This Week's Citation Classic

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Wilson E B. Some mathematical methods for the study of molecular vibrations.
J. Chem. Phys. **9**:7684, 1941.
[Mallinckrodt Chem. Lab., Harvard Univ., Cambridge, MA]

Developments which simplify the calculation of vibration frequencies of molecules are described. A vectorial scheme yields the inverse G of the matrix of the kinetic energy. Symmetry, redundancy, the isotope product rule, and splitting of high from low frequencies are also discussed. [The *SCI*® indicates that this paper has been cited over 400 times since 1961.]

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"This publication was actually the second of a pair of papers which introduced the socalled FG method for setting up the equations which connect the vibrational frequencies of a polyatomic molecule with the force constants of the chemical bonds, i.e., the stiffness with respect to stretching and bending of the bonds. It is chemically more interesting to describe the potential energy of a molecule in a distorted instantaneous configuration in terms of bond stretches and bends but, before these publications appeared, no convenient general approach had been published for handling the kinetic energy in terms of the time derivatives of these 'valence bond' coordinates. The first paper[1], showed how to get the necessary equation for the vibration frequencies in expanded algebraic form using the elements F_{ij} for the force constants and the numbers C_{ij} the G matrix elements, which are functions of the atomic masses and molecular geometry and take care of the kinetic energy part of the problem.

"The second paper showed improved methods for evaluating the C matrix elements, particularly by introducing vectors *skt* one for each atom t and each valence type coordinate k. These can be written down with very simple rules.

"This method was central in the later book, *Molecular Vibrations,*[2] by myself, J.C. Decius, and Paul C. Cross, and this is probably one reason for the frequency of the citation.

"The development of this approach came at a time when I had been deeply involved with molecular vibrational spectroscopy at Harvard, using infrared and Raman spectroscopy. I had the exceptional luck of having an extremely able group of collaborators. It was a very exciting period during which we built spectrometers, worked on the theory, obtained and analyzed spectra, and used the results to calculate thermodynamic properties such as heat capacity and entropy. These latter we compared with measured values being obtained then by Kistiakowsky's group. Some of the molecules studied showed hindered internal rotation, a topic of great interest at Harvard at that time. Since we were immersed in force constant calculations, it was natural to be seeking more convenient methods and so I was constantly trying various approaches.

"A very interesting aspect of this work is that, unbeknownst to me at the time, a Russian spectroscopist, M.A. Eliashevich, at Leningrad, was following a somewhat similar track. His first contribution[3] appeared in 1940, therefore in between my two papers. He also later coauthored a book[4] on molecular vibrations, published in 1949.

"Incidentally, in looking back at the *Chemical Abstracts* entry for my two FG papers, I note that the total abstract for the first one, beside the title and reference, was 'math.' The second one was not even considered worthy of that; only the title and reference were given.

"It has been a pleasure to see the ramifications which have followed from these papers, which certainly at the time of publication could not have appealed to more than a very small group of specialists."

1. **Wilson E B.** A method of obtaining the expanded secular equation for the vibration frequencies of a molecule. *J. Chem. Phys.* **7**:104752, 1939.
2. **Wilson E B, Decius J C & Cross P C.** *Molecular vibrations.* New York: McGrawHill, 1955.
3. **Eliashevich M A.** Simple method for calculation of vibrational frequencies of polyatomic molecules. *C.R. (Oaklady) Acad. Sci. URSS* **28**:6058, 1940.
4. **U Vol kenshtein M, Eliashevich M A & Stepanov B I.** *Vibrations of molecules 2.* Moscow: Gosudarst. Izd. Tekh. Teoret. Lit., 1949. 2 vols.