CLASSIFICATION OF MOLECULAR TERMS WITH RESPECT TO TOTAL NUCLEAR SPIN

E. G. KAPLAN

Institute of Chemical Physics, Academy of Sciences, U.S.S.R.

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A method is proposed for finding nuclear multiplicities of molecular terms, for nuclei of arbitrary spin. The relation between Young tableaus and total spin, on the one hand, and between the permutation group and the point symmetry group of the molecule, on the other, is used.

1. FORMULATION OF THE PROBLEM

THOUGH the nuclear spin has a negligible direct influence on molecular term values, it has a significant indirect effect on their symmetry. Namely, only those types of point symmetry groups of the molecule occur which correspond to the permutation symmetry of the nuclear spins. Existing methods enable one to find these allowed symmetry types together with their nuclear statistical weights.[1] However, each type of symmetry of the terms occurs only for definite values of the total nuclear spin. It is of interest to find this relation. The solutions of the analogous problem for electronic terms are very complicated, and have been achieved[2,3] only for spin $\frac{1}{2}$. The method presented in this paper allows one relatively easily to assign to terms the value of the total nuclear spin, for nuclei with arbitrary spin i, and at the same time automatically gives the allowed terms and their statistical weights.

2. BASIS OF THE METHOD

Let us consider a system of n identical nuclei, each having spin i. The permutation symmetry of the coordinate wave function of the system is determined by the Young tableaus which are consistent with the given spin value i.[1] Each Young tableau defines an irreducible representation of the group of permutations of n particles, whose characters are given in the tables of characters of the symmetric groups[4,5]. However, this representation may be reducible with respect to the point group of the molecule. By resolving into irreducible representations of the point group, we find the relation between symmetry types of the molecule and its coordinate Young tableaus. On the other hand, there is a one-to-one correspondence between the coordinate and spin Young tableaus, which is determined by the Pauli principle. But each spin Young tableau corresponds to definite values of the total spin of the particles. Thus we find the relation between the total nuclear spin and the molecular terms. Terms which do not appear in the representations of the coordinate Young tableaus are forbidden.

3. YOUNG TABLEAUS AND TOTAL SPIN

In the general case of arbitrary spin i, a single Young tableau may correspond to several values of the total spin of the system. This connection can be found by adding cells to Young tableaus which have already been investigated, and corresponds to successive vector addition of spins.[6] The permutation symmetry of the state corresponding to the product of two Young tableaus is given by Littlewood's theorem (reference 5, p. 94).*

The results of the calculation for n = 3, 4, and i = 1, $\frac{3}{2}$, are given in the table.

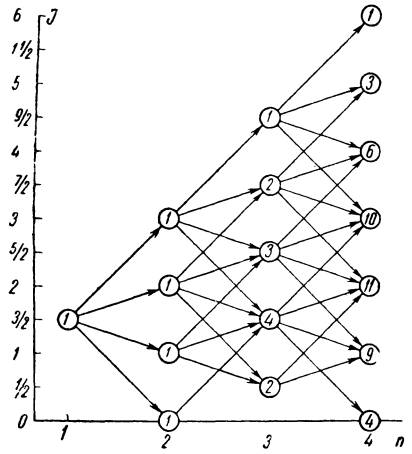
Young tableau*	Dimensionality of representation	i = 1	i = 3/2 †
[1³]	1	0	3/2
[2,1]	2	1; 2	1/2; 3/2; 5/2; 7/2
[3]	1	1; 3	3/2; 5/2; 9/2;
[1⁴]	1	—	0
[2,1²]	3	1	1; 2; 3
[2²]	2	0; 2	0; 2 (2); 4
[3,1]	3	1; 2; 3;	1 (2); 2; 3 (2); 4; 5
[4]	1	0; 2; 4	0; 2; 3; 4; 6

*$[\lambda_1^{(a)}, \lambda_2^{(b)}, \cdots]$ denotes a Young tableau in which the first a rows contain λ_1 boxes, the next b rows have λ_2 boxes, etc.

†The numbers in parentheses give the number of times a given total spin occurs, if this number is greater than unity.

*The formulation of Littlewood's theorem is also in reference 6, p. 527.

We note that to check the results we can make use of the fact that the total number of states of a system of n particles which give total spin I is equal to the sum of the dimensionalities of the irreducible representations of those Young tableaus which occur for the given value of I. On the other hand this same number can be found from the vector addition diagrams used by Van Vleck for electronic configurations.[7] The figure shows the diagram for $i = 3/2$. The numbers in circles given the total number of states for given I and n.



4. MOLECULES WITH A TOTAL SPIN WHICH IS DETERMINED BY IDENTICAL NUCLEI

Let us consider molecules whose nuclei can be divided into two groups. In the one group there are identical nuclei with $i \neq 0$, while the nuclei of the other group have $i = 0$. Then the total spin of the molecule will be determined by the total spin of the group of nuclei with $i \neq 0$.

Suppose that a molecule of type YX_4 ($i(Y) = 0$) has point symmetry T_d.* Any symmetry operation of the molecule can be considered as a permutation of the nuclei. Thus we can associate with each class of the point symmetry group the corresponding class of the permutation group:

Classes of group T_d	E	C_3	C_2	σ_d	S_4
Classes of the permutation group	$[1^4]$	[1,3]	$[2^2]$	$[1^2,2]$	[4]

Next, resolving the characters of the irreducible representations of the coordinate Young tableaus in characters of the point group, we find the correspondence between symmetry types of the molecule and coordinate Young tableaus. In the case of symmetry T_d, there is a one-to-one correspondence, since the group T_d is isomorphic to the group of permutations of four objects:

$$[4] \leftrightarrow A_1, \quad [1^4] \leftrightarrow A_2, \quad [2^2] \leftrightarrow E, \quad [2, 1^2] \leftrightarrow F_1, \quad [3, 1] \leftrightarrow F_2.$$

*We shall use the notation of reference 1.

a) $C^{12}H_4^1$; $i(C^{12}) = 0$, $i(H^1) = 1/2$. The allowed spin tableaus are [4], $I = 2$; [3,1], $I = 1$; $[2^2]$, $I = 0$. The corresponding coordinate tableaus are $[1^4]$, $[2,1^2]$, $[2^2]$. Consequently, the possible levels are $^5A_2$, $^3F_1$, ^1E.

b) $C^{12}H_4^2$; $i(H^2) = 1$. The spin and coordinate tableaus have the same symmetry. The allowed spin patterns are [4], [3,1], $[2^2]$, $[2,1^2]$. The corresponding values of total spin are given in the table. Thus the possible levels are $^{9,5,1}A_1$; $^{5,1}E$; $^{7,5,3}F_2$; $^3F_1$. The sum of the multiplicities of each level gives its nuclear degeneracy (statistical weight).

c) $C^{12}Cl_4^{35}$; $i(Cl^{35}) = 3/2$. All spin patterns for $n = 4$ are allowed. Using the fact that the coordinate patterns are dual to the spin patterns, and taking the total spin values from the table, we find the following level multiplicities:

$$^1A_1; \ ^{13,9,7,5,1}A_2; \ ^{9,5(2),1}E; \ ^{11,9,7(2),5,3(2)}F_1; \ ^{7,5,3}F_2.$$

As another example we consider the benzene molecule $C_6^{12}H_6^1$, with point symmetry D_{6h}. Since the molecule is planar, inversion is equivalent to a rotation, so we can restrict ourselves to the symmetry D_6. We have a system of six identical nuclei with $i = 1/2$. The allowed coordinate patterns are $[1^6]$, $[2.1^4]$, $[2^2, 1^2]$, $[2^3]$, with total spins of 3, 2, 1, and 0 respectively. Resolution into irreducible representations of the point group gives the following term multiplicities:

$$^{5,1(2)}A_1; \ ^3A_2; \ ^{7,3(2)}B_1; \ ^1B_2; \ ^{5,3(2)}E_1; \ ^{5,3,1}E_2.$$

5. MOLECULES CONSISTING OF SEVERAL GROUPS OF IDENTICAL NUCLEI WITH $i \neq 0$.

In this case we can find the total spin of each of the groups for each molecular term. We then construct direct products of the irreducible representations of each of the groups. The resolution of these direct products into irreducible parts gives the allowed symmetry types. The total statistical weight of a term is given by the sum of the statistical weights of the direct products (in whose resolution the particular term occurs), multiplied by the number of times the term appears in the direct product. We note that if we want only to find the total statistical weights of the terms, this can be done more simply for complicated molecules by the method of reference 1.

If the molecule has one group of identical nuclei, while all the other nuclei with $i \neq 0$ are different, the allowed terms can be found by considering the permutation symmetry of the identical nuclei. To

find the total statistical weight we must multiply the multiplicity found in this way by the number of different projections of spin of the remaining nuclei.

Let us consider, as an example, the molecule $C^{13}H^{1}Cl_3^{35}$, $i(C^{13}) = 1/2$; symmetry group C_{3V}. From the character tables, we find the correspondence $[3] \leftrightarrow A_1$; $[2,1] \leftrightarrow E$; $[1^3] \leftrightarrow A_2$. Noting that the spin patterns for $i = 3/2$ must be dual to the coordinate patterns, we find that to a level of symmetry A_1 there correspond total spins of the chlorine nuclei equal to $3/2$; to A_2 the spins $3/2$, $5/2$, $9/2$; to E $-$ $1/2$, $3/2$, $5/2$, $7/2$. We find the total statistical weight by multiplying the statistical weight due to the chlorine nuclei by four. As a result we get: $16\,A_1$, $80\,A_2$, $80\,E$.

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