

Short Communications

New Secular Equations in the Problem of Molecular Vibrations

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The well-known secular equation in the problem of harmonic vibrations of polyatomic molecules may be put in the form ^{1,2}

$$|GF - E\lambda| = 0 \quad (1)$$

Here G and F are the energy matrices introduced by Wilson,¹ and E is the identity matrix. The G matrix is composed of the atomic masses and occasionally the structural parameters of the molecule, the F matrix containing the force constants included the interaction terms. Eqn. (1) yields the familiar relations connecting the force constants with the normal frequencies of the molecule. The values of λ are proportional to the squares of the frequencies (ν) according to the equation

$$\lambda_k = 4\pi^2\nu_k^2 \quad (2)$$

It should be emphasized that the number of normal frequencies of a polyatomic molecule in most cases is not sufficient for the complete determination of the harmonic force field. Therefore usually a simplified force field, e.g. a valence force field is assumed, or additional information, e.g. normal frequencies from isotopically substituted molecules, or force constant values from related molecules, are utilized.

Let now S be a column matrix consisting of a complete set of internal displacement coordinates and connected with the vibrational normal coordinates (Q) through the linear transformation

$$S = LQ \quad (3)$$

The following relations involving the transformation matrix L exist.

$$\widetilde{L}FL = \Lambda \quad (4)$$

$$G = L\widetilde{L} \quad (5)$$

Here \sim denotes the transpose of a matrix, and Λ is a diagonal matrix with the elements λ_k given by eqn. (2). The symbol $\langle \rangle$ will be used to indicate that the mean value of each element of the matrix in question has been taken, and the matrix

$$\Sigma = \langle S\widetilde{S} \rangle \quad (6)$$

will be considered. The elements on its main diagonal, viz.

$$\Sigma_{ii} = \langle S_i^2 \rangle \quad (7)$$

have been called the "mean-square amplitudes of vibration" and are of considerable interest in molecular structure studies (see, e.g. Refs.³⁻⁵).

The matrix Σ of eqn. (6) may be computed by means of the L matrix according to

$$\Sigma = L \Delta \widetilde{L} \quad (8)$$

where $\Delta = \langle Q\widetilde{Q} \rangle$ is a diagonal matrix with the elements

$$\Delta_k = (h/8\pi^2\nu_k)\coth(h\nu_k/2kT) \quad (9)$$

If the F matrix has been established, and with the knowledge of the normal frequencies, the L matrix may be obtained according to eqn. (1) by means of the standard method of characteristic vectors applied to the GF matrix. This is the method for computing mean-square amplitudes of vibration which has been evaluated by Morino *et al.*⁴

The progress in gas electron diffraction techniques has made it possible to produce experimental values of root-mean-square

amplitudes of vibration,⁵ and it has been proposed to utilize such measurements in force constant determinations. It seems to be doubtful whether the present electron diffraction data of root-mean-square amplitudes are of sufficient accuracy to be of practical value for this purpose. Nevertheless, we may hope that the accuracy still will increase in the future. This discussion indicates the desire of evaluating a method for obtaining some information about the force constants from given values of root-mean-square amplitudes of vibration. The above mentioned method of Morino *et al.*⁴ is in practice not convenient for such computations.

From eqns. (5) and (8) a new secular equation may be derived and written in the form

$$|\Sigma G^{-1} - E\Delta| = 0 \quad (10)$$

This equation makes it possible to treat the mean-square amplitudes of vibration similarly to the treatment of force constants. It may be applied to establish relations connecting the normal frequencies and the mean-square amplitudes including the interaction terms, *i.e.* the off-diagonal Σ matrix elements. Here again the number of normal frequencies is usually not sufficient for the complete determination of the Σ matrix, but approximations may be performed, and additional information about the mean-square amplitudes may be utilized. This method represents a new approach to the calculation of mean-square amplitudes of vibration from spectroscopic data, being different from the method of Morino *et al.*⁴ Furthermore, if the complete Σ matrix could be established, it would be possible to determine the L matrix by the method of characteristic vectors applied to the ΣG^{-1} matrix. In consequence, the potential energy matrix could be obtained from the equation *

$$F = \tilde{L}^{-1} \wedge L^{-1} \quad (11)$$

being a modification of eqn. (4).

Still another secular equation will be reported, *viz.*

$$|\Sigma F - E\lambda\Delta| = 0 \quad (12)$$

which may be deduced from eqns. (4) and

* The L^{-1} matrix may be computed directly by means of a modified form of equation (10), *viz.* $|G^{-1}\Sigma - E\Delta| = 0$.

(8). According to eqns. (2) and (9), the characteristic values of the ΣF matrix are

$$\lambda_k \Delta_k = \frac{1}{2} h\nu_k \coth(h\nu_k/2kT) \quad (13)$$

Eqn. (12) yields relations containing the elements from both of the matrices Σ and F . These relations will be useful in combination with the relations obtained from (1) and (12) if it is desirable to apply some information about the Σ matrix elements for determination of the elements of the F matrix, and *vice versa*. Accordingly, such computations may be performed without determination of the L matrix.

It should be pointed out that the new secular eqns. (10) and (12) will factorize in precisely the same manner as the ordinary secular eqn. (1) if a set of *symmetry* coordinates is chosen.

Finally an isotope rule for mean-square amplitudes of vibration will be reported. The ordinary product rule for isotopically substituted molecules as derived from eqn. (1) may be written in the form¹

$$\Pi_i(v_i/v_i^*) = |G|^{1/2}/|G^*|^{1/2} \quad (14)$$

where the quantities of the isotopically substituted molecule are identified by an asterisk. Using the analogous notation, one obtains from eqn. (12)

$$|\Sigma|/|\Sigma^*| = \Pi_i \frac{v_i \coth(h\nu_i/2kT)}{v_i^* \coth(h\nu_i^*/2kT)} \quad (15)$$

If the mean-square amplitudes at the absolute zero are considered, and the corresponding matrices are identified by the subscript 0 , one obtains

$$|\Sigma_0|/|\Sigma_0^*| = \Pi_i(v_i/v_i^*) = |G|^{1/2}/|G^*|^{1/2} \quad (16)$$

Some applications of the here presented secular equations to specific problems, are under preparation.

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