SOVIET PHYSICS JETP VOLUME 28, NUMBER 5 MAY 1969

A METHOD FOR DETERMINING ALLOWED MULTIPLETS OF MANY-ELECTRON POLYATOMIC SYSTEMS

V. I. CHEREPANOV and A. A. SHCHETKOV

Ural State University

Submitted February 27, 1968

Zh. Eksp. Teor. Fiz. 55, 1805–1817 (November 1968)

A method is proposed for determining allowed multiplets of many-electron polyatomic systems (molecules or complexes of impurity paramagnetic ions in a crystal) encountered in the Heitler–London scheme on the basis of the states of separate atoms (ions) of the system. Underlying the method is the relation between the total spin of the system and the type of interchange symmetry of the coordinate wave functions (Young pattern) and also the allowance for the transformation properties of the coordinate wave functions of the system with respect to space (point) and interchange permutative transformations of the electron coordinates. Tables of the point group characters and permutation groups are used in the method. The CH_4 molecule is considered as an example.

1. INTRODUCTION

THE method of determining allowed electronic terms from the specified states $\alpha_i w_i S_i L_i$ of the atoms making up the molecule (L_i and S_i are the quantum numbers of the total orbital angular momentum and of the total spin of the i-th atom, w_i is the parity, and α_i are additional quantum numbers) was proposed by Kotani,[1] for polyatomic molecules, and by Wigner and Witmer[2] for diatomic molecules. This method was generalized in [3] for impurity pairs and complexes in a crystal matrix.

The Kotani method, however, calls for rather laborious calculations of the spin factor $\mathcal{T}_S(g)$. This shortcoming can be overcome by taking into account (besides the spatial symmetry of the system) also the symmetry with respect to permutation of the electron coordinates. Some work was done in this direction by Kaplan.[4,5] In the latest of his papers[5] he proposed a method of determining the allowed multiplets of polyatomic molecules, based on the use of the representations of the permutation group, but Kaplan's method is applicable only to certain particular cases (for example, when the atoms of the molecule are only in the $^2S_+$ and $^1S_+$ states).

The purpose of the present paper is to propose a general method of determining allowed multiplets of multielectron polyatomic systems (molecules or complexes of impurity ions in crystals) from the states that make up the system of multielectron atoms (ions).1) This method, like the Kaplan method,[5] is based on the use of the well known connection between the permutation symmetry of the coordinate wave functions and the values of the total spin of the electron system (see in this respect, for example, [6], page 265).

2. SYMMETRY OF SYSTEM

We denote the point symmetry group of a free molecule by G_C^M (C—center of the point transformations of the molecule2)), and the permutation group of its electrons by S_Δ (where $\Delta = n_1 + n_2 + \ldots + n_N$, n_i is the number of electrons in the i-th atom, and N is the number of atoms in the molecule). Then the total symmetry group of the molecule is $S_\Delta \times G_C^M$.

The point symmetry group of the impurity complex in a crystal matrix can be determined[3] as the meet of two point groups

$$G_{C^K} = G_{C^M} \cap G_C, \tag{2.1}$$

where G_C^M is the point symmetry group of the "impurity molecule," taken from the crystal, and G_C is the local symmetry group for the position C in an impurity-free crystal (with "holes" on the sites, where impurity atoms (ions) of the substitution type are located). The total symmetry group of the impurity complex is $S_\Delta \times G_C^K$.3)

In the case of a free molecule, our problem consists of determining the allowed electronic terms $^{2S+1}\Gamma$ of the molecule from the specified states $\alpha_i w_i S_i L_i$ of its atoms (S—quantum number of the total electron spin and Γ—irreducible representation of the group G_C^M, characterizing the orbital state of the molecule). In the case of an impurity ion, the problem consists in determining the terms $^{2S+1}\Gamma$ of the complex from the specified states of the individual impurity ions in the crystal environment (S has the same meaning, and Γ is the irreducible representation of the group G_C^K). In the former case, the orbital degeneracy of each i-th ion is characterized by an irreducible representation $D_{(w_i L_i)}$ of the group of rotations with inversion $\bar{R}_i$. In the latter case, the orbital state of each i-th impurity ion is characterized by an irreducible representation Γ_i of a local symmetry group G_i of the given ion in the impurity-free crystal environment.

---

1) As in [5] in this article we deal with the determination of the symmetry of the electronic states of a system at fixed nuclei.

2) In some cases the choice of the center is arbitrary to a certain degree (for example, for $C_{\infty v}$ at any point of the symmetry axis, for C_s at any point of the symmetry plane).

3) We do not include in the considered system the electrons of the main atoms (ions) of the crystal, a procedure that can be justified if only the impurity ions have unfilled shells, and the covalency is weak.

We note that in this case the initial states are indeed the states of the impurity ion in an impurity-free crystal environment. A preliminary analysis of the influence of other impurity ions on the states of each given ion (with appropriately altered local symmetry G_i of each ion) leads to the same results (for details see [3c]). Obviously, the conclusion drawn for the impurity complex is more general and includes the case of a free molecule as a particular case, when all the $G_i \equiv \bar{R}_i$ and $G_C \equiv \bar{R}_C$, i.e., from (2.1) we get $G_C^K = G_C^M$. We shall therefore consider from now on directly the more general case of an impurity complex.

3. COORDINATE WAVE FUNCTIONS OF A COMPLEX

As is well known, for particles with spin $1/2$ there exists a one-to-one correspondence between the total spin S of the system of particles and the Young pattern, which characterizes the permutation symmetry of the coordinate wave function of the system.[6] Therefore, instead of specifying S, it is possible to indicate the Young pattern $[\lambda]$ of the coordinate wave function of the system. If the number of rows in the coordinate pattern $[\lambda]$, containing only one cell, is equal to k, then the total spin of the system of electrons in this state equals $S = k/2$.[6] This pertains not only to the complex as a whole, but also to the states of the individual ions (which generally speaking, are multielectronic), which can also be characterized in place of S_i by the coordinates of the Young patterns $[\lambda_i]$ of the permutation groups S_{n_i}.

The coordinate wave functions of impurity ions will be denoted by

$$\Phi(A_i t_i \alpha_i \Gamma_i M_i [\lambda_i] r_i | 1 \ldots n_i),$$

where A_i indicates the location of the nucleus of the ion, t_i is the type of ion (with allowance not only of the species of the ion, but also of its crystal environment, i.e., t_i distinguishes equivalent ions from the nonequivalent ones), M_i is the "row" of the representation Γ_i of the group G_i, r_i is the "row" of the representation $[\lambda_i]$, and the numbers 1, 2, ..., n_i following the bar denote the coordinates of the electrons. For a free atom, M_i is the projection of the angular momentum L_i on the quantization axis. For ions in a crystal, M_i can be understood as the projection of a certain "quasimomentum[7] on the principal symmetry axis of the group G_i.

If we write the coordinate wave functions of the complex in the form of all possible products

$$\begin{gathered}\Phi(A_1 t_1 \varkappa_1 M_1 r_1; \ldots; A_N t_N \varkappa_N M_N r_N | 1\,2 \ldots \Delta) \\ = \Phi(A_1 t_1 \varkappa_1 M_1 r_1 | 1\,2 \ldots n_1) \ldots \Phi(A_N t_N \varkappa_N M_N r_N | \Delta - n_N + 1 \ldots \Delta),\end{gathered} \quad (3.1)$$

where $\kappa_i = \alpha_i \Gamma_i [\lambda_i]$, then they still do not form a basis for the representation of the permutation group S_Δ (they form the basis of the representation $[\lambda_1] \times [\lambda_2] \times \ldots \times [\lambda_N]$ of the subgroup $S_0 \equiv S_{n_1} \times \ldots \times S_{n_N}$ of the "internal" permutations of the electrons and ions). Nor do the functions (3.1) form in the general case a basis for the representation of the group G_C^K, since G_C^K is generally speaking not a subgroup of the group $G_1 \times G_2 \times \ldots \ltimes G_N$.

Let us expand the group S_Δ into left-side co-sets in the subgroup S_0:

$$S_\Delta = S_0 + Q_1 S_0 + \ldots + Q_k S_0. \quad (3.2)$$

The chosen permutations 1, Q_1, Q_2, ... will be called the Q-set.[4] The number of co-sets (i.e., the number of permutations in the Q-set, including the identical permutation), as is well known, is equal to the order of the group S_Δ, divided by the order of the group S_0, i.e., $N_Q = \Delta!/n_1! \ldots n_N!$. From each function (3.1) it is possible to form N_Q new independent functions

$$\begin{gathered}\Phi_{(Q) r_1 \ldots r_N}(A_1 t_1 \varkappa_1 M_1; \ldots; A_N t_N \varkappa_N M_N | 1\,2 \ldots \Delta) \\ = Q\Phi(A_1 t_1 \varkappa_1 M_1 r_1; \ldots; A_N t_N \varkappa_N M_N r_N | 1\,2 \ldots \Delta).\end{gathered} \quad (3.3)$$

Account must also be taken of the degeneracy with respect to the exchange of unlike states between equivalent ions, which can take place for excited states. Thus, the set (3.3) contains functions that differ from one another in all possible permutations of the unlike κ_i between equivalent ions, and also in the different $M_i r_i$ and different Q.

The basis (3.3) specifies a certain representation T_S of the group S_Δ and a certain representation T_G of the group G_C^M. The first statement is obvious, and the second can be proved by using the fact that the permutations QPQ^{-1} differ from P in the permutation of Q over all the cycles of the permutation P. The representation T_S is the so-called "external product" of the representations $[\lambda_i]$ (see [8], page 297):

$$T_S = [\lambda_1] \otimes [\lambda_2] \otimes \ldots \otimes [\lambda_N]. \quad (3.4)$$

The representation T_S can be expanded in terms of irreducible representations $[\lambda]$ of the group S_Δ:

$$T_S = \sum_\lambda a_\lambda [\lambda]. \quad (3.5)$$

This expansion can actually be performed on the basis of the Littlewood theorem[9] as applied to permutation groups.[4, 8] Thus, it is possible to construct out of the functions (3.3) new linear combinations that transform in accordance with the irreducible representations of the group $S_\Delta - [\lambda]$:

$$\begin{gathered}\psi_{\xi[\lambda] r}(A_1 t_1 \varkappa_1 M_1; \ldots; A_N t_N \varkappa_N M_N | 12 \ldots \Delta) \\ = \sum_Q \sum_{r_i} \langle \xi [\lambda] r | (Q) r_1 \ldots r_N \rangle \Phi_{(Q) r_1 \ldots r_N}(A_1 t_1 \varkappa_1 M_1; \ldots | 12 \ldots \Delta),\end{gathered} \quad (3.6)$$

where ξ "numbers" the repeated $[\lambda]$ in the expansion (3.5), and $\langle \xi [\lambda] r | (Q_1) r_1 \ldots r_N \rangle$ is a unitary matrix that realizes the reduction of the representation T_S.

We shall call all the possible linear combinations of the functions of the set (3.3) L-space. This space is invariant against transformations of the group G_C^K. Using this invariance, we can prove that the functions (3.6), which have different admissible permutations of the states κ_i and all possible values of $\xi M_1 \ldots M_N$ (with fixed $[\lambda] r$), form a basis of a certain representation Γ_λ of the group G_C^K, whereas the functions (3.6) with different r (but fixed $\kappa_i M_i$ and $\xi[\lambda]$) form the basis of the irreducible representation $[\lambda]$ of the group S_Δ.

---

[4] The choice of the permutation Q_1 is not unique, but the "content" of the co-sets does not depend on this choice. We shall assume the set Q_1 to be chosen once and for all.

This statement is a generalization of the corresponding statement that holds for the construction of coordinate wave functions of a many-particle system from products of single-particle functions ([10], page 137). The regular coordinate wave functions of the complex (3.6), pertaining to a definite representation $[\lambda] \times \Gamma_\lambda$ of the group $S_\Delta \times G_C^K$, pertain to a definite value of the total spin S, corresponding to the coordinate Young pattern $[\lambda] \to S$.

4. METHOD OF DETERMINING THE ALLOWED MULTIPLETS

Our purpose will be reached if we derive a formula for determining the characters of the representation Γ_λ. Knowing these characters, we can expand Γ_λ in terms of the irreducible representations of the group G_C^K:

$$\Gamma_\lambda = \sum_\Gamma b_\Gamma D^{(\Gamma)}. \tag{4.1}$$

The irreducible representations obtained by such an expansion determine the allowed terms of the complex with multiplicity 2S + 1, where S corresponds to the coordinate Young pattern $[\lambda]$.

We divide the L-space into two parts:

$$L = L_\lambda + L', \tag{4.2}$$

where L_λ is a linear space "stretched" over the basis unit vectors (3.6), with fixed $[\lambda]$, and L' is orthogonal to L_λ. The characters of the representation of the group $S_\Delta \times G_C^K$, constructed on the basis (3.6) of L-space (or the equivalent basis (3.3)) are equal to

$$X^{(L)}(Pg) = X^{(L_\lambda)}(Pg) + X^{(L')}(Pg). \tag{4.3}$$

Multiplying by $(1/\Delta!)X^{[\lambda]}(P)$, summing over all the permutations P, and taking into account the orthogonality of the spaces L_λ and L', we get

$$X^{(\Gamma_\lambda)}(g) = \frac{1}{\Delta!}\sum_P X^{[\lambda]}(P)X^{(L)}(Pg). \tag{4.4}$$

Inasmuch as the character $X^{(L)}$ of the representation constructed on the complete set of basis functions does not depend on the choice of the basis in the form (3.6) or (3.3), we shall use the basis (3.3) for the determination of $X^{(L)}(Pg)$.

To each element g of the group G_C^K there corresponds a certain permutation $P_g(A_1 \ldots A_N)$ of the ions of the complex, which can always be represented in the form of a product of ion cycles:[5]

$$P_g(A_1 \ldots A_N) \to P_g(A_1 \ldots A_a)P_g(B_1B_2 \ldots B_b) \ldots \tag{4.5}$$

Obviously, one cycle can contain only equivalent ions (i.e., ions with identical $\kappa_i t_i$ and n_i). The breakdown of the ions of the complex into ion cycles is determined by the element g. For a unit element (and possibly for a number of others) $P_g = 1$, i.e., each ion forms a separate cycle.

It is always possible to choose local coordinate systems in which the ion functions are determined in such a way that the following chain of equations is satisfied for the ions of each cycle:[3]

$$\begin{gathered} g\Phi(A_1\varkappa_1M_1r_1|R_1) = \Phi(A_2\varkappa_1M_1r_1|R_1), . \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ g\Phi(A_{a-1}\varkappa_{a-1}M_{a-1}r_{a-1}|R_{a-1}) = \Phi(A_a\varkappa_{a-1}M_{a-1}r_{a-1}|R_{a-1}), \\ g\Phi(A_a\varkappa_aM_ar_a|R_a) = g^a\Phi(A_1\varkappa_aM_ar_a|R_a). \end{gathered} \tag{4.6}$$

Here

$$R_1 = (1, 2, \ldots, n_A), \quad R_2 = (n_A + 1, \; n_A + 2, \ldots, 2n_A), \ldots, \\ R_a = ((a-1)n_A + 1, \ldots, an_A),$$

$n_1 = n_2 = \ldots = n_a = n_A$ is the number of electrons in each ion of the cycle, and the indices t_i have been omitted since they are the same for all the ions of the cycle. The presence of g^a in the last equation is connected with the fact that an a-fold application of the coordinate transformation g to the local system of coordinates of the ion A_1 may not lead to the initial local system, for example, $S_3^3 \neq E$. For free molecules, the atomic functions can be determined in the same coordinate system (and then each equation of (4.6) will contain on the right side the operator g in front of the function, but the subsequent results are not affected by this). For an impurity complex, each function $\Phi(A_i)$ is defined with respect to the crystal axis of the local system of coordinates (point group G_i). The elements $g \in G_C^K$ may be missing from the group G_i. (For free molecules this may not occur, since the group $\overline{R}_i$ contains all the point transformations.) However, the element g^a leaves in place all the ions of the cycle, and therefore must be present in each local point group G_i. Inasmuch as the "notation" of the element g^a can be different for different ion cycles, we shall mark g^a with the index of the cycle, g_A^a, etc. Taking (4.6) into account, we get

$$\begin{aligned} &Pg\Phi_{(Q)r_1\ldots{}_N}(A_1t_1\varkappa_1M_1; \ldots; A_Nt_N\varkappa_NM_N|12\ldots\Delta) \\ &= PQ\Big\{\Big[\sum_{M'} D^{(\Gamma_a)}_{M_a'M_a}(g_A{}^a)P_g(A_1A_2\ldots A_a)\Phi(A_1\varkappa_1M_1r_1|R_1)\ldots \\ &\qquad \ldots\Phi(A_a\varkappa_aM_a'r_a|R_a)\Big]\ldots\Big\}, \end{aligned} \tag{4.7}$$

where the dots following the square bracket will henceforth denote analogous expressions for the other ion cycles. Representing $P_g(A_1A_2 \ldots A_a)$ in the form $P_g^{-1}(R_1 \ldots R_a)P_g(R_1 \ldots R_a)P_g(A_1 \ldots A_a)$ and taking into account the fact that the action of the operator $P_g(R_1R_2 \ldots R_a)P_g(A_1A_2 \ldots A_a)$ on the function in (4.7) is equivalent to the action of the operator of the inverse permutation of the states, we obtain

$$P_g(A_1A_2\ldots A_a) = P_g{}^{-1}(R_1\ldots R_a)P_g{}^{-1}(\varkappa_1M_1r_1; \ldots; \varkappa_aM_a'r_a).$$

According to (3.2), any permutation can be represented in the form of the product $Q\overline{P}$, where Q is the permutation from the Q-set, and $\overline{P}$ is the permutation of the subgroup S_0, having the form of the product of the permutations $\overline{P}_i$ of the electrons within each of the ions. In particular, we represent in this form the permutation

$$PQ\{P_g{}^{-1}(R_1R_2\ldots R_a)]\ldots\} = PQP_g{}^{-1}(R_1\ldots R_N) = \overline{Q}\overline{P}_1\overline{P}_2\ldots\overline{P}_N. \tag{4.8}$$

We then get from (4.7)

$$\begin{aligned} &Pg\Phi_{(Q)r_1\ldots r_N}(A_1t_1\varkappa_1M_1; \ldots; A_Nt_N\varkappa_NM_N|12\ldots\Delta) \\ &= \Big\{\Big[\sum_{M_a'} D^{(\Gamma_a)}_{M_a'M_a}(g_A{}^a)P_g{}^{-1}(\varkappa_1M_1r_1; \ldots; \varkappa_aM_a'r_a) \\ &\quad \cdot \sum_{r_i'} D^{[\lambda_1]}_{r_1'r_1}(\overline{P}_1)D^{[\lambda_2]}_{r_2'r_2}(\overline{P}_2)\ldots D^{[\lambda_a]}_{r_a'r_a}(\overline{P}_a)\Big]\ldots\Big\}\cdot \end{aligned}$$

---

[5] Starting with (4.5), the ions entering in different cycles will be denoted by different letters A_i, B_i, etc. The numbers of the ions in the cycles will be denoted by a, b, etc., respectively.

$$\times\Phi_{(\bar{Q})r_1'\ldots r_N'}(A_1t_1\varkappa_1M_1;\ldots;A_Nt_N\varkappa_NM_N|12\ldots\Delta). \qquad (4.9)$$

The representation (4.8) depends on Q and g. It is clear from (4.9) that a nonzero contribution to a character can be made only by functions with $\kappa_1 M_1 = \kappa_2 M_2 = \ldots \kappa_a M_a$ (and analogously for other cycles), and with Q satisfying the operator equation

$$PQP_g^{-1}(R_1R_2\ldots R_N) = Q\bar{P}_1\bar{P}_2\ldots\bar{P}_N \qquad (4.10)$$

or the equivalent equation

$$Q^{-1}PQ = \bar{P}_1\bar{P}_2\ldots\bar{P}_N\cdot P_g(R_1R_2\ldots R_N). \qquad (4.11)$$

If at least in one ion cycle the specified states of the ions κ_i do not coincide with one another, then, as follows from (4.9), the contribution to the character will vanish, i.e., $X^{(L)}(Pg) = 0$. Therefore the subsequent deduction will pertain to the case when the states of the ions in each ion cycle are the same. In this case the character will equal

$$X^{(L)}(Pg) = \sum{}' \sum_Q{}' \Big\{\Big[X^{(\Gamma_A)}(g_A{}^a)\sum_{r_i'} P_g{}^{-1}(r_1r_2\ldots r_a)$$
$$\times D^{[\lambda_A]}_{r_1'r_1}(\bar{P}_1)D^{[\lambda_A]}_{r_2'r_2}(\bar{P}_2)\ldots D^{[\lambda_A]}_{r_a'r_a}(\bar{P}_a)\Big]\ldots\Big\}, \qquad (4.12)$$

where $\sum'$ denotes the sum over all the sets of the states (taking into account the degeneracy with respect to exchange of unlike states between equivalent ion cycles) under the condition that the states of the ions in each cycle are identical:

$$\alpha_1\Gamma_1[\lambda_1] = \ldots = \alpha_a\Gamma_a[\lambda_a] = \alpha_A\Gamma_A[\lambda_A]$$

etc., and the sum $\sum_Q{}'$ denotes the sum over the Q-set under the condition (4.11) or

$$Q^{-1}PQ \in S_0 \times P_g(R_1R_2\ldots R_N). \qquad (4.13)$$

In view of the equality of the number of electrons in the equivalent ions of one ion cycle, the permutation groups $S_{n1}, S_{n2}, \ldots, S_a$ are isomorphic. Therefore each of the permutations $\bar{P}_1, \bar{P}_2, \ldots, \bar{P}_a$ can be "reduced" to one center (say the first), and we then obtain

$$\sum_{r_i'} P_g{}^{-1}(r_1r_2\ldots r_a)D^{[\lambda_A]}_{r_1'r_1}(\bar{P}_1)\ldots D^{[\lambda_A]}_{r_a'r_a}(\bar{P}_a) = X^{[\lambda_A]}(\bar{P}_{a\to1}\ldots\bar{P}_{2\to1}\bar{P}_1), \qquad (4.14)$$

where $\bar{P}_{i\to1}$ denotes the permutation $\bar{P}_i$ "reduced" to the center 1 (i.e., acting on the coordinates 1, 2, ..., n_A in place of $n_A(i-1)+1, \ldots, in_A$ respectively). Taking (4.14) into account, we get from (4.12)

$$X^{(L)}(Pg) = \sum{}'\sum_Q{}' \{[X^{(\Gamma_A)}(g_A{}^a)X^{[\lambda_A]}(\bar{P}_{a\to1}\ldots\bar{P}_1)]\ldots\}. \qquad (4.15)$$

The condition (4.11) shows that (4.15) can give a nonzero result only if the cyclic structure of the permutation P coincides with the cyclic structure of any permutation from the co-set $S_0 \times P_g(R_1 \times R_2 \ldots R_N)$, i.e., if the meet of the class of conjugate elements K, to which P belongs, with the co-set $S_0 \times P_g(R_1 \ldots R_N)$ is not empty. Substituting (4.15) in (4.4), we recognize that the sum over all P can be broken up into sums over individual classes of the conjugate elements of the group S_Δ. When P "runs through" all the permutations of one such class K, then (at a fixed Q) the elements $Q^{-1}PQ$ also "run through" all the permutations of the class K (once each).

Although the concrete form of the permutations $\bar{P}_1, \bar{P}_2, \ldots, \bar{P}_N$ depends not only on P and g, but also on Q (see (4.11)), the cyclic structure of each permutation $[\bar{P}_{a\to1}\ldots\bar{P}_1], [\bar{P}_{a+b\to a+1}\ldots P_{a+1}]\ldots$ is determined only by the cyclic structure of the permutations P and g (see the appendix). Then the characters in the right side of (4.4), following substitution of (4.15), do not depend on Q and the role of the sum $\sum_Q{}'$ subject to the condition (4.11), reduces to limiting the sum $\sum_{P\in K}$ for each Q to the sum over $P \in K \cap S \times P_g(R_1 \ldots R_N)$. Denoting the number of permutations in this meet by $N_g(K)$, we obtain after substituting (4.15) in (4.4)

$$X^{[\Gamma_\lambda]}(g) = \frac{1}{\Lambda!}\sum{}'\sum_K N_QN_g(K)X^{[\lambda]}(K)$$
$$\times\{[X^{(\Gamma_A)}(g_A{}^a)X^{[\lambda_A]}(\bar{P}_{a\to1}\ldots\bar{P}_{2\to1}\bar{P}_1)]\ldots\}, \qquad (4.16)$$

where N_Q is the number of permutations in the Q-set, and the first sum is taken over the sets κ_i.

It is shown in the appendix that the cyclic structures $K_A, K_B, \ldots$ of the permutations $[\bar{P}_{a\to1}\ldots\bar{P}_{2\to1}\bar{P}_1]$, $[\bar{P}_{a+b\to a+1}\ldots\bar{P}_{a+2\to a+1}\bar{P}_{a+1}]\ldots$ are connected with the cyclic structure K as follows:

$$K = \{K_A^{(a)}, K_B^{(b)}, \ldots\}, \qquad (4.17)$$

where $K_A^{(a)}$ is the cyclic structure K_A, each cycle of which is "lengthened" by a factor a, $K_B^{(b)}$ is the cyclic structure K_B in which each cycle is "lengthened" by a factor b, etc., and K is obtained by joining the structures $K_A^{(a)}$, $K_B^{(b)}$, into one. For example, in the case $P_g = (A_1A_2A_3)(B_1B_2B_3B_4)$ and $n_A = 3$, $n_B = 2$ for $K_A = \{3\}$ and $K_B = \{1^2\}$ we get: $K_A^{(3)} = \{9\}$ and $K_B^{(4)} = \{4^2\}$, and consequently $K = \{4^2, 9\}$. The number of permutations $N_g(K)$ is

$$N_g(K) \equiv N_g(K_A^{(a)}, K_B^{(b)}, \ldots) = \bar{N}_g(K_A)\bar{N}_g(K_B)\ldots, \qquad (4.18)$$

where $\bar{N}_g(K_A)$ is the number of permutations in the a-fold product S^a_{nA}, having the cyclic structure K_A, $\bar{N}_g(K_B)$ is the number of permutations in the b-fold product S^b_{nB} having the cyclic structure K_B, etc.[6] The latter, however, are obviously equal to

$$\bar{N}_g(K_A) = (n_A!)^{a-1}N(K_A), \qquad \bar{N}_g(K_B) = (n_B!)^{b-1}N(K_B), \ldots, \qquad (4.19)$$

where $N(K_A)$ is the number of permutations of the group S_{nA} in the class with structure K_A, $N(K_B)$ is the number of permutations of the group S_{nB} in the class with structure K_B, etc. Taking into account the values of (4.19) and the value of N_Q from (4.16), we obtain finally

$$X^{(\Gamma_\lambda)}(g) = \sum{}' \sum_{K_A, K_B, \ldots} X^{[\lambda]}(K_A^{(a)}, K_B^{(b)}, \ldots)$$
$$\times\Big\{\Big[\frac{N(K_A)}{n_A!}X^{[\lambda_A]}(K_A)X^{(\Gamma_A)}(g_A{}^a)\Big]\Big[\frac{N(K_B)}{n_B!}X^{[\lambda_B]}(K_B)X^{(\Gamma_B)}(g_B{}^b)\Big]\ldots\Big\}. \qquad (4.20)$$

---

[6] g determines the distribution of the ions over the ion cycles, i.e., g determines the numbers a, b, ... etc.

The sum over the sets of the states is extended only over those sets, in which the states of the ions in each ion cycle are the same. This sum can appear only in the case when certain ions are in excited states. If the given states of the ions are not the same at least in one cycle, then it must be assumed that the sum over the sets of states in (4.20) vanishes. Further, the sum over K_A, K_B, ... denotes the sum over all possible classes of the groups S_{nA}, S_{nB}, ... respectively.

In the particular case when the element g does not change the positions of the ions of the complex, i.e., $P_g \equiv 1$ (we shall denote it in this case as g^0), formula (4.20) can be simplified. In this case, each ion forms a separate cycle and all a = b = ... = 1. Then the sum over the permutations in (4.20) leads to the expression

$$\frac{1}{\Delta!}\sum_P X^{[\lambda]}(P)\, X^{[\lambda_1]\otimes[\lambda_2]\otimes\ldots\otimes[\lambda_N]}(P) = a_\lambda, \tag{4.21}$$

which shows how many times[7] [λ] is encountered in the expansion of the external product (3.4). Thus we obtain for g^0 the simpler formula

$$X^{(\Gamma_\lambda)}(g^0) = a_\lambda \quad \sum{}' \; X^{(\Gamma_1)}(g_1{}^0)\ldots X^{(\Gamma_N)}(g_N{}^0). \tag{4.22}$$

The obtained formulas allow us to calculate in each concrete case (using only the tables of the characters of the point groups and permutations groups) the characters of the representation Γ_λ, and after expanding Γ_λ in terms of the irreducible representations of the group G_C^K, to determine all the allowed terms with specified multiplicity 2S + 1 (i.e., with specified [λ]).

It should be noted that an important role is played only by electrons with uncompensated spin (more accurately, single-cell columns of spin Young patterns or single-cell rows of coordinate Young patterns). This allows us to consider, in place of the groups S_{n1}, ... S_{nN}, the groups $S_{\bar{n}1}$, $S_{\bar{n}2}$, ... , $S_{\bar{n}N}$, where $\bar{n}_i$ is the number of electrons with uncompensated spin, which equals $\bar{n}_i = 2S_i$.

5. PARTICULAR CASES

Let us consider several particular cases of formulas (4.20) and (4.22). We note first that in the case of a free molecule these formulas retain their form, but the representations Γ_i of the point groups G_i of local symmetry are replaced by the representations $D^{(W_i L_i)}$ of the groups $\bar{R}_i$.

A. Spin of Each Ion of the Complex Equals ½

In this case it is possible to assume that each ion has only one electron (since the number of electrons with uncompensated spin is equal to unity), i.e., all the groups of electron permutations within the ions are transformed into S_1. This group contains one identical element (i.e., we have one class of conjugate elements), having the structure {1}. Consequently, it is necessary to put in (4.20)

$$K_A = K_B = \ldots = \{1\}, \quad \{K_A^{(a)}, K_B^{(b)}, \ldots\} = \{a, b, \ldots\},$$
$$n_A = n_B = \ldots = 1, \quad N(K_A) = N(K_B) = \ldots = 1.$$

We then get

$$X^{(\Gamma_\lambda)}(g) = \sum{}' X^{[\lambda]}(\{a, b, \ldots\})\,\{[X^{(\Gamma_A)}(g_A{}^a)]\ldots\}. \tag{5.1}$$

In this case the group of electron permutations S_Δ coincides with the group of ion permutations, and since the cyclic structure {a, b, ... } is the cyclic structure of the permutation of the ions P_g, we can write (5.1) in the form

$$X^{(\Gamma_\lambda)}(g) = \sum{}' X^{[\lambda]}(P_g)\,\{[X^{(\Gamma_A)}(g_A{}^a)]\ldots\}. \tag{5.2}$$

Thus, in the case when each ion is in a state with one uncompensated spin ($S_i = ½$) we can use instead of the electron permutation group the group of permutations of the ions of the complex S_N.

B. Each Ion of the Complex Has a State $^2A_1$ (for the Free Molecule $^2S_+$)

A more particular case is obtained if we assume in the preceding case that the orbital state of each ion is fully symmetrical, i.e., is characterized by a single representation A_1 of the local-symmetry group G_i. For the atoms of the free molecules this denotes an S-state with positive parity (S_+) of the group $\bar{R}_i$. In this case we obtain from (5.2)

$$X^{(\Gamma_\lambda)}(g) = \sum{}' X^{[\lambda]}(P_g). \tag{5.3}$$

The sum in (5.3) gives the number of sets of states $\alpha_i^2 A_1$ that remain invariant under the action of the elements g. (Although the type of the state $^2A_1$ is the same for all ions, the additional quantum numbers may be different.)

If any of the ions of the complex have no uncompensated spins at all, i.e., are in the state $^1A_1$ ($^1S_+$), and the remaining ions are in the states $^2A_1$ (or $^2S_+$), then formula (5.3) remains valid, but the sum in (5.3), generally speaking, breaks up into several separate sums over the types of sets having the same character $X^{[\lambda]}(P_g)$, so that each of these sums gives the number of sets of the given type, which remain invariant under the action of g.

In this particular case, as seen from (5.3), we arrive at the method proposed in [5].

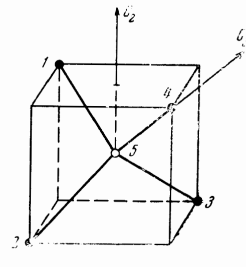
6. THE MOLECULE CH_4

By way of an example, let us consider the determination of the multiplets of the molecule CH_4.

The molecule CH_4 has a symmetry T_d (see the figure). The comparison $g \to P_g$ is of the form

g:	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
P_g:	1	(123) (4) (5)	(14)(23)(5)	(1)(23)(4)(5)	(1342)(5)

We have chosen here one element out of each class, and have written down in the lower line the corresponding



Model of the molecule CH_4. ○ – C atom, ● – H atom.

---

[7] The same number a_λ is equal to the number of the repeated values of the total spin S in the addition of the spin momenta $S_1 + S_2 + \ldots + S_N$ (where S is the value of the total spin corresponding to the coordinate Young pattern [λ].

permutation of the atoms, each permutation being represented in the form of cycles.

The main configurations of the atoms are as follows: $C(1s^2 2s^2 2p^2)$ and $H(1s^1)$. Since the closed shells do not play any role, we shall consider the case $C(2p^2)$. We specify that the carbon atom is in the ground state $(2p^2)^3P_+$. For the states of the four hydrogen atoms we consider two cases: a) all atoms are in the ground state $(1s^1)^2S_+$, b) one is excited to the state $(2s^1)^2S_+^*$ (the asterisk will replace the additional quantum number n = 2). The sets of states for these two cases are written out below:[8]

Atom:	H	H	H	H	C
Number of atom:	1	2	3	4	5
Case a:	$^2S_+$	$^2S_+$	$^2S_+$	$^2S_+$	$^3P_+$
Case b:	$^2S_+{}^*$	$^2S_+$	$^2S_+$	$^2S_+$	$^3P_+$
	$^2S_+$	$^2S_+{}^*$	$^2S_+$	$^2S_+$	$^3P_+$
	$^2S_+$	$^2S_+$	$^2S_+^*$	$^2S_+$	$^3P_+$
	$^2S_+$	$^2S_+$	$^2S_+$	$^2S_+{}^*$	$^3P_+$

The possible values of the total spin in both cases are the same: S = 0, 1, 2, 3, and the corresponding coordinate Young patterns of the group S_6, and also the values of a_λ, are as follows:

S:	0	1	2	3
$[\lambda]$:	$[2^3]$	$[2^2, 1^2]$	$[2, 1^4]$	$[1^6]$
a_λ:	3	6	4	1

The coordinate Young patterns for the atoms H, H, H, H, C are $[1], [1], [1], [1], [1^2]$, corresponding to spins ½, ½, ½, ½, 1.

Let us determine, for example, the character of the representation Γ_λ for the element σ_d in the case b, using formula (4.20). Let us see first what sets of states enter in $\sum'$. Since the chosen element σ_d permutes the positions of the atoms 2 and 3, their states should be the same, i.e., only $^2S_+$ and $^2S_+$. Thus, the sum Σ' is limited to two sets having identical characteristics:

CH_4 atoms:	H	H	H	H	C
Number of atom:	1	2	3	4	5
Number of states in the sum:	$^2S_+{}^*$ $^2S_+$	$^2S_+$ $^2S_+$	$^2S_+$ $^2S_+$	$^2S_+$ $^2S_+{}^*$	$^3P_+$ $^3P_+$
Number of atoms in cycle:	$a = 1$	$b = 2$		$c = 1$	$d = 1$
Number of electrons in atom:	$n_A = 1$	$n_B = 1$		$n_C = 1$	$n_D = 2$
Permutation groups of electrons of atom:	S_1	S_1		S_1	S_2
Classes	$K_A = \{1\}$	$K_B = \{1\}$		$K_C = \{1\}$	$K_D = \{1^2\}$ и $\{2\}$
Number of permutations in class:	$N(K_A) = 1$	$N(K_B) = 1$		$N(K_C) = 1$	$N(K_D) = 1$ и 1

According to (4.20) we get

$$X^{(\Gamma_\lambda)}(\sigma_d) = 2 \sum_{K_D = \{1^2\}, \{2\}} X^{[\lambda]}(\{1^2, 2\} K_D)[X^{[1]}(\{1\}) X^{(S+)}(\sigma_d)]^2 \cdot$$

$$\times [X^{[1]}(\{1\}) X^{(S+)}(\sigma_d^2)] \left[\frac{N(K_D)}{2!} X^{[1^2]}(K_D) X^{(P+)}(\sigma_d) \right].$$

Recognizing that

$$X^{(S+)} = 1,\ X^{[1]}(\{1\}) = 1,\ X^{(P+)}(\sigma_d) = -1,$$

we obtain

$$X^{(\Gamma_\lambda)}(\sigma_d) = -[X^{[\lambda]}\{1^4, 2\} - X^{[\lambda]}\{1^2, 2^2\}].$$

S	$[\lambda]$	g: E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$	Expansion Γ_λ
				Case a)			
0	$[2^3]$	9	0	1	1	1	$A_1 + E + F_1 + F_2$
1	$[2^2, 1^2]$	18	0	−2	2	0	$A_1 + E + 2F_1 + 3F_2$
2	$[2, 1^4]$	12	0	0	2	0	$A_1 + E + F_1 + 2F_2$
3	$[1^6]$	3	0	−1	1	−1	F_2
				Case b)			
0	$[2^3]$	36	0	0	2	0	$2A_1 + A_2 + 3E + 5F_2 + 4F_1$
1	$[2^2, 1^2]$	72	0	0	4	0	$4A_1 + 2A_2 + 6E + 10F_2 + 8F_1$
2	$[2, 1^4]$	48	0	0	4	0	$3A_1 + A_2 + 4E + 7F_2 + 5F_1$
3	$[1^6]$	12	0	0	2	0	$A_1 + E + 2F_2 + F_1$

Using the tables of the characters of the permutation group S_6 for $[\lambda] = [2^3], [2^2, 1^2], [2, 1^4], [1^6]$, we obtain $X^{(\Gamma_\lambda)}(\sigma_d) = 2, 4, 4, 2$. We calculate analogously the characters of the other elements. The results of the calculation of $X^{(\Gamma_\lambda)}$ are listed in the table. The expansions of Γ_λ, given here on the right, determine the types of multiplets. For the case a, the allowed multiplets were determined also by Kotani.[1] The multiplets obtained in [1] coincide with those obtained by us, thus confirming the correctness of the described method.

7. CONCLUSION

The proposed method of determining allowed multiplets of a many-electron system from the states of the atoms (ions) of a system having point symmetry, has been developed on the basis of taking into account the transformation properties of the coordinate wave functions both under the action of coordinate transformations corresponding to elements of a point symmetry group, and under the action of coordinate permutations corresponding to the permutation group of the electrons of the system, and also on the basis of an account of the known connection[6] between the permutation symmetry of the coordinate wave functions with a total spin S of the system (i.e., the multiplicity 2S + 1). Unlike [5], this method is not limited by any conditions imposed on the number of electrons in the atoms (ions) of the system and on the states of these atoms (ions). Unlike [1,3C], this method is more convenient, since it requires for its application only tables of the characters of the point groups (rotation groups) and permutation groups, whereas in [1,3C] the latter are not used. The method can also be used (in somewhat modified form) for many-shell configurations of nucleons in a nucleus.

APPENDIX

CONNECTION BETWEEN THE CYCLIC STRUCTURE OF THE PERMUTATION P, SATISFYING THE CONDITION (4.11), WITH THE CYCLIC STRUCTURE OF THE PERMUTATION

$$[\overline{P}_{a\to 1} \cdots \overline{P}_{2\to 1}\overline{P}_1][\overline{P}_{a+b\to a+1} \cdots \overline{P}_{a+2\to a+1}\ \overline{P}_{a+1}] \cdots$$

The condition (4.11) shows that the cyclic structure P coincides with the cyclic structure

$$I \equiv \overline{P}_1 \overline{P}_2 \ldots \overline{P}_N P_g (R_1 R_2 \ldots R_N).$$

Since the $\overline{P}_i$ commute with one another and the cyclic structure of the product of permutations does not

---

[8] The four sets in case b) denote four terms in the sum over the sets of states Σ' in formula (4.20).

change under cyclic permutation of the co-factors, then $I \sim P_g(R_1 \dots R_N)\overline{P}_N \dots P_1$ (where $\sim$ denotes coincidence of the cyclic structures). Putting $P_\kappa = P_g(R_1 \dots R_N)$, we rewrite the preceding relation in the form $I \sim P_\kappa \overline{P}_N P_\kappa^{-1} P_\kappa \dots P_\kappa \overline{P}_2 P_\kappa^{-1} P_\kappa \overline{P}_1 P_\kappa^{-1} P_\kappa$. Representing P_κ and P_κ^{-1} in the form of a product of simple transpositions

$$\begin{gathered} P_\varkappa = [(1, n_A(a-1)+1) \dots (1, 2n_A+1)(1, n_A+1)] \\ \times[(2, n_A(a-1)+2) \dots (2, n_A+2)] \cdot \\ \dots [(n_A, an_A) \dots (n_A, 3n_A)(n_A, 2n_A)] \dots \end{gathered}$$

and taking into account the connection

$$\begin{gathered} \overline{P}_{i\to1} = (1, (i-1)n_A+1)(2, (i-1)n_A+2) \dots (n_A, in_A) \\ \times \overline{P}_i(1, (i-1)n_A+1)(2, (i-1)n_A+2) \dots (n_A, in_A) \end{gathered}$$

(analogously for other ionic cycles), we get

$$\begin{gathered} I \sim \{\overline{P}_{a\to1}[(1, n_A(a-1)+1) \dots (n_A, n_A a)] \cdot \\ \times \overline{P}_{a-1\to1}[(1, n_A(a-2)+1) \dots (n_A, n_A(a-1))]\overline{P}_{a-2\to1} \dots \\ \dots [(1, 2n_A+1) \dots (n_A, 3n_A)]\overline{P}_{2\to1}[(1, n_A+1) \cdot \\ \dots (n_A, 2n_A)]\overline{P}_1\} \dots = \{\overline{P}_{a\to1} \dots \overline{P}_{2\to1}\overline{P}_1 P_\varkappa'(A)\} \dots, \end{gathered}$$

where

$$\begin{gathered} P_\varkappa'(A) = \overline{P}_1^{-1}\overline{P}_{2\to1}^{-1} \dots \overline{P}_{a-1\to1}^{-1}[(1, h_A(a-1)+1) \dots (n_A, an_A)]\overline{P}_{a-1\to1} \cdot \\ \dots [(1, 2n_A+1) \dots (n_A, 3n_A)\overline{P}_{2\to1}[(1, n_A+1) \dots (n_A, 2n_A)]\overline{P}_1 \end{gathered}$$

and analogously for other ionic cycles. It is easy to show that P_κ' is of the form

$$\begin{gathered} P_\varkappa'(A) = (\overline{1}, \overline{n_A+1}, \dots, \overline{n_A(a-1)+1}) \cdot \\ \times (\overline{2}, \overline{n_A+2}, \dots, \overline{n_A(a-1)+2}) \dots (\overline{n}_A, \overline{2n_A}, \dots, \overline{an_A}), \end{gathered}$$

where the superior bars denote that the first numbers in each cycle represent a certain permutation of the numbers $1, 2, \dots, n_A$, the second a certain permutation of the numbers $n_A + 1$, $n_A + 2, \dots, 2n_A$, etc. The permutation $P_\kappa'(A)$ has the property that when the permutations $\overline{P}_1$ are multiplied by it, all the cycles of the permutation $\overline{P}_1$ become elongated by a factor a. An analogous property is possessed by $P_\kappa'(B)$, etc.

It is clear therefore that the cyclic structure of the permutation I can be obtained from the cyclic structure $[\overline{P}_{a\to1} \dots \overline{P}_{2\to1}\overline{P}_1] \cdot [\overline{P}_{a+b\to a+1} \dots P_{a+2\to a+1}\overline{P}_{a+1}]$ ... by lengthening all the cycles of the permutation $[\overline{P}_{a\to1} \dots \overline{P}_{2\to1}\overline{P}_1]$ by a factor a, all the cycles of the permutation $\overline{P}_{a+b\to a+1} \dots \overline{P}_{a+1}]$ by a factor b, etc. Since the cyclic structure of P, satisfying the condition (4.11), coincides with the cyclic structure of I, it is possible to obtain analogously also the cyclic structure of P.

---

[1] M. Kotani, Proc. Phys. Math. Soc. Jap. **19**, 460 (1937).

[2] E. Wigner and E. E. Witmer, Z. Physik **51**, 859 (1928).

[3] S. V. Vonsovskiĭ, V. I. Cherepanov, A. N. Men', and A. E. Nikiforov, a) Dokl. Akad. Nauk SSSR **170**, 1288 (1966) [Sov. Phys.-Doklady **11**, 877 (1967)]; b) ibid., **174**, 783 (1967) [**12**, 570 (1967)]; c) Phys. Stat. Sol. **24**, 51 (1967).

[4] I. G. Kaplan, Zh. Eksp. Teor. Fiz. **41**, 560, 790 (1961) [Sov. Phys.-JETP **14**, 401, 568 (1962)]; TEKh **1**, 601 (1965).

[5] I. G. Kaplan, Zh. Eksp. Teor. Fiz. **51**, 169 (1966) [Sov. Phys.-JETP **24**, 114 (1967)].

[6] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika, Fizmatgiz, 1963, [Quantum Mechanics, Addison-Wesley, 1965].

[7] M. A. El'yashevich, Spektry redkikh zemel' (Spectra of Rare Earths), Gostekhizdat, 1953.

[8] M. Hamermesh, Group Theory and Its Application to the Problems of Physics, (Russ. transl. Mir, 1966) [Addison-Wesley, 1962].

[9] D. E. Littlewood, Theory of Group Characters, Oxford, 1940.

[10] B. F. Beĭman, Lektsii po primeneniyu teorii grupp v yadernoĭ spektroskopii (Lectures on the Application of Group Theory in Nuclear Spectroscopy), Fizmatgiz, 1961.

Translated by J. G. Adashko
199