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GROUP THEORETICAL CLASSIFICATION OF STATES IN CALCULATION OF MOLECULAR SYSTEMS

I. G. KAPLAN and O. B. RODIMOVA

Karpov Physico-chemical Institute; Siberian Physico-technical Institute of the Tomsk State University

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A general method is proposed of finding allowed molecular multiplets that can be constructed from specified atomic states with allowance for the interaction of the configurations. The method starts from a description of the molecule by a coordinate wave function with a specified permutation symmetry of the Young pattern $[\lambda]$. Concrete particular cases of different molecular configurations are analyzed. All the 100 multiplets that can be constructed on four 2p orbitals of the O atoms and two 1s orbitals of the H atoms are determined for the H_2O molecule.

1. INTRODUCTION

WHEN spin interactions are neglected, the states of symmetrical molecules are classified by specifying the total spin S and the irreducible representation Γ of the point symmetry group of the molecule. Such states, in analogy with the terminology used in atomic spectroscopy, are called molecular multiplets and are designated $^{2S+1}\Gamma$. In the case of the calculation of molecular systems by a variational method, or else with the aid of perturbation theory, it is necessary to solve the secular equation. The order of the secular equation increases rapidly when account is taken of the interaction of different electronic configurations. The construction of the eigenfunctions of the molecular multiplets from the initial variational functions leads to an essential lowering of the order of the secular equation (see[1], Secs. 6–9).

Before proceeding to calculate any concrete system, it is of interest to determine the allowed molecular multiplets and the order of the secular equations that are encountered in the calculation. A problem of this kind was solved by one of the authors[2] in the case when one nondegenerate orbital is specified for each atom[1)]. The present paper contains a generalization to include the case when degenerate orbitals and an arbitrary number of valence electrons are specified for the atoms.

The problem of finding the possible molecular multiplets from specified atomic ones was considered by Kotani[3]. However, the general formulas given by Kotani for the character of the sought reducible representation are expressed not in terms of the characters of the irreducible representations of the group of orthogonal transformations in three-dimensional space, but in terms of a product of matrix elements of the corresponding matrices of this group. In addition, calculations by the Kotani method require cumbersome calculations of the spin factor. As will be shown below, allowance for the permutation symmetry of the coordinate wave function makes it possible to simplify greatly the procedure of finding the characters of the representations formed by the initial set of the wave functions.

2. DERIVATION OF FORMULAS FOR THE CHARACTERS

In all the quantum-mechanical problems in which no account is taken of the spin interaction, the total spin of the system is a good quantum number. In this approximation, the total wave function is separated into a coordinate function and a spin function. All the properties of the considered systems are determined fully by specifying the coordinate wave function, which has a permutation symmetry uniquely connected with the spin of the Young pattern $[\lambda]$[4]. In finding the formulas for the characters of the representations that can be constructed on the initial set of the wave functions, we shall always start from the coordinate wave functions symmetrized in accordance with the Young pattern $[\lambda]$. We start the consideration with the simplest cases, after which we investigate an arbitrary molecular system.

A. One Valence Electron Specified on Each Atom (Covalent Configurations)

Assume that there are N equivalent atoms, on each of which is specified an identical degenerate orbital $\varphi^{(l)}$, where l is the orbital angular momentum and m is its projection on the z axis. The number of valence electrons is assumed equal to the number of atoms. The total number of coordinate states is obviously $(2l+1)^N$. Each of them corresponds to a non-symmetrized coordinate function

$$\Phi^{(l)}_{m_1m_2\ldots m_N} = \varphi^{(l)}_{m_1a}(1)\,\varphi^{(l)}_{m_2b}(2)\ldots\varphi^{(l)}_{m_Nq}(N), \tag{1}$$

where the indices a, b, ..., q number the atoms. By making all the possible permutations of the arguments in the function (1), we obtain N! functions for each set of values $m_1, m_2, \ldots, m_N$. It is possible to construct from them the basis functions of the irreducible representations $\Gamma^{[\lambda]}$ of the permutation group π_N, characterized by the Young pattern $[\lambda]$, by acting on the function (1) with the Young operators $\omega^{(\lambda)}_{rt}$[1]:

[1)] This case is realized, for example, in calculations of π-electron systems of conjugate and aromatic hydrocarbons in systems with 1s-valent electrons.

$$\Phi_{rt}^{[\lambda]}(\varphi_{m_1a}^{(l)}\varphi_{m_2b}^{(l)}\dots\varphi_{m_Nq}^{(l)}) = \omega_{rt}^{[\lambda]}\Phi_{m_1m_2\dots\ N}^{(l)}. \tag{2}$$

For each set of values $m_1, m_2, \dots, m_N$ there are f_λ^2 functions (2) (the indices r and t run through f_λ values each). These functions break up into f_λ independent basis sets of f_λ functions in each set. Under the action of the permutations through one another, the function (2) is transformed with fixed indices t and $m_1, m_2, \dots, m_N$; they correspond to one state (see[1,4]). Consequently the number of independent states having the permutation symmetry of the Young pattern $[\lambda]$ is equal to $f_\lambda(2l+1)^N$.

The action of the operation of the point symmetry group of the molecule (we denote such an operation, specified at the origin, by $\mathfrak{R}$) on the configuration of localized orbitals reduces to a permutation $\overline{P}$ of the centers of the orbitals and to operations of point symmetry, specified at the center of each orbital; we denote such operation by R_a. With respect to the group of point transformations, the set of functions (2) with fixed indices $[\lambda]$ and r, forms a basis for a certain reducible representation of dimension $f_\lambda(2l+1)^N$. Let us find the characters of such a representation.

The operations of the point symmetry and permutations of the coordinates of the electrons commute, and therefore

$$\mathfrak{R}\Phi_{rt}^{[\lambda]}(\varphi_{m_1a}^{(l)}\,{}_{m_2b}^{(l)}\cdots\varphi_{m_Nq}^{(l)}) = \Phi_{rt}^{[\lambda]}(\overline{P}(R_a\varphi_{m_1a}^{(l)})(R_b\varphi_{m_2b}^{(l)})\cdots(R_q\varphi_{m_Nq}^{(l)}))$$
$$= \sum_{m_1'm_2'\cdots m_N'} D_{m_1'm_1}^{(l)}(R)\,D_{m_2'm_2}^{(l)}(R)\cdots D_{m'\ _Nm_N}^{(l)}(R)\Phi_{rt}^{[\lambda]}(\varphi_{m_1'\overline{a}}^{(l)}\varphi_{m_2'\overline{b}}^{(l)}\cdots\varphi_{m_N'q}^{(l)}), \tag{3}$$

where $D_{m_i'm_i}^{(l)}(R)$ are the matrix elements of the irreducible representations of the group of orthogonal transformations in three-dimensional space $\mathbf{O}_3$, corresponding to the operations R of the point group[2]). The permutation $\overline{P}$ is defined as

$$\overline{P} = \begin{pmatrix} a & b & \cdots & q \\ \overline{a} & \overline{b} & \cdots & \overline{q} \end{pmatrix}.$$

We denote by P the electron-coordinate permutation that returns the electrons to "their own" atoms. Then the function in the right side of (3) can be represented by

$$\Phi_{rt}^{[\lambda]}(\varphi_{m_1'\overline{a}}^{(l)}\varphi_{m_2'\overline{b}}^{(l)}\cdots\varphi_{m_N'\overline{q}}^{(l)}) = \omega_{rt}^{[\lambda]}\varphi_{m_1'\overline{a}}^{(l)}(1)\,\varphi_{m_2'\overline{b}}^{(l)}(2)\cdots\varphi_{m_N'\overline{q}}^{(l)}(N)$$
$$= \omega_{rt}^{[\lambda]}P^{-1}\varphi_{\overline{m}_1'a}^{(l)}(1)\,\varphi_{\overline{m}_2'b}^{(l)}(2)\cdots\varphi_{\overline{m}_N'q}^{(l)}(N). \tag{4}$$

Using relation (2.34) of[1], we write

$$\omega_{rt}^{[\lambda]}P^{-1} = \sum_u \Gamma_{tu}^{[\lambda]}(P^{-1})\,\omega_{ru}^{[\lambda]} = \sum_u \Gamma_{ut}^{[\lambda]}(P)\,\omega_{ru}^{[\lambda]}, \tag{5}$$

where $\Gamma_{ut}^{[\lambda]}(P)$ are the matrix elements of the orthogonal irreducible representation $\Gamma^{[\lambda]}$ of the group π_N. Substituting (4) and (5) in (3) we get

$$\mathfrak{R}\Phi_{rt}^{[\lambda]}(\varphi_{m_1a}^{(l)}\cdots\varphi_{m_Nq}^{(l)})$$
$$= \sum_u \sum_{\overline{m}_1'\cdots\overline{m}_N'} \Gamma_{ut}^{[\lambda]}(P)\,D_{\overline{m}_1'\overline{m}_1}^{(l)}(R)\cdots D_{\overline{m}_N'\overline{m}_N}^{(l)}(R)\,\Phi_{ru}^{[\lambda]}(\varphi_{\overline{m}_1'a}^{(l)}\cdots\varphi_{\overline{m}'\ _Nq}^{(l)}). \tag{6}$$

The $D_{m_1'm_1}^{(l)}(R)$ in (6) are regrouped in such a way that the order of their arrangements corresponds to the order of the arrangement of $\varphi_{\overline{m}_1'a}^{(l)}\dots\varphi_{\overline{m}_N'q}^{(l)}$, and the sum over $m_1'\dots m_N'$ is replaced by the equivalent summation over $\overline{m}_1'\dots\overline{m}_N'$.

In order to obtain the character, it is necessary to to take the "diagonal" term in the sum (6), i.e., equate $u = t$, $\overline{m}_1' = m_1, \dots, \overline{m}_N' = m_N$, and sum over t and over all the sets $m_1, m_2, \dots, m_N$. As a result we obtain

$$X^{[\lambda]}(\mathfrak{R}) = \chi^{[\lambda]}(P)\sum_{m_1\cdots m_N} D_{m_1\overline{m}_1}^{(l)}(R)\cdots D_{m_N\overline{m}_N}^{(l)}(R). \tag{7}$$

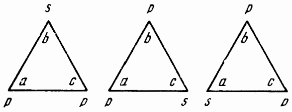
This expression can be easily simplified. To this end we take into account the fact that the corresponding operation $\mathfrak{R}$ of the permutation $\overline{P}$ can always be represented in the form of a product of cycles. Accordingly, all the atoms break up into cycles, in which the atoms go over one into the other. The sequence of the values $\overline{m}_1\overline{m}_2\dots\overline{m}_N$ is made up of $m_1m_2\dots m_N$ by the action of the permutation P^{-1}, which has the same cycle structure as $\overline{P}$. Therefore the products $D_{m_i\overline{m}_i}^{(l)}(R)$ in (7) can be broken up into cyclic aggregates, making it possible to express them in terms of the characters (see[5], Sec. 25). Let us examine, for example, that part of the sum of (7) which corresponds to a cycle of length k (we renumber successively the indices of this cycle)

$$\sum_{m_1\cdots m_k} D_{m_1m_2}^{(l)}(R)\,D_{m_2m_3}^{(l)}(R)\cdots D_{m_km_1}^{(l)}(R) = \sum_{m_1} D_{m_1m_1}^{(l)}(R^k) = \chi^{(l)}(R^k). \tag{8}$$

For the operation $\mathfrak{R}$ corresponding to the permutation $\overline{P}$ with the cyclic structure $\{1^{\nu_1}2^{\nu_2}\dots k^{\nu_k}\}$, the formula for the character assumes the form

$$X^{[\lambda]}(\mathfrak{R}) = \chi^{[\lambda]}(P)\,[\chi^{(l)}(R)]^{\nu_1}[\chi^{(l)}(R^2)]^{\nu_2}\dots[\chi^{(l)}(R^k)]^{\nu_k}. \tag{9}$$

In the case when orbitals of different types are specified on the atoms, several covalent configurations are possible, differing in the permutations of the orbitals among the identical points. Since the different covalent configurations go over into one another following the operation of the point group, the only configurations contributing to the character are those that go over into themselves following the operation $\mathfrak{R}$. The number of such configurations will be denoted by $\tau(\mathfrak{R})$. The procedure for finding $\tau(\mathfrak{R})$ coincides with the procedure described in detail in[2] for finding the number of ionic structures remaining invariant under the action of the operation $\mathfrak{R}$. The formula for the characters takes the form



Different covalent configurations for the case when two p-orbitals and one s-orbital are specified on the atoms.

$$X^{[\lambda]}(\mathfrak{R}) = \chi^{[\lambda]}(P)\chi^{(l_1)}(R^{n_1})\chi^{(l_2)}(R^{n_2})\dots\chi^{(l_k)}(R^{n_k})\tau(\mathfrak{R}). \tag{10}$$

Some of the orbital momenta l_i, as well as the lengths of the cycles n_i in formula (10), may coincide. If all the atoms are identical and all the l_i are equal, then we get $\tau(\mathfrak{R}) = 1$, inasmuch as only one covalent con-

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[2]) We recall that all the point groups are subgroups of the group $\mathbf{O}_3$, and the group $\mathbf{O}_3$ itself is determined as the direct product of the group of three-dimensional rotations $\mathbf{R}_3'$ by the group $\mathbf{C}_i$ of the inversion operator.

figuration is possible in this case, and formula (10) goes over into (9).

The characters of the operations of the point group corresponding to the irreducible representations of the group O_3 can be readily found from the formulas[6]. The character of the operation of rotation through an angle φ is

$$\chi^{(l)}(C_\varphi)=\frac{\sin(l+{}^1/_2)\varphi}{\sin(\varphi/2)}, \tag{11}$$

the character of the inversion operation

$$\chi^{(l)}(I)=\pm(2l+1), \tag{12}$$

the plus sign is for even states and the minus sign for odd states. Finally, the characters of reflection in the plane σ and of mirror rotation S_φ are calculated by representing these operations in the form $\sigma = IC_2$ and $S_\varphi = IC_{\pi+\varphi}$, which leads to the following formulas:

$$\chi^{(l)}(\sigma)=\pm\chi^{(l)}(C_2), \quad \chi^{(l)}(S_\varphi)=\pm\chi^{(l)}(C_{\pi+\varphi}) \tag{13}$$

depending on the parity of the state.

Let us consider by way of an example a symmetrical system of three equivalent atoms, with p-orbitals specified on two of them and an s-orbital on one. Three covalent configurations are possible (see the figure). Assume that we are interested in the state of the system with total spin $S = {}^3/_2$. The permutation symmetry of the coordinate wave function is characterized in this state by the Young pattern[13]. The point symmetry group C_{3v} contains three classes of operations. For the single class E all three configurations of the figure make a contribution to the character, i.e., $\tau(E) = 3$. Each of the operations of the class σ_v leaves invariant one configuration, therefore $\tau(\sigma_v) = 1$. Finally, under the action of the operations of class C_3 the configurations go over into one another, i.e., $\tau(C_3) = 0$. The character of the representation made up by the s-orbital is always equal to unity. The characters of the representations formed by the p-orbitals are expressed, in this case for all the operations in therms $\chi^{(1)}(E) = 3$. Taking $\chi^{[1^3]}(P)$ from[1], we can readily find with the aid of formula (10) the characters of the reducible representation. Their values, and also the results of expansion in irreducible representations of the group C_{3v}, are given below:

Classes π_3:	$\{1^3\}$	$\{3\}$	$\{12\}$
Classes C_{3v}:	E	$2C_3$	$3\sigma_v$
$X^{[1^3]}(\mathfrak{R})$:	27	0	—3
Allowed multiplets	$3\,{}^4A_1$,	$6\,{}^4A_2$,	$9\,{}^4E$

B. Several Valence Electrons Specified on One of the Atoms

In the preceding section it was assumed that one valence electron is specified on each atom. Formula (10) can be easily generalized to the case when n_1 valence atoms are specified on one of the atoms. We start here from a definite state of this multi-electron atom, characterized by a set of quantum numbers $[\lambda_1]\alpha_1 L_1 M_1$, where α_1 distinguishes between states with identical value of the total orbital angular momentum L_1. In all the symmetry transformations, the multi-electron atom remains in place, and only the atoms with one valence electrons are permuted. We denote such permutations by P_2. In formula (10) it is necessary to replace $\chi^{[\lambda]}(P)$ by $\chi^{[\lambda_2]}(P_2)$, where $[\lambda_2]$ denotes the permutation symmetry of the electrons of the monovalent atoms. Further, since we are specifying only the permutation symmetry $[\lambda]$ of all the electrons and $[\lambda_1]$ of the electrons on one atom, it is necessary to sum the formula for the character over all possible $[\lambda_2]$. As a result, (10) goes over into

$$X^{[\lambda]}(\mathfrak{R})=\sum_{[\lambda_2]}\chi^{[\lambda_2]}(P_2)\chi^{(L_1)}(R)\chi^{(l_2)}(R^{n_2})\ldots\chi^{(l_k)}(R^{n_k})\tau(\mathfrak{R}). \tag{14}$$

In the case of ionic configurations it may turn out that the operation $\mathfrak{R}$ corresponds, for different configurations of a given set, to different permutations P_2. It is then necessary to replace $\tau(\mathfrak{R})$ by $\tau_{P_2}(\mathfrak{R})$ and to sum expression (14) over the possible P_2.

The possible Young patterns $[\lambda_2]$ are determined by expanding the representation $\Gamma^{[\lambda]}$ on the subgroup $\pi_{n_1}\times\pi_{n_2}$ at fixed $\Gamma^{[\lambda_1]}$:

$$\Gamma^{[\lambda]}\rightarrow\sum_{\lambda_2}\Gamma^{[\lambda_1]}\times\Gamma^{[\lambda_2]}. \tag{15}$$

The expansion (15) can be found, for example, with the aid of the Littlewood theorem, see[1,7][3)].

By way of an example let us consider determination of allowed triplets of the methane molecule CH_4 in the case of a carbon atom in the state $2s2p^3\ {}^3P$, i.e., with $[\lambda_1] = [21^2]$, $L_1 = 1$. The electrons of the H atoms are assumed to be in the 1s state. The permutation symmetry of the total wave function is characterized by a Young pattern $[\lambda] = [2^3 1^2]$. Specified $[\lambda]$ and $[\lambda_1]$ satisfy all three possible Young patterns for four electrons of the atoms H, i.e., $[\lambda_2] = [2^2]$, $[21^2]$ and $[1^4]$. T_d is the point symmetry group of methane. In this case there is one covalent configuration, therefore $\tau(\mathfrak{R}) = 1$ for all $\mathfrak{R}$. Formula (14) takes the simple form

$$X^{[2^3 1^2]}(\mathfrak{R})=\sum_{\lambda_2}\chi^{[\lambda_2]}(P_2)\chi^{(1)}(R). \tag{16}$$

We take the characters $\chi^{[\lambda_2]}$ from[1]. The characters $\chi^{(1)}(R)$ corresponding to the operations of the group T_d are obtained from formulas (11)—(13). We recall that the parity of the state of the system of k electrons with orbital angular momenta $l_1, l_2, \ldots, l_k$ is determined from the formula[6]:

$$(-1)^{l_1+l_2+\ldots+l_k}. \tag{17}$$

Consequently, a carbon atom with the considered electron configuration $2s2p^3$ is in an odd state. From formula (16) we find the characters of the reducible representation:

Classes π_4:	$\{1^4\}$	$\{13\}$	$\{2^2\}$	$\{1^2 2\}$	$\{4\}$
Classes T_d	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
$X^{[2^3 1^2]}[\mathfrak{R}]$:	18	0	—2	—2	0

Expansion of this representation into irreducible

[3)] An alternate method is based on the one-two-one correspondence between the Young patterns of an N-electron system and the value of the total spin S. To find $[\lambda_2]$ it is sufficient to find the possible values of the spin S_2 which are compatible with the vector equation $S = S_1 + S$

representations of the group T_d yields the following set of allowed triplets: $^3A_2$, ^3E, 3^3F_1, 2^3F_2 (in full accord with[3]).

C. Diatomic Molecule

Let us consider a diatomic molecule consisting of identical atoms. The states of the atoms are specified by a set of quantum numbers $[\lambda_i]\alpha_i L_i M_i$. The coordinate wave function of the molecule, having permutation symmetry of the Young pattern $[\lambda]$, is constructed in the following manner from the coordinate wave functions of the atoms (see (7.56) in[1]):

$$\Phi_r^{[\lambda]}(A_1[\lambda_1]\alpha_1 L_1 M_1,\ A_2[\lambda_2]\alpha_2 L_2 M_2)$$
$$= C\sum_{r_1 r_2}\sum_{m}\langle r|Q|r_1 r_2\rangle^{[\lambda]} Q\Phi_{r_1}^{[\lambda_1]}(A_1\alpha_1 L_1 M_1)\,\Phi_{r_2}^{[\lambda_2]}(A_2\alpha_2 L_2 M_2), \tag{18}$$

where C is a normalization factor, Q the permutations of the electrons among the atoms retaining an increasing order of numbers of the electrons of each atom. The molecule point symmetry group is $D_{\infty h}$. Let us find the characters of the representation made up of the functions (18) for the operations of the group $D_{\infty h}$.

The result of the action of the operation $\mathfrak{R} = P_{A_1A_2}R_{A_1}R_{A_2}$ on the function (18) is equal to

$$P_{A_1A_2}R_{A_1}R_{A_2}\Phi_r^{[\lambda]} = C\sum_{\substack{r_1 r_2\\ M_1' M_2'}}\sum_{Q} D^{(L_1)}_{M_1' M_1}(R)\,D^{(L_2)}_{M_2' M_2}(R)\langle r|Q|r_1 r_2\rangle^{[\lambda]} Q$$
$$\times\Phi_{r_1}^{[\lambda_1]}(A_2\alpha_1 L_1 M_1'|12\cdots n)\,\Phi_{r_2}^{[\lambda_2]}(A_1\alpha_2 L_2 M_2'|n+1\cdots 2n). \tag{19}$$

Let P be the electron-coordinate permutation that returns them to "their own" atoms with conservation of the increasing order of the numbers of the electrons of each atom. Then that part of (19) which is connected with the permutations can be written in the form:

$$\sum_{Q}\langle r|Q|r_1 r_2\rangle^{[\lambda]} QP^{-1}\Phi_{r_2}^{[\lambda_2]}(A_1\alpha_2 L_2 M_2'|12\cdots n)$$
$$\times\Phi_{r_1}^{[\lambda_1]}(A_2\alpha_1 L_1 M_1'|n+1\cdots 2n). \tag{20}$$

We put $QP^{-1} = U$, whence $Q = UP$ and

$$\langle r|UP|r_1 r_2\rangle^{[\lambda]} = \sum_{\bar\lambda_1 t_1\bar\lambda_2 t_2}\langle r|U|[\bar\lambda_1]t_1,\ [\bar\lambda_2]t_2\rangle^{[\lambda]}$$
$$\times\langle[\bar\lambda_1]t_1,\ [\bar\lambda_2]t_2|P|[\lambda_1]r_1,\ [\lambda_2]r_2\rangle^{[\lambda]}. \tag{21}$$

The matrix $\langle\ |P|\rangle$ from (21) belongs to the class of matrices considered in[8], is diagonal in $[\lambda_i]$, and does not depend on the Young tableaux r_i:

$$\langle[\bar\lambda_1]t_1,\ [\bar\lambda_2]t_2|P|[\lambda_1]r_1,\ [\lambda_2]r_2\rangle^{[\lambda]} = \delta_{t_1r_2}\delta_{t_2r_1}\langle\lambda_1\lambda_1\|P\|\lambda_1\lambda_1\rangle^{[\lambda]}. \tag{22}$$

The double bar in the matrix element in the right side of (22) denotes independence of the Young tableaus. A convenient method of expressing such matrix elements in terms of the characters is given in the Appendix (see (37), (38) and Table II).

Substituting (20)—(22) in (19) and using the definition of the function (18), we obtain

$$P_{A_1A_2}R_{A_1}R_{A_2}\Phi_r^{[\lambda]}(A_1[\lambda_1]\alpha_1 L_1 M_1,\ A_2[\lambda_2]\alpha_2 L_2 M_2) = \delta_{\lambda_1\lambda_2}\langle\lambda_1\lambda_1\|P\|\lambda_1\lambda_1\rangle^{[\lambda]}$$
$$\times\sum_{M_1' M_2'} D^{(L_1)}_{M_1' M_1}(R)\,D^{(L_2)}_{M_2' M_2}(R)\,\Phi_r^{[\lambda]}(A_1[\lambda_2]\alpha_2 L_2 M_2',\ A_2[\lambda_1]\alpha_1 L_1 M_1'). \tag{23}$$

To find the character it is necessary to equate in (23) $\alpha_1 = \alpha_2$, $L_1 = L_2$, $M_2' = M_1$, and $M_1' = M_2$, and to sum over M_1 and M_2. As a result we obtain

$$X^{[\lambda]}(P_{A_1A_2}R_{A_1}R_{A_2}) = \langle\lambda_1\lambda_1\|P\|\lambda_1\lambda_1\rangle^{[\lambda]}\chi^{(L_1)}(R^2). \tag{24}$$

In the case when the atoms have different sets $[\lambda_i]\alpha_i L_i$, the character (24) equals zero. For the operations $\mathfrak{R}$ which are not connected with permutation of the nuclei, it is not necessary to satisfy the equations $\alpha_1 = \alpha_2$ and $[\lambda_1] = [\lambda_2]$. The corresponding formula for the character is

$$X^{[\lambda]}(R_{A_1}R_{A_2}) = \chi^{(L_1)}(R)\,\chi^{(L_2)}(R)\,\tau_{L_1L_2}, \tag{24a}$$

where $\tau_{L_1L_2} = 2$ for $L_1 \neq L_2$, since two configurations are possible, differing in permutations of the orbital angular momenta; obviously $\tau_{L_1L_1} = 1$.

By way of an example, let us consider the N_2 molecule. We find the allowed singlets arising from the state $p^3\ {}^3P$ of the N atoms. According to Table II of the Appendix, the permutation factor $\langle[21][21]\|P\|[21][21]\rangle^{[2^3]}$ entering in (24) is equal to unity. The formulas (24) and (24a) take on the simple form

$$X^{[2^3]}(P_{A_1A_2}R_{A_1}R_{A_2}) = \chi^{(1)}(R^2), \tag{25}$$

$$X^{[2^3]}(R_{A_1}R_{A_2}) = [\chi^{(1)}(R)]^2. \tag{25a}$$

Calculating the characters by means of formulas (11)—(13), we obtain

$D_{\infty h}$:	E	C_φ	σ_v	I	IC_φ	$I\sigma_v$
$X^{[2^3]}(\mathfrak{R})$	9	$\dfrac{\sin^2(^3/_2\varphi)}{\sin^2(\varphi/2)}$	1	3	$\dfrac{\sin 3\varphi}{\sin\varphi}$	3

Expansion of this representation into irreducible representations of the group $D_{\infty h}$ yields the following singlet states:

$$2^1\Sigma_g^+,\quad {}^1\Sigma_u^-,\quad {}^1\Pi_g,\quad {}^1\Pi_u,\quad {}^1\Delta_g.$$

D. General Case

Let us consider a molecule consisting of an arbitrary number of atoms. The state of each atom is specified by a set of quantum numbers $[\lambda_i]\alpha_i L_i M_i$. Let us find the characters of the representation, formed by the coordinate wave functions of the molecule in the state with definite permutation symmetry $[\lambda]$. The coordinate wave functions of the molecule are constructed from the coordinate wave functions of the atoms in accordance with formula (21) from[8]. For the sake of clarity we consider a molecule consisting of three identical atoms. The result of the action of the cyclic permutation $P_{A_1A_2A_3}$ on the wave function of such a molecule is

$$P_{A_1A_2A_3}\Phi_r^{[\lambda]}((A_1[\lambda_1]\alpha_1 L_1 M_1,\ A_2[\lambda_2]\alpha_2 L_2 M_2)[\lambda_{12}]\,A_3[\lambda_3]\alpha_3 L_3 M_3)$$
$$= C\sum_{r_1 r_2 r_3}\sum_{Q}\langle r|Q|(r_1 r_2)\lambda_{12} r_3\rangle^{[\lambda]} QP^{-1}\Phi_{r_1}^{[\lambda_1]}(A_2\alpha_1 L_1 M_1)\,\Phi_{r_2}^{[\lambda_2]}$$
$$\times(A_3\alpha_2 L_2 M_2)\,\Phi_{r_3}^{[\lambda_3]}(A_1\alpha_3 L_3 M_3). \tag{26}$$

The permutation P, just as in (20), returns the electrons to "their own" atoms while conserving the increasing order of numbers of electrons of the atom. It can be written as P_{123}, where the symbol P_{123} denotes that the electrons of the atom 1 are replaced by the electrons of the atom 2, etc. Putting $QP^{-1} = U$, we represent

$$\langle r|UP|(r_1 r_2)\lambda_{12} r_3\rangle^{[\lambda]} = \sum_{\substack{\text{interm.}\\ \text{state}}}\langle r|U|(t_1 t_2)\bar\lambda_{12} t_3\rangle^{[\lambda]}$$
$$\times\langle(t_1 t_2)\bar\lambda_{12} t_3|P|(r_1 r_2)\lambda_{12} r_3\rangle^{[\lambda]}. \tag{27}$$

In analogy with (22)

$$\langle (t_1t_2)\bar{\lambda}_{12}t_3|P|(r_1r_2)\lambda_{12}r_3\rangle^{[\lambda]} = \delta_{t_1r_2}\delta_{t_2r_3}\delta_{t_3r_1}\langle(\lambda_1\lambda_1)\bar{\lambda}_{12}\lambda_1\|P\|(\lambda_1\lambda_1)\lambda_{12}\lambda_1\rangle^{[\lambda]}. \qquad (28)$$

Substituting (27) and (28) in (26) and taking into account the definition of the function $\Phi_r^{[\lambda]}$ in (26), we obtain

$$P_{A_1A_2A_3}\Phi_r^{[\lambda]}(\cdots) = C\sum_{\bar{\lambda}_{12}}\langle(\lambda_1\lambda_1)\bar{\lambda}_{12}\lambda_1\|P\|(\lambda_1\lambda_1)\lambda_{12}\lambda_1\rangle^{[\lambda]}$$
$$\cdot\Phi_r^{[\lambda]}((A_1[\lambda_3]\alpha_3L_3M_3,\ A_2[\lambda_1]\alpha_1L_1M_1)[\bar{\lambda}_{12}]A_3[\lambda_2]\alpha_2L_2M_2). \qquad (29)$$

For the character of the operation $\Re = P_{A_1A_2A_3}R_{A_1}R_{A_2}R_{A_3}$ we obtain the expression

$$X^{[\lambda]}(\Re) = \sum_{\lambda_{12}}\langle(\lambda_1\lambda_1)\lambda_{12}\lambda_1\|P\|(\lambda_1\lambda_1)\lambda_{12}\lambda_1\rangle^{[\lambda]}\chi^{(L)}(R^3). \qquad (30)$$

It is obvious that in the case of a cycle of n atoms we have

$$X^{[\lambda]}(\Re) = \sum_{\lambda_{\text{interm}}}\langle(\lambda_1\ldots\lambda_1)\lambda_{\text{interm}}\|P\|(\lambda_1\ldots\lambda_1)\lambda_{\text{interm}}\rangle^{[\lambda]}\chi^{(L)}(R^n), \qquad (31)$$

where λ_{interm} denotes the set of $(n-2)$ intermediate Young patterns, necessary for a complete description of the permutation symmetry of the state of n particles (see Sec. 2—10 in[1]). We note that for a cycle of n atoms, on each of which v valence electrons are specified, the permutation P belongs to the class $\{n^v\}$.

We introduce for the sum over λ_{interm} in (31) the special symbol

$$\sum_{\lambda_{\text{interm}}}\langle(\underbrace{\lambda_1\ldots\lambda_1}_{n})\lambda_{\text{interm}}\|P\|(\lambda_1\ldots\lambda_1)\lambda_{\text{interm}}\rangle^{[\lambda]} = w_n(\lambda_1,\lambda). \qquad (32)$$

Formula (31) assumes the compact form

$$X^{[\lambda]}(\Re) = w_n(\lambda_1,\lambda)\chi^{(L)}(R^n). \qquad (33)$$

In the general case the operation $\Re$ corresponds to permutation with arbitrary cyclic structure. The formula for the character,with allowance for (33), can be written in the form

$$X^{[\lambda]}(\Re) = \Big\{\sum_{\lambda^{(1)}\ldots\lambda^{(k)}}\sum_{\lambda_{\text{interm}}} w_{n_1}(\lambda_1,\lambda^{(1)})\chi^{(L_1)}(R^{n_1})\ldots w_{n_k}(\lambda_k,\lambda^{(k)})\chi^{(L_k)}(R^{n_k})\Big\}\tau(\Re), \qquad (34)$$

where n_i is the number of atoms in a cycle in which each atom is characterized by the permutation symmetry $[\lambda_i]$ and total orbital angular momentum L_i, and $[\lambda^{(i)}]$ is the overall permutation symmetry of the atoms of the i-th cycle. Since in the construction of the permutation state $[\lambda]$ one specifies only the permutation state $[\lambda_i]$ of the atoms, it is necessary to sum in (34) over all possible permutation symmetries $[\lambda^{(i)}]$ of the cycles, and also over the intermediate symmetry patterns $[\lambda_{\text{interm}}]$ which relate $[\lambda^{(i)}]$ with $[\lambda]$. The possible Young patterns $[\lambda^{(i)}]$ at a fixed overall Young pattern $[\lambda]$ are obtained by using the Littlewood theorem[1,7] (see also footnote[3]). The cyclic structure of the expression (34) is determined by the operation $\Re$. We note that the permutation factors $w_{n_i}(\lambda_i,\lambda^{(i)})$ for each cycle are calculated separately. In the Appendix we give a method of their calculation in terms of the character. They also give the values of $w_n(\lambda_1,\lambda)$ for all possible symmetries of the systems with a total number of electrons $N \leq 8$. Finally, $\tau(\Re)$, just as in formula (10) and (14), denotes the number of electronic configurations of the molecules, which remain invariant under the action of the operation $\Re$ (see, e.g., the next section).

In concrete particular cases formula (34) goes over into formulas (10), (14), and (24) of the preceding sections.

3. DETERMINATION OF ALLOWED MULTIPLETS OF THE MOLECULE H_2O

Let us find all the multiplets that can be constructed for the molecule H_2O with account taken of four 2p-electrons of the atom O and two 1s-electrons of the atoms H. The overall dimensionality of the secular equation which appears in this case is, in accordance with formula (6.54) of[1], equal to 10!/6!4! = 210. The point symmetry group of the water molecule is C_{2v}. The molecular configurations include one covalent and five different types of ionic configurations. Let us consider them in sequence.

I. $(p^4)_O(s)_H(s)_H$. The characters of the representations induced by the coordinate wave functions of different covalent structures are given in the upper lines of Table I. They can be readily found from formula (14) with $\tau(\Re) = 1$ for all $\Re$.

II—IV. Ionic configurations $(p^5)_O(s)_H$, $(p^4)_O(s^2)_H$, and $(p^3)_O(s)_H(s)_H$. For each allowed O atom state characterized by an orbital angular momentum L, there are two configurations of such types. The characters are calculated by the formula $X^{[\lambda]}(\Re) = \chi^{(L)}(R)\tau(R)$, in which $\tau(E) = \tau(\sigma_2) = 2$ and $\tau(C_2) = \tau(\sigma_1) = 0$.

V. $(p^2)_O(s^2)_H(s^2)_H$. The formula for the characters is obtained from the general formula (34) with

Table I*

	Coordinate functions of molecular configurations	Characters of reducible representations				Multiplicities of entry of irreducible representations			
		e	C_2	σ_1	σ_2	A_1	A_2	B_1	B_2
I	$\Phi^{[21^4]}(p^4[21^2]P;\ (s;\ s)[1^2])$	3	1	1	—1	1	1	0	1
	$\Phi^{[2^21^2]}(p^4[2^2]S;\ (s;\ s)[1^2])$	1	—1	—1	1	0	0	1	0
	$\Phi^{[2^21^2]}(p^4[2^2]D;\ (s;\ s)[1^2])$	5	—1	—1	1	1	1	2	1
	$\Phi^{[2^21^2]}(p^4[21^2]P;\ (s;\ s)[2])$ $\Phi^{[2^21^2]}(p^4[21^2]P;\ (s;\ s)[1^2])$ }	6	0	0	—2	1	2	1	2
	$\Phi^{[2^3]}(p^4[2^2]S;\ (s;\ s)[2])$	1	1	1	1	1	0	0	0
	$\Phi^{[2^3]}(p^4[2^2]D;\ (s;\ s)[1^2])$	5	1	1	1	2	1	1	1
	$\Phi^{[2^3]}(p^4[21^2]P;\ (s;\ s)[1^2])$	3	1	1	—1	1	1	0	1
II	$\Phi^{[2^21^2]}(p^5[2^21]P;\ s[1]S)$	6	0	0	2	2	1	2	1
	$\Phi^{[2^3]}(p^5[2^21]P;\ s[1]S)$	6	0	0	2	2	1	2	1
III	$\Phi^{[2^21^2]}(p^4[21^2]P;\ s^2[2]S)$	6	0	0	—2	1	2	1	2
	$\Phi^{[2^3]}(p^4[2^2]S;\ s^2[2]S)$	2	0	0	2	1	0	1	0
	$\Phi^{[2^3]}(p^4[2^2]D;\ s^2[2]S)$	10	0	0	2	3	2	3	2
IV	$\Phi^{[21^4]}(p^3[1^3]S;\ (s^2[2]S;\ s)[21])$	2	0	0	—2	0	1	0	1
	$\Phi^{[2^21^2]}(p^3[1^3]S;\ (s^2[2]S;\ s)[21])$	2	0	0	—2	0	1	0	1
	$\Phi^{[2^21^2]}(p^3[21]P;\ (s^2[2]S;\ s)[21])$	6	0	0	2	2	1	2	1
	$\Phi^{[2^21^2]}(p^3[21]D;\ (s^2[2]S;\ s)[21])$	10	0	0	—2	2	3	2	3
	$\Phi^{[2^3]}(p^3[21]P;\ (s^2[2]S;\ s)[21])$	6	0	0	2	2	1	2	1
	$\Phi^{[2^3]}(p^3[21]D;\ (s^2[2]S;\ s)[21])$	10	0	0	—2	2	3	2	3
V	$\Phi^{[2^21^2]}(p^2[1^2]P;\ (s^2[2]S;\ s^2[2]S)[2^2])$	3	—1	—1	—1	0	1	1	1
	$\Phi^{[2^3]}(p^2[2]S;\ (s^2[2]S;\ s^2[2]S)[2^2])$	1	1	1	1	1	0	0	0
	$\Phi^{[2^3]}(p^2[2]D;\ (s^2[2]S;\ s^2[2]S)[2^2])$	5	1	1	1	2	1	1	1
VI	$\Phi^{[2^3]}(p^6[2^3]S)$	1	1	1	1	1	0	0	0

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*The operation σ_2 denotes reflection in the plane of the molecule, and σ_1 reflection in the perpendicular plane.

Table II.

	$[\lambda_1]$	$[\lambda]$										
		$N=4$		$N=6$				$N=8$				
		$[2^2]$	$[21^2]$	$[2^3]$	$[2^21^2]$	$[21^4]$	$[1^6]$	$[2^4]$	$[2^31^2]$	$[2^21^4]$	$[21^6]$	$[1^8]$
w_2	$[2]$	1										
	$[1^2]$	1	−1									
	$[21]$			1	−1							
	$[1^3]$			1	−1	1	−1					
	$[2^2]$							1				
	$[21^2]$							1	−1	1		
	$[1^4]$							1	−1	1	−1	1
w_3	$[2]$			1								
	$[1^2]$			1	0	−1	1					
w_4	$[2]$							1				
	$[1^2]$							1	0	0	−1	1

$\tau(\Re) = 1$ for all the operations $\Re$, and has the following simple form: $\chi^{[\lambda]}(\Re) = \chi^{(L)}(R)$, since, in accordance with Table II, $w_2([2], [2^2]) = 1$.

VI. $(p^6)_O$. A single configuration of this type is possible.

The values of the characters of the reducible representations of the group C_{2v}, induced on the coordinate functions of the configurations I—VI, are listed in Table I. Their expansion in irreducible representations yields the following allowed multiplets: $1\,{}^5A_1$, $2\,{}^5A_2$, $2\,{}^5B_2$; $9\,{}^3A_1$, $12\,{}^3A_2$, $12\,{}^3B_1$, $12\,{}^3B_2$; $18\,{}^1A_1$, $10\,{}^1A_2$, $12\,{}^1B_1$, and $10\,{}^1B_2$. The total number of multiplets is 100, and the maximum order of the secular equation is obtained for the ground state ${}^1A_1$ and equals 18, which coincides with Slater's unpublished data (see[9], p. 278).

APPENDIX

CALCULATION OF THE PERMUTATION FACTORS $w_n(\lambda_1, \lambda)$

The matrix elements $\langle \| P \| \rangle$ which enter in the definition of $w_n(\lambda_1, \lambda)$ (see (32)) belong to a nonstandard representation of the permutation group and can be obtained by direct calculation with the aid of the corresponding transformation matrices ([1], Chap. II). It is possible, however, to formulate a system of equations which relate the sought factors $w_n(\lambda_1, \lambda)$ with the characters $\chi^{[\lambda_1]}$ and $\chi^{[\lambda]}$.

In the general case, the permutation of n groups of electrons can always be represented in the form $Q = PU_1 \ldots U_n$, where P is the permutation of the electrons among the groups and U_i is the permutation of the electrons inside the i-th group. If the matrix element $\langle (r)^B | PU_1 \ldots U_n | (r)^B \rangle^{[\lambda]}$, where $(r)^B$ is the symbol numbering the basis functions of the nonstandard representation reduced on n equal-number subgroups, is represented in the form of a product of matrix elements, then, by summing both parts of the obtained equation over $(r)^B$, we arrive at the following equation:

$$\sum_{\lambda_1} \chi^{[\lambda_1]}(U_1U_2 \ldots U_n)\, w_n(\lambda_1, \lambda) = \chi^{[\lambda]}(PU_1U_2 \ldots U_n). \tag{35}$$

The electron permutation P for each operation of the point symmetry is determined uniquely by the permutation of the atoms. Each of the permutations U_i in the right side of (35) acts on the electrons of different atoms, whereas the permutations U_i which enter in the character $\chi^{[\lambda_1]}$ act on the electrons of one atom.

If we put in (35) all U_i equal to unit permutations and take into account the fact that the permutations P belong to the class $\{n^\nu\}$, then (35) goes over into

$$\sum_{\lambda_1} f_{\lambda_1} w_n(\lambda_1, \lambda) = \chi^{[\lambda]}(\{n^\nu\}). \tag{36}$$

Equations (35) and (36) for the determination of $w_n(\lambda_1, \lambda)$ are very simple and as a rule make it possible to find the required factors without particular difficulty. In the particular case of a cycle of two atoms, the permutation factors

$$w_2(\lambda_1, \lambda) = \langle \lambda_1\lambda_1 \| P \| \lambda_1\lambda_1 \rangle^{[\lambda]} \tag{37}$$

satisfy the equation

$$\sum_{\lambda_1} \chi^{[\lambda_1]}(U_2U_1)\, w_2(\lambda_1, \lambda) = \chi^{[\lambda]}(PU_1U_2). \tag{38}$$

Let us consider by way of an example the determination of the factors $w_2([\lambda_1], [2^3])$. The two possible Young patterns are $[\lambda_1] = [21]$ and $[1^3]$, and are compatible with $[\lambda] = [2^3]$. We choose for U_1U_2 in (38) the two sets of permutations:

$$1.\ U_1 \text{ and } U_2 \subset \{1^3\};\quad 2.\ U_1 \subset \{3\},\quad U_2 \subset \{1^3\}.$$

This leads to the two equations

$$f_{[21]}w_2([21], [2^3]) + f_{[1^3]}w_2([1^3], [2^3]) = \chi^{[2^3]}(\{2^3\}),$$

$$\chi^{[21]}(\{3\})w_2([21], [2^2]) + \chi^{[1^3]}(\{3\})w_2([1^3], [2^3]) = \chi^{[2^3]}(\{6\}), \tag{39}$$

from which it follows that

$$w_2([21], [2^3]) = w_2([1^3], [2^3]) = 1.$$

Table II lists the values of the permutation factors for all possible symmetries of systems of electrons with $N \leq 8$.

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[1] I. G. Kaplan, Simmetriya mnogoelektronnykh sistem (Symmetry of Multielectronic Systems) Nauka, 1968).

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

[3] M. Kotani, Proc. Phys. Math. Soc. Japan, 19, 460 (1937).

[4] I. G. Kaplan, Teor. I. Eksp. khimiya 1, 608, 619 (1965); 2, 441 (1966); 3, 150, 287 (1967).

[5] G. Ya. Lyubarskiĭ, Teoriya grupp i ee primenenie v fizike (Group Theory and its Application in Physics) Fizmatizdat, 1958.

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

[7] M. Hamermesh, Group Theory and Its Application to Physical Problems, Addison-Wesley, 1962, Ch. 7.

[8] I. G. Kaplan, Zh. Eksp. Teor. Fiz. 41, 560 (1961) [Sov. Phys.-JETP 14, 401 (1962)].

[9] J. C. Slater, Quantum Theory of Molecules and Solids, Vol. 1, McGraw Hill, 1963.

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208