The Secular Equation for Molecular Vibrations

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It is well known that when the potential and kinetic energies of a vibrating N atomic molecule are expressed in terms of the $3N$ Cartesian coordinates of the atoms, the secular equation for the vibration frequencies has $3N$ rows and columns and $3N$ roots, six of which are equal to zero. Recently, Redlich and Tompa[1] have published a method for manipulating such a secular equation so as to eliminate the zero roots and obtain a new equation of only $3N-6$ rows and columns. It is the purpose of this letter to give a much simpler method which accomplishes essentially the same results as theirs and to outline the drawbacks of both these methods as contrasted with a number of others which have been previously described.

By direct elimination of p_2 between Eq. (13) and (14) of Redlich and Tompa's paper, one obtains

$$\{B_{11}-B_{12}M_{22}^{-1}F_{22}^{-1}F_{21}M_{11}-\omega^2 M_{11}\}p_1=0,$$

in which their notation has been employed. If the F matrix is adjusted so that $F_{22}=E$, as they recommend, the secular equation becomes

$$|B_{fg}-\sum_u B_{fu}F_{ug}M_g/Mu-\omega^2 M_g\delta_{fg}|=0.$$

This equation requires all the potential constants B_{ij} but involves only one summation, whereas Redlich and Tompa's equation requires somewhat fewer constants but two summations.

Unfortunately, both these methods suffer from the very grave defect of yielding an unsymmetrical secular equation. The two easiest methods of solution of large secular equations, the method of numerical approximation[2] and the mechanical method,[3] both require an equation symmetrical with respect to the principle diagonal. The numerical method can be modified to remove this limitation, but it then becomes very considerably more laborious. Since this is true, and since any manipulation which yields a symmetrical secular equation is equivalent to a change of coordinates,[4] we believe that the older methods of eliminating the zero roots are still to be preferred.

The problem of the elimination of zero roots is independent of the question of the factoring of the secular equation by the use of the symmetry of the molecule. In symmetrical molecules, $3N$ linear combinations of the Cartesian coordinates can be constructed, not involving the relative masses of the atoms, which have the proper symmetries to factor the secular equation. These *external symmetry coordinates*, which Redlich and Tompa denote by p, can be used instead of the Cartesian coordinates with the result that the discussions of this letter then apply to each factor instead of to the whole secular equation. The number of zero roots in a given factor may be less than six.

If the number of rows of a given factor of the secular equation is small, say three, it is simplest to expand the determinantal equation into an ordinary algebraic equation, from which the zero roots can be eliminated immediately. For larger factors there are several possible procedures. One is to leave the secular equation unaltered and solve by numerical or mechanical methods. This has the drawback of requiring the solution of a larger secular equation than would be required if the zero roots were removed, but has the advantage that the secular equation is quickly and easily set up.

Another method is to employ *internal* coordinates ($3N-6$ in number) such as interatomic distances and angles. This gives a secular equation with no zero roots and $3N-6$ rows and columns. ("Geometrical symmetry coordinates"[5] are of this type and in addition utilize the symmetry to factor the equation.) The drawbacks of this type are, first, the difficulty of obtaining the kinetic energy expression, and second, the fact that the kinetic energy contains cross terms, so that the numerical solution is more difficult and the mechanical method inapplicable.

Still another procedure is to eliminate six of the Cartesian coordinates from the kinetic and potential energy expressions by means of the conditions of the linear and angular momenta. This gives a symmetrical secular equation but the kinetic energy again contains cross terms, and in addition the whole process is rather cumbersome.

Finally, a set of coordinates[6] may be used with the following properties: (a) Six of them represent the motions of translation and rotation. (b) In terms of these coordinates the kinetic energy matrix is the unit matrix. Such a set of coordinates produces a secular equation which is symmetrical, has no cross terms in the kinetic energy, and has the zero roots factored out. It is therefore in the form best suited for either numerical or mechanical solution. However, it is sometimes fairly troublesome to obtain these coordinates.

In conclusion, it is our experience that for small factors (less than four rows) it is best to expand the secular equation, which is originally set up in terms of external symmetry coordinates and therefore may contain zero roots. For larger factors, it seems best either to leave the zero roots in the equation and suffer the consequent larger sizes of the factors, or to transform to the type of symmetry coordinates which conserve momenta and therefore reduce the sizes of the factors.

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[4] M. Bocher, *Introduction to Higher Algebra*, p. 299 ff.
[5] J. E. Rosenthal and G. M. Murphy, Rev. Mod. Phys. **8**, 317 (1936).
[6] If it is required in addition that these coordinates have the proper symmetry properties to factor the secular equation, they become the "symmetry coordinates" of Howard and Wilson, (J. Chem. Phys. **2**, 630 (1934)). These coordinates have been criticized as unsuitable for use in connection with the isotope effect because they involve the atomic masses. We cannot understand this criticism because the secular equation will always contain the atomic masses in any event, and to change from one isotopic molecule to another of the same symmetry requires the same operations no matter what coordinates are used, whereas if the introduction of the isotopic atom lowers the symmetry, a new secular equation is necessary anyway. We have found these coordinates very useful.