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

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ADJUSTER

A FORCE CONSTANT ADJUSTER PROGRAM TO OBTAIN LEAST SQUARES FIT

TO OBSERVED FREQUENCIES OF MOLECULES AND CRYSTALS

(PPCo 40*0930)

by

J. K. Boyter and H. L. McMurry

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 J input cards may be punched by the program MACS J(PPCo 40*0929), described in IN-1147.

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ADJUSTER

A FORCE CONSTANT ADJUSTER PROGRAM TO OBTAIN LEAST SQUARES FIT

TO OBSERVED FREQUENCIES OF MOLECULES AND CRYSTALS

PROGRAM NO. 40*0930

I. PURPOSE

Let $\tilde{\nu}_o$ 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 $\tilde{\nu}^{(0)}$ be a column matrix the n elements of which are the calculated vibration frequencies corresponding to the ones in $\tilde{\nu}_o$. This superscript (0) denotes that these are obtained with some initial set of the m force constants.

Let $\tilde{J}$ denote an $n \times m$ matrix such that $J_{st} = -\frac{\Delta \nu_s}{\Delta f_t}$. Here $\Delta \nu_s$ 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 $\tilde{W}$ denote a diagonal weight factor matrix with n rows and n columns such that $W_{tt} = \frac{1}{\nu_{ot}^2}$ where ν_{ot} is the observed value of the t^{th} element in $\tilde{\nu}_o$.

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

Let $\tilde{V} = \tilde{\nu}^{(0)} - \tilde{\nu}_o$, 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, $n \geq m$.

$\underline{W}$, 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:

* 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.

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

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

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

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

Eq. (2) gives the predicted value for $\underline{v}^{(1)} - \underline{v}^{(0)}$ and indicates what may be expected from a full calculation of $\underline{v}^{(1)}$. Usually, the $\underline{\Delta v}$ 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. In certain nontrivial cases, (2) is exact. This point is discussed in more detail by J. K. Boyter and A. W. Solbrig, Jr., in IN-1147 (in preparation).

The program also calculates a predicted

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

III. RESTRICTIONS

The program is dimensioned to take 32×32 matrices.

IV. GENERAL INPUT-OUTPUT INFORMATION

Summary of output:

1. The input is printed out and identified.
2. $\underline{V}' \underline{W} \underline{V}$, the initial sum of squares.
3. The determinant of $[\underline{J}' \underline{W} \underline{J}]$.
4. $[\underline{J}' \underline{W} \underline{J}]^{-1} [\underline{J}' \underline{W} \underline{J}]$, a check on the computations.

5. $\Delta f.$
6. $\Delta v = - J \Delta f.$
7. $\tilde{v}^{(1)} = \tilde{v} + \Delta v = \tilde{v} - J \Delta f.$
8. $[\tilde{v}^{(1)}]^T W \tilde{v}^{(1)}$, the final sum of squares.

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 J matrix
	6-10	I	M	The number of columns in the J matrix
3	1-12	E	$J_{1,1}$	The J matrix is read row by row,
	13-24	E	$J_{1,2}$	6 per card. When one row is
	.	.	.	completed, the next row starts on
	.	.	.	a new card. Cards for the J matrix
	.	.	.	may be punched by the program
	61-72	E	$J_{1,6}$	MACS J (PPCo 40*0939) described in
	1-12	E	$J_{1,7}$	IN-1147.
	.	.	.	
	.	.	.	
	.	.	.	
	1-12	E	$J_{i,1}$	
	13-24	E	$J_{i,2}$	
	.	.	.	
	.	.	.	
	.	.	.	
	61-72	E	$J_{i,6}$	

(Continued)

<u>Type</u>	<u>Column</u>	<u>Format</u>	<u>Mnemonics</u>	<u>Description</u>
	1-12	E	$J_{i,7}$	
	.	.	.	
	.	.	.	
	.	.	.	
4	1-10	F	$W_{1,1}$	The diagonal elements of W are
	11-20	F	$W_{2,2}$	read 8 per card, using as many
	.	.	.	cards as needed.
	.	.	.	
	.	.	.	
	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
	11-20	F	V_2	read 8 per card, using as many
	.	.	.	cards as needed.
	.	.	.	
	.	.	.	
	71-80	F	V_8	
	1-10	F	V_9	
	.	.	.	
	.	.	.	
	.	.	.	

If the user desires a test example, see the Appendix to IN-1077
(April 1967) by J. K. Boyter and H. L. McMurry. After the format of

the input $\underline{J}$ matrix is adapted to the present program, this test example will provide a check on the functioning of most of the present program.