INVESTIGATIONS ON THE APPLICATIONS OF GROUP THEORY TO ROTATIONS

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A THESIS

Submitted to Women's University College
Ain Shams University

For
The Degree of
M. Sc. In Applied Mathematics

1979

ACKNOWLEDGMENT

I wish to express my sincere thanks to Professor, A.A. Sabry, Head of the Mathematic Department, Faculty of Girls, Ain Shams University, for suggesting the topics of this thesis and for his great help and the time he spent in the discussions during the preparation of this thesis.

بسم الله الرحمن الرحيم

CONTENTS

INTRODUCTION

A thorough investigation on the important problem of rotation is given, with the application of the group theory. Such an investigation is quite essential for the further applications of rotations in higher dimensions in the modern developments of Elementary particle Physics.

In the first chapter, the essentials of the theory of group representations with important formulas are summarised.

In the second chapter, the representation of the classical three dimensional rotation group is given with a thorough investigation of the proper and improper rotation representations and their additions. The quantum mechanical rotation is also sketched with its general representation in the Hilbert space.

The introduction of the Clebsch-Gordan coefficients, and the Wigners 3-j symbols and their symmetries is discussed in the problem of addition of angular momenta in quantum mechanics. For three coupled angular momenta, the Racah W-coefficients and the 6-j symbols are also discussed together with their symmetry relations.

In chapter III, numerical values are given for some important integrals containing a product of three spherical harmonic functions, after establishing some recurrence relations for their numerical computations. These tables find wide use in many applications.

In chapter IV, the energy levels and eigen vectors of a general asymmetric molecule is discussed with implicit values for low values of the quantum numbers defining the rotation.

In the last chapter V, the electronic part of the angular momenta of molecules is discussed with some investigations on the important problem of electronic orbitals and their symmetries.

CHAPTER I

GENERAL THEORY OF GROUP REPRESENTATIONS

In this chapter we shall summarise all the important postulate of group theory which are very important in the applications to the angular momenta of molecules as a whole and in particular to the electronic angular momenta of molecules.

We shall say that a representation T of a group G is given in a certain linear space L, if to each element R of G there is a corresponding operator T (g) in the space L such that to each product of the element of the group there is a corresponding product of the operators

$$T\,(R_1)\;T\,(R_2) = T\,(R_1R_2) \qquad (1)$$

The dimensionality of space L is said to be the dimensionality of the representation. Two representations T(R) and T'(R) which are connected by a relation such as

$$T'(R) = A\;T(R)\;A^{-1} \qquad (2)$$

are said to be equivalent.

A transformation which converts a representation into an equivalent one is called a similarity transformation.

All representations equivalent to a given one are equivalent to each other. Hence all the representations of a given group G can be split into classes of mutually equivalent representations. Each class of equivalent representations of a finite group contains unitary representations.

A representation T of a group G in space L is called reducible, if there exists in L at least one nontrivial subspace L_1 invariant with respect to all operators T(R), $(R \in G)$.

The representation T of G in space L is called irreducible, if in L there is no nontrivial subspace L_1 invariant with respect to all the operators T(R), $(R \in G)$.
A space L can be expanded into a sum of mutually orthogonal invariant subspaces

$$L = L^{(1)} + L^{(2)} + \ldots\ldots + L^{(m)} \qquad (3)$$

We quote without proof the following important properties of irreducible representations of finite groups [1,2] :

1- The number of non equivalent irreducible representations of a group is equal to the number of classes in the group.

2- The sum of the squares of the dimensions of the non-equivalent irreducible representations is equal to the order of the group, i.e.,

$$f_1^2 + f_2^2 + \dots + f_r^2 = g \tag{4}$$

where f_α denotes the dimension of the $\alpha^{\underline{th}}$ irreducible representation.

3- The dimension of an irreducible representation of a finite group is a divisor of the order of the group.

4- The following orthogonality relations hold for the matrix elements of irreducible represenations :-

$$\sum_R T_{ik}^{(\alpha)}(R)^* \, T_{\ell m}^{(\beta)}(R) = (g/f_\alpha)\, \delta_{\alpha\beta}\, \delta_{i\ell}\, \delta_{km} \tag{5}$$

$$\sum_{\alpha, i, k} (f_\alpha / g)\, T_{ik}^{(\alpha)}(R_1)^* \, T_{ik}^{(\alpha)}(R_2)\ \delta_{R_1 R_2} \tag{6}$$

The character $\chi(R)$ of the representation $T(R)$ is defined as the sum of diagonal elements of the matrix that correspond to the operator $T(R)$ for any basis. i.e.,[3]

$$\chi^{(\alpha)}(R) = \sum_i T_{ii}^{(\alpha)}(R) \tag{7}$$

The characters of equivalent representations are identical. The characters of irreducible representations satisfy the following orthogonality relation :-

$$\sum_R \chi^{(\alpha)}(R)^* \, \chi^{(\beta)}(R) = g\, \delta_{\alpha\beta} \tag{8}$$

Since the characters of all the elements belonging to a given class are equal, eq. (8) can be written in the form

$$\sum_{c} g_c \chi^{(\alpha)}(c)^* \chi^{(\beta)}(c) = g\,\delta_{\alpha\beta} \qquad (9)$$

where the sum is taken over all classes C of the group, and g_c denotes the number of elements in C. Another orthogonality relation for the characters of irreducible representations is

$$\sum_{\alpha} \chi^{(\alpha)}(C_i)^* \chi^{(\alpha)}(C_k) = (g/g_{c_i})\,\delta_{C_i C_k} \qquad (10)$$

(4)
<u>The point groups :-</u>

We use a symbol σ for reflection in a plane. Since two reflections in the same plane return us to initial position :- we have

$$\sigma^2 = E \qquad (11)$$

We denote by σ_h reflection in an axis perpendicular to rotation axis, and by σ_v reflection in a plane passing through the axis.

A product of two reflections is equal to a rotation through double the angle between planes. The matrix representation of a reflection is equal to the matrix representation of a rotation with $\alpha = \pi$ ($R_{ij} = -\delta_{ij} + 2\,K_iK_j$) multiplied by a matrix representation of inversion. Hence it is equal to

$$R = \begin{pmatrix} 1 - 2K_1^2 & -2K_1K_2 & -2K_1K_3 \\ -2K_2K_1 & 1 - 2K_2^2 & -2K_2K_3 \\ -2K_3K_1 & -2K_3K_2 & 1 - 2K_3^2 \end{pmatrix} \quad (12)$$

Every subgroup of the full orthogonal group is called a point group.

1- The group C_n has elements C_n, C_n^2, ..., C_n^{n-1}, e is a cyclic group. The axis C_n is called a two - sided axis if C_n and C_n^{-1} are conjugate. Other wise C_n is called a one sided axis. Every operation of this group forms a class, and the irreducible represent-ation are all one - dimensional.

2- The group D_n has one $n^{\underline{th}}$ order C_n axis and n second order axes perpendicular to it. These axes are denoted by u_1, u_2, ..., u_n the angle between two of them is $\frac{\pi}{n}$. the group contains 2 n operations : n rotations C_n^k about the vertical axis and n rotations through π about the horizontal axis. The number of classes of the group D_n are ($\frac{n}{2}$ + 3) if n is even and ($\frac{n+3}{2}$) if n is odd.

3- The group S_{2n} consists of powers of the rotation inversion $S_{2n} = S\left(\frac{\pi}{n}\right)$. It has 2 n elements : $e, S_{2n}, S_{2n}^{2}, \ldots, S_{2n}^{2n-1}$. The even powers of S_{2n} form a subgroup coinciding with C_n. S_{2n} is a cyclic group. It has (n + 1) classes

$$\{e\}, \{S_{2n}, S_{2n}^{2n-1}\} \ldots \{S_{2n}^{n-1}, S_{2n}^{n+1}\}, \{S_{2n}^{n}\} .$$

4- The group C_{nh} consists of rotations and rotation - inversions. It thus contains 2 n elements, C_n^k , $\sigma_h C_n^k$ ($k = 0, 1, 2, \ldots, n-1$). The C_{nh} group is commutative. Each element constitute a class by itself.

5- The group C_{nv} contains one n^{th} order axis and n vertical planes $\sigma_1, \sigma_2, \ldots, \sigma_n$ that pass through the axis C_n. The group C_{nv} has 2 n elements $e, C_n, C_n^2, \ldots, C_n^{n-1}, \sigma_1, \sigma_2, \ldots, \sigma_n$. It is isomorphic to the group D_n and therefore, the number of their classes and elements are equal , so that the number of classes is equal to $\left(\frac{n}{2} + 3\right)$ if n is even or to $\left(\frac{n+3}{2}\right)$ if n is odd.

6- The group D_{nh} has the 2 n elements of the group C_{nh}, n horizontal second order axes $u_1, u_2, \ldots, u_n$ and n vertical reflection planes $\sigma_1, \sigma_2, \ldots, \sigma_n$ passing through these axes. The number of classes of this group is equal to $(n + 10)$ if n is even or $(n + 5)$ if n is odd.

7- The group D_{nd} contains one rotation - inversion axis S_{2n} of order 2 n, n vertical reflection planes σ_1, σ_2, ..., σ_n and n horizontal second order axes u_1, u_2, ..., u_n. The total number of classes is $(n + 3)$.

8- The group T has four axes C_3 and three axes C_2. The second order axes are u_{12}, u_{13}, u_{14}. Thus T contains beside the unit element four rotations of $\frac{2\pi}{3}$, four rotations of $\frac{4\pi}{3}$ and three rotations of π i.e. altogether 12 elements. We have then following classes

$$\{e\} , \{C_3^{(i)}\} , \{C_3^{(i)^2}\} , \{u_{1i}\}.$$

9- The group T_d contains the group T as a subgroup. In addition to the 12 elements of T, the group T_d contains the 6 reflection planes σ_{12}, σ_{13}, σ_{14}, σ_{23}, σ_{24}, σ_{34} and the two rotation - inversions S_4, S_4^3 about each of the three second order axes. Thus it has 24 elements. It decomposes into 5 classes as follows

$$\{e\} , \{C_3^{(i)}, C_3^{(i)^2}\}, \{u_{1i}\}, \{S_4^{(ik)}, S_4^{(ik)^3}\} , \{\sigma_{ik}\} .$$

10- The group T_h is obtained from T by adding the inversion and carrying out inversion on all the elements of the group T. The product of the inversion and the rotation $C_3^{(1)}$ is the rotation inversion $IC_3^{(1)} = S_6^{(1)^5}$ also $IC_3^{(1)^2} = S_6^{(1)}$. The product of inversion I and a π - rotation is equal to a reflection in a plane perpendicular to the axis of rotation. Thus the total number of elements of this group is 24 its classes are

$$\{e\}, \{C_3^{(1)}\}, \{C_3^{(1)^2}\}, \{u_{1k}\}, \{I\}, \{S_6^{(1)}\}, \{S_6^{(1)^5}\}, \{\sigma_{1k}\}.$$

11- The group O contains three fourth order axes $C_4^{(1)}$, $C_4^{(2)}$ and $C_4^{(3)}$; four third order axes $C_3^{(1)}$, $C_3^{(2)}$, $C_3^{(3)}$ and $C_3^{(4)}$ and six second order axes u_{12}, u_{23}, u_{34}, u_{41}, u_{26} and u_{37}, beside the unit element. The group O contains three rotations of $\frac{\pi}{2}$, three rotations of π and three of $\frac{3\pi}{2}$; four rotations of $\frac{2\pi}{3}$, four rotations of $\frac{4\pi}{3}$ and finally six rotations of π.
i.e. altogether 24 elements. We have the following classes

$$\{e\}, \{C_4^{(1)}, C_4^{(1)^3}\}, \{C_4^{(1)^2}\}, \{C_3^{(1)}, C_3^{(1)^2}\}, \{u_{1k}\}.$$

12- The group O_h contains 48 elements. These elements belong to 12 classes.