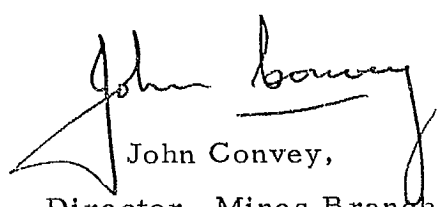C 197

FOREWORD

The Spectrochemistry Section of the Mineral Sciences Division, Mines Branch, has been investigating the application of infra-red vibration spectra to the study of the structure of a number of the sulphide and arsenide minerals.

The complexity of the secular equations relating to the vibration frequencies, geometry and force-constants of the molecules requires the use of a computer.

The mathematical method of greatest value to the problem is, in the opinion of our spectroscopist (Dr. A. H. Gillieson), that of Dr. Alois Fadini, which had appeared in German only. For the guidance, initially, of the Department's Computer Sciences Division, his paper was translated into English. The method is, however, of such a fundamental character and of such wide interest to infra-red spectroscopists that it was felt the translation would merit a wider distribution than Departmental.

It is therefore being issued as an Information Circular as a general contribution to the science in English-speaking countries and to assist infra-red research in universities and research establishments.
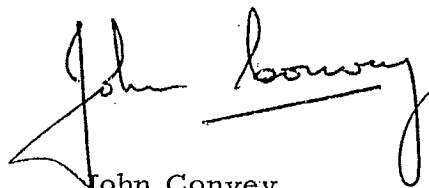
John Convey,
Director, Mines Branch

AVANT-PROPOS

La Section de la spectrochimie de la Division des sciences minérales, Direction des mines, a examiné les possibilités d'application des spectres des vibrations infrarouges à l'étude de la structure d'un certain nombre de minéraux sulfurés et arsénieux.

La complexité des équations décrivant les fréquences de vibration, la géométrie et les constantes de force des molécules exige le recours à l'ordinateur.

La méthode mathématique la plus utile pour cette étude, est, de l'avis de notre spectroscopiste (Dr. A.H. Gillieson), celle du Dr. Alois Fadini, qui n'a été publiée qu'en allemand. On a fait traduire en anglais l'étude de Fadini pour les besoins de la Division des sciences de l'ordination du ministère; mais cette méthode se révéla un instrument de travail fondamental et intéressa tellement les spectroscopistes spécialisés en infrarouge qu'on devrait diffuser la version traduite de cet exposé en dehors des cadres du ministère.

Cette étude est donc publiée comme Circulaire d'information au titre de contribution à la science dans les pays anglophones et d'aide à la recherche en infrarouge dans les universités et les institutions de recherches.

John Convey,
Directeur,
Direction des mines.

APPLICATION OF A NEW METHOD FOR THE CALCULATION OF FORCE CONSTANTS

by

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(Laboratory for Inorganic Chemistry of the Technische Hochschule, Stuttgart.)
Received 13th August, 1964.
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Translated by

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ABSTRACT

A method is presented which permits calculation, by means of a digital computer, of a complete set of force constants, using only the vibrational frequencies and the geometry of a molecule. The eigenvalues containing the vibrational frequencies are connected with the force constant matrix by the CAYLEY-HAMILTON theorem. This is resolved by the NEWTON method. As a first approximation the normal vibrations are assumed to be completely uncoupled. Then the known interactions of the kinetic energy are introduced stepwise and so a set of force constants is obtained which contains all the interaction terms of the potential energy.

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#By permission of the authors, December 20, 1967.

Circulaire d'information IC 197

Direction des mines

NOUVELLE MÉTHODE DE CALCUL DES CONSTANTES DE FORCE

par

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Technische Hochschule, Stuttgart)
Document reçu le 13 août 1964

Traduit de l'allemand à l'anglais

par

A.H. Gillieson*#

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RÉSUMÉ

Cette méthode permet, au moyen d'un calculateur digital, d'établir une série complète de constantes de force en utilisant uniquement des fréquences de vibration et la géométrie d'une molécule. Les valeurs propres contenant les fréquences de vibration sont reliées à la matrice de la constante de force par le théorème de Cayley-Hamilton. On résout l'équation par la méthode de Newton. Dans une première approche, on assume que les vibrations normales sont tout à fait libres. On introduit alors graduellement dans les calculs les interactions connues de l'énergie cinétique, de sorte qu'on obtient une série de constantes de forces contenant tous les termes d'interaction de l'énergie potentielle.

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CONTENTS

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INTRODUCTION

By neglecting the cubic and higher terms of the potential energy, which at sufficiently small amplitudes of vibration have only a minute effect, the problem of molecular vibrations can be reduced to a purely mechanical, harmonically vibrating system, for which the equation

$$|G.F - E\lambda| = 0 \qquad \qquad \ldots (1)$$

is valid [1,2]. In this, G is a matrix which contains the coefficients of kinetic energy - given by the masses, angles and separations of the atoms forming the molecule. E is the unit matrix and λ is proportional to the square of the frequencies of the normal vibrations of the molecule. The matrix F is formed from the coefficients of the potential energy - the force constants. It seemed sensible to choose a mechanical model such that the forces of a stretching between atoms in the direction of the bond, and of a change in the angle between bonds, would act against one another. This is called the general valence-force field = GVFF. The terms of the F matrix are then a measure of the binding, angular-stability and interaction forces.

Equation (1) is known in mathematics as the characteristic equation of the Eigenvalue Function, and can be solved for the eigenvalues λ by various methods [3]. In the application to the theory of molecular vibrations, it is not the eigenvalues (which can be found from the vibration spectra) but the terms of the F matrix which are the values sought. Thus we are presented, as it were, with an inverse eigenvalue problem, which stems from the basic difficulty, that for n given eigenvalues and a symmetrical F-matrix, n(n+1)/2 force constants have to be calculated.

It has been recommended either to obtain further determinantal equations from ancillary data, or to reduce the number of force constants to n by the assumption of a simplified force field. For the first method suggested, there can be employed the normal vibrations of isotopically substituted molecules, vibration-rotation interactions such as Coriolis-coupling or centrifugal-expansion constants, and vibration amplitudes or band intensities [4]. Since such data are only known for a few, mostly simple, molecules, the applicability of this method is very limited. To reduce the number of force constants sought to the number of normal vibrations available, there have been developed a number of simplified potential expressions. In the modified valence-force field = MVFF, carefully selected constants of the general valence-force field (GVFF) are neglected, so that of the above-mentioned n(n+1)/2 constants, only n remain for calculation. However, this simplification is, in general, not possible if the central atom is light in comparison with the ligand atoms, owing to the appearance of strong couplings, which cannot be neglected. Another method consists of choosing a model such that certain constants are given a defined relation to one

another, and their total number is thus diminished. The most useful model - developed by Urey and Bradley (UBFF) - describes all coupling constants as repulsion forces between unlinked atoms, but does not always give satisfactory results [6, 7]. Heath and Linnett [8] originated a potential expression which defines the coupling and deformation constants by the distortion of the ligand electron cloud, taking place during the vibration, and the change in hybridisation resulting - (orbital valence-force field = OVFF). This force field in a more developed form yields good force constants [7, 9], but is also only applicable to relatively simple molecules.

Another difficulty is calculation time, which is so long, particularly for molecules with many atoms and of low symmetry, that calculation by hand can no longer be considered practical. For this reason, in the last few years a number of procedures have been described in which digital computers have been used to determine force constants [10, 11]. All these procedures start from an assumed solution of F, which is varied by an iteration procedure until the calculated normal vibrations agree as well as possible with those found experimentally. At the same time, equation (1) is solved for eigenvalues λ. Until now, for the converse problem only one method of solution [12] has been known which permitted the iterative calculation of an F-matrix - and only a diagonal one at that - from known eigenvalues. The MVFF constants in the normal and usual form are directly accessible by this procedure. However, with very many molecules the coupling constants $f_{ik}(i \neq k)$ do not appear, and as these cannot be neglected, no sound solution can be obtained by this method.

In the following, a new procedure is described, which permits the calculation of a complete F-matrix containing the GVFF constants, by suitable choice of an initial solution.

DESCRIPTION OF THE CALCULATION PROCEDURE [13]

From n known eigenvalues λ of the determinantal equation (1), it is possible to calculate, by Vieta's expression for roots, the coefficients c_i of the characteristic equation:

$$\lambda^n + c_{n-1}\lambda^{n-1} + c_{n-2}\lambda^{n-2} + \ldots \ldots c_1\lambda^1 + c_o = 0 \qquad \ldots \ (2)$$

which is connected with the matrix product

$$A = G.F \qquad \ldots \ (3)$$

by the Cayley-Hamilton Theorem [3] among others.

$$A^n + c_{n-1}A^{n-1} + c_{n-2}A^{n-2} + \ldots\ldots + c_1A^1 + c_0E = 0 \qquad \ldots\, (4)$$

Since 0 is an n-rowed square null matrix, equation (4) produces a system of n^2 algebraic equations, which can be drawn on for the determination of the n^2 elements of the F-matrix. In general, the system of equations can be solved iteratively by Newton's procedure, if a sufficiently accurate approximate solution F_N is known and if the convergence requirements are satisfied [14]. By neglecting the quadratic, cubic and higher terms of the correction matrix F_K, there is obtained:

$$F = F_N + F_K \qquad \ldots\, (5)$$

and by this equation (4) becomes:

$$\sum_{\nu=0}^{n} c_\nu \left[G(F_N + F_K) \right]^\nu = 0 \quad \text{with} \quad \left[G(F_N + F_K) \right]^0 = E \qquad \ldots\, (6)$$

If, for simplification, one puts $F_K = X$ and $G.F_N = A_N$, one obtains, for the corrector X, the linear matrix equation:

$$\sum_{\nu=0}^{n} (-c_\nu).A_N = \sum_{\nu=1}^{n} \sum_{\rho=0}^{n-1} (A_N^\rho.G).X.(c_\nu.A_N^{\nu-\rho-1}) \qquad \ldots\, (7)$$

which with

$$J_N = \sum_{\nu=0}^{n} (-c_\nu).A_N : P_\rho = A_N^\rho.G \quad \text{and} \quad Q_\rho = c_\nu.A_N^{\nu-\rho-1} \quad (\rho = 1, 2, \ldots n)$$

reads in simplified form:

$$J_N = \sum_{\nu-1}^{n} \sum_{\rho=0}^{n-1} P_\rho.X.Q_\rho \qquad \ldots\, (7a)$$

By the introduction of new coefficients r_{st}, which are defined by:

$$j_{ik} = \sum_{\nu=1}^{n} \sum_{\rho=0}^{n-1} \sum_{h=1}^{n} \sum_{\ell=1}^{n} P_{ih}.x_{h\ell}.q_{ik} = \sum_{\nu=1}^{n} \sum_{\rho=0}^{n-1} r_{st}.x_{h\ell} \ldots\, (8)$$

$s = n(i-1) + k; \; t = n(h-1) + \ell; \; i,h,k,\ell = 1, 2 \ldots.n; \; s,t = 1, 2 \ldots.n^2;$

there results:

$$R_N.x = j_N \qquad \ldots\, (9)$$

an inhomogeneous linear system of equations, in which R_N is an n-rowed, square matrix, obtainable, as can be seen from equations (7), (7a) and (8) from the coefficients c_ν and the matrix product $A_N = G.F_N$ (F_N is the

approximate solution), by fourfold summation. j_N and x are column matrices with n^2 terms, which contain the known values $j_{11} \ldots\ldots j_{nn}$ of matrix J_N from equation (7a) and the corrections sought for the correction matrix F_K or X, $x_{11} \ldots x_{nn}$.

$$\begin{vmatrix} r_{11} \; r_{12} \cdots\cdots r_{1n}^{\,2} \\[1em] r_{21} \; r_{22} \cdots\cdots r_{2n}^{\,2} \\[1em] \\ r_{n\,^2 1}\,r_{n\,^2 2} \cdots\cdots r_{n\,^2 n\,^2} \end{vmatrix} \cdot \begin{vmatrix} x_{11} \\[1em] x_{12} \\[1em] \\ x_{nn} \end{vmatrix} = \begin{vmatrix} j_{11} \\[1em] j_{12} \\[1em] \\ j_{nn} \end{vmatrix} \qquad \ldots\, (9a)$$

If the rank of matrix R_N is n^2 and at least one term of j_N is not zero, there exists an unique solution for x, which can be determined by Gaussian algorithm [3]. This requirement is satisfied for $n \geqslant 3$. (For $n = 2$, on the other hand, the rank of R_N is smaller than 4, so that this case cannot be dealt with by the procedure without additional information.) In this way the inverse eigenvalue problem is solved in so far as the convergence of the Newton procedure is assured. From equation (4), however, there still arises an ambiguity in the solution of the F-matrix, which results from the free choice of the various initial solutions F_N (cf., for example, the investigation of the multiplicity of solutions in the force constant calculations, using an analogue computer, by Mecke et al. in Spectrochimica Acta, 19, 1540 (1963) and 20, 1295 (1964). It is therefore a question of finding a method of separating, from this multiplicity of solutions, one which has meaning for the given problem.

We set about this from the following consideration: In the discussion of molecular spectra, the concept of the characteristic vibration plays a major role, i.e. it is assumed that each normal frequency is defined as far as possible by only one symmetry co-ordinate, and therefore the coupling between different vibrations is as small as possible. Moreover, much use has been made, with considerable success, of a modified valence-force model which indeed considers all the coupling terms of the G-matrix but disregards all the non-diagonal terms of the F-matrix. Thus to a first approximation there should be a usable solution, in which the normal vibrations are assumed to be fully decoupled.

If, in the G-matrix, only the g_{ii} values are retained and all g_{ik} $(i \neq k)$ are taken as zero, from equation (1) is obtained:

$$F_D = G_D^{-1} \cdot L \qquad \ldots\, (10)$$

in which the index D means that F and G are now diagonal matrices. L is also a diagonal matrix, containing the eigenvalues λ. Since the sequence of λ-values in L is given by the arrangement of the vibration spectrum, from equation (10) there is obtained an unique solution for F_D. This is now used

to calculate an F-matrix according to equations (6) and (9), whereby, in a number of iteration cycles, the known g_{ik} values are built up stepwise:

$$F_\mu = F_{\mu-1} + X \quad \text{with } F_o = F_D \qquad \qquad \dots \text{ (11a)}$$

$$G_\mu = G_D + \mu/m\ (G - G_D) \quad \text{with } \mu = 1, 2, \dots\dots m : G_m = G \ \text{.. (11b)}$$

Necessary assumptions for the convergence of the Newton procedure are that no second solution lies in the region G_D to G, that the stepwidth m is chosen so that $F_{\mu-1}$ is a sufficiently exact approximation to $F\mu$, and that continuous partial derivatives up to the second order exist for the algebraic system of equations (4) [14].

PROGRAMMING

The calculation procedure described in the previous section was programmed for the digital computer, Standard Electric ER 56. The details can be taken from the flow diagram, Figure 1. The most difficult problem is presented by the determination of the n^4 coefficients of matrix R in equation (9). The course of this calculation is therefore reproduced in full in Figure 2. The memory requirement grows rapidly with increasing size of A. In addition to the programme memory of about 1500, an $(n^4 + n^3 + 8n^2 + 3n + 1)$ memory is required for the data - for n = 3, this is 190, but at n = 6, reaches 1820. Because of the high matrix powers arising in the solutions of the system of equations (9), the number range of the machine can be exceeded. In this case, equation (9) must be multiplied by a suitable factor (e.g. 10^{-4}).

The procedure converges very rapidly; with the examples calculated to date, a step number of m = 5-10 has always been sufficient. Post-iterations are only necessary with the last step ($\mu = m$). Their number is limited by the accuracy attainable in the solution of the inhomogeneous system of equations (9), since as $x \to 0$, so also does $j \to 0$, and from this a marked diminution in the places of the determination of x occurs. This makes itself noticeable in the loss of symmetry of the F-matrix. In general, one or two post-iterations suffice to reproduce the eigenvalues accurate to 6-7 places and concurrently to return the experimentally obtained vibration frequencies exactly. The F-matrix appears - as required - symmetrical (x_{ik} is calculated by another equation as x_{ki}). Small rounding-off errors can, however, appear due to the limited calculation. To avoid an accumulation of these errors by the iteration, before the beginning of each iteration cycle a symmetrisation of matrix F_N is carried out. Calculation time with the digital computer ER 56 (mean addition time 300 microsec.) amounts to 1.5 minutes for n = 3, and 30 minutes for n = 6. At present the programme

Ⓐ

Frequency → Eigenvalue
$C_{U_\tau}^2 \rightarrow \lambda_\tau$

Charact. Polynomial
$\prod\limits_{\tau=1}^{n} (\lambda - \lambda_\tau) = \sum\limits_{\tau=0}^{n} C_\tau \lambda^\tau$

Prime Diagonal of G
$g_{ii} \rightarrow g_\sigma^x$

First Approximation
F_o
$\lambda_\tau / g_\sigma^x \rightarrow f_{ii}$
$(f_{ik} = 0)$

$\mu = 0$

$\mu + 1 \rightarrow \mu$

μ

$\geqslant m + 1$

$< m + 1$

Ω

No

Post − iteration

Yes

$\mu - 1 \rightarrow \mu$

Addition
$F_{\mu-1} + X \rightarrow F_\mu$

Symmetrisation of F
$(F + F^T) / 2 \rightarrow F$

$> \epsilon$

Conditional Stop

$\geqslant \epsilon$

Symmetrisation Proof
$|x_{ik} - x_{ki}|$

Setting−up of $G\mu$
$\frac{\mu}{m} g_{ik} \rightarrow g_{ik}(n)$
$g_\sigma^x \rightarrow g_{ii}(\mu)$

Solution of the Equation Systems
$R_N \cdot x_N = j_N$
$x_N \rightarrow X$

Setting−up of the Equation Systems
(See Fig. 2)
$R_N \cdot x_N = j_N$

Fig. 1. Flow Diagram

A

$\nu = 0$

$J_0 = -c_0 E$
$R = 0$

$\nu + 1 \to \nu$
$\rho = -1$

Ω

$> n$

ν

$\leq n$

$-c\nu A^{\nu-1} + J_{\nu-1} \to J_\nu$

$\rho + 1 \to \rho$
$1 = 0$

$\geq \nu$

ρ

$< \nu$

$P_\rho \to P$
$Q_\rho \to Q$

$1 + 1 \to 1$
$i, \sigma = 0$

$> n$

1

$\leq n$

$i + 1 \to i$
$h = 0$

$> n$

i

$\leq n$

$h + 1 = h$
$k = 0$

$> n$

h

$\leq n$

$k + 1 \to k$
$\sigma + 1 \to \sigma$

$> n$

k

$\leq n$

$p_{1i} \cdot q_{1k} + r_\sigma^{\rho-1} \to r_\sigma^\rho$
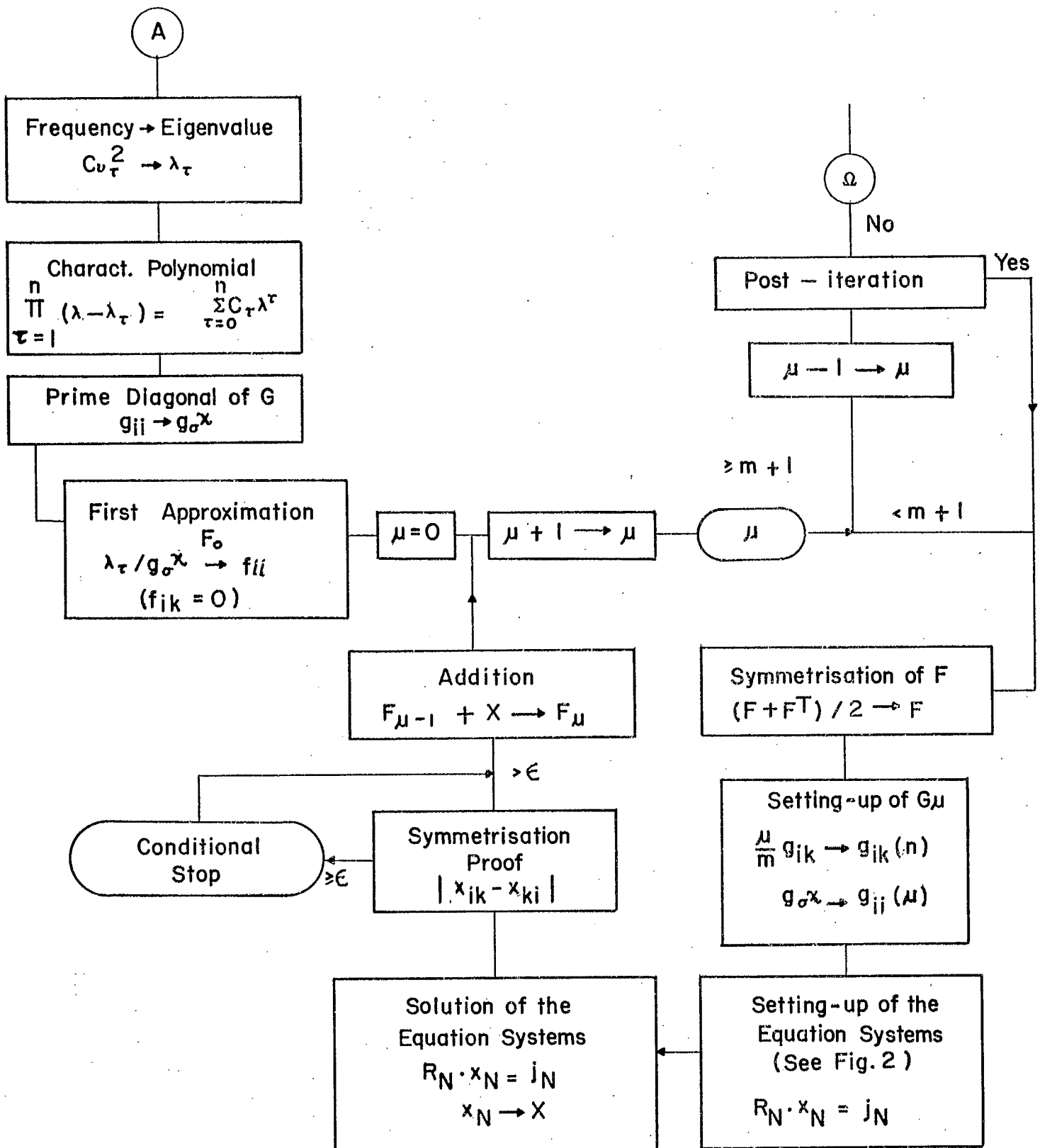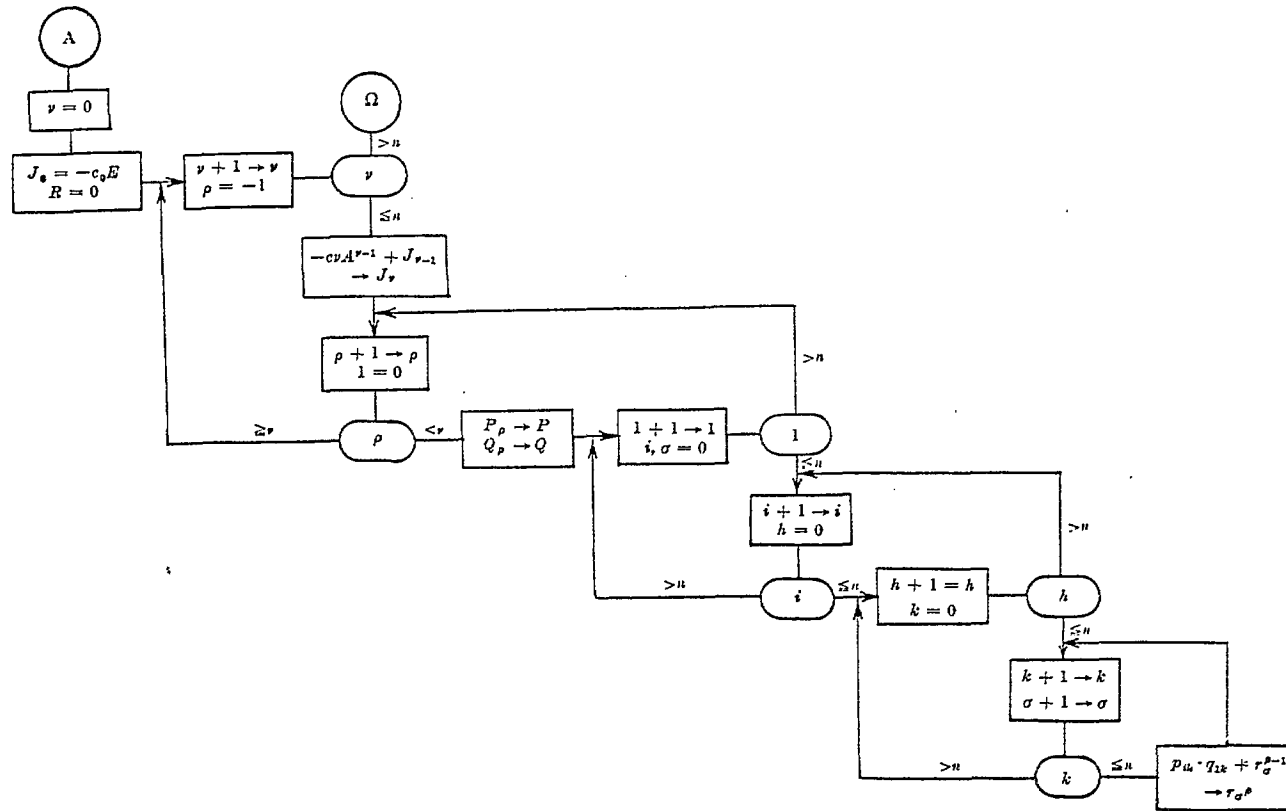
Fig. 2. Setting-up of Equation Systems $R_N \cdot x_N = j_N$.

exists only in the ER 56 machine code, but a reprogramming in Algol code will be undertaken shortly.

EXAMPLES OF MOLECULES CALCULATED

A few calculation results should serve as proof of the serviceability of the method. A series of unsymmetrical bent molecules, which possessed three normal vibrations of one type, were investigated. The geometric data and vibrations frequencies are given in Table 1.

From these were obtained the force constants listed in Table 2. The constants for NSF and the valence-force constants $f_R(NO)$ of the nitrosyl halides agree with the values quoted in the literature [16, 17, 19, 20]. On the other hand, the constants $f_r(NX)$ are throughout found to be higher. This is due to the coupling magnitudes $f_{r\alpha}$, which were neglected in all the previous calculations made.

The usability of the procedure is also shown by the results for ONCℓ with ^{14}N and ^{15}N. The deviation between the separately calculated force constant expressions amounts only to circa 1% with the diagonal terms and up to 10% in the coupling constants. With an averaged force constant expression, the frequencies reproduced for $O^{14}NC\ell$ and $O^{15}NC\ell$ are:

$$O^{14}NC\ell: 1800.9 \; ; \; 604.6 \; ; \; 332.4 \; cm^{-1}.$$
$$O^{15}NC\ell: 1768.0 \; ; \; 589.7 \; ; \; 330.6 \; cm^{-1}.$$

The error is less than 1 per cent.

Force constant expressions for molecules of the type YZX$_3$ are also quoted. Table 3 contains the geometric data and vibration frequencies used. Because of the surplus co-ordinates in the species A_1, too few defining values are obtained to be able to specify the force constants for the linear co-ordinates. In Table 4 the force constants for the symmetry co-ordinates are presented, while in Table 5 are reproduced only the valence-force constants calculated from inner co-ordinates, together with comparative values from the literature [18, 20, 22, 24, 25] . (All constants in mdyne/Å).

The valence-force constants for NSF and OPF$_3$ lie in the ranges which have previously been obtained by other methods of calculation. With FCℓ0$_3$, for which no previous calculation was available, there is found an FCℓ-force constant of the order of the value for CℓF$_3$ (3.93 mdyne/Å [2G]), while the Cℓ0-force constant equals the value in C$\ell_2$0$_7$ (9.10 mdyne/Å [20]). This agrees with the value expected from the standpoint of bond theory. Reasonable values were found throughout for the deformation and interaction magnitudes.

TABLE 1

	ONF	$O^{14}NC\ell$		$O^{15}NC\ell$	ONBr	NSF
r_{ZX} (A)	1.52	1.95			2.14	1.646
r_{ZY}	1.13	1.14			1.15	1.44
$\measuredangle$ XZY	110°	116°			117°	116°52
ν_1 cm^{-1}	1844	1800		1769	1801	1372
ν_2	765.9	604.7		589.7	542	640
ν_3	521	332.4		330.6	265	366
Lit.	[15]	[16]		[16]	[17]	[18]

TABLE 2

	ONF	$O^{14}NC\ell$	$O^{15}NC\ell$	ONBr	NSF
f_R	14.833	14.133	14.157	14.157	10.721
f_r	2.791	2.246	2.227	2.210	2.884
f_α	0.751	0.300	0.302	0.204	0.410
f_{rR}	0.121	0.067	0.060	0.073	0.008
$f_{R\alpha}$	0.143	0.064	0.060	0.052	0.014
$f_{r\alpha}$	0.278	0.131	0.128	0.115	0.023

All data in mdyne/Å.

TABLE 3

	NSF$_3$	OPF$_3$	FCℓO$_3$
r_{ZX}(A)	1.55	1.53	1.45
r_{ZY}	1.42	1.45	1.66
$\angle$XZX	94°2′	102°30′	109°27′
A$_1$ ν_1	1515	1395	715
ν_2	775	875	1061
ν_3	521	473	549
E ν_4	811	986	1314
ν_5	429	337	588
ν_6	342	485	408
Lit.	[18] [21]	[22]	[23]

TABLE 4

Force Constants

	A$_1$			E		
NSF$_3$	12.549	0.124	-0.172	4.257	-0.064	0.049
		4.957	0.224		0.841	0.009
			1.402			0.296
OPF$_3$	11.380	0.305	-0.135	5.916	-0.045	0.120
		7.202	0.090		0.443	0.001
			0.593			0.659
FCℓO$_3$	3.912	-0.033	-0.438	9.800	-0.093	0.044
		8.641	0.126		1.027	0.002
			1.815			0.618

TABLE 5
Valence-Force Constants

	$f_r(ZX)$	Lit.	$f_R(ZY)$	Lit.
NSF_3	4.49	4.8 - 5.6	12.55	12.3 - 12.4
OPF_3	6.35	4.8 - 6.3	11.38	9.9 - 11.4
$FC\ell0_3$	9.41	-	3.91	-

TABLE 6
Force Constants

		f_r	f_{rr}	$f_{ra} - f_{ra}'$	$f_a - f_{aa}$
BF_3	Lit. [28]	7.15-7.88	0.47-0.84	-0.25 to -0.64	0.50-0.53
	O.T. [29]	7.148	0.838	-0.319	0.528
	This work	7.287	0.768	-0.328	0.519
$BC\ell_3$	Lit.	1.87-3.97	0.33-1.01	-0.29 to +0.14	0.23-0.38
	O.T.	3.293	0.799	0.030	0.274
	This work	3.808	0.442	-0.205	0.227
BBr_3	Lit.	2.74-3.43	0.10-0.46	-0.14 to -0.29	0.18-0.22
	O.T.	2.951	0.402	-0.137	0.212
	This work	3.172	0.247	-0.232	0.186
BI_3	Lit.	2.054	0.323	-0.035	0.151
	O.T.	1.877	0.411	0.021	0.177
	This work	2.403	0.147	-0.147	0.128

SOLUTION OF DETERMINANTS WITH n = 2

As was shown previously, the inhomogeneous system of equations (9) is soluble only for $n \geqslant 3$, and this could be an inconvenient limitation of the method. However, it has been shown in practice that,in the case of n = 2, solutions can be obtained by an artifice. Either, two determinants of degree n = 2 are combined, or one such is combined with a single equation, as shown in Figure 3.

$$
\begin{vmatrix}
a_{11} - \lambda & a_{12} & 0 & 0 \\
a_{21} & a_{22} - \lambda & 0 & 0 \\
0 & 0 & a_{33} - \lambda & a_{34} \\
0 & 0 & a_{43} & a_{44} - \lambda
\end{vmatrix} = 0
$$

$$
\begin{vmatrix}
a_{11} - \lambda & 0 & 0 \\
0 & a_{22} - \lambda & a_{23} \\
0 & a_{32} & a_{33} - \lambda
\end{vmatrix} = 0
$$

Figure 3.

The resulting determinants of degree n = 4 and 3 can be solved for the force constants by the method described. It is true that values are obtained for the terms of the zero-blocks, but, in contrast with the true force constants, they are small enough to be disregarded ($<10^{-4}$).

The boron halides BX_3 are quoted as examples of this kind of application. With these molecules, the introduction of the ^{10}B isotope data leads to no unique force constant expressions, because the isotope effect is too small [27]. Table 6 reproduces the force constants obtained by averaging the separate ^{10}B and ^{11}B values. For comparison the literature values [28] are presented in condensed form, except that the most recent results [29] receive separate mention.

In each case the calculated force constants lie within the expected range and also in that of the other authors. On the other hand,the values of Orville-Thomas et al. [29] show marked differences. While by our calculations the interaction constants $f_{r\alpha}-f_{r\alpha}$, except for a small deviation

with BBr_3, show a uniform shift, but, especially as required by Mills [9], are always negative, with Orville-Thomas marked differences occur, even changes in sign in the series. In our results, also, the bond degree calculated by the Siebert [26] formula shows - after a large jump from the fluorine to the chlorine compound - a regular decrease, while the bond degrees arrived at from the Orville-Thomas force constants show a large jump from BF_3 to BCl_3, then a small increase to BBr_3, before, at BI_3, an almost unitary bonding is reached at the lowest value (cf. Table 7).

CONCLUSION

The procedure described in this work for the calculation of force constants takes into account all the coupling terms of the general valence-force field, without additional data being necessary other than the normal vibrations and the molecular geometry. In our view this represents a significant advance over the previously much-used simplified potential functions, and extends the applicability of force-constant calculations.

As well as the choice of a suitable molecular model and a meaningful assignment, both of which are indeed assumptions in the calculation of force constants, the choice of the first approximation, which is made here from the viewpoint of the characteristic vibration, is the only additional assumption. For weakly coupled systems, at least, this should be an acceptable approximation, but even a number of molecules with strong coupling have been successfully calculated by the method described.

In what manner the interaction terms of the F-matrix are built up, is not ascertainable without further data, because of the complicated mathematical relationships. Work on this point is, however, in progress. Investigations are also being carried out into how far the potentials obtained by our method agree with other force fields, especially with the general valence-force field (GVFF) produced with the aid of isotope- and rotation-interaction data. The results to date indicate that the answer lies in the direction of a modified valence-force field (MVFF) developed from the GVFF.

The complete argument and detailed proof of the so-called "Stepwise-Coupling Procedure" (30) is to be found in reference 13. Other initial starting solutions are employed in reference 30. In (31) there is given a comprehensive description, which includes the form suitable for computer programming, the working method, and numerous additional examples. The force constants of over 100 molecules and ions, calculated by the stepwise-coupling procedure and arranged according to type and symmetry group, are compiled (33) in Siebert's book (32). A procedure described in (34), the so-called "Nearest-solution Procedure", permits very simple interpretation by a closely related mininum principle.

TABLE 7

	$f_1[26]$	ORVILLE-THOMAS [29]		This work	
		f_r	N	f_r	N
BF_3	5.06	7.15	1.29	7.29	1.31
BCl_3	2.84	3.29	1.11	3.81	1.24
BBr_3	2.46	2.95	1.14	3.17	1.21
BI_3	1.93	1.88	0.98	2.41	1.17

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