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Abstract

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CALCULATION OF THE FREQUENCIES AND FORMS OF NORMAL VIBRATIONS OF MOLECULES BY THE PERTURBATION METHOD

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Indications of the possibility of using the perturbation method as a computational device for approximate estimates of the frequencies of normal vibrations (see [1,2,12]) assign this method, in essence, a very modest place in the analysis of the frequencies of normal vibrations of polyatomic molecules. For calculating the forms of normal vibrations, the perturbation method is in fact regarded as ineffective.

The perturbation method for an operator of simple structure formulated in work [3] can be applied not only in solving special problems, such as, for example, the influence of free rotation in molecules on the frequencies of normal vibrations, considered in work [4]*, but also, as specific calculations show [5], directly to the analysis of normal vibrations. This means that the vibration operator of a molecule can always be represented in the form

$$W = W_0 + \Delta W, \tag{1}$$

where the operator ΔW plays the role of the perturbation, and its influence on the frequencies and forms of normal vibrations is determined by formulas (13), (15), (16), (13′), (20), or (23) of work [3].

If, in the space of natural coordinates, it is impossible to isolate ΔW as a perturbation, then one should first perform a transformation of the basis of the system of natural coordinates, taking into account the strongest interactions. It can be shown that the operator W is then transformed according to the law $W' = \widetilde{P}_0 W X_0$ [2,11], where P_0 and X_0 are matrices composed respectively of the column vectors $P_0^{(i)}$ and $X_0^{(i)}$, corresponding to the operator W_0.

Let us divide the set of vibrational coordinates of a molecule A into nonintersecting sets

$$A_1, A_2, \ldots, A_n, \tag{2}$$

corresponding to the respective selected groups in the molecule. Such a division is, of course, not unique, but this circumstance is by no means of fundamental importance, since in the course of the calculation one can always transform the

sequence $A_1, A_2, \ldots, A_n$ into another sequence $A'_1, A'_2, \ldots, A'_n$ of nonintersecting sets, which also exhausts the set of coordinates A and corresponds to a somewhat different division of the molecule into groups**.

* See also applications of the perturbation method for small changes in the masses of atoms forming a molecule ([2,9,10]).

** The transformation of the operator basis described above is meant.

To each set of coordinates A_m from sequence (2) there corresponds its own vibration operator $W_0^{(m)}$. The operator-matrix

$$W_0 = \begin{Vmatrix} W_0^{(1)} & & 0 \\ 0 & W_0^{(2)} & \\ & & \ddots\ W_0^{(n)} \end{Vmatrix} \tag{3}$$

then characterizes the vibration of the molecule considered as a system of noninteracting groups.

If in (2) there are identical sets, then their interaction, determined by the operator-matrix

$$\Delta W^{(\mathrm{T})} = W^{(\mathrm{T})} - W_0^{(\mathrm{T})}, \tag{4}$$

where $W^{(\mathrm{T})}$ is the operator-matrix of that part of the molecule which is described by the sum of identical sets of coordinates, and $W_0^{(\mathrm{T})}$ is constructed in accordance with (3) for the identical groups under consideration, is computed by successive application of formulas (13′) and (20) for the degenerate case, and then (15) and (16), from paper ([3]). The frequency spectrum and normal-vibration forms calculated in this way correspond to the entire system of identical groups, i.e., the identical sets of coordinates are merged into one set, which leads to the transformation of sequence (2) mentioned above. A similar partial unification of sets in sequence (2) may also be carried out for nonidentical sets*.

The expediency of transforming sequence (2) is established in each specific case depending on whether ΔW from relation (1) satisfies the conditions for applicability of the perturbation method or not. On the other hand, an important principle in constructing sequence (2) is the separation of groups of equivalent coordinates, to which Hermitian operators $W_0^{(m)}$ with coinciding $X_0^{(i)}$- and $P_0^{(i)}$-vectors correspond in W_0. In doing so, the symmetry of individual groups is used to the maximum extent, even if the molecule as a whole has no symmetry elements. Moreover, it is essential that dependent coordinates not fall into different groups. The exclusion of superfluous coordinates is undesirable, since, when symmetry is present within a group of dependent coordinates, there automatically arises a vibration with zero frequency and with such a form that the

interaction of this vibration with any other is equal to zero; hence the presence of such "superfluous" vibrations with zero frequencies has no effect whatsoever on the results of the calculations.

It should be noted that the perturbation method makes it possible to find, rather simply, the so-called symmetry coefficients ([1],[2],[6]); however, in contrast to other methods ([2],[7],[8]), obtaining them does not precede the operation of reducing the vibration matrix by symmetry, but is one of the results of such reduction, which is carried out by the perturbation method in the particular case when the formulas of this method give not approximate but exact corrections to the zeroth approximation. For example, if in (12a) from [3]

$$\widetilde{P}_0^{(in')}\Delta W X_0^{(j)} = 0, \qquad i \neq j, \qquad n' = 1, 2, \ldots, s,$$

then from equations (13′) and (20) of [3] one obtains the exact corrections $\Delta\lambda^{(i)}$ and the coefficients $a_i^{(in')}$.

* In some cases, and especially when the symmetry of the molecule is not lower than the symmetry of the combined subgroups of coordinates, it is more rational to cut out the corresponding blocks $W_0^{(m')}$ directly from the matrix W.

The interaction of vibrations with close but unequal frequencies, as is easily shown, can be reduced to the degenerate case by introducing, for example, the mean frequency of these vibrations

$$\overline{\lambda_0^{(i)}} = \sum_{n=1}^{s} \lambda_0^{(i_n)}/s. \tag{5}$$

In this case the secular equation (13′) from [3] is modified, namely:

$$\left\| \tilde{P}_0^{(i_{n'})}\Delta W X_0^{(i_n)} + \delta\lambda_0^{(i_{n'})}\delta_{n'n} - \Delta\lambda^{(i)}\delta_{n'n} \right\| = 0, \tag{6}$$

where $\delta_{n'n}$ is the Kronecker symbol, and

$$\delta\lambda_0^{(i_{n'})} = \lambda_0^{(i_{n'})} - \overline{\lambda_0^{(i)}}. \tag{7}$$

The system of equations (20) in [3] is modified in an analogous way.

The operator W_0 generates a system of eigenvalues λ_0 (the squares of the frequencies of the normal vibrations) and eigenvectors X_0 (the forms of the normal vibrations). If this operator is not Hermitian, then, in order to calculate corrections by the perturbation method according to [3], it is necessary, in addition to λ_0 and X_0, to know the corresponding eigenvectors P_0 of the operator $\tilde{W}_0$.

The application of formulas (13), (15), (16), (13′), (20) from [3] makes it possible to find λ and X—the vectors of the operator W. By the same formulas, replacing

in them ΔW by $\Delta\tilde{W}$ and X_0 by P_0, and P_0 by X_0, the P-vectors of the operator W are also determined.

The special features of the analysis of vibrations by the perturbation method include: 1) the speed of calculating the frequencies and forms of vibrations of large molecules, since the order of the secular equations and of the corresponding systems usually does not exceed two; 2) automatic allowance for the symmetry of the molecule as a whole; 3) maximal allowance for the symmetry of individual groups of the molecule; 4) additional information on the interaction of vibrations of isolated groups.

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Note: Figure translations are in progress. See original paper for figures.