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MASTER

MATRIX
A FORCE CONSTANT ADJUSTER PROGRAM
TO OBTAIN LEAST SQUARES FIT
TO OBSERVED FREQUENCIES OF MOLECULES AND CRYSTALS

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ABSTRACT

This report describes a Fortran program for the IBM 7040 which is a force constant adjuster to obtain a least squares fit to observed frequencies of molecules and crystals.

The input data are explained and an illustrative application to diamond is presented.

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MATRIX

A FORCE CONSTANT ADJUSTER PROGRAM TO OBTAIN LEAST SQUARES FIT TO OBSERVED FREQUENCIES OF MOLECULES AND CRYSTALS

PROGRAM NO. 40-0832

I. PURPOSE

Let $\underline{v}_o$ denote a column matrix the n elements of which are observed vibration frequencies (or energies) for a molecule or a crystal (or any other system for that matter) where these frequencies can be calculated using a force field defined by m force constants. Let $\underline{v}^{(0)}$ be a column matrix the n elements of which are the calculated vibration frequencies corresponding to the ones in $\underline{v}_o$. This superscript (0) denotes that these are obtained with some initial set of the m force constants.

Let $\underline{J}$ denote an $n \times m$ matrix such that $J_{st} = -\frac{\Delta v_s}{\Delta f_t}$. Here Δv_s denotes the change in the s^{th} calculated frequency when the force constant f_t is changed by Δf_t , all other force constants are held fixed. The negative sign has been inserted so that Eq. (1) below appears with a positive sign on the right side.

Let $\underline{W}$ denote a diagonal weight factor matrix with n rows and n columns such that $W_{tt} = \frac{1}{v_{ot}^2}$ where v_{ot} is the observed value of the t^{th} element in $\underline{v}_o$.

Let $\underline{f}^{(0)}$ denote a column matrix of m elements which are the initial set of force constants used to compute the $\underline{v}^{(0)}$.

Let $\underline{V} = \underline{v}^{(0)} - \underline{v}_o$, a column matrix with n elements. Then, following D. E. Mann, T. Shimanouchi, J. H. Meal and L. Fano (J. Chem. Phys. 27, 43 (1957)), it can be shown that the force constants must be altered according to the following equation if the sum of the squared

deviations between calculated and observed frequencies is to be minimized*

$$\Delta \underline{f} = [\underline{J}' \underline{W} \underline{J}]^{-1} \underline{J}' \underline{W} \underline{V} \quad (1)$$

In (1), $\Delta \underline{f}$ is a column matrix of m elements which are the predicted changes in the force constants such that a new set $\underline{f}^{(1)}$ given by

$$\underline{f}^{(1)} = \underline{f}^{(0)} + \Delta \underline{f}$$

will lead toward new calculated frequencies $\underline{v}^{(1)}$ which yield a minimum sum of squared deviations between observed and calculated frequencies (weighted, however, by $\underline{W}$). Thus, the minimized sum is

$$[\underline{v}^{(1)}]' \underline{W} [\underline{v}^{(1)}] = S^{(1)} < \underline{v}' \underline{W} \underline{v}$$

where

$$\underline{v}^{(1)} = \underline{v}^{(1)} - \underline{v}_0$$

$$\underline{v} = \underline{v}^{(0)} - \underline{v}_0$$

II. PROCEDURE

The program takes the three matrices:

$\underline{J}$, the $n \times m$ matrix,

$\underline{W}$, the diagonal $n \times n$ matrix,

$\underline{V}$, the $n \times 1$ column vector.

With these matrices, the following $m \times 1$ vector is calculated:

$$(\underline{J}' \underline{W} \underline{J})^{-1} \underline{J}' \underline{W} \underline{V} = \Delta \underline{f}.$$

In calculating $\Delta \underline{f}$ the matrix $(\underline{J}' \underline{W} \underline{J})$ and its inverse are multiplied together so the precision of the inversion may be observed.

*Mann et al should give this equation with a negative sign in front because their $\underline{J}$ is the negative of that used here. They have a sign error in their published work.

A $n \times 1$ vector is calculated from $\underline{J}$ and $\Delta \underline{f}$:

$$\Delta \underline{v} = - \underline{J} \Delta \underline{f} . \quad (2)$$

Eq. (2) gives the predicted value for $\underline{v}^{(1)} - \underline{v}^{(0)}$ and indicates what may be expected from a full calculation of $\underline{v}^{(1)}$. Actually, the $\Delta \underline{v}$ calculated from (2) will not be the same as $\underline{v}^{(1)} - \underline{v}^{(0)}$ calculated from the program because the frequencies are not really linear functions of the force constants as (2) implies.

The program also calculates a predicted

$$\begin{aligned} \underline{v}^{(1)} - \underline{v}_0 &= \underline{v}^{(1)} \\ &= \underline{v} - \underline{J} \Delta \underline{f} \end{aligned} \quad (3)$$

III. GENERAL INPUT-OUTPUT INFORMATION

Summary of output

1. The input is printed out and identified.
2. The determinant of $[\underline{J}' \quad \underline{W} \quad \underline{J}]$.
3. $[\underline{J}' \quad \underline{W} \quad \underline{J}]^{-1} [\underline{J}' \quad \underline{W} \quad \underline{J}]$ A check on the computations.
4. $\Delta \underline{f}$.
5. $\Delta \underline{v} = - \underline{J} \Delta \underline{f}$.
6. $\underline{v}^{(1)} = \underline{v} + \Delta \underline{v} = \underline{v} - \underline{J} \Delta \underline{f}$.

The input format is as follows:

<u>Type</u>	<u>Column</u>	<u>Format</u>	<u>Mnemonics</u>	<u>Description</u>
1	1-80	A	N	Comments
2	1-5	I	N	The number of rows in the $\underline{J}$ matrix
	6-10	I	M	The number of columns in the $\underline{J}$ matrix
3	1-10	F	J_{11}	The $\underline{J}$ matrix is read row by row,
	11-20	F	J_{12}	8 per card. When one row is
	.	.	.	completed, the next row starts on
	.	.	.	a new card.
	.	.	.	
	71-80	F	J_{18}	
	1-10	F	J_{19}	
	.	.	.	
	.	.	.	
	.	.	.	
	1-10	F	J_{11}	
	11-20	F	J_{12}	
	.	.	.	
	.	.	.	
	.	.	.	
	71-80	F	J_{18}	
	1-10	F	J_{19}	
	.	.	.	
	.	.	.	
	.	.	.	

<u>Type</u>	<u>Column</u>	<u>Format</u>	<u>Mnemonics</u>	<u>Description</u>
4	1-10	F	$W_{1,1}$	The diagonal elements of W are read 8 per card, using as many cards as needed.
	11-20	F	$W_{2,2}$	
	.	.	.	
	.	.	.	
	.	.	.	
	71-80	F	$W_{8,8}$	
	1-10	F	$W_{9,9}$	
	.	.	.	
	.	.	.	
	.	.	.	
5	1-10	F	V_1	The elements of the vector V are read 8 per card, using as many cards as needed.
	11-20	F	V_2	
	.	.	.	
	.	.	.	
	.	.	.	
	71-80	F	V_8	
	1-10	F	V_9	
	.	.	.	
	.	.	.	
	.	.	.	

APPENDIX

Test Example

This example is given as a test for the program. The listing is self explanatory.

LEAST SQUARES FIT FOR DIAMOND

DIMENSIONS OF J MATRIX IS 13 BY 6

GIVEN J MATRIX

0.033000	0.187000	-0.265000	-0.016600	=0.133000	0.000147
-0.001240	-0.002380	=0.003050	-0.000509	=0.001550	0.000000
-0.002150	0.000000	=0.008650	-0.000357	=0.004320	0.008650
0.000186	-0.000963	=0.006760	-0.000091	=0.003400	0.005530
0.000579	-0.003020	=0.003870	-0.000278	=0.001970	0.000000
-0.006880	0.070100	=0.139000	-0.008540	=0.128000	0.000000
-0.088100	0.085400	=0.175000	-0.011500	=0.108000	0.095600
0.035900	0.136000	=0.152000	-0.018000	=0.085200	0.036700
0.036400	0.078600	=0.025900	-0.018200	=0.045200	0.000000
-0.007430	-0.008870	=0.018200	-0.011800	=0.016700	0.000000
-0.024200	0.029300	=0.132000	-0.007500	=0.079600	0.118000
0.000427	=0.002060	=0.014100	-0.006211	=0.077800	0.082500
0.003910	-0.011000	=0.005930	-0.019400	=0.085800	0.000000

THE DIAGONAL ELEMENTS OF W

I	W(I,I)
1	0.366900E 02
2	0.180200E 05
3	0.151800E 05
4	0.428700E 05
5	0.284400E 05
6	0.407200E 02
7	0.394000E 02
8	0.453600E 02
9	0.513800E 02
10	0.688700E 02
11	0.577400E 02
12	0.227500E 03
13	0.122800E 03

GIVEN V MATRIX

I	V(I)
1	=0.800000E-03
2	0.500000E-04
3	=0.100000E-03
4	=0.500000E-04
5	0.500000E-04
6	=0.400000E-03
7	0,
8	0.210000E-02
9	=0.200000E-02
10	0.100000E-02
11	0.600000E-03
12	0.300000E-02
13	0.490000E-02

DETERMINANT = 0.135300E 01

COMPUTED PRODUCT OF JTWJ AND THE INVERSE OF JTWJ

1.000000	-0.000000	0.000000	0.000000	-0.000000	0.000000
-0.000000	1.000000	0.000000	0.000000	0.000000	-0.000000
-0.000000	0.000000	1.000000	-0.000000	-0.000000	0.000000
-0.000000	0.000000	-0.000000	1.000000	-0.000000	0.000000
0.000000	-0.000000	0.000000	0.000000	1.000000	-0.000000
0.000000	-0.000000	0.000000	0.000000	0.000000	1.000000

THE DELTA F MATRIX

I	DELTA F(I)
1	-0.857023E-03
2	-0.926370E-02
3	0.218039E-01
4	-0.584292E-01
5	-0.385906E-01
6	-0.416841E-02

THE DELTA NU MATRIX

I	DELTA NU(I)
1	0.143675E-02
2	-0.461645E-04
3	0.352469E-04
4	0.251471E-04
5	-0.353660E-04
6	-0.176436E-02
7	0.900696E-04
8	0.418151E-03
9	-0.148367E-02
10	-0.102563E-02
11	0.110637E-03
12	-0.273264E-02
13	-0.441386E-02

THE V = V + DELTA NU MATRIX

I	V(I)
1	0.636753E-03
2	0.383555E-05
3	-0.647531E-04
4	-0.248529E-04
5	0.146340E-04
6	-0.216436E-02
7	0.900696E-04
8	0.251815E-02
9	-0.348367E-02
10	-0.256346E-04
11	0.710637E-03
12	0.267357E-03
13	0.486145E-03