

Note on a Form of the Secular Equation for Molecular Vibrations

E. Bright Wilson Jr.

Citation: [The Journal of Chemical Physics](#) **15**, 736 (1947); doi: 10.1063/1.1746308

View online: <http://dx.doi.org/10.1063/1.1746308>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/15/10?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[The Cubic Secular Equation for Molecular Vibrations](#)

J. Chem. Phys. **18**, 773 (1950); 10.1063/1.1747772

[Developments in the Theory of the Secular Equation for Molecular Vibrations](#)

J. Chem. Phys. **17**, 1026 (1949); 10.1063/1.1747108

[Note on the Solution of Secular Equations](#)

J. Chem. Phys. **8**, 569 (1940); 10.1063/1.1750714

[The Secular Equation for Molecular Vibrations](#)

J. Chem. Phys. **6**, 223 (1938); 10.1063/1.1750232

[A Mechanical Analyzer for the Solution of Secular Equations and the Calculation of Molecular Vibration Frequencies](#)

J. Chem. Phys. **5**, 940 (1937); 10.1063/1.1749967



to the considerable increase in molal volume between CCl_4 and SiCl_4 ; although the attraction is less, the attraction constant is greater, increasing almost linearly with molecular dimensions in the order CCl_4 , SiCl_4 , GeCl_4 , TiCl_4 , SnCl_4 . None of the properties herein examined, including Raman frequencies, indicates any exceptional character for SiCl_4 , such as the double-bond resonance that others have assumed to account for the somewhat short M - X distance.

5. The only members of these series that appear to call for any unique explanation are CCl_4 and CBr_4 , which have (a) high melting points and low entropies of fusion, which seem to be connected with crystal structure; (b) high boiling points, which require a totally different explanation; (c) slightly high Raman frequencies, which

may be ascribed to interhalogen repulsions and covalent bonds; and (d) attraction constants and polarizabilities slightly in excess of the linear relationship to molecular dimensions exhibited by the higher members of the series.

It seems appropriate, in conclusion, to call attention to certain gaps in the experimental data for these important substances which should by all means be filled. They include crystal structures of the solids, densities and expansivities of the solids, heat capacities and heats of fusion, a redetermination of the M - X distance for TiCl_4 and VCl_4 by the same investigator; Raman spectrum of VCl_4 ; additional accurate mutual solubility data; vapor pressures for SnBr_4 and nearly every thermodynamic property for the fluorides.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 15, NUMBER 10 OCTOBER, 1947

Note on a Form of the Secular Equation for Molecular Vibrations

E. BRIGHT WILSON, JR.

Mallinckrodt Chemical Laboratory, Harvard University, Cambridge, Massachusetts

(Received July 21, 1947)

By starting with the Hamiltonian form of the equations of motion, the problem of the small vibrations of a polyatomic molecule can be solved with the aid of a secular equation twice the usual size. This equation, however, is readily adapted to solution by electrical circuits and has the important advantage of having as elements the force constants and inverse kinetic energy coefficients ("G" matrix elements) directly. The force constant matrix elements occupy one off-diagonal corner of the secular equation, the G matrix elements are in the other off-diagonal corner, the circular frequencies ($2\pi\nu$) appear on the principal diagonal, and all other elements are zero.

THE problem of small amplitude vibrations of the atoms of a polyatomic molecule has been extensively treated.¹ Its solution, as is well known, involves some type of determinantal or secular equation, which can assume many forms. It is the purpose of this note to point out the useful properties of one of the lesser known forms.

Consider that a set of "internal" coordinates has been selected, such as $3N-6$ independent interatomic distances and valence angles, where N is the number of atoms. Let R_i be the deviation of the i th coordinate from its equilibrium value. Then the potential energy V of the molecule can

be expressed in the form

$$2V = \sum_{ij} F_{ij} R_i R_j, \quad (1)$$

if the zero of energy is properly chosen and if higher order terms (anharmonic terms) are neglected. The constants F_{ij} are the force constants.

The kinetic energy can be expressed in terms of the velocities \dot{R}_i or in terms of the momenta P_i , conjugate to the coordinates R_i . Let the kinetic energy T be written as

$$2T = \sum_{ij} G_{ij} \dot{R}_i \dot{R}_j, \quad (2)$$

where the G_{ij} are coefficients involving the masses of the atoms and the geometry of the molecule and are constants to the approximation ordi-

¹ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, New York, 1945).

narily used. Simple vectorial rules have been formulated for calculating these coefficients,² or they can be tabulated for various types of pairs of internal coordinates.³

The equations of motion in Hamiltonian form are

$$\dot{R}_i = \partial H / \partial P_i = \sum_j G_{ij} P_j, \quad (3)$$

and

$$\dot{P}_i = -\partial H / \partial R_i = -\sum_j F_{ij} R_j, \quad (4)$$

since $H = T + V$ for this system.

As a solution of these equations, try

$$R_j = A_j \cos(2\pi\nu t + \epsilon), \quad (5)$$

and

$$P_j = B_j \sin(2\pi\nu t + \epsilon), \quad (6)$$

where ν is the frequency of vibration, t the time, and ϵ an arbitrary phase constant. These expressions lead to the following equations which must be satisfied by the amplitudes A_j and B_j :

$$\begin{aligned} 2\pi\nu A_i + \sum_j G_{ij} B_j &= 0, \quad i = 1, 2, \dots, 3N-6, \\ \sum_j F_{ij} A_j + 2\pi\nu B_i &= 0, \quad i = 1, 2, \dots, 3N-6. \end{aligned} \quad (7)$$

This set of $2n = 2(3N-6)$ equations for the $2n$ unknown amplitudes A_i and B_i , has solutions differing from zero only if the determinantal or secular equation formed from its coefficients is satisfied; i.e., only if (with $\omega = 2\pi\nu$)

$$\begin{vmatrix} \omega & 0 & 0 & \cdots & G_{11} & G_{12} & G_{13} \\ 0 & \omega & 0 & \cdots & G_{21} & G_{22} & G_{23} \\ 0 & 0 & \omega & \cdots & G_{31} & G_{32} & G_{33} \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ F_{11} & F_{12} & F_{13} & \cdots & \omega & 0 & 0 \\ F_{21} & F_{22} & F_{23} & \cdots & 0 & \omega & 0 \\ F_{31} & F_{32} & F_{33} & \cdots & 0 & 0 & \omega \end{vmatrix} = 0. \quad (8)$$

This is the form of the secular equation in question. It has certain important properties. *First*: it is twice as large as the usual forms. This is a drawback but not as serious as might be supposed. *Second*: it involves $\omega = 2\pi\nu$ instead of $\lambda = 4\pi^2\nu^2$ as is usual. *Third*: the roots come in pairs, positive and negative; i.e., if $+\omega$ is a root so is $-\omega$. This accounts for the extra n roots required by its double size. *Fourth*: it is unsymmetrical with respect to the principal diagonal. *Fifth*: it has nothing in the principal diagonal

except the unknowns ω . *Sixth*: its off-diagonal elements are the force constants F_{ij} and the coefficients G_{ij} directly.

It is the last property which makes this form of the secular equation of interest in molecular vibrational problems. In all other forms of the secular equation it is necessary to carry out some algebraic manipulation on the force constants or the G_{ij} 's before obtaining the elements of the final equation. In this form the F s and G s occur directly.

This advantage is particularly profitable when a machine is used to solve the secular equation. For example it is possible to make obvious modifications of the direct-current resistance network computer described by Frost and Tamres⁴ for the solution of this type of equation. With this device the coefficients G_{ij} and also the force constants F_{ij} are set directly on dials of the machine so that trial of different force constants, for example, can be carried out by resetting the appropriate dial and determining the new roots.

The double size of the equation is not as objectionable as might be suspected since each row contains only $n+1$ elements because of the $n-1$ zeros. Therefore there are no more resistances required than in Frost and Tamres' general design for n rows. The switching and wiring is somewhat more complicated but not seriously so. In use, it will require more time to find each root because the method of successive approximations increases in difficulty as the number of rows increases.

Unfortunately the form of Eq. (8) precludes the use of the inductance-capacity network type of machine,^{5,6} which will not handle unsymmetrical equations.

Naturally, if the molecule has any symmetry, internal symmetry coordinates¹ would be used instead of internal coordinates in setting up the equations, so that one factor of the secular equation at a time would be placed on the machine. This form of the secular equation could be used with other types of coordinates, such as

⁴ A. A. Frost and M. Tamres, J. Chem. Phys. **15**, 383 (1947).

⁵ G. Kron, J. Chem. Phys. **14**, 19 (1946); G. K. Carter and G. Kron, J. Chem. Phys. **14**, 32 (1946).

⁶ R. H. Hughes and E. B. Wilson, Jr., Rev. Sci. Inst. **18**, 103 (1947).

² E. Bright Wilson, Jr., J. Chem. Phys. **9**, 76 (1941).

³ For example, all the coefficients occurring in substituted methanes and ethanes have been tabulated by J. C. Decius, Thesis 1947, Harvard University.

Cartesians, but would then probably be inferior to the usual forms in convenience.

The amplitudes A_j of Eq. (5), when properly normalized, provide the coefficients in the transformation from normal coordinates Q_k to internal coordinates R_j . The coefficients B_j of Eq. (6), on the other hand, are related to the coefficients of the inverse transformation from R_j s to Q_k s. To see this, let

$$R = LQ \quad (9)$$

in matrix notation, where L is the matrix of the coefficients of the transformation from Q_k s to R_j s. Q and R are the appropriate column matrices. Then it has been shown that²

$$G = LL', \quad (10)$$

where G is the matrix of the elements G_{ij} and the prime denotes the transpose. Consequently,

$$L^{-1} = L'G^{-1}. \quad (11)$$

But $L = AK$ where A is the matrix $\|A_{jk}\|$ of the amplitudes in Eq. (5), the subscript k labelling the normal mode involved. K is a diagonal matrix which is used to normalize the coefficients. Therefore,

$$L^{-1} = KA'G^{-1}. \quad (12)$$

But from Eq. (7) one sees that

$$-A\omega = GB, \quad (13)$$

where ω is the diagonal matrix with diagonal elements ω_k . Consequently, since $G' = G$,

$$B' = -\omega A'G^{-1} = -\omega K^{-1}L^{-1}, \quad (14)$$

or

$$L^{-1} = -K\omega^{-1}B', \quad (15)$$

so that, except for the normalization factor $(-K\omega^{-1})$, the coefficients B_{jk} provide the elements of L^{-1} as stated above. To determine K ,

one may use*

$$L'FL = \Lambda = KA'FAK, \quad (16)$$

where F is $\|F_{ij}\|$ and Λ is the diagonal matrix with diagonal elements $4\pi^2\nu_k^2 = \omega_k^2$. This equation arises because the normal coordinates, by definition, diagonalize the potential energy.² Thus, from Eq. (16),

$$K_k = \omega_k / (\sum_{ij} F_{ij} A_{ik} A_{jk})^{1/2}, \quad (17)$$

so that

$$L_{jk} = A_{jk}\omega_k / (\sum_{il} F_{il} A_{ik} A_{lk})^{1/2}, \quad (18)$$

and

$$L_{kj}^{-1} = -B_{jk} / (\sum_{il} F_{il} A_{ik} A_{lk})^{1/2}. \quad (19)$$

APPENDIX

A simple proof of the equivalence of this form of the secular equation and other more usual forms follows. Consider

$$\begin{vmatrix} \omega E & G \\ F & \omega E \end{vmatrix} = 0, \quad (20)$$

which is a symbolic way of writing Eq. (8), F and G here representing the corresponding sets of coefficients. E represents the n -by- n unit matrix. If a given value of ω satisfies this equation, it will also satisfy the equation

$$\begin{vmatrix} \omega E & -G \\ -F & \omega E \end{vmatrix} = 0. \quad (21)$$

Multiplication of these two equations by the rule for multiplication of determinants (which is the same as the rule for matrix multiplication) gives

$$\begin{vmatrix} \omega^2 E - GF & 0 \\ 0 & \omega^2 E - FG \end{vmatrix} = 0, \quad (22)$$

or

$$|GF - \omega^2 E| = 0 \quad \text{or} \quad |FG - \omega^2 E| = 0. \quad (23)$$

These are two equivalent and previously known⁷ forms of the secular equation.

* This procedure for normalization was pointed out to me by Dr. R. S. Rasmussen, Shell Development Company, Emeryville, California.

⁷ E. B. Wilson, Jr., J. Chem. Phys. **7**, 1047 (1939); also, M. A. Eliashevich, Comptes rendus U.R.S.S. **28**, 604 (1940).