# FORCE CONSTANTS IN THE POTENTIAL ENERGY OF A VIBRATING MOLECULE

**(Determination of the Maximum Number by a Group Theoretical Method)**

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## 1. INTRODUCTION

THE potential energy V of a molecule, consisting of $n$ atoms and performing small vibrations about its equilibrium configuration, can be expressed as a quadratic form in the $3n$ cartesian displacements ($x_i$; $i = 1$ to $3n$) of the atoms with constant coefficients as in (1).

$$2V = \sum_{i,j=1}^{3n} b_{ij}x_ix_j. \tag{1}$$

In the above expression, $b_{ij} = b_{ji}$. Since the potential energy does not depend on bodily translations and rotations of the molecule, a new set of $3n-6$ orthogonal co-ordinates ($S_i$) which may be called internal co-ordinates, which are linear combinations of the cartesian displacements and are orthogonal to the translational and rotational modes of motion can be formed. The potential energy, in this new set of co-ordinates, will have the form

$$\sum_{i,j=1}^{3n-6} F_{ij}S_iS_j. \tag{2}$$

In the above expression, $F_{ij} = F_{ji}$. It follows that there can be $\frac{1}{2}(3n-6)(3n-5)$ independent constants in the potential energy expression of a completely unsymmetrical molecule composed of $n$ atoms. Such a case is regarded as possessing only one element of symmetry, namely the identity operation. The presence of other symmetry elements in the molecule results in further relations between ($F_{ij}$).

The application of symmetry operations belonging to the point group appropriate to a molecule transform the set of internal co-ordinates and transformation matrices which connect the old and new sets of internal co-ordinates form a reducible representation of the point group under consideration. When this representation $\Gamma$ is completely reduced, it consists of a number of irreducible representations $\Gamma_i$, a fact which may be symbolically written as in (3).

$$\Gamma = \sum_i n_i \Gamma_i \tag{3}$$

$n_i$ is the number of times the $i$-th irreducible representation occurs in the completely reduced representation. It is easy to show that for a molecule whose symmetry results in the completely reduced representation having a structure given by (3), the maximum number of independent constants required for writing out the potential energy is given by (4).

$$\sum_i \tfrac{1}{2} n_i (n_i + 1) \tag{4}$$

The present available method for evaluating (4) in respect of a particular molecule consists in determining the structure of the completely reduced representation, which involves the determination of $n_i$ for all $i$. $n_i$ is given by formula (5) (Bhagavantam and Venkatarayudu, 1963).

$$n_i = \frac{1}{N} \sum_\rho h_\rho \chi_\rho (R) \chi_i (R) \tag{5}$$

where

N is the order of the group.

$h_\rho$ is the number of elements in the $\rho$-th class.

$\chi_\rho$ (R) is the character of the group element R belonging to $\rho$-th class in the reducible representation.

$\chi_i$ (R) is the character of same R in the $i$-th irreducible representation.

Thus, this method requires a knowledge of the complete character table of the group and the determination of $n_i$ for each irreducible representation.

## 2. Description of a New Method

The purpose of this paper is to present a more elegant method of deriving the same result. It is an adaptation of the method suggested by Bhagavantam (1942) for obtaining the maximum number of independent constants required to describe a physical property of a crystal of given symmetry.

From the potential energy expression (2), it is evident that ($F_{ij}$) transform like the products of the components of a $3n - 6$ dimensional vector ($S_1, S_2, \ldots, S_{3n-6}$) amongst themselves, *i.e.*, as a symmetric tensor of rank 2 which consists of $\frac{1}{2}(3n - 6)(3n - 5)$ components. The transformation properties of ($F_{ij}$) under the set of symmetry operations of the point group

can be worked out. The transformation matrices form a multi-dimensional representation of the point group, the $F_{ij}$ components forming a basis for such a representation. By forming suitable linear combinations of $F_{ij}$ components, a new basis of the same dimension can be formed in which the representation is completely reduced.

Since a symmetry operation leaves a molecule identical with itself, the potential energy expression can have only coefficients which remain invariant under all symmetry operations This consideration applies to a linear combination of them as well. Therefore it follows that those linear combinations of the coefficients, which remain invariant under all symmetry operations will alone remain and the rest vanish. The linear combinations of $(F_{ij})$ which remain invariant under all symmetry operations come under the total symmetric irreducible representation. Thus, the maximum number of independent force constants is given by the number of times the total symmetric irreducible representation occurs in the completely reduced representation formed with linear combinations of $(F_{ij})$ as basis. This number is found by applying formula (5) in which we have to take the proper $\chi_p$ (R). It may be noted that the formula need be applied only once and that to find the $n_i$ for total symmetric representation. Since $\chi_i$ (R) = 1 for all R for that irreducible representation, we do not need to know the character table at all.

Further, there is no need to form the potential energy expression in internal co-ordinates for applying this method. The potential energy in cartesian displacements can be taken; but the proper $\chi_p$ (R), in which the character arising from translational and rotational modes of motion is removed has to be employed.

The compound character of a symmetry operation $R_\phi$ in the $3n$-dimensional cartesian representation, after removing the character arising from translations and rotations, is given by (Bhagavantam and Venkatarayudu, 1963);

$$\chi_p(R_\phi) = (U_R - 2)(1 + 2\cos\phi) \text{ when } R_\phi \text{ is a pure rotation through } \phi; \quad (6)$$

$$\chi_p(R_\phi) = (U_R)(-1 + 2\cos\phi) \text{ when } R_\phi \text{ is a rotation reflection through } \phi; \quad (7)$$

The suffix $p$ used in (6) and (7) is equal to $3n$.

$U_R$ is the number of atoms which remain unmoved on applying $R_\phi$.

The character of the symmetry operation $R_\phi$ in the representation formed by $(b_{ij})$ as basis, excluding translational and rotational contributions, is

$$\chi_{pps}(R_\phi) = \tfrac{1}{2}\chi_p(R_{2\phi}) + \tfrac{1}{2}\{\chi_p(R_\phi)\}^2. \quad (8)$$

The subscript *pps* has been used for indicating that $\chi_{pps}$ is the character in the symmetrized Kronecker square representation. In (8), when $R_\phi$ is a rotation-reflection, $\chi_p(R_{2\phi})$ is the character of a pure rotation through $2\phi$ given by (6) and $\chi_p(R_\phi)$ is the character of a rotation-reflection given by (7). On the other hand, when $R_\phi$ is a pure rotation, $\chi_p(R_{2\phi})$ and $\chi_p(R_\phi)$ are both given by (6) only. The derivation of (8) follows from the expression for the spur of the symmetrized Kronecker square of a matrix (Bhagavantam and Venkatarayudu, 1963).

Using the compound character $\chi_{pps}(R_\phi)$ in (5), we get the number of total symmetric irreducible representations contained in the completely reduced representation. This number is also the maximum number of force constants needed for expressing the potential energy, when a molecule of $n$ atoms and a given point group symmetry is executing small vibrations about its equilibrium configuration.

## 3. Application to Some Particular Examples

(*a*) *Water molecule* ($H_2O$); *point group* ($C_{2v}$); $N = 4$; $n = 3$.

| $R_\phi$ | E | $C_2$ | $\sigma_v$ | $\sigma_h$ |
|---|---|---|---|---|
| $\chi_{pps}(R_\phi)$ | 6 | 2 | 2 | 6 |

$n_i = \frac{1}{4}(6 + 2 + 2 + 6) = 4.$

(*b*) *Ammonia* ($NH_3$); *point group* ($C_{3v}$); $N = 6$; $n = 4$.

| $R_\phi$ | E | $2C_3$ | $3\sigma_v$ |
|---|---|---|---|
| $\chi_{pps}(R_\phi)$ | 21 | 0 | 5 |

$n_i = \frac{1}{6}(21 + 2 \times 0 + 3 \times 5) = 6.$

(*c*) *Carbonate ion* ($CO_3^{--}$); *point group* ($D_{3h}$); $N = 12$; $n = 4$.

| $R_\phi$ | E | $2C_3$ | $3C_2$ | $\sigma_h$ | $2S_3$ | $3\sigma_v$ |
|---|---|---|---|---|---|---|
| $\chi_{pps}(R_\phi)$ | 21 | 0 | 3 | 11 | 2 | 5 |

$$n_i = \frac{1}{12}(21 + 2 \times 0 + 3 \times 3 + 11 + 2 \times 2 + 3 \times 5) = 5.$$

(*d*) *Methane* ($CH_4$); *point group* ($T_d$); $N = 24$; $n = 5$.

| $R_\phi$ | E | $8C_3$ | $3C_2$ | $6\sigma$ | $6S_4$ |
|---|---|---|---|---|---|
| $\chi_{pos}(R_\phi)$ | 45 | 0 | 5 | 9 | -1 |

$$n_i = \frac{1}{24}(45 + 8 \times 0 + 3 \times 5 + 6 \times 9 + 6 \times 1) = 5.$$

As may be expected, the numbers obtained in the four selected examples cited above are identical with the results that one can get by a detailed process involving the writing out of the full character table in each case and the use of formula (4).

## 4. Summary

A new and elegant method, based on group theory, has been given for obtaining the maximum number of force constants needed in expressing the potential energy of a vibrating molecule characterised by a certain point group symmetry.

## References

Bhagavantam, S. .. *Proc. Ind. Acad. Sci.*, 1942, **16**, 356.

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