1,N
      DO 14 J=1,N
      IF(I-J)12,11,12
   11 U(I,J)=1.0
      GO TO 14
   12 U(I,J)=0.0
   14 CONTINUE
   15 NR = 0
      IF (N-1) 1000,1000,17
   17 NMI1=N-1
      DO 30 I=1,NMI1
      X(I) = 0.0
      IPL1=I+1
      DO 30 J=IPL1,N
      IF(X(I)-ABS ( H(I,J))) 20,20,30
   20 X(I)=ABS (H(I,J))
      IQ(I)=J
   30 CONTINUE
      RAP=7.450580596E-9
      HDTEST=1.0E30
   40 DO 70  I=1,NMI1
      IF (I-1) 60,60,45
   45 IF(XMAX-X(I)) 60,70,70
   60 XMAX=X(I)
      IPIV=I
      JPIV=IQ(I)
   70 CONTINUE
      IF (XMAX) 1000,1000,80
   80 IF( HDTEST) 90,90,85
   85 IF (XMAX - HDTEST) 90,90,148
   90 HDIMIN = ABS  ( H (1,1) )
      DO 110  I=2,N
      IF (HDIMIN - ABS  ( H (I,I))) 110,110,100
  100 HDIMIN=ABS  (H(I,I))
  110 CONTINUE
      HDTEST = HDIMIN*RAP
      IF (HDTEST-XMAX) 148,1000,1000
  148 NR= NR+1
  150 TANG=SIGN (2.0,(H(IPIV,IPIV)-H(JPIV,JPIV)))*H(IPIV,JPIV)/(ABS (H(I
     1PIV,IPIV)-H(JPIV,JPIV))+SQRT ((H(IPIV,IPIV)-H(JPIV,JPIV))**2+4.0*H
     2(IPIV,JPIV)**2))
      COSINE=1.0/DSQRT(1.0+TANG*TANG)
      SINE=TANG*COSINE
      HII=H(IPIV,IPIV)
      H(IPIV,IPIV)=COSINE**2*(HII+TANG*(2.*H(IPIV,JPIV)+TANG*H(JPIV,JPIV
     1)))
      H(JPIV,JPIV)=COSINE**2*(H(JPIV,JPIV)-TANG*(2.*H(IPIV,JPIV)-TANG*H
     1II))
      H(IPIV,JPIV)=0.0
      IF ( H(IPIV,IPIV) - H(JPIV,JPIV)) 152,153,153
  152 HTEMP = H(IPIV,IPIV)
      H(IPIV,IPIV) = H(JPIV,JPIV)
      H(JPIV,JPIV) =HTEMP
      HTEMP=DSIGN(1.0,-SINE)*COSINE
      COSINE=DABS(SINE)
      SINE =HTEMP
  153 CONTINUE
      DO 350 I=1,NMI1
      IF(I-IPIV)210,350,200
  200 IF (I-JPIV) 210,350,210
  210 IF(IQ(I)-IPIV) 230,240,230
  230 IF(IQ(I)-JPIV) 350,240,350
  240 K=IQ(I)
  250 HTEMP=H(I,K)
```

```
      H(I,K)=0.0
      IPL1=I+1
      X(I) =0.0
      DO 320 J=IPL1,N
      IF ( X(I) -ABS ( H(I,J)) ) 300,300,320
  300 X(I)=ABS(H(I,J))
      IQ(I)=J
  320 CONTINUE
      H(I,K)=HTEMP
  350 CONTINUE
      X(IPIV) =0.0
      X(JPIV) =0.0
      DO 530 I=1,N
      IF (I-IPIV) 370,530,420
  370 HTEMP = H(I,IPIV)
      H(I,IPIV)= COSINE*HTEMP + SINE*H(I,JPIV)
      IF ( X(I) - ABS (H(I,IPIV)) )380,390,390
  380 X(I) = ABS (H(I,IPIV))
      IQ(I) = IPIV
  390 H(I,JPIV) = - SINE*HTEMP + COSINE*H(I,JPIV)
      IF ( X(I) - ABS  ( H(I,JPIV)) ) 400,530,530
  400 X(I) = ABS (H(I,JPIV))
      IQ(I) = JPIV
      GO TO 530
  420 IF(I-JPIV) 430,530,480
  430 HTEMP = H(IPIV,I)
      H(IPIV,I) = COSINE*HTEMP + SINE*H(I,JPIV)
      IF ( X(IPIV) - ABS (H(IPIV,I)) ) 440,450,450
  440 X(IPIV) = ABS (H(IPIV,I))
      IQ(IPIV) = I
  450 H(I,JPIV) = - SINE*HTEMP + COSINE*H(I,JPIV)
      IF (X(I) - ABS (H(I,JPIV)) ) 400,530,530
  480 HTEMP = H(IPIV,I)
      H(IPIV,I) = COSINE*HTEMP + SINE*H(JPIV,I)
      IF ( X(IPIV) - ABS ( H(IPIV,I)) ) 490,500,500
  490 X(IPIV) = ABS (H(IPIV,I))
      IQ(IPIV) = I
  500 H(JPIV,I) = - SINE*HTEMP + COSINE*H(JPIV,I)
      IF ( X(JPIV) - ABS ( H(JPIV,I)) )510,530,530
  510 X(JPIV) = ABS (H(JPIV,I))
      IQ(JPIV) = I
  530 CONTINUE
      IF(IEGEN) 40,540,40
  540 DO 550 I=1,N
      HTEMP=U(I,IPIV)
      U(I,IPIV)=COSINE*HTEMP+SINE*U(I,JPIV)
  550 U(I,JPIV)= -SINE*HTEMP+COSINE*U(I,JPIV)
      GO TO 40
 1000 RETURN
      END

END OF SEGMENT, LENGTH  1401, NAME  HDIAG
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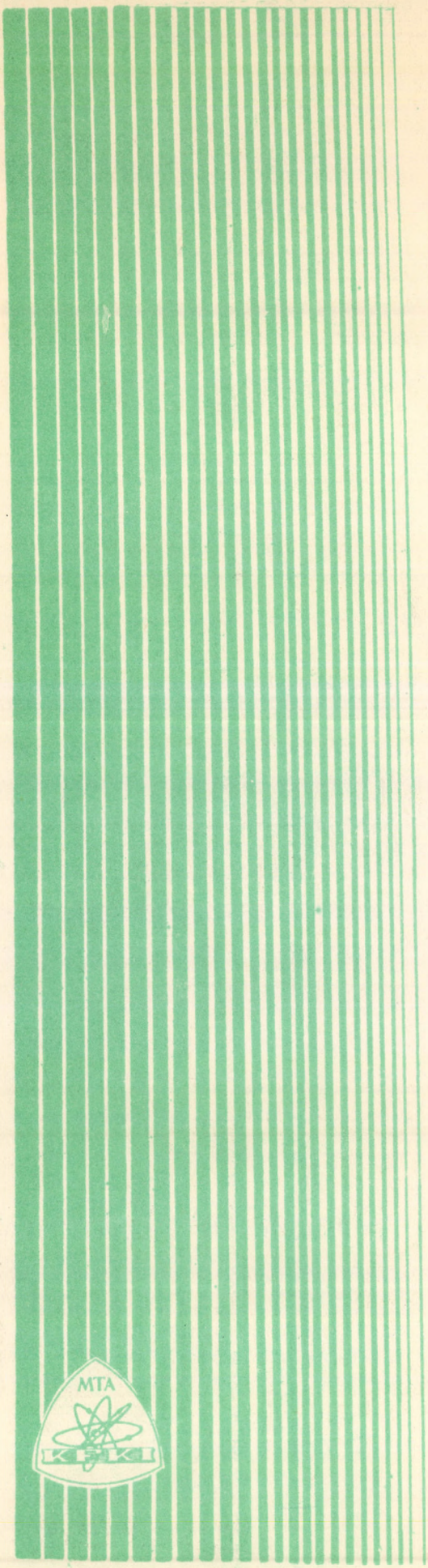

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