ACTA CHEMICA SCANDINAVICA 15 (1961) 483–486

Vibrational Mean-Square Amplitude Matrices

XIII. Remarks on Computing Mean-Square Amplitude Matrices

Y. MORINO* and S. J. CYVIN

Institutt for teoretisk kjemi, Norges tekniske høgskole, Trondheim, Norway

The previously evaluated secular equations involving the mean-square amplitude matrix (Σ) have been extended to

$$|\Sigma G^{-1} (GF)^m - \delta\lambda^m E| = 0$$

where $m = 0, \pm 1, \pm 2, \ldots$. For the negative values of m, $(GF)^m$ must be interpreted as $(F^{-1} G^{-1})^{-m}$. It is pointed out that in cases where the F matrix is known, the extended secular equations give sufficient relations to compute the complete Σ matrix in the general case of polyatomic molecules.

The mean-square amplitude matrix Σ in the theory of small harmonic vibrations is defined in terms of its elements by

$$\Sigma_{ii} = \langle S_i^2 \rangle, \ \Sigma_{ij} = \langle S_i S_j \rangle \quad (1)$$

where S_i and S_j denote some arbitrary internal displacement coordinates. The following secular equations have previously been deduced for the Σ matrix.

$$|\Sigma G^{-1} - \delta E| = 0 \quad (2)$$

$$|\Sigma F - \delta\lambda E| = 0 \quad (3)$$

For details of the theory and further explanation of the symbols, see [1,2]. The applicability of these secular equations in practical computations has been discussed previously [2,3]. In the present article some additional remarks will be given as to the methods of computing the Σ matrix in the case when the force constants (F matrix elements) are known. In this connection an extension of the secular eqns. (2) and (3) will be communicated.

L MATRIX METHOD

The well-stablished method of computing mean-square amplitudes of vibration or Σ matrix elements in general may be termed the L matrix method. If

* Permanent address: Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-Ku, Tokyo, Japan.

the F matrix is known, the noımal coordinate transformation matrix L ($S = LQ$) is obtainable according to

$$GFL = L\Lambda \quad (4)$$

by the generally adopted normal coordinate treatment proposed by Wilson [4]. Hence the Σ matrix may be computed according to [1–3]

$$\Sigma = L\Delta\tilde{L} \quad (5)$$

SECULAR EQUATION METHOD

In the special case of linear triatomic molecules another method of calculating the mean-square amplitude quantities has been described [5]. In this case the relations obtained from the secular eqns. (2) and (3) were given. The four resulting equations contained three independent equations sufficient for calculating the three unknown quantities. This procedure of calculating mean-square amplitude quantities, which does not involve the computation of the L matrix, may be extended to the general case of polyatomic molecules. The extended secular equantions for the Σ matrix given in the next paragraph, must always provide a sufficient number of independent equations for computing all of the Σ matrix elements. The method involves namely completely the same information as regard to the vibrational problem as given alternatively by the L matrix.

EXTENSION OF THE SECULAR EQUATIONS

The two given secular eqns. (2) and (3) follow from the matrix relations

$$\Sigma G^{-1}L = L\,\Delta \quad (6)$$

and

$$\Sigma FL = L\Delta\Lambda \quad (7)$$

respectively. From eqn. (7) one has $\Sigma F = L\Delta\Lambda L^{-1}$, which may be combined with $GF = L\Lambda L^{-1}$, obtained from eqn. (4). From the resulting relation $\Sigma FGF = L\Delta\Lambda^2 L^{-1}$ it is obtained

$$\Sigma FGFL = L\Delta\Lambda^2 \quad (8)$$

The procedure may be repeated and leads to the general equation

$$\Sigma F(GF)^n L = L\Delta\Lambda^{n+1} \quad (9)$$

By putting $m = n + 1$ eqn. (9) may be written

$$\Sigma G^{-1}(GF)^m L = L\Delta\Lambda^m \quad (10)$$

This equation contains (6) and (7) as special cases for $m = 0$ ($n = -1$) and $m = 1$ ($n = 0$), respectively. The secular equations corresponding to eqn. (10) read

$$|\Sigma G^{-1}(GF)^m - \delta\lambda^m E| = 0 \quad (11)$$

Negative values of m may also have a meaning, if eqn. (10) for m = —p is interpreted as

$$\Sigma G^{-1}(F^{-1}G^{-1})^{p}L = L\Lambda(\Lambda^{-1})^{p} \tag{12}$$

In the general case with the number of internal coordinates equal to N, the number of unknown Σ matrix elements is $\frac{1}{2}N(N + 1)$. The number of equations obtained from one of the secular equations is N. Hence for computing the complete Σ matrix we must take so many of the secular equations (t) to make

$$tN \geqq \tfrac{1}{2}N(N + 1) \tag{13}$$

From the tN equations it is possible to select a set being sufficient for computing the complete Σ matrix. The excess equations must evidently be dependent on the selected set. Consequently it is possible to calculate all of the Σ matrix elements without computing the L matrix.

EXAMPLE

The bent symmetrical XY_2 molecular model will be considered. The relations for the Σ matrix elements (based on symmetry coordinates) obtained from eqn. (2) or eqn. (11) with m = 0 have been reported previously [2,6]. For m = 1 one has with the same notation as used in Ref.[6]

$$\delta_1\lambda_1 + \delta_2\lambda_2 = \Sigma_1F_1 + \Sigma_2F_2 + 2\Sigma_{12}F_{12} \tag{14}$$

$$\delta_1\lambda_1\delta_2\lambda_2 = (\Sigma_1\Sigma_2 - \Sigma_{12}^2)(F_1F_2 - F_{12}^2) \tag{15}$$

$$\delta_3\lambda_3 = \Sigma_3F_3 \tag{16}$$

For m = 2 it has been found

$$\delta_1\lambda_1^2 + \delta_2\lambda_2^2 = \Sigma_1[F_1^2(2\mu_X\cos^2A + \mu_Y) + 2F_{12}^2(2\mu_X\sin^2A + \mu_Y) - 2\sqrt{2}F_1F_{12}\mu_X\sin2A] + \Sigma_2[F_{12}^2(2\mu_X\cos^2A + \mu_Y) + 2F_2^2(2\mu_X\sin^2A + \mu_Y) - 2\sqrt{2}F_2F_{12}\mu_X\sin2A] + 2\Sigma_{12}[F_1F_{12}(2\mu_X\cos^2A + \mu_Y) + 2F_2F_{12}(2\mu_X\sin^2A + \mu_Y) - \sqrt{2}(F_1F_2 + F_{12}^2)\mu_X\sin2A] \tag{17}$$

$$\delta_1\lambda_1^2\delta_2\lambda_2^2 = 2(\Sigma_1\Sigma_2 - \Sigma_{12}^2)(F_1F_2 - F_{12}^2)(2\mu_X + \mu_Y)\mu_Y \tag{18}$$

$$\delta_3\lambda_3^2 = \Sigma_3F_3^2(2\mu_X\sin^2A + \mu_Y) \tag{19}$$

To establish these equations, only the F and G matrices have been employed, not the inverse G matrix. The Σ matrix elements of the A_1 species (*viz.* Σ_1, Σ_2 and Σ_{12}) may be calculated from eqns. (14), (15), and (17). Eqn. (18) is equivalent to eqn. (15). The identity of these equations is evident from the relation [*cf.* eqn. (6) of Ref.[6]]

$$\lambda_1\lambda_2 = 2(F_1F_2 - F_{12}^2)(2\mu_X + \mu_Y)\mu_Y \tag{20}$$

It should be noted too that the linear equation for Σ_1, Σ_2 and Σ_{12} corresponding to m = 0, *viz.* eqn. (8) of Ref.[6], is linearly dependent on eqns. (14) and (17).

CONCLUSION

The new method of computing the Σ matrix outlined in the present article is mainly of theoretical interest. For practical calculations the conventional $\mathbf{L}$ matrix method seems to be the most convenient one in the majority of special cases. But still the extended secular equations may give valuable relations of practical use between force constants and mean-square amplitude quantities, even in the cases where the secular equation method for computing the complete Σ matrix would be too complicated.

REFERENCES

1. Cyvin, S. J. *Spectrochim. Acta* **15** (1959) 828.
2. Cyvin, S. J. *Acta Polytechn. Scand.* (279/1960) Ph No. 6, Chapter 4.
3. Cyvin, S. J. *Acta Chem. Scand.* **13** (1959) 2135.
4. Wilson, E. B., Jr. *J. Chem. Phys.* **7** (1939) 1047; **9** (1941) 76; Wilson, E. B., Jr., Decius, J. C. and Cross, P. C. *Molecular Vibrations*, McGraw-Hill, New York 1955.
5. Cyvin, S. J. *Spectrochim. Acta* **15** (1959) 958.
6. Cyvin, S. J. *Acta Chem. Scand.* **13** (1959) 1400.

Received September 30, 1960.