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Configurations of Equivalent Electrons[†]

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We derive here a comprehensive set of formulas for determining the overall spin and spatial symmetry of wave functions arising from a partially filled degenerate orbital. We extend the usual arguments for the case of weak coupling between spin and spatial angular momenta to the *jj*-coupling case.

I. Introduction

The derivation of the electronic states allowed by the Pauli principle for "equivalent electrons", that is, an incompletely filled degenerate orbital, is brushed aside in most elementary treatments of group theory, commonly replaced by an enumeration technique for an example such as the p^2 occupation in an atom based on "microstates": specific combinations of electrons listed by values of the overall M_L and M_S, which are then used to deduce which *LS*-coupled states result. This approach is elementary enough to be used in undergraduate courses but is neither elegant nor conveniently transferred to the (arguably more common) situation of a degenerate molecular orbital in a system belonging to a finite point group.

The general approach to this problem is of course well-known. Any wave function for an allowed state of, e.g., N electrons in a k-fold degenerate orbital must be antisymmetric with respect to particle interchange; more formally, it must transform as a basis function for the alternating (totally antisymmetric) representation of the symmetric group $\mathscr{S}(N)$. The case of $N = 1$ is trivial and the case of N is identical to that of $2k - N$, so at most half-filled shells need be considered explicitly. Since in the limit of small spin−orbit coupling our goal is to identify the electronic states by spin labels and by irreducible representations (irreps) of the molecular point group, it is natural to view the wave function as a product of appropriate spin and spatial functions. These are in turn conveniently expressed as functions with well-defined permutational symmetry, which further lends itself to treatment using $\mathscr{S}(N)$. Historically, this is the approach usually associated with Kotani,[1] although it was presented earlier in the fairly advanced group-theory text by Lomont.[2] Other formulations of this approach in the literature include a very elaborate and comprehensive derivation by Goscinski and Öhrn[3] and a pedagogical one by Ford.[4] It should be emphasized, however, that while symmetric group methods are used to derive the final formulas the latter are completely general and apply irrespective of how spin- and symmetry-adapted functions are to be constructed. This can be seen in treatments by Slater[5] or by Hurley[6] that actually use determinants throughout, although this approach rapidly becomes clumsy as k increases since it involves manipulating $k!$ terms.

The final formulas for different values of N and k are scattered through the literature, and although the cases for $N = 2$ and $N = 3$ are well-known, the explicit formula for $N = 4$ is harder to find (see, e.g., ref 7) and $N = 5$ is commonly arrived at by arguments based on atomic d^N configurations. The analogous results for cases of strong coupling between spin and spatial coordinates—*jj* -coupling in atoms, and for convenience we will use this term for the molecular case throughout this work—are considerably more difficult to find in the literature. The purpose of the present work is to give a list that is (for practical purposes) complete for any application to molecular electronic structure for both weak and strong spin−orbit coupling. In the next section we review the necessary background for the use of the symmetric group and derive the formulas which give the various electronic states arising from occupancies k^N, and in the following section give a brief discussion and enumeration of some particular cases. We emphasize that the methodology is well-known and we claim no originality for it, although a key result that has simply been assumed in previous work is actually proved here. Our aim is to provide a comprehensive derivation and listing of the final formulas, providing a single source for configurations of equivalent electrons for any spin−orbit coupling situation. The final formulas are equally applicable to the atomic (or diatomic/linear) case as to finite point groups, but for atoms it is far more convenient to use angular momentum coupling techniques (see, e.g., refs 8−10 and references therein) than to use the formulas here. We will thus deal only with the molecular case.

Consistent with our intention to make this work self-contained, the reader will need only a set of character tables to apply the various formulas. The examples presented in section III were analyzed using the extensive tables of Altmann and Herzig.[11] We note here that we have followed their notation unconditionally, so that triply degenerate irreducible representations are labeled T, 4-fold degenerate ones F, and 5-fold H. This conflicts with some tables, but in view of the completeness and superiority of the presentation in ref 11 we prefer it.

II. Derivation: Group-Theoretical Background

We review very briefly here material relevant to our use of the symmetric group. Much more detail on these groups can be found in group theory texts such as Hamermesh.[8]

The symmetric group on N objects is denoted $\mathscr{S}(N)$ (we use a different typeface to avoid any confusion with the point groups S_N) and comprises all permutations P on N objects. $\mathscr{S}(N)$ is a group of order $N!$ and is non-Abelian for $N > 2$. Irreps of $\mathscr{S}(N)$ can be labeled by a partition of N, that is, a set of nonincreasing positive integers $\lambda_1, \lambda_2, \ldots$ such that $\lambda_1 + \lambda_2 + \ldots = N$. It is conventional to write $\lambda_i^{m_i}$ to indicate that the integer λ_1 occurs m_1 times in the partition, so the partition $3 + 1 + 1 + 1$ of 6 is written $[31^3]$. Distinct partitions of N thus label the irreps of

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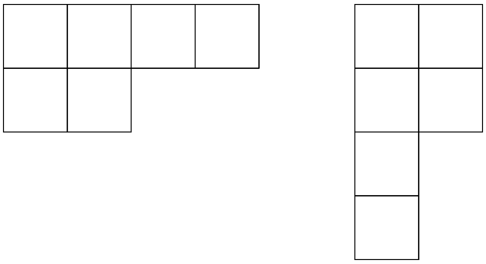

Figure 1. Young shapes: [42] (left) and its dual [$2^2 1^2$] (right).

$\mathscr{S}(N)$, and these can be represented if desired by Young shapes as shown in Figure 1.

The elements $P \in \mathscr{S}(N)$ fall into classes that are uniquely specified by the cycle structure of P: that is, the decomposition of P into disjoint cyclic permutations. If P comprises q_1 1-cycles, q_2 2-cycles, etc., then the cycle structure of P is denoted $(1^{q_1}2^{q_2}...)$. Clearly, this label is another partition of N—the number of classes of a finite group equals the number of irreps. We note in passing that the permutation is designated odd or even according to whether $q_2 + q_4 + q_6$ ... is odd or even, and the parity (or signature or sign) ε_p of P is then -1 or $+1$, respectively. Given the character table for $\mathscr{S}(N)$ we have the usual projection operators

$$O^{\pi} = (N!)^{-1} \sum_q \mu_q \chi_q^{\pi} P_q \tag{1}$$

where π is an irrep of $\mathscr{S}(N)$, μ_q is the order of the class q, and χ_q^{π} is the character of irrep π for class q. The sum runs over distinct classes of $\mathscr{S}(N)$ and P_q is an arbitrary element chosen from class q. The class order is given by the cycle structure of the class as

$$\mu_q = \frac{N!}{q_1! 2^{q_2} q_2! ... n^{q_n} q_n!} \tag{2}$$

We use the label π to denote an irrep of a symmetric group; α will denote an irrep of the molecular point group $\mathscr{G}$, which may be a double group.

We consider first the case of a Hamiltonian with no dependence on electron spin, so that the total electron spin of the system is a good quantum number. It is well-known that since there are only two elementary spin projections $m_S = \pm 1/2$ only those irreps of $\mathscr{S}(N)$ with at most two rows are admissible as spin eigenfunctions, and for the wave function to be antisymmetric with respect to particle interchange the spatial part must correspond to the dual or conjugate of the spin irrep, which hence has at most two columns (Figure 1). Allowable irreps for the spatial part thus correspond to partitions $2^{(N-2S)/2}1^{2S}$. We can find the appropriate permutational symmetry-adapted functions by applying a projection operator. The question we wish to answer is, what is the spatial symmetry (that is, what is the behavior under the molecular point group) of these permutational symmetry-adapted functions when they comprise partly filled degenerate orbitals?

The *derivation* (but not the use) of the final formulas of this section requires a knowledge of at least part of the character table for $\mathscr{S}(N)$. For molecular cases we will need $N = 2$, 3, 4, and 5. The cases of $N \leq 4$ can be obtained from point group character tables since those symmetric groups are isomorphic to point groups C_2, C_{3v}, and T_d, respectively: the correspondences between classes of symmetry elements and permutations and between irrep labels used in this work are given in Table 1. $\mathscr{S}(5)$ is not isomorphic to a point group and for convenience and in the interests of completeness we give its character table here in Table 2.

TABLE 1: Symmetric Groups $\mathscr{S}(N)$ for $N = 2, 3, 4$ as Isomorphisms from Point Groups

group elements		irreps	
	$\mathscr{S}(2)$ from C_2		
(1^2)	E	$[2]$	A
(2)	C_2	$[1^2]$	B
	$\mathscr{S}(3)$ from C_{3v}		
(1^3)	E	$[3]$	A_1
(12)	σ_v	$[1^3]$	A_2
(3)	C_3	$[21]$	E
	$\mathscr{S}(4)$ from T_d		
(1^4)	E	$[4]$	A_1
$(1^2 2)$	σ_d	$[1^4]$	A_2
(13)	C_3	$[2^2]$	E
(2^2)	C_2	$[21^2]$	T_1
(4)	S_4	$[31]$	T_2

TABLE 2: Character Table for $\mathscr{S}(5)$[a]

	(1^5) 1	$(1^3 2)$ 10	$(1^2 3)$ 20	(14) 30	(12^2) 15	(23) 20	(5) 24
$[5]$	1	1	1	1	1	1	1
$[41]$	4	2	1	0	0	-1	-1
$[32]$	5	1	-1	-1	1	1	0
$[31^2]$	6	0	0	0	-2	0	1
$[2^2 1]$	5	-1	-1	1	1	-1	0
$[21^3]$	4	-2	1	0	0	1	-1
$[1^5]$	1	-1	1	-1	1	-1	1

[a] The order of each class is listed below its cycle structure.

We assume that for a k-fold degenerate irrep α of the molecular point group we have a set of partner basis functions related by

$$Gf^{\alpha}(i) = \sum_{j=1}^{k} f^{\alpha}(j)\, D^{\alpha}(j,i;G) \tag{3}$$

where $D^{\alpha}(j,i;G)$ is the jith element of irreducible representation matrix $\mathbf{D}^{\alpha}(G)$ and $G \in \mathscr{G}$ is the molecular point group. (We use this in-line notation rather than the more conventional subscript indexing of $\mathbf{D}$ and f because otherwise our subsequent derivation requires too many levels of subscripts.) Consider now, for N electrons in this k-fold degenerate orbital, an N-fold product of partner functions f (which may include duplication of basis functions) $f^{\alpha}(i_1)f^{\alpha}(i_2)\,...f^{\alpha}(i_N)$. The effect of $G \in \mathscr{G}$ on this product can be written as

$$\begin{aligned} Gf^{\alpha}(i_1)...f^{\alpha}(i_N) &= \sum_{j_1}...\sum_{j_N} f^{\alpha}(j_1)...f^{\alpha}(j_N) D^{\alpha}(j_1,i_1;G)...D^{\alpha}(j_N,i_N;G) \\ &\equiv \sum_{j_1}...\sum_{j_N} f^{\alpha}(j_1)...f^{\alpha}(j_N) D^{\mathrm{prod}}(j_1 j_2...j_N,i_1 i_2...i_N;G) \end{aligned} \tag{4}$$

where in the second line we have written the products of irrep matrix elements as elements of a direct product representation $\mathbf{D}^{\mathrm{prod}}$. This form more clearly illustrates taking the trace to obtain characters: set $j_k = i_k$ and sum over i_k.

We have already mentioned that a function of a desired permutational symmetry can be obtained using the projection operator of eq 1. The question here is what are the spatial symmetry properties of the function obtained by applying this projection operator to our orbital product—properties defined by the character

$$\chi^{N,S;\alpha}(G) = \mathrm{Tr}(O^{N,S} G f^{\alpha}(i_1)..f^{\alpha}(i_N)) \tag{5}$$

where the label on $O^{N,S}$ indicates the irrep $2^{(N-2S)/2}1^{2S}$ of $\mathscr{S}(N)$, or more explicitly as

$$\chi^{N,S;\alpha}(G) = \mathrm{Tr}((N!)^{-1} \sum_q \mu_q \chi_q^{N,S} P_q G f^{\alpha}(i_1)..f^{\alpha}(i_N)) \tag{6}$$

We note first that the permutations P_q that appear in O^{π} are given as products of disjoint m-cycles. This means that $\chi^{N,S;\alpha}(G)$ can be written using a product of disjoint terms

$$\chi^{N,S;\alpha}(G) = \mathrm{Tr}((N!)^{-1} \sum_q \mu_q \chi_q^{N,S} \prod_m^N m^{q_m} G f^{\alpha}(i_1)..f^{\alpha}(i_N)) \tag{7}$$

identified with cycles of specific order, where the cycle structure of P_q is $(1^{q_1}2^{q_2}...N^{q_N})$; without loss of generality we can choose from the class q the permutation in which the first q_1 labels (the 1-cycles) are unpermuted, the next q_2 pairs of labels are permuted within the pairs, then the next q_3 triples, etc. First, since there are no permutations of the first q_1 indices, the contributions to the direct product of irrep matrix elements when applying P_q to $Gf^{\alpha}(i_1)...f^{\alpha}(i_N)$ of eq 7 from the 1-cycles is simply

$$\sum_{j_1} ... \sum_{j_{q_1}} D^{\alpha}(j_1,i_1;G)...D^{\alpha}(j_{q_1},i_{q_1};G) \tag{8}$$

and we obtain a contribution from the 1-cycles to the overall trace $\chi^{N,S;\alpha}(G)$ of $\Sigma_i D^{\alpha}(i,i;G)]^{q_1}$ or $[\chi^{\alpha}(G)]^{q_1}$.

Consider next the term in eq 7 from the 2-cycles in P_q. This results in the expression

$$D^{\alpha}(j_{q_1+2},i_{q_1+1};G)\, D^{\alpha}(j_{q_1+1},i_{q_1+2};G)...D^{\alpha}(j_{q_1+q_2},i_{q_1+q_2-1};G)\, D^{\alpha}(j_{q_1+q_2-1},i_{q_1+q_2};G) \tag{9}$$

On taking the trace by setting $j_k = i_k$ and summing over the latter, each pairwise product here contributes a term of the form $\Sigma_{i_1 i_2} D^{\alpha}(i_1,i_2;G)\, D^{\alpha}(i_2,i_1;G)$, and since

$$\sum_{i_2} D^{\alpha}(i_1,i_2;G)\, D^{\alpha}(i_2,i_1;G) = D^{\alpha}(i_1,i_1;G^2) \tag{10}$$

we obtain a contribution to the trace from all the 2-cycles in P_q of $[\chi^{\alpha}(G^2)]^{q_2}$. At this point it seems evident that m-cycles in P_q will make a contribution of $[\chi^{\alpha}(G^m)]^{q_m}$ to the trace. This is simply inferred, using a 3-cycle for illustration, by Goscinski and Öhrn,[3] and stated without proof or comment by Ford,[4] but is in fact no trouble to establish by induction.

We wish to establish that for the m-cycle contribution to the trace we have

$$\mathrm{Tr}\{ \sum_{j_1} ... \sum_{j_m} D^{\alpha}(j_2,i_1;G)\, D^{\alpha}(j_3,i_2;G)...D^{\alpha}(j_m,i_{m-1};G)\, D^{\alpha}(j_1,i_m;G)\} = \chi^{\alpha}(G^m) \tag{11}$$

The trace operation requires that we set all $j_k = i_k$ and sum over all i_k, so our aim is to establish that

$$\sum_{i_1} ... \sum_{i_m} D^{\alpha}(i_2,i_1;G)\, D^{\alpha}(i_3,i_2;G)...D^{\alpha}(i_m,i_{m-1};G)\, D^{\alpha}(i_1,i_m;G) = \sum_{i_1} D^{\alpha}(i_1,i_1;\mathrm{G}^m) \equiv \chi^{\alpha}(G^m) \tag{12}$$

Consider now the corresponding expression for the (m+1)-cycle:

$$\mathrm{Tr}\{ \sum_{j_1} ... \sum_{j_{m+1}} D^{\alpha}(j_2,i_1;G)\, D^{\alpha}(j_3,i_2;G)...D^{\alpha}(j_{m+1},i_m;G) \times D^{\alpha}(j_1,i_{m+1};G)\} \tag{13}$$

On taking the trace, we obtain

$$\sum_{i_1} ... \sum_{i_m+1} D^{\alpha}(i_2,i_1;G)\, D^{\alpha}(i_3,i_2;G)...D^{\alpha}(i_{m+1},i_m;G) \times D^{\alpha}(i_1,i_{m+1};G) \tag{14}$$

and if eq 12 holds, this reduces to

$$\sum_{i_1} \sum_{i_m+1} D^{\alpha}(i_{m+1},i_1;G^m)\, D^{\alpha}(i_1,i_{m+1};G) = \sum_{i_{m+1}} D^{\alpha}(i_{m+1},i_{m+1};G^{m+1}) \equiv \chi^{\alpha}(G^{m+1}) \tag{15}$$

Hence, if eq 12 holds for the m-cycle, it holds for the (m+1)-cycle, and since it certainly holds for the case $m = 2$, this is enough to establish it for all values of m.

Thus the trace in eq 6 is given by

$$\chi^{N,S;\alpha}(G) = (N!)^{-1} \sum_q \mu_q \chi_q^{\pi} [\chi^{\alpha}(G)]^{q_1} [\chi^{\alpha}(G^2)]^{q_2} ... [\chi^{\alpha}(G^N)]^{q_N} \tag{16}$$

or more compactly as

$$\chi^{N,S;\alpha}(G) = (N!)^{-1} \sum_q \mu_q \chi_q^{\pi} \prod_i [\chi^{\alpha}(G^i)]^{q_i} \tag{17}$$

where in both cases the sum is again over classes of $\mathscr{S}(N)$ and the q_i specify the cycle structure of each class q. In general, $\chi^{N,S;\alpha}(G)$ will be a reducible representation of $\mathscr{G}$, and its reduction will yield a list of states of well-defined spin and spatial symmetry. The explicit expressions for $\chi^{N,S;\alpha}(G)$ for the cases of two, three, four, and five electrons in a degenerate orbital are given in Table 3, and several examples of the use of these formulas are given in the next section.

Up to this point we have assumed that spin is a good quantum number and have selected a particular spin state initially.

TABLE 3: Explicit Formulas for *N* Equivalent Electrons

$$\begin{aligned}\chi^{2,S=1;\alpha}(G) &= \frac{1}{2}([\chi^{\alpha}(G)]^2 - \chi^{\alpha}(G^2)) \\ &\equiv \chi^{2,jj,\alpha}(G)\end{aligned}$$

$$\chi^{2,S=0;\alpha}(G) = \frac{1}{2}([\chi^{\alpha}(G)]^2 + \chi^{\alpha}(G^2))$$

$$\begin{aligned}\chi^{3,S=3/2;\alpha}(G) &= \frac{1}{6}([\chi^{\alpha}(G)]^3 - 3\chi^{\alpha}(G^2)\chi^{\alpha}(G) + 2\chi^{\alpha}(G^3)) \\ &\equiv \chi^{3,jj;\alpha}(G)\end{aligned}$$

$$\chi^{3,S=1/2;\alpha}(G) = \frac{1}{3}([\chi^{\alpha}(G)]^3 - \chi^{\alpha}(G^3))$$

$$\begin{aligned}\chi^{4,S=2;\alpha}(G) &= \frac{1}{24}([\chi^{\alpha}(G)]^4 + 3[\chi^{\alpha}(G^2)]^2 - 6[\chi^{\alpha}(G)]^2\chi^{\alpha}(G^2) + 8\chi^{\alpha}(G^3)\chi^{\alpha}(G) - 6\chi^{\alpha}(G^4)) \\ &\equiv \chi^{4,jj;\alpha}(G)\end{aligned}$$

$$\chi^{4,S=1;\alpha}(G) = \frac{1}{8}([\chi^{\alpha}(G)]^4 - [\chi^{\alpha}(G^2)]^2 - 2[\chi^{\alpha}(G)]^2\chi^{\alpha}(G^2) + 2\chi^{\alpha}(G^4))$$

$$\chi^{4,S=0;\alpha}(G) = \frac{1}{12}([\chi^{\alpha}(G)]^4 + 3[\chi^{\alpha}(G^2)]^2 - 4\chi^{\alpha}(G^3)\chi^{\alpha}(G))$$

$$\begin{aligned}\chi^{5,S=5/2;\alpha}(G) &= \frac{1}{120}([\chi^{\alpha}(G)]^5 - 10[\chi^{\alpha}(G)]^3\chi^{\alpha}(G^2) + 15[\chi^{\alpha}(G^2)]^2\chi^{\alpha}(G) + 20[\chi^{\alpha}(G)]^2\chi^{\alpha}(G^3) - 20\chi^{\alpha}(G^3)\chi^{\alpha}(G^2) - 30\chi^{\alpha}(G^4)\chi^{\alpha}(G) + 24\chi^{\alpha}(G^5)) \\ &\equiv \chi^{5,jj;\alpha}(G)\end{aligned}$$

$$\chi^{5,S=3/2;\alpha}(G) = \frac{1}{30}([\chi^{\alpha}(G)]^5 - 5[\chi^{\alpha}(G)]^3\chi^{\alpha}(G^2) + 5[\chi^{\alpha}(G)]^2\chi^{\alpha}(G^3) + 5\chi^{\alpha}(G^3)\chi^{\alpha}(G^2) - 6\chi^{\alpha}(G^5))$$

$$\chi^{5,S=1/2;\alpha}(G) = \frac{1}{24}([\chi^{\alpha}(G)]^5 - 2[\chi^{\alpha}(G)]^3\chi^{\alpha}(G^2) + 3[\chi^{\alpha}(G^2)]^2\chi^{\alpha}(G) - 4[\chi^{\alpha}(G)]^2\chi^{\alpha}(G^3) - 4\chi^{\alpha}(G^3)\chi^{\alpha}(G^2) + 6\chi^{\alpha}(G^4)\chi^{\alpha}(G))$$

Permutational symmetry and the symmetry of the degenerate orbital that is partially occupied then lead to a particular (reducible) representation $\chi^{N,S;\alpha}(G)$ of the point group $\mathcal{G}$. If the Hamiltonian contains spin-dependent terms, we can proceed in two ways to classify the resulting states of equivalent electrons under the appropriate double point group. If we have already constructed the list of states for the spin-free case, using the formula above, we have reduced a particular $\chi^{N,S;\alpha}(G)$ or set thereof. Each such state has well-defined spin symmetry S and spatial symmetry (for example) γ. Obviously, we need only reduce the direct product $\chi^{S}(G) \otimes \chi^{\gamma}(G)$ to determine the symmetry of each possible state when the Hamiltonian contains spin-dependent terms. This approach has its shortcomings, however. It is the same procedure used for atomic states of well-defined L and S to determine the possible J values, and this atomic case is most appropriately applied where spin−orbit coupling is weak. Although it gives the same list of final J values as a treatment using explicit *jj*-coupling, it is only via *jj*-coupling that we can identify which J values arise from which occupations of one-electron (spinor) *j*-states. As a concrete example, from Russell−Saunders coupling we know that the atomic occupation p^2 gives rise to J values of 2, 2, 1, 0, and 0 via ^3P, ^1D, and ^1S, but it is only by explicitly considering the occupancies $(3/2, 1/2)^2$ in *jj*-coupling that we can identify these J values with spinor occupations. [We note that in *jj*-coupling we will encounter cases such as $(3/2)^1(1/2)^1$ here, which do not involve equivalent electrons, and this situation of course also arises in the molecular analog.]

An alternative approach for equivalent electrons is then desirable for the molecular analog of *jj*-coupling. We should consider the transformation properties of products of one-particle functions that are labeled by spinor representations of the double group, such as the occupation $f^2_{3/2}$ from the double group I and apply the appropriate projector for a representation of the symmetric group. Since the overall wave function should be antisymmetric and there is no separation of spin and spatial symmetry, the only relevant projector is the antisymmetrizer. This is especially straightforward since all characters are $\varepsilon_P = \pm 1$ according to whether the permutations in a given class are even or odd. A further simplification is the that whereas in the spin-free case our *k*-fold degenerate orbital could hold $2k$ electrons, in the *jj*-coupling case a $k(=2j + 1)$-fold degenerate spinor representation can hold at most *k* electrons. The highest degeneracy we can encounter in molecular double groups is the 6-fold degenerate irrep $I_{5/2}$ in I^*, and thus the most complicated case involves only three electrons (the half-filled shell here). The relevant formulas for the *jj*-coupling case are identified in Table 3 where they are denoted $\chi^{N,jj;\alpha}(G)$.

III. Examples

Weak Spin−Orbit Coupling. If we assume that spin is a good quantum number, acceptable spatial wave functions will transform as a basis for the representation of $\mathcal{S}(N)$ corresponding to the desired spin S, and the spatial symmetry will be given by the usual point group—the double group is not necessary. In molecules we will deal with at most 5-fold degenerate irreps, and we will therefore consider here values of N from 2 to 5. In groups that contain the inversion operation i determining the parity of the electronic states is trivial and it is never necessary to consider such groups explicitly, only the appropriate subgroup, such as I instead of I_h.

The formulas for two electrons in Table 3 are certainly the best-known cases of equivalent electrons and can easily be used with any set of point group tables to show that, e.g., e^2 in C_{3v} yields $^3A_2$, $^1A_1$, and ^1E; e^2 in C_{4v} yields $^3A_2$, $^1A_1$, $^1B_1$, and $^1B_2$; or t_2^2 in T_d yields $^1A_1$, ^1E, $^1T_2$, and $^3T_1$.

TABLE 4: Contributions to $\chi^{N,S,;\alpha}(G)$ for t_1^3 in O

$\{G\}$	E	$3C_2$	$8C_3$	$6C_4$	$6C_2'$
$\{G^2\}$	E	$3E$	$8C_3$	$6C_2'$	$6E$
$\{G^3\}$	E	$3C_2$	$8E$	$6C_4$	$6C_2'$
$\chi^{T_1}(G)$	3	−1	0	1	−1
$[\chi^{T_1}(G)]^3$	27	−1	0	1	−1
$\chi^{T_1}(G^2)$	3	3	0	−1	3
$\chi^{T_1}(G^3)$	3	−1	3	1	−1
$\chi^{3,S=3/2;\alpha}(G)$	1	1	1	1	1
$\chi^{3,S=1/2;\alpha}(G)$	8	0	−1	0	0

TABLE 5: Contributions to $\chi^{N,S;\alpha}(G)$ for λ^2 in $C_{\infty v}$

$\{G\}$	E	C_ϕ	σ_v
$\{G^2\}$	E	$C_{2\phi}$	E
$\chi^\lambda(G)$	2	$2\cos\lambda\phi$	0
$[\chi^\lambda(G)]^2$	4	$4\cos^2\lambda\phi$	0
$\chi^\lambda(G^2)$	2	$2\cos 2\lambda\phi$	2
$\chi^{2,S=1;\alpha}(G)$	1	1	−1
$\chi^{2,S=0;\alpha}(G)$	3	$2\cos 2\lambda\phi + 1$	1

As a more detailed worked example, we consider the three-electron occupation t_{1u}^3 in O_h. The parity is trivial, since three electrons in a u orbital necessarily give u many-electron states. We may therefore work with O to obtain the irrep labels. In Table 4 we list first, after the classes of group elements G, the corresponding classes of G^2 and G^3. We note in passing that if G_i and G_j are in the same class, $G_i = G_aG_jG_a^{-1}$ for some element(s) $G_a \in \mathcal{G}$, and since

$$G_i^p = (G_aG_jG_a^{-1})^p = G_aG_j^pG_a^{-1} \tag{18}$$

so G_i^p and G_j^p are also in the same class (which may of course be different from that of G_i). This obviates the need to have a complete multiplication table for the group, since we can identify the classes of G^2 and G^3 by examining the square and cube of one element of the original class.

In the lower part of Table 4 we list the characters $\chi^{T_1}(G)$ and then both the powers of those characters $[\chi^{T_1}(G)]^3$ and the characters $\chi^{T_1}(G^2)$ and $\chi^{T_1}(G^3)$ that are required to construct the characters $\chi^{3,S=3/2;\alpha}(G)$ and $\chi^{3,S=1/2;\alpha}(G)$. Reduction of these representations, together with the knowledge that the states are all odd parity yields ${}^4A_{1u}$, ${}^2E_u$, ${}^2T_{1u}$, and ${}^2T_{2u}$. Similarly, f^3 in I yields ${}^4F$, ${}^2T_1$, ${}^2T_2$, ${}^2F$, and $2{}^2H$.

For the cases of four electrons we obtain for f^4 in I ${}^5A$, ${}^3T_1$, ${}^3T_2$, ${}^3F$, ${}^3F$, ${}^1A$, ${}^1F$, and $3{}^1H$; while for h^4 we obtain ${}^5H$, $3{}^3T_1$, $3{}^3T_2$, $3{}^3F$, $3{}^3H$, $3{}^1A$, ${}^1T_1$, ${}^1T_2$, $4{}^1F$, and $5{}^1H$.

Finally, h^5 in I yields ${}^6A$, ${}^4T_1$, ${}^4T_2$, $2{}^4F$, $2{}^4H$, $2{}^2A$, $3{}^2T_1$, $3{}^2T_2$, $5{}^2F$, and $7{}^2H$.

Some laborious trigonometry could be used with for example the $N = 5$ formulas to derive the states arising from d^5 in an atom, but as discussed in the Introduction, the case of spherical symmetry is better dealt with using angular momentum coupling techniques. It would be futile therefore to have derived in the previous section the formulas for six or seven electrons, since they would be applicable only to atomic occupations f^6 or f^7 and these are even more advantageously dealt with using such angular momentum coupling techniques. The continuous axial group $C_{\infty v}$ can, however, be treated using Table 3 without requiring too much trigonometry. We list in Table 5 the operations for $C_{\infty v}$ and the characters for an arbitrary degenerate representation with angular momentum projection λ.

The characters for the only case of interest, the occupation λ^2, for both singlets and triplets are also given, where we have used the identity $2\cos^2\lambda\phi - 1 = \cos 2\lambda\phi$. Hence the triplet state is ${}^3\Sigma^-$. The character of the singlet states can be seen by inspection to reduce to ${}^1\Sigma^+$ and ${}^1\Lambda$, where $\Lambda = 2\lambda$. In this way we obtain the familiar ${}^3\Sigma^-$, ${}^1\Sigma^+$, and ${}^1\Delta$ from π^2, for example. Extension to $D_{\infty h}$ is trivial since with two electrons the many-electron state must be a g state.

Strong Spin−Orbit Coupling. When relativistic effects are important the separation of the wave function into space and spin parts becomes inappropriate. Here we are simply interested in obtaining an antisymmetric wave function for various occupancies of degenerate one-electron states.

In the case of two electrons in a doubly degenerate spinor there is of course only one result from applying O^{1^N}. For all axial double groups, that is, $C_{\infty v}^*$, $D_{\infty h}^*$, and the subgroups C_n^*, C_{nv}^*, C_{nh}^*, D_n^*, D_{nh}^*, D_{nd}^*, and S_{2n}^*, derived from them by restricting the principal rotation to an integer divisor of 2π, the degenerate spinor representations of the double group are at most two-dimensional, and thus in all cases we obtain only one function by projection with O^{1^N}. This can be thought of as a closed shell, with two electrons having opposite "m_j" values, and thus transforms as a basis function for the totally symmetric irrep of the molecular double group.[12]

For these groups the product of a degenerate irrep for a spatial orbital with a spinor irrep gives a reducible representation, for example, in C_{3v} we have $E \otimes E_{1/2} = E_{1/2} \oplus E_{3/2}$, so that the *jj*-coupling case of two electrons allocated to an e orbital becomes $(e_{1/2}, e_{3/2})^2$. This corresponds to three possible spinor occupations: $e_{1/2}^2$, $e_{3/2}^2$, and $e_{1/2}^1e_{3/2}^1$. The first two are "closed shells" and thus A_1, while the last is of symmetry type $E_{1/2} \otimes E_{3/2} = 2E$. The overall result of $2A_1 + 2E$ could have been obtained by explicitly multiplying the spin-free result of e^2, ${}^3A_2$, ${}^1A_1$, and ${}^1E$, by the spin functions, giving respectively $A_1 + E$, A_1, and E. This approach provides a correlation between the strong spin−orbit or relativistic limit and the weak spin−orbit limit, but it does not yield any information about which spinor occupations give rise to which electronic states.

We now consider cases where spinor irreps are of dimension greater than two. For molecules the only cases that occur are of dimension four and six, for the cubic and icosahedral groups, and up through half-filled shells this implies consideration of $N = 2$ and $N = 3$. We will see that cases in which the *spatial* occupation involves four and five equivalent electrons reduce to $N = 2$ and $N = 3$ equivalent electrons under *jj*-coupling. As examples we consider states derived from the spatial occupations t_1^3 in T_d^* and h^5 in I^*.

For t_1^3 in T_d^* the six possible spinors form a basis for the reducible representation $e_{1/2} \oplus f_{3/2}$. The possible occupations are then $e_{1/2}^2f_{3/2}^1$, $e_{1/2}^1f_{3/2}^2$, and $f_{3/2}^3$. The only case that involves equivalent electrons here is the second, since the first and third are $F_{3/2}$ states. $f_{3/2}^2$ yields $A_1 + E + T_2$, and thus $e_{1/2}^1f_{3/2}^2$ yields $E_{1/2} + 2F_{3/2} + E_{5/2}$. In toto, t_1^3 in *jj*-coupling therefore gives an $E_{1/2}$ state, an $E_{5/2}$ state, and $4F_{3/2}$ states, as confirmed by multiplying the spin irreps into the spatial irreps given in the previous subsection for the weak coupling case.

For h^5 in I^*, which is arguably the most elaborate molecular possibility, the ten possible spinors form a basis for the reducible representation $F_{3/2} \oplus I_{5/2}$. This gives five occupations, which we consider separately:

$f_{3/2}^4 i_{5/2}^1$ $I_{5/2}$
$f_{3/2}^3 i_{5/2}^2$ $F_{3/2} \otimes (A + F + 2H) = 2E_{1/2} + 2E_{7/2} + 4F_{3/2} + 6I_{5/2}$
$f_{3/2}^2 i_{5/2}^3$ $(A + H) \otimes (2F_{3/2} + 2I_{5/2}) = 4E_{1/2} + 4E_{7/2} + 8F_{3/2} + 12I_{5/2}$
$f_{3/2}^1 i_{5/2}^4$ $F_{3/2} \otimes (A + F + 2H) = 2E_{1/2} + 2E_{7/2} + 4F_{3/2} + 6I_{5/2}$
$f_{3/2}^0 i_{5/2}^5$ $I_{5/2}$

and which yield a grand total of 8 $E_{1/2}$ states, 8 $E_{7/2}$ states, 16 $F_{3/2}$ states, and 26 $I_{5/2}$ states, in agreement with the result of multiplying out the spin and spatial irreps in the weak coupling case.

IV. Conclusions

We have derived a complete set of formulas for molecular electronic states arising from equivalent electrons in a degenerate orbital, and given several illustrative examples of their use for both weak and strong spin−orbit coupling cases. Although the formulas are derived using symmetric group methods, the final formulas are quite independent of the method used to obtain spin eigenfunctions: if the actual configurational wave functions are desired, then any method of spin coupling and symmetry projection can be used to obtain them.

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