THEORY OF POINT GROUP APPLIED IN MOLECULAR PHYSICS★

DANA-ORTANSA DOROHOI[1], STELA GOSAV[2], MIRELA PRAISLER[2]

[1] Faculty of Physics, "Al. I. Cuza" University, Iași-700506, Romania
[2] Faculty of Sciences, "Dunărea de Jos" University, Galați, Romania

Received September 26, 2006

Some theorems of the point group algebra are discussed in correlation with their applications in the molecular physics. The symmetry of the components of electric and magnetic dipole moments as well as of the polarizability for the molecules belonging to C_{2v} and D_{3h} point groups is given in this paper.

Key words: group representations, classes of equivalency, polarizability, electric dipole moment.

INTRODUCTION

Theory of Groups has large applications in Physics. A part of this theory describes the Point Groups of symmetry, defined for geometrical objects. A series of physical properties of the molecules are obtained directly, without calculations, on the basis of the concepts of the Point Group Theory. This theory offers a direct and simple method for obtaining information about molecular dipole moments, polarity, and chirality or about other anisotropic properties of the molecules. From this point of view, some theorems from the Group Algebra must be known and applied to the molecular physics or to the molecular spectroscopy.

A set of elements $G\{g_1, g_2, \ldots, g_n\}$ with a composition law, which assigns to an ordered pair $\{g_1, g_2\}$ another element $g_1 \cdot g_2 \in G,$ is named group if its law of composition satisfies the following axioms:

a) The associativity (for each set of elements $\{g_1, g_2, g_3\}$ from G the following relation is true: $g_1 \cdot (g_2 \cdot g_3) = (g_1 \cdot g_2) \cdot g_3$;

b) The existence of the unit element $e \in G,$ which satisfies the relation: $e \cdot g = g \cdot e,$ for each $g \in G$;

c) The existence of the inverse: for each element $g \in G$ there exists an unique element $g^{-1} \in G$ satisfying the relation $g^{-1} \cdot g = g \cdot g^{-1} = e$;

★ Paper presented at the National Conference on Applied Physics, June 9–10, 2006, Galați, Romania

Rom. Journ. Phys., Vol. 53, Nos. 1–2, P. 49–55, Bucharest, 2008

d) The commutability $g_i \cdot g_j = g_j \cdot g_i$ for each set $\{g_i, g_j\} \in G$

The last axiom is accomplished only for the so called Abelian or commutative groups.

The point groups [1–3], defined for geometrical objects contain operations of symmetry that transform the identical parts of the objects one into another. All symmetry operations that transform the identical parts of an object into one another keep unchanged at least a point belonging to the object. The point groups contain symmetry operations such as identity, spatial rotations around the symmetry axes, reflections in the symmetry planes, inversions relative to an inversion center identity.

All the symmetry operations transform a molecule in such a way that identical atoms are changed between themselves. The singular atoms of the molecules must be transformed into themselves at all symmetry operations of the point group.

2. REPRESENTATIONS OF THE POINT GROUPS

The effect of a symmetry operation on a polyatomic molecule with N atoms may be represented analytically by a linear transformation connecting the new values of the displacement coordinates $\{x'_\alpha,\ y'_\alpha,\ z'_\alpha;\ \alpha = 1, 2, 3, \ldots, N\}$ with their old values $\{x_\alpha, y_\alpha, z_\alpha; \alpha = 1, 2, 3 \ldots, N\}$.

Let us consider, as an example, the action of the rotation around of the two-fold axis, $C_2^{(z)}$ of the C_{2v}, group at which classifies the water molecule [4, 5] on the Cartesian coordinates of its atoms. In Fig. 1 the symmetry elements of a water molecule are given (the identity, the two-fold axis $C_2^{(z)}$; two symmetry planes – the molecular plane *xoz* and the plane *yoz*, bisector of the dihedral angle determined by the O-H bonds).

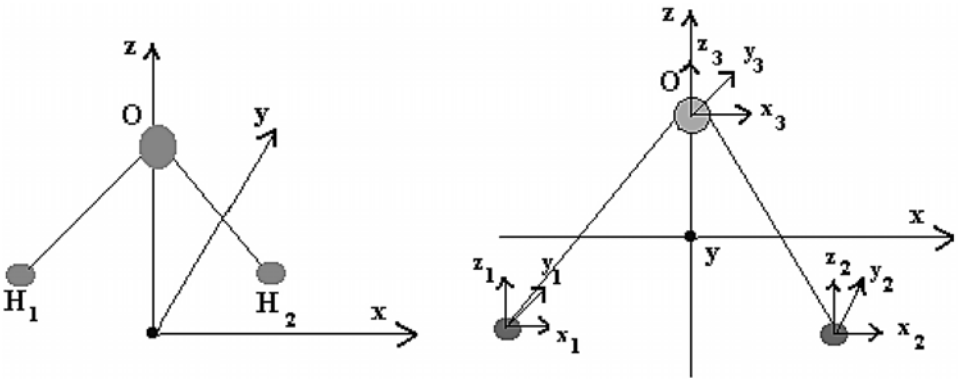

Fig. 1 – a) Symmetry elements of water molecule; b) Cartesian coordinates attached to each atom of water.

Let be the coordinates (x_1, y_1, z_1) and (x_2, y_2, z_2) for the two hydrogen atoms and the coordinates (x_3, y_3, z_3) for the oxygen atom. When the rotation is made, the hydrogen atoms change their places while the oxygen atom keeps its place.

$$\begin{vmatrix} x_1' \\ y_1' \\ z_1' \\ x_2' \\ y_2' \\ z_2' \\ x_3' \\ y_3' \\ z_3' \end{vmatrix} = \begin{vmatrix} 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{vmatrix} \cdot \begin{vmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{vmatrix} \tag{1}$$

Relation (1) contains the matrix describing the changes of the Cartesian coordinates of the water atoms as a consequence of rotation around $C_2^{(z)}$ axis.

Each symmetry operation can be described by a matrix. The result of applying two succesive symmetry operations may be described by a linear transformation which is called the product of the first two. If we note the initial displacements by q_i, $q = x, y, z$; $i = 1, 2, \ldots$ and by q_i', $q' = x, y, z$; $i = 1, 2, \ldots$ the final displacements obtained after applying the symmetry operation O_1,

$$q_j' = \sum_j a_{ji} q_i; \quad j = 1, 2, \ldots \tag{2}$$

and also q_i'', $q'' = x, y, z$; $i = 1, 2, \ldots$ the displacements after aplying the symmetry operation O_2, one obtains a similar linear transformation:

$$q_k'' = \sum_j a_{kj} q_j; \quad k = 1, 2, ... \tag{3}$$

By introducing expression (2) in (3), it is seen that:

$$q_k'' = \sum_j c_{kl} q_l; \quad k = 1, 2, \ldots \tag{4}$$

where:

$$c_{kl} = \sum_j b_{kj} a_{ji}; \quad k = 1, 2, \ldots \tag{5}$$

or in the matriceal form:

$$\boldsymbol{C} = \boldsymbol{BA} \tag{5'}$$

The relations (2) and (3) represent the results of symmetry operations' applied to the molecule and (4) – the result of their succesive application (their product).

To each element of the point group (to each symmetry operation) corresponds a matrix that describes the transformation of the displacement coordinates. The product of the two individual matrices corresponds to the product of the symmetry operations. In both cases (the succesion of symmetry operations and product of the corresponding linear transformations) the law of composition is the same.

The coordinates q_i, $q = x, y, z$; $i = 1, 2, \ldots$ in term of which the transformations are written are said to form the basis of the representation. The basis of a linear representation can be arbitrarily chosen. If another basis is selected, similar results will be obtained. The coefficients in relations (2), (3), (4) could be different, but the general remarks would be equally true for the new transformations.

The linear transformations which represent the symmetry operations of the point groups have the same multiplication properties as the corresponding operations themselves; multiplication is evidently associative.

The product of two or more members of a set of linear transformations is therefore a member of the set. Furthermore, there exists an identity transformation $q_i' = q_i$; $q = x, y, z$; $i = 1, 2, \ldots N$ correlated with the identity operation E.

Each linear transformation possesses an inverse transformation.

Consequently, since the set of linear transformation possesses all the required properties as well as the corresponding symmetry operations, it is said to constitue a group, named the group of representations. The point group to which the molecule belongs and the group formed by the linear transformations correlated to the point group symmetry operations are evidently closely related.

The character of a linear transformation is equal to the summ of the diagonal elements of the representation matrix.

$$\chi_R = \sum_{i=1}^{3N} R_{ii} \tag{6}$$

The subscript R denotes the transformation to which χ belongs. For example, the character of the matrix from relation (1) is –1. The character of a linear reprezentation shows the proportion in which the atoms of a molecule are transformed into themselves by the corresponding operation. The character is dependent on the chosen basis.

The multitude of the matrices representing all the group operations is named matriceal reprezentation of the point group, for a given basis [2, 6]. When two representations of a group differ only in that the basis coordinates of one are

linear combinations of the basis coordinates of the other, the two representations are said to be equivalent. Equivalent representations may be recognised by the fact that the corresponding transformations in the two representations have the same characters.

The representation that can not be reduced to a simpler one is named irreducible (irrep). The Table of a given point group is a list of the characters of all its irreps. The origin of the characters is the symmetry operations of the point groups.

The Table of the C_{2v} point group of water molecule and the Table of D_{3h} point group at which belong the molecules BF_3 or CO_3^- are given below. (For more examples, see [3]).

In the last row of Table 1 the characters corresponding to the Chartezian coordinates of the water atoms are listed. The Abelian group C_{2v} has four symmetry operations that transform the symmetry axis of this group into itself.

Information about the symmetry of the components of dipole moment (P) magnetic dipole moment (μ) and molecular polarizability (α) of the molecules

Table 1

Table characters of C_{2v} group; symmetry of translations and rotations, characters of reducible representation of Cartesian atomic coordinates [3]

Type of symmetry	E	$C_2^{(z)}$	σ_{xoz}	σ_{yoz}	
A_1	1	1	1	1	P_z; α_{xx}; α_{yy}; α_{zz}
A_2	1	1	–1	–1	μ_z; α_{xy}
B_1	1	–1	–1	1	P_x; μ_y; α_{xz}
B_2	1	–1	1	–1	P_y; μ_z; α_{yz}
D^{3N}	9	–1	3	1	

Table 2

Table characters of D_{3h} group; symmetry of translations and rotations, characters of reducible representation of Cartesian atomic coordinates [3]

Type of symmetry	E	$2C_3$	$3\sigma_v$	σ_h	$2S_3$	$3C_2$	
A_1'	1	1	1	1	1	1	α_{zz}; $\alpha_{xx} + \alpha_{yy}$
A_1''	1	1	–1	–1	1	1	
A_2'	1	1	–1	1	1	–1	μ_z
A_2''	1	1	1	–1	–1	–1	P_z
E'	2	–1	0	2	–1	0	P_x; P_y; $\alpha_{xx} - \alpha_{yy}$; α_{xy}
E''	2	–1	0	–2	1	0	α_{xz}; α_{zy}; μ_x; μ_y

clasified to C_{2v} and D_{3h} point groups are given in the last column of Tables 1 and 2. From these tables it results that the molecules belonging to D_{nh} with $n > 3$ are not dipolar molecules from the electric point of view. The molecules possessing only a C_n axis of symmetry and $n\sigma_v$ vertical planes must have their electric dipole moment along this axis.

3. CLASSES OF SYMMETRY OF THE POINT GROUPS

The concept of class of symmetry, or class of equivalence simplifies the group theory applications [2]. The symmetry operations of each point group can be devided into classes with the property that the members of any class always have the same character χ. Therefore it is not necessary to fiind the character for each operation, but merely for a sample operation in each class. Usually, on the Tables of the irreps, the characters for each class are given, not for each symmetry operation. These observations permit to obtain information about the number $n^{(\gamma)}$ of times the irrep $\Gamma^{(\gamma)}$ appears in the reduced reprezentation Γ.

$$n^{(\gamma)} = \frac{1}{g}\sum_j g_j \cdot \chi_j^{(\gamma)} * \cdot \chi_j \tag{7}$$

In relation (6) the following notations were made: g and g_j the numbers of symmetry operations in the point group and in the j class; χ_j and $\chi_j^{(\gamma)}$ – the character of each operation in a class and character of the γ^{th} irrep.

From the mathematical point of view, the fundamental definition of a class is:

Let be the operations O_1 and O_2 in the group G, if relation:

$$X^{-1}O_1X = O_2, \quad \text{or} \quad O_1X = XO_2 \tag{8}$$

is true for some operation of the group, then O_1 and O_2 are said to belong to the same class. The Abelian group C_{2v} has 4 classes of operations. In each class only one symmetry operation is classified. The number of the classes is equal to the order of the group. The molecules classified to this group possess only non-degenerate energetic states. The group D_{3h} has two equivalent operations C_3 which belong to the class of rotations by $2\pi/3$ radians; three reflections $\sigma_v^{(1)}$; $\sigma_v^{(2)}$; $\sigma_v^{(3)}$ in the equivalent vertical planes of symmetry; two reflection-rotation operations corresponding to the axes S_3 and three equivalent rotations by π around the three corresponding axes. The molecules belonging to this group have degenerated energetical levels.

Operations in the same class have the same character. When in a given representation of the point group, the coefficients of the transformations from relation (6) are $O_{ij}^{(1)}$; $O_{ij}^{(2)}$; X_{ij} and $(X^{-1})_{ij}$ respectively, then the character of O_2 is:

$$\chi_{O_2} = \sum_i O_{ii}^{(2)} \tag{9}$$

and

$$\chi_{(X^{-1}O_1X)} = \sum_{i,j,k} \left(X^{-1}\right)_{ij} \cdot O_{jk}^{(1)} \cdot X_{ki} = \sum_{j,k} O_{jk}^{(1)} \sum_i \left(X^{-1}\right)_{ij} X_{ki} = \sum_j A_{jj} \tag{10}$$

The rule of product of transformations has been used in order to obtain Eq. (10) which shows that the characters of the equivalent operations are the same.

$$\chi_{(X^{-1}O_1X)} = \chi_{O_2}, \quad \text{or} \quad \chi_{O_1} = \chi_{O_2} \tag{11}$$

The classes for all point groups are included in the Tables of irreducible representations.

4. CONCLUSIONS

When a molecule is attributed to a point group of symmetry, some of its physical properties can be easily described without supplementar calculations. The molecules belonging to the point groups of high symmetry are nonpolar and can have only Raman vibrational spectra, while the molecules with fewer elements of symmetry are polar from the electrical point of view and have vibrational spectra in the infrared range [7, 8].

REFERENCES

1. P. W. Atkins, *Physical Chemistry*, Oxford University Press, Oxford, Melbourne, Tokyo, 1994.
2. H. F. Jones, *Groups. Representations and Physics*, Imperial College of London, 1989.
3. M. Eliaşevici, *Spectroscopie atomică şi moleculară*, (traducere din limba rusă), Ed. Acad. Române, Bucureşti, 1968.
4. A. Streitwieser Jr., *Molecular Orbital Theory of Organic Chemists*, Wiley, London, 1961.
5. P. Gans, *Vibrating Molecules*, Ed. Chapman and Hall LTD, 1970.
6. *Molecular Vibrations, The Theory of Infrared and Raman Vibrational Spectra*, Eds. E.B. Wilson, J. C. Decius, P. C. Cross, Mc Graw Hill, New York, 1955.
7. D. O. Dorohoi, S. Gosav, S. Picoş, *Selection rules in vibrational spectra and molecular symmetry*, National Conference "Strategii XXI", Bucharest, 13–14 aprilie 2006, pp. 282–287.
8. D. O. DOROHOI, S. GOSAV, *Theory group representations applied to molecular vibrations*, National Conference "Strategii XXI", Bucharest, 13–14 aprilie 2006, pp. 7–17.