1971

Permutational symmetry in electronic systems

William Irwin Salmon
Iowa State University

Recommended Citation

Salmon, William Irwin, "Permutational symmetry in electronic systems " (1971). *Retrospective Theses and Dissertations*. 4916.
https://lib.dr.iastate.edu/rtd/4916

71-26,890

SALMON, William Irwin, 1942-
PERMUTATIONAL SYMMETRY IN ELECTRONIC
SYSTEMS.

Iowa State University, Ph.D., 1971
Chemistry, physical

University Microfilms, A XEROX Company, Ann Arbor, Michigan

Permutational symmetry in electronic systems

by

William Irwin Salmon

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology

1971

TABLE OF CONTENTS

PREFACE

This dissertation is concerned with the simplification of calculations on electronic systems through the exploitation of permutational symmetry.

Accurate theoretical descriptions of chemical phenomena are made easier when secular equations can be factored in terms of commuting operators. It is impractical to ignore this possibility in any but the simplest cases. In most quantum-chemical calculations, it is therefore desirable to construct wave functions from antisymmetrized space-spin functions that are also eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$.

Two problems must be solved. First of all, one must be able to generate spin eigenfunctions for any desired eigenvalues S and M_S. In other words, one must be able to find a basis for any given irreducible representation of the symmetric group. For systems with more than a few electrons, this is more difficult than it might seem. The problem has received much attention in recent years, and a survey of the techniques available appears in the third and fourth chapters.

The second problem is to structure the wave function in such a way that expectation values can be calculated conveniently. It is particularly important to obtain a simple formula for the energy. Previous attempts have yielded expressions involving sums over many permutation matrix elements or other complicated coefficients. This subject is discussed

in the second chapter.

We introduce a particular construction for unrestricted configuration-interaction wave functions which simplifies the calculation of expectation values. General wave functions are expressed in terms of pure-spin components of determinantal functions. The building blocks, called "spin-adapted antisymmetrized products", or SAAP's, are designed to exploit double occupancy.

It is shown that SAAP's, when constructed from orthonormal orbitals, can be handled in calculations more easily than Slater determinants. Simple formulas are derived for matrix elements of the Hamiltonian and $\hat{L}^2$. A computer program is given for the evaluation of coefficients occurring in the energy matrix elements.

Two new methods are described for the construction of suitable spin eigenfunctions. The first of these is an algorithm for generating Serber functions by diagonalization of the $\hat{S}^2$-matrix. The other is a direct procedure for obtaining orthogonal matric bases spanning Yamanouchi-Kotani and Serber representations of the symmetric group algebra.

A computer program is given for generating simultaneous eigenfunctions of $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, and $\hat{S}_z$.

In the discussion that follows, certain special symbols and conventions are used. These are explained in Appendices A and B.

GENERAL CONSIDERATIONS

Indistinguishability of Electrons

Electrons are identical, meaning that no experiment can tell them apart. This implies that expectation values are independent of any electron numbering scheme. Suppose that $\Psi(1,2,...,N)$ is the exact wave function (a solution of the Schrodinger equation) for an N-electron system, and that P is any of the N! permutations of the electrons. Then for any observable operator $\hat{O}$,

$$\langle P\Psi(1,2,...,N)|\hat{O}P\Psi(1,2,...,N)\rangle = \langle\Psi(1,2,...,N)|\hat{O}\Psi(1,2,...,N)\rangle . \qquad (1)$$

Since permutations are unitary operators (Appendix B), it follows that

$$\langle\Psi(1,2,...,N)|P^{-1}\hat{O}P\Psi(1,2,...,N)\rangle = \langle\Psi(1,2,...,N)|\hat{O}\Psi(1,2,...,N)\rangle$$

for any wave function. Thus it must be that

$$\hat{O} = P^{-1}\hat{O}P \quad : \qquad (2)$$

every observable operator is invariant under similarity transformations that permute its electron labels. In other words, every observable operator affects electrons symmetrically.

If it should happen that Ψ is permutationally symmetric or antisymmetric,

$$P\Psi(1,2,\ldots,N) = \pm\Psi(1,2,\ldots,N),$$

then it is clear that (1) is satisfied. However, (1) does not imply that the wave function has this property. In fact, any product function

$$\Psi(1,2,\ldots,N) = a(1)b(2) \cdots c(N)$$

will satisfy (1).

The behavior of the operators does induce a behavior in the wave functions. It follows from (2) that observable operators commute with all electronic permutations, and group-theoretical arguments then lead to the conclusion that eigenfunctions of observable operators span representations of the symmetric group.

Suppose that the operator $\hat{O}$ has, for a given eigenvalue, a set $\{\phi_1,\phi_2,\ldots,\phi_m\}$ of m linearly independent, degenerate eigenfunctions. Then (2) guarantees that the result $(P\phi_i)$ of permuting any eigenfunction in the set is a new function

$$P\phi_i = \sum_j \phi_j [P]_{ji} ,$$

which is itself a vector in the space spanned by the ϕ_i. The number $[P]_{ji}$ is the (j,i)-element of the matrix $[P]$ representing P, and the functions $\{\phi_i\}$ are said to form a basis for the representation.

If the symmetric group S_N contains <u>every</u> symmetry transformation commuting with $\hat{O}$, then the degenerate functions $\{\phi_i\}$ span an <u>irreducible</u> representation of S_N (apart from accidental degeneracies), and each $\hat{O}$-eigenvalue will be associated with a particular irreducible representation.

Exclusion Principle

Since permutations commute with the Hamiltonian, the implication of the argument above is that solutions of the N-electron Schrödinger equation for a given energy must span a representation of the symmetric group. Permutations of electrons do not comprise every symmetry transformation commuting with the Hamiltonian, so there is no theoretical reason to suppose that such a representation will be irreducible.

Nevertheless, experiment demands that solutions of the Schrödinger equation for fermion systems must span the one-dimensional (thus irreducible) antisymmetric representation of the symmetric group. In other words, for every P in S_N,

$$P\Psi(1,2,\ldots,N) = \varepsilon(P)\Psi(1,2,\ldots,N),$$

where $\varepsilon(P)$ is +1 when P is even and -1 when P is odd. Here P is a transformation which permutes the space <u>and</u>

spin coordinates of the fermions.

This result is the Pauli Exclusion Principle for fermions.

Spin Eigenfunctions

It happens that S_N contains every symmetry transformation commuting with the total spin operator $\hat{S}^2$. Thus spin eigenfunctions $\Theta_\alpha(NSM)$, satisfying the equations

$$\hat{S}^2\Theta_\alpha(NSM) = \hbar^2 S(S+1)\Theta_\alpha(NSM),$$
$$\hat{S}_z\Theta_\alpha(NSM) = \hbar M\Theta_\alpha(NSM),$$

are basis functions for irreducible representations of S_N. Here the permutations transform only the spin coordinates of the electrons.

Spin eigenfunctions are important in quantum chemistry because, for many atoms and molecules, the Hamiltonian, $\hat{H}$, very nearly commutes with $\hat{S}^2$ and $\hat{S}_z$. This means that eigenfunctions of $\hat{H}$ can be chosen to be also eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$. Doing so simplifies energy calculations by factoring the energy matrix: if two trial wave functions $\psi_\alpha(NSM)$ and $\psi_\beta(NS'M')$ are spin eigenfunctions for which $S'\neq S$ or $M'\neq M$,

$$<\psi_\alpha(NSM)|\hat{H}\psi_\beta(NS'M')> = 0.$$

The energy matrix reduces to a direct sum of blocks within which S and M are constant.

Thus the Pauli and Indistinguishability Principles lead to two conclusions regarding electronic wave functions:

(i) the wave functions are antisymmetric with respect to simultaneous permutations of the space and spin coordinates of the electrons;

(ii) they can often be chosen to be eigenfunctions of $\hat{S}^2$, implying that they transform according to irreducible representations of the symmetric group permuting only the spin coordinates of the electrons.

Spin-Adapted Antisymmetrized Products

Slater determinants (Slater, 1929, 1931) are antisymmetric with respect to simultaneous permutations of space and spin and are $\hat{S}_z$-eigenfunctions, but they are not in general eigenfunctions of $\hat{S}^2$. An approximate wave function which is to be a spin eigenfunction is usually constructed as a linear combination of Slater determinants. In fact, <u>any</u> antisymmetric wave function can be expanded in Slater determinants: such determinants span the configuration space (Löwdin, 1955a).

A Slater determinant for N electrons is obtained by applying the antisymmetrizer (Appendix B) to the product of a space product function $\phi(N)$ and a spin product function $\Theta(NM)$ having the $\hat{S}_z$-eigenvalue M:

$$\Phi(NM) = \mathcal{A}[\phi(N)\Theta(NM)].$$

($\mathcal{A}$ has been defined in such a way that it is idempotent, but $\Phi(NM)$ is not normalized.) In the discussion that follows, the orbitals of which $\phi(N)$ is composed will not be discussed. They may be atomic or molecular orbitals: what they are in particular does not concern us at this stage. The pertinent fact is that $\phi(N)$ is some product of one-electron orbitals, which we shall for convenience assume to be orthonormal.

In analogy to the Slater determinant $\Phi(NM)$, we can define an antisymmetric eigenfunction of $\hat{S}_z$ which is also an eigenfunction of $\hat{S}^2$ by replacing the spin product function $\Theta(NM)$ with a spin eigenfunction $\Theta_\alpha(NSM)$. The new function,

$$\Phi_\alpha(NSM) = \mathcal{A}[\phi(N)\Theta_\alpha(NSM)], \tag{3}$$

will be an eigenfunction of $\hat{S}^2$ because the spin operator commutes with $\mathcal{A}$. Functions like that given in (3) can be projected out of Slater determinants by suitable operators, and we shall refer to them as "spin-adapted antisymmetrized products", or SAAP's. Since each spin eigenfunction $\Theta_\alpha(NSM)$ is a linear combination of spin products, a SAAP is a linear combination of Slater determinants.

Spin-adapted antisymmetrized products span the N-electron configuration space: any antisymmetric wave function can be expanded in terms of them. Furthermore, SAAP's possess an advantage over Slater determinants, in that they are eigenfunctions of $\hat{S}^2$. Slater determinants are easy to handle without the use of group theory, and lead to convenient formulas for the matrix elements of observable operators. We shall show, using group theory, that SAAP's lead to formulas no less simple, and thus that they are more efficient building blocks for wave functions when S is a good quantum number.

The antisymmetrizer in (3) masks the true relationship between the space and spin components of the SAAP. Suppose that there are d(NS) spin eigenfunctions $\Theta_\alpha(NSM)$ for a given M. Then these functions span an irreducible matrix representation $[P]^{NS}$ of S_N: for any permutation P transforming the spin coordinates of the electrons 1,2,...,N,

$$P\Theta_\alpha(NSM) = \sum_\beta \Theta_\beta(NSM)[P]^{NS}_{\beta\alpha} \quad . \tag{4}$$

This will be called the <u>spin</u> <u>representation</u> of S_N. Using this relation in (3),

$$\begin{aligned}\Phi_\alpha(NSM) &= (N!)^{-1} \sum_P \varepsilon(P)(P\phi)(P\Theta_\alpha)\\ &= (N!)^{-1} \sum_P \varepsilon(P)(P\phi)\{\sum_\beta \Theta_\beta [P]^{NS}_{\beta\alpha}\}\\ &= (N!)^{-1} \sum_\beta \{\sum_P \varepsilon(P)[P]^{NS}_{\beta\alpha}(P\phi)\}\ \Theta_\beta \ ,\end{aligned}$$

or $$\Phi_\alpha(\mathrm{NSM}) = [d(\mathrm{NS})]^{-1} \sum_\beta \phi_\beta(\mathrm{NS}\alpha)\Theta_\beta(\mathrm{NSM}), \tag{5}$$

where $$\phi_\beta(\mathrm{NS}\alpha) = [d(\mathrm{NS})/N!] \sum_P \varepsilon(P)[P]^{\mathrm{NS}}_{\beta\alpha}(P\phi). \tag{6}$$

Equation (5) shows that the SAAP is a sum of terms, each of which is the product of a spin eigenfunction and some kind of space function. The space function, as shown in (6), is projected out of the "primitive" space product function ϕ by a Wigner operator (Wigner, 1931). As a consequence, these space functions form a basis for an irreducible representation of S_N, called the <u>space representation</u>: if $k=d(\mathrm{NS})/N!$,

$$\begin{aligned}
P\phi_\beta(\mathrm{NS}\alpha) &= k \sum_{P'} \varepsilon(P')[P']^{\mathrm{NS}}_{\beta\alpha}(PP'\phi) \\
&= k \sum_{P''} \varepsilon(P^{-1}P'')[P^{-1}P'']^{\mathrm{NS}}_{\beta\alpha}(P''\phi) \\
&= k \sum_{P''} \varepsilon(P^{-1})\varepsilon(P'') \sum_\gamma [P^{-1}]^{\mathrm{NS}}_{\beta\gamma}[P'']^{\mathrm{NS}}_{\gamma\alpha}(P''\phi) \\
&= \varepsilon(P^{-1}) \sum_\gamma \{k\sum_{P''} \varepsilon(P'')[P'']^{\mathrm{NS}}_{\gamma\alpha}(P''\phi)\} \; [P^{-1}]^{\mathrm{NS}}_{\beta\gamma} \\
&= \varepsilon(P) \sum_\gamma \phi_\gamma(\mathrm{NS}\alpha)[P^{-1}]^{\mathrm{NS}}_{\beta\gamma} .
\end{aligned} \tag{7}$$

Comparison of (7) and (4) shows that the spin functions transform under P according to the matrix $[P]^{\mathrm{NS}}$, while the space functions $\phi_\beta(\mathrm{NS}\alpha)$ transform according to the transpose of $\varepsilon(P)[P^{-1}]^{\mathrm{NS}}$. Thus there is a close relationship between the spin and space representations: they are reciprocal to each other in such a way that the SAAP is antisymmetric. These representations are said to be dual (Kotani *et al.*, 1955).

The spin-adapted antisymmetrized products have been displayed in two equivalent forms. Either form demands a procedure for obtaining spin eigenfunctions, and one of them requires dual space functions. We shall see later how these might be obtained. First we examine the usefulness of SAAP's.

ELECTRONIC WAVE FUNCTIONS AS SUPERPOSITIONS OF SPIN-ADAPTED ANTISYMMETRIZED PRODUCTS

Linear Dependence of SAAP's

Any antisymmetric wave function that is an eigenfunction of $\hat{S}^2$ and $\hat{S}_z$ can be written as a linear combination of SAAP's having N, S, and M fixed:

$$\Psi(NSM) = \sum_{\phi} \sum_{\alpha} c(\phi,\alpha)\mathcal{A}[\phi(N)\Theta_{\alpha}(NSM)] \ . \tag{8}$$

If the sum over space products includes contributions from different configurations, Ψ is a configuration-interaction (CI) function. We assume for generality that this is the case.

In (8), the sums run over every space product for the configurations of interest, and every spin eigenfunction for the given N, S, and M. In general, some of the SAAP's will then be linearly dependent. In order that the coefficients $c(\phi,\alpha)$ will be unique and the secular equation will be soluble, it is essential to remove this dependence. Two sources of linear dependence are easily identified.

Suppose that Ψ includes every SAAP containing the space product ϕ. SAAP's containing a space product $\phi' = P\phi$ differing from ϕ by only a permutation should not be included in Ψ. For

$$\mathcal{A}[\phi'\Theta_{\alpha}] = \mathcal{A}[(P\phi)\Theta_{\alpha}] = \mathcal{A}P[\phi\cdot P^{-1}\Theta_{\alpha}] = \varepsilon(P)\sum_{\beta}[P^{-1}]^{NS}_{\beta\alpha}\mathcal{A}[\phi\Theta_{\beta}] .$$

Thus any SAAP containing ϕ' is linearly dependent on SAAP's already included in Ψ. The additional one contributes nothing new.

It follows that, in (8), it is sufficient to sum over just those space products containing different orbitals.

Double occupancy is a second source of linear dependence. If a space product ϕ contains a doubly-occupied orbital, there exists a transposition $t=t^{-1}$ such that $t\phi=\phi$. It follows that

$$\mathcal{A}[\phi\Theta_\alpha] = \Phi_\alpha(\mathrm{NSM}) = \mathcal{A}[(t\phi)\Theta_\alpha] = \mathcal{A}t[\phi t\Theta_\alpha] = -\mathcal{A}[\phi t\Theta_\alpha]$$

$$= -\sum_\beta [t]^{NS}_{\beta\alpha}\mathcal{A}[\phi\Theta_\beta]$$

$$= -\sum_\beta [t]^{NS}_{\beta\alpha}\ \Phi_\beta(\mathrm{NSM}),$$

or

$$\sum_\beta \Phi_\beta(\mathrm{NSM})\cdot\{[t]^{NS}_{\beta\alpha}+\delta_{\beta\alpha}\} = 0.$$

Thus the only way to avoid having all the SAAP's for given N, S, and M linearly dependent is to construct the spin eigenfunctions $\Theta_\alpha(\mathrm{NSM})$ in such a way that

$$[t]^{NS}_{\beta\alpha} = -\delta_{\beta\alpha}$$

for every transposition t under which ϕ is invariant. A procedure for doing this is introduced in the next two sections.

Space Products

It is possible to structure space products and spin eigenfunctions in such a way as to greatly simplify calculations on systems with double occupancy. For this purpose, we will introduce two conventions.

In the following, we shall refer to doubly-occupied orbitals as *doubles*, and to singly-occupied orbitals as *singles*. Two electrons labelled $2\lambda-1$ and 2λ, where $\lambda=1,2,\ldots$, will be referred to as a *geminal pair*. Orbitals containing a geminal pair of electrons will be said to occupy *geminal positions*. Two-cycle permutations of the form $(2\lambda-1,2\lambda)$ will be called *geminal transpositions*, and a product of geminal transpositions will be called a *geminal permutation*. The subgroup of S_N containing every product of the geminal transpositions

$$(1,2),\ (3,4),\ \ldots,\ (2\mu-1,2\mu),$$

including the identity, will be called the *geminal group* $\mathcal{G}_{\mu}$. Whereas we use P to denote a general element of S_N, a geminal permutation will be denoted by G, and a geminal transposition by g.

The discussion of the last section showed that, of all possible space products containing the same orbitals, a CI wave function need contain only one - any one. We are free to make a convention as to how such a space product shall be chosen. We have assumed for convenience that the space orbitals are orthonormal. In addition, we adopt the *following convention for the structure of space products*: they will have all their doubles listed first, with ascending labels, followed by the singles, in the order of ascending labels. For example, of twelve possible space products containing the atomic orbitals $(1s)^2 2s2p_o$, we pick the function

$$\phi_1 = [1s(1)1s(2)2s(3)2p_o(4)].$$

As in this example, space products containing π doubles will be denoted by that subscript: e.g., ϕ_π , ϕ'_π. Space products with the subscript π are invariant under the geminal permutations belonging to $\mathcal{G}_{\pi'}$, where $\pi' \leqslant \pi$.

Geminally-Adapted Spin Eigenfunctions

There are infinitely many ways to make spin functions for given N, S, and M, corresponding to infinitely many equivalent spin representations of S_N. We choose the following *convention for spin functions*:

(i) The spin eigenfunctions will be orthonormal.

(ii) They will be constructed by coupling the spins of each geminal pair of electrons separately, then coupling the pair-spins to each other. If N is odd, the spin of the remaining electron will then be coupled to the resultant spin.

Spin eigenfunctions constructed in this way, using Clebsch-Gordon coefficients, were first described by Serber (1934a, 1934b). They contain a singlet or triplet component for every geminal pair of electrons, and thus are either symmetric or antisymmetric with respect to every geminal transposition in S_N. The Serber functions for N=4, S=1, M=0 are:

$$\begin{gathered}[\alpha(1)\beta(2)+\beta(1)\alpha(2)][\alpha(3)\beta(4)-\beta(3)\alpha(4)]/2, \\ [\alpha(1)\alpha(2)\beta(3)\beta(4)-\beta(1)\beta(2)\alpha(3)\alpha(4)]/\sqrt{2}, \\ [\alpha(1)\beta(2)-\beta(1)\alpha(2)][\alpha(3)\beta(4)+\beta(3)\alpha(4)]/2.\end{gathered} \tag{9}$$

We shall denote a spin function antisymmetric in the first π geminal pairs, but symmetric in the next one, by the subscript π. If there are several such functions, they will be called $\Theta_{\pi 1}(NSM)$, $\Theta_{\pi 2}(NSM)$, etc. Using this notation, the functions in the example above would be labelled $\Theta_{01}(410)$, $\Theta_{02}(410)$, and $\Theta_{11}(410)$. As a result of the notation,

$$g\Theta_{\pi\alpha} = \pm\Theta_{\pi\alpha} \quad \text{for every } g \text{ in } S_N,$$

but in particular,

$$g\Theta_{\pi\alpha} = -\Theta_{\pi\alpha} \text{ if } g \text{ belongs to } \mathfrak{G}_{\pi'}, \text{ where } \pi' \leqslant \pi.$$

These relations imply that the matrices representing geminal transpositions in the spin representation spanned by Serber spin functions are <u>diagonal</u>: since the functions are orthonormal,

$$[g]^{NS}_{\pi''\beta,\pi\alpha} = \langle\Theta_{\pi''\beta}(NSM)|g\Theta_{\pi\alpha}(NSM)\rangle = \pm\langle\Theta_{\pi''\beta}(NSM)|\Theta_{\pi\alpha}(NSM)\rangle$$

$$= \pm\delta(\pi''\beta,\pi\alpha)$$

for every g in S_N. In particular, if g belongs to $\mathfrak{G}_{\pi'}$, where $\pi'\leq\pi$ or $\pi'\leq\pi''$,

$$[g]^{NS}_{\pi''\beta,\pi\alpha} = -\delta(\pi''\beta,\pi\alpha).$$

Since geminal permutations G are products of geminal transpositions, we have the more general result

$$[G]^{NS}_{\pi''\beta,\pi\alpha} = \pm\delta(\pi''\beta,\pi\alpha) \quad \text{for every G in } S_N.$$

In particular, if G belongs to $\mathfrak{G}_{\pi'}$, where $\pi'\leq\pi$ or $\pi'\leq\pi''$,

$$[G]^{NS}_{\pi''\beta,\pi\alpha} = \varepsilon(G)\ \delta(\pi''\beta,\pi\alpha), \tag{10}$$

in which $\varepsilon(G)$ is +1 when G is even and -1 when G is odd.

This result has a special consequence that will prove useful. We write "$G\varepsilon\mathfrak{G}_{\pi'}$" to mean "G belongs to $\mathfrak{G}_{\pi'}$". Since every geminal permutation is a product of mutually commuting geminal transpositions, with a factor I or $(2\mu-1,2\mu)$ from the μth geminal pair, the order of $\mathfrak{G}_{\pi'}$ is $2^{\pi'}$, and (10) gives

$$\sum_{G\varepsilon\mathfrak{G}_{\pi'}} \varepsilon(G)\,[G]^{NS}_{\pi''\beta,\pi\alpha} = \sum_{G\varepsilon\mathfrak{G}_{\pi'}} \varepsilon(G)\,\varepsilon(G)\,\delta(\pi''\beta,\pi\alpha)$$

$$= \delta(\pi''\beta,\pi\alpha) \sum_{G\varepsilon\mathfrak{G}_{\pi'}} (+1),$$

or
$$\sum_{G\in\mathcal{G}_{\pi'}} \varepsilon(G)\,[G]^{NS}_{\pi''\beta,\pi\alpha} = 2^{\pi'}\,\delta(\pi''\beta,\pi\alpha) \qquad (11)$$

when $\pi' \leqslant \pi$ or $\pi' \leqslant \pi''$. This result is, as we shall see, a great aid in simplifying the expressions for expectation values.

Linearly Independent SAAP's

The two conventions we have adopted further simplify the wave function (8) when the space products contain doubly-occupied orbitals. We have already reduced the number of space products required to the bare minimum: one product for each choice of orbitals. The conventions reduce the number of spin eigenfunctions required.

Consider the SAAP $\mathcal{A}[\phi_\pi \Theta_{\pi'\alpha}]$, where $\pi' < \pi$. The geminal transposition $g = g^{-1} = (2\pi'+1, 2\pi'+2)$, which belongs to $\mathcal{G}_\pi$ but not to $\mathcal{G}_{\pi'}$, has the properties

$$g\phi_\pi = \phi_\pi \quad \text{and} \quad g\Theta_{\pi'\alpha} = +\Theta_{\pi'\alpha}.$$

As a result,

$$\mathcal{A}[\phi_\pi \Theta_{\pi'\alpha}] = \mathcal{A}[(g\phi_\pi)\Theta_{\pi'\alpha}] = \mathcal{A}g[\phi_\pi \cdot g\Theta_{\pi'\alpha}] = -\mathcal{A}[\phi_\pi \Theta_{\pi'\alpha}],$$

so that the SAAP is zero. In other words, if a SAAP contains a space product with doubles in geminal positions in which the associated spin function is not antisymmetric, then that SAAP vanishes.

This result reduces the sum over spin functions in the CI wave function: we have now

$$\Psi = \sum_{\substack{\phi_\pi \\ \pi\leq\pi'}} \sum_{\pi'\alpha} c(\phi_\pi,\pi'\alpha)\mathcal{A}[\phi_\pi\theta_{\pi'\alpha}], \tag{12}$$

where the sum over space products ϕ_π includes only one product for each choice of orbitals, and the sum over spin functions includes only some of them.

The wave function has been reduced to the bare minimum: the SAAP's in (12) are all linearly independent. In fact, we now show that they are all orthogonal.

The overlap between two SAAP's with the same values of N, S, and M is

$$\Delta = \langle\mathcal{A}[\phi_\pi\theta_{\pi'\alpha}]|\mathcal{A}[\phi_\rho\theta_{\rho'\beta}]\rangle$$

$$= \langle\phi_\pi\theta_{\pi'\alpha}|\mathcal{A}[\phi_\rho\theta_{\rho'\beta}]$$

$$= (N!)^{-1}\sum_P \varepsilon(P)\langle\theta_{\pi'\alpha}|P\theta_{\rho'\beta}\rangle\langle\phi_\pi|P\phi_\rho\rangle.$$

Here we assume that $\pi'\geq\pi$ and $\rho'\geq\rho$, for otherwise the SAAP's would vanish. The first integral on the right is the $(\pi'\alpha,\rho'\beta)$-element of the matrix representing P in the Serber spin representation for N, S. Thus

$$\Delta = (N!)^{-1} \sum_P \varepsilon(P)[P]^{NS}_{\pi'\alpha,\rho'\beta}\langle\phi_\pi|P\phi_\rho\rangle.$$

No two space products in the CI wave function contain the same orbitals, so $\langle\phi_\pi|P\phi_\rho\rangle$ is zero unless $\phi_\pi=\phi_\rho$:

$$\Delta = \delta(\phi_\pi,\phi_\rho)(N!)^{-1} \sum_P \varepsilon(P)[P]^{NS}_{\pi'\alpha,\rho'\beta}\langle\phi_\pi|P\phi_\pi\rangle.$$

The integral on the right is zero unless P belongs to the geminal group $\mathcal{G}_\pi$ under which ϕ_π is invariant:

$$\Delta = \delta(\phi_\pi, \phi_\rho) \ (N!)^{-1} \sum_{G \in \mathcal{G}_\pi} \varepsilon(G) [G]^{NS}_{\pi'\alpha, \rho'\beta} \cdot$$

Using (11),

$$\Delta = \delta(\phi_\pi, \phi_\rho) \delta(\pi'\alpha, \rho'\beta) \cdot 2^\pi / N! \qquad (13)$$

This proves that the functions

$$\left(\frac{N!}{2^\pi}\right)^{1/2} \mathcal{A}[\phi_\pi(N) \Theta_{\pi'\alpha}(NSM)],$$

where $\pi \leqslant \pi'$ and only one space product is included for each choice of orbitals, form a complete orthonormal set spanning the space of N-electron antisymmetric wave functions having spin eigenvalues S and M. These SAAP's are therefore efficient building blocks for CI wave functions when S is a good quantum number.

Energy Matrix Elements between SAAP's Constructed from Orthonormal Orbitals

General formula

The importance of the space and spin conventions introduced in the last sections lies in the way in which they simplify the calculation of expectation values. It has been shown that they facilitate the removal of linear dependence in the wave function. We now show that they simplify the calculation of energy matrix elements.

It is assumed that the wave function (12) is constructed from orthonormal orbitals, and that the Hamiltonian is, for practical purposes, spin-free. Except for these conditions, our results will be perfectly general, and applicable to either atomic or molecular systems.

The immediate result of (12) is that the energy is a sum of Hamiltonian matrix elements between spin-adapted antisymmetrized products. The problem is to express such matrix elements in terms of elementary one- and two-electron integrals.

Just as SAAP's are generalizations of Slater determinants, we shall obtain matrix element formulas which are generalizations of Slater's matrix element rules. Despite the fact that the derivations are complicated by group theory, the results are very nearly as simple as those for determinantal functions. Before proceeding to the derivation, we define notation and display the formulas obtained.

We consider the two SAAP's $\mathcal{A}[\phi_\pi(N)\Theta_{\pi'\alpha}(NSM)]$ and $\mathcal{A}[\phi_\rho(N)\Theta_{\rho'\beta}(NSM)]$, where the space products are

$$\phi_\pi = \pi_1\pi_2 \cdots \pi_N$$

$$\text{and} \qquad \phi_\rho = \rho_1\rho_2 \cdots \rho_N \, . \tag{14}$$

Here π_k and ρ_k are the orbitals occupied by electron k in ϕ_π and ϕ_ρ. According to convention, ϕ_π and ϕ_ρ contain π and

ρ doubles, respectively. It should be noted that an orbital π_k in ϕ_π can occur also in ϕ_ρ, and an orbital ρ_m in ϕ_ρ can occur in ϕ_π. We write, for example, $n(\pi_k,\phi_\pi)$ and $n(\pi_k,\phi_\rho)$ to denote the occupancies of π_k in ϕ_π and ϕ_ρ.

It is assumed that ϕ_π and ϕ_ρ differ by no more than two orbitals, and that $\pi \leqslant \pi'$ and $\rho \leqslant \rho'$. Otherwise, the energy matrix element is zero.

There is a permutation, $\mathcal{L}$, that rearranges ϕ_ρ so as to place it in "maximum coincidence" with ϕ_π. This means that $(\mathcal{L}\phi_\rho)$ and ϕ_π are identical except possibly for the orbitals occupied by one or two electrons.

We break down the Hamiltonian in terms of the one-electron Hamiltonians h_i and the electronic interactions g_{ij}:

$$\hat{H} = \sum_{i<j}\sum H_{ij} \ ,$$

where

$$H_{ij} = (N-1)^{-1}(h_i+h_j) + g_{ij} \ .$$

The general formula for the energy matrix element turns out to be [when the SAAP's are normalized according to (13)]

$$\begin{aligned}
&\langle \mathcal{A}[\phi_\pi \Theta_{\pi'\alpha}] | \hat{H} | \mathcal{A}[\phi_\rho \Theta_{\rho'\beta}] \rangle \\
&\quad = \varepsilon(\mathcal{L}) \sum_{\pi_i \leq \pi_j} \sum N(\pi_i,\pi_j;\rho_r,\rho_s) \times \\
&\quad\quad \times \{ [\mathcal{L}]^{NS}_{\pi'\alpha,\rho'\beta} \langle \pi_i \pi_j | H_{ij} | \rho_r \rho_s \rangle \\
&\quad\quad\quad - [(i,j)\mathcal{L}]^{NS}_{\pi'\alpha,\rho'\beta} \langle \pi_i \pi_j | H_{ij} | \rho_s \rho_r \rangle \} ,
\end{aligned} \tag{15}$$

in which

$$\varepsilon(\mathcal{L}) = \begin{Bmatrix}+1\\-1\end{Bmatrix} \text{ when } \mathcal{L} \text{ is } \begin{Bmatrix}\text{even}\\\text{odd}\end{Bmatrix} ,$$

$$N(\pi_i,\pi_j;\rho_r\rho_s) = \left\{\frac{n(\pi_i,\phi_\pi)n(\pi_j,\phi_\pi)n(\rho_r,\phi_\rho)n(\rho_s,\phi_\rho)}{[1+\delta(\pi_i,\pi_j)]^3[1+\delta(\rho_r,\rho_s)]^3}\right\}^{1/2} ,$$

$$[P]^{NS}_{\pi\alpha',\rho\beta'} = \langle\Theta_{\pi\alpha'}(NSM)|P|\Theta_{\rho\beta'}(NSM)\rangle ,$$

$$\langle\pi_i\pi_j|H_{ij}|\rho_r\rho_s\rangle = \iint \pi_i^*(i)\pi_j^*(j)H_{ij}\rho_r(i)\rho_s(j)\ d\underline{x}_i d\underline{x}_j ,$$

and ρ_r and ρ_s are the orbitals occupied in $(\mathcal{L}\phi_\rho)$ by electrons i and j, respectively.

If $\phi_\pi=\phi_\rho$, the sum in (15) is over every <u>distinct</u> pair of orbitals in the space product. For example, if $\pi_1=\pi_2$ is a double, but π_3 and π_4 are singles, then the sum may include the pairs (π_1,π_2), (π_1,π_3), (π_1,π_4), (π_3,π_4), in which case it does <u>not</u> include (π_2,π_1), (π_2,π_3), or (π_2,π_4). Or it may include (π_1,π_2), (π_2,π_3), (π_2,π_4), and (π_3,π_4), in which case it does not include (π_2,π_1), (π_1,π_3), or (π_1,π_4). In other words, doubles do not contribute duplicate terms to the sum. When $\phi_\pi=\phi_\rho$, the alignment permutation is $\mathcal{L}=I$.

If ϕ_π and ϕ_ρ differ by one orbital, the sum is over every <u>distinct</u> orbital pair in ϕ_π containing the differing orbital. For example, suppose that a, b, c, d are orbitals, and $\phi_\pi=\pi_1\pi_2\pi_3\pi_4=aabc$ while $\phi_\rho=\rho_1\rho_2\rho_3\rho_4=abcd$. The differing orbital in ϕ_π is a, and in ϕ_ρ is d. Then the sum in (15) may include the orbital pairs $(\pi_1,\pi_2)=(a,a)$, $(\pi_1,\pi_3)=(a,b)$, and

$(\pi_1,\pi_4)=(a,c)$, but not (π_2,π_3) or (π_2,π_4) as well. In this example, $\mathcal{L}=(1,2,3,4)$.

If ϕ_π and ϕ_ρ differ by two orbitals, the only term occurring in the sum is that for which π_i and π_j are the differing orbitals.

The full power of the SAAP formalism becomes evident when one evaluates the matrix element in specific cases, expressing it in terms of one- and two-electron integrals. We save the derivations until later, and give here only the results.

<u>Case when $\phi_\pi=\phi_\rho$</u>

In this event, $\rho_r=\pi_i$, $\rho_s=\pi_j$, and $\mathcal{L}=I$. Writing $n(\pi_i) = n(\pi_i,\phi_\pi) = n(\pi_i,\phi_\rho)$, we have

$$\begin{aligned}
&\langle \mathcal{A}[\phi_\pi \Theta_{\pi'\alpha}]|\hat{H}|\mathcal{A}[\phi_\rho\Theta_{\rho'\beta}]\rangle \\
&\quad = \delta(\pi'\alpha,\rho'\beta) \sum_{\pi_i} \{n(\pi_i)\langle\pi_i|h|\pi_i\rangle + [n(\pi_i)-1]\langle\pi_i\pi_i|g|\pi_i\pi_i\rangle\} \\
&\qquad + \sum_{\pi_i<}\sum_{\pi_j} n(\pi_i)n(\pi_j)\{\delta(\pi'\alpha,\rho'\beta)\langle\pi_i\pi_j|g|\pi_i\pi_j\rangle \\
&\qquad\qquad - [(i,j)]^{NS}_{\pi'\alpha,\rho'\beta}\langle\pi_i\pi_j|g|\pi_j\pi_i\rangle\} ,
\end{aligned} \tag{16}$$

the sums being over distinct orbitals (i.e., only one from each double). Here $g=(e^2/r_{12})$ and h is a one-electron Hamiltonian.

<u>Case when ϕ_π and ϕ_ρ differ by one orbital</u>

Let the differing orbital be π_μ in ϕ_π and ρ_σ in ϕ_ρ. Then

$$\begin{aligned}
&\langle \mathcal{A}[\phi_\pi \Theta_{\pi'\alpha}]|\hat{H}|\mathcal{A}[\phi_\rho \Theta_{\rho'\beta}]\rangle \\
&\quad = [n(\pi_\mu,\phi_\pi)n(\rho_\sigma,\phi_\rho)]^{1/2}\,\varepsilon(\mathcal{L}) \times \\
&\quad \times \Big\{ \{ [\mathcal{L}]^{NS}_{\pi'\alpha,\rho'\beta} \langle \pi_\mu|h|\rho_\sigma\rangle + [n(\pi_\mu,\phi_\pi)-1]\langle \pi_\mu\pi_\mu|g|\rho_\sigma\pi_\mu\rangle \\
&\qquad\qquad + [n(\rho_\sigma,\phi_\rho)-1]\langle \pi_\mu\rho_\sigma|g|\rho_\sigma\rho_\sigma\rangle \} \\
&\qquad + \sum_{\substack{\pi_j \\ (\neq \pi_\mu,\rho_\sigma)}} n(\pi_j,\phi_\pi)\{ [\mathcal{L}]^{NS}_{\pi'\alpha,\rho'\beta}\langle \pi_\mu\pi_j|g|\rho_\sigma\pi_j\rangle \\
&\qquad\qquad - [(\mu,j)\mathcal{L}]^{NS}_{\pi'\alpha,\rho'\beta}\langle \pi_\mu\pi_j|g|\pi_j\rho_\sigma\rangle \} \Big\}, \qquad (17)
\end{aligned}$$

where the sum is over distinct orbitals in ϕ_π other than the orbitals π_μ and ρ_σ. A double makes only one contribution.

Case when ϕ_π and ϕ_ρ differ by two orbitals

We take the differing orbitals to be π_μ, π_ν in ϕ_π, and ρ_σ, ρ_τ in ϕ_ρ. There are no sums in the formula and no one-electron integrals arise. The result is, then,

$$\begin{aligned}
&\langle \mathcal{A}[\phi_\pi \Theta_{\pi'\alpha}]|\hat{H}|\mathcal{A}[\phi_\rho \Theta_{\rho'\beta}]\rangle \\
&\quad = N(\pi_\mu,\pi_\nu;\rho_\sigma,\rho_\tau)\cdot\varepsilon(\mathcal{L}) \times \\
&\quad \times \{ [\mathcal{L}]^{NS}_{\pi'\alpha,\rho'\beta}\langle \pi_\mu\pi_\nu|g|\rho_\sigma\rho_\tau\rangle \\
&\qquad\qquad - [(\mu,\nu)\mathcal{L}]^{NS}_{\pi'\alpha,\rho'\beta}\langle \pi_\mu\pi_\nu|g|\rho_\tau\rho_\sigma\rangle \}. \qquad (18)
\end{aligned}$$

Discussion

These formulas are very nearly as simple as Slater's rules for matrix elements between determinants (Slater, 1929), the difference being that certain delta functions for one-electron spins have been replaced by spin representation matrix elements for the permutations $\mathcal{L}$ and $(i,j)\mathcal{L}$.

Formula (15) was first obtained, in a slightly less simple form, by K. Ruedenberg (private communication, Iowa State University, Ames, Iowa, 1968). The formulas shown here, as well as formulas for the matrix elements of p-electron operators and pth-order reduced density matrices, will be reported by Ruedenberg and Poshusta (1971).

There have been previous attempts to obtain formulas of this type. Kotani *et al*. (1955) used group theory to simplify the expressions for energy matrix elements between spin components of determinantal functions. Harris (1967) extended this work, and gave closed- and open-shell formulas for matrix elements of one- and two-electron operators, without assuming that the orbitals are orthogonal. Even with this assumption, his results were complicated, involving sums over many permutations. Karplus *et al*. (1958) obtained matrix element formulas for one-electron operators.

The case when the wave function is expressed as one SAAP is similar to the extended Hartree-Fock approximation of Löwdin (1955b, 1960). Matrix elements for spin-free operators in this formalism were obtained by Pauncz, de Heer, and Löwdin (1962) for application to the alternant molecular orbital method. The formulas were generalized by Pauncz (1962, 1969). The results involved various complicated coefficients, closed expressions for which were found by a number of workers (Percus and Rotenberg, 1962; Sasaki and Ohno, 1963; Smith, 1964; Shapiro, 1965; Smith and Harris, 1967). Reviews have been given by Harris (1967) and Pauncz (1967, 1969).

The formulas presented here avoid these difficulties. Their close relation to Slater's rules is emphasized by the ease with which they can be reduced to those rules when the SAAP's involved happen to be Slater determinants. Consider, for example, the case when $\phi_\pi=\phi_\rho$ and $M=S=\frac{N}{2}$: $\Theta_{\pi'\alpha}=\Theta_{\rho'\beta}=\alpha\alpha\cdots\alpha$. Since these spin functions contain no antisymmetric factors, it must be that $\pi=\rho=0$ and $n(\pi_i)=1$ for every orbital π_i in ϕ_0. We have $\delta(\pi'\alpha,\rho'\beta)=1$ and

$$[(i,j)]^{NS}_{\pi'\alpha,\rho'\beta}=\langle\alpha\alpha\cdots\alpha|(i,j)\alpha\alpha\cdots\alpha\rangle = 1$$

in (16). The result is the formula

$$\begin{aligned}&\langle\mathcal{A}[\phi_0(\alpha\alpha\cdots\alpha)]|\hat{H}|\mathcal{A}[\phi_0(\alpha\alpha\cdots\alpha)]\rangle \qquad (19)\\ &\quad=\sum_{\pi_i}\langle\pi_i|h_i|\pi_i\rangle+\sum_{\pi_i<\pi_j}\sum\{\langle\pi_i\pi_j|g_{ij}|\pi_i\pi_j\rangle-\langle\pi_i\pi_j|g_{ij}|\pi_j\pi_i\rangle\}.\end{aligned}$$

Since $\mathcal{A}[\phi_0(\alpha\alpha\cdots\alpha)] = (\alpha\alpha\cdots\alpha)\mathcal{A}[\phi_0]$, (19) is the formula for the matrix element $\langle\mathcal{A}(\phi_0)|\hat{H}|\mathcal{A}(\phi_0)\rangle$, where ϕ_0 consists entirely of singly-occupied orbitals. Thus $\mathcal{A}(\phi_0)$ is a "space only" Slater determinant, and (19) is analogous to the familiar formula for the energy of a determinantal wave function.

Appendix D contains a listing for a Fortran program to implement formulas (16)-(18). It finds the alignment permutation $\mathcal{L}$, evaluates the representation matrix elements for

$\mathcal{L}$ and $(i,j)\mathcal{L}$ from knowledge of the spin functions, and calculates the coefficients of the one- and two-electron integrals occurring in the energy matrix element between two SAAP's. This program was based on earlier, more complicated, formulas than those given here. An updated version is being written.

The Serber spin functions used with this program will be discussed in the next chapter. As is mentioned there, it is found more convenient to generate the spin functions and then obtain the representation matrices from them, than to calculate these matrices directly.

Derivation of the General Energy Matrix Element Formula

We seek to evaluate the integral

$$\begin{aligned} E &\overset{d}{\equiv} <\mathcal{A}[\phi_{\pi}\Theta_{\pi'\alpha}]|\hat{H}|\mathcal{A}[\phi_{\rho}\Theta_{\rho'\beta}]> = <\phi_{\pi}\Theta_{\pi'\alpha}|\hat{H}|\mathcal{A}[\phi_{\rho}\Theta_{\rho'\beta}]> \\ &= (N!)^{-1}\sum_{P}\varepsilon(P)<\phi_{\pi}\Theta_{\pi'\alpha}|\hat{H}|P[\phi_{\rho}\Theta_{\rho'\beta}]> \ , \end{aligned}$$

where $\pi\leqslant\pi'$, $\rho\leqslant\rho'$, and the sum runs over all of S_N. Since the Hamiltonian is assumed to contain no spin operators, space and spin separate:

$$\begin{aligned} E &= (N!)^{-1}\sum_{P}\varepsilon(P)\,[P]^{NS}_{\pi'\alpha,\rho'\beta}<\phi_{\pi}|\hat{H}|P\phi_{\rho}> \\ &= (N!)^{-1}\sum_{P}\varepsilon(P)\,[P]^{NS}_{\pi'\alpha,\rho'\beta}<\hat{H}\phi_{\pi}|P\phi_{\rho}> \ , \end{aligned} \tag{20}$$

where we have used the fact that H is Hermitian.

In terms of the one-electron Hamiltonians h_i and the electron repulsions g_{ij}, the N-electron Hamiltonian is

$$\hat{H} = \sum_i h_i + \sum_{i<j}\sum g_{ij} .$$

In order to simplify the derivation that follows, we shall write

$$\hat{H} = \sum_{i<j}\sum H_{ij} ,$$

in terms of the operators

$$H_{ij} = (N-1)^{-1}(h_i+h_j) + g_{ij}.$$

Thus the Hamiltonian is written in terms of two-electron operators. From (20), we have

$$E = (N!)^{-1} \sum_{i<j}\sum \sum_P \varepsilon(P)\,[P]^{NS}_{\pi\alpha,\rho\beta}\langle H_{ij}\phi_\pi|P\phi_\rho\rangle, \tag{21}$$

the sums on i and j being over electron labels, and the sum on P being over the symmetric group, S_N. The rest of the derivation is devoted to the simplification of this equation.

Reduction of the sum over permutations

We assume that ϕ_π and ϕ_ρ are the following products of orthonormal one-electron orbitals:

$$\phi_\pi(1,2,\ldots,N) = \pi_1(1) \cdots \pi_N(N),$$

$$\phi_\rho(1,2,\ldots,N) = \rho_1(1) \cdots \rho_N(N).$$

We write $(\phi_\rho)_{k,\ell,\ldots,m}$ to denote that part of ϕ_ρ occupied by electrons $k,\ell,\ldots,m$. For example, $(\phi_\rho)_k = \rho_k$. Then

$$\langle H_{ij}\phi_\pi | P\phi_\rho\rangle = \langle \pi_1 | (P\phi_\rho)_1\rangle \cdots \langle H_{ij}\pi_i\pi_j | (P\phi_\rho)_{i,j}\rangle \cdots \langle \pi_N | (P\phi_\rho)_N\rangle .$$

This integral is zero unless $\langle \pi_k | (P\phi_\rho)_k\rangle = 1$ for every k other than i and j.

It is clear that not every P in (21) will make a nonzero contribution to the i,j-term. Suppose that Q_{ij} is a permutation aligning ϕ_ρ with ϕ_π in such a way that $(Q_{ij}\phi_\rho)_k = \pi_k$ for every k other than i and j. Then

$$\langle H_{ij}\phi_\pi | Q_{ij}\phi_\rho\rangle = \langle H_{ij}\pi_i\pi_j | (Q_{ij}\phi_\rho)_{i,j}\rangle \neq 0 .$$

Furthermore, for any geminal permutation G in $\mathcal{G}_\rho$, $G\phi_\rho = \phi_\rho$ and

$$\langle H_{ij}\phi_\pi | Q_{ij}G\phi_\rho\rangle = \langle H_{ij}\phi_\pi | Q_{ij}\phi_\rho\rangle \neq 0 .$$

Thus the set of permutations $\{Q_{ij}G | G \in \mathcal{G}_\rho\}$ makes nonzero contributions to the i,j-term in (21). We will show that other permutations may do this.

The two orbitals from ϕ_ρ that are occupied in $(Q_{ij}\phi_\rho)$ by electrons i and j are uniquely determined by the condition that $\langle H_{ij}\phi_\pi | Q_{ij}\phi_\rho\rangle$ not vanish. Let these two orbitals be ρ_r and ρ_s:

$$(Q_{ij}\phi_\rho)_i = \rho_r , \qquad (Q_{ij}\phi_\rho)_j = \rho_s .$$

This is not meant to suggest that r and s are uniquely determined by i and j. If ρ_r or ρ_s is a double in ϕ_ρ, then there may be more than one possible value of r or s.

We see that $(Q_{ij}\phi_\rho)$ is a rearrangement of ϕ_ρ that coincides with ϕ_π except possibly in the orbitals occupied by electrons i and j:

$$\phi_\pi = \pi_1 \cdots \pi_{i-1}\cdot\pi_i\cdot\pi_{i+1} \cdots \pi_{j-1}\cdot\pi_j\cdot\pi_{j+1} \cdots \pi_N \;,$$

$$(Q_{ij}\phi_\rho) = \pi_1 \cdots \pi_{i-1}\cdot\rho_r\cdot\pi_{i+1} \cdots \pi_{j-1}\cdot\rho_s\cdot\pi_{j+1} \cdots \pi_N \;.$$

In order to suggest this, we adopt the notation Q^{ij}_{rs} for Q_{ij}. The reader should note that Q^{ij}_{rs} has the following properties:

$$\text{(i)} \qquad (i,j)Q^{ij}_{rs} = Q^{ij}_{rs}\cdot(r,s) = Q^{ij}_{sr} \;;$$

$$\text{(ii)} \qquad Q^{ij}_{rs} = Q^{ji}_{sr} \;.$$

It is easy to see that not only

$$\langle H_{ij}\phi_\pi | Q^{ij}_{rs}\phi_\rho\rangle = \langle H_{ij}\pi_i\pi_j | (Q^{ij}_{rs}\phi_\rho)_{i,j}\rangle = \langle H_{ij}\pi_i\pi_j | \rho_r\rho_s\rangle \neq 0,$$

but also

$$\langle H_{ij}\phi_\pi | (i,j)\cdot Q^{ij}_{rs}\phi_\rho\rangle = \langle H_{ij}\pi_i\pi_j | \rho_s\rho_r\rangle \neq 0.$$

Clearly _every_ permutation making a nonzero contribution to the i,j-term of (21) is of the form

$$(Q^{ij}_{rs}G) \qquad \text{or} \qquad [(i,j)Q^{ij}_{rs}G], \tag{22}$$

where G is a geminal permutation belonging to $\mathcal{G}_\rho$.

The result is that the sum over N! permutations in (21) reduces to a sum over just those permutations with the forms

(22). It must be kept in mind that these permutations may not all be distinct. The sets

$$\{Q_{rs}^{ij}G \mid G\varepsilon\mathcal{G}_\rho\} \text{ and } \{(i,j)Q_{rs}^{ij}G \mid G\varepsilon\mathcal{G}_\rho\} \qquad (23)$$

each consist of distinct permutations. We now investigate the conditions under which the sets may overlap.

The two sets share an element if and only if there are two geminal permutations G and G' in $\mathcal{G}_\rho$ such that

$$\begin{array}{l} (i,j)Q_{rs}^{ij}G' = Q_{rs}^{ij}G \\ \qquad \| \\ Q_{rs}^{ij}\cdot(r,s)G' \end{array}$$

But then $\quad (r,s) = (Q_{rs}^{ij})^{-1}Q_{rs}^{ij}GG'^{-1} = GG'^{-1}\varepsilon\mathcal{G}_\rho$.

Thus $\{Q_{rs}^{ij}G\}$ and $\{(i,j)Q_{rs}^{ij}G\} = \{Q_{rs}^{ij}\cdot(r,s)G\}$ share an element only if $(r,s)\varepsilon\mathcal{G}_\rho$: in fact, then they share <u>all</u> their elements.

Therefore, the sum in (21) over all permutations reduces to a sum over the permutations in the two sets (23), but this sum should be divided by two if r and s are in geminal positions and $(r,s)\varepsilon\mathcal{G}_\rho$ (i.e., if $\rho_r=\rho_s$). Using this result in (21), we obtain

$$E = (N!)^{-1}\sum_{i<j}\sum 2^{-\delta(\rho_r,\rho_s)}\sum_{G\varepsilon\mathcal{G}_\rho}\{\varepsilon(Q_{rs}^{ij}G)\,[Q_{rs}^{ij}G]_{\pi\alpha,\rho\beta}^{NS}\langle H_{ij}\phi_\pi|Q_{rs}^{ij}\phi_\rho\rangle$$

$$+\ \varepsilon[(i,j)Q_{rs}^{ij}G]\,[(i,j)Q_{rs}^{ij}G]_{\pi\alpha,\rho\beta}^{NS}\langle H_{ij}\phi_\pi|(i,j)Q_{rs}^{ij}\phi_\rho\rangle\},$$

or

$$E = (N!)^{-1}\sum_{i<j}\sum 2^{-\delta(\rho_r,\rho_s)}\varepsilon(Q^{ij}_{rs})\sum_{G\varepsilon\mathcal{G}_\rho}\varepsilon(G)\times$$

$$\times\{[Q^{ij}_{rs}G]^{NS}_{\pi'\alpha,\rho'\beta}\langle H_{ij}\pi_i\pi_j|\rho_r\rho_s\rangle$$

$$-[(i,j)Q^{ij}_{rs}G]^{NS}_{\pi'\alpha,\rho'\beta}\langle H_{ij}\pi_i\pi_j|\rho_s\rho_r\rangle\},$$

where $\delta(\rho_r,\rho_s)$ is the Kronecker delta.

This result can be simplified by noticing that

(i) for any permutation P, $[PG]^{NS}_{\pi'\alpha,\rho'\beta} = [P]^{NS}_{\pi'\alpha,\rho'\beta}[G]^{NS}_{\rho'\beta,\rho'\beta}$ because the matrices representing geminal permutations are diagonal;

(ii) $\sum_{G\varepsilon\mathcal{G}_\rho}\varepsilon(G)[G]^{NS}_{\rho'\beta,\rho'\beta} = 2^\rho$, from (11).

Thus we obtain

$$E = (2^\rho/N!)\sum_{i<j}\sum 2^{-\delta(\rho_r,\rho_s)}\varepsilon(Q^{ij}_{rs})\times$$

$$\times\{[Q^{ij}_{rs}]^{NS}_{\pi'\alpha,\rho'\beta}\langle H_{ij}\pi_i\pi_j|\rho_r\rho_s\rangle$$

$$-[(i,j)Q^{ij}_{rs}]^{NS}_{\pi'\alpha,\rho'\beta}\langle H_{ij}\pi_i\pi_j|\rho_s\rho_r\rangle\}, \tag{24}$$

the sums running over electrons.

Reduction of the sum over electron pairs

Equation (24) contains redundancies. Suppose that $\pi_i=\pi_k$. We make the following observations:

(i) It must be that $k=i\pm1$ and (i,k) is a geminal transposition.

(ii) The integrals arising from the k,j-term in (24) are $\langle H_{kj}\pi_k\pi_j|\rho_r\rho_s\rangle$ and $\langle H_{kj}\pi_k\pi_j|\rho_s\rho_r\rangle$, having the same values as $\langle H_{ij}\pi_i\pi_j|\rho_r\rho_s\rangle$ and $\langle H_{ij}\pi_i\pi_j|\rho_s\rho_r\rangle$, the integrals arising from the i,j-term. Orbitals ρ_r and ρ_s are the same in each case.

(iii) The alignment permutation Q^{kj}_{rs} arising from the k,j-term is

$$Q^{kj}_{rs} = (i,k)Q^{ij}_{rs} \qquad [\underline{\text{not}}\ (i,k)Q^{ij}_{rs}(i,k)^{-1}],$$

and since (i,k) is a geminal transposition belonging to $\mathscr{S}_\pi$,

$$\begin{aligned}\varepsilon(Q^{kj}_{rs})\,[Q^{kj}_{rs}]^{NS}_{\pi'\alpha,\rho'\beta} &= -\varepsilon(Q^{ij}_{rs})\,[(i,k)]^{NS}_{\pi'\alpha,\pi'\alpha} \times \\ &\qquad\qquad \times\ [Q^{ij}_{rs}]^{NS}_{\pi'\alpha,\rho'\beta} \\ &= \varepsilon(Q^{ij}_{rs})\,[Q^{ij}_{rs}]^{NS}_{\pi'\alpha,\rho'\beta}\ .\end{aligned}$$

Similarly,

$$\varepsilon(Q^{kj}_{rs})\,[(k,j)Q^{kj}_{rs}]^{NS}_{\pi'\alpha,\rho'\beta} = \varepsilon(Q^{ij}_{rs})\,[(i,j)Q^{ij}_{rs}]^{NS}_{\pi'\alpha,\rho'\beta}\ .$$

As a result, if $\pi_k=\pi_i$, the k,j-term in (24) makes the same contribution as the i,j-term. Generalizing this, all cases can be summarized as follows:

if π_i is:	and π_j is:	the number of equal contributions in (24) is:
double	same double	1
double	different double	4
double	single	2
single	double	2
single	single	1

In general, the number of equal contributions is

$$2^{[d_{ij}(\phi_\pi)-\delta(\pi_i,\pi_j)]},$$

where $d_{ij}(\phi_\pi)$ is the number of doubles in ϕ_π represented by the orbitals π_i and π_j.

Equation (24) is simplified by collecting together all the equal terms, summing only over distinct contributions. This is the same as *summing over different pairs of orbitals* in ϕ_π. Normalizing the SAAP's according to (13), we have

$$\begin{aligned} E = \sum_{\pi_i \leqslant \pi_j} \sum \, & 2^{p(i,j;r,s)} \varepsilon(Q^{ij}_{rs}) \times \\ & \times \{[Q^{ij}_{rs}]^{NS}_{\pi\alpha,\rho\beta} \langle H_{ij} \pi_i \pi_j | \rho_r \rho_s \rangle \\ & - [(i,j) Q^{ij}_{rs}]^{NS}_{\pi\alpha,\rho\beta} \langle H_{ij} \pi_i \pi_j | \rho_s \rho_r \rangle\}, \qquad (25) \end{aligned}$$

where

$$p(i,j;r,s) = [(\rho-\pi)/2] + d_{ij}(\phi_\pi) - \delta(\pi_i,\pi_j) - \delta(\rho_r,\rho_s).$$

The meaning of the sum needs clarification. If $\phi_\pi=\phi_\rho$, the sum runs over every *distinct* pair of orbitals. For example, if $\phi_\pi=\phi_\rho=\pi_1\pi_2\pi_3\pi_4=aabc$, the sum includes the orbital pairs (a,a), (a,b), (a,c), and (b,c). Each of these appears once: doubles do not cause duplicate contributions. If ϕ_π and ϕ_ρ differ by two orbitals, π_α and $\pi_\beta \geqslant \pi_\alpha$ in ϕ_π, then the sum reduces to the one term with $\pi_i = \pi_\alpha$ and $\pi_j = \pi_\beta$. In every other term, the integrals are zero. If ϕ_π and ϕ_ρ differ by one orbital, π_α in ϕ_π, then the sum is over every distinct orbital pair in ϕ_π that contains π_α. For example, if ϕ_π=aabc and ϕ_ρ=aabd, then the sum is over the orbital pairs (a,c), (b,c).

If π_i or π_j is doubly-occupied in ϕ_π, there is an ambiguity in the meanings of H_{ij} and Q^{ij}_{rs}, which are defined in terms of electron labels. We adopt the following convention: whenever double occupancy in π_i or π_j makes the choice of i or j ambiguous, we choose the lower electron number. If, for example, ϕ_π=aabc and ϕ_ρ=ddbc, so that $\pi_i = \pi_j$=a is the only orbital pair occurring in the sum, i and j are unambiguously defined to be 1 and 2 (it does not matter which is which). On the other hand, if ϕ_π=aabc and ϕ_ρ=aabd, then the sum contains a term with π_i=a, π_j=c, for which we choose i=1 and not i=2.

It is not necessary to have a different alignment permutation for each term of (25). Let $\mathcal{L}$ be a "maximal alignment" permutation for ϕ_π and ϕ_ρ which, when operating on ϕ_ρ, has the property that orbitals common to ϕ_π and ϕ_ρ are occupied by the same electrons in ϕ_π and $(\mathcal{L}\phi_\rho)$. This means that the differing orbitals in ϕ_π and $(\mathcal{L}\phi_\rho)$ are also occupied by the same electrons. The electrons occupying the differing orbitals in ϕ_π are unambiguously defined by the convention adopted for i and j.

Any $\mathcal{L}$ with this behavior will perform the duties of every Q_{rs}^{ij} in the sum of (25). Thus we obtain a simpler result:

$$E = \varepsilon(\mathcal{L}) \sum_{\pi_i \leqslant \pi_j} \sum 2^{p(i,j;r,s)} \times$$

$$\times \{[\mathcal{L}]^{NS}_{\pi'\alpha,\rho'\beta} \langle H_{ij}\pi_i\pi_j|\rho_r\rho_s\rangle$$

$$- [(i,j)\mathcal{L}]^{NS}_{\pi'\alpha,\rho'\beta} \langle H_{ij}\pi_i\pi_j|\rho_s\rho_r\rangle\} \ . \qquad (26)$$

The exponent of two appearing in this equation is

$$p(i,j;r,s) = [(\rho-\pi)/2] + d_{ij}(\phi_\pi) - \delta(\pi_i,\pi_j) - \delta(\rho_r,\rho_s),$$

a number apparently not symmetric in its arguments. However,

$$d_{ij}(\phi_\pi) = \pi - \tilde{\pi}_{ij} \quad ,$$

where $\tilde{\pi}_{ij} = \tilde{\rho}_{rs}$ is the number of doubles in ϕ_π other than π_i and π_j or the number of doubles in ϕ_ρ other than ρ_r and ρ_s. Thus

$$p(i,j;r,s) = [(\pi/2) - (\tilde{\pi}_{ij}/2) - \delta(\pi_i,\pi_j)]$$

$$+ [(\rho/2) - (\tilde{\rho}_{rs}/2) - \delta(\rho_r,\rho_s)]$$

$$= [\tfrac{1}{2}d_{ij}(\phi_\pi) - \delta(\pi_i,\pi_j)]$$

$$+ [\tfrac{1}{2}d_{rs}(\phi_\rho) - \delta(\rho_r,\rho_s)],$$

or $$p(i,j;r,s) = p(i,j) + p(r,s),$$

where $$p(i,j) = [\tfrac{1}{2}d_{ij}(\phi_\pi) - \delta(\pi_i,\pi_j)]$$

and $$p(r,s) = [\tfrac{1}{2}d_{rs}(\phi_\rho) - \delta(\rho_r,\rho_s)].$$

This can be cast into a form more convenient for programming by noticing that

$$2^{p(i,j)} = \left\{\frac{n(\pi_i,\phi_\pi)\,n(\pi_j,\phi_\pi)}{[1+\delta(\pi_i,\pi_j)]^3}\right\}^{1/2},$$

a result obtained by considering all possible cases:

π_i	π_j	$p(i,j)$	$\left\{\frac{n(\pi_i,\phi_\pi)\,n(\pi_j,\phi_\pi)}{[1+\delta(\pi_i,\pi_j)]^3}\right\}^{1/2}$
double	same double	$\frac{1}{2} - 1 = -\frac{1}{2}$	$(4/8)^{1/2} = 1/\sqrt{2}$
double	different double	$1 - 0 = 1$	$(4/1)^{1/2} = 2$
double	single	$\frac{1}{2} - 0 = \frac{1}{2}$	$(2/1)^{1/2} = \sqrt{2}$
single	double	$\frac{1}{2} - 0 = \frac{1}{2}$	$(2/1)^{1/2} = \sqrt{2}$
single	single	$0 - 0 = 0$	$(1/1)^{1/2} = 1$

We obtain the final results

$$2^{p(i,j;r,s)} = N(\pi_i,\pi_j;\rho_r,\rho_s)$$

$$= \left\{\frac{n(\pi_i,\phi_\pi)\,n(\pi_j,\phi_\pi)\,n(\rho_r,\phi_\rho)\,n(\rho_s,\phi_\rho)}{[1+\delta(\pi_i,\pi_j)]^3\,[1+\delta(\rho_r,\rho_s)]^3}\right\}^{1/2}$$

and

$$\begin{aligned}
E &\overset{d}{=} \langle \mathcal{A}[\phi_{\pi}\Theta_{\pi'\alpha}]|\hat{H}|\mathcal{A}[\phi_{\rho}\Theta_{\rho'\beta}]\rangle \\
&= \varepsilon(\mathcal{L}) \sum_{\pi_i \leq \pi_j}\sum N(\pi_i,\pi_j;\rho_r,\rho_s) \times \\
&\quad \times \ \{[\mathcal{L}]^{NS}_{\pi'\alpha,\rho'\beta}\langle H_{ij}\pi_i\pi_j|\rho_r\rho_s\rangle \\
&\qquad\qquad - [(i,j)\mathcal{L}]^{NS}_{\pi'\alpha,\rho'\beta}\langle H_{ij}\pi_i\pi_j|\rho_s\rho_r\rangle\} \ .
\end{aligned}$$

This is the general energy matrix element formula quoted in (15) on page 20. It is also, of course, the matrix element between SAAP's of any operator expressible as a sum of two-electron operators.

The only properties of the spin eigenfunctions that were used in deriving this equation were those of (10) and (11). In other words, we have assumed that the spin function in a SAAP is antisymmetric in every geminal pair which is a double in the space product. We have also assumed that the spin functions can be labelled $\Theta_{\pi'\alpha}$, indicating that the functions are antisymmetric in the first π' geminal pairs, and symmetric in the next one. As we shall see, Serber spin functions are not the only ones with these properties. It will turn out, though, that Serber functions are particularly easy to generate.

Derivation of the Matrix Element Formula in Specific Cases

The general formula derived above needs no discussion when ϕ_π and ϕ_ρ differ by two orbitals. The sum reduces to just one term, and no one-electron integrals arise. One obtains (18) immediately. The other two cases are more complicated, however.

Case when $\Phi_\pi = \Phi_\rho$

In this event, $\rho_r=\pi_i$, $\rho_s=\pi_j$, and the alignment permutation is $\mathcal{L}=I$. Defining $n(\pi_i) = n(\pi_i,\phi_\pi) = n(\pi_i,\phi_\rho)$,

$$E = \sum_{\pi_i\leq\pi_j}\sum \{n(\pi_i)n(\pi_j)/[1+\delta(\pi_i,\pi_j)]^3\} \times$$

$$\times \quad \{\delta(\pi'\alpha,\rho'\beta)\langle H_{ij}\pi_i\pi_j|\pi_i\pi_j\rangle - [(i,j)]^{NS}_{\pi'\alpha,\rho'\beta}\langle H_{ij}\pi_i\pi_j|\pi_j\pi_i\rangle\}.$$

Breaking the sum into terms with $\pi_j=\pi_i$ (when π_i is a double) and terms with $\pi_j>\pi_i$, and substituting the definition of H_{ij}, one obtains

$$\begin{aligned}
E = {} & \delta(\pi'\alpha,\rho'\beta)\sum_{\pi_i} [n(\pi_i)-1][(\tfrac{2}{N-1})\langle\pi_i|h|\pi_i\rangle + \langle\pi_i\pi_i|g|\pi_i\pi_i\rangle] \\
& + \sum_{\pi_i<\pi_j}\sum [n(\pi_i)n(\pi_j)] \times \\
& \times \Big\{\delta(\pi'\alpha,\rho'\beta)\{(N-1)^{-1}[\langle\pi_i|h|\pi_i\rangle+\langle\pi_j|h|\pi_j\rangle]+\langle\pi_i\pi_j|g|\pi_i\pi_j\rangle\} \\
& \qquad -[(i,j)]^{NS}_{\pi'\alpha,\rho'\beta}\langle\pi_i\pi_j|g|\pi_j\pi_i\rangle\Big\},
\end{aligned}$$

where $g=(e^2/r_{12})$ and h is a one-electron Hamiltonian.

Since

$$\sum_{\pi_i<\pi_j}\sum n(\pi_i)n(\pi_j)\,[<\pi_i|h|\pi_i>+<\pi_j|h|\pi_j>] + 2\sum_{\pi_i}[n(\pi_i)-1]<\pi_i|h|\pi_i>$$

$$= (N-1)\sum_{\pi_i} n(\pi_i)<\pi_i|h|\pi_i> ,$$

the final result is

$$E = \delta(\pi'\alpha,\rho'\beta)\sum_{\pi_i}\{n(\pi_i)<\pi_i|h|\pi_i> + [n(\pi_i)-1]<\pi_i\pi_i|g|\pi_i\pi_i>\}$$

$$+ \sum_{\pi_i<\pi_j}\sum n(\pi_i)n(\pi_j)\ \times$$

$$\times\ \{\delta(\pi'\alpha,\rho'\beta)<\pi_i\pi_j|g|\pi_i\pi_j> - [(i,j)]^{NS}_{\pi'\alpha,\rho'\beta}<\pi_i\pi_j|g|\pi_j\pi_i>\} ,$$

where the sums run over distinct orbitals. This is the result quoted in (16), on page 22.

<u>Case when ϕ_π and ϕ_ρ differ by one orbital</u>

Suppose that the differing orbital is π_μ in ϕ_π and ρ_σ in ϕ_ρ. There is only one sum in the matrix element:

$$E = \varepsilon(\mathcal{L})\ \sum_{\pi_j}^{c} N(\pi_\mu,\pi_j;\rho_\sigma,\pi_j)\ \times$$

$$\times\{[\mathcal{L}]^{NS}_{\pi'\alpha,\rho'\beta}<H_{\mu j}\pi_\mu\pi_j|\rho_\sigma\pi_j> - [(\mu,j)\mathcal{L}]^{NS}_{\pi'\alpha,\rho'\beta}<H_{\mu j}\pi_\mu\pi_j|\pi_j\rho_\sigma>\},$$

where the sum is over distinct orbitals in ϕ_π that are also in ϕ_ρ, and

$$N(\pi_\mu,\pi_j;\rho_\sigma,\pi_j) = \left\{\frac{n(\pi_\mu,\phi_\pi)\,n(\pi_j,\phi_\pi)\,n(\rho_\sigma,\phi_\rho)\,n(\pi_j,\phi_\rho)}{[1+\delta(\pi_\mu,\pi_j)]^3\,[1+\delta(\rho_\sigma,\pi_j)]^3}\right\}^{1/2} .$$

This case is much more complex than the other two. If π_μ or ρ_σ is a double, the sum includes a term with π_j equal to π_μ or ρ_σ. It is possible that π_μ occurs in ϕ_ρ, and ρ_σ can occur in ϕ_π. Altogether, there are twelve possible cases, shown in Table 1.

Using $[n(\pi_\mu,\phi_\pi)-1]$ as a "delta function" for double occupancy in π_μ in ϕ_π, the matrix element breaks down as follows:

$$\begin{aligned}
E = \varepsilon(\mathcal{L})\,[\mathcal{L}]^{NS}_{\pi'\alpha,\rho'\beta}\{&[n(\pi_\mu,\phi_\pi)-1][2n(\rho_\sigma,\phi_\rho)]^{1/2} \times \\
&\times[(N-1)^{-1}\langle\pi_\mu|h|\rho_\sigma\rangle + \langle\pi_\mu\pi_\mu|g|\rho_\sigma\pi_\mu\rangle] \\
&+ [n(\rho_\sigma,\phi_\rho)-1][2n(\pi_\mu,\phi_\pi)]^{1/2}\times \\
&\times[(N-1)^{-1}\langle\pi_\mu|h|\rho_\sigma\rangle + \langle\pi_\mu\rho_\sigma|g|\rho_\sigma\rho_\sigma\rangle]\} \\
+ \varepsilon(\mathcal{L}) \sum_{\substack{\pi_j \\ (\neq\pi_\mu,\rho_\sigma)}} &[n(\pi_\mu,\phi_\pi)\,n(\pi_j,\phi_\pi)\,n(\pi_j,\phi_\rho)\,n(\rho_\sigma,\phi_\rho)]^{1/2} \times \\
\times \{&[\mathcal{L}]^{NS}_{\pi'\alpha,\rho'\beta}[(N-1)^{-1}\langle\pi_\mu|h|\rho_\sigma\rangle + \langle\pi_\mu\pi_j|g|\rho_\sigma\pi_j\rangle] \\
&- [(\mu,j)\mathcal{L}]^{NS}_{\pi'\alpha,\rho'\beta}\langle\pi_\mu\pi_j|g|\pi_j\rho_\sigma\rangle\} .
\end{aligned}$$

The coefficient of $\langle\pi_\mu|h|\rho_\sigma\rangle$ in this equation contains the quantity

Table 1. Situations occurring when ϕ_π and ϕ_ρ differ by one

π_μ		π_j (in ϕ_π)[a]	Example[b] of ϕ_π	ρ_σ		π_j (in ϕ_ρ)[a]	Example[b] of ϕ_ρ
s		s	$(\mu j/\cdots m)$	s		s	$(\sigma j/\cdots m)$
				d		s	$(mj/\cdots m)$
				d	=	d	$(jj/\cdots m)$
s		d	$(\mu j/\cdots jm)$	s		d	$(\sigma j/\cdots jm)$
				d	≠	d	$(mj/\cdots jm)$
d		s	$(\mu j/\cdots \mu m)$	s		s	$(\sigma j/\cdots \mu m)$
				d		s	$(mj/\cdots \mu m)$
				d	=	d	$(jj/\cdots \mu m)$
d	≠	d	$(\mu j/\cdots \mu jm)$	s		d	$(\sigma j/\cdots \mu jm)$
				d	≠	d	$(mj/\cdots \mu jm)$
d	=	d	$(jj/\cdots m)$	s		s	$(\sigma j/\cdots m)$
				d		s	$(mj/\cdots m)$

[a] Notation: "d" means double, "s" means single.

[b] In the examples, orbitals are represented by their subscripts. The orbitals occupied by electrons μ and j are listed to the left of the slash. The differing orbital is listed first.

$$\mathcal{N} \overset{d}{=} [n(\pi_\mu,\phi_\pi)-1][2n(\rho_\sigma,\phi_\rho)]^{1/2}+[n(\rho_\sigma,\phi_\rho)-1][2n(\pi_\mu,\phi_\pi)]^{1/2}$$
$$+ [n(\pi_\mu,\phi_\pi)n(\rho_\sigma,\phi_\rho)]^{1/2} \sum_{\substack{\pi_j \\ (\neq\pi_\mu,\rho_\sigma)}} [n(\pi_j,\phi_\pi)n(\pi_j,\phi_\rho)]^{1/2} .$$

It can be seen from Table 1 that, when π_j does not equal π_μ or ρ_σ, it is a double or single in both ϕ_π and ϕ_ρ. Thus

$$\sum_{\substack{\pi_j \\ (\neq\pi_\mu,\rho_\sigma)}} [n(\pi_j,\phi_\pi)n(\pi_j,\phi_\rho)]^{1/2} = 2\cdot(\text{number of doubles other than } \pi_\mu \text{ and } \rho_\sigma) + 1\cdot(\text{number of singles other than } \pi_\mu \text{ and } \rho_\sigma)$$

$$= \text{number of electrons occupying orbitals other than } \pi_\mu \text{ and } \rho_\sigma .$$

Because of this, the possible values of $\mathcal{N}$ are:

π_μ (in ϕ_π)	ρ_σ (in ϕ_ρ)	$\mathcal{N}$
s	s	$[0+0+\ 1\ (N-1)] = \quad (N-1)$
s	d	$[0+\sqrt{2}+\sqrt{2}\cdot(N-2)] = \sqrt{2}(N-1)$
d	s	$[\sqrt{2}+0+\sqrt{2}\cdot(N-2)] = \sqrt{2}(N-1)$
d	d	$[2+2+\ 2\ (N-3)] = \ 2(N-1)$

The result is that $\mathcal{N} = (N-1)[n(\pi_\mu,\phi_\pi)n(\rho_\sigma,\phi_\rho)]^{1/2}$, and so the matrix element is

$$\begin{aligned}
E = {} & [n(\pi_\mu,\phi_\pi)\,n(\rho_\sigma,\phi_\rho)]^{1/2}\,\varepsilon(\mathcal{L}) \times \\
& \times \Bigl\{ [\mathcal{L}]^{NS}_{\pi'\alpha,\rho'\beta} \{ \langle\pi_\mu|h|\rho_\sigma\rangle + [n(\pi_\mu,\phi_\pi)-1]\langle\pi_\mu\pi_\mu|g|\rho_\sigma\pi_\mu\rangle \\
& \qquad\qquad + [n(\rho_\sigma,\phi_\rho)-1]\langle\pi_\mu\rho_\sigma|g|\rho_\sigma\rho_\sigma\rangle \} \\
& + \sum_{\substack{\pi_j \\ (\neq\pi_\mu,\rho_\sigma)}} n(\pi_j,\phi_\pi)\{ [\mathcal{L}]^{NS}_{\pi'\alpha,\rho'\beta}\langle\pi_\mu\pi_j|g|\rho_\sigma\pi_j\rangle \\
& \qquad\qquad - [(\mu,j)\mathcal{L}]^{NS}_{\pi'\alpha,\rho'\beta}\langle\pi_\mu\pi_j|g|\pi_j\rho_\sigma\rangle \} \Bigr\} .
\end{aligned}$$

This was the result quoted in (17) on page 23.

GENERATING SPIN EIGENFUNCTIONS WITHOUT USING GROUP ALGEBRA THEORY

Construction of Spin Eigenfunctions by Spin-Coupling Techniques

Yamanouchi-Kotani functions

The entire spin space for N electrons is spanned by the 2^N elementary spin product functions $\Theta_k(NM)$:

$$\Theta_1(N,\tfrac{N}{2}) = [\alpha(1)\alpha(2)\cdots\alpha(N)];$$

$$\{\Theta_k(N,\tfrac{N}{2}-1)\} = \{[\beta(1)\alpha(2)\cdots\alpha(N)], \ldots, [\alpha(1)\alpha(2)\cdots\beta(N)]\};$$

$$\cdots$$

$$\Theta_1(N,-\tfrac{N}{2}) = [\beta(1)\beta(2)\cdots\beta(N)].$$

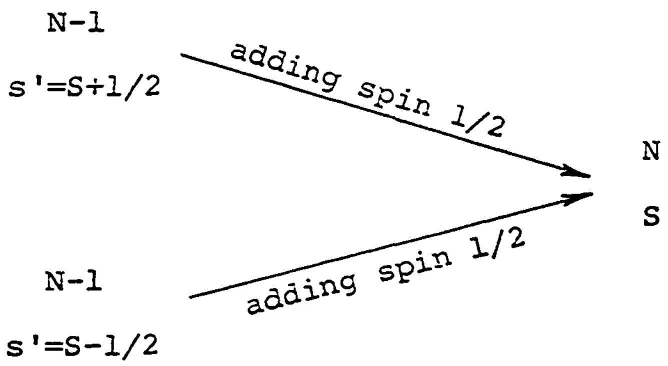
Of these, the products $\{\Theta_k(NM)\,|\,k=1,2,\ldots,\binom{N}{\frac{N}{2}+M}\}$ span the part of the N-spin space that is specific to $\hat{S}_z$-eigenvalue M.

On the other hand, this subspace is also spanned by spin eigenfunctions $\Theta_j(NSM)$, where j and S take on all possible values. Thus there is a transformation from the elementary spin products to the spin eigenfunctions:

$$\Theta_j(NSM) = \sum_k \Theta_k(NM)\gamma_{kj}(NSM). \qquad (27)$$

Here the product functions $\Theta_k(NM)$ belong to the reducible direct-product spin space for N fermions. The coefficients γ_{kj} must be chosen in a special way that forces $\Theta_j(NSM)$ into a subspace for the irreducible spin representation defined by N and S.

This is special case of the vector-coupling problem solved by Wigner (1931). The solution is given stepwise, by coupling spins one at a time. One starts with the spin of a single electron, couples it to the spin of another, and proceeds by coupling the spin of the Nth electron to the resultant spin of the first (N-1). At each stage, there are two ways in which one can obtain spin S for N electrons. Pictorially,



This sort of spin-coupling picture is called a <u>branching diagram</u>, and the two <u>routes</u> shown correspond to the two equations

$$\Theta_j(NSM) = -\sqrt{\frac{S-M+1}{2S+2}}\ \Theta_j(N-1,S+\tfrac{1}{2},M-\tfrac{1}{2})\cdot\alpha(N) + \sqrt{\frac{S+M+1}{2S+2}}\ \Theta_j(N-1,S+\tfrac{1}{2},M+\tfrac{1}{2})\cdot\beta(N) \qquad (28a)$$

and

$$\Theta_j(NSM) = \sqrt{\frac{S+M}{2S}}\ \Theta_j(N-1,S-\tfrac{1}{2},M-\tfrac{1}{2})\cdot\alpha(N) + \sqrt{\frac{S-M}{2S}}\ \Theta_j(N-1,S-\tfrac{1}{2},M+\tfrac{1}{2})\cdot\beta(N). \qquad (28b)$$

The coefficients appearing here are examples of Clebsch-Gordan or Wigner coefficients, which guarantee that the $\Theta_j(NSM)$ form an orthonormal basis for an irreducible representation of S_N.

In applying these equations recursively for given N, S, and M, one makes a spin-coupling choice at each stage - a choice between Equations (28a) and (28b). In the end, there are a number of ways in which N one-electron spins can be coupled so that the resultant spin is S. Each of these "spin-coupling schemes" is labelled by a value of the subscript j in (28). The schemes can be represented pictorially as routes on an N-electron branching diagram like the one given in Figure 1, where we have given at each intersection the number of spin functions resulting for the corresponding values of N and S. This number, which is independent of M, is

$$d(NS) = \frac{(2S+1)(N!)}{(\frac{N}{2}+S+1)!(\frac{N}{2}-S)!} = \frac{(2S+1)}{(N+1)}\binom{N+1}{\frac{N}{2}-S} .$$

Thus, for example, there are three spin eigenfunctions for N=4, S=1, _for each value of M_.

Since each N-electron spin function is derived from a chain of predecessors, this procedure is often called a "genealogical construction". It was introduced by Yamanouchi (1936, 1937, 1938), and a full account has been given by Kotani _et al_. (1955). We shall hereafter refer to spin functions constructed according to (28) as Yamanouchi-Kotani (YK)

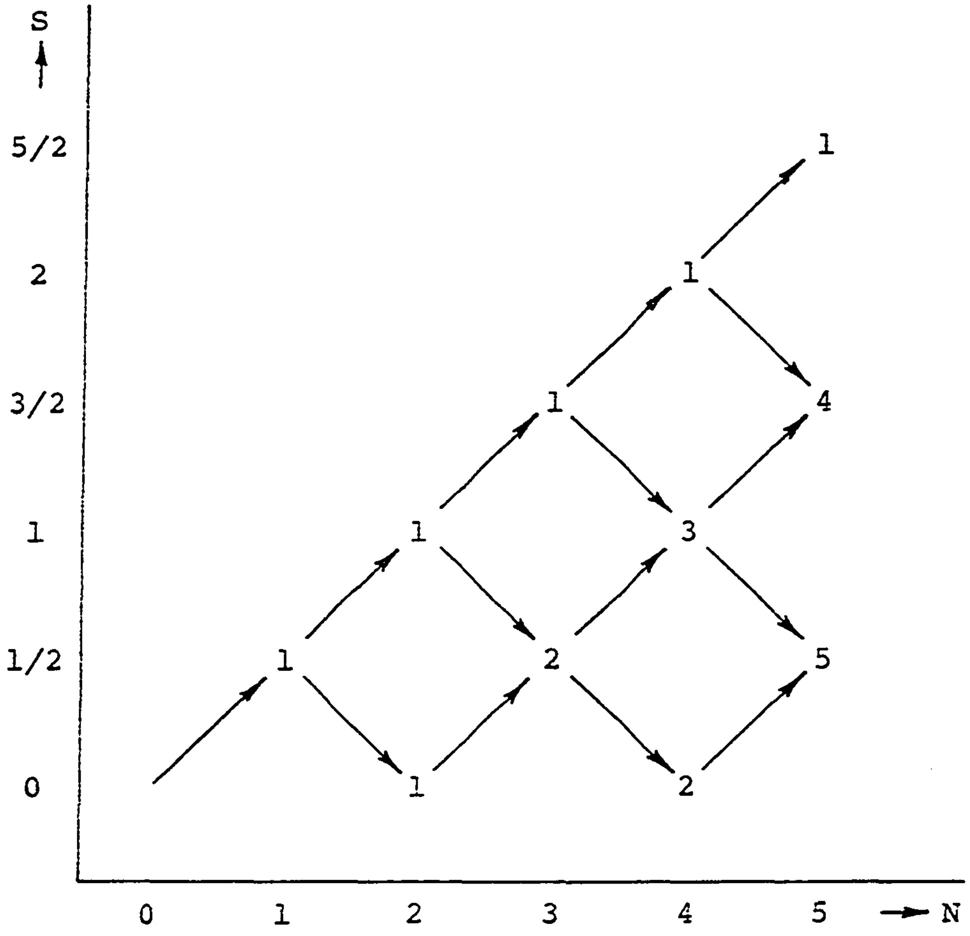


Figure 1. Yamanouchi-Kotani branching diagram

spin functions, and to Figure 1 as a YK branching diagram.

The YK functions are a basis for a very special orthogonal representation of S_N. Not only are the matrices representing permutations in S_N fully reduced, but it will be observed from (28) that the representation of the subgroup S_{N-1} is also reduced. In fact, the recursive nature of these equations has the result that the representations of the subgroups S_{N-1}, S_{N-2}, ..., S_1 are <u>all</u> fully reduced. The YK spin representation is said to be adapted to the sequence

$$S_N, S_{N-1}, S_{N-2}, \ldots, S_1$$

of nested symmetric groups (Klein, Carlisle, and Matsen, 1970). We shall return to this point later.

Serber functions

In the last chapter, we found it useful to have orthogonal eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$ that were simultaneously eigenfunctions of all the geminal spin operators $\hat{S}^2(2\mu-1,2\mu)$, where μ labels a geminal pair of electrons. Such functions were first obtained by Serber (1934a, 1934b), using a genealogical procedure in which spins were coupled two at a time.

Assume for the moment that N=2n is even. Then, defining geminal spin functions $w_\mu(s_\mu,m_\mu)$ for the μth geminal pair,

$$\begin{aligned}
w_\mu(1,1) &= \alpha(2\mu-1)\alpha(2\mu), \\
w_\mu(1,0) &= [\alpha(2\mu-1)\beta(2\mu)+\beta(2\mu-1)\alpha(2\mu)]/\surd 2, \\
w_\mu(1,-1) &= \beta(2\mu-1)\beta(2\mu), \\
w_\mu(0,0) &= [\alpha(2\mu-1)\beta(2\mu)-\beta(2\mu-1)\alpha(2\mu)]/\surd 2,
\end{aligned} \qquad (29)$$

it is possible to make 2n-electron spin eigenfunctions from these:

$$\Theta_{\pi\alpha}(NSM) = \sum_{\{m_\mu\}} c_{\pi\alpha}(m_1,\ldots,m_n)[w_1(s_1,m_1) \cdots w_n(s_n,m_n)]. \qquad (30)$$

Here the sum runs over all choices of $m_1, m_2, \ldots, m_n$ such that $\Sigma m_\mu = M$. Since each s_μ is fixed, the functions (30) will be automatically eigenfunctions of $\hat{S}^2(2\mu-1,2\mu)$ for each μ. The subscript "π" on $\Theta_{\pi\alpha}(NSM)$ indicates that

$$s_1=m_1=s_2=m_2= \ldots =s_\pi=m_\pi=0.$$

Thus $\Theta_{\pi\alpha}(NSM)$ is antisymmetric under the geminal transpositions of $\mathscr{G}_\pi$.

Each geminal spin function $w_\mu(s_\mu,m_\mu)$ belongs to an irreducible representation $\Gamma(s_\mu)$ for two electrons, so $\Theta_{\pi\alpha}(NSM)$ automatically belongs to the space for the direct-product representation

$$\Gamma(s_1) \otimes \Gamma(s_2) \otimes \cdots \otimes \Gamma(s_n).$$

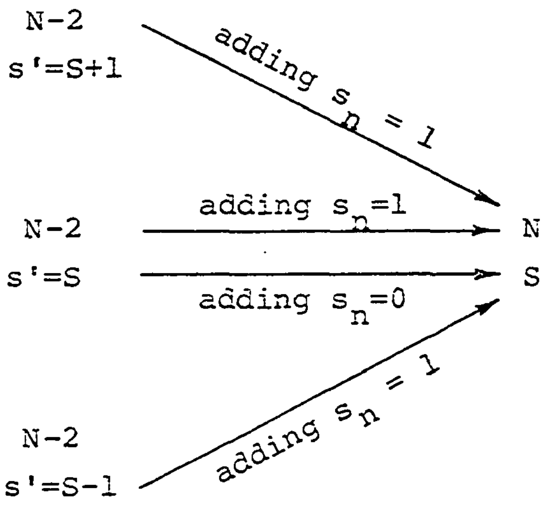
The coefficients must be chosen in a special way that forces $\Theta_{\pi\alpha}(NSM)$ into the irreducible space defined by N and S.

As before, the solution is given stepwise, in this case by coupling spins two at a time:

$$\Theta_{\pi\alpha}(NSM) = \sum_{m_n} W_{\pi\alpha}(s',s_n,S;M-m_n,m_n,M) \times \times \Theta_{\pi\alpha}(N-2,s',M-m_n)\cdot w_n(s_n,m_n) \qquad (31)$$

Here $\Theta_{\pi\alpha}(N-2,s',M-m_n)$ is an (N-2)-electron spin function for spin s'. Since s_n can be 0 or 1, s' can be S+1, S, or S-1. The numbers $W_{\pi\alpha}(s',s_n,S;M-m_n,m_n,M)$ are the Wigner coefficients.

There are four equations like (31), corresponding to the four spin-coupling ("branching") routes shown in the following diagram:



The ten Wigner coefficients involved are available in standard references (Wigner, 1959, p. 193; Condon and Shortley, 1951, p. 76).

The different subscripts $\pi\alpha$ occurring in (31) correspond to different routes on a Serber branching diagram like that in Figure 2. As in the previous case, the values of d(NS) are shown at each intersection.

It follows from (31) that Serber spin functions are a basis for a representation of S_N that is adapted to the sequence

$$S_N,\ S_{N-2},\ S_{N-4},\ \ldots,\ S_2$$

of nested symmetric groups. It also follows from this equation that the representation of every geminal two-electron subgroup is fully reduced. These facts will prove useful

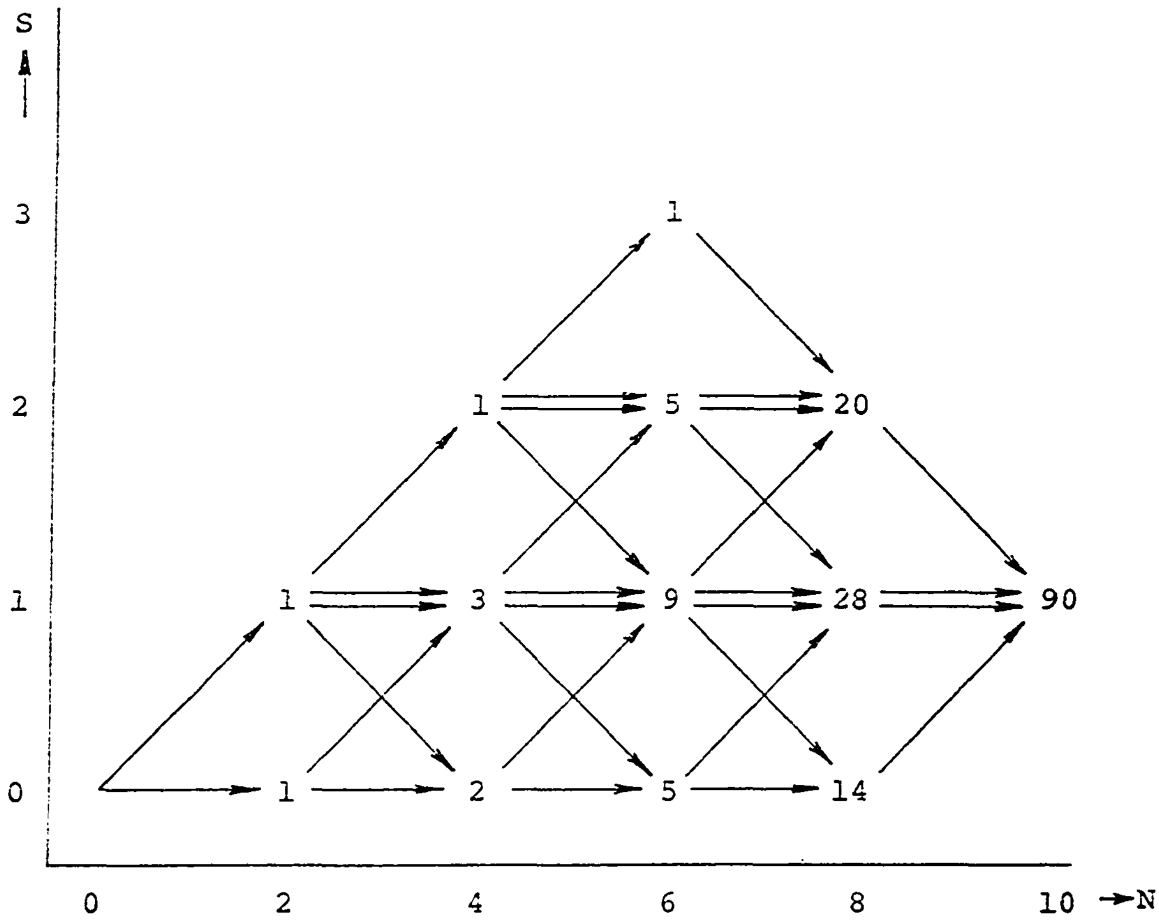


Figure 2. Serber branching diagram for states leading to N=10, S=1

later on.

"Serber-type" functions for odd N can be made by coupling the spin of the Nth electron to Serber functions for N'=N-1. The resulting functions will then have Serber-type behavior up to electron N'.

Comparison of YK and Serber functions

The differences between YK and Serber spin functions are not made obvious by the branching diagrams, Figures 1 and 2. The easiest way to reveal the differences is to examine the functions resulting from both genealogical schemes when, say, N=4, S=1, M=0. We use the notation introduced previously, and show with each function its branching route.

The YK functions turn out to be

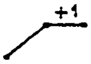
: $\theta_1(410) = (\alpha\beta-\beta\alpha)(\alpha\beta+\beta\alpha)/2;$

: $\theta_2(410) = [2\alpha\alpha\beta\beta-2\beta\beta\alpha\alpha-(\alpha\beta+\beta\alpha)(\alpha\beta-\beta\alpha)]/2\sqrt{3};$

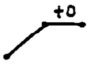
: $\theta_3(410) = [\alpha\alpha\beta\beta-\beta\beta\alpha\alpha+(\alpha\beta+\beta\alpha)(\alpha\beta-\beta\alpha)]/\sqrt{6}.$

On the other hand, the Serber functions are

: $\theta_{11}(410) = (\alpha\beta-\beta\alpha)(\alpha\beta+\beta\alpha)/2;$



: $\theta_{01}(410) = (\alpha\alpha\beta\beta-\beta\beta\alpha\alpha)/\sqrt{2};$



$: \Theta_{02}(410) = (\alpha\beta+\beta\alpha)(\alpha\beta-\beta\alpha)/2.$

The Serber functions are symmetric or antisymmetric in each geminal pair: they are simultaneous eigenfunctions of $\hat{S}^2$, $\hat{S}_z$, $\hat{s}_1^2$, and $\hat{s}_2^2$. The YK functions are less simple. The first one happens to be the same as the Serber function Θ_{11} because its branching diagram unambiguously fixes the spin of the first geminal pair to be zero. Since the total spin is one, the spin of the second pair must be $s_2=1$. In the other two YK functions, the spin of the first geminal pair is unambiguously $s_1=1$, but the second pair has no definite spin. In other words, the functions Θ_2 and Θ_3 are simultaneous eigenfunctions of $\hat{S}^2$, $\hat{S}_z$, and $\hat{s}_1^2$, but not of $\hat{s}_2^2$. This is because either $s_2=1$ or $s_2=0$ can couple with $s_1=1$ to give $S=1$. Rather than containing a pure contribution from $s_2=1$ or $s_2=0$, the YK functions Θ_2 and Θ_3 contain mixtures of both.

However, these functions can be labelled with the subscript "π", just as the Serber functions were. One merely defines the YK function $Y_{\pi\alpha}$(NSM) to be one for which the branching route has the form $\wedge$ for the first π geminal pairs, then turns upward for the next. In the example above,

$$\Theta_1 = Y_{11}, \quad \Theta_2 = Y_{01}, \quad \Theta_3 = Y_{02} .$$

The consequence of this notation is that the YK function $Y_{\pi\alpha}$ and the Serber function $\Theta_{\pi\alpha}$ will both be antisymmetric in the first π geminal pairs, symmetric in the next, then bear no fixed relation in the rest.

As was pointed out in the last chapter, this is the only behavior required of spin functions in the SAAP formalism. Either YK or Serber functions can be used, the choice depending on convenience in generating the functions.

Practicality of spin-coupling techniques

The genealogical construction of spin functions is inconvenient because it is recursive. In order to make an N-electron spin function, one must first generate every predecessor in the genealogical scheme. It can be seen from the branching diagrams that the complexity of the problem increases rapidly with N.

In order to make the three YK functions for N=4, S=1, M=0, one must generate the following fifteen functions:

N	S	functions for each M	M values required	total functions
1	1/2	1	+1/2, -1/2	2
2	0	1	0	1
2	1	1	1, 0, -1	3
3	1/2	2	+1/2, -1/2	4
3	3/2	1	+1/2, -1/2	2
4	1	3	0	3
				15

The calculations are so simple that this is no problem. But there are 90 spin functions for N=10, S=1, M=0. In order to get them, one must generate 660 functions altogether, some containing as many as 252 product functions.

At least one computer program is available for YK functions (Mattheiss, 1958), but the genealogical construction of spin functions is practical only for small N. In other cases, the programs require too much storage.

Löwdin's Projection Operators

By inverting (27), one can express any elementary spin product function $\theta_k(NM)$ in terms of all the spin eigenfunctions $\theta_j(NSM)$ having the same N and M:

$$\theta_k(NM) = \sum_S \sum_j \theta_j(NSM)c_{jk}(NSM). \tag{32}$$

It is apparent that the quantity

$$\sum_j \theta_j(NSM)c_{jk}(NSM) \tag{33}$$

is the <u>projection</u> of the spin product $\theta_k(NM)$ on the subspace for spin-eigenvalue S, a subspace spanned by the vectors $\{\theta_j(NSM)|\text{all } j\}$. This quantity is also called the <u>S-component</u> of $\theta_k(NM)$. Equation (32) says that, in general, an elementary spin product function may contain components for every value of S.

Löwdin (1955b, 1960, 1964) has introduced the operator

$$\hat{O}_S = \prod_{\substack{S' \\ (\neq S)}} \left[\frac{\hat{S}^2 - S'(S'+1)}{S(S+1)-S'(S'+1)}\right], \tag{34}$$

which, when operating on $\Theta_k(NM)$, successively annihilates every spin-component except the one shown in (33). Thus $\hat{O}_S$ projects an eigenfunction of $\hat{S}^2$ from any spin product function.

The application of (34) is straightforward, since the Dirac identity gives (McWeeny and Sutcliffe, 1969)

$$\hat{S}^2\Theta_k(NM) = [(M^2+\tfrac{N}{2})I + \sum_{\mu<\nu} \varepsilon_{\mu\nu}(NMk)\cdot(\mu,\nu)]\Theta_k(NM),$$

where I is the identity permutation, (μ,ν) is the transposition interchanging electrons μ and ν, and

$$\varepsilon_{\mu\nu}(NMk) = \begin{Bmatrix}0\\1\end{Bmatrix} \text{ if the spins of } \mu \text{ and } \nu \text{ are } \begin{Bmatrix}\text{the same}\\\text{different}\end{Bmatrix} \text{ in } \Theta_k(NM).$$

If $\hat{O}_S$ is applied to all the spin products for given N and M, the results will be redundant, but enough linearly independent spin eigenfunctions will be generated to span the spin-space for N and S. Löwdin (1964) has developed a procedure for choosing spin products that lead to independent eigenfunctions. A computer program is available (Rotenberg, 1963).

The resulting functions can be orthogonalized without difficulty. In order to obtain the sort of spin functions which are useful in the SAAP formalism, however, one must transform the Löwdin spin functions by diagonalizing the representation matrices for geminal transpositions. While this could be done with high-speed computers, it would not be as practical as other methods to be discussed.

Wigner Operators

There are several group-theoretical approaches to spin functions. The Wigner shift operators (Wigner, 1931, 1959)

$$\mathcal{P}_{\alpha}(NS\beta) = [d(NS)/N!]\sum_{P}[P^{-1}]^{NS}_{\beta\alpha}\,P, \tag{35}$$

with β fixed, will generate from a spin product $d(NS)$ spin eigenfunctions spanning the spin-space for N and S. Different values of β produce different bases for the same representation. Setting $\alpha=\beta$ produces a Wigner projection operator, which can be shown to be idempotent.

In order to make spin functions with these operators, it is necessary to know the N! spin representation matrices $[P]^{NS}$, for every P in S_N. These can all be generated from the (N-1) matrices representing the elementary transpositions (k-1,k), where k runs from 2 to N.

A spin-coupling procedure for evaluating these matrices was given by Yamanouchi (1936, 1937) and discussed by Kotani et al. (1955). The method was extended to the Serber spin representation by Mattheiss (1959), following a scheme suggested by Corson (1951). These procedures are recursive, and suffer from the disadvantages mentioned earlier.

It so happens (Pauncz, 1967) that the YK spin representation is the same as Young's orthogonal representation

(Young, 1932; Thrall, 1941), obtained by nonphysical arguments. Young's analysis leads to useful rules for evaluating the representation matrices for transpositions (Rutherford, 1948; Goddard, 1967a; Coleman, 1968). This method is quite practical.

It is possible to get along without the representation matrices. Setting $\beta=\alpha$ in (35) and summing over α, one obtains the new operator

$$\mathcal{P}_{\chi}(NS) = [d(NS)/N!] \sum_{P} \chi^{NS}(P)P, \tag{36}$$

where $\chi^{NS}(P)$ is the character of the permutation P in the representation given by the matrices $[P]^{NS}$. This operator, when applied to a spin product, does not in general produce one of the spin eigenfunctions $\Theta_{\alpha}(NSM)$, but some function in the (N,S)-space spanned by them. Thus (36) is the group-theoretical equivalent of Löwdin's operator.

The fly in the ointment is that, for ten electrons, there are 10! = 3,628,800 terms in the sum of (35) or (36). It would be extremely time-consuming to generate this many representation matrices from the nine elementary matrices. Even to get the characters required by (36) would be inefficient compared to Löwdin's method. The operators (35) and (36) have been used to make spin functions for small N (Smith and Harris, 1967; Harris, 1967), but they are not practical for many systems of interest.

Young's theory of the symmetric group leads to a more viable approach to projection operators through group theory. Only <u>some</u> permutations are required in projectors made in this way, and the calculations do not become so unwieldy. A discussion and further extension of this method is presented in the next chapter.

Serber Spin Functions
by Diagonalization of $\hat{S}^2$

The first new method suggested here for the construction of Serber spin functions is largely numerical in character.

We seek to construct spin eigenfunctions $\Theta_{\pi\alpha}(NSM)$ having the following properties:

$$\hat{S}^2\Theta_{\pi\alpha}(NSM) = \hbar^2 S(S+1)\Theta_{\pi\alpha}(NSM); \tag{37}$$

$$\hat{S}_z\Theta_{\pi\alpha}(NSM) = \hbar M\,\Theta_{\pi\alpha}(NSM); \tag{38}$$

$$g\Theta_{\pi\alpha}(NSM) = \pm\Theta_{\pi\alpha}(NSM) \text{ for every geminal transposition } g \text{ in } S_N; \tag{39}$$

$$g\Theta_{\pi\alpha}(NSM) = -\Theta_{\pi\alpha}(NSM) \text{ for every geminal transposition } g \text{ in } \mathcal{G}_\pi. \tag{40}$$

Properties (39) and (40) can be reworded: $\Theta_{\pi\alpha}(NSM)$ is to be an eigenfunction of every geminal spin operator $\hat{S}^2(2\mu-1,2\mu)$, and in particular, its eigenvalue under such an operator is to be zero when $\mu \leqslant \pi$.

It is natural to think of such functions as linear combinations of products, not of one-electron spin functions α and β, but of the geminal spin functions introduced in (29):

$$\begin{aligned} \sigma_\mu &= w_\mu(0,0) &&= [\alpha(2\mu-1)\beta(2\mu) - \beta(2\mu-1)\alpha(2\mu)]/\surd 2, \\ \bar{\tau}_\mu &= w_\mu(1,1) &&= \alpha(2\mu-1)\alpha(2\mu), \\ \tau_\mu &= w_\mu(1,0) &&= [\alpha(2\mu-1)\beta(2\mu) + \beta(2\mu-1)\alpha(2\mu)]/\surd 2, \\ \underline{\tau}_\mu &= w_\mu(1,-1) &&= \beta(2\mu-1)\beta(2\mu). \end{aligned} \tag{41}$$

For the moment we consider only the case when $N=2n$ is even. The product

$$W_M(s_1,\ldots,s_n;m_1,\ldots,m_n) = \prod_{\mu=1}^{n} w_\mu(s_\mu,m_\mu), \tag{42}$$

where $M=\Sigma m_\mu$, we shall call a <u>geminal spin product</u>. Obviously, each geminal spin product W_M is an eigenfunction of the geminal spin operators $\hat{S}^2(2\mu-1,2\mu)$ and $\hat{S}_z(2\mu-1,2\mu)$, for every μ.

The spin eigenfunction $\Theta_{\pi\alpha}(NSM)$, which is some linear combination

$$\begin{aligned} \Theta_{\pi\alpha}(NSM) = \sum_{\{s_\mu\}} \sum_{\{m_\mu\}} c_{\pi\alpha}^{NSM}(\{s_\mu\},\{m_\mu\}) \times \\ \times W_M(s_1,\ldots,s_n;m_1,\ldots,m_n), \end{aligned} \tag{43}$$

where $M=\Sigma m_\mu$ is fixed, is itself an eigenfunction of the operators $\hat{S}^2(2\mu-1,2\mu)$. Thus $\Theta_{\pi\alpha}(NSM)$ contains only those geminal spin products having the same geminal pair-spins: <u>each linear combination (43) has</u> $\{s_1,s_2,\ldots,s_n\}$ <u>fixed</u>.

We say that each linear combination has a certain "pair-spin combination", or "PSC". Each geminal pair spin is called a "PS". Furthermore, the subscript "π" on $\Theta_{\pi\alpha}$(NSM) means that every W_M in (43) has $s_\mu=0$ for $\mu=1,2,\ldots,\pi$. This follows from (40).

Now, given that the linear combinations (43), for fixed N, S, M, and π, are subject to the three conditions

(i) the PSC is fixed;

(ii) $s_\mu=0$ for $\mu\leqslant\pi$;

(iii) $\Sigma m_\mu=M$;

only one more condition is required to produce the $\Theta_{\pi\alpha}$(NSM): the linear combinations must diagonalize the $\hat{S}^2$-matrix. This, of course, forces the linear combinations to be eigenfunctions of $\hat{S}^2$.

Serber spin functions can be made, then, by the very simple algorithm shown in Figure 3. The algorithm is so simple that only one part of it requires further explanation - the calculation of the $\hat{S}^2$-matrix over geminal spin products.

The N-electron operators $\hat{S}_\pm$, $\hat{S}_z$, and $\hat{S}^2$ are related by

$$\hat{S}_-\hat{S}_+ = (\hat{S}_x-i\hat{S}_y)(\hat{S}_x+i\hat{S}_y) = \hat{S}_x^2 + \hat{S}_y^2 + i[\hat{S}_x,\hat{S}_y]$$

$$= \hat{S}^2 - \hat{S}_z^2 - \hat{S}_z,$$

or

$$\hat{S}^2 = \hat{S}_-\hat{S}_+ + \hat{S}_z(\hat{S}_z+1).$$

```
Determine all PSC's having the properties
    (i)   $s_\mu=0$ for $\mu=1,2,\ldots,\pi$;
    (ii)  $\sum_{\mu=1}^{n} s_\mu > |M|$.
  For each of these, do the following:
    construct every possible geminal spin product having $\Sigma m_\mu=M$;
    calculate the $\hat{S}^2$-matrix between these geminal spin products;
    diagonalize this $\hat{S}^2$-matrix;
    keep only those eigenvectors having the desired eigenvalue S.
```

Figure 3. Algorithm for construction of Serber spin functions with eigenvalues S, M, for use with a space product function having π doubles

Writing $\hat{S}_{\pm} = \sum_{\mu=1}^{n} \hat{s}_{\pm}(\mu)$ in terms of the geminal pairs,

$$\hat{S}^2 = \hat{S}_z(\hat{S}_z+1) + \sum_{\mu} \hat{s}_-(\mu)\hat{s}_+(\mu) + \sum_{\mu<\nu}\sum [\hat{s}_-(\mu)\hat{s}_+(\nu)+\hat{s}_-(\nu)\hat{s}_+(\mu)] .$$

The calculation of the $\hat{S}^2$-matrix is trivial when the operator is written in this form. The action of the second term on the geminal spin functions (41) is given by

$w_\mu(s_\mu,m_\mu)$	$[\hat{s}_-(\mu)\hat{s}_+(\mu)w_\mu(s_\mu,m_\mu)]$
σ	0
$\bar{\tau}$	0
τ	2τ
$\underline{\tau}$	$2\underline{\tau}$

Thus

$$\sum_{\mu} \hat{s}_-(\mu)\hat{s}_+(\mu)W_M = 2[n(\tau) + n(\underline{\tau})]W_M ,$$

where $n(\tau)$, for example, is the number of times that $w(1,0)=\tau$ occurs in W_M.

Since the geminal spin products (42) are orthogonal, the $\hat{S}^2$-matrix elements between such products (with M fixed) are given by

$$\langle W'_M|\hat{S}^2W_M\rangle = \{M(M+1) + 2[n(\tau)+n(\underline{\tau})]\} \delta(W'_M , W_M)$$

$$+ \langle W'_M| \sum_{\mu<\nu}\sum [\hat{s}_-(\mu)\hat{s}_+(\nu)+\hat{s}_-(\nu)\hat{s}_+(\mu)]W_M\rangle .$$

The contribution in {}-brackets is zero unless $W_M' = W_M$. On the other hand, the last term is zero unless W_M and W_M' differ in two geminal pairs, say those numbered κ and λ. In that case, the last term is [note that all geminal spins s_μ are the same in any two products W_M' and W_M in (43)]

$$<w_\kappa'(s_\kappa,m_\kappa')w_\lambda'(s_\lambda,m_\lambda')\,|\,[\hat{s}_-(\kappa)\hat{s}_+(\lambda)+\hat{s}_-(\lambda)\hat{s}_+(\kappa)]w_\kappa(s_\kappa,m_\kappa)w_\lambda(s_\lambda,m_\lambda)>$$

This integral is zero unless $m_\kappa'+m_\lambda' = m_\kappa+m_\lambda$. In fact, of 256 elements in the matrix of such integrals, only eight are nonzero: see Figure 4.

The algorithm of Figure 3 has been programmed in Fortran for the IBM System 360/65, and the listing is given in Appendix C. The speed of this program is limited by the matrix diagonalization procedure. The one listed, EIGEN, is an IBM Jacobi scheme improved by R. C. Raffenetti, D. M. Silver, and B. F. Sullivan, of the Theoretical Chemistry Group at Iowa State University, Ames, Iowa. The time required by EIGEN to produce double-precision eigenvectors of a matrix goes up roughly as the cube of the dimension: in this case, as the cube of the number of geminal spin products for a given PSC. EIGEN will handle a 10×10 case in less than 0.5 second, and a 25×25 in less than seven seconds.

As a practical matter, one is interested in using the spin functions to calculate the representation matrices of the permutations in the symmetric group. Such matrices are

$$
\begin{array}{c|cccc|cccc|cccc|cccc}
 & \sigma\sigma & \sigma\bar{\tau} & \sigma\tau & \sigma\underline{\tau} & \bar{\tau}\sigma & \bar{\tau}\bar{\tau} & \bar{\tau}\tau & \bar{\tau}\underline{\tau} & \tau\sigma & \tau\bar{\tau} & \tau\tau & \tau\underline{\tau} & \underline{\tau}\sigma & \underline{\tau}\bar{\tau} & \underline{\tau}\tau & \underline{\tau}\underline{\tau} \\
\hline
\sigma\sigma & & & & & & & & & & & & & & & & \\
\sigma\bar{\tau} & & & & & & & & & & & & & & & & \\
\sigma\tau & & & & & & & & & & & & & & & & \\
\sigma\underline{\tau} & & & & & & & & & & & & & & & & \\
\hline
\bar{\tau}\sigma & & & & & & & & & & & & & & & & \\
\bar{\tau}\bar{\tau} & & & & & & & & & & & & & & & & \\
\bar{\tau}\tau & & & & & & & & & & 2 & & & & & & \\
\bar{\tau}\underline{\tau} & & & & & & & & & & & 2 & & & & & \\
\hline
\tau\sigma & & & & & & & & & & & & & & & & \\
\tau\bar{\tau} & & & & & & & 2 & & & & & & & & & \\
\tau\tau & & & & & & & & 2 & & & & & & 2 & & \\
\tau\underline{\tau} & & & & & & & & & & & & & & & 2 & \\
\hline
\underline{\tau}\sigma & & & & & & & & & & & & & & & & \\
\underline{\tau}\bar{\tau} & & & & & & & & & & & 2 & & & & & \\
\underline{\tau}\tau & & & & & & & & & & & & 2 & & & & \\
\underline{\tau}\underline{\tau} & & & & & & & & & & & & & & & &
\end{array}
$$

Figure 4. Matrix of elements

$\langle w'_\kappa w'_\lambda | [\hat{s}_-(\kappa)\hat{s}_+(\lambda)+\hat{s}_-(\lambda)\hat{s}_+(\kappa)] w_\kappa w_\lambda \rangle$

(All elements not given explicitly are zero.)

needed for the evaluation of expectation values in terms of wave functions containing the spin functions.

The N! permutations belonging to S_N are products of the (N-1) elementary transpositions $t_k=(k-1,k)$, where k runs from 2 to N. In practical applications, one therefore generates only the t_k-matrices from the spin functions.

A program has been written which generates all Serber spin functions for given N, S, and M, and then evaluates all of the t_k-matrices from them. Sample running times in single precision are:

N	S	M	spin functions	elem. matrices	CPU time (sec)
4	1	1	3	3	0.4
4	0	0	2	3	0.3
6	3	3	1	5	0.2
6	2	2	5	5	3.0
6	2	1	5	5	14.0
6	2	0	5	5	23.7
6	1	1	9	5	31.1
6	1	0	9	5	51.7

These running times reflect the fact that the complexity of spin functions depends on $|M|$.

An application of these techniques is the program to generate simultaneous eigenfunctions of spin and orbital angular momentum, listed in Appendix E. Subprograms SSQEIG and SEIGEN generate Serber spin functions, and FPMAT is used to evaluate permutation matrices. The operation of this program is explained in the last chapter.

The preceding discussion leads to the following conclusions. The most convenient computer technique for obtaining Serber spin representation matrices is to generate spin functions first, and obtain the matrices from them. This requires many arithmetical operations, but most involve only integer arithmetic, and are quickly done. Attempts to obtain matrices directly from genealogical schemes usually require a very large amount of storage when more than a few electrons are involved. The exception is that YK matrices may be obtained conveniently from Young tableaux. This approach is useful when spin functions are not required.

CONSTRUCTION OF SPIN EIGENFUNCTIONS BY GROUP-ALGEBRAIC TECHNIQUES

We have described how the group-theoretical Wigner operators can be used to generate spin functions. It seems reasonable to expect that group theory might lead to simpler expressions for such operators, ones which do not involve sums over every group element. We present in this chapter a new method to accomplish this, a method by which YK and Serber spin functions can be generated directly from Young tableaux without the need to evaluate representation matrices. As a bonus, this approach also gives directly the dual space functions.

The operators we shall describe form matric bases in the symmetric group algebra. The theory behind them is abstract and relatively unfamiliar to chemists. For this reason, we shall begin by outlining the application of group algebra theory to the symmetric group. The reader seeking a more complete treatment is referred elsewhere (Weyl, 1931; van der Waerden, 1950; Johnson, 1960; Boerner, 1963; Löwdin, 1967; Poshusta, 1969; Matsen, 1970; Salmon, 1971).

Despite the abstractness of the theory, the operators obtained turn out to be "conceptualizable" and easy to apply.

The Group Algebra for S_N; the Regular Representation

While the method of the last section dealt with linear combinations of spin product functions, we now construct linear combinations of permutations which, when operating on a single product function, produce basis functions for irreducible representations of S_N.

Two such operators are familiar. The antisymmetrizer,

$$\mathcal{A} = (N!)^{-1} \sum_{\underset{\sim}{P}} \varepsilon(P)P,$$

has already been introduced, and there is, similarly, a symmetrizer:

$$\mathcal{S} = (N!)^{-1} \sum_{\underset{\sim}{P}} P.$$

These operators are idempotent and are projection operators for the antisymmetric and symmetric representations, respectively.

For $N>2$, however, there are other irreducible representations. This chapter is concerned with the construction of projectors for all of the irreducible representations. In group-theoretical language, we seek a way to completely reduce the regular representation of S_N. Let us start with the functional approach of the last chapter, and show how it leads to a powerful abstract method for this reduction.

Consider an N-electron function f, such that the N!

functions

$$f(1,2,\ldots,N),\ f(2,1,\ldots,N),\ \ldots\ ,\ f(N,3,1,\ldots),\ \ldots$$

are all distinct. It is convenient to label these functions with the permutations that generate them from $f(1,2,\ldots,N)$: let $f_I(1,2,\ldots,N) = f(1,2,\ldots,N)$ and, if

$$P = \begin{pmatrix} 1 & 2 & 3 & \ldots & N \\ p_1 & p_2 & p_3 & \ldots & p_N \end{pmatrix},$$

let $f_P(1,2,\ldots,N) = f(p_1,p_2,\ldots,p_N) = Pf(1,2,\ldots,N)$, etc.

The set $\{f_P\}$ is a basis for an important representation of S_N: for every P and f_Q, there is in the set an f_R such that

$$P\cdot f_Q = f_R, \text{ where } R = PQ.$$

In other words,

$$P\cdot f_Q = \sum_S \Gamma_{SQ}(P) f_S \quad \text{with} \quad \Gamma_{SQ}(P) = \delta_{SR}. \tag{44}$$

It is easy to show that the matrices $\Gamma(P)$ multiply like the permutations. They constitute the regular representation of S_N, which is shown in elementary texts to be reducible and to contain every distinct (i.e., nonequivalent) irrep of S_N. It should be noted that the permutations play a dual role in the regular representation: they are both the transformations and the labels for the basis functions.

The N!-dimensional linear space $F(S_N)$ spanned by the f_P

is said to be the carrier space for the regular representation. It consists of every linear combination

$$X(1,2,\ldots,N) = \sum_{P\varepsilon S_N} x(P) f_P(1,2,\ldots,N)$$

of the basis functions f_P.

Since the regular representation is reducible, its carrier space $F(S_N)$ is decomposable into the direct sum of subspaces invariant and irreducible with respect to the operations of the group. Since the regular representation contains every nonequivalent irrep, $F(S_N)$ contains a carrier space for every distinct irrep.

The meaning of these terms can be clarified through an example. Suppose that $f(1,2,3) = a(1)b(2)c(3) = abc$. Then $F(S_3)$ consists of every linear combination of the form

$$X(1,2,3) = x_1abc + x_2bac + x_3cba + x_4acb + x_5cab + x_6bca.$$

It turns out that this linear space can be decomposed as the direct sum of the following four irreducible subspaces:

subspace 1, spanned by $\theta_{11} = abc+bac+cba+acb+cab+bca$;

subspace 2, spanned by $\begin{cases}\theta_{21} = 2abc+2bac-cba-bca-cab-acb, \\ \theta_{22} = acb+bca-cab-cba;\end{cases}$

subspace 3, spanned by $\begin{cases}\theta_{31} = acb-bca+cab-cba, \\ \theta_{32} = 2abc-2bac+cba-bca-cab+acb;\end{cases}$

subspace 4, spanned by $\theta_{41} = abc-bac-cba-acb+cab+bca$.

By "direct sum" is meant the following:

(i) Every function in $F(S_3)$ can be written as a sum of functions in the subspaces.

(ii) The subspaces share no functions other than the null - they are independent. Here, in fact, their basis functions are all orthogonal.

The subspaces are said to be "invariant" under S_N because the result of operating with a permutation on a vector from one of the subspaces is again a vector in that subspace. For example,

$$(1,2)\theta_{21} = \theta_{21}, \quad (1,2)\theta_{22} = -\theta_{22};$$

$$(2,3)\theta_{21} = \tfrac{1}{2}(-\theta_{21}+3\theta_{22}), \quad (2,3)\theta_{22} = \tfrac{1}{2}(\theta_{21}+\theta_{22}).$$

The invariant subspaces are "minimal" or "irreducible" because they cannot be decomposed into smaller invariant subspaces. Here, in fact, two of the subspaces are one-dimensional.

The carrier space $F(S_N)$ for the regular representation of S_N is decomposed by finding projection operators for the various minimal invariant subspaces. To this end, we recast the linear function space $F(S_N)$ in terms of operators: an element

$$X(1,2,\ldots,N) = \sum_{P\varepsilon S_N} x(P) f_P(1,2,\ldots,N)$$

is written in the form

$$X(1,2,\ldots,N) = [\sum_{P\varepsilon S_N} x(P)P]\ f(1,2,\ldots,N).$$

From this point of view, each element $X(1,2,\ldots,N)$ in $F(S_N)$ corresponds to an operator like $[\sum_P x(P)P]$. The "primitive function" $f(1,2,\ldots,N)$ is the same in every case, and is thus superfluous. The properties of $F(S_N)$ can be discussed without mentioning the primitive function.

For this reason, the space $F(S_N)$ of <u>functions</u> can be replaced by the equivalent linear space $A(S_N)$, consisting of all <u>operators</u> of the form

$$X = \sum_{P\varepsilon S_N} x(P)P.$$

The space $A(S_N)$ is called the <u>group algebra</u> of S_N. It is to be considered not only as a set of operators, but also as a linear vector space spanned by the group elements.

Like $F(S_N)$, $A(S_N)$ is a carrier space for the regular representation of S_N. Finding operator bases for minimal invariant subspaces of $A(S_N)$ corresponds to finding basis functions for minimal invariant subspaces of $F(S_N)$, and in this sense is equivalent to finding basis functions for irreps of S_N.

We shall see, for example, that a basis for a certain minimal invariant subspace of $A(S_4)$ consists of the operators

$$o_1 = \mathcal{S}_{12}\mathcal{A}_{34}\cdot I\cdot \mathcal{P} \,,$$

$$o_2 = \mathcal{S}_{12}\mathcal{S}_{34}\cdot(3,4)\cdot \mathcal{P} \,, \qquad (45)$$

$$o_3 = \mathcal{A}_{12}\mathcal{S}_{34}\cdot(2,3,4)\cdot \mathcal{P} \,,$$

where $\mathcal{S}_{i,\ldots,k}$ and $\mathcal{A}_{i,\ldots,k}$ are the symmetrizer and antisymmetrizer on the numbers $i,\ldots,k$, respectively, and

$$\mathcal{P} = \mathcal{A}_{14}\mathcal{S}_{123}\mathcal{A}_{14}\mathcal{A}_{34}\mathcal{S}_{12} \,.$$

These operators, applied to the spin primitive $\alpha\beta\alpha\beta = \alpha(1)\beta(2)\alpha(3)\beta(4)$, generate the basis functions

$$\Theta_1 = (\alpha\beta+\beta\alpha)(\alpha\beta-\beta\alpha) \,,$$

$$\Theta_2 = \alpha\alpha\beta\beta - \beta\beta\alpha\alpha \,, \qquad (46)$$

$$\Theta_3 = (\alpha\beta-\beta\alpha)(\alpha\beta+\beta\alpha) \,.$$

Comparison with (9) shows that these are Serber spin functions for $N=4$, $S=1$, $M=0$. Either the operators of (45) or the functions of (46) can be thought of as a basis for the corresponding irrep of S_N.

Just as the group algebra is an abstraction from the function space $F(S_N)$, the regular representation has a more abstract meaning in terms of $A(S_N)$. Equation (44) defines a matrix representative for each group element when the basis in $A(S_N)$ is chosen to be those same group elements. Again, the permutations in S_N play the dual role of transformations and basis elements. This implies a dual role for the group algebra.

Since the regular representation defines a matrix

$$\Gamma(P) \leftrightarrow P$$

representing each permutation, it automatically defines a matrix

$$\Gamma(X) \overset{d}{\equiv} \sum_{P} x(P)\Gamma(P)$$

representing each $X=\Sigma x(P)P$ in $A(S_N)$. This is the <u>regular representation of the group algebra</u>, a generalization of the regular representation of the group. Hereafter, we shall understand the word "representation" to mean a representation of $A(S_N)$.

In the regular representation, then, the group algebra is to be considered as the set of operators being represented and also as the carrier space for the representation. The basis vectors in the carrier space are taken to be the permutations P. The representation matrices $\Gamma(X)$ for each X in $A(S_N)$ are related to the basis vectors P by the equations

$$XP = \sum_{P'\varepsilon S_N} \Gamma_{P'P}(X)P'.$$

In these equations, the basis vectors of the carrier space are being transformed according to left-multiplications by elements of $A(S_N)$.

Minimal Left Ideals, Primitive Idempotents, and Matric Bases

Carrier spaces of representations into which the regular representation reduces are subspaces of $A(S_N)$ that are invariant under left-multiplications by group algebra elements. Given an element U in $A(S_N)$, it is easy to see that the set of elements

$$L = \{XU \mid X \varepsilon A(S_N)\}$$

is such a subspace. The set L is said to be the <u>left ideal</u> generated by U, and U is called its <u>generator</u>. Every subspace of $A(S_N)$ that is invariant under all left-multiplications is a left ideal. Left ideals are thus carrier spaces for the representations into which the regular representation reduces.

Corresponding to the reduction of the regular representation, its carrier space $A(S_N)$ decomposes as the direct sum of certain left ideals: we write

$$A(S_N) = L_1 \oplus L_2 \oplus \ldots \oplus L_k \, .$$

It may be that a left ideal L_i contains left ideals of smaller dimension, in which case L_i itself decomposes. By carrying this process as far as it will go, $A(S_N)$ can be written as the direct sum of certain <u>minimal left ideals</u>, each of which is nondecomposable, or irreducible. *The minimal left ideals into which $A(S_N)$ decomposes are carrier spaces for the irreducible representations contained in the regular representation*. As is well-known, the irrep "α" occurs d^α times in the regular representation if it has dimension d^α. Similarly, d^α equivalent minimal left ideals $\{L_i^\alpha | i=1,2,\ldots,d^\alpha\}$ for irrep α occur in the decomposition of $A(S_N)$. We write

$$A(S_N) = \sum_\alpha (L_1^\alpha \oplus L_2^\alpha \oplus \ldots \oplus L_{d^\alpha}^\alpha) \ ,$$

in which the sums are *direct*.

We wish to obtain operator bases for these minimal left ideals, for such operators can be used to generate basis functions for the irreps.

It can be shown that every left ideal contains at least one idempotent generator, e, called a *generating unit*. A generating unit for a *minimal* left ideal is called a *primitive idempotent*. It turns out that an element e is a primitive idempotent if and only if

$$eXe = \lambda(X)e, \tag{47}$$

where X is *any* element of $A(S_N)$ and $\lambda(X)$ is a number that depends on X. Obviously, if e is to be idempotent, it must be that $\lambda(I)=1$. Property (47) is used to identify generating units for *irreducible* carrier spaces.

Idempotents that generate different minimal left ideals occurring in the decomposition of $A(S_N)$ annihilate each other.

If L_i^α and L_j^β are generated by idempotents e_i^α and e_j^β, respectively, it can be shown that

$$e_i^\alpha e_j^\beta = e_j^\beta e_i^\alpha = \delta^{\alpha\beta}\delta_{ij}e_i^\alpha \ . \tag{48}$$

These idempotents are the diagonal elements $\{e_i^\alpha = e_{ii}^\alpha\}$ of a set

$$\{e_{ij}^\alpha \,|\, \text{all } \alpha;\ i,j=1,2,\ldots,d^\alpha\}$$

of operators in $A(S_N)$ having the multiplicative property

$$e_{ij}^\alpha e_{mn}^\beta = \delta^{\alpha\beta}\delta_{jm}e_{in}^\alpha \ . \tag{49}$$

This property guarantees that the $\sum_\alpha (d^\alpha)^2 = N!$ elements $\{e_{ij}^\alpha\}$ are linearly independent. For if

$$\sum_\alpha\sum_i\sum_j c(\alpha;i,j)e_{ij}^\alpha = 0 \ ,$$

then from (49),

$$e_{kk}^\beta \cdot \sum_\alpha\sum_i\sum_j c(\alpha;i,j)e_{ij}^\alpha \cdot e_{nn}^\beta = 0 = c(\beta;k,n)e_{kn}^\beta \ ,$$

or

$$c(\beta;k,n) = 0$$

for any β, k, and n.

Like the permutations, then, *the* e_{ij}^α *form a basis for the whole group algebra*, and there is a transformation between the two basis sets:

$$P = \sum_\alpha\sum_i\sum_j [P]_{ij}^\alpha e_{ij}^\alpha \ . \tag{50}$$

Because of this and the fact that the e_{ij}^α multiply like the "elementary matrices" $\underline{\underline{e}}_{ij} = (\delta_{ij})$, they are given the name <u>matric</u> <u>basis</u>.

It is important to note that $e^{\alpha}_{ij} = e^{\alpha}_{ij} e^{\alpha}_{jj} = e^{\alpha}_{ij} e^{\alpha}_{j}$. This means that the subset

$$B^{\alpha}_{j} = \{e^{\alpha}_{ij} | i=1,2,\ldots,d^{\alpha}\}$$

of the matric basis belongs to the minimal left ideal generated by e^{α}_{j}. Since the matric basis elements are linearly independent, B^{α}_{j} <u>constitutes a basis for the jth minimal left ideal for irrep α occurring in the decomposition of the group algebra</u>. From

$$Pe^{\alpha}_{ij} = \sum_{\beta k \ell}\sum\sum [P]^{\beta}_{k\ell}\, e^{\beta}_{k\ell} e^{\alpha}_{ij} = \sum_{k} [P]^{\alpha}_{ki} e^{\alpha}_{kj} \ , \qquad (51)$$

it follows that the coefficients $[P]^{\alpha}_{ij}$ in (50) are elements of an <u>irreducible</u> representation matrix for P. It can be seen from (51) that the sets B^{α}_{j} and B^{α}_{k} , where $k \neq j$, span two carrier spaces for the <u>same</u> irrep.

Multiplying (50) by $[P^{-1}]^{\beta}_{\ell k}$, summing over P, and applying the Orthogonality Theorem for irrep matrices, one obtains the expressions

$$e^{\beta}_{k\ell} = (d^{\beta}/N!) \sum_{P} [P^{-1}]^{\beta}_{\ell k} P \ . \qquad (52)$$

These relations are often used to find the matric basis elements.

Now it is possible to see what property of the matric basis corresponds to orthogonality in the irrep matrices. We define for each element $X = \sum_P x(P)P$ in $A(S_N)$

an <u>adjoint</u> $X^\dagger = \sum_P x^*(P)P^{-1} = \sum_P x^*(P^{-1})P$,

where $x^*(P)$ is the complex conjugate of the number $x(P)$. This definition is reasonable in view of its application to integrals over functions: if ϕ and ψ are well-behaved functions,

$$\langle X\phi|\psi\rangle = \sum_P x^*(P)\langle P\phi|\psi\rangle = \sum_P x^*(P)\langle\phi|P^{-1}\psi\rangle = \langle\phi|X^\dagger\psi\rangle .$$

The adjoint of e^α_{ij} is, therefore,

$$e^{\alpha\dagger}_{ij} = (d^\alpha/N!)\sum_P [P^{-1}]^{\alpha *}_{ji}P^{-1} = (d^\alpha/N!)\sum_P [P]^{\alpha *}_{ji}P .$$

Comparing this with

$$e^\alpha_{ji} = (d^\alpha/N!)\sum_P [P^{-1}]^\alpha_{ij}P ,$$

we see that the property

$$e^{\alpha\dagger}_{ij} = e^\alpha_{ji} \tag{53}$$

implies that $[P]^{\alpha *}_{ji} = [P^{-1}]^\alpha_{ij}$.

Thus a matric basis with property (53) spans carrier spaces for <u>unitary</u> irreps. If the coefficients in the matric basis elements are real, then the irrep matrices are <u>orthogonal</u>, and

$$e^\alpha_{ij} = (d^\alpha/N!)\sum_P [P]^\alpha_{ij}P . \tag{54}$$

In order to generate basis functions for orthogonal irreducible representations of the symmetric group, therefore, we require a matric basis of operators with the multiplicative property (49) and the adjoint property (53). This matric basis is to be associated with the irreps of S_N by building it around primitive idempotents for the minimal left ideals occurring in the decomposition of the group algebra.

The primitive idempotents $e^\alpha_{ii}=e^\alpha_i$ are to be constructed to have the properties

$$e^\alpha_i e^\beta_j = \delta^{\alpha\beta}\delta_{ij}e^\alpha_i, \quad e^{\alpha\dagger}_i = e^\alpha_i .$$

It will follow that (see page 137)

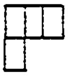
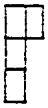
$$\sum_\alpha\sum_i e^\alpha_i = \sum_\alpha\sum_i e^\alpha_{ii} = I .$$

Thus the idempotent diagonal elements of the matric basis will be <u>projection operators</u> for irreducible carrier spaces.

Young Idempotents, Young Operators

Minimal left ideals of $A(S_N)$ can be generated using a method developed by Alfred Young (1901, 1902, 1928, 1930, 1932). An account of this method, with a complete bibliography, has been given by Rutherford (1948). Weyl (1931) and Boerner (1963) have described the connection between Young's work and group algebra theory.

Since there are as many classes of S_N as there are partitions of N, the partitions of N provide a way of labelling the irreps of S_N: for N=4, the labels are

partition	pictorial label
$\{4,0\}$	
$\{3,1\}$	
$\{2,2\} = \{2^2\}$	
$\{2,1,1\} = \{2,1^2\}$	
$\{1,1,1,1\} = \{1^4\}$	

These pictorial labels for irreps are called Young diagrams or patterns. If the row lengths of a Young diagram are $\rho_1, \rho_2, \ldots, \rho_r$, (where $\rho_1 \geqslant \rho_2 \geqslant \ldots \geqslant \rho_r$), the diagram is named $\{\rho\}$.

The diagrams are used to make Young tableaux. A tableau is a particular way of arranging the numbers $1,2,\ldots,N$ in the boxes of the diagram. For example, the diagram  for $N=3$ gives rise to the following tableaux:

$$\begin{array}{llllll} 1\ 2 & 1\ 3 & 2\ 1 & 3\ 1 & 2\ 3 & 3\ 2 \\ 3 & 2 & 3 & 2 & 1 & 1 \end{array}$$

(We shall often omit the boxes for convenience.)

Each tableau is used to build operators. Given a tableau T, let $\mathcal{R} = \{r\}$ be the set of all permutations which interchange only numbers on the same row. This set is a group - the row group. We similarly define a column group, $\mathcal{C} = \{c\}$. For the tableau $\begin{matrix} 1 & 2 \\ 3 & 4 \\ 5 & \end{matrix}$, these are

$$\mathcal{R} = \{I,\ (1,2),\ (3,4),\ (1,2)(3,4)\}\ ,$$

$$\begin{aligned} \mathcal{C} = \{I,\ &(1,3),\ (1,5),\ (3,5),\ (1,3,5),\ (1,5,3), \\ &(2,4),\ (1,3)(2,4),\ (1,5)(2,4),\ (3,5)(2,4), \\ &(1,3,5)(2,4),\ (1,5,3)(2,4)\}\ . \end{aligned}$$

Note that $\mathcal{R}$ is the direct product of the groups for individual rows, and that $\mathcal{C}$ is the direct product of individual column groups.

The <u>row operator</u> is defined to be a symmetrizer on the row group:

$$R = \sum_{r \varepsilon \mathcal{R}} r.$$

This is the product of symmetrizers for the individual rows.

The <u>column operator</u> is defined to be an antisymmetrizer on the column group:

$$C = \sum_{c \varepsilon \mathcal{C}} \varepsilon(c) c,$$

where $\varepsilon(c)$ is +1 when c is even and -1 if c is odd. This is the product of individual column antisymmetrizers.

The tableau operator is the column operator followed by the row operator:

$$E(T) = RC = \sum_{r} r \sum_{c} \varepsilon(c)c. \tag{55}$$

(Some authors define E(T)=CR.) This operator is given the special symbol E because it is essentially idempotent (idempotent within a numerical factor) and generates a minimal left ideal. It is called the Young idempotent for tableau T, and it satisfies (47).

Young tableaux and idempotents have the following important property: if T and T' are tableaux belonging to the same diagram, then E(T) and E(T') generate minimal invariant subspaces for equivalent representations; if T and T' belong to different diagrams, E(T) and E(T') generate minimal left ideals for nonequivalent representations. Since each diagram labels a distinct irreducible representation, the Young idempotents can be used to generate irreducible subspaces for every distinct irrep.

One further definition is required in order to clarify the correspondence between diagrams and irreps. A standard tableau is defined to be a tableau in which the numbers along each row increase to the right and numbers on each column increase downward. The diagrams, standard tableaux, and Young idempotents for N=4 are shown in Figure 5.

It can be shown that the number of standard tableaux for the diagram $D=\{\rho\}=\{\rho_1,\rho_2,\ldots,\rho_r\}$ is

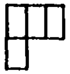
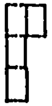
Diagram, D	Standard tableaux, T_i^D	Number of standard tableaux, d^D	Young idempotents, E_i^D
	$\begin{matrix}1&2&3&4\end{matrix}$	1	$\mathcal{S}_{1234}$
	$\begin{matrix}1&2&3\\4\end{matrix}$ $\begin{matrix}1&2&4\\3\end{matrix}$ $\begin{matrix}1&3&4\\2\end{matrix}$	3	$\mathcal{S}_{123}\mathcal{A}_{14}$ $\mathcal{S}_{124}\mathcal{A}_{13}$ $\mathcal{S}_{134}\mathcal{A}_{12}$
	$\begin{matrix}1&2\\3&4\end{matrix}$ $\begin{matrix}1&3\\2&4\end{matrix}$	2	$\mathcal{S}_{12}\mathcal{S}_{34}\mathcal{A}_{13}\mathcal{A}_{24}$ $\mathcal{S}_{13}\mathcal{S}_{24}\mathcal{A}_{12}\mathcal{A}_{34}$
	$\begin{matrix}1&2\\3\\4\end{matrix}$ $\begin{matrix}1&3\\2\\4\end{matrix}$ $\begin{matrix}1&4\\2\\3\end{matrix}$	3	$\mathcal{S}_{12}\mathcal{A}_{134}$ $\mathcal{S}_{13}\mathcal{A}_{124}$ $\mathcal{S}_{14}\mathcal{A}_{123}$
	$\begin{matrix}1\\2\\3\\4\end{matrix}$	1	$\mathcal{A}_{1234}$

Figure 5. Example of N=4

$$d^D = (N!)\left\{\frac{\prod_{i<j}^{r}(\rho_i-\rho_j+j-i)}{\prod_{i=1}^{r}[(\rho_i+r-i)!]}\right\} \quad , \tag{56}$$

that these numbers satisfy the equation

$$\sum_D (d^D)^2 = N!,$$

and hence that d^D is the dimension of the irrep of S_N corresponding to the diagram D.

The situation is as follows. Each Young diagram D labels a distinct irreducible representation Γ^D, the dimension of which is given by d^D, the number of standard tableaux. This number is also the number of equivalent carrier spaces for Γ^D occurring in the decomposition of the group algebra. Thus there is a one-to-one relation between the standard tableaux $\{T_i^D |\ i=1,2,\ldots,d^D\}$ for diagram D and the equivalent carrier spaces for Γ^D occurring in the decomposition of $A(S_N)$. Since the Young idempotent for each standard tableau generates an irreducible subspace of $A(S_N)$, there is a one-to-one relation between these minimal left ideals and the irreducible carrier spaces occurring in the decomposition of the group algebra. Just what this relation is will become clearer as we proceed.

Suppose that the standard tableaux for diagram D are related by permutations p_{ij}^D :

$$T_i^D = p_{ij}^D T_j^D ,$$

where $p_{ii}^D = I$ and $(p_{ij}^D)^{-1} = p_{ji}^D$. It can be shown that the d^D elements

$$p_{1k}^D E_k^D , p_{2k}^D E_k^D , \ldots$$

where E_k^D is the Young idempotent for T_k^D, are all linearly independent. Since these elements belong to the left ideal generated by E_k^D, *they span a carrier space for the irreducible representation associated with the diagram D*. These operators, called *Young operators*, thus form a basis for an irreducible carrier space, and can be used to make basis functions. We shall give an example shortly.

Spin Diagrams

Diagrams with one or two rows correspond to spin representations of S_N. Other diagrams are associated with Young idempotents containing column antisymmetrizers for more than two numbers. Such an operator will annihilate any spin primitive function to which it is applied, since spin functions contain only two one-electron functions - α and β. For example,

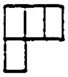
$$E\begin{pmatrix}12\\3\\4\end{pmatrix}\alpha\beta\alpha\beta = \mathcal{S}_{12}\mathcal{A}_{134}\alpha\beta\alpha\beta = \mathcal{S}_{12}(\alpha\beta\alpha\beta-\alpha\beta\alpha\beta-\beta\beta\alpha\alpha-\alpha\beta\beta\alpha+\beta\beta\alpha\alpha+\alpha\beta\beta\alpha)$$
$$= 0.$$

We can now see which diagram labels a particular spin representation. For a diagram containing two rows at most, (56) becomes

$$d^D = \frac{N!(\rho_1-\rho_2+1)}{(\rho_1+1)!\rho_2!} \; .$$

This gives the dimension of the spin representation corresponding to diagram D. Using the example of N=4, we have the spin representations

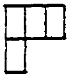

(dimension 1),


(dimension 3),


(dimension 2).

Comparison with the branching diagrams, Figures 1 and 2, reveals the following correspondence:


$\leftrightarrow$ S=2,


$\leftrightarrow$ S=1,


$\leftrightarrow$ S=0.

Indeed, the general relation between the diagram $\{\rho_1,\rho_2\}$ and the spin representation labelled by N and S is given by

$$(\rho_1-\rho_2)/2 = S, \quad \rho_1+\rho_2 = N,$$

or $$\rho_1 = (N/2) + S,\ \rho_2 = (N/2) - S.$$

Let us use the techniques described on the last several pages to derive spin functions for N=4, S=1, M=0. The standard tableaux are

$$T_1^D = \begin{array}{l}123\\4\end{array},\quad T_2^D = \begin{array}{l}124\\3\end{array},\quad T_3^D = \begin{array}{l}134\\2\end{array},$$

so that $P_{11}^D = I,\quad P_{21}^D = (3,4),\quad P_{31}^D = (2,3)(3,4).$

The Young operators for T_1^D are

$$E_{11}^D = E_1^D,\quad E_{21}^D = (3,4)E_1^D,\quad E_{31}^D = (2,3)(3,4)E_1^D,$$

where $$E_1^D = \mathcal{S}_{123}\mathcal{A}_{14}\ .$$

These operators, applied to the spin product $\Theta=\alpha\beta\alpha\beta$ for M=0, give three linearly independent spin functions:

$$\begin{aligned}\Theta_1^D = E_1^D\Theta = \mathcal{S}_{123}\mathcal{A}_{14}\alpha\beta\alpha\beta &= 2(\alpha\beta\alpha\beta+\alpha\alpha\beta\beta+\beta\alpha\alpha\beta\\ &\qquad -\beta\beta\alpha\alpha-\alpha\beta\beta\alpha-\beta\alpha\beta\alpha)\\ &= 2[\alpha\alpha\beta\beta-\beta\beta\alpha\alpha+(\alpha\beta+\beta\alpha)(\alpha\beta-\beta\alpha)];\end{aligned}$$

$$\begin{aligned}\Theta_2^D = (3,4)\Theta_1^D &= 2(\alpha\beta\beta\alpha+\alpha\alpha\beta\beta+\beta\alpha\beta\alpha-\beta\beta\alpha\alpha-\alpha\beta\alpha\beta-\beta\alpha\alpha\beta)\\ &= 2[\alpha\alpha\beta\beta-\beta\beta\alpha\alpha-(\alpha\beta+\beta\alpha)(\alpha\beta-\beta\alpha)];\end{aligned}$$

$$\begin{aligned}\Theta_3^D = (2,3)\Theta_2^D &= 2(\alpha\beta\beta\alpha+\alpha\beta\alpha\beta+\beta\beta\alpha\alpha-\beta\alpha\beta\alpha-\alpha\alpha\beta\beta-\beta\alpha\alpha\beta)\\ &= 2[\beta\beta\alpha\alpha-\alpha\alpha\beta\beta+(\alpha\beta-\beta\alpha)(\alpha\beta+\beta\alpha)].\end{aligned}$$

Direct application of $\hat{S}^2$ shows that these functions <u>are</u> spin eigenfunctions, with eigenvalue S=1.

Deficiencies of Young Operators

From a practical point of view, spin functions generated by Young operators have two shortcomings: they are not orthogonal, and they correspond to neither the YK nor the Serber spin-coupling scheme. Consequently, these functions do not have the properties demanded by the SAAP formalism.

One reason for this is that Young operators do not compose an orthogonal matric basis. It can be shown that they multiply, not according to (49), but according to the equations

$$E^{D}_{ij}E^{D'}_{mn} = \delta^{DD'}\hat{\delta}_{jm}E^{D}_{in}\cdot(\text{a number}),$$

where $\hat{\delta}_{jm}$ is not always zero when $j \neq m$.

In addition, there is nothing about the construction of Young operators that would associate them with any particular spin-coupling scheme.

Neither do these operators possess the adjoint property of (53). Since row and column operators are self-adjoint (symmetrizers and antisymmetrizers are Hermitian),

$$E^{D\dagger}_{ij} = (p^{D}_{ij}E^{D}_{j})^{\dagger} = E^{D\dagger}_{j}(p^{D}_{ij})^{-1} = (R^{D}_{j}C^{D}_{j})^{\dagger}\, p^{D}_{ji}$$

$$= C^{D}_{j}R^{D}_{j}p^{D}_{ji} = p^{D}_{ji}C^{D}_{i}R^{D}_{i} \neq E^{D}_{ji}.$$

This last deficiency can be remedied by defining new operators $p^{D}_{ij}C^{D}_{j}R^{D}_{j}C^{D}_{j}$ or $p^{D}_{ij}R^{D}_{j}C^{D}_{j}R^{D}_{j}$. Such operators are easily seen to satisfy (53). Their properties have been studied by

Gallup (1968, 1969), who has used them to generate projected Hartree-product wave functions.

According to (49), the diagonal elements of a matric basis multiply according to

$$e_{ii}^{D} e_{jj}^{D'} = \delta^{DD'} \delta_{ij} \, e_{ii}^{D} \; .$$

That is, these elements are idempotent and they annihilate each other from the left and right. It can be shown that the generating units for the minimal left ideals into which the group algebra decomposes also have this property, as well as the property (47) characteristic of primitive idempotents.

Young idempotents are primitive. Two Young idempotents from different diagrams annihilate each other from the left and right. However, two Young idempotents from the <u>same</u> diagram may not do this. In other words, Young idempotents "almost" multiply like the diagonal elements of a matric basis (McIntosh, 1960).

Examining the situation more closely, we may draw the following conclusion. There occur in the decomposition of $A(S_N)$ d^D equivalent irreducible carrier spaces for the irrep labelled by diagram D. These carrier spaces are generated by the matric basis idempotents e_1^D, e_2^D, ..., $e_{d^D}^D$. The Young idempotents E_1^D, E_2^D, ..., $E_{d^D}^D$ generate carrier spaces for this representation also. Thus there must be equivalence transformations relating the Young idempotents and the matric basis idempotents.

In constructing from Young idempotents a matric basis suited to the SAAP formalism, we must, therefore, build operators that

(i) are related to a spin-coupling scheme;
(ii) multiply like a matric basis;
(iii) have the adjoint property (53).

As we shall see, this can be accomplished by multiplying Young idempotents from the left and right by certain operators.

Tableau Chains

It is well-known that standard tableaux can be derived from a genealogical scheme similar to that involved in spin-coupling (Jahn and van Wieringen, 1951; Pauncz, 1967; Coleman, 1968; McWeeny and Sutcliffe, 1969; Klein _et_ _al_., 1970). Since Young spin diagrams $\{\rho_1,\rho_2\}$ label spin representations of S_N through the relations $\rho_1=(N/2)+S$, $\rho_2=(N/2)-S$, the YK branching diagram can be given in the form shown in Figure 6. In other words, the Young diagrams can be considered the result of a "box-coupling" procedure: one starts with $\square$ and adds boxes one by one, subject to the condition that $\rho_1 \geqslant \rho_2$.

Figure 6 is a kind of shorthand for the genealogical construction of standard tableaux. If we start with the tableau $\boxed{1}$ and add, one by one, the numbers 2,3,...,N in

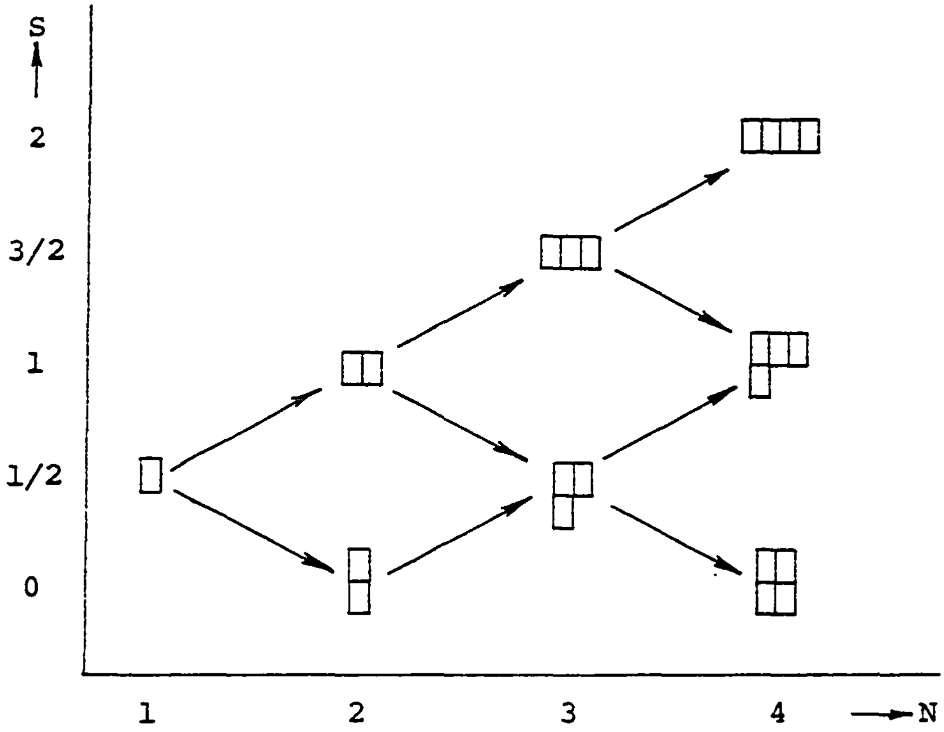


Figure 6. YK branching diagram for Young diagrams

such a way that the resulting tableaux are standard, we obtain Figure 7.

Each route in this figure results in a unique standard tableau. Conversely, each standard tableau uniquely defines its predecessors along the route. This follows from the fact that removal of the highest number from a standard tableau for N numbers produces a standard tableau for (N-1) numbers. Thus, for example, one can work backward from $\begin{smallmatrix}1&2&4\\3\end{smallmatrix}$ in the following way:

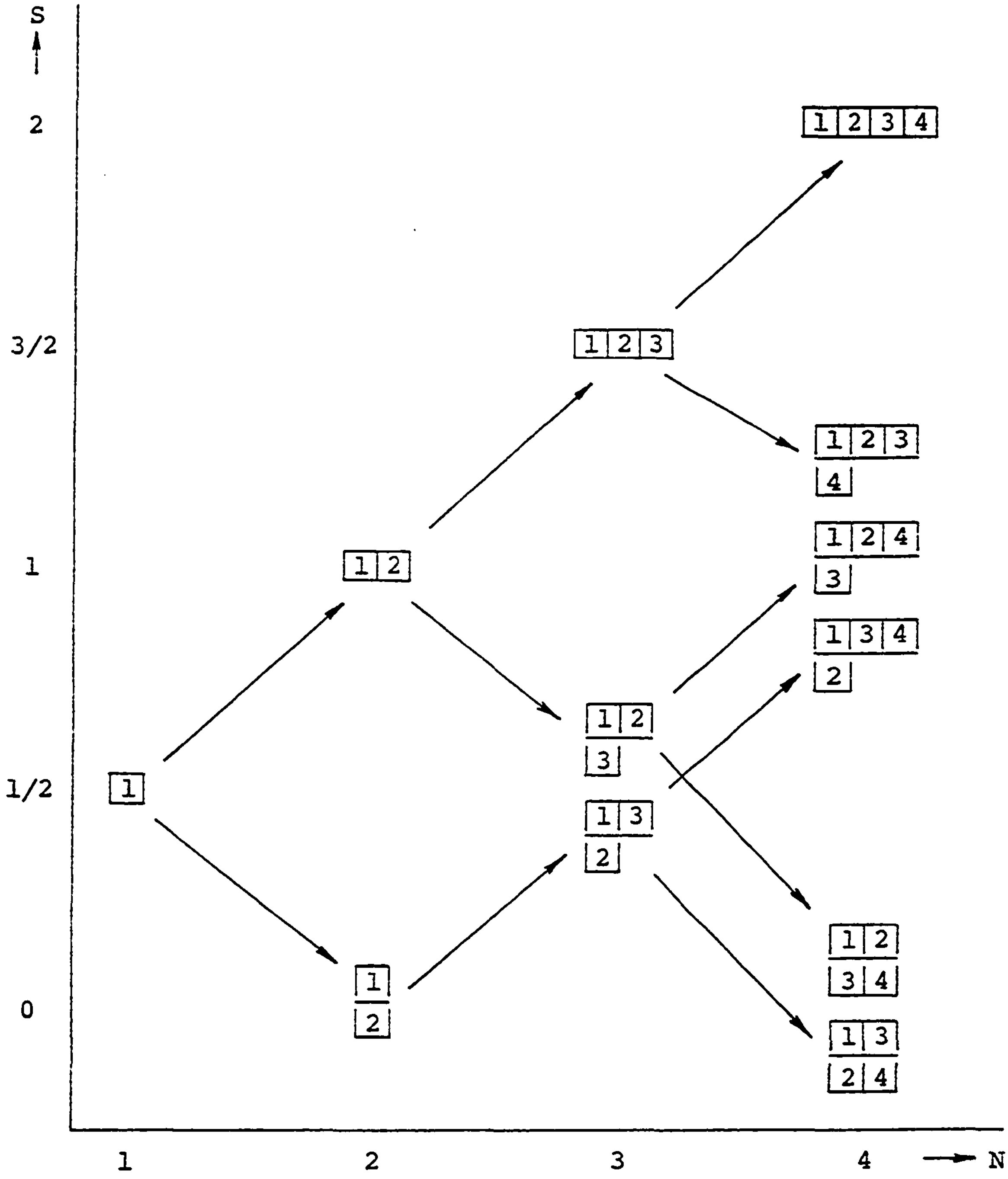
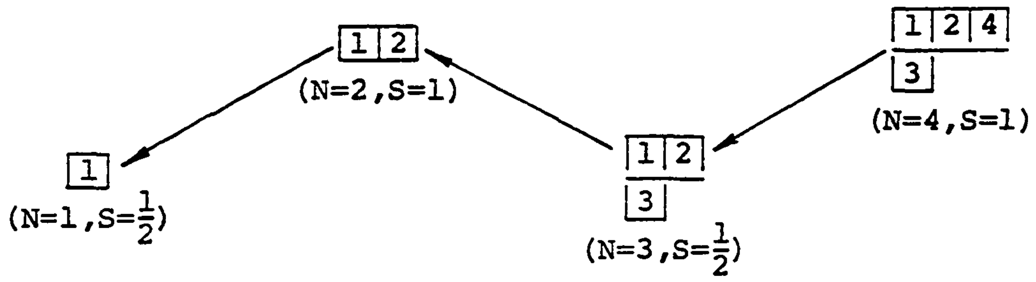


Figure 7. YK branching diagram for standard Young tableaux



The significance of this is that each standard tableau can be uniquely associated with a YK branching route, and therefore can be uniquely associated with a YK spin function. To use the example of page 52, N=4, S=1 (or D= ), we have the correspondence

Standard tableau	Branching route
1 2 3 4	
1 2 4 3	
1 3 4 2	

It will be observed that each number on the upper row of a standard tableau corresponds to an upward movement in the associated branching route, and each number on the lower row corresponds to a downward movement.

Strictly speaking, it is not the tableau itself that corresponds to a YK branching route, but the unique "chain" of tableau predecessors from which it derives. For example, the branching route  is a shorthand for the tableau chain

$$\begin{array}{|c|}\hline 1\\\hline\end{array} \longrightarrow \begin{array}{|c|}\hline 1\\\hline 2\\\hline\end{array} \longrightarrow \begin{array}{|c|c|}\hline 1&3\\\hline 2\\\cline{1-1}\end{array} \longrightarrow \begin{array}{|c|c|c|}\hline 1&3&4\\\hline 2\\\cline{1-1}\end{array}$$

Such a chain involves the addition of one number at a time, and is called a <u>1-chain.</u>

In general, we denote by $T_r^{D,k}$ the standard tableau obtained from T_r^D by removing its k highest numbers, viz. N, N-1, ..., N-k+1. Thus the 1-chain defined by T_r^D is written

$$T_r^{D,N-1} \longrightarrow T_r^{D,N-2} \longrightarrow \ldots \longrightarrow T_r^{D,1} \longrightarrow T_r^D \quad .$$

Each standard tableau is also associated with a unique <u>2-chain</u>, if N is even. Removal of two numbers from a standard tableau results in a smaller tableau which is also standard. Thus one can work backward from a given standard tableau and define its predecessors in a Serber-type genealogical scheme. For example,

$$\begin{array}{|c|c|}\hline 1&2\\\hline\end{array} \longrightarrow \begin{array}{|c|c|c|}\hline 1&2&4\\\hline 3\\\cline{1-1}\end{array} \longrightarrow \begin{array}{|c|c|c|c|}\hline 1&2&4&6\\\hline 3&5\\\cline{1-2}\end{array}$$

In general,

$$T_r^{D,N-2} \longrightarrow T_r^{D,N-4} \longrightarrow \ldots \longrightarrow T_r^{D,2} \longrightarrow T_r^D$$

In other words, standard tableaux can be considered constructed according to the Serber branching diagram of Figure 8.

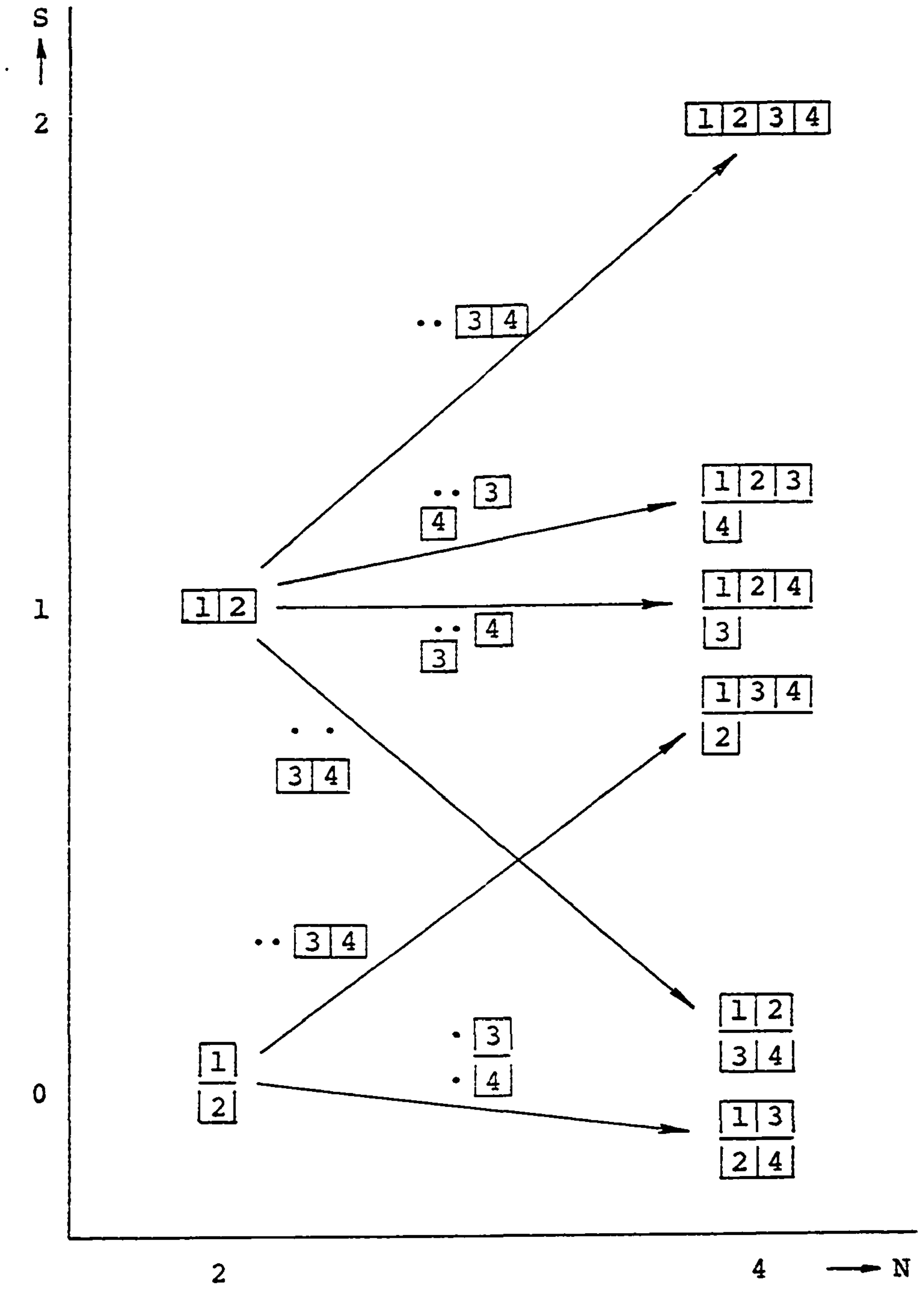


Figure 8. Serber branching diagram for standard Young tableaux

We have indicated in each case the pair of numbers being added, and their positions relative to the original tableau.

At each stage in such a branching diagram, a geminal pair of numbers $2\mu-1, 2\mu$ is added to a tableau containing $\mu-1$ geminal pairs. It will be observed that the addition of $\cdots \boxed{2\mu-1}\boxed{2\mu}$ always corresponds to $s_\mu=1$, and the addition of two numbers on the same column always has the effect of adding $s_\mu=0$. There is an ambiguity, however, when $2\mu-1$ and 2μ are on neither the same row nor the same column. One case must correspond to the addition of $s_\mu=1$ and the other to $s_\mu=0$. We are free to make a choice, so long as we are consistent. In the following pages, we shall associate

$$\begin{array}{ll} \cdots & \boxed{2\mu} \\ \boxed{2\mu-1} & \end{array} \quad \text{with} \quad s_\mu = 1$$

and

$$\begin{array}{ll} \cdots & \boxed{2\mu-1} \\ \boxed{2\mu} & \end{array} \quad \text{with} \quad s_\mu = 0.$$

Now it is clear that the concept of tableau chains provides the link between Young's theory of the symmetric group and the genealogical construction of spin functions. However, we have already pointed out that Young operators do not generate YK or Serber spin functions. Clearly, this is because they do not, in themselves, carry information specific to 1-chains or 2-chains.

We begin to remedy this deficiency by defining <u>chains</u>

of Young idempotents. Suppose that E_r^D and $E_r^{D,k}$ are the Young idempotents for the tableaux T_r^D and $T_r^{D,k}$, respectively. Then the m-chain of standard tableaux

$$T_r^{D,N-m} \longrightarrow T_r^{D,N-2m} \longrightarrow \cdots \longrightarrow T_r^{D,m} \longrightarrow T_r^D$$

is associated with the m-chain

$$E_r^{D,N-m} \longrightarrow E_r^{D,N-2m} \longrightarrow \cdots \longrightarrow E_r^{D,m} \longrightarrow E_r^D$$

of Young idempotents. (We assume that N is a multiple of m.)

Carrying this one step further, we define $L_r^{D,k}$ to be the minimal left ideal generated by the Young idempotent $E_r^{D,k}$. Thus each standard tableau T_r^D defines a unique m-chain

$$L_r^{D,N-m} \longrightarrow L_r^{D,N-2m} \longrightarrow \cdots \longrightarrow L_r^{D,m} \longrightarrow L_r^D$$

of minimal left ideals.

Chains of Young Idempotents and Genealogical Spin Functions: an Heuristic Argument

It was mentioned previously that the YK spin functions for fixed N and S form a basis for that special orthogonal irrep of S_N in which S_{N-1}, S_{N-2}, ..., S_1 are also represented by orthogonal, irreducible matrices. The representation is said to be adapted to the sequence of groups

$$S_N,\ S_{N-1},\ S_{N-2},\ \ldots,\ S_1.$$

We shall say that a representation with this property is <u>YK-adapted</u>.

In a similar way, the Serber functions (for even N) are adapted to the sequence

$$S_N,\ S_{N-2},\ S_{N-4},\ \ldots,\ S_2.$$

In addition, every geminal two-electron subgroup of S_N is represented irreducibly. A representation with these two properties is said to be <u>Serber-adapted</u>.

<u>The adaptation of representations to sequences of nested symmetric groups is the group-theoretical significance of a genealogical spin-coupling scheme.</u>

Now suppose that L_Y is a subspace of the group algebra, $A(S_N)$, with the following properties:

(i) L_Y is invariant under left-multiplications by elements of S_N and transforms according to the minimal left ideal L_r^D;

(ii) the elements of L_Y transform among themselves under left-multiplications by elements of S_{N-k} like elements of the minimal left ideal $L_r^{D,k}$, for k=1,2,...,N-1.

Property (i) means that L_Y is a carrier space for an irreducible representation of S_N. From property (ii), we see that L_Y is also a carrier space for irreducible representations of

S_{N-1}, S_{N-2}, ..., S_1. Thus L_Y is a carrier space for a YK-adapted representation of S_N.

In a similar way, a subspace L_S of $A(S_N)$ is a carrier space for a Serber-adapted representation of S_N if

(i) L_S is invariant under left-multiplications by elements of S_N and transforms like L_r^D;

(ii) the elements of L_S transform among themselves under left-multiplications by elements of S_{N-k} like elements of $L_r^{D,k}$, for $k=2,4,\ldots,N-2$;

(iii) the elements of L_S are either symmetric or antisymmetric with respect to left-multiplications by geminal transpositions.

Before defining orthogonal matric bases for genealogical representations, it is instructive to see what predictions can be made about the structure of such operators by extending the present argument. We shall see that idempotent generators for YK- and Serber-adapted carrier spaces can be deduced rather easily.

The minimal left ideal associated with the standard tableau T_r^D is defined to be $L_r^D=\{XE_r^D\}$, where X sweeps the whole group algebra. It can be shown (Rutherford, 1948, p. 20) that Young idempotents have the property

$$E_r^D X E_r^D = \theta^D \cdot i[XE_r^D]\ E_r^D\ ,$$

where $\theta^D = (N!/d^D) > 0$ does not depend on r, and $i[XE_r^D]$ is the coefficient of the identity in XE_r^D, when it is expanded in terms of the group elements. It follows that

$$(XE_r^D)(XE_r^D) = \theta^D \cdot i[XE_r^D]\ (XE_r^D),$$

so that (XE_r^D) is essentially idempotent if it contains the identity. In other words, *new idempotent generators of L_r^D can be made by left-multiplying E_r^D.*

Consider, for example, the element

$$E_Y(D,r) = E_r^{D,N-1}E_r^{D,N-2} \cdots E_r^{D,1}E_r^D.$$

This operator belongs to L_r^D. To the left, it has

$E_r^{D,N-1}$, which generates $L_r^{D,N-1}$;

$(E_r^{D,N-1}E_r^{D,N-2})$, belonging to $L_r^{D,N-2}$;

$(E_r^{D,N-1}E_r^{D,N-2}E_r^{D,N-3})$, belonging to $L_r^{D,N-3}$;

etc.

Thus $E_Y(D,r)$ behaves under left-multiplications by elements of S_{N-k} (where k=1,2,...,N-1) like an element of $L_r^{D,k}$. The Young idempotent E_r^D has been "YK-adapted" by multiplying it from the left by the 1-chain

$$E_1^{D,N-1} \longrightarrow E_r^{D,N-2} \longrightarrow \cdots \longrightarrow E_r^{D,1}$$

of Young idempotents from which it derives.

Similarly, we may expect a Serber-adapted idempotent to take the form

$$E_S(D,r) = S_r^{D,N-2}E_r^{D,N-2}S_r^{D,N-4}E_r^{D,N-4} \cdots S_r^{D,2}E_r^{D,2}S_r^D E_r^D,$$

where $S_r^{D,2k}$ either symmetrizes or antisymmetrizes the geminal pair (N-2k-1, N-2k). Since the operators to the left of $S_r^{D,2k}$ do not contain the electron labels on which it operates, the pair-symmetry operators can all be brought out to the left:

$$E_S(D,r) = (S_r^{D,N-2}S_r^{D,N-4}\cdots S_r^{D,2}S_r^D)\cdot(E_r^{D,N-2}E_r^{D,N-4}\cdots E_r^{D,2}E_r^D)$$

Thus, when $E_S(D,r)$ is applied to a primitive function, it will generate a function which is either symmetric or antisymmetric in each geminal pair.

Assuming that $E_Y(D,r)$ and $E_S(D,r)$, when expanded in terms of the group elements, contain the identity, they are essentially idempotent. However, they are not Hermitian, so they cannot be the idempotent diagonal elements of the matric bases we seek.

It is easy to see that the following operators *are* Hermitian:

$$E_Y(D,r)E_Y^\dagger(D,r) = E_r^{D,N-1}\cdots E_r^{D,1}E_r^D E_r^{D\dagger}E_r^{D,1\dagger}\cdots E_r^{D,N-1\dagger} \;;$$

$$E_S(D,r)E_S^\dagger(D,r) = G_r^D E_r^{D,N-2}\cdots E_r^{D,2}E_r^D E_r^{D\dagger}E_r^{D,2\dagger}\cdots E_r^{D,N-2\dagger}G_r^D \;;$$

in which $G_r^D = (S_r^{D,N-2} \cdots S_r^{D,2} S_r^D) = G_r^{D\dagger}$.

It can be shown that these operators are, in fact, Hermitian idempotents generating YK- and Serber-adapted carrier spaces for irreducible representations of S_N. It can also be shown, however, that they do not multiply like the diagonal elements of a matric basis. It may be that

$$[E_Y(D,r)E_Y^\dagger(D,r)][E_Y(D,s)E_Y^\dagger(D,s)] \neq 0,$$

for example. Thus these operators cannot be used to generate orthogonal basis functions.

We present in the next section matric bases for YK- and Serber-adapted orthogonal representations. It will be seen that these matric bases are symmetry-adapted in a way similar to $E_Y E_Y^\dagger$ and $E_S E_S^\dagger$. Their definitions differ only to the degree necessary in order to obtain the correct multiplication properties.

Definitions of Orthogonal Matric Bases

Glossary of notation

Let T_r^D be a standard tableau for a diagram D with N boxes, and let $\mathcal{R}_r^D$ and $\mathcal{C}_r^D$ be its row and column groups. Let R_r^D and C_r^D be the row and column operators for T_r^D, and let $E_r^D = R_r^D C_r^D$ be its Young idempotent. Then E_r^D has the property

$$E^D_r X E^D_r = \theta^D \, i[XE^D_r] \; E^D_r \; ,$$

where $\theta^D > 0$ depends only on D, X is any element of the group algebra, and $i[XE^D_r]$ is the coefficient of the identity, I, in the expansion of XE^D_r in terms of group elements. In particular, $i[E^D_r]=1$ (Rutherford, 1948, p.14), so that

$$E^D_r E^D_r = \theta^D E^D_r \; .$$

It can be shown (Rutherford, 1948, p.65) that $\theta^D = (N!/d^D)$, where d^D is the dimension of the representation labelled by diagram D.

The row and column operators are self-adjoint, so that

$$E^{D\dagger}_r = (R^D_r C^D_r)^\dagger = C^{D\dagger}_r R^{D\dagger}_r = C^D_r R^D_r \; .$$

Letting $o^D_{\mathcal{R}}$ be the order of the row group for any tableau belonging to diagram D,

$$R^D_r R^D_r = o^D_{\mathcal{R}} \, R^D_r \; ,$$

so that

$$E^{D\dagger}_r E^D_r = C^D_r R^D_r R^D_r C^D_r = o^D_{\mathcal{R}} \, C^D_r R^D_r C^D_r = o^D_{\mathcal{R}} \, C^D_r E^D_r \; .$$

We define p^D_{rs} to be the permutation that rearranges the numbers in T^D_s to form T^D_r:

$$T^D_r = p^D_{rs} T^D_s \; .$$

Thus p^D_{rs} is such that $p^D_{rr}=I$ and $p^D_{sr} = (p^D_{rs})^{-1}$. Furthermore, the tableau operators have the properties

$$R_r^D = p_{rs}^D R_s^D p_{sr}^D \ , \qquad C_r^D = p_{rs}^D C_s^D p_{sr}^D \ ,$$

and

$$E_r^D = p_{rs}^D E_s^D p_{sr}^D \ .$$

We denote by $T_r^{D,m}$ the standard tableau obtained from T_r^D by removing the m highest numbers, i.e., N, N-1, ..., N-m+1. Then if m is a factor of N, T_r^D defines the m-chain of standard tableaux

$$T_r^{D,N-m} \longrightarrow \ldots \longrightarrow T_r^{D,m} \longrightarrow T_r^D \ .$$

There corresponds an m-chain

$$E_r^{D,N-m} \longrightarrow \ldots \longrightarrow E_r^{D,m} \longrightarrow E_r^D$$

of Young idempotents.

A matric basis for orthogonal YK-adapted representations

The standard tableau T_r^D defines the 1-chain

$$T_r^{D,N-1} \longrightarrow T_r^{D,N-2} \longrightarrow \ldots \longrightarrow T_r^{D,1} \longrightarrow T_r^D$$

of standard tableaux, where $T_r^{D,N-1} = \boxed{1}$ for every D and r.

We define for this 1-chain a chain of idempotent operators, in the following manner:

$$e_r^{D,N-1} = I \ ,$$

$$e_r^{D,N-2} = (E_r^{D,N-2} e_r^{D,N-1})^{\dagger} (E_r^{D,N-2} e_r^{D,N-1}) / k_r^{D,N-2} \ ,$$

$$. \; . \; . \; ,$$

$$e_r^{D,i} = (E_r^{D,i} e_r^{D,i+1})^{\dagger} (E_r^{D,i} e_r^{D,i+1})/k_r^{D,i} ,$$

$$. \; . \; . \; ,$$

$$e_r^{D} = (E_r^{D} e_r^{D,1})^{\dagger} (E_r^{D} e_r^{D,1})/k_r^{D} , \qquad (57)$$

where k_r^D is the number

$$k_r^D = o_{\mathcal{R}}^D \cdot \theta^D \cdot \rho_r^D ,$$

in which

$$\rho_r^D = i \, [C_r^D E_r^D e_r^{D,1}] .$$

It should be noted that these operators are Hermitian.

The idempotents e_r^D are used to construct the matric basis elements

$$e_{rs}^D = (E_r^D e_r^{D,1})^{\dagger} p_{rs}^D (E_s^D e_s^{D,1})/(k_r^D k_s^D)^{1/2} \qquad (58)$$

The diagonal elements e_{rr}^D of this basis are identical to the idempotents e_r^D defined by (57).

For application to primitive functions, it is more convenient to use an alternative expression for the matric basis:

$$\begin{aligned} e_{rs}^D &= e_r^{D,1} C_r^D R_r^D p_{rs}^D R_s^D C_s^D e_s^{D,1}/(k_r^D k_s^D)^{1/2} \\ &= e_r^{D,1} p_{rs}^D C_s^D R_s^D R_s^D C_s^D e_s^{D,1}/[\theta^D o_{\mathcal{R}}^D (\rho_r^D \rho_s^D)^{1/2}] \\ &= e_r^{D,1} p_{rs}^D C_s^D R_s^D C_s^D e_s^{D,1}/[\theta^D (\rho_r^D \rho_s^D)^{1/2}] , \end{aligned}$$

or $$e^D_{rs} = e^{D,1}_r P^D_{rs} C^D_s E^D_s e^{D,1}_s / [\Theta^D (\rho^D_r \rho^D_s)^{1/2}] . \qquad (59)$$

These equations define operators built around Young operators, but adapted to the genealogy of 1-chains through equations (57).

The definitions are most easily understood by working an example. Let $D=\begin{array}{|c|c|}\hline & \\ \hline \\ \cline{1-1}\end{array}$, for which the standard tableaux are

$$T^D_1 = \begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 \\ \cline{1-1}\end{array} \text{ and } T^D_2 = \begin{array}{|c|c|}\hline 1 & 3 \\ \hline 2 \\ \cline{1-1}\end{array} ,$$

so that $$P^D_{12} = (2,3) = P^D_{21} \quad .$$

The 1-chain defined by T^D_1 is

$$T^{D,2}_1 = \boxed{1} \longrightarrow T^{D,1}_1 = \begin{array}{|c|c|}\hline 1 & 2 \\ \hline\end{array} \longrightarrow T^D_1 = \begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 \\ \cline{1-1}\end{array} \quad ,$$

for which the Young idempotents are

$$E^{D,2}_1 = I \longrightarrow E^{D,1}_1 = \mathcal{S}_{12} \longrightarrow E^D_1 = \mathcal{S}_{12}\mathcal{A}_{13} \quad .$$

Neglecting numerical factors,

$$e^{D,2}_1 \overset{d}{=} I,$$

$$e^{D,1}_1 = e^{D,2}_1 C^{D,1}_1 E^{D,1}_1 e^{D,2}_1 = I \cdot I \cdot \mathcal{S}_{12} \cdot I = \mathcal{S}_{12} ,$$

$$e^D_1 = e^{D,1}_1 C^D_1 E^D_1 e^{D,1}_1 = \mathcal{S}_{12}\mathcal{A}_{13}\mathcal{S}_{12}\mathcal{A}_{13}\mathcal{S}_{12} \quad .$$

The 1-chain defined by T_2^D is

$$T_2^{D,2} = \boxed{1} \longrightarrow T_2^{D,1} = \begin{array}{|c|}\hline 1 \\ \hline 2 \\ \hline \end{array} \longrightarrow T_2^D = \begin{array}{|c|c|}\hline 1 & 3 \\ \hline 2 \\ \cline{1-1} \end{array} ,$$

for which the Young idempotents are

$$E_2^{D,2} = I \longrightarrow E_2^{D,1} = \mathcal{A}_{12} \longrightarrow E_2^D = \mathcal{S}_{13}\mathcal{A}_{12} .$$

Neglecting numerical factors,

$$e_2^{D,2} \overset{d}{=} I,$$

$$e_2^{D,1} = e_2^{D,2}C_2^{D,1}E_2^{D,1}e_2^{D,2} = I\cdot\mathcal{A}_{12}\mathcal{A}_{12}\cdot I = 2\mathcal{A}_{12} ,$$

$$e_2^D = e_2^{D,1}C_2^DE_2^De_2^{D,1} = 4\mathcal{A}_{12}\mathcal{A}_{12}\mathcal{S}_{13}\mathcal{A}_{12}\mathcal{A}_{12} = 16\mathcal{A}_{12}\mathcal{S}_{13}\mathcal{A}_{12} .$$

The entire matric basis, then, consists of the operators

$$e_{11}^D = e_1^D = \mathcal{S}_{12}\mathcal{A}_{13}\mathcal{S}_{12}\mathcal{A}_{13}\mathcal{S}_{12} ,$$

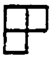
$$e_{21}^D = e_2^{D,1}p_{21}^DC_1^DE_1^De_1^{D,1} = 2\mathcal{A}_{12}\cdot(2,3)\cdot\mathcal{A}_{13}\mathcal{S}_{12}\mathcal{A}_{13}\mathcal{S}_{12} ,$$

$$\begin{aligned} e_{12}^D = e_1^{D,1}p_{12}^DC_2^DE_2^De_2^{D,1} &= 2\mathcal{S}_{12}\cdot(2,3)\cdot\mathcal{A}_{12}\mathcal{S}_{13}\mathcal{A}_{12}\mathcal{A}_{12} \\ &= 4\mathcal{S}_{12}\cdot(2,3)\cdot\mathcal{A}_{12}\mathcal{S}_{13}\mathcal{A}_{12} , \end{aligned}$$

$$e_{22}^D = e_2^D = 16\mathcal{A}_{12}\mathcal{S}_{13}\mathcal{A}_{12} .$$

The whole matric basis is not required for the construction of basis functions for the irrep. The operators

$\{e^D_{11}, e^D_{21}\}$ span a minimal left ideal associated with T^D_1; similarly, $\{e^D_{12}, e^D_{22}\}$ span a minimal left ideal associated with T^D_2. Either of these subsets can be used to generate basis functions.

As an example, we apply e^D_{12} and e^D_{22} to the spin product function $\theta=\alpha\beta\alpha$. Since the diagram D=  corresponds to S=1/2, we should obtain YK spin functions for N=3, S=M=1/2. We have $e^D_{12} = 4\mathcal{S}_{12}\cdot(2,3)\cdot\mathcal{P}$ and $e^D_{22} = 16\mathcal{P}$, where $\mathcal{P} = \mathcal{A}_{12}\mathcal{S}_{13}\mathcal{A}_{12}$. Thus

$$\begin{aligned}\mathcal{P}\,\theta &= \mathcal{A}_{12}\mathcal{S}_{13}(\alpha\beta\alpha-\beta\alpha\alpha) = \mathcal{A}_{12}(2\alpha\beta\alpha-\beta\alpha\alpha-\alpha\alpha\beta)\\ &= (2\alpha\beta\alpha-2\beta\alpha\alpha-\beta\alpha\alpha+\alpha\beta\alpha)\\ &= 3(\alpha\beta\alpha-\beta\alpha\alpha),\end{aligned}$$

so

$$\begin{aligned}e^D_{12}\theta &= 12\mathcal{S}_{12}\cdot(2,3)\cdot(\alpha\beta\alpha-\beta\alpha\alpha) = 12\mathcal{S}_{12}(\alpha\alpha\beta-\beta\alpha\alpha)\\ &= 12(2\alpha\alpha\beta-\beta\alpha\alpha-\alpha\beta\alpha)\\ &= 12[2\alpha\alpha\beta-(\alpha\beta+\beta\alpha)\alpha]\end{aligned}$$

and

$$e^D_{22}\theta = 16\mathcal{P}\theta = 48(\alpha\beta-\beta\alpha)\alpha.$$

These are, indeed, the (unnormalized) YK spin functions obtained for N=3, S=1/2, M=1/2 from the spin-coupling equations (28). Notice that $e^D_{12}\theta$ corresponds to the branching route , while e^D_{22} corresponds to , and that these functions are orthogonal.

The same functions, within a numerical factor, are obtained by means of the matric basis elements e^D_{11} and e^D_{21}.

A matric basis for orthogonal Serber-adapted representations

When N is even, the standard tableau T_r^D defines the 2-chain

$$T_r^{D,N-2} \longrightarrow T_r^{D,N-4} \longrightarrow \cdots \longrightarrow T_r^{D,2} \longrightarrow T_r^{D} ,$$

where $T_r^{D,N-2}$ is either $\begin{array}{|c|c|}\hline 1 & 2 \\ \hline\end{array}$ or $\begin{array}{|c|}\hline 1 \\ \hline 2 \\ \hline\end{array}$, depending on T_r^D.

For T_r^D, a geminal operator S_r^D is defined in terms of the positions of the two highest numbers, N-1 and N. Denoting the row and column on which a number k appears as r_k and c_k, we define

$$S_r^D = \begin{cases} [I+(N-1,N)]/2 \text{ if } r_{N-1}=r_N \text{ or } r_{N-1}>r_N \;; \\ [I-(N-1,N)]/2 \text{ if } c_{N-1}=c_N \text{ or } (r_{N-1}<r_N,\ c_{N-1}\neq c_N) \end{cases}$$

In other words, S_r^D symmetrizes the numbers (N-1) and N if T_r^D contains these numbers in the positions $\cdots\begin{array}{|c|c|}\hline (N-1) & N \\ \hline\end{array}$ or $\begin{array}{l} \cdot\;\cdot\;\cdot\,\boxed{N} \\ \boxed{N-1} \end{array}$, but antisymmetrizes them if T_r^D contains $\begin{array}{l} \cdot\;\cdot\;\cdot\,\boxed{N-1} \\ \boxed{N} \end{array}$ or $\begin{array}{c} \vdots \\ \hline \multicolumn{1}{|c|}{N-1} \\ \hline \multicolumn{1}{|c|}{N} \\ \hline \end{array}$

Geminal operators $S_r^{D,2k}$ for other tableaux $T_r^{D,2k}$ in the 2-chain are defined analogously.

A set of Hermitian idempotents is defined recursively for the 2-chain:

$$e_r^{D,N-2} = S_r^{D,N-2},$$

$$e_r^{D,N-4} = (E_r^{D,N-4} S_r^{D,N-4} e_r^{D,N-2})^{\dagger} (E_r^{D,N-4} S_r^{D,N-4} e_r^{D,N-2})/k_r^{D,N-4},$$

$$\ldots,$$

$$e_r^D = (E_r^D S_r^D e_r^{D,2})^\dagger (E_r^D S_r^D e_r^{D,2})/k_r^D \;, \tag{60}$$

where k_r^D is the number

$$k_r^D = o_{\mathfrak{a}}^D \cdot \theta^D \cdot \rho_r^D \;,$$

in which

$$\rho_r^D = i\,[C_r^D E_r^D S_r^D e_r^{D,2}] \;.$$

The idempotents e_r^D are used to construct the matric basis elements

$$e_{rs}^D = (E_r^D S_r^D e_r^{D,2})^\dagger p_{rs}^D (E_s^D S_s^D e_s^{D,2})/(k_r^D k_s^D)^{1/2} \tag{61}$$

It should be noted that a diagonal element e_{rr}^D in this basis is identical to the element e_r^D defined by (60).

As in the previous case, the matric basis elements can be given in a slightly simpler form. The result is

$$e_{rs}^D = e_r^{D,2} S_r^D p_{rs}^D C_s^D E_s^D S_s^D e_s^{D,2}/[\theta^D (\rho_r^D \rho_s^D)^{1/2}]. \tag{62}$$

As an example of the application of these operators, we generate the Serber spin functions for N=4, S=1, M=0, using the primitive function $\alpha\beta\alpha\beta$. The Young diagram is $D = \begin{array}{|c|c|c|}\hline \; & \; & \; \\ \hline \; \\ \cline{1-1} \end{array}$, for which the standard tableaux are

$$T_1^D = \begin{array}{|c|c|c|}\hline 1 & 2 & 3 \\ \hline 4 \\ \cline{1-1} \end{array}\,, \qquad T_2^D = \begin{array}{|c|c|c|}\hline 1 & 2 & 4 \\ \hline 3 \\ \cline{1-1} \end{array}\,, \qquad T_3^D = \begin{array}{|c|c|c|}\hline 1 & 3 & 4 \\ \hline 2 \\ \cline{1-1} \end{array}\,,$$

so that

$$p_{11}^D = I, \qquad p_{21}^D = (3,4), \qquad p_{31}^D = (2,3)(3,4),$$

and $$E_1^D = \mathcal{S}_{123}\mathcal{A}_{14}, \quad E_2^D = \mathcal{S}_{124}\mathcal{A}_{13}, \quad E_3^D = \mathcal{S}_{134}\mathcal{A}_{12} .$$

The 2-chain defined by T_1^D is

$$T_1^{D,2} = \begin{array}{|c|c|}\hline 1 & 2 \\ \hline\end{array} \longrightarrow T_1^D = \begin{array}{|c|c|c|}\hline 1 & 2 & 3 \\ \hline 4 \\ \cline{1-1}\end{array} .$$

Thus $$e_1^{D,2} = e_{11}^{D,2} = s_1^{D,2} = \mathcal{S}_{12}$$

and $$s_1^D = \mathcal{A}_{34} .$$

The 2-chain defined by T_2^D is

$$T_2^{D,2} = \begin{array}{|c|c|}\hline 1 & 2 \\ \hline\end{array} \longrightarrow T_2^D = \begin{array}{|c|c|c|}\hline 1 & 2 & 4 \\ \hline 3 \\ \cline{1-1}\end{array} .$$

Thus $$e_2^{D,2} = e_{22}^{D,2} = s_2^{D,2} = \mathcal{S}_{12}$$

and $$s_2^D = \mathcal{S}_{34} .$$

The 2-chain defined by T_3^D is

$$T_3^{D,2} = \begin{array}{|c|}\hline 1 \\ \hline 2 \\ \hline\end{array} \longrightarrow T_3^D = \begin{array}{|c|c|c|}\hline 1 & 3 & 4 \\ \hline 2 \\ \cline{1-1}\end{array} ,$$

so that $$e_3^{D,2} = e_{33}^{D,2} = s_3^{D,2} = \mathcal{A}_{12}$$

and $$s_3^D = \mathcal{S}_{34} .$$

The matric basis elements $\{e_{k1}^D \,|\, k=1,2,3\}$, which span a minimal left ideal associated with T_1^D, are therefore [using

(62) and neglecting numerical factors]

$$e^D_{11} = \mathcal{S}_{12}\mathcal{A}_{34}\mathcal{P} ,$$

$$e^D_{21} = \mathcal{S}_{12}\mathcal{S}_{34}\cdot(3,4)\cdot\mathcal{P} ,$$

$$e^D_{31} = \mathcal{A}_{12}\mathcal{S}_{34}\cdot(2,3)(3,4)\cdot\mathcal{P} ,$$

where $$\mathcal{P} = \mathcal{A}_{14}\mathcal{S}_{123}\mathcal{A}_{14}\mathcal{A}_{34}\mathcal{S}_{12} .$$

These are the operators that were displayed in (45) on page 74. Applying them to $\Theta=\alpha\beta\alpha\beta$, one obtains the Serber functions shown in (46) on that page. The branching routes can be read directly from the geminal symmetrizers and antisymmetrizers in the matric basis elements.

General definition of the orthogonal matric bases

It is convenient to treat the matric bases for 1-chains and 2-chains together, under one master formula. Let the m-chain defined by the standard tableau T^D_r be denoted by

$$T^{D,N-m}_r \longrightarrow T^{D,N-2m}_r \longrightarrow \cdots \longrightarrow T^{D,m}_r \longrightarrow T^D_r ,$$

where m is a factor of N.

For each standard tableau $T^{D,jm}_r$ in this chain, an Hermitian operator $M^{D,jm}_r$ is defined in terms of only the highest m numbers, i.e., the numbers N-jm, N-jm-1, ..., N-(j+1)m+1. When m=1, this operator is taken to be the identity. When m=2, it is defined to be a two-electron symmetrizer or antisymmetrizer, as discussed previously.

A set of Hermitian idempotents is defined recursively in terms of each m-chain:

$$e_r^{D,N-m} = M_r^{D,N-m} \quad ,$$

$$e_r^{D,N-2m} = (E_r^{D,N-2m} M_r^{D,N-2m} e_r^{D,N-m})^{\dagger} \times$$

$$\times \quad (E_r^{D,N-2m} M_r^{D,N-2m} e_r^{D,N-m})/k_r^{D,N-2m} \quad ,$$

$$\cdot \; \cdot \; \cdot \; ,$$

$$e_r^{D} = (E_r^{D} M_r^{D} e_r^{D,m})^{\dagger} (E_r^{D} M_r^{D} e_r^{D,m})/k_r^{D} \quad ,$$

where $$k_r^D = o_\alpha^D \cdot \theta^D \cdot \rho_r^D \quad ,$$

in which $$\rho_r^D = i[C_r^D E_r^D M_r^D e_r^{D,m}] .$$

These idempotents are used to define the matric basis

$$e_{rs}^D = (E_r^D M_r^D e_r^{D,m})^{\dagger} p_{rs}^D (E_s^D M_s^D e_s^{D,m})/(k_r^D k_s^D)^{1/2}, \qquad (63)$$

in which, it will be noted, $e_{rr}^D = e_r^D$.

It is convenient to use the matric basis elements in the simpler form

$$e_{rs}^D = e_r^{D,m} M_r^D p_{rs}^D C_s^D E_s^D M_s^D e_s^{D,m}/[\theta^D (\rho_r^D \rho_s^D)^{1/2}] . \qquad (64)$$

For use in generating basis functions for the irrep of S_N labelled by D, a subset $\{e_{rs}^D | s \text{ fixed}\}$ of the matric basis is used. The operators in this subset all have the form

$$e^D_{rs} = (\text{number})\cdot\ e^{D,m}_r M^D_r p^D_{rs} \wp^D_s \ , \qquad (65a)$$

where $$\wp^D_s = C^D_s E^D_s M^D_s e^{D,m}_s \qquad (65b)$$

is <u>fixed</u>.

Discussion

We shall prove in the next section that the matric bases defined by (58)-(64) can be used to generate basis functions for orthogonal representations of S_N. More precisely, we will show that

(i) none of the elements e^D_{rs} vanishes;

(ii) these elements multiply like a matric basis;

(iii) they possess the adjoint property $e^{D\dagger}_{rs} = e^D_{sr}$;

(iv) they are linearly independent and span the group algebra, $A(S_N)$;

(v) the diagonal elements e^D_{rr} are primitive idempotents generating the minimal left ideals occurring in the decomposition of $A(S_N)$.

That the matric bases are YK-adapted (when m = 1) or Serber-adapted (when m = 2) is easier to see. Using (64), neglecting numerical factors, and noting that M^D_r commutes with $e^{D,m}_r$, $e^{D,2m}_r$, etc.,

$$e^D_{rs} = e^{D,m}_r M^D_r p^D_{rs} C^D_s E^D_s M^D_s e^{D,m}_s$$

$$= M^D_r e^{D,m}_r C^D_r E^D_r p^D_{rs} e^{D,m}_s M^D_s$$

$$= M^D_r (e^{D,2m}_r M^{D,m}_r C^{D,m}_r E^{D,m}_r M^{D,m}_r e^{D,2m}_r) \times$$

$$\times\ C^D_r E^D_r p^D_{rs} \times (e^{D,2m}_s M^{D,m}_s C^{D,m}_s E^{D,m}_s M^{D,m}_s e^{D,2m}_s) M^D_s$$

$$= M^D_r M^{D,m}_r (e^{D,2m}_r C^{D,m}_r E^{D,m}_r M^{D,m}_r e^{D,2m}_r) C^D_r E^D_r p^D_{rs} \cdots$$

$$= \ldots$$

$$= G^D_r\, E^{D,N-m}_r \cdots E^{D,N-2m}_r \cdots E^{D,m}_r \cdots E^D_r \cdots \qquad (66)$$

where $\quad G^D_r = M^D_r M^{D,m}_r \cdots M^{D,N-m}_r$

is a product of commuting operators. When m=1, G^D_r is simply the identity. When m=2, it is a string of geminal symmetrizers and antisymmetrizers.

Comparison of (66) with the heuristically-derived operators $E_Y E_Y^\dagger$ and $E_S E_S^\dagger$ of the previous section shows that e^D_{rs} is YK-adapted when m=1 and Serber-adapted when m=2.

Orthogonal YK-adapted representation matrices were first obtained by Young (1932, p. 218). This is the representation known in the literature as "Young's orthogonal representation". Pauncz (1967) has shown that this representation is identical to that obtained by Yamanouchi. A matric basis for such a representation can be obtained from the relations (54) between orthogonal matric basis elements and permutations. One obtains the so-called "orthogonal units" (Rutherford, 1948, p. 50)

$$o^D_{rs} = (d^D/N!) \sum_P [P]^D_{rs} P, \tag{67}$$

where the sum runs over the entire symmetric group. Goddard (1967a, 1967b, 1968) has employed this matric basis in quantum-chemical calculations.

In nuclear theory, Jahn and co-workers (Jahn and van Wieringen, 1951; Elliott, Hope, and Jahn, 1953; Jahn, 1954) have used matric bases for orthogonal YK- and Serber-adapted representations. The latter were obtained from the orthogonal units (67) by finding the transformation between YK and Serber representations.

General discussions of matric bases, considered according to their expansions in permutations, have been given by Matsen and co-workers (Matsen, 1964; Klein, Carlisle, and Matsen, 1970).

In all of these accounts, matric basis elements were described as linear combinations of all N! permutations in S_N. Thus matric bases were expressed as sets of Wigner operators. The disadvantages of this approach were discussed in the last chapter.

To the author's knowledge, the only previous attempt to obtain matric bases directly from the standard Young tableaux was the derivation by Thrall (1941) of "Young's semi-normal units". These have been discussed by Rutherford (1948). The work reported in the present chapter is an extension of Thrall's approach to orthogonal representations useful in quantum chemistry.

The formulas given in the previous section would appear to avoid the drawbacks of other methods for obtaining basis functions. Referring to equation (65), one sees that basis functions for any irrep of S_N can be generated by a set of operators constructed from symmetrizers, antisymmetrizers, and the permutations p^D_{rs} relating standard tableaux. Furthermore, the "right half" of each operator, given by (65b), is fixed throughout the calculation.

Although the matric bases presented here are defined recursively, this does not cause serious computational difficulties. The recursion gives rise to a number of row and column operators which must be applied in succession to a primitive function. As can be seen from the examples in the last section, one applies a symmetrizer or antisymmetrizer to the primitive, collects terms, and then applies another. The operators are all "read" directly from the standard tableaux. A computer program for such a procedure would not require large amounts of storage - the chief drawback of other approaches. Such a program would have to perform very many permutations and collections of terms, but these operations involve only data transferrals and integer arithmetic, and can be performed quickly.

A computer program is being written to generate Serber spin functions by means of the matric basis elements (62).

Basic Lemmas

Before proceeding to the lemmas and theorems specific to orthogonal matric bases, we summarize some elementary results that will be needed.

The definitions (57)-(64) used in the construction of matric bases involve numerical factors i[x], the coefficient of the identity in an element x of the group algebra. This function defined on $A(S_N)$ has two properties which we shall find useful.

Lemma 1:

If μ is a number and x is an element of $A(S_N)$, then

$$i[\mu x] = \mu \cdot i[x].$$

Proof: If $x = \sum \xi(P)P$, then $\mu x = \sum \mu\xi(P)P$, so that $i[\mu x] = \mu\xi(I)$. But $\mu i[x] = \mu\xi(I)$ also.

Lemma 2:

If x and y are elements of $A(S_N)$, then $i[xy] = i[yx]$.

Proof: If $x = \sum \xi(P)P$ and $y = \sum \eta(P')P'$, then

$$i[xy] = \sum \xi(P)\eta(P^{-1})$$

$$\text{and} \quad i[yx] = \sum \eta(P)\xi(P^{-1}).$$

Since the sums run over an entire group, these expressions are identical.

Notice that Lemma 2 implies the following cyclic property:

$$i[xyz] = i[zxy] = i[yzx],$$

for any elements x, y, z of the group algebra.

We now repeat the definition of the adjoint operation and prove two results.

Definition:

For any element $x = \sum \xi(P)P$ in $A(S_N)$, the adjoint element is defined to be

$$x^{\dagger} = \sum \xi^{*}(P)P^{-1},$$

where * denotes the complex conjugate.

Lemma 3:

For any x and y in $A(S_N)$, $(xy)^{\dagger} = y^{\dagger}x^{\dagger}$.

Proof: Defining x and y as before,

$$(xy)^{\dagger} = [\sum_{P}\sum_{P'} \xi(P)\eta(P')PP']^{\dagger} = \sum_{P}\sum_{P'} \xi^{*}(P)\eta^{*}(P')P'^{-1}P^{-1}$$

$$= [\sum_{P'} \eta^{*}(P')P'^{-1}][\sum_{P} \xi^{*}(P)P^{-1}] = y^{\dagger}x^{\dagger}.$$

Lemma 4:

For any x in $A(S_N)$ other than the null, $i[xx^{\dagger}] > 0$.

Proof: If $x = \sum \xi(P)P$, then $x^{\dagger} = \sum \xi^{*}(P)P^{-1}$, so that

$$i[xx^{\dagger}] = \sum_{P} |\xi(P)|^{2} > 0,$$

if at least one coefficient $\xi(P)$ is nonzero.

We shall make frequent use of two properties of the tableau operators R_r^D, C_r^D, and E_r^D. These are proved in Rutherford (1948), so they are quoted here without proof.

Lemma 5:

For every D, r, and s,

$$p_{rs}^{D}\, R_s^D = R_r^D\, p_{rs}^{D} \quad \text{and} \quad p_{rs}^{D}\, C_s^D = C_r^D\, p_{rs}^{D} ,$$

so that

$$p_{rs}^{D}\, E_s^D = E_r^D\, p_{rs}^{D} .$$

Lemma 6:

For every D, D', r, s, and every x in $A(S_N)$,

$$E_r^D\, x\, E_s^{D'} = \delta^{DD'}\, E_{rs}^D \cdot \theta^D\, i[E_{sr}^D x],$$

where $\theta^D = [N!/d^D] > 0$, and $E_{rs}^D = p_{rs}^D E_s^D = E_r^D p_{rs}^D$.

Lemmas Concerning the Matric Bases

Lemma 7:

If the numbers N-1 and N are on different rows and different columns in a standard tableau T_r^D containing N numbers, then $E_r^D\, e_r^{D,2}$ does not contain the transposition $(N-1,N)$: i.e., the coefficient of $(N-1,N)$ in $E_r^D\, e_r^{D,2}$ is zero.

Proof: The element $e_r^{D,2}$ does not operate on the numbers $N-1$ and N. Therefore, if $E_r^D\, e_r^{D,2}$ were to contain $(N-1,N)$, E_r^D would have to contain a permutation of the form $(N-1,N)\tilde{p}$, where $\tilde{p}$ is a permutation which does not affect $N-1$ or N. We shall show that E_r^D can contain no such permutation.

There are two forms possible for T_r^D, namely

$$\begin{array}{cccc} & \vdots & & \vdots \\ \cdots & k & \cdots & N-1 \\ & \vdots & & \\ \cdots & N & & \end{array} \tag{68}$$

and

$$\begin{array}{cccc} & \vdots & & \vdots \\ \cdots & k & \cdots & N \\ & \vdots & & \\ \cdots & N-1 & & \end{array} \tag{69}$$

It is sufficient to consider only the former. With T_r^D of the form (68), E_r^D will contain only permutations of the form $\tilde{r}\, r_{N-1} r_N c_N c_{N-1}\, \tilde{c}$, where r_N is a row permutation for the row containing N, etc., and $\tilde{r}$, $\tilde{c}$ are permutations which do not operate on $N-1$ or N.

If $$\tilde{r}\, r_{N-1} r_N c_N c_{N-1}\, \tilde{c} = (N-1,N)\tilde{p},$$

then $$r_{N-1} r_N c_N c_{N-1} = (N-1,N)\tilde{r}^{-1}\tilde{p}\tilde{c}^{-1} = (N-1,N)\tilde{q}, \tag{70}$$

where $\tilde{q}$ does not operate on N-1 or N. We will prove that (70) is impossible.

According to (70), $r_{N-1}r_Nc_Nc_{N-1}$ must be a permutation in which N is replaced by N-1, and N-1 by N. We know from the form (68) of the tableau, however, that $r_{N-1}r_Nc_Nc_{N-1}$ has the form

$$(\ldots k \ldots N-1)(\ldots N)(\ldots k \ldots N)(\ldots N-1), \qquad (71)$$

where the dots represent numbers other than k, N-1, or N. Now, because of the form of the tableau, <u>no two of these permutations can share any numbers other than k, N-1, and N</u>. Thus if, in $c_N = (\ldots k \ldots N)$, N is replaced by a number ℓ other than k or N-1, the product $r_{N-1}r_Nc_Nc_{N-1}$ will be a permutation $(\ldots N\ell)$ because neither r_{N-1} nor r_N will operate on ℓ. Consequently, if any permutation of the form (71) can satisfy (70), it will be one in which the numbers represented by dots play no part at all. We may just as well consider the simpler tableau

$$T_r^D = \begin{matrix} k & N-1 \\ N & \end{matrix} .$$

But then

$$\begin{aligned} E_r^D &= [I+(k,N-1)][I-(k,N)] \\ &= I + (k,N-1) - (k,N) - (k,N,N-1). \end{aligned}$$

We have proven that E_r^D can contain no permutation of the form $(N-1,N)\tilde{p}$ if T_r^D is of the form (68). The proof for (69) is similar.

Lemma 8:

$$i[E_r^D\, M_r^D\, e_r^{D,m}] = k \cdot i[E_r^{D,m}\, e_r^{D,m}],\ k>0,$$

for every D and r, and for m=1 or m=2.

Proof: We deal here with operators defined in terms of a single standard tableau and its m-chain. We therefore drop the superscripts and subscripts, and denote E_r^D by E, M_r^D by M, and $e_r^{D,m}$ by e^-.

For a 1-chain, it can be shown (Rutherford, 1948, p. 28) that

$$\begin{aligned} E &= E^- + (\text{terms operating on } N) \\ &= E^- + t_N\ . \end{aligned}$$

Therefore, $i[Ee^-] = i[E^-e^-] + i[t_Ne^-]$. The last term is zero because e^- does not operate on N, and t_N is made up only of permutations that operate on N. Thus t_Ne^- cannot contain the identity. This proves the theorem when m=1.

For a 2-chain, there are three cases.

(i) If N-1 and N appear on the same row of T_r^D, then $M_r^DR_r^D = R_r^D$ because R_r^D contains the idempotent M_r^D and is a group sum. Thus

$$\begin{aligned} i[EMe^-] &= i[RCMe^-] = i[RCe^-M] = i[MRCe^-] \\ &= i[RCe^-] = i[Ee^-]. \end{aligned}$$

We have used Lemma 2 and the fact that M commutes with e^-.

(ii) If N-1 and N appear on the same column of T_r^D, the argument is similar: $C_r^D M_r^D = C_r^D$, so that

$$i[EMe^-] = i[RCMe^-] = i[RCe^-] = i[Ee^-].$$

(iii) If N-1 and N occur on different rows and different columns in T_r^D, then

$$\begin{aligned} i[EMe^-] &= i[E \cdot (1/2)\{I \pm (N-1,N)\} \cdot e^-] \\ &= (1/2)i[Ee^-] \pm (1/2)i[E\cdot(N-1,N)\cdot e^-] \end{aligned}$$

The last term contains $i[E\cdot(N-1,N)\cdot e^-] = i[Ee^-\cdot(N-1,N)]$, which is zero unless Ee^- contains (N-1,N). We proved in Lemma 7 that this is impossible.

In all three cases, $i[EMe^-] = k\cdot i[Ee^-]$, where $k>0$. By an argument exactly parallel to that for 1-chains, it can be shown that $i[Ee^-] = i[E^-e^-]$. This proves the theorem for $m=2$.

Existence Proofs

Our purpose in this section is to show that none of the matric basis elements vanish or blow up. The definitions involve factors ρ_r^D in the denominators. We begin by proving that these quantities are never zero. As a by-product, we are able to show that the diagonal elements of the matric basis are idempotent.

Theorem 1:

For any D and r, and for m=1 or m=2,

(a) $\rho^D_r \overset{d}{=} i[C^D_r E^D_r M^D_r e^{D,m}_r] = i[C^D_r R^D_r C^D_r M^D_r e^{D,m}_r] > 0;$

(b) $i[E^D_r M^D_r e^{D,m}_r] \neq 0;$

(c) e^D_r is idempotent and self-adjoint.

Proof: The proof is by induction. Using the notation of the previous lemma, we assume that

$$i[E^- e^-] \neq 0, \quad e^- e^- = e^-, \quad e^{-\dagger} = e^-,$$

then show that these properties recur: that

$$i[Ee] \neq 0, \quad ee = e, \quad e^\dagger = e, \tag{72}$$

and also that $i[CEMe^-] > 0$, $i[EMe^-] \neq 0$.
This is shown in five steps.

(i) We assume that $i[E^- e^-] \neq 0$, so that $i[EMe^-] \neq 0$ by Lemma 8. This is the induction for part (b). Therefore, $x \overset{d}{=} EMe^-$ is not the null, and $i[xx^\dagger] > 0$ by Lemma 4.

(ii) $i[CEMe^-] = i[CRCMe^-] = i[CR\ RCMe^-]/o^D_{\mathcal{R}}$

$$= i[RCMe^- CR]/o^D_{\mathcal{R}},$$

using Lemmas 1 and 2. By construction, M is idempotent and commutes with e^-: $Me^- = Me^- M$. In addition, we assume that e^- idempotent, so $Me^- = Me^- e^- M$, and

$$i[CEMe^{-}] = i[(RCMe^{-})(e^{-}MCR)]/o_{\alpha}^{D}.$$

Furthermore, $(RCMe^{-})^{\dagger} = e^{-\dagger}M^{\dagger}C^{\dagger}R^{\dagger}$. We assume that $e^{-\dagger} = e^{-}$, and $M^{\dagger} = M$, $C^{\dagger} = C$, $R^{\dagger} = R$ by construction. Thus

$$(RCMe^{-})^{\dagger} = (e^{-}MCR)$$

and $\quad i[CEMe^{-}] = i[(RCMe^{-})(RCMe^{-})^{\dagger}]/o_{\alpha}^{D} = i[xx^{\dagger}]/o_{\alpha}^{D} > 0.$

This is the induction for part (a). We have yet to justify equations (72).

(iii) Since $\rho = i[CEMe^{-}] \neq 0$ by (ii), the quantity $i[Ee] = i[Ee^{-}MCEMe^{-}]/(\theta\rho)$ is defined. But

$$\begin{aligned} Ee^{-}MCE &= E\cdot\theta i[Ee^{-}MC] \text{ by Lemma 6,} \\ &= E\cdot\theta i[CEMe^{-}] \text{ using Lemma 2,} \\ &= E\cdot\theta\rho \ , \end{aligned}$$

so that $\qquad i[Ee] = i[EMe^{-}] \neq 0$ by (i).

(iv) Assuming that e^{-} is idempotent,

$$\begin{aligned} ee &= e^{-}MCEMe^{-}e^{-}MCEMe^{-} \ / \ (\theta\rho)^{2} \\ &= e^{-}MC\cdot EMe^{-}CE\cdot Me^{-} \ / \ (\theta\rho)^{2} \\ &= e^{-}MC\cdot E\theta\rho\cdot Me^{-} \ / \ (\theta\rho)^{2} \quad \text{[as in (iii)]} \\ &= e^{-}MCEMe^{-} \ / \ (\theta\rho) \\ &= e \ . \end{aligned}$$

(v) $e^{\dagger} = (e^{-}MCRCMe^{-})^{\dagger}/(\theta\rho)$, since θ and ρ are real. We assume that $e^{-\dagger} = e^{-}$, so that

$$\begin{aligned} e^{\dagger} &= e^{-}M^{\dagger}C^{\dagger}R^{\dagger}C^{\dagger}M^{\dagger}e^{-}/(\theta\rho) \\ &= e^{-}MCRCMe^{-}/(\theta\rho) \\ &= e. \end{aligned}$$

This completes the induction scheme. We now prove that the induction has a base.

For a 1-chain, $E_r^{D,N-1} = e_r^{D,N-1} = I$, so that $e_r^{D,N-1}$ is idempotent and self-adjoint, and

$$i[E_r^{D,N-1}e_r^{D,N-1}] = i[I] = 1 \neq 0.$$

For 2-chains, $E_r^{D,N-2} = e_r^{D,N-2} = [I\pm(1,2)]/2$, so that $e_r^{D,N-2}$ is idempotent and self-adjoint, and

$$i[E_r^{D,N-2}e_r^{D,N-2}] = i[e_r^{D,N-2}] = 1/2 \neq 0. \qquad \underline{\text{Q.E.D.}}$$

<u>Theorem</u> <u>2</u>:

None of the elements e_{rs}^D is the null.

Proof: We prove that $E_r^D e_{rs}^D E_s^D$ does not vanish. This is

$$E_r^D\, e_{rs}^D\, E_s^D = \underline{E_r^D\, e_r^{D,m}\, M_r^D\, C_r^D\, E_r^D}\, p_{rs}^D\, M_s^D\, e_s^{D,m}\, E_s^D\, /[\theta^D(\rho_r^D\rho_s^D)^{1/2}]$$

The underlined part is $E_r^D\theta^D\rho_r^D$ by Lemmas 6 and 2 [the argument is similar to that in step (iii) of Theorem 1], so that

$$E_r^D\, e_{rs}^D\, E_s^D = E_r^D\, p_{rs}^D\, M_s^D\, e_s^{D,m}\, E_s^D\, (\rho_r^D/\rho_s^D)^{1/2},$$

or $$E_r^D\, e_{rs}^D\, E_s^D = p_{rs}^D\, E_s^D\, M_s^D\, e_s^{D,m}\, E_s^D\, (\rho_r^D/\rho_s^D)^{1/2}$$

$$= p_{rs}^D\, E_s^D\, \theta^D\, i[E_s^D M_s^D e_s^{D,m}]\, (\rho_r^D/\rho_r^D)^{1/2}.$$

It was shown in Theorem 1 that ρ_r^D, ρ_s^D, and $i[E_s^D M_s^D e_s^{D,m}]$ are nonzero. Also, $\theta^D>0$ by Lemma 6 and $p_{rs}^D E_s^D$ is not the null (Rutherford, 1948, p. 16). This completes the proof.

We have now proved that the definitions (57)-(64) of the orthogonal matric bases yield existing, nonvanishing operators.

Multiplicative Properties

Theorem 1 has already shown that the diagonal elements $e_r^D = e_{rr}^D$ are idempotent. This fact, and the two lemmas that follow, are enough to establish the matric basis multiplication relation.

First we must show that

$$M_r^D\, e_r^{D,m}\, e_s^{D,m}\, M_s^D = \delta_{rs}\, M_r^D\, e_r^{D,m}\ . \qquad (73)$$

It is clear to begin with that

$$M_r^D\, e_r^{D,m}\, e_r^{D,m}\, M_r^D = M_r^D\, e_r^{D,m}\ ,$$

because M_r^D and $e_r^{D,m}$ are idempotent and commuting. It remains only to show that

$$M_r^D\, e_r^{D,m}\, e_s^{D,m}\, M_s^D = \text{null} \quad \text{if } r \neq s.$$

This is the purpose of Lemmas 9 and 10.

Lemma 9:

(For 1-chains) Suppose that two standard tableaux T_r^D and T_s^D belong to the same diagram, D, and differ in the position of the highest number, N. Then $T_r^{D,1}$ and $T_s^{D,1}$ belong to different diagrams, and

$$E_r^{D,1}\, x\, E_s^{D,1} = \text{null} = E_s^{D,1}\, x\, E_r^{D,1}$$

for every x in the group algebra.

(For 2-chains) Let two standard tableaux, T_r^D and T_s^D, belonging to the same diagram, D, differ in the position of at least one of the two highest numbers, N-1 and N. Then either

$$M_r^D\, M_s^D = \text{null} = M_s^D\, M_r^D$$

or $T_r^{D,2}$ and $T_s^{D,2}$ belong to different diagrams. In the latter case,

$$E_r^{D,2}\, x\, E_s^{D,2} = \text{null} = E_s^{D,2}\, x\, E_r^{D,2}$$

for every x in $A(S_N)$.

Proof: For 1-chains, it is obvious that $T_r^{D,1}$ and $T_s^{D,1}$ will belong to different diagrams. The conclusion follows from Lemma 6.

For 2-chains, the argument is similar except when

$T_r^D = (N-1,N)T_s^D$. In such a case, $T_r^{D,2}$ and $T_s^{D,2}$ will belong to the same diagram, but we have defined M_r^D and M_s^D such that one will symmetrize N-1 and N, and the other will antisymmetrize them. In this case,

$$M_r^D\, M_s^D = \text{null} = M_s^D\, M_r^D \ .$$

<u>Lemma</u> <u>10</u>:

Let T_r^D and T_s^D be different standard tableaux belonging to the same diagram, D. Then

$$M_r^D\, e_r^{D,m}\, e_s^{D,m}\, M_s^D = \text{null}.$$

Proof: If T_r^D and T_s^D differ in the positions of their highest one (for 1-chains) or two (for 2-chains) numbers, then Lemma 9 applies directly, and, since M_s^D commutes with $e_t^{D,m}$ for every t,

$$\begin{aligned} M_r^D e_r^{D,m} e_s^{D,m} M_s^D &= M_r^D M_s^D e_r^{D,m} e_s^{D,m} \\ &= (\text{number})\ \underline{M_r^D M_s^D} e_r^{D,2m} M_r^{D,m} C_r^{D,m} \times \\ &\quad \times\ \underline{E_r^{D,m} M_r^{D,m} e_r^{D,2m} e_s^{D,2m} M_s^{D,m} C_s^{D,m} E_s^{D,m}} M_s^{D,m} e_s^{D,2m} \end{aligned}$$

where one or the other of the underlined factors is the null.

Otherwise, there is a number k such that removal of the highest km numbers from T_r^D and T_s^D results in tableaux $T_r^{D,km}$ and $T_s^{D,km}$ differing in the positions of their highest m numbers. Then recursive substitution gives

$$M_r^D e_r^{D,m} e_s^{D,m} M_s^D$$

$$= (\text{number})\ M_r^D e_r^{D,2m} M_r^{D,m} C_r^{D,m} \times$$

$$\times\ E_r^{D,m} M_r^{D,m} e_r^{D,2m} e_s^{D,2m} M_s^{D,m} C_s^{D,m} E_s^{D,m} M_s^{D,m} e_s^{D,2m} M_s^D$$

$$= \ .\ .\ .$$

$$= (\text{number})\ M_r^D \cdots \underline{M_r^{D,km} e_r^{D,(k+1)m} e_s^{D,(k+1)m} M_s^{D,km}} \cdots M_s^D$$

where the underlined factor is the null, by the argument given above. This proves the lemma.

Lemmas 6 and 10 and Theorem 1(c) put us in position to show how the elements e_{rs}^D multiply.

<u>Theorem</u> <u>3</u>:

$$e_{rs}^D\ e_{tu}^{D'} = \delta^{DD'} \delta_{st}\ e_{ru}^D$$

Proof:

$$e_{rs}^D e_{tu}^{D'} = [\theta^D \theta^{D'} (\rho_r^D \rho_s^D \rho_t^{D'} \rho_u^{D'})^{1/2}]^{-1} \times$$

$$\times\ e_r^{D,m} M_r^D P_{rs}^D C_s^D \underline{E_s^D M_s^D e_s^{D,m} e_t^{D',m} M_t^{D'} P_{tu}^{D'} C_u^{D'} E_u^{D'}} M_u^{D'} e_u^{D',m}$$

where the underlined factor vanishes if D≠D', by Lemma 6. Therefore,

$$e^D_{rs}e^{D'}_{tu} = \delta^{DD'} e^{D,m}_r M^D_r p^D_{rs} C^D_s E^D_s \underline{M^D_s e^{D,m}_s e^{D,m}_t M^D_t} p^D_{tu} C^D_u E^D_u M^D_u e^{D,m}_u \times$$
$$\times \ (\theta^D)^{-2} (\rho^D_r \rho^D_s \rho^D_t \rho^D_u)^{-1/2}$$

By Lemma 10, the underlined factor is $\delta_{st} M^D_s e^{D,m}_s$, so

$$e^D_{rs}e^{D'}_{tu} = \delta^{DD'} \delta_{st}\, e^{D,m}_r M^D_r p^D_{rs} C^D_s E^D_s M^D_s e^{D,m}_s p^D_{su} C^D_u E^D_u M^D_u e^{D,m}_u \times$$
$$\times \ (\theta^D)^{-2} (\rho^D_s)^{-1} (\rho^D_r \rho^D_u)^{-1/2} .$$

Using the fact that $p^D_{su} C^D_u E^D_u = C^D_s E^D_s p^D_{su}$, from Lemma 5,

$$e^D_{rs}e^{D'}_{tu} = \delta^{DD'} \delta_{st}\, e^{D,m}_r M^D_r p^D_{rs} C^D_s \underline{E^D_s M^D_s e^{D,m}_s C^D_s E^D_s} p^D_{su} M^D_u e^{D,m}_u \times$$
$$\times \ (\theta^D)^{-2} (\rho^D_s)^{-1} (\rho^D_r \rho^D_u)^{-1/2}$$

By Lemmas 6 and 2, the underlined part is

$$E^D_s \ \theta^D i\,[E^D_s M^D_s e^{D,m}_s C^D_s] = E^D_s \ \theta^D i\,[C^D_s E^D_s M^D_s e^{D,m}_s] = E^D_s \ \theta^D \rho^D_s ,$$

so that

$$e^D_{rs}e^{D'}_{st} = \delta^{DD'} \delta_{st}\, e^{D,m}_r M^D_r p^D_{rs} C^D_s E^D_s p^D_{su} M^D_u e^{D,m}_u \ / \ [\theta^D (\rho^D_r \rho^D_u)^{1/2}]$$

$$= \delta^{DD'} \delta_{st}\, e^{D,m}_r M^D_r p^D_{rs} p^D_{su} C^D_u E^D_u M^D_u e^{D,m}_u \ / \ [\theta^D (\rho^D_r \rho^D_u)^{1/2}]$$

$$= \delta^{DD'} \delta_{st}\, e^{D,m}_r M^D_r p^D_{ru} C^D_u E^D_u M^D_u e^{D,m}_u \ / \ [\theta^D (\rho^D_r \rho^D_u)^{1/2}]$$

$$= \delta^{DD'} \delta_{st}\, e^D_{ru}$$

This proves the theorem.

Orthogonal Operator Bases for Every Irreducible Representation

It follows from Theorem 3 that a matric basis $\{e^D_{rs} | \text{all } D,r,s\}$ consists of

$$\sum_D (d^D)^2 = N!$$

linearly independent elements. The argument was given on page 78. Thus the YK- and Serber-adapted matric bases introduced here <u>span the entire group algebra</u>.

Furthermore, they have been defined in such a way that

$$e^{D\dagger}_{rs} = [(E^D_r M^D_r e^{D,m}_r)^\dagger p^D_{rs} (E^D_s M^D_s e^{D,m}_s)]^\dagger / (k^D_r k^D_s)^{1/2}$$

$$= [(E^D_s M^D_s e^{D,m}_s)^\dagger p^D_{sr} (E^D_r M^D_r e^{D,m}_r)] / (k^D_s k^D_r)^{1/2}$$

$$= e^D_{sr}$$

Thus these matric bases have the adjoint property (53). It follows that a subset

$$B^D_s = \{e^D_{rs} | s \text{ fixed, all } r\}$$

spans a carrier space for an <u>orthogonal</u> representation of S_N. We say that B^D_s is an operator basis for an orthogonal representation, or for short, an <u>orthogonal operator basis.</u>

Now B^D_s consists of elements $e^D_{rs} = e^D_{rs} e^D_{ss}$, with s fixed, spanning a left ideal generated by the idempotent e_{ss}^{D}. As a matter of fact, this left ideal is *minimal*, for we now show that e_{ss}^{D} is a *primitive idempotent*.

Theorem 4:

For any D, D', r, and s, and any element x in the group algebra,

$$e_{r}^{D}\ x\ e_{s}^{D'} = e_{rr}^{D}\ x\ e_{ss}^{D'} = \delta^{DD'}\lambda(x)e_{rs}^{D} \ ,$$

where $\lambda(x)$ is a number that depends on x.

Proof:

$$e_{r}^{D}xe_{s}^{D'} = e_{r}^{D,m}M_{r}^{D}C_{r}^{D}\underline{E_{r}^{D}M_{r}^{D}e_{r}^{D,m}xe_{s}^{D',m}M_{s}^{D'}C_{s}^{D'}E_{s}^{D'}}M_{s}^{D'}e_{s}^{D',m} \quad \times$$

$$\times \quad (\theta^{D}\theta^{D'}\rho_{r}^{D}\rho_{s}^{D'})^{-1}$$

Applying Lemma 6 to the underlined portion,

$$e_{r}^{D}xe_{s}^{D'} = \delta^{DD'}e_{r}^{D,m}M_{r}^{D}C_{r}^{D}p_{rs}^{D}E_{s}^{D}M_{s}^{D}e_{s}^{D,m} \quad \times$$

$$\times \quad i[p_{sr}^{D}E_{r}^{D}M_{r}^{D}e_{r}^{D,m}xe_{s}^{D,m}M_{s}^{D}C_{s}^{D}](\theta^{D})^{-2}(\rho_{r}^{D}\rho_{s}^{D})^{-1}$$

$$= \delta^{DD'}\cdot(\text{number})\cdot e_{rs}^{D}$$

We have as a special case of this result,

$$e_{r}^{D}\ x\ e_{r}^{D} = \lambda(x)e_{r}^{D} \ ,$$

for arbitrary x. Thus e_{r}^{D} has the property (47): the diagonal elements of the matric bases are *primitive idempotents*.

These idempotents, unlike the Young idempotents, generate the minimal left ideals occurring in the decomposition of the group algebra. This we prove by showing that the identity, the generating unit of the whole group algebra, decomposes as the sum of the linearly independent elements e_r^D, which generate minimal left ideals.

Theorem 5:

$$\sum_D\sum_r e_r^D = \sum_D\sum_r e_{rr}^D = I$$

Proof: Let $T = \sum_D\sum_r e_{rr}^D$. Since the matric basis spans $A(S_N)$, an arbitrary element x can be expanded in the form

$$x = \sum_D\sum_r\sum_s \xi_{rs}^D e_{rs}^D .$$

It follows that

$$\begin{aligned} xT &= \sum_D\sum_r\sum_s \xi_{rs}^D e_{rs}^D \sum_{D'}\sum_t e_{tt}^{D'} = \sum_D\sum_r\sum_s\sum_{D'}\sum_t \xi_{rs}^D (e_{rs}^D e_{tt}^{D'}) \\ &= \sum_D\sum_r\sum_s\sum_{D'}\sum_t \xi_{rs}^D (\delta^{DD'}\delta_{st} e_{rs}^D) = \sum_D\sum_r\sum_s \xi_{rs}^D e_{rs}^D \\ &= x, \end{aligned}$$

for arbitrary x. Similarly, $Tx = x$. It follows that $T = I$.

It should be noted that this theorem cannot be proved with Young idempotents E_r^D in place of the e_r^D. This is because $E_r^D E_s^D \neq \delta_{rs} E_r^D$, in general. Young operators do not multiply like a matric basis.

The d^D minimal left ideals for irrep D that occur in the decomposition of the group algebra are those generated by the idempotents $\{e_r^D | r=1,2,...,d^D\}$. The minimal left ideals generated by $\{E_r^D | r=1,2,...,d^D\}$ can be shown to differ from these by equivalence transformations.

We conclude by summarizing the useful properties of the matric basis elements e_{rs}^D.

Each distinct irreducible representation of the symmetric group is labelled by a Young diagram, D. Spin representations are labelled by diagrams with one or two rows.

The irrep labelled by D occurs d^D times in the regular representation. Similarly, d^D carrier spaces for that irrep occur in the decomposition of the group algebra. Each of these irreducible carrier spaces is a minimal left ideal associated with a standard tableau T_s^D belonging to the diagram D.

The minimal left ideal associated with T_s^D is generated by $e_s^D = e_{ss}^D$, and spanned by the subset

$$B_s^D = \{e_{rs}^D | s \text{ fixed, all } r\}$$

of the matric basis.

We have shown how to construct matric bases for orthogonal YK- and Serber-adapted irreps. Basis functions for these irreps are generated by applying the operators in B_s^D, for suitable D and arbitrary s, to a primitive function, ϕ. These basis functions will be orthogonal, since

$$
\begin{aligned}
<e^D_{rs}\phi | e^D_{ts}\phi> &= <\phi | e^{D\dagger}_{rs} e^D_{ts}\phi> \\
&= <\phi | e^D_{sr} e^D_{ts}\phi> \\
&= \delta_{rt} <\phi | e^D_{ss}\phi> \ .
\end{aligned}
$$

CONSTRUCTION OF SPACE FUNCTIONS

Generating Dual Space Functions by Means of the Matric Bases

Sometimes it is convenient to consider a SAAP, not in the form

$$\Phi_\alpha(NSM) = \mathcal{A}[\phi(N)\Theta_\alpha(NSM)], \tag{74}$$

but in the alternate form

$$\Phi_\alpha(NSM) = [d(NS)]^{-1}\sum_\beta \phi_\beta(NS\alpha)\Theta_\beta(NSM), \tag{75}$$

where ϕ_β and Θ_β are dual space and spin functions. This subject was discussed on pages 7-9. The spin functions span an irreducible representation

$$[P]^{NS} \leftrightarrow P$$

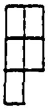
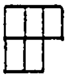
of the symmetric group. The space functions span the <u>dual representation</u>

$$\varepsilon(P)\left([P^{-1}]^{NS}\right)^t \leftrightarrow P\ .$$

When a SAAP is constructed in the form (75), there is no sum over N! permutations, as there is in (74). Thus it may be more convenient to construct SAAP's from dual space and spin functions, if these can be generated easily. The construction of dual functions by means of Wigner operators has been discussed by Kotani <u>et al</u>. (1955), Harris (1967), and Sullivan (1968). Goddard (1967a, 1967b, 1968) has made extensive use of matric basis elements (Young's orthogonal units) for this purpose.

We now discuss how dual space and spin functions are related in terms of Young diagrams. We have shown that spin representations are labelled by diagrams with one or two rows. It turns out that space functions transform according to irreducible representations associated with diagrams having one or two columns.

A diagram obtained from another diagram by interchanging rows and columns is said to be conjugate to it. For example,

 is conjugate to  ,

while  is self-conjugate. Thus space and spin diagrams are conjugate. This fact seems to have been first mentioned by Weyl (1931), who gave the proof by tensor methods. The proof that follows uses multiplication properties of Young idempotents, and is more in keeping with the rest of our discussion. The proof consists of two theorems.

Theorem 6:

Let Γ^D be the irreducible representation of S_N corresponding to the Young diagram D. In particular, let Γ^A be the antisymmetric representation, corresponding to the diagram $\{1^N\}$. Then the direct product $\Gamma^A \otimes \Gamma^D$ is the irreducible representation corresponding to the diagram conjugate to D.

Proof: Since Γ^A is one-dimensional, $\Gamma^A \otimes \Gamma^D$ is irreducible, and is therefore labelled by some Young diagram, D':

$$\Gamma^{D'} \overset{d}{=} \Gamma^{A} \otimes \Gamma^{D} .$$

We consider the symmetries of functions transforming according to these three representations. The carrier spaces can be considered to be generated by Young idempotents, since carrier spaces generated by matric basis idempotents differ from these only by equivalence transformations.

A function f_A transforming according to Γ^A is antisymmetric with respect to any transposition, and can be generated from a primitive function f by applying the antisymmetrizer: $f_A = \mathcal{A}f$.

Functions f_D , transforming according to Γ^D, can be generated from f by operating on it with $(X_t E_t^D)$, where E_t^D is the Young idempotent for some standard tableau T_t^D belonging to D, and

$$X_t = \sum_s c_s p_{st}^D$$

is a linear combination of the p_{st}^D, with t fixed. This is discussed on page 87.

Thus a function transforming according to $\Gamma^{D'}$ is given by

$$f_{D'} = \sum_s c_s p_{su}^{D'} E_u^{D'} f = \sum_s c_s E_s^{D'} p_{su}^{D'} f ,$$

where u is arbitrary. It follows that $E_r^{D'} f_{D'} \neq 0$ for at least one value of r.

Let f_A and f_D be functions transforming according to

Γ^A and Γ^D, respectively. Then $f_A f_D$ transforms according to $\Gamma^{D'}$. Thus <u>it must be that</u>

$$E_s^{D'} f_A f_D \neq 0 \ , \tag{76}$$

<u>for at least one value of s</u>.

We now evaluate $E_s^{D'} f_A f_D$ directly, making use of the fact that $f_D = X_t E_t^D f$, for some value of t. In the following, we denote the row and column groups for a standard tableau $T_v^{D''}$ by $\mathcal{R}_v^{D''}$ and $\mathcal{C}_v^{D''}$, respectively. We use the symbols $\mathcal{A}(\mathfrak{G})$ and $\mathcal{S}(\mathfrak{G})$ to mean the antisymmetrizer and symmetrizer for a group $\mathfrak{G}$. Then

$$E_s^{D'} f_A f_D = \sum_r r \sum_c \varepsilon(c) c(f_A f_D) = \sum_{rc}\sum \varepsilon(c)(rcf_A)(rcf_D)$$

$$= \sum_{rc}\sum \varepsilon(c)\varepsilon(r)\varepsilon(c) \ \ f_A(rcf_D)$$

$$= f_A \sum_r \varepsilon(r) r \sum_c c \ f_D \ ,$$

where the sums run over $r \varepsilon \mathcal{R}_s^{D'}$ and $c \varepsilon \mathcal{C}_s^{D'}$. Thus

$$E_s^{D'} f_A f_D = f_A \cdot \mathcal{A}(\mathcal{R}_s^{D'}) \mathcal{S}(\mathcal{C}_s^{D'}) f_D \ .$$

Now let $\tilde{D}'$ be the Young diagram conjugate to D', and $T_q^{\tilde{D}'}$ be the standard tableau conjugate to $T_s^{D'}$. Then

$$\mathcal{R}_s^{D'} = \mathcal{C}_q^{\tilde{D}'} \quad \text{and} \quad \mathcal{C}_s^{D'} = \mathcal{R}_q^{\tilde{D}'} ,$$

so that

$$\begin{aligned} E_s^{D'} f_A f_D &= f_A \mathcal{A}(\mathcal{C}_q^{\tilde{D}'}) \mathcal{S}(\mathcal{R}_q^{\tilde{D}'}) f_D = f_A\, C_q^{\tilde{D}'} R_q^{\tilde{D}'} f_D \\ &= f_A\, C_q^{\tilde{D}'} R_q^{\tilde{D}'} X_t R_t^D C_t^D\, f \\ &= f_A\, \underline{E_q^{\tilde{D}'\dagger} X_t E_t^D}\, f\ . \end{aligned}$$

The underlined operator is the null unless $\tilde{D}'=D$ (Rutherford, 1948, p. 21). Thus

$$E_s^{D'} f_A f_D = 0 \quad \text{unless} \quad \tilde{D}' = D.$$

Comparing this result with (76), it is seen that D' must be the diagram conjugate to D. This completes the proof.

Theorem 7:

Let Γ^D and $\Gamma^{D'}$ be real irreducible representations of S_N corresponding to Young diagrams D and D'. Let Γ^A be the antisymmetric representation, corresponding to the diagram $\{1^N\} = \{1,1,\ldots,1\}$.

Then the direct product $\Gamma^D \otimes \Gamma^{D'}$ contains Γ^A only if D and D' are conjugate diagrams. If D and D' are conjugate, $\Gamma^D \otimes \Gamma^{D'}$ contains Γ^A once only.

Proof: The number of times that Γ^A is contained in $\Gamma^D \otimes \Gamma^{D'}$ is

$$a(A,D\otimes D') = (N!)^{-1} \sum_P \chi^A(P)\chi^D(P)\chi^{D'}(P),$$

where $\chi^{D}(P)$ is the character of the permutation P in Γ^{D}.

However, it was shown in Theorem 6 that $\Gamma^{A}\otimes\Gamma^{D} = \Gamma^{\tilde{D}}$, where $\tilde{D}$ is conjugate to D. Thus $\chi^{A}(P)\chi^{D}(P) = \chi^{\tilde{D}}(P)$. Using the orthogonality property of real simple characters,

$$a(A,D\otimes D') = (N!)^{-1}\sum_{P} \chi^{\tilde{D}}(P)\chi^{D'}(P)$$

$$= \delta(\tilde{D},D'). \qquad \text{Q.E.D.}$$

We have proved that basis functions $\{\phi_{\beta}\}$ and $\{\theta_{\beta}\}$ for irreducible representations of S_N can be used to construct antisymmetric functions of the form

$$\Phi = \sum_{\beta} \phi_{\beta}\theta_{\beta}$$

<u>only</u> if the irreps spanned by $\{\phi_{\beta}\}$ and $\{\theta_{\beta}\}$ are associated with conjugate Young diagrams.

Suppose that ϕ is a space primitive function and θ, a spin primitive. As discussed in the last chapter, spin functions for the spin diagram D can be generated from θ by operating on it with the set

$$B_s^D = \{e_{rs}^D | s \text{ fixed, all } r\}$$

of matric basis elements, for arbitrary s. Similarly, space functions for the diagram $\tilde{D}$ conjugate to D can be generated from ϕ by means of the operators

$$B_u^{\tilde{D}} = \{e_{tu}^{\tilde{D}} | u \text{ fixed, all } t\} ,$$

for arbitrary u.

A space-spin wave function of the form

$$\Phi = \sum_r (e_{ru}^{\tilde{D}}\phi)(e_{rs}^{D}\theta) \tag{77}$$

will satisfy the Pauli Principle. For

$$P\Phi = \sum_r (Pe_{ru}^{\tilde{D}}\phi)(Pe_{rs}^{D}\theta) ,$$

and, using (51),

$$P\Phi = \sum_{r}\sum_{i}\sum_{j} [P]_{ir}^{\tilde{D}}[P]_{jr}^{D} \ (e_{iu}^{\tilde{D}}\phi)(e_{js}^{D}\theta) .$$

But conjugate diagrams correspond to dual irreps, so

$$[P]_{ir}^{\tilde{D}} = \varepsilon(P)[P^{-1}]_{ri}^{D} ,$$

and

$$\begin{aligned} P\Phi &= \varepsilon(P)\sum_{i}\sum_{j}\cdot\sum_{r} [P]_{jr}^{D}[P^{-1}]_{ri}^{D}\cdot(e_{iu}^{\tilde{D}}\phi)(e_{js}^{D}\theta) \\ &= \varepsilon(P)\sum_{i}\sum_{j} [I]_{ji}^{D} \ (e_{iu}^{\tilde{D}}\phi)(e_{js}^{D}\theta) \\ &= \varepsilon(P)\sum_{i}\sum_{j} \delta_{ij} \ (e_{iu}^{\tilde{D}}\phi)(e_{js}^{D}\theta) \\ &= \varepsilon(P)\sum_{i} (e_{iu}^{\tilde{D}}\phi)(e_{is}^{D}\theta) \\ &= \varepsilon(P)\Phi . \end{aligned}$$

We assume that the spin primitive, Θ, is chosen to be an eigenfunction of $\hat{S}_z$. Then Φ will be an eigenfunction of $\hat{S}^2$ and $\hat{S}_z$, since its spin components are generated by an operator basis for a spin representation. Thus (77) shows the construction of a SAAP by means of matric basis elements.

Simultaneous Eigenfunctions of $\hat{L}^2$ and $\hat{S}^2$ by Matrix Diagonalization

Since spin-free atomic Hamiltonians are spherically symmetric, they commute with the orbital angular momentum operators $\hat{L}^2$ and $\hat{L}_z$. For this reason, it is usually convenient in atomic calculations to use a trial wave function which is an eigenfunction of $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, and $\hat{S}_z$. It is easy to extend the method of pages 59-67 to cover orbital angular momentum.

The general CI wave function is of the form (12):

$$\Psi(NSM_S) = \sum_{\substack{\phi_\pi \\ \pi\leqslant\pi'}} \sum_{\pi'\alpha} c(\phi_\pi, \pi'\alpha)\mathcal{A}[\phi_\pi(N)\Theta_{\pi'\alpha}(NSM_S)] .$$

The sum over ϕ_π includes only space products containing different orbitals: no two space products are related by a permutation. The wave function $\Psi(NSM_S)$ is general in the sense that it may contain one configuration or many, depending on the SAAP's included. It is already an eigenfunction of $\hat{S}^2$ and $\hat{S}_z$, and we assume that the $\Theta_{\pi'\alpha}$ have been constructed by one of the methods described earlier.

Each space product is an eigenfunction of $\hat{L}_z$: we write $\phi_\pi(NM_L)$. If the summation includes only space products with one value of M_L, then Ψ will be an eigenfunction of $\hat{L}_z$ with that eigenvalue:

$$\Psi(N,M_L,S,M_S) = \sum_{\substack{\phi_\pi \\ \pi<\pi'}} \sum_{\pi'\alpha} c(\phi_\pi,\pi'\alpha)\mathcal{A}[\phi_\pi(N,M_L)\Theta_{\pi'\alpha}(N,S,M_S)]$$

It is possible to choose the coefficients $c(\phi_\pi,\pi'\alpha)$ in such a way that Ψ is also an eigenfunction of $\hat{L}^2$. The procedure is similar to that used for spin functions. One calculates the $\hat{L}^2$-matrix over SAAP's

$$\mathcal{A}[\phi_\pi(N,M_L)\Theta_{\pi'\alpha}(N,S,M_S)]$$

with N, M_L, S, and M_S fixed, then finds the linear combinations of SAAP's that diagonalize the matrix.

The calculation of the $\hat{L}^2$-matrix is more complicated than that of the spin matrix, but, again, the computation is greatly simplified by the space and spin conventions we have introduced.

Since $$\hat{L}^2 = \hat{L}_-\hat{L}_+ + \hat{L}_z(\hat{L}_z+1),$$

$$\begin{aligned}\langle\mathcal{A}[\phi_\pi\Theta_{\pi'\alpha}]|\hat{L}^2\mathcal{A}[\phi_\rho\Theta_{\rho'\beta}]\rangle &= \langle\hat{L}^2\mathcal{A}[\phi_\pi\Theta_{\pi'\alpha}]|\mathcal{A}[\phi_\rho\Theta_{\rho'\beta}]\rangle \\ &= \langle\hat{L}^2(\phi_\pi\Theta_{\pi'\alpha})|\mathcal{A}[\phi_\rho\Theta_{\rho'\beta}]\rangle\ ,\end{aligned}$$

$$\langle\mathcal{A}[\phi_\pi\Theta_{\pi'\alpha}]|\hat{L}^2\mathcal{A}[\phi_\rho\Theta_{\rho'\beta}]\rangle = \langle\hat{L}_-\hat{L}_+(\phi_\pi\Theta_{\pi'\alpha})|\mathcal{A}[\phi_\rho\Theta_{\rho'\beta}]\rangle + M_L(M_L+1)\langle\phi_\pi\Theta_{\pi'\alpha}|\mathcal{A}[\phi_\rho\Theta_{\rho'\beta}]\rangle \tag{78}$$

The second integral is

$$\delta(\phi_\pi,\phi_\rho)\delta(\pi'\alpha,\rho'\beta)(2^\pi/N!), \tag{79}$$

by equation (13). This leaves only the integral

$$I \overset{d}{=} \langle\hat{L}_-\hat{L}_+(\phi_\pi\Theta_{\pi'\alpha})|\mathcal{A}[\phi_\rho\Theta_{\rho'\beta}]\rangle$$

$$= (N!)^{-1}\sum_P \varepsilon(P)[P]^{NS}_{\pi'\alpha,\rho'\beta}\langle\hat{L}_-\hat{L}_+\phi_\pi|P\phi_\rho\rangle$$

$$= \langle\hat{L}_-\hat{L}_+\phi_\pi|\mathcal{P}^{NS}_{\pi'\alpha,\rho'\beta}\phi_\beta\rangle \ ,$$

where
$$\mathcal{P}^{NS}_{\pi'\alpha,\rho'\beta} \overset{d}{=} (N!)^{-1}\sum_P\varepsilon(P)[P]^{NS}_{\pi'\alpha,\rho'\beta}P.$$

In terms of one-electron ladder operators,

$$I = \sum_{ij}\langle\hat{L}_-(i)\hat{L}_+(j)\phi_\pi|\mathcal{P}^{NS}_{\pi'\alpha,\rho'\beta}\phi_\rho\rangle \ ,$$

the sums running over all electrons.

We define

$$\Delta_{\pi\rho}(i,j) = \begin{cases} 1 \text{ if } \hat{L}_-(i)\hat{L}_+(j)\phi_\pi \text{ contains} \\ \quad \text{the same orbitals as } \phi_\rho; \\ 0 \text{ otherwise.} \end{cases}$$

If $\Delta_{\pi\rho}(i,j) = 1$, define $P^{\pi\rho}_{ij}$ to be _any_ permutation which converts ϕ_ρ into $\hat{L}_-(i)\hat{L}_+(j)\phi_\pi$. Then

$$I = (N!)^{-1} \sum_{ij}\sum \Delta_{\pi\rho}(i,j)\varepsilon(P^{\pi\rho}_{ij}) \sum_{G\varepsilon\mathfrak{G}_\rho} \varepsilon(G)\,[P^{\pi\rho}_{ij}G]^{NS}_{\pi\alpha',\rho\beta'} ,$$

or, since the matrices representing geminal permutations are diagonal,

$$I = (N!)^{-1} \sum_{ij}\sum \Delta_{\pi\rho}(i,j)\varepsilon(P^{\pi\rho}_{ij})\,[P^{\pi\rho}_{ij}]^{NS}_{\pi\alpha',\rho\beta'} \sum_{G\varepsilon\mathfrak{G}_\rho} \varepsilon(G)\,[G]^{NS}_{\rho\beta',\rho\beta'}$$

$$= (2^\rho/N!) \sum_{ij}\sum \Delta_{\pi\rho}(i,j)\varepsilon(P^{\pi\rho}_{ij})\,[P^{\pi\rho}_{ij}]^{NS}_{\pi\alpha',\rho\beta'} . \qquad (80)$$

We have used equation (11).

Putting (79) and (80) into (78), we obtain the result

$$\langle \mathcal{A}[\phi_\pi\theta_{\pi\alpha'}]\,|\hat{L}^2\mathcal{A}[\phi_\rho\theta_{\rho\beta'}]\rangle$$

$$= (N!)^{-1}\,\{2^\pi M_L(M_L+1)\,\delta(\phi_\pi,\phi_\rho)\,\delta(\pi\alpha',\rho\beta') \qquad (81)$$

$$+ 2^\rho \sum_{ij}\sum \Delta_{\pi\rho}(i,j)\varepsilon(P^{\pi\rho}_{ij})\,[P^{\pi\rho}_{ij}]^{NS}_{\pi\alpha',\rho\beta'}\} .$$

Appendix E contains a Fortran listing for a program that generates simultaneous eigenfunctions of $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, and $\hat{S}_z$ for any eigenvalues. Equation (81) is used in this program - in Subroutine FLSQME - to calculate the $\hat{L}^2$-matrix elements between SAAP's. In all, the program contains six subprograms. Their interrelations are shown in Figure 9.

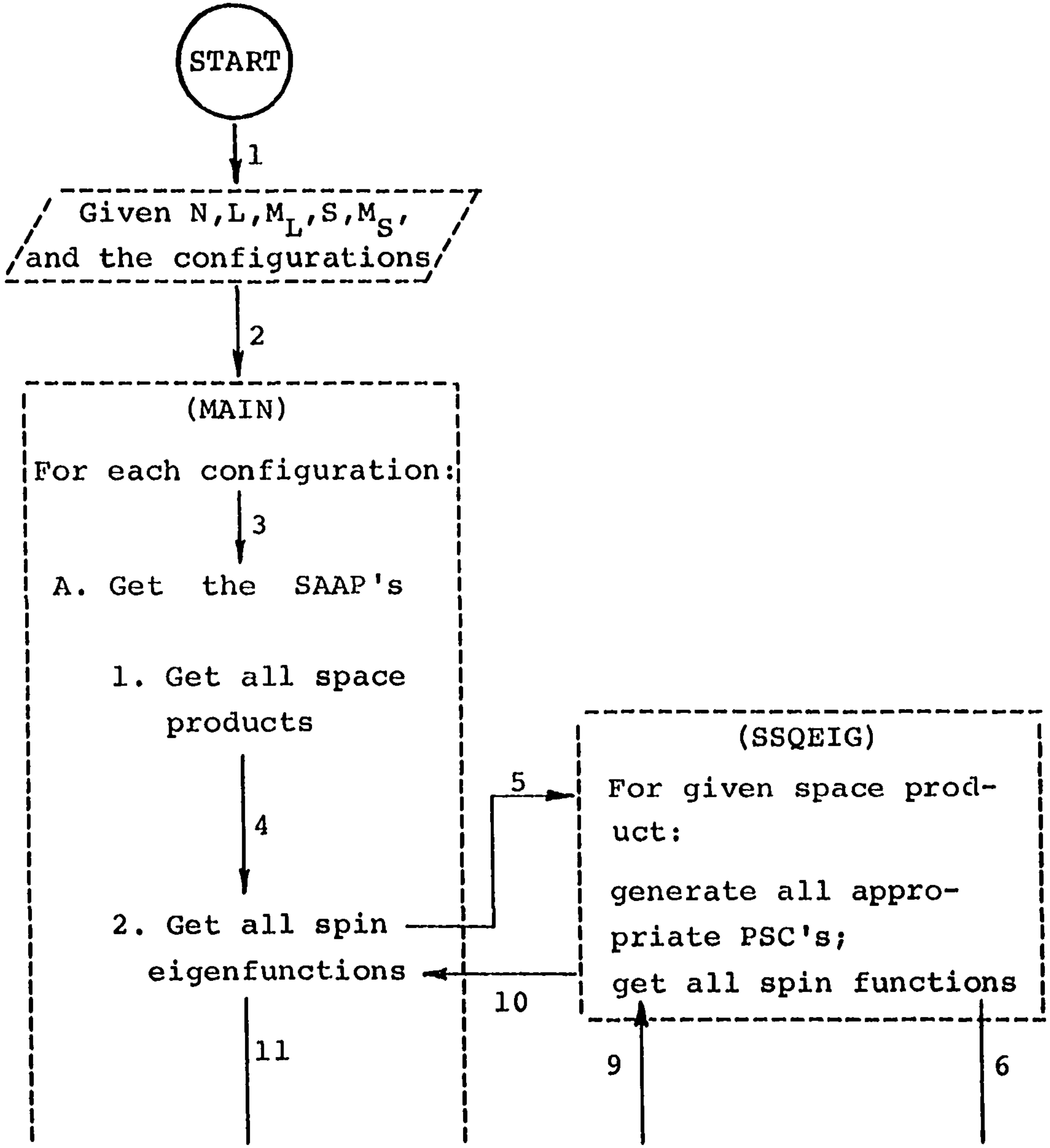
Sample running times, to obtain eigenfunctions for <u>every</u> eigenvalue L, are shown below:

N	S	M_S	M_L	Configuration	SAAP's	CPU time (sec)
2	1	0	0	p^2	1	0.4
4	0	0	0	p^4	2	0.6
4	0	0	0	p^3d	8	1.3
4	0	0	0	d^4	8	2.0
4	1	0	0	d^4	7	1.9
6	0	0	0	sp^3d^2	34	8.4

It should be noted that these are "worst-case" times. The CPU times include the internal processing of large amounts of testing output. Also, higher values of $|M_L|$ would reduce the number of orbital products required, and so lower the running time.

Schaeffer and Harris (1968) have reported a method for constructing L-S eigenfunctions as linear combinations of Slater determinants, using matrix diagonalization. They deal only with $M_L=L$, $M_S=S$. Running times are comparable to those reported here. Rotenberg (1963) wrote a machine-language program for the IBM 7090 to generate L-S eigenfunctions by means of Löwdin projection operators. Running times for the examples above were not reported. Neither of these procedures, of course, generates wave functions as linear combinations of SAAP's.

All programs that generate L-S eigenfunctions require a great deal of storage if they are to deal with more than, say, eight electrons. In fact, this seems to be the chief limitation on their use. The program given in Appendix E is designed to handle a maximum of eight electrons. A similar program, but with different storage arrangements, is being developed to handle as many as fourteen electrons.


START
1
Given N,L,M_L,S,M_S, and the configurations
2
(MAIN)
For each configuration:
3
A. Get the SAAP's
1. Get all space products
4
2. Get all spin eigenfunctions
11
5
10
(SSQEIG)
For given space product:
generate all appropriate PSC's;
get all spin functions
9
6

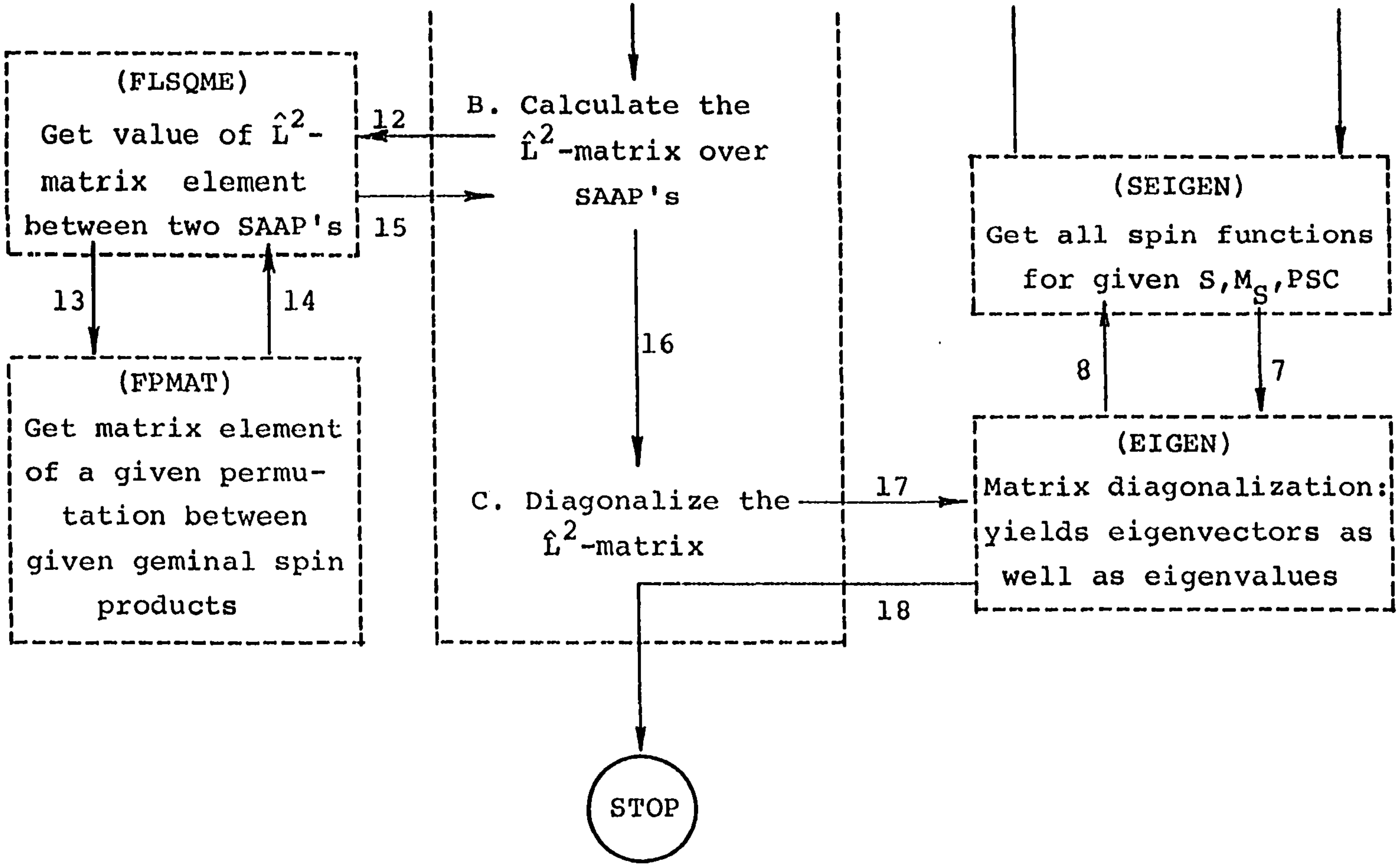


Figure 9. Organization of program generating simultaneous eigenfunctions of $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, and $\hat{S}_z$

APPENDIX A: NOTATION

(i) The symbol "$\overset{d}{=}$" is used to mean "is defined to be".

(ii) "Irrep" means "irreducible representation".

(iii) The set $X = \{x_1, x_2, \ldots, x_n\}$ is sometimes denoted
by $X = \{x_i | i=1,2,\ldots,n\}$
or by $X = \{x_i | \text{all } i\}$.

(iv) The symbol "ε" means "belongs to". For example, $x_i \varepsilon X$ in (iii).

(v) When a summation is written without explicit limits, it should be understood to run over the entire set to which the index belongs.

(vii) Dirac bra-ket notation is used for integrals:

$$<u_i u_j | v_r v_s> = \iint u_i^*(1) u_j^*(2) v_r(1) v_s(2) d\underline{x}_1 d\underline{x}_2;$$

$$<u_i u_j | \hat{H} | v_r v_s> = \iint u_i^*(1) u_j^*(2) \hat{H} v_r(1) v_s(2) d\underline{x}_1 d\underline{x}_2.$$

APPENDIX B: THE SYMMETRIC GROUP

The symmetric group, S_N, consists of the N! permutations of N objects. Here we consider permutations of electron labels, as though electrons could be labelled.

Let a, b, and c be three one-electron orbitals. By a(1)b(2)c(3), we denote that space product in which orbital a is occupied by electron 1, b by 2, and c by 3. The transformation that changes a(1)b(2)c(3) into the new product a(3)b(1)c(2), say, is a permutation of all three electrons: it replaces electron 1 by electron 3, 2 by 1, and 3 by 2. One standard notation for this permutation would be

$$a(3)b(1)c(2) = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix} a(1)b(2)c(3).$$

This is the so-called "two-row" notation. The same permutation is sometimes written $\begin{pmatrix} 1 & 2 & 3 \\ \downarrow & \downarrow & \downarrow \\ 3 & 1 & 2 \end{pmatrix}$.

A more compact notation for the same example would be

$$a(3)b(1)c(2) = (1,3,2)\ a(1)b(2)c(3).$$

The symbol "(1,3,2)" is cyclic: it reads, starting at the left, "electron 1 is replaced by electron 3, 3 by 2, and 2 by 1". In this notation, the permutation $(n_1,n_2,\ldots,n_k)$ is called a "k-cycle". Our example was of a 3-cycle. A 2-cycle permutation interchanges two objects, and is called a transposition. The identity, I, is a one-cycle.

All permutations can be written as products of transpositions. For example, (1,3,2) = (1,2)(1,3) = (1,3)(2,3) = (2,3)(1,2). If a permutation is the product of an even number of transpositions, it is said to be an even permutation; otherwise, it is odd.

The cycle structure of a permutation is a list of the cycles occurring in it, given in the order of decreasing cycle length. The notation is similar to that for partitions of the number N. The following are examples from S_4:

permutation	cycle structure
(1,3,4,2)	{4}
(1,3)·(2,4)	{2,2}
(1,2,3) = (1,2,3)·I	{3,1}
(1,3) = (1,3)·I·I	$\{2,1^2\}$
I	$\{1^4\}$

The cycle structures of permutations can be used to classify them: it can be shown that all permutations with the same cycle structure are equivalent. It is also true that a permutation and its inverse have the same cycle structure. Transpositions are their own inverses.

It is convenient to introduce a shorthand for manipulating permutations. Our first example could be written

$$bca = (1,3,2)abc,$$

in which the orbitals are listed in the order of the occupying electron labels. Operations with permutations are simplified if, in this notation, the permutation is read: "move the orbital in the first position to the third position, that in the third position to the second position, and that in the second position to the first position". The result is the same as before, but we think in terms of orbital permutations.

Using the cyclic permutation notation, the symmetric group for three objects, S_3, consists of the following six permutations: I, (1,2), (1,3), (2,3), (1,2,3), and (1,3,2), where I is the identity. The multiplication table for this group is

I	(1,2)	(1,3)	(2,3)	(1,2,3)	(1,3,2)
(1,2)	I	(1,3,2)	(1,2,3)	(2,3)	(1,3)
(1,3)	(1,2,3)	I	(1,3,2)	(1,2)	(2,3)
(2,3)	(1,3,2)	(1,2,3)	I	(1,3)	(1,2)
(1,2,3)	(1,3)	(2,3)	(1,2)	(1,3,2)	I
(1,3,2)	(2,3)	(1,2)	(1,3)	I	(1,2,3)

The <u>antisymmetrizer</u> for S_N is defined to be

$$\mathcal{A} = (N!)^{-1} \sum_{P} \varepsilon(P) P \ ,$$

where the sum runs over the whole group and $\varepsilon(P)$ is +1 when P is even and -1 when P is odd. Since the sum extends over a complete group, the antisymmetrizer is essentially invariant under left- and right-multiplications by permutations:

$$P'\mathcal{A} = (N!)^{-1}\sum_{P}\varepsilon(P)P'P = (N!)^{-1}\sum_{P''}\varepsilon(P'^{-1}P'')P''$$

$$= (N!)^{-1}\,\varepsilon(P'^{-1})\sum_{P''}\varepsilon(P'')P'' = \varepsilon(P')\mathcal{A} \quad .$$

Similarly, $\mathcal{A}P' = \varepsilon(P')\mathcal{A}$.

From this it follows that $\mathcal{A}$ is <u>idempotent</u>:

$$\mathcal{A}\mathcal{A} = (N!)^{-1}\sum_{P}\varepsilon(P)P\mathcal{A} = (N!)^{-1}\sum_{P}\varepsilon(P)\varepsilon(P)\mathcal{A} = \mathcal{A}(N!)^{-1}\sum_{P}(+1) = \mathcal{A} \; .$$

We now find the Hermitian adjoints of permutations and antisymmetrizers. Consider the N-electron integral $<P\psi|\phi>$, where ψ and ϕ are well-behaved functions. The Hermitian conjugate of P, $P^\dagger$, is defined by $<P\psi|\phi> = <\psi|P^\dagger\phi>$. On the other hand, the integral is a number and is unaffected by a permutation of the dummy variables. Thus

$$<P\psi|\phi> = P^{-1}[<P\psi|\phi>] = <P^{-1}P\psi|P^{-1}\phi> = <\psi|P^{-1}\phi>.$$

Comparison shows that <u>$P^\dagger = P^{-1}$</u>.

It follows that <u>the antisymmetrizer is self-adjoint</u>:

$$\langle \mathcal{A}\psi|\phi\rangle = (N!)^{-1}\sum_P \varepsilon(P)\langle P\psi|\phi\rangle = (N!)^{-1}\sum_P \varepsilon(P)\langle\psi|P^{-1}\phi\rangle$$

$$= (N!)^{-1}\sum_{P'} \varepsilon(P'^{-1})\langle\psi|P'\phi\rangle = (N!)^{-1}\sum_{P'} \varepsilon(P')\langle\psi|P'\phi\rangle$$

$$= \langle\psi|\mathcal{A}\phi\rangle \quad .$$

Thus $\mathcal{A}^\dagger = \mathcal{A}$. Since $\mathcal{A}\mathcal{A} = \mathcal{A}$, it follows that

$$\langle \mathcal{A}\psi|\mathcal{A}\phi\rangle = \langle\psi|\mathcal{A}\mathcal{A}\phi\rangle = \langle\psi|\mathcal{A}\phi\rangle$$

We have merely summarized some important results needed here. For a complete account of this material, the reader is referred to the book by Hamermesh (1962).

APPENDIX C: COMPUTER PROGRAM FOR SERBER SPIN EIGENFUNCTIONS

SUBPROGRAM 1.

```
      IMPLICIT REAL*8(F), INTEGER(A-E,G-Z)
      DIMENSION PS(4),L(13,4),SEIGV(13),FLEIG(169),
     1  FC(13,13)
C
C
C     * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
C     SSOEIG GENERATES SERBER SPIN EIGENFUNCTIONS FOR USE
C     IN SAAP'S WITH NDO DOUBLY-OCCUPIED ORBITALS: I.E,
C     SPIN FUNCTIONS ANTISYMMETRIC IN THE FIRST NDO GEMINAL
C     PAIRS.
C
C
C     INPUT -
C        NP =
C           NUMBER OF GEMINAL PAIRS, OR ONE-HALF THE NUMBER
C           OF ELECTRONS, WHICH IS ASSUMED EVEN.
C        NDO =
C           NUMBER OF DOUBLY-OCCUPIED ORBS IN THE SAAP.
C        SKEEP =
C           TOTAL S QUANTUM NUMBER.
C        MKEEP =
C           TOTAL SZ-EIGENVALUE.
C
C     * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
C
      FACT2 = 7.071067811865475D-01
      TNP = NP + NP
      TTNP = 2**NP
    5 MAGMT = IABS(MKEEP)
      NPS = 0
C     SWEEP DECIMAL REPS OF PS'S
      DO 40 DPS=1,TTNP
      TD = DPS - 1
C     CONVERT DEC REP TO PS'S
      PSSUM = 0
      DO 10 P=1,NP
      PI = 2**(NP-P)
      PSP = TD/PI
      PS(P) = PSP
      IF(P.GT.NDO) GO TO 9
      IF(PSP.NE.0) GO TO 40
    9 TD = TD - PSP*PI
   10 PSSUM = PSSUM + PSP
C     KEEP ONLY PS COMBINATIONS APPROPRIATE TO MKEEP
      IF(PSSUM.LT.MAGMT) GO TO 40
```

```
      NPS = NPS + 1
C     GET SSQ-EIGENFUNCTIONS CORRESPONDING TO MKEEP AND
C     GIVEN PS'S
      CALL SEIGEN(NP,PS,MKEEP,SEIGV,FLEIG,NPROD,L)
      IF(NPROD.NE.0) GO TO 15
      NPS = NPS - 1
      GO TO 40
   15 NSF = 0
      DO 37 ISEF=1,NPROD
      N2 = (ISEF-1)*NPROD
      IF(SEIGV(ISEF).NE.SKEEP) GO TO 37
      NSF = NSF + 1
      DO 30 IPROD=1,NPROD
   30 FC(NSF,IPROD) = FLEIG(N2+IPROD)
   37 CONTINUE
      IF(NSF.EQ.0) GO TO 39
C
C     OUTPUT AVAILABLE AT THIS POINT -
C        NPS =
C           INDEX OF THE PAIR-SPIN COMBINATION (PSC).
C        PS(P) =
C           SPIN OF THE PTH GEMINAL PAIR.
C        NSF =
C           NUMBER OF SPIN EIGENFUNCTIONS HAVING TOTAL SPIN
C           SKEEP AND SZ-EIGENVALUE MKEEP, FOR THE PSC WITH
C           INDEX NPS.
C        NPROD =
C           NUMBER OF GEMINAL SPIN PRODUCTS (GEMPRODS)
C           FROM WHICH THE SPIN FUNCTIONS FOR THE PSC
C           LABELLED NPS ARE CONSTRUCTED.
C        FC(I,J) =
C           COEFFICIENT OF THE JTH GEMPROD IN THE ITH
C           SPIN FUNCTION FOR THIS PSC.
C        L(J,P) =
C           CODE LABEL FOR THE TWO-ELECTRON SPIN FUNCTION
C           OCCUPIED BY THE GEMINAL PAIR 'P' IN THE JTH
C           GEMPROD. THE CODE IS AS FOLLOWS:
C                '0' MEANS (AB-BA)/DSQRT(2)
C                '3' MEANS (AA)
C                '2' MEANS (AB+BA)/DSQRT(2)
C                '1' MEANS (BB).
C
C
   39 IF(NSF.EQ.0) NPS=NPS-1
   40 CONTINUE
      RETURN
      END
```

SUBPROGRAM 2.

```
      SUBROUTINE SEIGEN(NP,SFIX,MTFIX,SEIGV,FLEIG,NPROD,L)
      IMPLICIT REAL*8(F), INTEGER(A-E,G-Z)
      REAL*8 DSQRT
      DIMENSION SFIX(4),LABEL(4),TS(4),TM(4),S(13,4),
     1  M(13,4),L(13,4),FLINT(91),SEIGV(13),IDX(13),
     2  FLEIG(169)
C
C * * * * * * * * * * * * * * *
C     SEIGEN RECEIVES PAIR-SPINS AND TOTAL MS FROM SSOEIG,
C     AND FINDS SSO-EIGENFUNCTIONS SATISFYING THAT DATA.
C
C     INPUT REQUIRED - TOTAL MS (MTFIX), PAIR-SPINS (SFIX
C     VECTOR), AND THE NUMBER OF GEMINAL PAIRS (NP).
C * * * * * * * * * * * * * * *
C
C     THIS SECTION PRODUCES NPROD GEMINAL SPIN PRODUCTS OF
C     THE SPECIFIED TYPE, THE NTH ONE HAVING THE PAIR-
C     FUNCTION LABELS (L(N,I),I=1,NP), PAIR-SPINS
C     (S(N,I),I=1,NP), AND PAIR-MS'S (M(N,I),I=1,NP).
  100 NPROD = 0
      LLIMP1 = 4**NP
      DO 200 I1=1,LLIMP1
      TMT = 0
      NMBR = I1-1
      TN = NMBR
      DO 170 I2=1,NP
      PI = 4**(NP-I2)
      LABEL(I2) = TN/PI
      TN = TN - LABEL(I2)*PI
      TS(I2) = 1
      IF(LABEL(I2).EQ.0) TS(I2)=0
      IF(TS(I2).NE.SFIX(I2)) GO TO 200
      TM(I2) = TS(I2)*(LABEL(I2)-2)
  170 TMT = TMT + TM(I2)
      IF(TMT-MTFIX) 200,180,200
  180 NPROD = NPROD + 1
      DO 190 I2=1,NP
      S(NPROD,I2) = TS(I2)
      M(NPROD,I2) = TM(I2)
  190 L(NPROD,I2) = LABEL(I2)
  200 CONTINUE
      IF(NPROD.NE.0) GO TO 299
      RETURN
C
C * * * * * * * * * * * * *
C     SSO-MATRIX BETWEEN GEMPRODS. STORED AS THE MATRIX
C     'INT'.
```

```
C * * * * * * * * * * * * *
C
  299 COUNT = 0
      DO 560 I2=1,NPROD
      DO 560 I1=1,I2
      INT = 0
      COUNT = COUNT + 1
      ND = 0
      DO 420 I3=1,NP
      IF(L(I1,I3).NE.L(I2,I3)) ND=ND+1
  420 CONTINUE
      IF(ND.NE.0) GO TO 460
C
C     DIAGONAL ELEMENTS
C
  430 DO 450 I3=1,NP
      LBL = L(I1,I3)
      IF(LBL.EQ.0) GO TO 450
      IF(LBL.LE.2) ND=ND+1
  450 CONTINUE
      INT = MTFIX*(MTFIX+1) + 2*ND
      GO TO 540
C
C     OFF-DIAGONAL ELEMENTS
C
  460 IF(ND-2) 540,510,540
  510 DO 520 I3=2,NP
      IF(IABS(M(I1,I3)-M(I2,I3)).GT.1) GO TO 520
      I3M1 = I3 - 1
      DO 518 I4=1,I3M1
      IF(S(I1,I3)+S(I1,I4)+S(I2,I3)+S(I2,I4).NE.4) GO TO 518
      M134 = M(I1,I3) + M(I1,I4)
      IF(M134.NE.M(I2,I3)+M(I2,I4)) GO TO 518
      IF(IABS(M134).GT.1) GO TO 518
      INT = INT + 2
  518 CONTINUE
  520 CONTINUE
  540 FLINT(COUNT) = INT
  560 CONTINUE
      IF(NPROD-1) 970,600,610
  600 FLEIG(1) = 1.0D0
      GO TO 620
C
C * * * * * * * * * * * * * * * * *
C     DIAGONALIZE THE SSQ-MATRIX, GET SSQ-EIGENFUNCTIONS
C * * * * * * * * * * * * * * * * *
  610 CALL EIGEN(FLINT,FLEIG,NPROD,1,IDX,1.0D-14)
  620 DO 640 I1=1,NPROD
      N1 = I1*(I1+1)/2
      FD = FLINT(N1)
```

```
      FD = (DSQRT(1.0D0+4.0D0*FD)-1.0D0)/2.0D0
      SEIGV(I1) = FD
      FD = FD - SEIGV(I1)
      IF(FD.GT.0.5D0) SEIGV(I1) = SEIGV(I1) + 1
  640 CONTINUE
      RETURN
  970 STOP
      END
```

SUBPROGRAM 3.

```
C     (USE SUBROUTINE EIGEN, LISTED IN APPENDIX E)
```

APPENDIX D: COMPUTER PROGRAM FOR THE EVALUATION OF COEFFICIENTS IN THE ENERGY MATRIX ELEMENTS BETWEEN SAAP'S

SURPROGRAM 1.

```
      SUBROUTINE MED1(N,LABLIM,LBL,LAF,RAF,LOP,ROP,A,B,NGP,
     1FGC,TESL)
      IMPLICIT REAL*8(F,P),INTEGER(A-E,G-O,Q-Z)
      DIMENSION LBL(2,8),NOCC(2,30),ORB(2,30),ELOCC(2,30),
     1  NO(2),IDENT(1,1),DORB(2,2),DEL(2,2),LIST(8),E(8,2),
     2  IRR(1,1),ISS(1,1),IRS(1,1),IST(1,1,8),ID(1,8),
     3  BLANK(120),NGP(2),FGC(2,20),TESL(2,20,4),
     4  FSC(2,1,20),SL(2,20,4),PD(1,30),PRRSSE(1,30,30),
     5  PRS(1,1),PRRSSD(1,1,30),PRRSS(1,1),PRSRS(1,1),
     6  DBLS(2)
      COMMON BLANK,EPP.BL,A,B,LOCL,LOCLP,NLPROD,NRPROD,NP,
     1  TNP,TTNP,NCYC,FACT,FNORM,FPAB,FACT2,ORB,NOCC,FSC,SL
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
C     CALCULATES COEFFICIENTS OF ONE- AND TWO-ELECTRON
C     INTEGRALS OCCURRING IN AN ENERGY MATRIX ELEMENT
C     BETWEEN TWO SAAP'S CONSTRUCTED FROM ORTHONORMAL
C     ORBITALS AND SERBER SPIN FUNCTIONS.
C
C     VERSION A.  9/70.  CONTAINS TESTING OUTPUT.
C
C
C     INPUT -
C
C        N =
C           NUMBER OF ELECTRONS (ASSUMED EVEN)
C        LBL(SIDE,EL) =
C           NUMERICAL LABEL OF ORBITAL CONTAINING ELECTRON
C           'EL' IN LEFT SAAP (SIDE = 1) OR RIGHT SAAP
C           (SIDE = 2).
C        LABLIM =
C           THE HIGHEST NUMERICAL ORBITAL LABEL USED.
C        LAF =
C           INDEX LABELLING THE LEFT SAAP.
C        RAF =
C           INDEX LABELLING THE RIGHT SAAP.
C        A =
C           INDEX LABELLING THE LEFT SPIN FUNCTION.
C        B =
C           INDEX LABELLING THE RIGHT SPIN FUNCTION.
C        LOP =
C           INDEX LABELLING THE LEFT ORBITAL PRODUCT.
C        ROP =
C           INDEX LABELLING THE RIGHT ORBITAL PRODUCT.
C        NGP(SIDE) =
C           NUMBER OF GEMINAL SPIN PRODUCTS IN SPIN FUNC-
```

```
C             TION ON LEFT (SIDE=1) OR RIGHT (SIDE=2).
C          TESL(SIDE,GP,MU) =
C             NUMERICAL LABEL FOR THE TWO-ELECTRON SPIN FUNC-
C             TION CONTAINING THE GEMINAL PAIR (2*MU-1,2*MU)
C             IN THE GEMINAL SPIN PRODUCT 'GP', APPEARING IN
C             THE SERBER SPIN FUNCTION ASSOCIATED WITH 'SIDE'.
C          FGC(SIDE,GP) =
C             COEFFICIENT OF THE GEMINAL SPIN PRODUCT 'GP'
C             IN THE SERBER FUNCTION INDICATED BY 'SIDE'.
C
C
C      UPDATED VERSIONS OF THIS PROGRAM MAY BE OBTAINED
C      THROUGH THE THEORETICAL CHEMISTRY GROUP, IOWA STATE
C      UNIVERSITY, AMES, IOWA.
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
      FACT2 = 7.0710678118654750D-01
      NP = N/2
      NLPROD = NGP(1)
      NRPROD = NGP(2)
      TNP = N
      TTNP = 2**NP
      DO 10 S=1,2
      DO 10 L=1,LABLIM
   10 NOCC(S,L) = 0
      WRITE(3,11)
   11 FORMAT('1','* * * * * * * * * * * * * * * * * * *'///)
      WRITE(3,12) N
   12 FORMAT(' MED1 INPUT'///' * * * *'//
     1  ' NUMBER OF ELECTRONS- ',I1///)
      DO 18 SIDE=1,2
      NOGP = NGP(SIDE)
      IF(SIDE.EQ.2) GO TO 14
      WRITE(3,13) (LBL(1,EL),EL=1,N)
   13 FORMAT(' LEFT SAAP'///5X,' ORBITAL PRODUCT-',9X,
     1  8(I2,2X))
      GO TO 16
   14 WRITE(3,15) (LBL(2,EL),EL=1,N)
   15 FORMAT(' RIGHT SAAP'///5X,' ORBITAL PRODUCT-',9X,
     1  8(I2,2X))
   16 WRITE(3,17)
   17 FORMAT(///5X,' SPIN EIGENFUNCTION-')
      DO 18 GP=1,NOGP
      FSC(SIDE,1,GP) = FGC(SIDE,GP)
      DO 171 MU=1,NP
  171 SL(SIDE,GP,MU) = TESL(SIDE,GP,MU)
   18 WRITE(3,19) (FGC(SIDE,GP),(TESL(SIDE,GP,MU),MU=1,NP))
   19 FORMAT(28X,D25.16,6X,4I1)
      WRITE(3,191)
```

```
  191 FORMAT('1','* * * * * * * * * * * * * * * * * * *'///
     1' INTERMEDIATE RESULTS'///'* * * * * * * * * * * '////
     2/' ORBITAL DATA BLOCK')
C
C
C      MAKE LISTS OF LEFT AND RIGHT ORBITALS (ORB),
C      OCCUPANCIES (NOCC), AND HIGHEST-NUMBERED ELECTRON
C      LABELS OCCUPYING ORBITALS (ELOCC).
C
       S = 1
   20  NORB = 0
       DO 50 EL=1,N
       L = LBL(S,EL)
       SW = 0
       IF(NORB.EQ.0) GO TO 40
       DO 30 O=1,NORB
       IF(ORB(S,O).NE.L) GO TO 30
       SW = 1
   30  CONTINUE
       IF(SW.EQ.0) GO TO 40
       NOCC(S,L) = NOCC(S,L) + 1
       ELOCC(S,L) = EL
       GO TO 50
   40  NORB = NORB + 1
       ORB(S,NORB) = L
       NOCC(S,L) = 1
       ELOCC(S,L) = EL
   50  CONTINUE
       NO(S) = NORB
       WRITE(3,51) S,NO(S)
   51  FORMAT(//5X,' FOR SIDE ',I1,', THERE ARE ',I2,
      1  ' ORBITALS- '///30X,' ORB        NOCC        ELOCC'//)
       DBLS(S) = 0
       DO 52 I=1,NORB
       O = ORB(S,I)
       IF(NOCC(S,O).EQ.2) DBLS(S) = DBLS(S) + 1
   52  WRITE(3,53) O, NOCC(S,O),ELOCC(S,O)
   53  FORMAT(31X,I2,10X,I1,8X,I2)
       IF(S.EQ.2) GO TO 60
       S = 2
       GO TO 20
   60  S = 1
       FNORM = DFLOAT(2**(DBLS(1)+DBLS(2)))
       FNORM = DSQRT(FNORM)
       FACT = (DFLOAT(N-1))*FNORM
       BL = DBLS(1)
   70  DIFF = 0
       SP = 3-S
       DO 100 L=1,LABLIM
       D = NOCC(S,L)-NOCC(SP,L)
```

```
      IF(D.LE.0) GO TO 100
      DIFF = DIFF+D
      IF(DIFF.LE.2) GO TO 80
      IDENT(LOP,ROP) = 3
      WRITE(3,71)
   71 FORMAT(/////' ***** DIFF IS GREATER THAN 2- ',
     1'MED1 SETS IDENT(LOP,ROP) = 3 AND QUITS *****')
      RETURN
   80 EL = ELOCC(S,L)
      IF(D.GT.1) GO TO 90
      DORB(S,DIFF) = L
      DEL(S,DIFF) = EL
      GO TO 100
   90 DORB(S,1) = L
      DORB(S,2) = L
      DEL(S,1) = EL-1
      DEL(S,2) = EL
  100 CONTINUE
      IF(DIFF.EQ.0) GO TO 110
      IF(S.EQ.2) GO TO 110
      S = 2
      GO TO 70
  110 IDENT(LOP,ROP) = DIFF
      WRITE(3,111) DIFF
  111 FORMAT(////5X,' ** DIFF = IDENT(LOP,ROP) = ',I1)
      IF(DIFF.EQ.0) GO TO 120
      WRITE(3,112)
  112 FORMAT(//30X,' DIFFERING ORBITALS            ',
     1'ELECTRONS IN DIFFERING ORBITALS'/)
      DO 114 S=1,2
      WRITE(3,113) S,(DORB(S,I),I=1,DIFF)
  113 FORMAT(20X,' SIDE ',I1,10X,I2,2X,I2)
  114 WRITE(3,115) (DEL(S,I),I=1,DIFF)
  115 FORMAT('+',72X,I2,3X,I2)
  120 DO 130 EL=1,N
  130 LIST(EL) = LBL(1,EL)
      IF(DIFF.EQ.0) GO TO 150
      DO 140 EL=1,DIFF
  140 LIST(DEL(1,EL)) = DORB(2,EL)
C
C
C     CONVENTION - PERMUTATION CONVERTING ROP TO LOP IS
C     (E(1,1),E(1,2)) * * * (E(NCYC,1),E(NCYC,2)).
C     I.E., HIGHEST-NUMBERED CYCLE OPERATES FIRST ON ROP.
C
  150 NCYC = 0
      WRITE(3,151)
  151 FORMAT(/////' PERMUTATION BLOCK'//)
      DO 170 CHK1=1,N
      DO 160 CHK2=CHK1,N
```

```
      IF(LBL(2,CHK1).NE.LIST(CHK2)) GO TO 160
      IF(CHK1.EQ.CHK2) GO TO 170
      NCYC = NCYC+1
      E(NCYC,1) = CHK1
      E(NCYC,2) = CHK2
      SAVE = LIST(CHK1)
      LIST(CHK1) = LIST(CHK2)
      LIST(CHK2) = SAVE
      GO TO 170
  160 CONTINUE
  170 CONTINUE
      EPP = (-1)**NCYC
      DO 1701 S=1,2
 1701 WRITE(3,172) S,(LBL(S,EL),EL=1,N)
  172 FORMAT(20X,' ORB PROD ',I1,4X,8(2X,I2))
      WRITE(3,1721) NCYC
 1721 FORMAT(///20X,' NCYC = ',I1)
      IF(NCYC.EQ.0) GO TO 1731
      WRITE(3,173) ((E(CYC,S),S=1,2),CYC=1,NCYC)
  173 FORMAT(///20X,' PERMUTATION TO ALIGN RIGHT PROD WITH',
     1' LEFT PROD-  ',8('(',2I1,') '))
 1731 FPAB = FME(0,E)
      WRITE(3,174) A,B,FPAB
  174 FORMAT('0',21X,I1,',',I1,'-ELEMENT OF SPIN REP MATRI',
     1'X FOR ALIGNMENT PERMUTATION IS  FPAB = ',D25.16)
      WRITE(3,175)
  175 FORMAT(/////' P-COEFFICIENTS AND OTHER DATA REQUIRED',
     1' BY CI'//)
      D = DIFF+1
      GO TO (200,300,400),D
C     LOP = ROP
  200 DO 210 O=1,N
  210 ID(LAF,O) = 0
      NO1 = NO(1)
      WRITE(3,211) NO1
  211 FORMAT(20X,' INSTRUCTION BLOCK 200       NO1 = ',I1/)
      DO 220 OP=1,NO1
      LP = ORB(1,OP)
      LOCLP = ELOCC(1,LP)
C     ID(LAF,RAF) IS LABEL OF ORBITAL INDEXED 'OP'. THIS
C     LABEL IS ALSO CALLED 'LP'.
      ID(LAF,OP) = LP
      WRITE(3,212) OP,LP
  212 FORMAT(30X,' OP=',I1,', LP=ORB(1,OP)=',I2,' -        ',
     1'CALL FP1')
C     PD(LAF,OP) IS THE COEFF OF INTEGRAL (LP/H(1)/LP)
      PD(LAF,OP) = FP1(0,LP,LP,N,E,NO1)
      WRITE(3,213) LAF,OP,ID(LAF,OP),LAF,OP,PD(LAF,OP)
  213 FORMAT(35X,' ID(',I1,',',I1,') = ',I2/35X,
     1' PD(',I1,',',I1,') = ',D25.16)
```

```
      DO 220 O=OP,NO1
      L = ORB(1,O)
      LOCL = ELOCC(1,L)
      IF(LOCL.NE.LOCLP) GO TO 214
      IF(NOCC(1,L).EQ.2) LOCL = LOCL-1
C     PRRSSE(LAF,O,OP), WHERE O.GE.OP, IS COEFF OF INTEGRAL
C     (L,LP/G(1,2)/L,LP), IN DIRAC NOTATION.
  214 PRRSSE(LAF,O,OP) = FP2(O,L,LP,L,LP,0,E)
      WRITE(3,221) LAF,O,OP,PRRSSE(LAF,O,OP)
C     PRRSSE(LAF,OP,O) IS COEFF OF (L,LP/G(1,2)/LP,L).
      PRRSSE(LAF,OP,O) = FP2(O,L,LP,L,LP,1,E)
  220 WRITE(3,221) LAF,OP,O,PRRSSE(LAF,OP,O)
  221 FORMAT(35X,' PRRSSE(',I1,',',I1,',',I1,') = ',D25.16)
      RETURN
C
C     LOP AND ROP DIFFER BY ONE ORBITAL, VIZ.
C     IRS(LAF,RAF) = L IN LOP,
C     IRS(RAF,LAF) = R IN ROP.
  300 L = DORB(1,I)
      IRS(LAF,RAF) = L
      R = DORB(2,I)
      IRS(RAF,LAF) = R
      LOCL = DEL(1,I)
      NO1 = NO(1)
      NO2 = NO(2)
      I = 0
      DO 330 O1=1,NO1
      LP = ORB(1,O1)
      DO 310 O2=1,NO2
      IF(LP.EQ.ORB(2,O2)) GO TO 320
  310 CONTINUE
      GO TO 330
  320 I = I+1
C     IST(LAF,RAF,I) = ITH ORBITAL COMMON TO LOP AND ROP,
C     VIZ., LP.
      IST(LAF,RAF,I) = LP
  330 CONTINUE
      NI = I
C     PRS(LAF,RAF) = COEFF OF (L/H(1)/R).
  336 PRS(LAF,RAF) = FP1(1,L,R,N,E,NO1)
      DO 340 I=1,NI
      LP = IST(LAF,RAF,I)
      LOCLP = ELOCC(1,LP)
      IF(LOCLP.NE.LOCL) GO TO 337
      IF(NOCC(1,LP).EQ.2) LOCLP=LOCLP-1
C     PRRSSD(LAF,RAF,I) = COEFF OF (L,LP/G(1,2)/R,LP).
  337 PRRSSD(LAF,RAF,I) = FP2(1,L,LP,R,LP,0,E)
C     PRRSSD(RAF,LAF,I) = COEFF OF (L,LP/G(1,2)/LP,R).
  340 PRRSSD(RAF,LAF,I) = FP2(1,L,LP,R,LP,1,E)
      RETURN
```

```
C
C     LOP AND ROP DIFFER BY TWO ORBITALS, VIZ.,
C     IRR(LAF,RAF) = L  AND  ISS(LAF,RAF) = LP  IN LOP,
C     IRR(RAF,LAF) = R  AND  ISS(RAF,LAF) = RP  IN ROP.
  400 LP = DORB(1,2)
      ISS(LAF,RAF) = LP
      WRITE(3,410) LAF,RAF,LP
  410 FORMAT(35X,' ISS(',I1,',',I1,') = ',I2)
      RP = DORB(2,2)
      ISS(RAF,LAF) = RP
      WRITE(3,410) RAF,LAF,RP
      L = DORB(1,1)
      IRR(LAF,RAF) = L
      WRITE(3,420) LAF,RAF,L
  420 FORMAT(35X,' IRR(',I1,',',I1,') = ',I2)
      R = DORB(2,1)
      IRR(RAF,LAF) = R
      WRITE(3,420) RAF,LAF,R
      LOCL = DEL(1,1)
      LOCLP = DEL(1,2)
C     PRRSS(LAF,RAF) = COEFF OF (L,LP/G(1,2)/R,RP).
      PRRSS(LAF,RAF) = FP2(2,L,LP,R,RP,0,E)
      WRITE(3,430) LAF,RAF,PRRSS(LAF,RAF)
  430 FORMAT(35X,' PRRSS(',I1,',',I1,') = ',D25.16)
C     PRSRS(LAF,RAF) = COEFF OF (L,LP/G(1,2)/RP,R).
      PRSRS(LAF,RAF) = FP2(2,L,LP,R,RP,1,E)
      WRITE(3,440) LAF,RAF,PRSRS(LAF,RAF)
  440 FORMAT(35X,' PRSRS(',I1,',',I1,') = ',D25.16)
      RETURN
C
      END
```

SUBPROGRAM 2.

```
      DOUBLE PRECISION FUNCTION FP1(DIFF,L,R,N,P,NO1)
      IMPLICIT REAL*8(F),INTEGER(A-E,G-Z)
      DIMENSION ORB(2,30),P(8,2),NOCC(2,30),BLANK(120)
      COMMON BLANK,EPP,PL,A,B,LOCL,LOCLP,NLPROD,NRPROD,NP,
     1  TNP,TTNP,NCYC,FACT,FNORM,FPAB,FACT2,ORB,NOCC
C
C     CALCULATES COEFFICIENT OF ONE-ELECTRON INTEGRAL
C     (L/H(1)/R). LOP AND ROP DIFFER BY DIFF ORBITALS.
C
      F = 1.0D0
      O = L
      IF(DIFF.EQ.0) GO TO 25
```

```
      F = 2.0D0
      O = R
   25 FP1 = 0.0D0
      IF(NOCC(1,L).NE.2) GO TO 30
      FP1 = 4.0D0 * FPI(L,L,O,L,P,O)/F
   30 DO 50 I=1,NO1
      LP = ORB(1,I)
      IF(LP.EQ.L) GO TO 50
      FD = 1.0D0
      IF(DIFF.EQ.0) GO TO 40
      IF(LP.EQ.R) FD = 2.0D0
   40 FP1 = FP1 + FD*FPI(L,LP,O,LP,P,O)
   50 CONTINUE
   60 FP1 = FP1/FACT
      RETURN
      END
```

SUBPROGRAM 3.

```
      DOUBLE PRECISION FUNCTION FP2(DIFF,L,LP,R,RP,SW,P)
      IMPLICIT REAL*8(F), INTEGER(A-E,G-Z)
      DIMENSION P(8,2),ORB(2,30),NOCC(2,30),BLANK(120)
      COMMON BLANK,FPP,PL,A,B,LOCL,LOCLP,NLPROD,NRPROD,NP,
     1  TNP,TTNP,NCYC,FACT,FNORM,FPAB,FACT2,ORB,NOCC
C
C     CALCULATES COEFF OF INTEGRAL (L,LP/G(1,2)/R,RP) IF
C     SW=0, OR OF (L,LP/G(1,2)/RP,R) IF SW=1. LOP AND ROP
C     DIFFER BY DIFF ORBITALS.
C
      FC = 1.0D0
C
  300 IF(L.EQ.LP) GO TO 310
      IF(R.EQ.RP) GO TO 325
      GO TO 350
  310 IF(NOCC(1,L).EQ.2) GO TO 325
      FSTR = 0.0D0
      GO TO 375
  325 FC = 2.0D0
      IF(SW.EQ.1) GO TO 375
  350 FSTR = FC * FPI(L,LP,R,RP,P,SW) / FNORM
  375 FP2 = FSTR
      RETURN
      END
```

SUBPROGRAM 4.

```
      DOUBLE PRECISION FUNCTION FPI(L,LP,R,RP,P,SW)
      IMPLICIT REAL*8(F), INTEGER(A-E,G-Z)
      DIMENSION NOCC(2,30),P(8,2),ORB(2,30),BLANK(120)
      COMMON BLANK,EPP,PL,A,B,LOCL,LOCLP,NLPROD,NRPROD,NP,
     1  TNP,TTNP,NCYC,FACT,FNORM,FPAB,FACT2,ORB,NOCC
C
C     CALCULATES QUANTITY
C     (2**(PRS(L,LP)+PRS(R,RP)+PRS(LOPM))) * EPP *
C                                                    * FME(SW,P,A,B)
C     WHERE
C     PRS(L,LP) = NO. DIFFERENT DOUBLY-OCC ORBITALS REPRE-
C     SENTED BY L AND LP (IF L=LP, THIS NUMBER IS ZERO),
C     PRS(R,RP) = SIMILAR,
C     PRS(LOPM) = NO. OF DOUBLY-OCC ORBITALS IN LEFT ORB
C     PROD AFTER L AND LP ARE REMOVED,
C     EPP = +1 OR -1 IF P IS AN EVEN OR ODD PERMUTATION,
C     FME(SW,P,A,B) = (A,B)-ELEMENT OF SPIN REP MATRIX FOR
C     PERM 'P' IF SW=0, OR FOR PERM (I,J)*P IF SW=1 (WHERE
C     I AND J ARE THE ELECTRONS OCCUPYING L AND LP IN LEFT
C     ORB PROD).
C
      WRITE(3,1) L,LP,R,RP,SW
    1 FORMAT(80X,' FPI(',I2,4I3,')-')
      FMATEL = FPAB
      IF(SW.EQ.0) GO TO 10
      FMATEL = FME(1,P)
   10 PWR = PL
      IF(L.EQ.LP) PWR = PL-1
      PRRP = NOCC(2,R) + NOCC(2,RP) - 2
      IF(R.EQ.RP) PRRP=0
      FC = DFLOAT((2**(PWR+PRRP))*EPP)
      FPI = FC * FMATEL * (DFLOAT((-1)**SW))
      WRITE(3,19) PWR,PRRP,SW,EPP,FMATEL
   19 FORMAT(80X,' 2**(',I2,' +',I2,' )  *  (-1)**',I1,
     1 '  *  ',I2,'  *  ',D13.6)
      RETURN
      END
```

SUBPROGRAM 5.

```
      DOUBLE PRECISION FUNCTION FME(SW,E)
      IMPLICIT REAL*8(F), INTEGER(A-E,G-Z)
      DIMENSION FSC(2,1,20),L(2,20,4),T(4),M(4),SL(8),
     1  SEP(16),F(8,2),FCOEFF(16),NOCC(2,30),ORB(2,30),
     2  BLANK(120)
      COMMON BLANK,EPP,PL,A,B,LOCL,LOCLP,NLPROD,NRPROD,NP,
     1  TNP,TTNP,NCYC,FACT,FNORM,FPAB,FACT2,ORB,NOCC,FSC,L
C
C     CALCULATES (A,B)-ELEMENT OF SPIN REP MATRIX FOR PERM
C     'P' IF SW=0, FOR PERM (I,J)*P IF SW=1, WHERE I AND J
C     ARE THE ELECTRONS OCCUPYING ORBITALS L AND LP IN THE
C     LEFT ORB PROD.
C
      FME = 0.0D0
      DO 400 LPROD=1,NLPROD
      DO 400 RPROD=1,NRPROD
      FPMAT = 0.0D0
      IF(NCYC.NE.0) GO TO 305
      IF(SW.EQ.1) GO TO 305
C     WHEN NCYC=0, PERMUTATION IS TAKEN TO BE THE IDENTITY,
C     UF SW=0.
      DO 301 I3=1,NP
      IF(L(1,LPROD,I3).NE.L(2,RPROD,I3)) GO TO 370
  301 CONTINUE
      FPMAT = 1.0D0
      GO TO 370
C
  305 DO 365 SIDE=1,2
      PROD = LPROD
      IF(SIDE.EQ.1) GO TO 306
      PROD = RPROD
  306 COUNT = 0
C     FOR FIXED SIDE (LEFT OR RIGHT) AND GEMPROD, SWEEP ALL
C     SEPRODS AND CONVERT SUITABLE DECLABELS TO BINLABELS
      DO 360 I3=1,TTNP
      I3M = I3 - 1
      DO 310 I4=1,NP
      PI = 2**(NP-I4)
      T(I4) = I3M/PI + 1
      IF(L(SIDE,PROD,I4).NE.0) GO TO 307
      S = 0
      GO TO 308
  307 S = 1
  308 M(I4) = S*(L(SIDE,PROD,I4)-2)
      IF(T(I4).EQ.1) GO TO 310
C     SKIP SEPROD LABELS WH ARE NOT ASSOCIATED WITH THE
C     GIVEN GEMPROD
```

```
      IF(M(I4).NE.0) GO TO 360
  310 I3M = I3M - T(I4)*PI + PI
C     COUNT SEPRODS ASSOCIATED WITH GIVEN GEMPROD
      COUNT = COUNT + 1
C     FOR EACH SEPROD KEPT, GENERATE THE SINGLE-ELECTRON
C     SPIN FUNCTION LABELS (SL'S) AND THE COEFFICIENT (FC)
      FC = 1.0D0
      DO 330 I4=1,NP
      TI4 = 2*I4
      TI4M1 = TI4 - 1
      IF(M(I4).NE.0) GO TO 315
      IF(T(I4).NE.2) GO TO 325
      SL(TI4M1) = 0
      SL(TI4) = 1
      FC = FC*FACT2
      IF(L(SIDE,PROD,I4).EQ.2) GO TO 330
      FC = -FC
      GO TO 330
  315 SL(TI4M1) = 1
      IF(L(SIDE,PROD,I4).EQ.3) GO TO 320
      SL(TI4M1) = 0
  320 SL(TI4) = SL(TI4M1)
      GO TO 330
  325 SL(TI4M1) = 1
      SL(TI4) = 0
      FC = FC*FACT2
  330 CONTINUE
      IF(SIDE.EQ.1) GO TO 340
C     IF SIDE = 2, PERMUTE THE SL'S
      IF(NCYC.EQ.0) GO TO 337
      DO 336 K=1,NCYC
      I = NCYC + 1 - K
      TEMP = SL(E(I,2))
      SL(E(I,2)) = SL(E(I,1))
  336 SL(E(I,1)) = TEMP
  337 IF(SW.EQ.0) GO TO 340
      TEMP = SL(LOCL)
      SL(LOCL) = SL(LOCLP)
      SL(LOCLP) = TEMP
  340 SEPROD = 0
      DO 345 I4=1,TNP
  345 SEPROD = SEPROD + SL(I4)*(10**(TNP-I4))
C     IF SIDE=1 (LEFT), STORE SEPROD AS SEP(COUNT), FC AS
C     FCOEFF(COUNT)
      IF(SIDE.EQ.2) GO TO 350
      SEP(COUNT) = SEPROD
      FCOEFF(COUNT) = FC
      GO TO 360
  350 CONTINUE
      DO 355 I4=1,NSPL
```

```
      IF(SEPROD.NE.SEP(I4)) GO TO 355
      FPMAT = FPMAT + FC*FCOEFF(I4)
  355 CONTINUE
  360 CONTINUE
C     IF SIDE=1, STORE NUMBER OF SEPRODS ASSOCIATED WITH
C     LEFT GEMPROD
      IF(SIDE.EQ.2) GO TO 365
      NSPL = COUNT
  365 CONTINUE
  370 FME = FME + FSC(1,A,LPROD)*FSC(2,B,RPROD)*FPMAT
  400 CONTINUE
      RETURN
      END
C
C
C     SAMPLE DATA CARDS
C
C
    4    0    1    2    3    4
    2    3
   0.5773502691896257D 00             1    3
  -0.5773502691896257D 00             2    2
   0.5773502691896257D 00             3    1
    4    0    3    1    2    4
    2    3
   0.5773502691896257D 00             1    3
  -0.5773502691896257D 00             2    2
   0.5773502691896257D 00             3    1
```

APPENDIX E: COMPUTER PROGRAM FOR GENERATING SIMULTANEOUS EIGENFUNCTIONS OF SPIN AND ORBITAL ANGULAR MOMENTA AS LINEAR COMBINATIONS OF SAAP'S

SUBPROGRAM 1.

```
      IMPLICIT REAL*8(F),INTEGER(A-E,G-Z)
      REAL*8 DSQRT
      DIMENSION NQN(8),L(20,8),ML(20,8),LL(20,8),
     1  NSPROD(5,16),SL(2,13,4),FSC(2,13,13),NSEF(5,16),
     2  MS(2,13,4),PRS(5,20),NOCC(111),PL(5,20),NPS(5),
     3  FLINT(1275),NLP(5),LQN(8),FLEIG(2500),BLANK(4),
     4  IDX(50),PSCODE(5,16),M(8),SLDISK(5,16,13,4),
     5  FSCDSK(5,16,13,13)
      COMMON FSC,SL,MS,ML,L,LL,NSPROD,N,TTNP,PL
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
C     LSE2
C
C      THIS PROGRAM CONSTRUCTS SIMULTANEOUS EIGENFUNCTIONS
C      OF LSQ. LZ, SSQ, AND SZ, THESE EIGENFUNCTIONS BEING
C      LINEAR COMBINATIONS OF SAAP'S CONTAINING A SPACE PRO-
C      DUCT AND A SPIN EIGENFUNCTION. THE SPIN FUNCTIONS
C      SPAN A SERBER-TYPE REPRESENTATION OF THE SYMMETRIC
C      GROUP.
C
C      INPUT IS THE NUMBER OF ELECTRONS (N), TOTAL S (ST),
C      TOTAL MS (MST), TOTAL L (LT), TOTAL ML (MLT), HIGHEST
C      LQN OCCURRING (HIL), HIGHEST NQN OCCURRING (HIN),
C      AND THE NUMBER OF CONFIGURATIONS (NCONF). N IS
C      ASSUMED TO BE EVEN.
C
C      FOR EACH CONFIGURATION, THE PROGRAM NEEDS THE NUMBER
C      OF ORBITALS REQUIRED TO SPECIFY THAT CONFIGURATION
C      (NMNP) AND THE LIST OF NQN'S AND LQN'S.
C
C      NOTE TO THE USER - THIS DECK IS DIMENSIONED TO
C      HANDLE MOST CASES OF INTEREST  WITH UP TO 8 ELECTRONS.
C      CERTAIN CASES MAY REQUIRE HIGHER DIMENSIONS. THE
C      ARRAYS 'FSCDSK' AND 'SLDISK' SHOULD BE PLACED IN EX-
C      TERNAL STORAGE. THEY MAY THEMSELVES BE STORED IN BULK
C      CORE, OR THEIR FUNCTION MAY BE PERFORMED BY TAPE OR
C      DISK. STATEMENTS INVOLVING THESE ARRAYS ARE INDI-
C      CATED BY 'CTEMP' MARKERS.
C
C      UPDATED VERSIONS OF THIS PROGRAM MAY BE OBTAINED
C      THROUGH THE THEORETICAL CHEMISTRY GROUP, IOWA STATE
C      UNIVERSITY, AMES, IOWA.
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
C
```

```
C
C     FOLLOWING IS BLOCK TO SELECT ORBITAL PRODUCTS FOR
C     GIVEN MLT, INDIVIDUAL LON'S, SUBJECT TO CONDITIONS
C     THAT DOUBLES ARE LISTED FIRST, THAT DOUBLES ARE
C     LISTED WITH ASCENDING LABELS, AND THAT SINGLES ARE
C     LISTED WITH ASCENDING LABELS.
C
      READ(1,901) N,ST,MST,LT,MLT,HIL,HIN,NCONF
  901 FORMAT(8I5)
      WRITE(3,902) N,HIN,HIL,ST,MST,LT,MLT,NCONF
  902 FORMAT(//////////'  PROBLEM DESCRIPTION-'//10X,I2,
     1  ' ELECTRONS, HIGHEST NQN = ',I1,', HIGHEST LQN = ',
     2  I1//25X,'ST = ',I1,5X,'MST = ',I2/25X,'LT = ',I2,
     3  4X,'MLT = ',I3//26X,I1,' CONFIGURATIONS')
      ND2 = N/2
      TTNP = 2 ** ND2
      FACT2 = 7.071067811865475D-01
      HILP1 = HIL + 1
      HM = 2*HIL + 1
      LMMAX = (HIL+1)**2
      LABLIM = HIN*(HIN-1)*(2*HIN-1)/6 + LMMAX
      NPL = 0
C
C     SWEEP CONFIGURATIONS
      DO 113 C=1,NCONF
      COWNT = 0
      NRAF = 0
      NLPROD = 0
      READ(1,900) NMNP,(NQN(MU),LQN(MU),MU=1,NMNP)
  900 FORMAT(I2,2X,20(2I1,1X))
      WRITE(3,903) C,(NQN(MU),LQN(MU),MU=1,NMNP)
  903 FORMAT(//////////'1 **************************'//
     1  '  CONFIGURATION ',I1,'-     ',14(2I1,1X))
      WRITE(3,904)
  904 FORMAT(/////)
      NP = N - NMNP
      NPP1 = NP + 1
      NPP2 = NPP1 + 1
      NTP = NMNP - NP
      LTM = HM ** NMNP
C
C     SWEEP DECIMAL LABELS FOR SPACE PRODUCTS, KEEPING
C     ONLY THOSE WHICH SUIT THE INPUT DATA FOR THE GIVEN
C     CONFIGURATION
      DO 4 MU=1,NMNP
    4 M(MU) = - LQN(MU)
      U = 1
      V = 2
    6 NLPROD = NLPROD + 1
      DO 8 ORB=1,LABLIM
```

```
    8 NOCC(ORB) = 0
      MSUM = 0
      DO 10 MU=1,NMNP
      EM = M(MU)
      ML(NLPROD,MU) = EM
      IF(IABS(EM).GT.LQN(MU)) GO TO 40
      INC = 1
      IF(MU.LE.NP) INC=2
   10 MSUM = MSUM + INC*EM
      IF(MSUM.NE.MLT) GO TO 40
      DO 30 MU=1,NMNP
      EN = NQN(MU)
      EL = LQN(MU)
      L(NLPROD,MU) = EL
      LABEL = EN*(EN-1)*(2*EN-1)/6 + EL*(EL+1) + 1
     1                                         + ML(NLPROD,MU)
      LL(NLPROD,MU) = LABEL
      IF(MU.EQ.1) GO TO 20
      IF(MU.EQ.NPP1) GO TO 20
      MUM1 = MU - 1
      IF(LL(NLPROD,MU).LT.LL(NLPROD,MUM1)) GO TO 40
   20 INC = 1
      IF(MU.LE.NP) INC = 2
      NL = NOCC(LABEL)
      NL = NL + INC
      IF(NL.GT.2) GO TO 40
      NOCC(LABEL) = NL
   30 CONTINUE
      GO TO 50
   40 NLPROD = NLPROD-1
   50 IF(M(U).EQ.LQN(U)) GO TO 501
      M(U) = M(U) + 1
      GO TO 6
  501 U = U + 1
      IF(U.EQ.V) GO TO 502
      IF(M(U).EQ.LQN(U)) GO TO 501
      W = U
      GO TO 504
  502 IF(M(V).NE.LQN(V)) GO TO 503
      IF(V.EQ.NMNP) GO TO 506
      V = V + 1
      GO TO 502
  503 W = V
  504 U = 1
      WM1 = W - 1
      DO 505 MU=1,WM1
  505 M(MU) = -LQN(MU)
      M(W) = M(W) + 1
      GO TO 6
  506 NLP(C) = NLPROD
```

```
      IF(NLPROD.NE.0) GO TO 52
      WRITE(3,1014)
 1014 FORMAT(////' THERE ARE NO SUITABLE ORBITAL PRODUCTS -'
     1  'DATA ARE INCONSISTENT')
      GO TO 113
   52 MULIM = NMNP
C
C     FOR EACH CONFIGURATION, SWEEP ALL SUITABLE ORBITAL
C     PRODUCTS, CONVERT THEM TO STANDARD FORM
      DO 95 I=1,NLPROD
C     SHIFT BLOCK
      NMNP = MULIM
      NP = N - NMNP
      NTP = NMNP - NP
      IF(NPP2.GT.NMNP) GO TO 71
      DO 68 MU=NPP2,MULIM
      IF(MU.GT.NMNP) GO TO 71
      MUM1 = MU - 1
      IF(LL(I,MU).NE.LL(I,MUM1)) GO TO 68
      NMNP = NMNP - 1
      SAVE1 = LL(I,MUM1)
      SAVE2 = NP + 1
      IF(NP.EQ.0) GO TO 56
      DO 53 NU=1,NP
      IF(LL(I,NU).LE.SAVE1) GO TO 53
      SAVE2 = NU
      GO TO 56
   53 CONTINUE
   56 XILIM = MUM1 - SAVE2
      IF(XILIM.EQ.0) GO TO 62
      DO 59 XI=1,XILIM
      OM = MU - XI
   59 LL(I,OM) = LL(I,OM-1)
      LL(I,SAVE2) = SAVE1
   62 IF(NMNP.LT.MU) GO TO 67
      DO 65 XI=MU,NMNP
   65 LL(I,XI) = LL(I,XI+1)
   67 NP=N-NMNP
      NTP = NMNP - NP
   68 CONTINUE
   71 PRS(C,I) = NP
C     END SHIFT BLOCK
      GO TO 81
C
C     UNPACK MU SUBSCRIPT
      IF(NP.EQ.0) GO TO 81
      DO 80 MU=1,NMNP
      MUM1 = MU - 1
      J = 0
      K = NMNP - MUM1
```

```
      D = MUM1 - NTP
      IF(D.GT.0) J=D
      NEW = N-MUM1-J
      NEW1 = NEW - 1
      LABEL = LL(I,K)
      LL(I,NEW) = LABEL
      LL(I,NEW1)= LABEL
      CHKM1 = 0
      EN = 1
   72 CHK = EN*(EN+1)*(2*EN+1)/6
      IF(CHK.GE.LABEL) GO TO 725
      CHKM1 = CHK
      EN = EN + 1
      GO TO 72
  725 NQN(NEW) = EN
      NQN(NEW1) = EN
      LABEL = LABEL - CHKM1
      EL = 0
   73 CHK = (EL+1)**2
      IF(CHK.GE.LABEL) GO TO 735
      EL = EL+1
      GO TO 73
  735 L(I,NEW) = EL
      L(I,NEW1) = EL
      EM = LABEL - EL*(EL+1) - 1
      ML(I,NEW) = EM
      ML(I,NEW1) = EM
   80 CONTINUE
C     END MU EXPANSION BLOCK
C
C     GET SPIN EIGENFUNCTIONS TO GO WITH ITH SPACE PRODUCT
C     FOR CONFIGURATION C
   81 CLIM = C
      NPL = NPL + 1
      PL(C,I) = NPL
      SW = 0
      IF(I.NE.1) GO TO 83
      IF(CLIM.EQ.1) GO TO 88
      CLIM = C - 1
   83 DO 87 CC=1,CLIM
      JLIM = NLP(CC)
      IF(CC.EQ.C) JLIM = I-1
      DO 86 J=1,JLIM
      IF(SW.EQ.1) GO TO 84
      IF(PRS(C,I).NE.PRS(CC,J)) GO TO 86
      PL(C,I) = PL(CC,J)
      NPL = NPL - 1
      SW = 2
      CONF = CC
      PROD = J
```

```
      GO TO 880
   84 IF(PRS(CC,J).GE.PRS(C,I)) GO TO 86
      CONF = CC
      PROD = J
      GO TO 880
   86 CONTINUE
   87 CONTINUE
      IF(SW.NE.0) GO TO 88
      SW = 1
      GO TO 83
   88 CALL SSQEIG(ND2,NP,ST,MST,C,I,NPL,NPRSP,NSPROD,NSEF,
     1  PSCODE,FLEIG,FSCDSK,SLDISK)
      NPS(NPL) = NPRSP
      GO TO 89
C     NPRSP WILL BE ZERO IFF THERE ARE NO SUITABLE SPIN
C     EIGENFUNCTIONS TO GO WITH THE CURRENT ORB PROD
  880 PRGL = PL(CONF,PROD)
      PLI = PL(C,I)
      NPRSP = NPS(PRGL)
      NDO = PRS(C,I)
      CHK = 2**(ND2-NDO)
      COUNT = 0
      DO 881 PSC=1,NPRSP
      IF(SW.EQ.2) GO TO 8800
      IF(PSCODE(PRGL.PSC).GE.CHK) GO TO 881
 8800 COUNT = COUNT + 1
      NSF = NSEF(PRGL,PSC)
      NSP = NSPROD(PRGL,PSC)
      NSPROD(NPL,COUNT) = NSP
      NSEF(NPL,COUNT) = NSF
CTEMP
      DO 8802 ISP=1,NSP
      DO 8801 SEF=1,NSF
 8801 FSCDSK(PLI,COUNT,SEF,ISP) = FSCDSK(PRGL,PSC,SEF,ISP)
      DO 8802 PR=1,ND2
 8802 SLDISK(PLI,COUNT.ISP,PR) = SLDISK(PRGL.PSC,ISP,PR)
CTEMP
  881 CONTINUE
      IF(SW.EQ.2) GO TO 89
      NPS(NPL) = COUNT
C
C     FORM LSQ-MATRIX (UPPER TRIANGLE) FOR CURRENT CONFIG
   89 RPL = PL(C,I)
      NRPS = NPS(RPL)
      IF(NRPS.EQ.0) GO TO 95
      DO 94 RPS=1,NRPS
      NSP = NSPROD(RPL,RPS)
      NRSEF = NSEF(RPL,RPS)
      DO 93 RSEF=1,NRSEF
      NRAF = NRAF + 1
```

```
      SW = 0
CTEMP
      DO 8901 ISP=1,NSP
      FSC(2,RSEF,ISP) = FSCDSK(RPL,RPS,RSEF,ISP)
      DO 8901 PR=1,ND2
 8901 SL(2,ISP,PR) = SLDISK(RPL,RPS,ISP,PR)
CTEMP
      MU = 1
      WRITE(3,891) NRAF
  891 FORMAT(////5X,' SAAP NUMBER ',I3///20X,'SPACE ',
     1  'PRODUCT',48X,'SPIN EIGENFUNCTION'//23X,'N  L  M',
     2  40X,'COEFFICIENT',15X,'GEMINAL SPIN PRODUCT'///)
  892 IF(MU.GT.N) GO TO 894
      EL = L(I,MU)
      EM = ML(I,MU)
      EN = NQN(MU)
      WRITE(3,893) EN,EL,EM
  893 FORMAT('+',22X,3(I2))
      SW = 1
  894 IF(MU.GT.NSP) GO TO 896
      WRITE(3,895) FSC(2,RSEF,MU),(SL(2,MU,PR),PR=1,ND2)
  895 FORMAT('+',65X,F19.16,16X,7I1)
      SW = 1
  896 IF(SW.EQ.0) GO TO 898
      SW = 0
      WRITE(3,897)
  897 FORMAT(/)
      MU = MU+1
      GO TO 892
  898 WRITE(3,899)
  899 FORMAT(/////)
      NLAF = C
      DO 91 LPROD=1,NLPROD
      LPL = PL(C,LPROD)
      NLPS = NPS(LPL)
      IF(NLPS.EQ.0) GO TO 91
      DO 90 LPS=1,NLPS
      NLSP = NSPROD(LPL,LPS)
      NLSEF = NSEF(LPL,LPS)
      DO 90 LSEF=1,NLSEF
CTEMP
      DO 8991 ISP=1,NLSP
      FSC(1,LSEF,ISP) = FSCDSK(LPL,LPS,LSEF,ISP)
      DO 8991 PR=1,ND2
 8991 SL(1,ISP,PR) = SLDISK(LPL,LPS,ISP,PR)
CTEMP
      NLAF = NLAF + 1
      COWNT = COWNT + 1
      FLINT(COWNT) = FLSQME(C,LPROD,LPS,LSEF,C,I,RPS,RSEF,
     1  N,MLT,PRS,LABLIM)
```

```
      IF(NLAF.EQ.NRAF) GO TO 93
   90 CONTINUE
   91 CONTINUE
C
   93 CONTINUE
   94 CONTINUE
   95 CONTINUE
C     (95 IS END OF I-LOOP)
C
C
C     DIAGONALIZE THE LSQ MATRIX
      IF(NRAF.GT.1) GO TO 101
      FLEIG(1) = 1.0D0
      GO TO 104
  101 CALL EIGEN(FLINT,FLEIG,NRAF,1,IDX,1.0D-14)
  104 NLEF = 0
      WRITE(3,1012) C,LT,MLT,ST,MST
 1012 FORMAT('1CONFIGURATION ',I1,'.  LIST OF SIMULTANEOUS',
     1  ' EIGENFUNCTIONS OF LSQ. LZ, SSQ, AND SZ, WITH'/
     2  18X,'LT = ',I1,7X,'MLT = ',I1,7X,'ST = ',I1,7X,
     3  'MST = ',I1////4X,'EF NO.',22X,'COEFFICIENT',
     4  15X,'SAAP'///)
      DO 110 I1=1,NRAF
      N1 = I1*(I1+1)/2
      N2 = (I1-1)*NRAF
      FD = FLINT(N1)
      FD = (DSQRT(1.0D0+4.0D0*FD)-1.0D0)/2.0D0
      LEIGV = FD
      FD = FD-LEIGV
      IF(FD.GT.0.5) LEIGV = LEIGV + 1
      IF(LEIGV.NE.LT) GO TO 110
      NLEF = NLEF + 1
      WRITE(3,1013) NLEF,(FLEIG(N2+I2),I2,I2=1,NRAF)
 1013 FORMAT(//////'0',4X,I2,50(17X,D23.16,10X,'SAAP(',I2,
     1  ')'/7X))
      WRITE(3,1017) LEIGV
 1017 FORMAT('+',75X,'(CORRESP. TO L-EIGENVALUE OF ',I2,')')
  110 CONTINUE
      IF(NLEF.NE.0) GO TO 113
      WRITE(3,1101) LT
 1101 FORMAT(//////'0THE EIGENVALUE LT = ',I2,
     1  'DOES NOT OCCUR FOR THIS CONFIGURATION')
C
  113 CONTINUE
C     (113 IS END OF C-LOOP)
C
C
      RETURN
      END
```

SUBPROGRAM 2.

```
      SUBROUTINE SSQEIG(NP,NDO,SKEEP,MKEEP,C,ORBPRD,PRGL,
     1  NPS,NGP,NSEF,PSCODE,FLEIG,FSCDSK,SLDISK)
      IMPLICIT REAL*8(F), INTEGER(A-E,G-Z)
      DIMENSION PS(4),NGP(5,16),L(2,13,4),M(2,13,4),
     1  SEIGV(13),FLEIG(2500),NSEF(5,16),FC(2,13,13),
     2  PSCODE(5,16),FSCDSK(5,16,13,13),SLDISK(5,16,13,4)
      COMMON FC,L,M
C
C
C     SSQEIG FINDS EIGENFUNCTIONS OF S**2 AND SZ FOR THE
C     GIVEN PAIRING LABEL 'PRGL'.
C
C
      FACT2 = 7.0710678118654750-01
      TNP = NP + NP
      TTNP = 2**NP
    5 MAGMT = IABS(MKEEP)
      NPS = 0
C     SWEEP DECIMAL REPS OF PS'S
      DO 40 DPS=1,TTNP
      DPSM1 = DPS - 1
      TD = DPSM1
C     CONVERT DEC REP TO PS'S
      PSSUM = 0
      DO 10 P=1,NP
      PI = 2 ** (NP-P)
      PSP = TD/PI
      IF(P.GT.NDO) GO TO 9
      IF(PSP.NE.0) GO TO 40
    9 PS(P) = PSP
      TD = TD - PSP*PI
   10 PSSUM = PSSUM + PSP
C     KEEP ONLY PS COMBINATIONS APPROPRIATE TO MKEEP
      IF(PSSUM.LT.MAGMT) GO TO 40
      NPS = NPS + 1
C     GET SSQ-EIGENFUNCTIONS CORRESPONDING TO SZ-EIGENVALUE
C     'MKEEP', AND GIVEN PS'S
      CALL SEIGEN(NP,NPS,PS,MKEEP,SEIGV,FLEIG,NPROD,PRGL)
C     NGP(PRGL,I) IS NO. OF GEMPRODS ASSOCIATED WITH PSC
C     'I' AND PAIRING LABEL 'PRGL'
      NGP(PRGL,NPS) = NPROD
      PSCODE(PRGL,NPS) = DPSM1
      IF(NPROD.NE.0) GO TO 15
      NPS = NPS - 1
      GO TO 40
C     NSEF(PRGL,I) IS NO. OF SSQ-EIGENFUNCTIONS WITH GIVEN
C     EIGENVALUE WHICH ARISE FROM ITH PSC FOR PRGL
```

```
   15 NSF = 0
      DO 37 ISEF=1,NPROD
      N2 = (ISEF-1)*NPROD
      IF(SEIGV(ISEF).NE.SKEEP) GO TO 37
      NSF = NSF + 1
      DO 30 IPROD=1,NPROD
CTEMP
   30 FSCDSK(PRGL,NPS,NSF,IPROD) = FLEIG(N2+IPROD)
CTEMP
   37 CONTINUE
      NSEF(PRGL,NPS) = NSF
      IF(NSF.EQ.0) GO TO 39
CTEMP
      DO 38 IPROD=1,NPROD
      DO 38 P=1,NP
   38 SLDISK(PRGL,NPS,IPROD,P) = L(1,IPROD,P)
CTEMP
   39 WRITE(3,410) NSF
  410 FORMAT(100X,' AND NSEF = ',I2)
      IF(NSF.EQ.0) NPS=NPS-1
   40 CONTINUE
      RETURN
      END
```

SUBPROGRAM 3.

```
      SUBROUTINE SEIGEN(NP,NPS,SFIX,MTFIX,SEIGV,FLEIG,
     1  NPROD,PRGL)
      IMPLICIT REAL*8(F), INTEGER(A-E,G-Z)
      REAL*8 DSQRT
      DIMENSION SFIX(4),LABEL(4),TS(4),TM(4),S(13,4),
     1  M(2,13,4),L(2,13,4),FLINT(91),SEIGV(13),IDX(13),
     2  FBLANK(338),FLEIG(2500)
      COMMON FBLANK,L,M
C
C * * * * * * * * * * * * * * *
C     SEIGEN RECEIVES PAIR-SPINS AND TOTAL MS FROM SSQEIG,
C     AND FINDS SSQ-EIGENFUNCTIONS SATISFYING THAT DATA.
C
C     INPUT REQUIRED - TOTAL MS (MTFIX), PAIR-SPINS (SFIX
C     VECTOR), N/2 (NP).
C * * * * * * * * * * * * * * *
C
C     THIS SECTION PRODUCES NPROD PRODUCT FUNCTIONS OF THE
C     SPECIFIED TYPE, THE NTH ONE HAVING THE PAIR-FUNCTION
C     LABELS (L(PRGL,NPS,N,I),I=1,NP), PAIR-SPINS
```

```
C        (S(N,I),I=1,NP), AND PAIR-MS'S (M(NPS,N,I),I=1,NP).
  100 NPROD = 0
      LLIMP1 = 4**NP
      DO 200 I1=1,LLIMP1
      TMT = 0
      NMBR = I1-1
      TN = NMBR
      DO 170 I2=1,NP
      PI = 4**(NP-I2)
      LABEL(I2) = TN/PI
      TN = TN - LABEL(I2)*PI
      TS(I2) = 1
      IF(LABEL(I2).EQ.0) TS(I2)=0
      IF(TS(I2).NE.SFIX(I2)) GO TO 200
      TM(I2) = TS(I2)*(LABEL(I2)-2)
  170 TMT = TMT + TM(I2)
      IF(TMT-MTFIX) 200,180,200
  180 NPROD = NPROD + 1
      DO 190 I2=1,NP
      S(NPROD,I2) = TS(I2)
      M(1,NPROD,I2) = TM(I2)
  190 L(1,NPROD,I2) = LABEL(I2)
  200 CONTINUE
      IF(NPROD.NE.0) GO TO 299
      RETURN
C
C * * * * * * * * * * * * *
C        SSQ-MATRIX BETWEEN PRODS OF SPECIFIED TYPE. STORED AS
C        THE MATRIX 'INT'.
C * * * * * * * * * * * * *
C
  299 COUNT = 0
      DO 560 I2=1,NPROD
      DO 560 I1=1,I2
      INT = 0
      COUNT = COUNT + 1
      ND = 0
      DO 420 I3=1,NP
      IF(L(1,I1,I3).NE.L(1,I2,I3)) ND=ND+1
  420 CONTINUE
      IF(ND.NE.0) GO TO 460
C
C        DIAGONAL ELEMENTS
C
  430 DO 450 I3=1,NP
      LBL = L(1,I1,I3)
      IF(LBL.EQ.0) GO TO 450
      IF(LBL.LE.2) ND=ND+1
  450 CONTINUE
      INT = MTFIX*(MTFIX+1) + 2*ND
```

```
      GO TO 540
C
C     OFF-DIAGONAL ELEMENTS
C
  460 IF(ND-2) 540,510,540
  510 DO 520 I3=2,NP
      IF(IABS(M(1,I1,I3)-M(1,I2.I3)).GT.1) GO TO 520
      I3M1 = I3 - 1
      DO 518 I4=1,I3M1
      IF(S(I1,I3)+S(I1,I4)+S(I2,I3)+S(I2,I4).NE.4) GO TO 518
      M134 = M(1,I1,I3) + M(1,I1,I4)
      IF(M134.NE.M(1,I2,I3)+M(1.I2,I4)) GO TO 518
      IF(IABS(M134).GT.1) GO TO 518
      INT = INT + 2
  518 CONTINUE
  520 CONTINUE
  540 FLINT(COUNT) = INT
  560 CONTINUE
      IF(NPROD-1) 970,600,610
  600 FLEIG(1) = 1.0D0
      GO TO 620
C
C * * * * * * * * * * * * * * * * *
C     DIAGONALIZE THE SSQ-MATRIX, GET SSQ-EIGENFUNCTIONS
C * * * * * * * * * * * * * * * * *
  610 CALL EIGEN(FLINT,FLEIG,NPROD,1,IDX,1.0D-14)
  620 DO 640 I1=1,NPROD
      N1 = I1*(I1+1)/2
      FD = FLINT(N1)
      FD = (DSQRT(1.0D0+4.0D0*FD)-1.0D0)/2.0D0
      SEIGV(I1) = FD
      FD = FD - SEIGV(I1)
      IF(FD.GT.0.5D0) SEIGV(I1) = SEIGV(I1) + 1
  640 CONTINUE
      RETURN
  970 STOP
      END
```

SUBPROGRAM 4.

```
      FUNCTION FLSOME(CI,I,LPS,LSEF,CJ,J,RPS,RSEF,N,MLT,PRS,
     1  LABLTM)
      IMPLICIT REAL*8(F), INTEGER(A-E,G-Z)
      REAL*8 DSQRT
      DIMENSION PRS(5,20),M(20,8),LOCC(111),ROCC(111),
     1  LABEL(8),LBL(20,8),E(8,2),BLANK(208),FSC(2,13,13),
```

```
     2  PL(5,20),NSPROD(5,16),L(20,8)
      COMMON FSC,BLANK,M,L,LBL,NSPROD,TNP,TTNP,PL
C
C     FLSQME CALCULATES THE INTEGRAL OVER L**2 BETWEEN
C     TWO SAAP'S.
C
      FLSQME = 0.0D0
      ND2 = N/2
      PLL = PL(CI,I)
      PLR = PL(CJ,J)
      NLPROD = NSPROD(PLL,LPS)
      NRPROD = NSPROD(PLR,RPS)
      IF(CI.NE.CJ) GO TO 10
      IF(I.NE.J) GO TO 10
      IF(LPS.NE.RPS) GO TO 10
      IF(LSEF.NE.RSEF) GO TO 10
C
C     DIAGONAL-TERM CONTRIBUTION
      FLSME = MLT*(MLT+1)
   10 DO 70 NU=1,N
      MNU = M(I,NU)
      LNU = L(I,NU)
      IF(MNU.EQ.LNU) GO TO 70
      DO 68 MU=1,N
      DO 11 CHK1=1,LABLIM
      LOCC(CHK1) = 0
   11 ROCC(CHK1) = 0
      DO 12 CHK1=1,N
      LL = LBL(I,CHK1)
      RL = LBL(J,CHK1)
      LABEL(CHK1) = LL
      LOCC(LL) = LOCC(LL) + 1
   12 ROCC(RL) = ROCC(RL) + 1
      MMU = M(I,MU)
      LMU = L(I,MU)
      IF(MU.NE.NU) GO TO 15
      MMU = MMU + 1
      GO TO 20
   15 IF(MMU.EQ.-LMU) GO TO 68
C
C     APPLY OPERATOR L-(MU)L+(NU) TO LEFT ORBITAL PRODUCT
C     (I)
      LBLMU = LBL(I,MU)
      LBLNU = LBL(I,NU)
      LABEL(MU) = LBLMU - 1
      LABEL(NU) = LBLNU + 1
      LOCC(LBLMU) = LOCC(LBLMU) - 1
      LOCC(LBLNU) = LOCC(LBLNU) - 1
      LOCC(LABEL(MU)) = LOCC(LABEL(MU)) + 1
      LOCC(LABEL(NU)) = LOCC(LABEL(NU)) + 1
```

```
C     DOES (L-(MU)L+(NU)*I) CONTAIN THE SAME ORBITALS AS
C     THE RIGHT ORB PROD (J) ?
   20 DO 30 CHK1=1,LABLIM
      IF(ROCC(CHK1).NE.LOCC(CHK1)) GO TO 68
   30 CONTINUE
C     IF SO, FIND THE PERMUTATION (E) THAT CONVERTS
C     (L-(MU)L+(NU)*I) TO THE RIGHT ORB PROD J. THE PERM
C     IS FOUND AS A PRODUCT OF TWO-CYCLES.
      NCYC = 0
      DO 60 CHK1=1,N
      DO 58 CHK2=CHK1,N
      IF(LBL(J,CHK1).NE.LABEL(CHK2)) GO TO 58
      IF(CHK1.EQ.CHK2) GO TO 60
      NCYC = NCYC + 1
      E(NCYC,1) = CHK1
      E(NCYC,2) = CHK2
      SAVE = LABEL(CHK1)
      LABEL(CHK1) = LABEL(CHK2)
      LABEL(CHK2) = SAVE
      GO TO 60
   58 CONTINUE
   60 CONTINUE
C     GET THE CONTRIBUTION TO FLSQME FROM THE L-(MU)L+(NU)
C     TERM
      FME = 0.0D0
      DO 62 LPROD=1,NLPROD
      DO 62 RPROD=1,NRPROD
   62 FME = FME + FSC(1,LSEF,LPROD) * FSC(2,RSEF,RPROD) *
     1  FPMAT(ND2,NCYC,E,TNP,TTNP,PLL,LPS,LPROD,PLR,RPS,
     2  RPROD)
 1007 CONTINUE
      IF(FME.EQ.0.0D0) GO TO 68
      FCMUNU = (LMU-MMU+1)*(LMU+MMU)*(LNU-MNU)*(LNU+MNU+1)
      FCMUNU = DSQRT(FCMUNU)
      FLSQME = FLSQME + ((-1)**NCYC) * FME * FCMUNU
   68 CONTINUE
C     68 IS END OF MU-LOOP
   70 CONTINUE
C     70 IS END OF NU-LOOP
C
C     NORMALIZATION
      PWR = (PRS(CJ,J)-PRS(CI,I))
      IF(PWR.GE.0) GO TO 75
      PWR = -PWR
      FNORM = 1.0D0/(2**PWR)
      GO TO 80
   75 FNORM = 2 ** PWR
   80 FLSQME = FLSQME*DSQRT(FNORM)
      RETURN
      END
```

SUBPROGRAM 5.

```
      FUNCTION FPMAT(NP,NCYCS,E,TNP,TTNP,PLL,LPS,LPROD,PLR,
     1  RPS,RPROD)
      IMPLICIT REAL*8(F), INTEGER(A-E,G-Z)
      DIMENSION T(4),M(4),SL(8),L(2,13,4),SEP(16),E(8,2),
     1  FCOEFF(16),FBLANK(338)
      COMMON FBLANK,L
C
C     * * * * * * * * * * * * *
C     CALCULATES (LEFT GEMPROD/P/RIGHT GEMPROD), WHERE
C     GEMPROD DATA IS IN COMMON, AND PERMUTATION CONVENTION
C     IS THAT (123) MEANS'ORBITAL 1 REPLACES ORBITAL 2,
C     ETC.' E.G., (123)ABC = CAB.
C     * * * * * * * * * * * * *
C
      FACT2 = 7.0710678118654750-01
      FPMAT = 0.0D0
      IF(NCYCS.NE.0) GO TO 305
C     WHEN NCYCS=0, PERMUTATION IS TAKEN TO BE THE IDENTITY.
C     THEN FPMAT IS OVERLAP BETWEEN LEFT AND RIGHT SPIN
C     GEMPRODS.
      DO 301 I3=1,NP
      IF(L(1,LPROD,I3).NE.L(2,RPROD,I3)) GO TO 370
  301 CONTINUE
      FPMAT = 1.0D0
      GO TO 370
C
  305 DO 365 SIDE=1,2
      PL = PLL
      PS = LPS
      PROD = LPROD
      IF(SIDE.EQ.1) GO TO 306
      PL = PLR
      PS = RPS
      PROD = RPROD
  306 COUNT = 0
C     FOR FIXED SIDE AND GEMPROD, SWEEP ALL SEPREDS AND
C     CONVERT SUITABLE DECLABELS TO BINLABELS.
      DO 360 I3=1,TTNP
      I3M = I3 - 1
      DO 310 I4=1,NP
      PI = 2**(NP-I4)
      T(I4) = I3M/PI + 1
      IF(L(SIDE,PROD,I4).NE.0) GO TO 307
      S = 0
      GO TO 308
  307 S = 1
  308 M(I4) = S*(L(SIDE,PROD,I4)-2)
```

```
      IF(T(I4).EQ.1) GO TO 310
C     SKIP SEPROD LABELS WHICH ARE NOT ASSOCIATED WITH THE
C     GIVEN GEMPROD.
      IF(M(I4).NE.0) GO TO 360
  310 I3M = I3M - T(I4)*PI + PI
C     COUNT SEPRODS ASSOCIATED WITH GIVEN GEMPROD
      COUNT = COUNT + 1
C     FOR EACH SEPROD KEPT, GENERATE THE SINGLE-ELECTRON
C     SPIN FUNCTION LABELS (SL'S) AND THE COEFFICIENT (FC)
      FC = 1.0D0
      DO 330 I4=1,NP
      TI4 = 2*I4
      TI4M1 = TI4 - 1
      IF(M(I4).NE.0) GO TO 315
      IF(T(I4).NE.2) GO TO 325
      SL(TI4M1) = 0
      SL(TI4) = 1
      FC = FC*FACT2
      IF(L(SIDE,PROD,I4).EQ.2) GO TO 330
      FC = -FC
      GO TO 330
  315 SL(TI4M1) = 1
      IF(L(SIDE,PROD,I4).EQ.3) GO TO 320
      SL(TI4M1) = 0
  320 SL(TI4) = SL(TI4M1)
      GO TO 330
  325 SL(TI4M1) = 1
      SL(TI4) = 0
      FC = FC*FACT2
  330 CONTINUE
      IF(SIDE.EQ.1) GO TO 340
C     IF SIDE = 2, PERMUTE THE SL'S
      DO 336 K=1,NCYCS
      I = NCYCS + 1 - K
      TEMP = SL(E(I,2))
      SL(E(I,2)) = SL(E(I,1))
  336 SL(E(I,1)) = TEMP
C     GENERATE PRODUCT 'SEPROD' FROM SL'S
  340 SEPROD = 0
      DO 345 I4=1,TNP
  345 SEPROD = SEPROD + SL(I4)*(10**(TNP-I4))
C     IF SIDE=1, STORE SEPROD AS SEP(COUNT), FC AS
C     FCOEFF(COUNT)
      IF(SIDE.EQ.2) GO TO 350
      SEP(COUNT) = SEPROD
      FCOEFF(COUNT) = FC
      GO TO 360
  350 CONTINUE
      DO 355 I4=1,NSPL
      IF(SEPROD.NE.SEP(I4)) GO TO 355
```

```
      FPMAT = FPMAT + FC*FCOEFF(I4)
  355 CONTINUE
  360 CONTINUE
C     IF SIDE=1, STORE NUMBER OF SEPRODS ASSOCIATED WITH
C     LEFT GEMPROD
      IF(SIDE.EQ.2) GO TO 365
      NSPL = COUNT
  365 CONTINUE
  370 RETURN
      END
```

SUBPROGRAM 6.

```
      SUBROUTINE EIGEN(A,R,N,MV,IDX,CVG)
C
C     COMPUTE EIGENVALUES AND EIGENFUNCTIONS OF A REAL
C     SYMMETRIC MATRIX
C
C     DESCRIPTION OF PARAMETERS -
C          A - ORIGINAL MATRIX, DESTROYED IN COMPUTATION.
C              RESULTANT EIGENVALUES ARE DEVELOPED IN DIAGO-
C              NAL OF MATRIX A.
C          R - RESULTANT MATRIX OF EIGENVECTORS (STORED
C              COLUMNWISE, IN SAME SEQUENCE AS EIGENVALUES)
C          N - ORDER OF MATRICES A AND R
C          MV - INPUT CODE
C                 0  COMPUTE EIGENVALUES ONLY (R NEED NOT
C                    BE DIMENSIONED BUT MUST STILL APPEAR
C                    IN CALLING SEQUENCE)
C                 1  GENERATE R MATRIX---COMPUTE EIGEN-
C                                        VALUES ONLY
C                 1  GENERATE R MATRIX---COMPUTE EIGEN-
C                    VALUES AND EIGENVECTORS AND SORT
C                -1  SAME AS 1 EXCEPT R IS INPUT
C                 2  GENERATE R MATRIX---COMPUTE EIGEN-
C                    VALUES AND EIGENVECTORS BUT DO NOT
C                    SORT
C                -2  SAME AS 2 EXCEPT R IS INPUT
C         CVG - CRITERION FOR CONVERGENCE
C                CVG IS POSITIVE---FINAL NORM=CVG
C                CVG IS NEGATIVE---FINAL NORM IS COM-
C                                  PUTED FROM CVG
C
C
C    ORIGINAL MATRIX A MUST BE REAL SYMMETRIC (STORAGE
C    MODE=1). MATRIX A CANNOT BE IN THE SAME LOCATION AS
```

```
C     MATRIX R. A IS COLUMNWISE UPPER TRIANGULAR AND R IS
C     COLUMNWISE SQUARE, EACH STORED IN ONE-DIMENSIONAL
C     ARRAYS.
C
C
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(1),R(1),IDX(1)
C        GENERATE IDENTITY MATRIX
      IF(MV)21,21,10
   10 IJ=0
      DO 20 J=1,N
      DO 20 I=1,N
      IJ=IJ+1
      R(IJ) = 0.0D0
      IF(I.EQ.J)R(IJ) = 1.0D0
   20 CONTINUE
   21 MX=IABS(MV)
      IF(N.EQ.1)RETURN
C        COMPUTE INITIAL AND FINAL NORMS (ANORM AND ANORMX)
   25 ANORM=0.0D+00
      IDX(1)=0
      DO 35 I=2,N
      JLIM=I-1
      IDX(I)=IDX(JLIM)+JLIM
      IA=IDX(I)
      DO 35 J=1,JLIM
      IA=IA+1
   35 ANORM=ANORM+A(IA)*A(IA)
      IF(ANORM) 165,165,40
   40 ANORM=2.0D+00*DSQRT(ANORM)
      DIV = 2.0D0 / DFLOAT(IA + 1)
   41 ANRMX=CVG
      IF (ANRMX)42,43,43
   42 ANRMX = ANORM*DIV*DABS(ANRMX)
   43 IF(ANRMX.GT.ANORM) GO TO 165
C        INITIALIZE INDICATORS AND COMPUTE THRESHOLD, THR
      THR=ANORM
   45 THR=THR*DIV
  155 IND=0
      DO 1001  L=2,N
      LMO=L-1
      LQ=IDX(L)
      LL=L+LQ
      DO 1001 M=1,LMO
      MQ=IDX(M)
C        COMPUTE SIN AND COS
      LM=LQ+M
   62 IF(DABS(A(LM))-THR)1001,65,65
   65 IND=1
```

```
      MM=M+MQ
      X=0.5D+00*(A(LL)-A(MM))
   68 Y=-A(LM)/DSQRT(A(LM)*A(LM)+X*X)
      IF(X) 70,75,75
   70 Y=-Y
   75 SINX=Y/DSQRT(2.0D+00*(1.0D+00+(DSQRT(1.0D+00-Y*Y))))
      SINX2=SINX*SINX
   78 COSX=DSQRT(1.0D+00-SINX2)
      COSX2=COSX*COSX
      SINCS =SINX*COSX
C        ROTATE L AND M COLUMNS
      ILQ=N*(L-1)
      IMQ=N*(M-1)
      DO 125 I=1,N
      IQ=IDX(I)
      IF(I-L) 80,115,80
   80 IF(I-M) 85,115,90
   85 IM=I+MQ
      GO TO 95
   90 IM=M+IQ
   95 IF(I-L) 100,105,105
  100 IL=I+LQ
      GO TO 110
  105 IL=L+IQ
  110 X=A(IL)*COSX-A(IM)*SINX
      A(IM)=A(IL)*SINX+A(IM)*COSX
      A(IL)=X
  115 IF(MX)120,125,120
  120 ILR=ILQ+I
      IMR=IMQ+I
      X=R(ILR)*COSX-R(IMR)*SINX
      R(IMR)=R(ILR)*SINX+R(IMR)*COSX
      R(ILR)=X
  125 CONTINUE
      X=A(LM)*(SINCS+SINCS)
      Y=A(LL)*COSX2+A(MM)*SINX2-X
      X=A(LL)*SINX2+A(MM)*COSX2+X
      A(LM)=0.0D0
      A(LL)=Y
      A(MM)=X
 1001 CONTINUE
  150 IF(IND-1) 160,155,160
C        COMPARE THRESHOLD WITH FINAL NORM
  160 IF(THR-ANRMX)165,165,45
C        SORT EIGENVALUES AND EIGENVECTORS
  165 IF(MX.NE.1) RETURN
      IQ=0
      DO 185 I=2,N
      JLIM=I-1
      IQ=IQ+N
```

```
      LL=I+IDX(I)
      JQ=-N
      DO 185 J=1,JLIM
      JQ=JQ+N
      MM=J+IDX(J)
      IF(A(LL)-A(MM))170,185,185
  170 X=A(LL)
      A(LL)=A(MM)
      A(MM)=X
  175 DO 180 K=1,N
      ILR=IQ+K
      IMR=JQ+K
      X=R(ILR)
      R(ILR)=R(IMR)
  180 R(IMR)=X
  185 CONTINUE
      RETURN
      END
```

LITERATURE CITED

Boerner, Hermann. 1963. Representations of groups. Amsterdam, The Netherlands, North-Holland Pub. Co.

Coleman, A. J. 1968. The symmetric group made easy. Advan. Quantum Chem. 4, 83.

Condon, E. U. and Shortley, G. H. 1951. The theory of atomic spectra. Cambridge, England, Cambridge Univ. Press.

Corson, E. M. 1951. Perturbation methods in the quantum mechanics of n-electron systems. London, England, Blackie and Son, Ltd.

Elliott, J. P., Hope, J., and Jahn, H. A. 1953. Theoretical studies in nuclear structure. IV. Wave functions for the nuclear p-shell. Part B. <p(n)|p(n-2)p(2)> fractional parentage coefficients. Trans. Roy. Soc. (London) A246, 241.

Gallup, G. A. 1968. Projected Hartree product wavefunctions. J. Chem. Phys. 48, 1752.

Gallup, G. A. 1969. Projected Hartree product wavefunctions. II. General considerations of Young operators. J. Chem. Phys. 50, 1206.

Goddard, W. A. 1967a. Improved quantum theory of many-electron systems. I. Construction of eigenfunctions of $\hat{S}^2$ which satisfy Pauli's Principle. Phys. Rev. 157, 73.

Goddard, W. A. 1967b. Improved quantum theory of many-electron systems. II. The basic method. Phys. Rev. 157, 81.

Goddard, W. A. 1968. Improved quantum theory of many-electron systems. III. The GF method. J. Chem. Phys. 48, 450.

Hamermesh, Morton. 1962. Group theory. Reading, Mass., Addison-Wesley Pub. Co., Inc.

Harris, Frank E. 1967. Molecular orbital theory. Advan. Quantum Chem. 3, 61.

Jahn, H. A. 1954. Direct evaluation of fractional parentage coefficients using Young operators. General theory and <4|2,2> coefficients. Phys. Rev. 96, 989.

Jahn, H. A. and van Wieringen, H. 1951. Theoretical studies in nuclear structure. IV. Wave functions for the nuclear p-shell. Part A. <p(n)|p(n-1)p> fractional parentage coefficients. Proc. Roy. Soc. (London) A209, 502.

Johnson, D. F. 1960. Group theory in solid-state physics. Rept. Progr. Phys. 23, 66.

Karplus, M., Kuppermann, A., and Isaacson, L. M. 1958. Quantum-mechanical calculation of one-electron properties. I. General formulation. J. Chem. Phys. 29, 1240.

Klein, D. J., Carlisle, C. H., and Matsen, F. A. 1970. Symmetry adaptation to sequences of finite groups. Advan. Quantum Chem. 5, 219.

Kotani, M., Amemiya, A., Ishiguro, E., and Kimura, T. 1955. Tables of molecular integrals. Tokyo, Japan, Maruzen Co., Ltd.

Löwdin, P.-O. 1955a. Quantum theory of many-particle systems. I. Physical interpretations by means of density matrices, natural spin-orbitals, and convergence problems in the method of configurational interaction. Phys. Rev. 97, 1474.

Löwdin, P.-O. 1955b. Quantum theory of many-particle systems. III. Extension of the Hartree-Fock scheme to include degenerate systems and correlation effects. Phys. Rev. 97, 1509.

Löwdin, P.-O. 1960. Expansion theorems for the total wave function and extended Hartree-Fock schemes. Rev. Mod. Phys. 32, 328.

Löwdin, P.-O. 1964. Angular momentum wavefunctions constructed by projection operators. Rev. Mod. Phys. 36, 966.

Löwdin, P.-O. 1967. Group algebra, convolution algebra, and applications to quantum mechanics. Rev. Mod. Phys. 39, 259.

McIntosh, H. V. 1960. Symmetry-adapted functions belonging to the symmetric groups. J. Math. Phys. 1, 453.

McWeeny, R., and Sutcliffe, B. T. 1969. Methods of molecular quantum mechanics. New York, N. Y., Academic Press, Inc.

Matsen, F. A. 1964. Spin-free quantum chemistry. Advan. Quantum Chem. 1, 59.

Matsen, F. A. 1970. Vector spaces and algebras for chemistry and physics. New York, N. Y., Holt, Rinehart and Winston.

Mattheiss, L. F. 1958. IBM 704 program for generating the irreducible representations of the group of spin coordinate permutations. Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T. 30, 43.

Mattheiss, L. F. 1959. An inductive method for generating the irreducible representations of the group of spin coordinate permutations. Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T. 34, 58.

Pauncz, R. 1962. Studies on the alternant molecular orbital method. IV. Generalization of the method to states with different multiplicities. J. Chem. Phys. 37, 2739.

Pauncz, R. 1967. Alternant molecular orbital method. Philadelphia, Penna., W. B. Saunders Co.

Pauncz, R. 1969. Electron correlation in atoms and molecules. In Henderson, D., ed. Physical chemistry. Vol. 3. New York, N. Y., Academic Press, Inc.

Pauncz, R., de Heer, J., and Löwdin, P.-O. 1962. Studies on the alternant molecular orbital method. I. General energy expression for an alternant system with closed-shell structure. J. Chem. Phys. 36, 2247.

Percus, J. K. and Rotenberg, A. 1962. Exact eigenfunctions of angular momentum by rotational projection. J. Math. Phys. 3, 928.

Poshusta, R. D. 1969. Applications of the symmetric group in theoretical chemistry. Unpublished lecture notes. Ames, Iowa, Iowa State University.

Pratt, G. W., Jr. 1953. Eigenfunctions of S^2 by a spin operator method. Phys. Rev. 92, 278.

Rotenberg, A. 1963. Calculation of exact eigenfunctions of spin and orbital angular momentum using the projection operator method. J. Chem. Phys. 39, 512.

Ruedenberg, K. and Poshusta, R. D. 1971. Matrix elements and density matrices for many-electron spin eigenstates built from orthonormal orbitals. To be published.

Rutherford, D. E. 1948. Substitutional analysis. Edinburgh, Scotland, Edinburgh Univ. Press.

Salmon, W. I. 1971. The theory of group algebras. Unpublished lecture notes. Ames, Iowa, Iowa State University.

Sasaki, F. and Ohno, K. 1963. Spin-component analysis of single-determinant wavefunctions. J. Math. Phys. 4, 1140.

Schaeffer, H. F. III and Harris, Frank E. 1968. Construction and use of atomic L-S eigenfunctions. J. Comp. Phys. 3, 217.

Serber, R. 1934a. Extension of the Dirac vector model to include several configurations. Phys. Rev. 45, 461.

Serber, R. 1934b. The solution of problems involving permutation degeneracy. J. Chem. Phys. 2, 697.

Shapiro, J. 1965. Matrix representation of the angular momentum projection operator. J. Math. Phys. 6, 1680.

Slater, John C. 1929. The theory of complex spectra. Phys. Rev. 34, 1293.

Slater, John C. 1931. Molecular energy levels and valence bonds. Phys. Rev. 38, 1109.

Smith, V. H., Jr. 1964. Construction of exact spin eigenfunctions. J. Chem. Phys. 41, 277.

Smith, V. H., Jr. and Harris, F. E. 1967. Projection of exact spin eigenfunctions. Unpublished paper. Preprint No. 182. Uppsala, Sweden, Quantum Chemistry Group, University of Uppsala.

Sullivan, J. J. 1968. Antisymmetric projection in the approximation of no spin-orbit coupling. J. Math. Phys. 9, 1369.

Thrall, R. M. 1941. Young's semi-normal representation of the symmetric group. Duke Math. J. 8, 611.

van der Waerden, B. L. 1950. Modern algebra. Vol. 2. New York, N. Y., F. Ungar Pub. Co.

Weyl, Hermann. 1931. Gruppentheorie und Quantenmechanik. 2. Auflage. Leipzig, Germany, S. Hirzel. English edition, translated by Robertson, H. P. The theory of groups and quantum mechanics. New York, N. Y., Dover Publications, Inc. 1950.

Wigner, E. P. 1931. Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren. Braunschweig, Germany, F. Vieweg und Sohn Akt.-Ges.

Wigner, E. P. 1959. Group theory and its application to the quantum mechanics of atomic spectra. Expanded edition. Translated by Griffen, J. J. New York, N.Y., Academic Press, Inc.

Yamanouchi, Takahiko. 1935. On the calculation of atomic energy levels. Proc. Physico-Math. Soc. Japan 17, 274.

Yamanouchi, Takahiko. 1936. On the calculation of atomic energy levels. IV. Proc. Physico-Math. Soc. Japan 18, 623.

Yamanouchi, Takahiko. 1937. On the construction of unitary irreducible representations of the symmetric group. Proc. Physico-Math. Soc. Japan 19, 436.

Yamanouchi, Takahiko. 1938. On atomic energy levels of $p^n p$ configurations. Proc. Physico-Math. Soc. Japan 20, 547.

Young, A. 1901. On quantitative substitutional analysis. Proc. London Math. Soc. 33, 97.

Young, A. 1902. On quantitative substitutional analysis (second paper). Proc. London Math. Soc. 34, 361.

Young, A. 1928. On quantitative substitutional analysis (third paper). Proc. London Math. Soc. (2), 28, 255.

Young, A. 1930. On quantitative substitutional analysis (fourth paper). Proc. London Math. Soc. (2), 31, 253.

Young, A. 1932. On quantitative substitutional analysis (sixth paper). Proc. London Math. Soc. (2), 34, 196.

ACKNOWLEDGMENTS

The author is indebted to Professor Klaus Ruedenberg for suggesting this problem and guiding its solution. He also wishes to thank Professor R. D. Poshusta for helpful discussions concerning group algebras.

Special thanks are owed to that unknown person who, in 1950, left a chemistry textbook in a trash can, and thus inadvertently started the author's interest in chemistry.