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Utilization of Symmetry in Non-Linear Equations of the Inverse Vibrational Problem

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A new general technique is developed for solving the non-linear equations obtained from the secular equation in the inverse vibrational problem. The off-diagonal force constant elements are determined first and the resulting non-linear equations of various degrees in the secular equation are solved by Newton-Raphson's iterative method. This involves the computation of values of the functions and their derivatives for which the new technique exploiting the symmetry in the equations is utilised. The iterative method involves mainly the calculation of the values of the functions and their derivatives at the corresponding points. Here a new general procedure is developed to obtained these values of functions and derivatives using the symmetry in the secular equation.

INTRODUCTION

The determination of n(n + 1)/2 force constants from n fundamental frequencies is one of the major problems in the field of vibrational spectroscopy. Though the exact solution of this problem is indeterminate, the use of additional data like isotopic frequency shifts or Coriolis coupling constants leads to some effective values of force constants in molecules of high symmetry. Some mathematically constrained[1-6] methods have also been developed for this. Isotani[7] has introduced a method where the off-diagonal force constant element, F_{ij} is given in terms of the corresponing G_{ii}, G_{jj}, G_{ij}, λ_i and λ_j. This is derived as consequence of the studies of experimental force constants of simple molecules of the types of molecules like planar XY_2, planar XY_3, pyramidal XY_3 and tetrahedral XY_4 and their correlation with the mass coupling parameter.

For a third order problem, the off-diagonal F_{ij} is determined by considering the corresponding i and j moles only and the diagonal values F_{ii} and F_{jj} are obtained later using the secular equation considering this to be the second order problem. Similar calculations for all F_{ij} leads to two values for each f_{ii} and one set for F_{ij}. These values of F_{ii} appear close together and their average value is obtained as an approximate solution. In the same way, this procedure may be extended for higher order problems as well.

The new technique

In an $n \times n$ problem, it is found that the elements F_{ii} obtained $(n-1)$ times were all consistently close enough to justify the taking of the average. The values of F_{ii} together with the off-diagonal F_{ij} values satisfy the secular equations only approximately. To determine perfect sets of solutions, the F_{ij} values are fixed as obtained from Isotani's method and substituted into the secular equation to obtain 'n' nonlinear equations of varying degrees in n unknown elements F_{ii}. Newtons–Raphson's iterative method is applied to solve for the F_{ii} values. Here the average values of F_{ii} calculated earlier are used as initial set for the iterative procedure.

Newton– Raphson method consists in assuming a initial set of values for unknowns and substituting them in the non-linear equations and checking how far they satisfy them. The increments for each unknown is then calculated using expressions involving the evaluation of determinants consisting of values of functions of equations and their derivatives with respect to the unknowns. These increments are then added to the corresponding unknowns and new set of values for unknowns are obtained and the process of putting them back into the equations is continued followed by the calculation of further increments until the required accuracy is obtained.

So the iterative method involves mainly the calculation of the values of the functions and their derivatives at the corresponding points. Here a new general procedure is developed to obtain these values of functions and derivatives using the symmetry in the secular equation. This is explained below.

Second order problem

In a second order problem (2×2 case) the secular equation leads to the following two equations, one of first degree and the other of second degree in F_{ij}.

$$f_1 = H_{11} + H_{22} - (\lambda_1 + \lambda_2) = 0$$

$$f_2 = \begin{vmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{vmatrix} - \lambda_1\lambda_2 = 0$$

Here $H = GF$ and $|GF - \lambda E| = 0$ becomes $|H - \lambda E| = 0$. The elements of H are given by

$$H_{11} = G_{11}F_{11} + G_{12}F_{12} \qquad H^{12} = G^{11}F^{12} + G^{12}F^{22}$$

$$H_{21} = G_{12}F_{11} + G_{22}F_{12} \qquad H_{22} = G_{12}F_{12} + G_{22}F_{22}$$

Using these expressions for H_{ij} the derivatives are

$$\frac{\partial f_1}{\partial F_{11}} = G_{11} \qquad \frac{\partial f_1}{\partial F_{22}} = G_{22}$$

$$\frac{\partial f_2}{\partial F_{11}} = \begin{vmatrix} G_{11} & H_{12} \\ G_{12} & H_{22} \end{vmatrix} \text{ and } \frac{\partial f_2}{\partial F_{22}} = \begin{vmatrix} H_{11} & G_{12} \\ H_{21} & G_{22} \end{vmatrix}$$

Third order problem

In the third order problem (3 × 3 case) the secular equation leads to the following equations.

$$f_1 = H_{11} + H_{22} + H_{33} - (\lambda_1 + \lambda_2 + \lambda_3) = 0$$

$$f_2 = \begin{vmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{vmatrix} + \begin{vmatrix} H_{11} & H_{13} \\ H_{31} & H_{33} \end{vmatrix} + \begin{vmatrix} H_{22} & H_{23} \\ H_{32} & H_{33} \end{vmatrix} - (\lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_3\lambda_1) = 0$$

$$f_3 = \begin{vmatrix} H_{11} & H_{12} & H_{13} \\ H_{21} & H_{22} & H_{23} \\ H_{31} & H_{32} & H_{33} \end{vmatrix} - \lambda_1\lambda_2\lambda_3 = 0$$

The elements of H are given by

$$H_{11} = G_{11}F_{11} + G_{12}F_{12} + G_{13}F_{13}$$
$$H_{12} = G_{11}F_{12} + G_{12}F_{22} + G_{13}F_{23}$$
$$H_{13} = G_{11}F_{13} + G_{12}F_{23} + G_{13}F_{33}$$
$$H_{21} = G_{12}F_{11} + G_{22}F_{12} + G_{23}F_{13}$$
$$H_{22} = G_{12}F_{12} + G_{22}F_{22} + G_{23}F_{23}$$
$$H_{23} = G_{12}F_{13} + G_{22}F_{23} + G_{23}F_{33}$$
$$H_{31} = G_{13}F_{11} + G_{23}F_{12} + G_{33}F_{13}$$
$$H_{32} = G_{13}F_{12} + G_{23}F_{22} + G_{33}F_{23}$$
$$H_{33} = G_{13}F_{13} + G_{23}F_{23} + G_{33}F_{33}$$

The derivatives are

$$\frac{\partial f_1}{\partial F_{11}} = G_{11} \qquad \frac{\partial f_2}{\partial F_{22}} = G_{22} \qquad \frac{\partial f_3}{\partial F_{33}} = G_{33}$$

$$\frac{\partial f_2}{\partial F_{11}} = \begin{vmatrix} G_{11} & H_{12} \\ G_{12} & H_{22} \end{vmatrix} + \begin{vmatrix} G_{11} & H_{13} \\ G_{13} & H_{33} \end{vmatrix}$$

$$\frac{\partial f_2}{\partial F_{22}} = \begin{vmatrix} H_{11} & G_{12} \\ H_{21} & G_{22} \end{vmatrix} + \begin{vmatrix} G_{22} & H_{23} \\ G_{23} & H_{33} \end{vmatrix}$$

$$\frac{\partial f_2}{\partial F_{33}} = \begin{vmatrix} H_{11} & G_{13} \\ H_{31} & G_{33} \end{vmatrix} + \begin{vmatrix} H_{22} & G_{23} \\ H_{32} & G_{33} \end{vmatrix}$$

$$\frac{\partial f_3}{\partial F_{11}} = \begin{vmatrix} G_{11} & H_{12} & H_{13} \\ G_{12} & H_{22} & H_{23} \\ G_{13} & H_{32} & H_{33} \end{vmatrix}; \quad \frac{\partial f_3}{\partial F_{22}} = \begin{vmatrix} H_{11} & G_{12} & H_{13} \\ H_{21} & G_{22} & H_{23} \\ H_{31} & H_{23} & H_{33} \end{vmatrix}; \quad \frac{\partial f_3}{\partial F_{33}} = \begin{vmatrix} H_{11} & H_{12} & G_{13} \\ H_{21} & H_{22} & G_{23} \\ H_{31} & H_{32} & G_{33} \end{vmatrix}$$

The general n × n problem

It may be observed that there is a certain uniformity or symmetry in the functions and their derivatives which can be utilized to calculate their values. The function f_i consists of the difference between the sum of all the principal minors of order i of the matrix H and a similar sum for a diagonal matrix Λ having λ_i on their diagonals. The sum of all the principal minors of various orders can be directly obtained from the characteristic equation of the corresponding matrices.

The derivative of f_i with respect to F_{kk} involves the sum of all principal minors of order i involving H'_{kk} only, where H′ is the matrix obtained by replacing the *k*th column of H by the *k*th column of G–matrix. To obtain the derivative of f_i with respect to $F_{kk'}$ the *k*th column in H– matrix is replaced by the *k*th column of G –matrix and the sum of the principal minors of order i is determined and from this the sum of the principal minors of order i in a truncated H –matrix (leaving out the *k*th row and *k*th column) is subtratced.

The advantage of this general procedure is that it can be applied directly to a general *n*th order problem and there is no limitation on its extension to a general n × n case.

RESULTS AND DISCUSSION

Some examples of the solution of force constants obtained by this new technique coupling Isotani's method with Newton-Raphson iterative procedure are given in Table 1. Here in Table 1 the values of F_{ij} calculated by the method of Isotani by reducing to 3 different second order problems in 3 × 3 A′ species in HOF and ten different second order problems in 5 × 5 A′ species in HCOF are given. The average values of F_{ii} are also listed with the final converged values of solution of secular equations. Table-2 contains observed and calculated frequencies of HOF and HCOF.

The valence force constants determined in the present work are given along with literature values in Tables 3 and 4. The stretching and bending force constants agree well with literature values. The high values of C=O stretching force constants indicate the double bonded nature of C=O in this type of molecules. In general the bending force constants are always less than stretching force constants. The above general procedure is applicable to other methods also where constants involving off diagonal elements of force constants are introduced. The procedure can also be modified suitably to solve n equations in n unknowns, whether diagonal or off-diagonal. Possibility is also there for the extension to solve higher order problems involving isotopically substituted molecules.

To solve higher order problems, vibrational frequencies of additional isotopically substituted molecules are also combined. For example, in a fourth order problem, three isotopically substituted molecules are considered with totally 10 force constants to be determined. Corresponding to each molecule four equations, of degrees 1,2,3 and 4 are obtained from the secular equations. The three molecules yield 10 equations in 10 unknowns F_{ii} and F_{ij}, three each of degrees 1,2 and 3 and one of degree 4. (The last equation $|F||G| = |\Lambda|$ yields indentical equations of degree four because of the product rule). Newton-Raphson method may be used to solve these 10 equations in 10 unknowns with the values of functions and derivatives determined by the new procedure explained earlier. The derivatives with respect to off –diagonal elements may be derived in a similar mannar.

TABLE 1
SYMMETRIZED FORCE CONSTANTS OF A' SPECIES OF HOF AND HCOF (10^2 N/m)

Molecules	F_{11}	F_{22}	F_{33}	F_{44}	F_{55}	F_{ij}
HOF	7.15	4.25	—	—	—	-1.22
	7.16	—	0.66	—	—	0.27
	—	4.17	0.65	—	—	0.18
Mean values	7.16	4.21	0.66	—	—	—
Final values	7.16	4.39	0.66	—	—	—
HCOF	4.81	13.82	—	—	—	0.71
	4.84	—	0.42	—	—	-0.17
	4.89	—	—	4.97	—	0.50
	4.81	—	—	—	0.53	0.08
	—	13.92	0.42	—	—	0.38
	—	13.82	—	5.49	—	1.25
	—	13.44	—	—	0.55	0.04
	—	—	0.40	5.50	—	-0.37
	—	—	0.42	—	0.51	-0.05
	—	—	—	5.10	0.59	0.35
Mean values	4.84	13.74	0.41	5.26	0.54	—
Final values	4.81	14.14	0.45	5.40	0.96	—

TABLE 2
OBSERVED AND CALCULATED FREQUENCIES OF HOF AND HCOF (cm^{-1})

Mode	Stretch	Stretch	Stretch	bend	bend
		HOF			
Frequencies	ν_1(O–H)	ν_2(O–F)	—	ν_3(H$\hat{O}$F)	—
Obs. values	3578.5	889.0		1354.0	
cal. values	3578.5	889.0		1354.0	
		HCOF			
Frequencies	ν_1(C–F)	ν_2(C=O)	ν_3(C–H)	ν_4(F$\hat{C}$H)	ν_5(F$\hat{C}$O)
Obs. values	2976.0	1818.5	1064.0	1343.8	661.0
cal. values	2976.0	1818.4	1064.0	1348.7	666.1

TABLE 3
VALENCE FORCE CONSTANTS OF HOF (10^2 N/m)

$f_{(O-H)}$	$f_{(O-F)}$	$f_{(H\hat{O}F)}$	Ref.
7.16	4.39	0.66	present work
7.15	4.18	0.66	(8)

TABLE 4
VALENCE FORCE CONSTANTS OF HOF (10^2 N/m)

$f_{(C-F)}$	$f_{(C-O)}$	$f_{(C-H)}$	$f_{(F\hat{C}H)}$	$f_{(F\hat{C}O)}$	Ref.
4.81	14.14	5.40	0.41	1.30	present work
4.37	14.26	5.25	0.39	1.31	(9)

Thus the procedure outlined earlier may be extended to solve the general case of solving for force constants with the use of additional data of isotopic frequencies in any higher order vibrational problem. The magnitude of calculation involved increases with 15 non-linear equations in 15 force constants in a fifth order problem and with 21 equations in 21 force constants in a sixth order problem.

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