METHOD OF FINDING ALLOWED MULTIPLETS IN CALCULATIONS OF MANY-ELECTRON SYSTEMS

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A method is proposed for finding the allowed multiplets of a many-electron system when complete account is taken of the configuration interaction (this corresponds in the Heitler-London scheme to an account of covalent as well as all possible ionic structures). The method is based on the connection between the molecular symmetry point group and the nuclear commutation group and the connection between the Young scheme and the total spin of the system. The use of the developed procedure is illustrated with an example in which 248 allowed multiplets are obtained for a ring of six hydrogen atoms.

1. FORMULATION OF PROBLEM

IN those cases when the Hamiltonian of a system of N electrons does not contain spin variables, the states of the system are classified by the values of the summary spin S. The complete wave function is an eigenfunction of the operator $\hat{S}^2$ and is represented in the general case in the form of a linear combination of products of the coordinate wave function of the system and the spin wave function. The coefficients in this linear combination are chosen to satisfy the Pauli principle, i.e., such that the function is antisymmetrical against permutation of the electrons. In the presence of point symmetry, for example for symmetrical molecules, the coordinate wave functions belonging to a certain energy level of the system should transform in accord with the irreducible representations Γ of a point symmetry group. Consequently, neglecting spin interactions, each energy level of a symmetrical molecule is characterized by an irreducible representation Γ and a total spin S. In analogy with the terminology used in atomic spectroscopy, such states of the system are called multiplets and are designated $^{2S+1}\Gamma$.

An approximate solution of the problem by a variational method or with the aid of perturbation theory calls for the need for solving the secular equation. If the initial wave functions are chosen such that they are eigenfunctions of the multiplets, the initial secular equation is quasi-diagonalized and breaks up into separate secular equations, each of which corresponds to a certain multiplet $^{2S+1}\Gamma$. The order of the obtained secular equations is equal to the multiplicity of the given multiplet in the expansion of the representation formed by the initial set of basis functions.[1] The matrix elements of the Hamiltonian are best obtained with the aid of the procedure developed by us earlier.[2-4]

It is of interest, before we proceed to a direct calculation, to determine the allowed multiplets and the maximum order of the secular equations encountered in solving the problem. It is known that when account is taken of all the configurations obtained from the given set of atomic functions, calculation by the Heitler-London method and by the molecular-orbital method are equivalent.[1] Naturally, the resultant multiplet structure is also the same. In this article, when determining the allowed multiplets, we start from the concepts of covalent and ionic structures, introduced in molecular calculations by the Heitler-London method. The analysis is limited to the case when the number of interacting electrons is equal to the number of atoms and one atomic orbital is specified for each atom.

The existing method of finding the allowed multiplets has been described for covalent structures by Slater (see [1], p. 373). It is based on distributing the electron spins among the atoms in all possible ways and finding the characters of the obtained reducible representations, followed by subtraction from one another of the representations corresponding to different values of the total-spin projection. Slater's method is rather cumbersome and its use becomes difficult with increasing number of electrons. The method developed below is based on the connection between the permutation and point groups of the molecule, and calls for its

application for only knowledge of tables of the characters of the irreducible representations, which can be found in most texts on group theory.

2. THE METHOD

A. Covalent structures. As shown in [2], when there is no spin in the interaction operator, all the properties of the system of interacting particles can be adequately described by specifying the co-ordinate wave function which has the commutation symmetry of the corresponding Young scheme; we denote it by $[\lambda]$. If the spin function of the system has the permutation symmetry of the dual Young scheme $[\tilde{\lambda}]$, obtained from $[\lambda]$ by interchanging rows and columns, then the total wave function, made up of products of the coordinate wave function and the spin wave function, will be antisymmetrical. It is important for what follows that the coordinate wave functions $\Phi_r^{[\lambda]}$ form a basis of the irreducible representation of the permutation group, characterized by the Young scheme $[\lambda]$. The index r runs through f_λ values, where f_λ denotes the dimensionality of the irreducible representation $[\lambda]$. The spin wave function $\Omega_r^{[\lambda]}$ is the proper wave function of the operator $\hat{S}^2$, and a value of the spin is uniquely connected with each $[\tilde{\lambda}]$ for the electrons [2,5]. Consequently the set of f_λ functions $\Phi_r^{[\lambda]}$ corresponds to a state with a definite spin S. It is possible to make up f_λ independent states with a given spin S, since there is a total of f_λ independent bases for the representation $[\lambda]$ (see [2]).

The term "covalent structure" is usually used to define a certain configuration of neutral atoms, characterized by a definite method of adding the spins of the atomic elements to make up the total spin S. At fixed value of the total spin S, there usually exist several independent methods of adding the spins of the individual electrons. The number of such addition methods determines the number of independent covalent structures. It was shown in [2] that the coordinate functions of the covalent structures are linear combinations of the functions $\Phi_r^{[\lambda]}$ belonging to independent bases; consequently, the functions of the structures also form a certain basis of the irreducible representation $[\lambda]$, and the number of independent covalent structures is determined by the dimensionality of the irreducible representation $[\lambda]$.

For symmetrical molecules, the coordinate wave functions should belong to the basis of the irreducible representations Γ of the point symmetry group. The basis functions of the representations Γ can be constructed by taking the corre-

sponding linear combinations $\Phi_r^{[\lambda]}$. The procedure for finding such combinations is described in [4]. The determination of the possible point symmetry types that can be constructed from functions with permutation symmetry $[\lambda]$ can be readily realized from tables of the characters of the corresponding irreducible representations. This can be done because the point symmetry group of the molecule is a subgroup of the permutation group of the molecule atoms. Indeed, any operation of a point group can be represented as a permutation of atoms. At the same time, the operations of the point group run through not all the N! permutations, but only those corresponding to rotations and reflections of the molecule as a whole. It is shown that the irreducible representation of a certain group can become irreducible on going over to its subgroup. The expansion of the representation $[\lambda]$ into representations Γ is effected by means of a standard procedure—it is merely necessary beforehand to set in correspondence an appropriate permutation of the atoms to each operation of the point group. Tables of the characters of irreducible representations of the permutation group are given in the books by Lyubarskiĭ [6] and Murnaghan, [7] and tables of the characters of the irreducible representations of the point group can be taken, for example, from the book of Landau and Lifshitz. [5]

Thus, the method of finding the allowed multiplets for covalent structures can be represented by the following scheme: [1]

$$
\begin{array}{ccc}
[\lambda]_{\text{coord}} & \leftrightarrow & [\lambda]_{\text{spin}} \\
\downarrow & & \downarrow \\
\Gamma & \leftrightarrow & S
\end{array}
\tag{1}
$$

B. Ionic structures. The inclusion of ionic structures in the calculation takes into account configurations in which one or several electrons go over from their atoms to foreign atoms, forming pairs of positively and negatively charged atoms. To find the allowed multiplets it is necessary to subdivide first the aggregate of the ionic structures into individual sets, within which each structure is transformed in terms of the other by the molecule-symmetry operations. It is convenient to be guided here by the following rules:

1. If the ionic structure does not have symmetry elements, then the action of all the symmetry operations of the point group of the molecule (we denote the order of the group by the letter g) on

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[1] The connection between the types of symmetry of the coordinate wave function of the molecule and the values of the summary nuclear spin I for nuclei with arbitrary spin i is also determined by means of scheme (1)[8].

the ionic structure leads to g different structures forming a regular representation. The expansion of the regular representation is trivial: each irreducible representation enters in the expansion a number of times equal to its dimensionality.[5]

2. If the point group of the molecule has a certain subgroup H (we denote its order by k) with respect to which the given ionic structure is invariant, then the representation generated by the given structure is narrower than the regular one and has a dimensionality g/k.

To prove the latter statement let us break up all the elements of the group into adjacent classes relative to the subgroup H:[6] H, HR_1, HR_2, ..., HR_m. It is obvious that the action of the operations included in one adjacent class is equivalent. Inasmuch as there is a total of g/k adjacent classes, the number of different structures generated by the structure with symmetry group H is also equal to g/k.

For example, for a hypothetical molecule with a symmetry group D_4 (g = 8) there can exist two types of structures with one pair of ions (Fig. 1). Structure 1 does not have symmetry elements; consequently, it is possible to form eight different structures of type 1. Structure 2 is invariant with respect to the operations of group H of second order with elements E and U_2. Consequently there are only four structures of type 2.

It must be further taken into account that each ionic structure can exist in the form of several modifications corresponding to several independent methods of adding the unpaired spins to make up the total spin. An ionic structure with a definite manner of adding the unpaired spins to make up the total spin S will be called an ionic spin modification. For a given ionic structure, the number of independent spin modifications is determined in analogy with the number of independent covalent structures. Namely, it is equal to the dimensionality $f_{\lambda'}$ of the irreducible representation $[\lambda']$ [2] corresponding to a specified value of the total spin S. Consequently there are $f_{\lambda'}$ spin modifications for each of the g/k ionic structures forming the basis of the irreducible representation of the point group. The dimensionality of the irreducible representation formed by ionic spin modifications is equal to $f_{\lambda'} g/k$.

We can prove the correctness of the following theorem:

The characters of the representation formed by ionic spin modifications are equal to the products of the number of ionic structures remaining unchanged under the influence of the given operation, by the corresponding characters of the representation $[\lambda']$.

The proof of the theorem follows from the relative independence of the ionic structures and of their spin modifications. Therefore a representation made up of ionic spin modifications can be regarded as a direct product of a representation made up of the ionic structures, by a representation made up of spin modifications.

Once the characters of the irreducible representations are determined, the expansion of the representation into irreducible representations follows the standard procedure and yields the allowed multiplets. In the next section we describe the application of the developed procedure to the determination of the allowed multiplets of a ring of six atoms.

3. DETERMINATION OF THE ALLOWED MULTIPLETS OF A RING OF SIX HYDROGEN ATOMS

Let us consider six hydrogen atoms located at the vertices of a regular hexagon. Our problem is to find the energy levels of such an interacting system with allowance for all possible configurations which can be obtained from the six 1s-configurations. Since there are not more than two electrons on each 1s-orbital, the total number of different groups of six electrons from the 12 spin orbitals can be 12!/6!6! = 924. Consequently, the initial secular equation for the given variational problem should be of order 924. Its solution is possible only after preliminary quasi-diagonalization, which is accomplished by making up from the initial 924 functions linear combinations that are eigenfunctions of the multiplets. A problem of this type was solved by Mattheis[9] and is discussed in Slater's book.[1] In this section we shall show how it is possible to find without special difficulty, with the aid of the method developed by us, all the
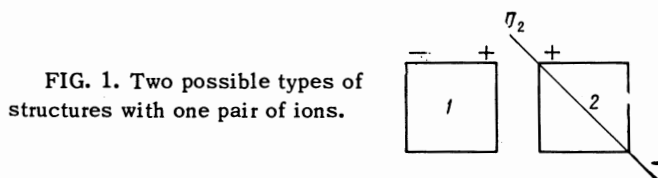
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[2] The prime in the notation for the Young scheme $[\tilde{\lambda}']$ indicates that this scheme is made up of spins of neutral atoms only; paired spins of negative ions in the scheme $[\tilde{\lambda}]$ are disregarded. We note that the dimensionalities of the representations $[\tilde{\lambda}]$ and $[\lambda]$ coincide.
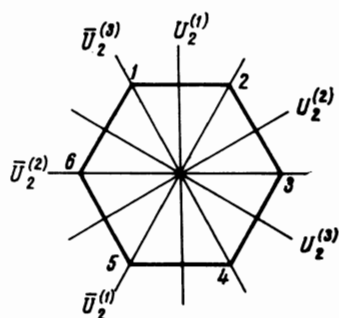
FIG. 1. Two possible types of structures with one pair of ions.

FIG. 2. Symmetry axes, lying in one plane, of regular hexagon.

FIG. 3. Types of structures $H_4H^+H^-$.

248 multiplets which are encountered in this problem.

A. Covalent structures. The point symmetry of the system is D_6. The symmetry axes which lie in the plane of the hexagon are shown in Fig. 2. The following spin Young schemes are possible

$$[\lambda]_{spin}: \quad [6] \quad [51] \quad [42] \quad [3^2]$$
$$S : \quad 3 \quad 2 \quad 1 \quad 0. \tag{2}$$

They correspond to coordinate Young schemes

$$[\lambda]_{coord}: \quad [1^6] \quad [21^4] \quad [2^21^2] \quad [2^3]. \tag{3}$$

Table I gives the correspondence between the classes of groups D_6 and π_6, and also the characters of the irreducible representations (3), as taken from [6]. The expansion of the representations given in Table I into irreducible representations of the group D_6 [3)] yields the allowed multiplets. As a result we find that the covalent structures form the following multiplets:

$$^7B_1; \quad ^5A_1, {}^5E_1, {}^5E_2; \quad ^3A_2, {}^3B_1(2), {}^3E_1(2), {}^3E_2;$$
$$^1A_1(2), {}^1B_2, {}^1E_2. \tag{4}$$

B. Ionic structures. Three types of ionic structures are possible in the system H_6: $H_4H^+H^-$, $H_2(H^+)_2(H^-)_2$, and $(H^+)_3(H^-)_3$. Let us consider each type separately.

I. $H_4H^+H^-$. The number of possible structures of this type is $2 \times 6!/2!4! = 30$ (double the number of combinations of six taken two at a time, since the permutation of plus and minus gives different structures). They can be broken into three

Table I

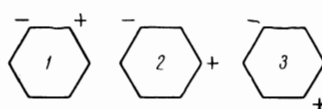| Classes D_6	E	C_2	$2C_3$	$2C_6$	$3U_2$	$3\bar{U}_2$
Classes π_6	$\{1^6\}$	$\{2^3\}$	$\{3^2\}$	$\{6\}$	$\{2^3\}$	$\{1^22^2\}$
$\chi^{[1^6]}$	1	-1	1	-1	-1	1
$\chi^{[21^4]}$	5	1	-1	1	1	1
$\chi^{[2^21^2]}$	9	-3	0	0	-3	1
$\chi^{[2^3]}$	5	3	2	0	3	1

sets (see Fig. 3). It is obvious that the structures shown in Fig. 3 do not transform into one another under the influence of the point-group operations. Structures 1 and 2 form regular sets, since they do not have any symmetry elements. Structure 3 is invariant against $\bar{U}_2^{(3)}$ rotation, and consequently its symmetry group consists of two elements E and $\bar{U}_2$. The set of structures of type 3 is narrower than the regular one and consists of $g/k = 6$ structures, in accordance with the rule 2 given in Sec. 2 (item B). Each of the ionic structures of the foregoing sets can be obtained in the form of $f_{\lambda'}$ spin modifications. Since only electrons of neutral atoms are taken into account, the following spin Young schemes are realized:

$$[4] \quad [31] \quad [2^2].$$
$$S = 2 \quad S = 1 \quad S = 0.$$

They correspond to the coordinate Young schemes:

$$[1^4] \quad [21^2] \quad [2^2]$$
$$f_{\lambda'} = 1 \quad f_{\lambda'} = 3 \quad f_{\lambda'} = 2.$$

The characters of the representations formed by the ionic spin modifications are determined in accordance with the rules given in Sec. 2. For the representations formed by regular sets (sets 1 and 2 of Fig. 3), the characters of all the operations, except E, are equal to zero; the character of the operation E is equal to the dimensionality of the representation, i.e., $12f_{\lambda'}$. For the representations made up by the set of structures of type 3, the character of the operation $\bar{U}_2$ is likewise not equal to zero. Since the action of the operation $\bar{U}_2$ leaves two structures of set 3 invariant, in accordance with the theorem given in Section 2, the character of the operation $\bar{U}_2$ is equal to $2\chi^{[\lambda']}(P)$ for the representation corresponding to the Young scheme $[\lambda']$. The operation $\bar{U}_2$ is equivalent to a permutation P belonging to the class $\{2^2\}$ of the group π_4. The characters of the irreducible representations of group π_4 were taken from [6]. Table II lists the characters of the representations formed by the sets 1 and 3 (the representations formed by the sets 1 and 2 are identical). In the right side are given the multiplicities of the irreducible representations of group D_6 in the expansion of the initial irreducible representations.

II. $H_4(H^+)_2(H^-)_2$. The number of structures of this type is equal to the products of the number of combinations from six by the number of the differ-
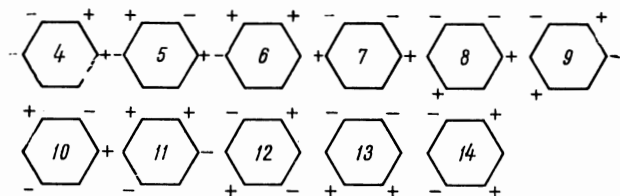

[3)] The characters of group D_3 were taken from [5]; operations U_2 and U'_2 of [5] are designated in our notation by $\bar{U}_2$ and U_2, respectively.

Table II

	Characters of irreducible representations						Multiplicities of irreducible representations					
	E	C_2	$2C_3$	$2C_6$	$3U_2$	$3\bar{U}_2$	A_1	A_2	B_1	B_2	E_1	E_2
$\chi_1\ (S=2)$	12	0	0	0	0	0	1	1	1	1	2	2
$\chi_1\ (S=1)$	36	0	0	0	0	0	3	3	3	3	6	6
$\chi_1\ (S=0)$	24	0	0	0	0	0	2	2	2	2	4	4
$\chi_3\ (S=2)$	6	0	0	0	0	2	1	0	1	0	1	1
$\chi_3\ (S=1)$	18	0	0	0	0	−2	1	2	1	2	3	3
$\chi_3\ (S=0)$	12	0	0	0	0	4	2	0	2	0	2	2
$\chi_6\ (S=1)$	6	0	0	0	−2	0	0	1	1	0	1	1
$\chi_6\ (S=0)$	6	0	0	0	2	0	1	0	0	1	1	1
$\chi_9\ (S=1)$	6	0	0	0	0	−2	0	1	0	1	1	1
$\chi_9\ (S=0)$	6	0	0	0	0	2	1	0	1	0	1	1
$\chi_{12}\ (S=1)$	6	−6	0	0	0	0	0	0	1	1	2	0
$\chi_{12}\ (S=0)$	6	6	0	0	0	0	1	1	0	0	0	2
$\chi_{14}\ (S=1)$	6	0	0	0	0	2	1	0	1	0	1	1
$\chi_{14}\ (S=0)$	6	0	0	0	0	2	1	0	1	0	1	1
$\chi_{15}\ (S=0)$	2	0	2	0	0	2	1	0	1	0	0	0

ent permutations of two pluses and two minuses, amounting to $(6!/4!2!)(4!/2!2!) = 90$. These 90 structures break up into 11 sets which do not transform in terms of one another. Figure 4 shows one structure of each set. Inasmuch as there is a total of only two unpaired spins, only triplet and singlet states are possible, corresponding to $[\lambda']$ equal respectively $[1^2]$ and $[2]$. In both cases $f_{\lambda'} = 1$; consequently the dimensionalities of the representations made up by the ionic spin modifications coincide with the dimensionality of the representations formed by the ionic structures.

FIG. 4. Types of structures $H_2(H^+)_2(H^-)_2$.

Structures 4, 5, 8, and 11 form regular sets. Since $f_{\lambda'} = 1$ for $S = 1$ and $S = 0$, the expansion of such sets does not depend on the multiplicity and can be written out immediately. Namely, the expansion of each of the foregoing sets contains

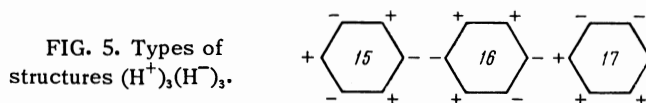$$^{3,1}A_1, \ ^{3,1}A_2, \ ^{3,1}B_1, \ ^{3,1}B_2, \ ^{3,1}E_1(2), \ ^{3,1}E_2(2). \tag{5}$$

The structures of sets 6, 7, and 13 have a symmetry axis U_2 (the axis designations are shown in Fig. 2) and form identical six-dimensional representations. The character of the operation U_2 is equal to $2\chi^{[\lambda']}(P) = \pm 2$; the upper sign is for $[\lambda'] = [2]$ and the lower for $[1^2]$.

The symmetry group of the structures of set 12 consists of elements E and C_2. Consequently we

have a six-dimensional representation. The operation C_2 leaves invariant all six ionic structures of the set. Therefore the character of the operation C_2 is equal to 2 ± 6, depending on $[\lambda']$.

The structures of sets 9, 10, and 14 have a symmetry axis $\bar{U}_2$ and also form six-dimensional representations. However, the characters of these representations for sets 9, 10 and for set 14 are different. The point is that for sets 9 and 10 the operation $\bar{U}_2$ corresponds to permutation of the unpaired spins; in set 14 the operation $\bar{U}_2$ leaves the unpaired spins untouched, since the $\bar{U}_2$ axis passes through the neutral atoms. The character of the noncoinciding representations, as well as their expansion into irreducible parts, are given in Table II.

III. $(H^+)_3(H^-)_3$. The number of such structures is equal to the number of combinations of three out of six, i.e., $6!/3!3! = 20$. There are three sets which do not transform in terms of one another (see Fig. 5). Inasmuch as all the spins are paired, only singlet states are possible.

FIG. 5. Types of structures $(H^+)_3(H^-)_3$.

The structures of set 15 are invariant against the group H with elements E, C_3, C_3^2, $3\bar{U}_2$. Consequently, they form a two-dimensional representation; its characters are given in Table II. Set 16 is regular. The characters of the representation formed by set 17 coincide with the characters $\chi_9\ (S = 0)$ from Table II.

The total number of multiplets in the expansions (4) and (5) and in Table II, with allowance for the coinciding representations, is 248. Consequently,

the interaction of a ring of six hydrogen atoms in the 1s-state leads to a splitting of a level degenerate in the zeroth approximation into 248 levels. The energies of these levels are obtained by solving the secular equations for each multiplet $^{2S+1}\Gamma$. The order of the secular equation is equal to the multiplicity with which the multiplet $^{2S+1}\Gamma$ enters in the expansion of the initial representation.

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