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Dual-Space-Operator Technique to Build Symmetry-Adapted Wave Functions. I. Molecules with Abelian Symmetry Group

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A general method is described of building up open-shell multideterminant wave functions which are eigenfunctions of the spin operators S^2 and S_z. In the present case, that of a molecule with an Abelian symmetry group, the wave functions obtained are easily adapted for spatial symmetry. The matrix elements of the Hamiltonian are derived. The method gives a building up of the matrix elements of the irreducible representation $[n_1, n_2]$ symmetric groups which, as far as the author knows, is original. While many of the specific results are not new, the author believes that the presentation which he used is both new and interesting. This method will be extended later to more general cases.

INTRODUCTION

There exist many ways to build up symmetry-adapted molecular or atomic wave functions and also many types of symmetry within the framework of the Pauli principle. The simplest case is the one we are dealing with, i.e., the eigenfunctions of S^2 with an Abelian spatial symmetry group. Increasingly complex are the antisymmetrized eigenfunctions of J^2 (j-j coupling), L^2, S^2 (L-S coupling), and S^2 with a non-Abelian spatial symmetry group.

The existing methods used in the problem of symmetry-adapted wave functions of S^2 are of two types: (i) those using the symmetric groups and constructing the eigenfunctions in a manner specific to S^2, and (ii) those dealing with the S^2 problem as an example of a general procedure for obtaining covariant eigenfunctions. The method of Van Vleck, Serber, and Yamanouchi[1-3] is of type (i). These authors were the first to use matrix representations of the permutation groups to construct the wave functions corresponding to different multiplicities. Goddard[4] used a similar procedure to derive eigenfunctions of S^2 which satisfy the Pauli principle. This author applied his method to a great number of problems: atoms, molecules, and solids. Of type (i) also is the use of Young's operator by Matsen.[5] This, however, is limited to a small number of electrons. From the group-theory point of view, McIntosh[6] discussed the symmetry-adapted functions belonging to the symmetric groups. The foregoing constructions deal specifically with the invariant S^2. The Löwdin[7] method, of type (ii), uses projection operators acting on Slater determinants to select the desired multiplicity; the Löwdin projection-operator method can be used for dynamic operators other than spin. It seems that the process is quite tedious; yet many useful applications have been given. Lefebvre and Prat[8] used a rotational projection operator, whereas Pratt[9] derived eigenfunctions of S^2 using a spin-operator method. Löwdin's method was studied also by Rotenberg[10] and Shapiro.[11] Another approach was given by Percus and Rotenberg[12] and by Harris and Pauncz.[13]

The method we present here is essentially algebraic and is closely related to annihilation and creation operators.[14] In the case of S^2, it also immediately gives the orthogonal standard representation of the permutation group, and is then connected with Yamanouchi symbols. The use of a dual space to construct spin eigenfunctions by means of spinor invariants is originally due to Kramers.[15,16] This method has been applied by a few other authors: Wolfe,[17] Brinkman,[18] and Bijl.[19] Orthogonal S^2 eigenfunctions with only integer coefficients have been given by the author[20] using D and A, Kramer's operators, and a very simple process.

I. BUILDING UP EIGENFUNCTIONS OF S^2

Generalities. Consider a system of electrons, the wave function of which is expanded in a set of spin orbitals $\psi^{\xi\sigma}(i)$, where i designates the number of an electron, ξ the set of quantum numbers of the spatial part, and $\sigma = \pm\frac{1}{2}$ the spin state:

$$\psi^{\xi\sigma}(i) = \varphi^{\xi}(i)\chi^{\sigma}(i) \quad . \tag{1}$$

Then considering the $SU(2)$ group, we construct a vectorial space E on the complex field $\mathbf{C}$ of representations for this group, such as to be a direct sum of irreducible vectorial subspaces $E^{[S]}$ (one for each S, with $S = 0, \frac{1}{2}, 1, \ldots,$ corresponding then to the spin)[21]:

$$E = \bigotimes_S E^{[S]} \quad . \tag{2}$$

We then choose a basis set in each $E^{[S]}$,

$$|z_M^S), \; M = -S, \; -S+1, \ldots, S \quad , \tag{3}$$

so that the spin states of an electron i are the components of a vector belonging to $E^{[1/2]}$:

$$^{[1/2]}\Theta(i)=\chi^{\sigma}(i)\,|z_{\sigma}^{1/2}) \tag{4}$$

[with the Einstein summation convention on the index $\sigma=\pm\frac{1}{2}$; (this convention will always be implicit in the following)]. In the same way, the spin states of an n-electron system for the values S and M are the components of a vector of $E^{[S]}$:

$$^{[S]}\Theta(1,2,\ldots,n)=\chi_S^M(1,\ldots,n)\,|z_M^S)\,. \tag{5}$$

It is useful to consider $E^{[S]}$ as a dual of the space with spin state S. $^{[S]}\Theta$ is then a duality bracket, that is, an invariant bilinear form (spinor invariants of Kramers). The χ_S^M are covariant irreducible tensors with respect to the $SU(2)_{\rm st}$ transformations of states; the $|z_M^S)$, contravariant irreducible tensors. $^{[S]}\Theta$ is invariant with respect to the $SU(2)_{\rm st}\otimes SU(2)$ set of all the diagonal pairs $[(g,g)\in SU(2)_{\rm st}\times SU(2)]$.

Introduction of operators in E. We now introduce the irreducible tensorial operators $[\hat{\Sigma}]^{\dagger}$ with respect to $E^{[1/2]}$, the components of which, for the basis $|z_\sigma^{1/2})$, are[22]

$$\mathbf{S}_{\sigma}^{\Sigma\dagger},\quad \mathbf{S}_{\sigma}^{\Sigma\dagger},\quad \sigma=\pm\tfrac{1}{2}. \tag{6}$$

They act in E and are such that for a vector $|z_M^S)\in E^{[S]}$, we have by definition

$$\mathbf{S}_{\sigma}^{\Sigma\dagger}|z_M^S)=[S]^{1/2}\begin{pmatrix}\frac{1}{2} & S & M+\sigma\\ \sigma & M & S+\Sigma\end{pmatrix}|z_{M+\sigma}^{S+\Sigma})\,, \tag{7}$$

where $\begin{pmatrix}j_1 & j_2 & m_3\\ m_1 & m_2 & j_3\end{pmatrix}$

is a Clebsch-Gordan coefficient in a covariant form, and $[S]=2S+1$ is the dimension of the space $E^{[S]}$.

There exist two $[\hat{\Sigma}]^{\dagger}$ operators which effect the decomposition

$$\begin{aligned} &E^{[1/2]}\otimes E^{[S]}\to E^{[S+1/2]}\,,\quad \Sigma=+\tfrac{1}{2}\,,\\ &E^{[1/2]}\otimes E^{[S]}\to E^{[S-1/2]}\,,\quad \Sigma=-\tfrac{1}{2}\,. \end{aligned} \tag{8}$$

Explicitly (7) gives

$$\begin{aligned} &\mathbf{S}_{1/2}^{1/2\dagger}|z_M^S)=(S+M+1)^{1/2}\,|z_{M+1/2}^{S+1/2})\,,\\ &\mathbf{S}_{-1/2}^{1/2\dagger}|z_M^S)=(S-M+1)^{1/2}\,|z_{M-1/2}^{S+1/2}),\\ &\mathbf{S}_{1/2}^{-1/2}\,|z_M^S)=(S-M)^{1/2}\,|z_{M+1/2}^{S-1/2}),\\ &\mathbf{S}_{-1/2}^{-1/2\dagger}|z_M^S)=-(S+M)^{1/2}\,|z_{M-1/2}^{S-1/2})\,. \end{aligned} \tag{9}$$

Realization (Ref. 21) of the $\mathbf{S}_{\sigma}^{\Sigma\dagger}$ operators in the polynomial space of two complex variables $z_\sigma(\sigma=\pm\frac{1}{2})$. We denote $z_+=z_{1/2}$; $z_-=z_{-1/2}$ and take for basis vectors in a space $E^{[S]}$ of homogeneous polynomials with degree $2S$:

$$|z_M^S)=\frac{z_+^{S+M}z_-^{S-M}}{[(S+M)!(S-M)!]^{1/2}}=\frac{z_+^{S+M}z_-^{S-M}}{N_{SM}}\,. \tag{10}$$

The $\mathbf{S}_{\sigma}^{\Sigma\dagger}$ operators have the realizations

$$\mathbf{S}_{1/2}^{1/2\dagger}=z_+;\quad \mathbf{S}_{-1/2}^{1/2\dagger}=z_-;$$

$$\mathbf{S}_{1/2}^{-1/2\dagger}=\frac{\partial}{\partial z_-}\,;\ \mathbf{S}_{-1/2}^{-1/2\dagger}=-\frac{\partial}{\partial z_+}\,. \tag{11}$$

Application to the building up of the spin functions. We use a step-by-step method in which every spin function χ_S^M obtained for a given n-electron system and a given S and M corresponds to a path γ on the branching diagram, or equivalently, to a Yamanouchi symbol.[1,20] Hence the mapping $\Theta\leftrightarrow\gamma$ is one to one.

Suppose we have built up eigenfunctions in the case of a $(n-1)$-electron system,

$$^{[\bar S]}\Theta_{\bar\gamma}(1,\ldots,n-1)\equiv\chi_{\bar\gamma\bar S}^{\bar M}(1,\ldots,n-1)\,|z_{\bar M}^{\bar S})\,, \tag{12}$$

where $\bar S$ is the spin quantum number and $\bar\gamma$ distinguishes any eigenvectors degenerated with respect to $\bar S$. [A bar is used in the $(n-1)$-electron systems; no bar in the n-electron systems.] If $\chi^{\sigma_n}(n)$ is the spin state of the nth electron, to which is associated the vector

$$^{[1/2]}\Theta(n)=\chi^{\sigma_n}(n)\,|z_{\sigma_n}^{1/2})\in E^{[1/2]}\,,$$

then the operator $[\Sigma_n]^{\dagger}$ corresponding to the foregoing vector is

$$\chi^{\sigma_n}(n)\,\mathbf{S}_{\sigma_n}^{\Sigma_n\dagger}\,. \tag{13}$$

These operators are precisely equivalent to the Kramers's D_n and A_n operators[16]

$$A_n\leftrightarrow\chi^{\sigma_n}(n)\,\mathbf{S}_{\sigma_n}^{1/2\dagger}\,,\qquad D_n\leftrightarrow\chi^{\sigma_n}(n)\,\mathbf{S}_{\sigma_n}^{-1/2\dagger}\,. \tag{14}$$

We will use the more concise notation

$$\chi^{\sigma_n}(n)\,\mathbf{S}_{\sigma_n}^{\Sigma_n\dagger}=\mathbf{S}_{\chi n}^{\Sigma_n\dagger}\,.$$

Applying these operators to $^{[S]}\Theta_{\bar\gamma}(1,\ldots,n-1)$, we obtain

$$\begin{aligned} &\mathbf{S}_{\chi n}^{\Sigma_n\dagger}\,{}^{[\bar S]}\Theta_{\bar\gamma}(1,\ldots,n-1)\\ &\quad=\chi^{\sigma_n}(n)\chi_{\bar\gamma\bar S}^{\bar M}(1,\ldots,n-1)\;\mathbf{S}_{\sigma_n}^{\Sigma_n\dagger}|z_{\bar M}^{\bar S})\\ &\quad=\chi^{\sigma_n}(n)\chi_{\bar\gamma\bar S}^{\bar M}(1,\ldots,n-1)\\ &\qquad\times[\bar S]^{1/2}\begin{pmatrix}\frac{1}{2} & \bar S & M+\sigma\\ \sigma_n & \bar M & \bar S+\Sigma_n\end{pmatrix}|z_{\bar M+\sigma_n}^{\bar S+\Sigma_n})\,, \end{aligned}$$

that is to say,

$$\mathbf{S}_{\chi(n)}^{\Sigma_n\dagger}\,{}^{[\bar S]}\Theta_{\bar\gamma}(1,\ldots,n-1)={}^{[S]}\Theta_{\gamma}(1,\ldots,n)\,, \tag{15}$$

$$\text{with}\quad S=\bar S+\Sigma_n,\quad \gamma=(\Sigma_n,\bar\gamma)\,, \tag{16}$$

$$\text{and}\quad \chi_{\gamma S}^M(1,\ldots,n)=[\bar S]^{1/2}\chi^{\sigma_n}(n)\chi_{\bar\gamma\bar S}^{\bar M}(1,\ldots,n-1)$$

$$\times \left(\begin{matrix} \frac{1}{2} & \bar{S} \\ \sigma_n & \bar{M} \end{matrix}\middle| \begin{matrix} M \\ S \end{matrix}\right). \tag{17}$$

It is now easy to build up the spin functions, starting from individual spin states:

$$\begin{aligned} {}^{[S]}\Theta_\gamma(1, \ldots, n) &= \mathbf{S}^{\Sigma_n\dagger}_{\chi(n)} \mathbf{S}^{\Sigma_{n-1}\dagger}_{\chi(n-1)} \cdots \mathbf{S}^{\Sigma_1\dagger}_{\chi(1)} |z^0) \\ &= \chi^{\sigma_n}(n)\chi^{\sigma_{n-1}}(n-)\cdots\chi^{\sigma_1}(1) \\ &\quad \times \mathbf{S}^{\Sigma_n\dagger}_{\sigma_n}\mathbf{S}^{\Sigma_{n-1}\dagger}_{\sigma_{n-1}}\cdots \mathbf{S}^{\Sigma_1\dagger}_{\sigma_1}|z^0) , \end{aligned} \tag{18}$$

where $|z^0)$ is the vector generating $E^{[0]}$.

The index γ which distinguishes the Θ with identical S can be identified with the ordered set $\Sigma_n\Sigma_{n-1}\cdots\Sigma_1$, that is to say, with a path γ on the branching diagram. S is simply given by

$$S = \Sigma_1 + \Sigma_2 + \cdots + \Sigma_n \ . \tag{19}$$

(The branching diagram for $S=1$; $n=4$ is shown in Fig. 1.) The paths are

Adjoint operator of $\mathbf{S}^{\Sigma\dagger}_\sigma$. An inner Hermitian product is defined in E, such that

$$(z^{S'}_{M'}|z^S_M) = \delta^{SS'}\delta_{MM'} \ . \tag{20}$$

We show in Appendix A that the adjoint of $\mathbf{S}^{\Sigma\dagger}_\sigma$ is then

$$(\mathbf{S}^{\Sigma\dagger}_\sigma)^\dagger = \mathbf{S}^{\Sigma}_\sigma = (-1)^{\Sigma+\sigma}\mathbf{S}^{-\Sigma\dagger}_{-\sigma} \ . \tag{21}$$

Commutation relations $[\mathbf{S}^{\Sigma_1\dagger}_{\sigma_1}, \mathbf{S}^{\Sigma_2\dagger}_{\sigma_2}]$. These are trivial if one used the realizations (11):

$$[\mathbf{S}^{\Sigma_1\dagger}_{\sigma_1}, \mathbf{S}^{\Sigma_2\dagger}_{\sigma_2}] = \delta^{\Sigma_1+\Sigma_2,0}\epsilon_{\sigma_1\sigma_2} , \tag{22}$$

where $$\epsilon_{\sigma_1\sigma_2} = (-1)^{1/2-\sigma_1}\delta_{\sigma_1+\sigma_2,0} \ . \tag{23}$$

II. BUILDING UP OF DETERMINANTAL COMBINATION EIGENFUNCTIONS OF S^2

One first forms spin-orbital combinations, eigenfunctions of S^2, using the preceding prescriptions:

$$\psi^{\xi_n\sigma_n}(n)\cdots\psi^{\xi_1\sigma_1}(1)\mathbf{S}^{\Sigma_n\dagger}_{\sigma_n}\cdots\mathbf{S}^{\Sigma_1\dagger}_{\sigma_1}|z^0); \tag{24}$$

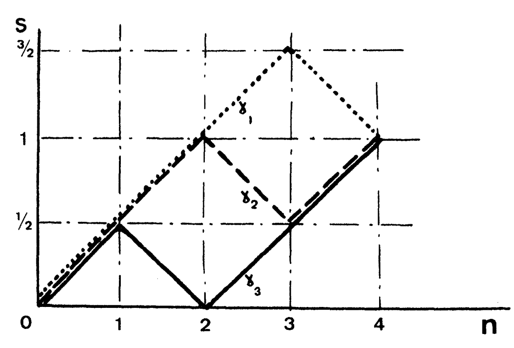

FIG. 1. Branching diagram for $S=1$ and $n=4$.

then, when antisymmetrized, the functions remain eigenfunctions of S^2 (S^2 commutes with the antisymmetrization operator):

$$\begin{aligned} {}^{[S]}\Psi_\gamma &= \psi^M_{\gamma S}\,|z^S_M) \\ &= C_\gamma\,\mathcal{A}\,(\psi^{\xi_n\sigma_n}\cdots\psi^{\xi_1\sigma_1})\mathbf{S}^{\Sigma_n\dagger}_{\sigma_n}\cdots\mathbf{S}^{\Sigma_1\dagger}_{\sigma_1}|z^0) \ . \end{aligned} \tag{25}$$

C_γ is a normalization constant, and $\mathcal{A} = (n!)^{-1}\sum_p \times(-1)^p p$, being the idempotent antisymmetrization operator (p is a permutation of the number of electrons).

III. RELATIONS BETWEEN THE DIFFERENT SCALAR PRODUCTS - REDUCED MATRIX ELEMENTS

The Hilbert space of the physical states is denoted by $\mathcal{E}$, and the scalar product in $\mathcal{E}$ is written $\langle\,|\,\rangle$. We consider the invariants ($A^{M_1}_{S_1}$ and $B^{M_2}_{S_2} \in \mathcal{E}$).

$${}^{[S_1]}A = A^{M_1}_{S_1}\,|z^{S_1}_{M_1}), \quad {}^{[S_2]}B = B^{M_2}_{S_2}|z^{S_2}_{M_2}) \tag{26}$$

and the scalar product

$$\langle A^{M_1}_{S_1}|O^M_S|B^{M_2}_{S_2}\rangle \ ,$$

where O_S is a tensorial irreducible operator acting in $\mathcal{E}$. The Wigner-Eckart theorem can be written[23]:

$$\langle A^{M_1}_{S_1}|O^M_S|B^{M_2}_{S_2}\rangle = \begin{pmatrix} S_1 & M & M_2 \\ M_1 & S & S_2 \end{pmatrix} \langle A_{S_1}\|O_S\|B_{S_2}\rangle \ . \tag{27}$$

Considering then the unit operator w^S (with components w^S_M) such that $(z^{S_1}\|w^S\|z^{S_2}) = 1$ and using the Wigner-Eckart theorem in the space E:

$$\begin{aligned} (z^{S_1}_{M_1}|w^S_M|z^{S_2}_{M_2}) &= (-)^{2S_1}\begin{pmatrix} M_1 & S & S_2 \\ S_1 & M & M_2 \end{pmatrix} (z^{S_1}\|w^S\|z^{S_2}) \\ &= (-)^{2S_1}\begin{pmatrix} M_1 & S & S_2 \\ S_1 & M & M_2 \end{pmatrix} \equiv \begin{pmatrix} S_1 & M & M_2 \\ M_1 & S & S_2 \end{pmatrix} \ . \end{aligned} \tag{28}$$

The reduced matrix element in (27) is connected with the two scalar products above by the relation (where summation goes over M, M_1, and M_2)

$$\begin{aligned} &\langle A^{M_1}_{S_1}|O^M_S|A^{M_2}_{S_2}\rangle\,(z^S_{M_1}|w^S_M|z^{S_2}_{M_2}) \\ &= (-)^{2S_1}\begin{pmatrix} S_1 & M & M_2 \\ M_1 & S & S_2 \end{pmatrix}\begin{pmatrix} M_1 & S & S_2 \\ S_1 & M & M_2 \end{pmatrix} \\ &\quad \times\langle A_{S_1}\|O_S\|A_{S_2}\rangle = \langle A_{S_1}\|O_S\|A_{S_2}\rangle \ . \end{aligned} \tag{29}$$

Since the left-hand side depends only on

$${}^{[S_1]}A = A^{M_1}_{S_1}|z^{S_1}_{M_1}), \quad {}^{[S_2]}B = B^{M_2}_{S_2}|z^{S_2}_{M_2}), \quad {}^{[S]}O = O^M_S w^S_M ; \tag{30}$$

we shall use the notation (30) in the reduced matrix elements, and (29) will be written

$$\begin{aligned} &\langle A^{M_1}_{S_1}|O^M_S|B^{M_2}_{S_2}\rangle\,(z^{S_1}_{M_1}|w^S_M|z^{S_2}_{M_2}) \\ &\equiv \langle({}^{[S_1]}A\,|\,{}^{[S]}O\,|\,{}^{[S_2]}B)\rangle = \langle A_{S_1}\|O_S\|B_{S_2}\rangle \ . \end{aligned} \tag{31}$$

Considering the fundamental relation to calculate the matrix elements, we suppose now that the states $A^{M_1}_{S_1}$, $B^{M_2}_{S_2}$ can be put in the form of linear combinations

$$A^{M_1}_{S_1} = a^{\mu} C^{S_1 M_1}_{\mu}, \quad B^{M_2}_{S_2} = b^{\nu} D^{S_2 M_2}_{\nu}, \quad a^{\nu}, b^{\nu} \in \mathcal{E},$$

and that there exists operators $\mathfrak{C}^{S_1}_{\mu}$ and $\mathfrak{D}^{S_2}_{\nu}$ in E such that

$$\mathfrak{C}^{S_1}_{\mu} |z^0) = C^{S_1 M_1}_{\mu} |z^{S_1}_{M_1}), \quad \mathfrak{D}^{S_2}_{\nu} |z^0) = D^{S_2 M_2}_{\nu} |z^{S_2}_{M_2}).$$

It has been proved in Appendix B that the reduced matrix elements take the form

$$\langle\langle {}^{[S_1]}A \,|\, {}^{[S]}O \,|\, {}^{[S_2]}B \rangle\rangle = \langle a^{\mu} | O^M_S | b^{\nu} \rangle \times (z^0 | \mathfrak{C}^{S_1 \dagger}_{\mu} w^S_M \mathfrak{D}^{S_2}_{\nu} | z^0). \tag{32}$$

IV. CALCULUS OF THE MATRIX ELEMENTS

Matrix elements of a polyelectronic symmetrical (Ref. 24) operator. Let O be a scalar polyelectronic symmetric operator acting on space coordinates. Then using (31) we can write

$$\langle \psi'^{M'}_{\gamma' S} | O | \psi^M_{\gamma S} \rangle = \delta^{MM'} \delta_{SS'} [S]^{-1/2} \langle\langle {}^{[S]}\Psi'_{\gamma'} | O | {}^{[S]}\Psi_{\gamma} \rangle\rangle, \tag{33}$$

where $O = O w^0_0 = [S_{\rm op}]^{-1/2} O$,

$${}^{[S]}\Psi'_{\gamma'} = C'_{\gamma'} \mathcal{A}\{\psi^{\xi'_n \sigma'_n} \cdots \psi^{\xi'_1 \sigma'_1}\} \prod_i (\mathbf{S}^{\Sigma'^{\dagger}_i}_{\sigma'_i}),$$

$${}^{[S]}\Psi_{\gamma} = C_{\gamma} \mathcal{A}\{\psi^{\xi_n \sigma_n} \cdots \psi^{\xi_1 \sigma_1}\} \prod_i (\mathbf{S}^{\Sigma_i^{\dagger}}_{\sigma_i}) | z^0).$$

Hence (32) gives

$$\langle\langle {}^{[S]}\Psi'_{\gamma'} | O | {}^{[S]}\Psi_{\gamma} \rangle\rangle = C'^{*}_{\gamma'} C_{\gamma} [S]^{-1/2} \times \langle \mathcal{A}\{\psi^{\xi'_n \sigma'_n} \cdots \psi^{\xi'_1 \sigma'_1}\} | O | \mathcal{A} \times \{\psi^{\xi_n \sigma_n} \cdots \psi^{\xi_1 \sigma_1}\} \rangle \times (z^0 | \mathbf{S}^{\Sigma'_1}_{\sigma'_1} \cdots \mathbf{S}^{\Sigma'_n}_{\sigma'_n} \mathbf{S}^{\Sigma_n^{\dagger}}_{\sigma_n} \cdots \mathbf{S}^{\Sigma_1^{\dagger}}_{\sigma_1} | z^0. \tag{34}$$

O is symmetric and does not act on spin space, so we obtain

$$\langle \mathcal{A}\{\psi^{\xi'_n \sigma'_n} \cdots \psi^{\xi'_1 \sigma'_1}\} | O | \mathcal{A}\{\psi^{\xi_n \sigma_n} \cdots \psi^{\xi_1 \sigma_1}\} \rangle$$
$$= \langle \psi^{\xi'_n \sigma'_n} \cdots \psi^{\xi'_1 \sigma_1} | O | \mathcal{A}\{\psi^{\xi_n \sigma_n} \cdots \psi^{\xi_1 \sigma_1}\} \rangle$$
$$= (n!)^{-1} \sum_p (-1)^p \langle \xi'_n \cdots \xi'_1 | O | p\,\xi_n \cdots p\,\xi_1 \rangle \times \prod_i \delta_{\sigma'_i, p\sigma_i}$$

after integration over spin. The last bracket is a concise form for

$$\langle \varphi^{\xi'_n} \cdots \varphi^{\xi'_1} | O | p \langle \varphi^{\xi_n} \cdots \varphi^{\xi_1} \rangle \rangle.$$

Now (34) becomes

$$\langle\langle {}^{[S]}\Psi'_{\gamma'} | O | {}^{[S]}\Psi_{\gamma} \rangle\rangle = [S]^{-1/2} (n!)^{-1} C'^{*}_{\gamma'} C_{\gamma} \times \sum_p (-1)^p \langle \xi'_n \cdots \xi'_1 | O | p\xi_n \cdots p\xi_1 \rangle \times \sum_{(\sigma)} (z^0 | \mathbf{S}^{\Sigma'_1}_{p\sigma_1} \cdots \mathbf{S}^{\Sigma'_n}_{p\sigma_n} \mathbf{S}^{\Sigma_n^{\dagger}}_{\sigma_n} \cdots \mathbf{S}^{\Sigma_1^{\dagger}}_{\sigma_1} | z^0)$$

It is demonstrated in Appendix D that

$$D^{S,n}_{\gamma'\gamma}(p) = (d_{\gamma'}(n) d_{\gamma}(n))^{-1/2} \sum_{(\sigma)} (z^0 | \mathbf{S}^{\Sigma'_1}_{p\sigma_1} \cdots \mathbf{S}^{\Sigma'_n}_{p\sigma_n} \times \mathbf{S}^{\Sigma_n^{\dagger}}_{\sigma_n} \cdots \mathbf{S}^{\Sigma_1^{\dagger}}_{\sigma_1} | z^0) \tag{35}$$

is a matrix element of the permutation p in the irreducible representation of $S(n)$ associated with the spin S. This representation is the standard one – i.e., orthogonal and with $\gamma = (\Sigma_n \cdots \Sigma_1)$, $\gamma' = (\Sigma'_n \cdots \Sigma'_1)$, in a one-to-one correspondence with the Yamanouchi symbols. $d_{\gamma}(n)$ are products of dimensions along a path γ, on the branching diagram:

$$d_{\gamma}(n) = [\Sigma_1] \times [\Sigma_1 + \Sigma_2] \times \cdots \times [\Sigma_1 + \Sigma_2 + \cdots + \Sigma_n]. \tag{36}$$

Equation (34) finally becomes

$$\langle\langle {}^{[S]}\Psi'_{\gamma'} | O | {}^{[S]}\Psi_{\gamma} \rangle\rangle = C'^{*}_{\gamma'} C_{\gamma} (d_{\gamma'}(n) d_{\gamma}(n))^{1/2} [S]^{-1/2} (n!)^{-1} \times \sum_p (-1)^p D^S_{\gamma'\gamma}(p) \langle \xi'_n \cdots \xi'_1 | O | p\xi_n \cdots p\xi_1 \rangle. \tag{37}$$

This particular result can be easily connected with the Yamanouchi-Kotani[1,3] and Goddard[4] methods. Our $\sum_p (-1)^p D^S_{\gamma'\gamma}(p) p$ is a Wigner projection operator of the same kind as the one which Yamanouchi and Kotani denote by $\sum_p \overline{U}^p_{km}(p)\, p$ and Goddard as $\sum_\tau U^{\mu}_{sr} \tau$.

Normalization of ${}^{[S]}\Psi_{\gamma}$ built up on an orthonormalized set of orbitals φ^{ξ_i}. Equation (37) can be written when all φ^{ξ_i} are singly occupied:

$$\langle\langle {}^{[S]}\Psi_{\gamma'} | {}^{[S]}\Psi_{\gamma} \rangle\rangle = \delta_{\gamma\gamma'} |C_{\gamma}|^2 d_{\gamma}(n)/n! [S]^{1/2} = \delta_{\gamma\gamma'} [S]^{1/2}.$$

Then we obtain

$$C_{\gamma} = (n! [S]/d_{\gamma}(n))^{1/2}. \tag{38}$$

In the case of c *doubly occupied orbitals*, the normalization constant is

$$C_{\gamma} N_c \text{ with } N_c = 2^{-c/2}. \tag{39}$$

(37) becomes

$$\langle\langle {}^{[S]}\Psi'_{\gamma'} | O | {}^{[S]}\Psi_{\gamma} \rangle\rangle = N_{c'} N_c \sum_p (-1)^p D^S_{\gamma'\gamma}(p) \times \langle \xi'_n \cdots | O | p\xi_n \cdots \rangle. \tag{40}$$

Creation and annihilation formalism. Using the creation and annihilation formalism, let $a^{\xi\sigma\dagger}$ create the state $\varphi^{\xi\sigma}$, and $a^{\xi\sigma}$ annihilate the same state; then a normalized n-electron determinantal product state is

$$a^{\xi_n\sigma_n\dagger}\cdots a^{\xi_1\sigma_1\dagger}\,|O\rangle=(n!)^{1/2}\,\mathcal{A}\{\varphi^{\xi_n\sigma_n}\cdots\varphi^{\xi_1\sigma_1}\}\ .$$

Then we may define creation and annihilation operators which act simultaneously in the two dual spaces like

$$\mathfrak{A}^{\xi\Sigma\dagger}=a^{\xi\sigma\dagger}\ \mathbf{S}_\sigma^{\Sigma\dagger}\quad\text{and its adjoint}\quad\mathfrak{A}^{\xi\Sigma}=a^{\xi\sigma}\,\mathbf{S}_\sigma^{\Sigma}$$

$$\mathfrak{A}^{\xi\Sigma}=(-1)^{\Sigma+\sigma}a^{\xi\sigma}\,\mathbf{S}_{-\sigma}^{-\Sigma\dagger}=(-1)^{1/2+\Sigma}\tilde{a}^{\xi\rho}\,\mathbf{S}_{\rho}^{-\Sigma\dagger}\tag{41}$$

where $\tilde{a}^{\xi\rho}$ is the tensorial operator[25] associated with $a^{\xi\sigma}$. This formalism will be developed in Paper II.

CONCLUSION

We have given a method for building up determinantal combinations, eigenfunctions of S^2 in the problem of n-electron Abelian molecules. Every combination obtained is directly associated with a path on the branching diagram. The wave functions, which are mutually orthogonal, are constructed by step-by-step application of irreducible tensorial operators $[\hat{\Sigma}]^\dagger$ acting in a dual space of the quantum state space. Being of a tensorial character, the process can be used to calculate the matrix elements of irreducible tensorial dynamic operators. We have given the matrix elements only for a symmetric scalar operator between two eigenstates. In this case, the matrix elements of irreducible standard representations of the permutation groups appear, and the commutation rules and contractions of the $[\hat{\Sigma}]^\dagger$ operators simplify their calculation. Moreover, the $[\hat{\Sigma}]^\dagger$ are closely connected with creation and annihilation techniques.

This formalism, using dual space operators, can be generalized to $(j\text{-}j)$ coupling and j^2 symmetry-adapted combinations of determinants. Graphs and mathematical apparatus of the theory of angular momentum [26] are then very useful. We hope this will be the object of a next paper.

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APPENDIX A: ADJOINT OPERATOR OF $\mathbf{S}_\sigma^{\Sigma\dagger}$

Using $(A^\dagger z_{M'}^{S'}|z_M^S)=(z_{M'}^{S'}|Az_M^S)$ for any S, S', M, M' to define the adjoint, we compare the scalar products

$$(z_{M'}^{S'}|\mathbf{S}_\sigma^{\Sigma\dagger}z_M^S)=[S]^{1/2}\begin{pmatrix}\frac12 & S & M'\\ \sigma & M & S'\end{pmatrix}\delta^{S'-S,\,\Sigma}\,\delta_{M'-M,\,\sigma},$$

$$(\mathbf{S}_{-\sigma}^{-\Sigma\dagger}z_{M'}^{S'}|z_M^S)=[S']^{1/2}\begin{pmatrix}-\sigma & M' & S\\ \frac12 & S' & M\end{pmatrix}\delta^{S'-S,\,\Sigma}\,\delta_{M'-M,\,\sigma},$$

$$(-1)^{\Sigma+\sigma}(\mathbf{S}_{-\sigma}^{-\Sigma\dagger}\ z_{M'}^{S'}|z_M^S)=(z_{M'}^{S'}|\mathbf{S}_\sigma^{\Sigma\dagger}z_M^S)$$

for any S, S', M, M'. Furthermore,

$$\mathbf{S}_\sigma^{\Sigma}=(-1)^{\Sigma+\sigma}\ \mathbf{S}_{-\sigma}^{-\Sigma\dagger}\qquad .$$

APPENDIX B: DEMONSTRATION OF EQ. (32)

If $\quad {}^{[S_1]}A=A_{S_1}^{M_1}\,|z_{M_1}^{S_1})\equiv a^\mu\,\mathfrak{C}_\mu^{S_1}|z^0)$

and $\quad {}^{[S_2]}B=B_{S_2}^{M_2}\,|z_{M_2}^{S_2})\equiv b^\nu\,\mathfrak{D}_\nu^{S_2}|z^0)$,

then the reduced matrix elements can be written, using (29):

$$\langle\!\langle({}^{[S_1]}A\,|\,{}^{[S]}O\,|\,{}^{[S_2]}B)\!\rangle$$

$$=\langle A_{M_1}^{S_1}|O_S^M|B_{S_2}^{M_2}\rangle\,(z_{M_1}^{S_1}|w_M^S|z_{M_2}^{S_2})$$

$$=\langle a^\mu|O_S^M|b^\nu\rangle\sum_{M_1M_2}(z^0|\mathfrak{C}_\mu^{S_1\dagger}|z_{M_1}^{S_1})$$

$$\times(z_{M_1}^{S_1}|w_M^S|z_{M_2}^{S_2})\,(z_{M_2}^{S_2}|\mathfrak{D}_\nu^{S_2}|z^0)\quad .$$

Furthermore, we have

$$\sum_{M_2}|z_{M_2}^{S_2})(z_{M_2}^{S_2}|\mathfrak{D}_\nu^{S_2}|z^0)$$

$$=\sum_{S_2'M_2'}|z_{M_2}^{S_2'})(z_{M_2'}^{S_2'}|\mathfrak{D}_\nu^{S_2}|z^0)=\mathfrak{D}_\nu^{S_2}|z^0),$$

because $\sum_{S_2'M_2'}|z_{M_2'}^{S_2'})(z_{M_2'}^{S_2'}|=1$. The same relation can be proved for S_1, and (32) is demonstrated.

APPENDIX C: DEMONSTRATION OF $\sum_\sigma\mathbf{S}_\sigma^{\Sigma'}\mathbf{S}_\sigma^{\Sigma\dagger}=\delta^{\Sigma\Sigma'}[\Sigma+S_{op}]$

Applying to an arbitrary $|z_M^S)$:

$$\textstyle\sum_\sigma\mathbf{S}_\sigma^{\Sigma'}\mathbf{S}_\sigma^{\Sigma\dagger}=|z_M^S)=\sum_\sigma(-1)^{\Sigma'+\sigma}\mathbf{S}_{-\sigma}^{-\Sigma'\dagger}\mathbf{S}_\sigma^{\Sigma\dagger}|z_M^S)$$

$$=[S]^{1/2}[S+\Sigma-\Sigma']^{1/2}\begin{pmatrix}\frac12 & S+\Sigma & S\\ \sigma & -M-\sigma & M\end{pmatrix}$$

$$\times\begin{pmatrix}\sigma & -M-\sigma & M\\ \frac12 & S+\Sigma & S+\Sigma-\Sigma'\end{pmatrix}|z_M^{S+\Sigma-\Sigma'})$$

(no summation on M)

$$=[S+\Sigma]\delta^{\Sigma\Sigma'}\qquad\text{(for any } S, M)$$

and $\sum_\sigma \mathbf{S}_\sigma^{\Sigma'} \mathbf{S}_\sigma^{\Sigma\dagger} = \delta^{\Sigma\Sigma'} [\Sigma + S_{op}]$,

where S_{op} is an operator in E such that $S_{op} |z_M^S) = S |z_M^S)$. Note that the foregoing expression is nothing else than the coupling of two $[\hat{\Sigma}]^\dagger$ operators in their scalar component.

APPENDIX D: CONNECTION BETWEEN $D_{\gamma'\gamma}^{S,n}(p)$ AND MATRIX ELEMENTS OF I.R. OF THE GROUP $S(n)$

(i) The $D_{\gamma'\gamma}^{S,n}(p)$ form a representation of $S(n)$; that is to say,

$$\sum_\gamma D_{\gamma'\gamma}^S(p) D_{\gamma\gamma''}^S(q) = D_{\gamma'\gamma''}^S(pq) \quad p, q \in S(n) \ .$$

In order to prove this, we use a summation formula on the Σ:

$$\sum_{S_i, \Sigma_{i+1}} \mathbf{S}_{\sigma_{i+1}}^{\Sigma_{i+1}\dagger} |z_{M_i}^{S_i})(z_{M_i}^{S_i}| \mathbf{S}_{\rho_{i+1}}^{\Sigma_{i+1}}$$

$$= \delta_{\sigma_{i+1}\rho_{i+1}} [S_{i+1}] \left| z_{M_{i+1}}^{S_{i+1}})(z_{M_{i+1}}^{S_{i+1}} \right|$$

with $S_{i+1} = S_i + \Sigma_{i+1}$; $M_{i+1} = M_i + \sigma_{i+1}$,

which is easily demonstrated using (7) and the relation

$$\sum_j \begin{pmatrix} j_1 & j_2 & \Big| m \\ m_1 & m_2 & \Big| j \end{pmatrix} \begin{pmatrix} j & m_1' & m_2' \\ m & j_1 & j_2 \end{pmatrix} = \delta_{m_1 m_1'} \delta_{m_2 m_2'} \ .$$

Then we have

$$\sum_\gamma D_{\gamma'\gamma}^S(p) D_{\gamma\gamma''}^S(q) = \sum_{(\sigma)(\sigma'')} \sum_\gamma \frac{[d_{\gamma'} d_{\gamma''}]^{-1/2}}{d_\gamma}$$

$$\times \ (z^0 | \mathbf{S}_{p\sigma_1}^{\Sigma_1'} \cdots \mathbf{S}_{p\sigma_n}^{\Sigma_n'} \mathbf{S}_{\sigma_n}^{\Sigma_n\dagger} \cdots \mathbf{S}_{\sigma_1}^{\Sigma_1\dagger} | z^0)$$

$$\times \ (z^0 | \mathbf{S}_{q\sigma_1'}^{\Sigma_1} \cdots \mathbf{S}_{q\sigma_n'}^{\Sigma_n} \mathbf{S}_{\sigma_n''}^{\Sigma_n''\dagger} \cdots \mathbf{S}_{\sigma_1''}^{\Sigma_1''\dagger} | z^0) \ .$$

Summation on γ is done as

$$\sum_\gamma = \sum_{\Sigma_n} \left(\sum_{\Sigma_{n-1}} \cdots \left(\sum_{\Sigma_1} \right.\right. \quad \text{with} \sum_i \Sigma_i = S$$

and one obtains

$$\prod_{i=1}^n [S_i] \delta_{\sigma_i, q\sigma_i''} = d_\gamma \prod_{i=1}^n \delta_{\sigma_i, q\sigma_i''} \ ;$$

then

$$\sum_\gamma D_{\gamma'\gamma}^S(p) D_{\gamma\gamma''}^S(q) = \sum_{(\sigma'')} (d_{\gamma'} d_{\gamma''})^{-1/2}$$

$$\times \ (z^0 | \mathbf{S}_{pq\sigma_1''}^{\Sigma_1'} \cdots \mathbf{S}_{pq\sigma_n''}^{\Sigma_n'}$$

$$\times \mathbf{S}_{\sigma_n''}^{\Sigma_n''\dagger} \cdots \mathbf{S}_{\sigma_1''}^{\Sigma_1''\dagger} | z^0)$$

$$= D_{\gamma'\gamma''}^S(pq) \ .$$

(ii) The matrices $D^S(p)$ are real because they are combinations of Clebsch-Gordan coefficients.

(iii) The matrices $D^S(p)$ are orthogonal:

$$D^S(p)^* = \left\{ (d_\gamma d_{\gamma'})^{-1/2} \sum_{(\sigma)} (z^0 | \prod_i (\mathbf{S}_{p\sigma_i}^{\Sigma_i'}) \prod_i \right.$$

$$\left. \times (\mathbf{S}_{\sigma_i}^{\Sigma_i\dagger}) | z^0) \right\}^*$$

$$= \{ (d_\gamma d_{\gamma'})^{-1/2} \sum_{(\sigma)} (z^0 | \prod_i (\mathbf{S}_{\sigma_i}^{\Sigma_i}) \prod_i (\mathbf{S}_{p\sigma_i}^{\Sigma_i'\dagger}) | z^0) \}$$

$$= \{ (d_{\gamma'} d_\gamma)^{-1/2} \sum_{(\sigma)} (z^0 | \prod_i (\mathbf{S}_{p^{-1}\sigma_i}^{\Sigma_i}) \prod_i (\mathbf{S}_{\sigma_i}^{\Sigma_i'\dagger}) | z^0) \}$$

$$= \tilde{D}^S(p^{-1}) \ .$$

Thus $D^S(p)^\dagger D^S(p) = 1$.

Finally, the matrices $D^S(p)$ are standard orthogonal irreducible representations of $S(n)$ corresponding to the partition $[\frac{1}{2}n + S, \ \frac{1}{2}n - S]$ of n.

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$$\mathfrak{S}_\sigma^{1/2\dagger}=a_\sigma^\dagger=z_\sigma;\ \mathfrak{S}_\sigma^{-1/2\dagger}=(-1)^{1/2-\sigma}a_{-\sigma}=(-1)^{1/2-\sigma}\frac{\partial}{\partial z_{-\sigma}}.$$

[23]We have adopted the definition of Racah.

[24]Here symmetrical is taken in the sense of "invariant by permutation of the electrons."

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