# Improved Quantum Theory of Many-Electron Systems. I. Construction of Eigenfunctions of $\hat{S}^2$ Which Satisfy Pauli's Principle*

WILLIAM A. GODDARD, III†
*Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California*
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A general method of obtaining many-electron wave functions which are eigenfunctions of $\hat{S}^2$ and which also satisfy Pauli's principle is developed. This method is based on the properties of the irreducible units of the group algebra of the symmetric group. Using this method, expansions of the exact wave function are found which will in succeeding articles form the basis of a powerful method of obtaining accurate *and quite useful* many-electron wave functions for atoms, molecules, and solids.

## INTRODUCTION

THIS series will be primarily concerned with constructing accurate and useful many-electron wave functions for atoms, molecules, and solids. We take our Hamiltonian $H$ as including only the kinetic-energy terms for the electrons and the electrostatic interactions among all the electrons and nuclei (i.e., we neglect relativistic effects, nuclear motions, and all spin interactions). Independently of the nuclear configuration this Hamiltonian has two general symmetries: $H$ is invariant under all permutations of the electrons, and $H$ commutes with all spin operators, including $\hat{S}^2$ and $\hat{S}_z$, the total-spin and total-spin-projection operators. This invariance of the Hamiltonian results in some important symmetry conditions on the wave function. We wish to introduce these symmetries into the wave function in an exact way, since, although of necessity any wave function we write down will be an approximation, we wish for the approximate wave function to behave as nearly as possible like the exact wave function so that we will be able to draw valid conclusions from considerations of the approximate wave functions. The proper permutational symmetry for the many-electron wave function is stated in the Pauli principle and is that the many-electron wave function changes sign upon transposition of the spatial-spin coordinates of any two electrons. A condition which ensures that the wave function possesses the proper spin symmetry is that the wave function be an eigenfunction of $\hat{S}^2$ and $\hat{S}_z$. In this paper we will discuss a general method of constructing many-electron wave functions that simultaneously are eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$ and satisfy Pauli's principle. Later papers will utilize this method for developing a general method of calculating accurate and useful many-electron wave functions.

It has been rather easy to construct a wave function which satisfies Pauli's principle, since if $\psi(1,2,\cdots,N)$ is any function of the spatial-spin coordinates of $N$ electrons, then $\Psi(1,\cdots,N)=\mathcal{A}\psi(1,\cdots,N)$ changes sign under any transposition [where $\mathcal{A}$ is the antisymmetrizer, $\sum_\tau(-1)^\tau\tau$]. We will use a method of constructing eigenfunctions of $\hat{S}^2$ satisfying Pauli's principle which is based on the group-theoretical properties of the symmetric group, and which has a form especially well suited for our purposes. This method is closely related to the method due to Yamanouchi[1] and Kotani.[2,3]

The basic operator is discussed in Sec. I, and some useful relations are obtained in Sec. II. In Sec. III we consider the expansion of the exact wave function in terms of the operators of the new method. Section IV includes a short discussion of the Löwdin[4] and Yamonouchi-Kotani methods and a comparison of the latter to the new method, and in Sec. V we consider some ways to use the results of Sec. III for the purpose of constructing approximate wave functions.

## I. THE SYMMETRIC GROUP AND THE $G_i^\mu$ OPERATOR

As was mentioned in the Introduction, the Hamiltonian $H$ for an $N$-electron system is invariant under all permutations of the $N$ electrons, i.e., is invariant under the operations of the *symmetric group*, $\mathcal{S}_N$. In this section, we will use the orthogonal units[5], $O_{ij}^\mu$, of the group algebra of $\mathcal{S}_N$ to construct an operator $G_i^\mu$ such that if $\psi$ is any function of the spatial-spin coordinates of $N$ electrons, then $G_i^\mu\psi$ satisfies Pauli's principle. Then we show that the $G_i^\mu$ operator also has the property that $G_i^\mu\psi$ is an eigenfunction of $\hat{S}^2$.

The orthogonal units and their properties were derived by Young and are described in detail in a quite clear and appealing treatment by Rutherford.[5] These units are Wigner projection operators,

$$O_{rs}^\mu=\left(\frac{1}{\Theta^\mu}\right)\sum_{\tau\in\mathcal{S}^N}U_{sr\tau}^\mu\tau, \tag{1}$$

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[1] T. Yamanouchi, Proc. Phys. Math. Soc. Japan **18**, 623 (1936); **20**, 560 (1938); see also M. Kotani and M. Siga, *ibid.* **19**, 471 (1937).

[2] M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, *Table of Molecular Integrals* (Maruzen Company, Ltd., Tokyo, 1963), 2nd ed.

[3] We wish to thank Dr. R. M. Pitzer for pointing out that Kotani describes a method which is related to the method described herein.

[4] P.-O. Löwdin, Phys. Rev. **97**, 1509 (1955).

[5] D. E. Rutherford, *Substitutional Analysis* (Edinburgh University Press, London, 1948).

defined in terms of a specific representation $U^\mu$ of the irreducible representations of the symmetric group. This representation is defined in Appendix A in terms of Young's shapes $S^\mu$ [e.g., as in Fig. 1(a)] and Young's tableau $S_i^\mu$ [e.g., as in Fig. 1(b)]. The resulting $U_\tau^\mu$ are real orthogonal matrices; hence

$$O_{rs}^\mu=\left(\frac{1}{\Theta^\mu}\right)\sum_\tau U_{rs\tau}^\mu\tau, \tag{2}$$

$$\tau=\sum_{\mu rs} U_{rs\tau}^\mu O_{rs}^\mu, \tag{3}$$

where $\Theta^\mu=N!/f^\mu$ and $f^\mu$ is the degree of the $\mu$ irreducible representation of $\mathcal{S}_N$. The $O_{rs}^\mu$ combine as follows:

$$O_{rs}^\mu O_{pq}^\beta=\delta^{\mu\beta}\delta_{sp}O_{rp}^\mu, \tag{4}$$

and the resolution of the identity becomes

$$\sum_\mu\sum_{i=1}^{f^\mu} O_{ii}^\mu=\epsilon. \tag{5}$$

The Young's shape containing one column is denoted by $[1^N]$ and leads to one tableau

$$O_{11}^{[1^N]}=\frac{1}{N!}\sum_\tau \zeta_\tau\tau, \tag{6}$$

where $\delta_\tau$ is the parity of $\tau$.

A shape which is obtained from a second shape by interchanging rows and columns is called the *associate* of the second shape, and the same is true for tableaux; the associate is denoted by a bar. Using the definition of axial distance from Appendix A, we see that $d_{(k+1,k)}{}^l=-d_{(k+1,k)}{}^{\bar{l}}$ and

$$\begin{aligned}&U_{i\bar{l}(k+1,k)}{}^{\bar{\mu}}=-U_{il(k+1,k)}{}^\mu,\\ &U_{i\bar{l}(k+1,k)}{}^{\bar{\mu}}=U_{il(k+1,k)}{}^\mu \quad \text{if} \quad l\neq i.\end{aligned} \tag{7}$$

We wish to consider linear combinations of permutations acting on two different spaces. We will let $O_{rs}{}^\alpha$ act only on the first space and $\omega_{pq}{}^\beta$ act only on the second space; of course, $O_{rs}{}^\alpha$ and $\omega_{pq}{}^\beta$ commute. Define the quantity $G_i{}^\mu$ as follows:

$$G_i{}^\mu\equiv\sum_\tau \zeta_{\sigma\tau i}O_{\tau i}{}^\mu\omega_{\bar{\tau}\bar{i}}{}^{\bar{\mu}}, \tag{8}$$

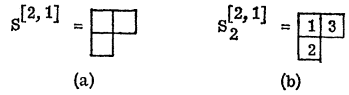
where $\sigma_{ri}$ is the permutation taking tableau $S_i{}^\mu$ into tableau $S_r{}^\mu$. Let the transposition $\tau$ act on $G_i{}^\mu$; it then acts on both $O^\mu$ and $\omega^\mu$. Using (3), we obtain

$$\begin{aligned}\tau G_i{}^\mu&=\sum_{\beta st}\sum_{\alpha\bar{p}\bar{q}}\sum_r \zeta_{\sigma ri}U_{st\tau}{}^\beta U_{\bar{p}\bar{q}\tau}{}^\alpha O_{si}{}^\beta O_{ri}{}^\mu\omega_{\bar{p}\bar{q}}{}^\alpha\omega_{\bar{r}\bar{i}}{}^{\bar{\mu}}\\ &=\sum_{spr}\zeta_{\sigma rp}\zeta_{\sigma pi}U_{sr\tau}{}^\mu U_{\bar{p}\bar{r}\tau}{}^{\bar{\mu}}O_{si}{}^\mu\omega_{\bar{p}\bar{i}}{}^{\bar{\mu}},\end{aligned} \tag{9}$$

where we have used $\sigma_{ri}=\sigma_{rp}\sigma_{pi}$, $\zeta_\tau\zeta_\sigma=\zeta_{\tau\sigma}$, and $\zeta_\tau=\zeta_{\tau^{-1}}$. If $\tau$ is an elementary transposition, then from Appendix B,

$$\zeta_{\sigma_{pr}}U_{\bar{p}\bar{r}\tau}{}^{\bar{\mu}}=-U_{pr\tau}{}^\mu.$$

FIG. 1. (a) A sample shape; (b) a sample standard tableau.




Thus,

$$\sum_\tau \zeta_{\sigma_{pr}}U_{sr\tau}{}^\mu U_{\bar{p}\bar{r}\tau}{}^{\bar{\mu}}=-\delta_{sp}. \tag{10}$$

Using (10) in (9) we obtain

$$(k,\,k+1)G_i{}^\mu=-\sum_s \zeta_{\sigma_{si}}O_{si}{}^\mu\omega_{\bar{s}\bar{i}}{}^{\bar{\mu}}=-G_i{}^\mu,$$

which is independent of $k$. But any permutation $\tau$ may be expressed in terms of elementary transpositions and $\tau$ will involve an even or odd number of elementary transpositions depending on whether $\tau$ is an even or odd permutation; hence,

$$\tau G_i{}^\mu=\zeta_\tau G_i{}^\mu. \tag{11}$$

Thus, the result of $G_i{}^\mu$ operating on any function of $N$ electrons is a function which satisfies the Pauli principle.

Now we must consider the spin symmetry. If $\chi$ is some product of the spin functions for $N$ electrons and $\omega_{sr}{}^\alpha$ is a Wigner projection operator for $\mathcal{S}_N$, such as in (2), then $\omega_{sr}{}^\alpha\chi$ is an eigenfunction of $\hat{S}^2$,

$$\hat{S}^2\omega_{sr}{}^\alpha\chi=S(S+1)\omega_{sr}{}^\alpha\chi. \tag{12}$$

This is due to the well-known direct relationship[6] between the irreducible representations of $N$th rank tensors [in this case based on the transformation group $SU(2)$] and the symmetric group on $N$ objects, $\mathcal{S}_N$. Since the transformation space for $SU(2)$ is two-dimensional, then $\omega_{sr}{}^\alpha\chi\neq 0$ only for $\alpha$ having two rows or less (see Appendix D). If these rows have lengths $n$ and $m$ with $n>m$, then $n+m=N$ and $S=(n-m)/2$. Thus, if $G_i{}^\mu\psi\neq 0$, then $\hat{S}^2G_i{}^\mu\psi=S(S+1)G_i{}^\mu\psi$ and *$G_i{}^\mu$ is an operator which upon operating on a function of the spatial-spin coordinates of $N$ electrons yields a function which is an eigenfunction of total spin and which satisfies Pauli's principle.* Before considering some important expansions using this operator, we will consider some of its properties.

## II. SOME PROPERTIES OF THE $G_i{}^\mu$ OPERATORS

### Expectation Values

Since the $U_\tau{}^\mu$ are orthogonal, the adjoint of $O_{ij}{}^\mu$ is $O_{ji}{}^\mu$. That is, for any $N$-electron spatial functions $\Phi_1$ and $\Phi_2$,

$$\begin{aligned}\langle\Phi_1|O_{ji}{}^\mu\Phi_2\rangle&=\frac{1}{\Theta^\mu}\sum_\tau U_{ji\tau}{}^\mu\langle\Phi_1|\tau\Phi_2\rangle\\ &=\frac{1}{\Theta^\mu}\sum_\tau U_{ji\tau}{}^\mu\langle\tau^{-1}\Phi_1|\Phi_2\rangle\\ &=\langle O_{ij}\Phi_1|\Phi_2\rangle.\end{aligned} \tag{13}$$

[6] M. Hamermesh, *Group Theory* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1962).

Hence if $H$ commutes with all permutations, then

$$\langle\Phi_1|H|O_{ji}{}^{\mu}\Phi_2\rangle=\langle O_{ij}{}^{\mu}\Phi_1|H|\Phi_2\rangle \tag{14}$$

and

$$\langle O_{ij}{}^{\mu}\Phi_1|H|O_{kl}{}^{\beta}\Phi_2\rangle=\delta^{\mu\beta}\delta_{ik}\langle\Phi_1|H|O_{jl}{}^{\beta}\Phi_2\rangle$$

using (4). Thus, if $\chi_1$ and $\chi_2$ are arbitrary $N$-electron spin functions,

$$\langle G_i{}^{\mu}\Phi_1\chi_1|H|G_k{}^{\beta}\Phi_2\chi_2\rangle = \delta^{\mu\beta}\zeta_{\sigma ik}f^{\mu}\langle\Phi_1|H|O_{ik}{}^{\mu}\Phi_2\rangle\langle\chi_1|\omega_{\bar{i}\bar{k}}\chi_2\rangle;$$

hence

$$E=\langle G_i{}^{\mu}\Phi\chi|H|G_i{}^{\mu}\Phi\chi\rangle/\langle G_i{}^{\mu}\Phi\chi|G_i{}^{\mu}\Phi\chi\rangle = \langle\Phi|H|O_{ii}{}^{\mu}\Phi\rangle/\langle\Phi|O_{ii}{}^{\mu}\Phi\rangle. \tag{15}$$

Consider the operator

$$T^{\mu}\equiv(1/f^{\mu})\sum_i G_i{}^{\mu}. \tag{16}$$

Then using (4) and (8) we find that $T^{\mu}T^{\beta}=\delta^{\mu\beta}T^{\mu}$. Thus the $T^{\mu}$ form an orthogonal set of idempotent operators.

Consider the operator $\sum_{\mu}T^{\mu}$. We obtain

$$\sum_{\mu}T^{\mu}=(1/\Theta^{\mu})\sum_{\tau}\zeta_{\tau}\tau\sum_{i,\mu}(1/f^{\mu})O_{ii}{}^{\mu},$$

where $O_{ii}{}^{\mu}$ operates on spatial coordinates only and $\tau$ operates on spatial-spin coordinates, and we have used

$$\sum_{r}\zeta_{\sigma ri}O_{ri}{}^{\mu}\omega_{\bar{r}\bar{i}}{}^{\mu}=(1/\Theta^{\mu})\sum_{\tau}\zeta_{\tau}\tau O_{ii}{}^{\mu}$$

from Appendix C. But $\Theta^{\mu}=N!/f^{\mu}$ and $\sum\mu,_i O_{ii}=\epsilon$, thus,[7]

$$\sum_{\mu}T^{\mu}=\frac{1}{N!}\sum_{\tau\in\mathfrak{S}^N}\zeta_{\tau}\tau\equiv\Omega_{11}{}^{[1^N]}. \tag{17}$$

That is, $\sum_{\mu}T^{\mu}$ projects out the totally antisymmetric component of any function of $N$ particles. Since $\Omega_{11}{}^{[1^N]}\Omega_{11}{}^{[1^N]}=\Omega_{11}{}^{[1^N]}$ then $(\sum T^{\mu})(\sum T^{\mu})=(\sum T^{\mu})$.

## III. EXPANSIONS OF THE EXACT MANY-ELECTRON WAVE FUNCTION

Next we shall consider some possible expansions of the exact many-electron wave function.

If $\{\psi_i\}$ is a complete set of spin orbitals, then the exact many-electron wave function can be expanded in a sum over tensor products of these spin-orbitals,[8]

$$\Psi_{\text{exact}}(1,2,\cdots,N) = \sum_{i,j,\cdots,k}C_{ij\ldots k}\psi_i(1)\psi_j(2)\cdots\psi_k(N). \tag{18}$$

If this wave function is to describe a system of electrons, then the coefficients in the expansion are not all independent. For example, in order that $\Psi_{\text{exact}}$ satisfy the Pauli principle, the coefficients must be related in a manner such that we can combine terms to obtain[7,8]

$$\Psi_{\text{exact}}=\sum_{i<j<\cdots<k}C_{ij\ldots k}\Omega_{11}{}^{[1^N]}\psi_i(1)\psi_j(2)\cdots\psi_k(N), \tag{19}$$

where $N!\Omega_{11}{}^{[1^N]}=\sum\tau\in\mathfrak{S}_N\,\zeta_{\tau}\tau$ is an antisymmetrizer and the set of spin-orbitals is presumed to have been ordered. But if no further restrictions are placed on the coefficients, (19) is in general not an eigenfunction of spin; in fact, from (17) we can expand $\Omega_{11}{}^{[1^N]}=\sum_{\mu}T^{\mu}$, where each $\mu$ corresponds to a different eigenfunction of $\hat{S}^2$ which satisfies Pauli's principle. Thus to ensure that $\Psi_{\text{exact}}$ is an eigenfunction of $\hat{S}^2$ and satisfies Pauli's principle, instead of operating on (18) with $\Omega_{11}{}^{[1^N]}{}_{\text{exact}}$ we should operate with $T^{\mu}$,

$$\Psi_{\text{exact}}{}^{S}=\sum_{j_1<j_2<\cdots<j_N}C_{\mathbf{j}}T^{\mu S}\psi_{\mathbf{j}}, \tag{20}$$

where $\mathbf{j}$ denotes the set of indices $j_1j_2\cdots j_N$ and $\psi_{\mathbf{j}}$ denotes $\psi_{j_1}\psi_{j_2}\cdots\psi_{j_N}$. We will generally suppress the subscript $S$ on $\mu$.

We are interested in a Hamiltonian which does not involve spin, so it is convenient to factor each spin orbital into a spatial part $\phi_j$ and a spin part $s_j$. We let $\{\phi_j\}$ be a complete set of spatial functions and $\{s_j\}=\{\alpha,\beta\}$ be a complete set of spin functions. Thus (20) becomes

$$\Psi_{\text{exact}}=\sum_{\mathbf{i},\mathbf{j}}C_{\mathbf{i},\mathbf{j}}T^{\mu}\Phi_{\mathbf{i}}\chi_{\mathbf{j}}, \tag{21}$$

where

$$\Phi_{\mathbf{i}}=\phi_{i_1}(1)\phi_{i_2}(2)\cdots\phi_{i_N}(N)$$

and

$$\chi_{\mathbf{j}}=s_{j_1}(1)s_{j_2}(2)\cdots s_{j_N}(N).$$

In order to define (21) properly, we must define an order for the double sum over spatial and spin tensor components, so that only linearly independent terms appear, just as was done for (19) and (20). It will be convenient to do this by ordering the spin components first and then the spatial components. Hence if $\psi_{\mathbf{k}}=\Phi_{\mathbf{i}}\chi_{\mathbf{j}}$ and $k$ is ordered $(k_1<k_2<\cdots<k_N)$, then $\mathbf{j}$ is ordered $(j_1\leqslant j_2\leqslant j_3\leqslant\cdots\leqslant j_N)$, and if $j_p=j_q$, then $i_p<i_q$. By this convention we have $\chi_{\mathbf{j}}=\alpha(1)\alpha(2)\cdots\alpha(\nu)\beta(\nu+1)\cdots\beta(N)$. If the exact wave function is an eigenfunction of $\hat{S}_z$, there is only one choice of $\mathbf{j}$ for a given $M$; also if $\nu=\frac{1}{2}N+M$, then the sum over $i$ in (21) becomes such that $i_1<i_2<\cdots<i_\nu$ and $i_{\nu+1}<i_{\nu+2}<\cdots<i_N$; such a pair of ordered sums is denoted by $\sum_{\mathrm{p},\mathrm{q}}{}^{0}$. Thus (21) becomes

$$\Psi_{\text{exact}}{}^{S,M}=\sum_{\mathrm{p},\mathrm{q}}{}^{0}C_{\mathrm{p},\mathrm{q}}T^{\mu}(\Phi_{\mathrm{p},\mathrm{q}}\chi_M) = (1/f^{\mu})\sum_{\mathrm{p},\mathrm{q}}{}^{0}C_{\mathrm{p},\mathrm{q}}{}'\sum_i G_i{}^{\mu}(\Phi_{\mathrm{p},\mathrm{q}}\chi_M). \tag{22}$$

In particular, if $M=S$ then $G_i{}^{\mu}\Phi\chi_S=\delta_{if}G_f{}^{\mu}\Phi\chi_S$ (see Appendix D); hence

$$\Psi_{\text{exact}}{}^{S,S}=\sum_{\mathrm{p},\mathrm{q}}{}^{0}C_{\mathrm{p},\mathrm{q}}{}''G_f{}^{\mu}(\Phi_{\mathrm{p},\mathrm{q}}\chi_S). \tag{23}$$

[7] We use the convention that $\Omega_{ij}{}^{\mu}$, $O_{ij}{}^{\mu}$, and $\omega_{ij}{}^{\mu}$ are operators on the spatial-spin, spatial, and spin coordinates, respectively.

[8] P.-O. Löwdin, Phys. Rev. **97**, 1474 (1955).

If we define $\Phi' \equiv \sum_{\mathbf{p},\mathbf{q}}{}^{0} C_{\mathbf{p},\mathbf{q}}{}'' \Phi_{\mathbf{p},\mathbf{q}}$, then

$$\Psi_{\text{exact}}{}^{S,S} = G_f{}^{\mu}(\Phi' \chi_S). \tag{24}$$

Applying $\hat{S}^-$ to (23) and (24), we find that they hold for any $M$ component (note that we are dealing with non-normalized wave functions). We have been considering the set of spatial functions to belong to some complete set of orthonormal functions; however, from (23) the sum over $\mathbf{p}$ and the sum over $\mathbf{q}$ are independent, thus we could actually consider two different complete, orthonormal sets of functions (over the same space) with no fixed relation between the sets and write (23) with

$$\Phi_{\mathbf{p},\mathbf{q}} = \phi_{p_1 a}\phi_{p_2 a}\cdots\phi_{p_n a}\phi_{q_1 b}\phi_{q_2 b}\cdots\phi_{q_m b}, \tag{25}$$

where $a$ and $b$ refer to the different sets of functions.

Equations (23) and (24) might seem to give a special place to the $G_f{}^{\mu}$ operator; actually this is not completely the case.[9] Write $\omega_{i1}{}^{\mu}\chi_S = W_{1j\sigma}{}^{\mu}\omega_{ij}\chi_f(S)$, where

$$\chi_f(S) = \alpha(1)\beta(2)\alpha(3)\beta(4)\cdots\alpha(2m-1)\beta(2m) \times\alpha(2m+1)\cdots\alpha(N) \quad \text{and} \quad \chi_S = \sigma\chi_f(S).$$

We can do this since $\omega_{i1}{}^{\mu}\chi_S \neq 0$ and $\omega_{ij}{}^{\mu}\chi_f(S) \neq 0$ and since there is only one linearly independent function $\omega_{ij}{}^{\mu}\chi(S)$ for all $j$ and $\chi$ such that $\hat{S}_z\chi = S\chi$. Then

$$\begin{aligned} G_f(\Phi'\chi_S) &= \sum_r \zeta_{\sigma rf}(O_{rf}\Phi')(\omega_{\bar{r}\bar{j}}\chi_S) \\ &= W_{\bar{j}\bar{i}\sigma}\sum_r \zeta_{\sigma rf}(O_{ri}O_{if}\Phi')[\omega_{\bar{r}\bar{i}}\chi_f(S)] \\ &= G_i[\Phi''\chi_f(S)], \end{aligned}$$

where

$$\Phi'' = \zeta_{\sigma if}W_{\bar{j}\bar{i}\sigma}O_{if}\Phi'.$$

Thus Eq. (24) becomes

$$\Psi_{\text{exact}}{}^{S,S} = G_i{}^{\mu}[\Phi''\chi_f(S)]. \tag{26}$$

However, the transformed (23) involves $\Phi''' = O_{if}\Phi_{\mathbf{p},\mathbf{q}}$ which is *not* a simple product of orbitals. We could expand

$$\Phi''' = (1/\Theta)\sum_\tau U_{if\tau}\tau\Phi_{\mathbf{p},\mathbf{q}},$$

simplify this slightly using the special properties of $U_{if\tau}$, and rewrite (23) in terms of $G_i{}^{\mu}$; however, the result is somewhat less convenient than (23). Thus $G_f{}^{\mu}$ does have some special convenience as an operator.

For systems with Hamiltonians that are independent of spin, the spin dependence integrates out of the matrix elements for operators which do not involve spin. Thus since the spin functions $\omega_{ri}\chi_f$ in (26) are linearly dependent, we can use the spatial function $O_{ri}{}^{\mu}\Phi'$ in place of the exact function (26) for all considerations which do not involve spin. For example, we immediately obtain (15) for the expectation value of a spin-independent operator.

## IV. COMPARISON WITH OTHER METHODS

Now that we have shown that $G_i{}^{\mu}\psi$ is an eigenfunction of $\hat{S}^2$ and satisfies Pauli's principle, this method of obtaining wave functions with these two properties will be compared with the Yamanouchi-Kotani[1,2] and Löwdin[4] methods.

Kotani[2] has described a method essentially due to Yamanouchi.[1] By a different approach, Kotani obtains the function $\Phi_{S,M}{}^{(m)}$ which is an eigenfunction of $\hat{S}^2$ and satisfies Pauli's principle. The $\Phi_{S,M}{}^{(m)}$ is defined as

$$\Phi_{S,M}{}^{(m)} = (1/f^S)^{1/2}\sum_k \psi_{S,k}{}^{(m)}\Theta_{S,M;k},$$

where

$$\psi_{S,k}{}^{(m)} = (f/N!)^{1/2}\sum_p \tilde{U}_{km}(p)p\psi^0,$$

$m$ takes on the values $1, 2, \cdots, f_S$, $\psi^0$ is a function of the spatial coordinates of $N$ electrons, $p$ goes through all permutations of $\mathcal{S}_N$, $\Theta_{S,M;k}$ is one of $f_S$ orthonormal spin functions which is an eigenfunction of $\hat{S}^2$ and $\hat{S}_z$ with eigenvalues $S(S+1)$ and $M$, respectively, and the $\Theta$ are obtained by vector coupling the $N$ spins in the $f_S$ different ways given by the branching diagram. The $\Theta$ transform as

$$p\Theta_{S,M;k} = \sum_h V_{hk}(p)\Theta_{S,M;h}$$

so that

$$U_{hk}(p) = \zeta_p V_{kh}(p^{-1})$$

in order that $\Phi_{S,M}$ satisfy Pauli's principle. We must compare the $\Phi_{S,M}{}^{(i)}$ to

$$G_i{}^{\mu}\Phi\chi = \sum_r \zeta_{\sigma ri}(O_{ri}{}^{\mu}\Phi)(\omega_{\bar{r}\bar{i}}{}^{\mu}\chi).$$

Here

$$p\omega_{\bar{r}\bar{i}}{}^{\mu}\chi = \sum_{\beta ks} U_{ksp}{}^{\beta}\omega_{ks}{}^{\beta}\omega_{\bar{r}\bar{i}}{}^{\mu}\chi = \sum_k U_{\bar{k}\bar{r}p}{}^{\mu}\omega_{\bar{k}\bar{i}}{}^{\mu}\chi.$$

We may identify $\omega_{\bar{r}\bar{i}}{}^{\mu}\chi$ with $\Theta_{S,M;r}$ in which case $U_{\bar{k}\bar{r}p}{}^{\mu} = V_{kr}(p)$. Also

$$p\psi_{S,r}{}^{(i)} = \sum_k U_{kr}(p)\psi_{S,k}{}^{(i)}$$

and

$$p(\zeta_{\sigma ri}O_{ri}\Phi) = \sum_k U_{kr}\zeta_{\sigma ri}O_{ki}\Phi = \sum_k \zeta_{\sigma kr}U_{krp}(\zeta_{\sigma ki}O_{ki}\Phi);$$

[9] Even the set of operators $\{G_i{}^{\mu}; i=1, \cdots f^{\mu}\}$ is arbitrary in a sense, since they depend on the $O_{ij}{}^{\mu}$ and $\omega_{ij}{}^{\mu}$ which depend on the specific basis chosen for the $\mu$ irreducible representation of $\mathcal{S}_N$. We could take any unitary transformation on these basis functions of the $\mu$ irreducible representation and obtain an equivalent set of basis functions. However, the new basis functions would lead to a different set of $G_i{}^{\mu}$ which are linear combinations of the previous ones. Actually, though, the set of basis functions we have used correspond to a quite natural way of building up the case for $N$ in an inductive way from the case of $N$-1 [which in the case of tensors transforming as $SU(2)$ corresponds to the natural inductive way of obtaining the spin states for $N$ particles from the spin states $N$-1 particles]. Hence, both mathematically and physically there is something special about the basis we have chosen. In addition, such results as (23) occur only for the particular $f$th basis function we have used; we shall in the future articles see other situations in which the basis we have used possesses a particular prominence.

thus

$$U_{kr}(p)=\zeta_{\sigma_{kr}}U_{krp}.$$

But from Appendix A

$$\zeta_{\sigma_{kr}}U_{krp}=\zeta_pU_{\bar{k}\bar{r}p};$$

hence,

$$U_{kr}(p)=\zeta_pU_{\bar{k}\bar{r}p}=\zeta_pU_{\bar{r}\bar{k}p^{-1}}.$$

Thus, we see that the Yamanouchi-Kotani function and the $G_i^\mu\Phi\chi$ are equivalent. An advantage of the $G_i^\mu$ form is the close relationship to the Young tableaux, permitting a pictorial visualization of the relationship between and the properties of the $G_i^\mu$; however, the $\Theta_{S,M;k}$ can be visualized using the branching diagrams and, indeed, there is a direct relation between the branching diagrams and the standard Young tableaux. The original work on this approach by Yamanouchi[1] actually dealt only with spinless functions and is equivalent to the alternative approach at the end of Sec. III. Some configuration-interaction calculations making use of the Yamanouchi-Kotani method have been reported by Kotani *et al.*[10]

Another method of obtaining $N$-electron wave functions which are eigenfunctions of $\hat{S}^2$ and simultaneously satisfy Pauli's principle is due to Löwdin.[4] Löwdin starts with a Slater determinant and then operates with a projection operator to select the component having a specified total spin. The projection operator is

$$^{2l+1}\mathcal{O}=\prod_{k\neq l}\frac{\hat{S}^2-k(k+1)}{l(l+1)-k(k+1)},$$

where the product is over all $k$ from 0 or $\frac{1}{2}$ to $N/2$ (except $l$) and[11]

$$\hat{S}^2=(\sum_{i=1}^{N}\hat{s}_i^+)(\sum_{j=1}^{N}\hat{s}_j^-)+(\sum_i\hat{s}_{zi})^2-(\sum_i\hat{s}_{zi}).$$

The problem is that the result of operating with $^{2l+1}\mathcal{O}$ on a Slater determinant includes, in general, a sum over very many Slater determinants and the spin integrations are not trivial even in the case where the operators are independent of spin. Thus, the use of this scheme can become quite tedious. Despite this, Löwdin and others have succeeded in deriving many useful expressions and in performing some interesting applications.[12] Of course, Löwdin's projection operator method can be used for cases other than spin; for example, it can be used for the group $SO(3)$ to project out a state of total orbital angular momentum (for an atom) and for Abelian spatial symmetry groups (e.g., the translation group, for crystals) to project out a state belonging to a specific irreducible representation.

Matsen[13] has suggested a different approach of constructing antisymmetrized eigenfunctions of $\hat{S}^2$ through the use of Young's operators. This method has been used for some calculations[13] but is not so appropriate for our purposes. Another approach has been described by Pratt,[14] and McIntosh[12] has given a group-theoretical discussion of antisymmetrized spin-projector operators.

## V. SUMMARY AND DISCUSSION

An operator $G_i^\mu$ has been defined which upon operating on any function of the coordinates of $N$ electrons yields a function which is an eigenfunction of total spin and satisfies Pauli's principle. Some general expansions of exact many-electron wave functions utilizing the $G_i^\mu$ operators were considered. In particular, it was found that the exact wave function, $\Psi_{\text{exact}}^{S,M}$, always can be written as

$$\Psi_{\text{exact}}^{S,M}=G_i^\mu\Phi\chi(M),$$

where $\mu$ corresponds to spin $S$, $i$ can have any integer value from 1 through $f^\mu$, $\chi(M)$ is any product of $N$ one-electron spin functions ($\alpha$ or $\beta$) such that $\hat{S}_z\chi=M\chi$ and such that $\omega_{\bar{r}i}^\mu\chi\neq0$ (there always is at least one such function if $|M|\leqslant S$), and $\Phi$ is a (very complicated) function of the spatial coordinates which depends (in a known way) on the specific choice of $i$ and $\chi(M)$. We may now try to find approximate many-electron wave functions by finding approximate functions $\Phi$. In particular, in Paper II[15] we will restrict $\Phi$ to be a general product of one-electron functions and then require that the best possible one-electron functions be used (i.e., require that the energy be stationary under variations of any of the one-electron functions). We shall find that the resulting wave functions are quite useful and accurate (e.g., they always yield a lower energy than does the Hartree-Fock wave function). Of course, one can take other restrictions on the $\Phi$. For example, we might take $\Phi$ to be a sum of several terms each of which is a product of one-electron functions; with a properly defined sequence of such functions we should be able to obtain arbitrarily accurate wave functions. One might take $\Phi$ to be $\mathcal{O}_s\Phi'$, where $\Phi'$ is a product of one-electron functions and $\mathcal{O}_s$ projects out a function with the proper

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spatial symmetry. Actually, we shall see in later papers that the case where $\Phi$ is a single product of orbitals yields quite good wave functions with extremely interesting properties. For example, in this case, even with the requirement that the $G_i{}^\mu\Phi\chi$ have the proper spatial symmetry, the many-electron wave function $G_i{}^\mu\Phi\chi$ for molecules (and solids) dissociates properly as the nuclei are removed; the individual one-electron functions in $\Phi$ can be given an independent-particle interpretation; and at least for some $i$, the individual orbitals are allowed to localize in such a way as to correspond to present concepts of localized inner-shell states, bonding states, etc.

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## APPENDIX A: THE REPRESENTATION FOR THE ORTHOGONAL UNITS

We wish to construct the elements $U_{ij}{}^\alpha\tau$ of the matrix representing the permutation $\tau$ for the various irreducible representations $\alpha$ of $S_N$.[5] Let each $\alpha$ be associated with a different shape and let each $i$ and $j$ be associated with a standard tableau of the shape $\alpha$ as in Fig. 2. Define the axial distance between two elements, say $p$ and $q$, of a tableau, $i$, as the number of rectilinear jumps form $p$ to $q$ where left and down are positive (e.g., $d_{32}{}^i=+1, -1, -2$, and $+2$ for the tableaux above). We need only determine the matrices for elementary permutations, $\tau_k=(k, k+1)$, since all other matrices can be constructed from these. The diagonal elements are defined as

$$U_{ii(k,k+1)}=1/d_{k+1,k}{}^i,$$

and the off-diagonal elements are zero unless the two tableaux differ only in the positions of the elements $k$ and $k+1$; in this case

$$U_{ij(k,k+1)}=[1-(1/d_{k+1,k}{}^i)^2]^{1/2}.$$

The matrices for $N=3$ are given in Fig. 2.

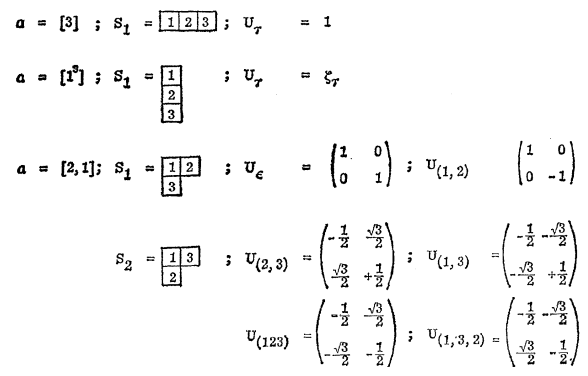


FIG. 2. The orthogonal irreducible representations for $S_3$.

## APPENDIX B: THEOREM

*Theorem.* $U_{\bar r\bar s\tau}{}^\mu=\zeta_\tau\zeta_{\sigma_{rs}}U_{rs\tau}{}^\mu$.

*Proof.* Consider $\tau=(k, k+1)$, then

$$U_{\bar r\bar s(k,k+1)}=[-\delta_{rs}+(1-\delta_{rs})]U_{rs(k,k+1)}$$

from (7). We write this as

$$U_{\bar r\bar s(k,k+1)}=\zeta_{(k,k+1)}\zeta_{\sigma_{rs}}U_{rs(k,k+1)},$$

since $\zeta_{\sigma_{rs}}=-1$ if $r\neq s$ and $U_{rs(k,k+1)}\neq 0$. For any $\tau$

$$U_{\bar r\bar s\tau}=\sum_{il\cdots m}U_{\bar r\bar i\tau_1}U_{\bar i\bar l\tau_2}\cdots U_{\bar m\bar s\tau_p},$$

where $\tau_1, \tau_2, \cdots, \tau_p$ are elementary transpositions. But $\zeta_{\sigma_{ri}}\zeta_{\sigma_{ij}}\cdots\zeta_{\sigma_{ms}}=\zeta_{\sigma_{rs}}$ and $\zeta_{\tau_1}\zeta_{\tau_2}\cdots\zeta_{\tau_p}=\zeta_\tau$; hence, the theorem follows.

## APPENDIX C: TRANSFORMATION OF $G_i{}^\mu\Phi\chi$ TO A CONVENIENT FORM

We wish to transform $G_i{}^\mu\Phi\chi$ to a convenient form. Expand

$$G_i{}^\mu\Phi\chi=\sum_r\zeta_{\sigma_{ri}}(O_{ri}{}^\mu\Phi)(\omega_{\bar r\bar i}{}^\mu\chi)$$
$$=\sum_r\zeta_{\sigma_{ri}}\sum_\tau(1/\Theta^\mu)U_{ri\tau}{}^\mu(\tau\Phi)\sum_t(1/\Theta^\mu)U_{\bar r\bar i t}{}^\mu(t\chi).$$

Letting $t=\tau t'$, we find

$$\sum_t(1/\Theta^\mu)U_{\bar r\bar i t}{}^\mu t\chi=\sum_{t'}(1/\Theta^\mu)\sum_s U_{\bar r\bar s\tau}{}^\mu U_{\bar s\bar i t'}{}^\mu(\tau t'\chi)$$
$$=\sum_s U_{\bar r\bar s\tau}(\tau\omega_{\bar s\bar i}{}^\mu\chi).$$

But $\zeta_{\sigma_{ri}}=\zeta_{\sigma_{rs}}\zeta_{\sigma_{si}}$, $\zeta_{\sigma_{rs}}=\zeta_{\sigma_{\bar r\bar s}}$, and $\zeta_{\sigma_{\bar r\bar s}}U_{\bar r\bar s\tau}{}^\mu=\zeta_\tau U_{rs\tau}{}^\mu$. Hence,

$$G_i{}^\mu\Phi\chi=\sum_{r,s}\sum_\tau\zeta_{\sigma_{si}}\zeta_\tau(1/\Theta^\mu)U_{ri\tau}{}^\mu U_{rs\tau}{}^\mu(\tau\Phi)(\tau\omega_{\bar s\bar i}{}^\mu\chi).$$

But

$$\sum_\tau U_{ri\tau}{}^\mu U_{rs\tau}{}^\mu=\delta_{is};$$

thus,

$$G_i{}^\mu\Phi\chi=\sum_\tau\zeta_\tau(1/\Theta^\mu)\tau[\Phi\omega_{\bar i\bar i}{}^\mu\chi],$$

where $\tau$ now operates on spatial and spin coordinates. Therefore,

$$G_i{}^\mu\Phi\chi=(N!/\Theta^\mu)\Omega_{11}{}^{[1^N]}[\Phi(\omega_{\bar i\bar i}{}^\mu\chi)] \quad (C1)$$
$$=(N!/\Theta^\mu)\Omega_{11}{}^{[1^N]}[(O_{ii}{}^\mu\Phi)\chi]. \quad (C2)$$

## APPENDIX D: DERIVATION OF SOME THEOREMS CONCERNING TRANSFORMATIONS ON TENSOR SPACES

Here we derive some theorems concerning transformations on tensor spaces.

The $d$-dimensional space transformed by the group $G$ (with elements $a$) is called the transformation space. The $d^n$-dimensional vector space spanned by the $n$th-rank tensors $\mathfrak{T}$ is called the tensor space. A component of $\mathfrak{T}$ is denoted by $F_{i_1 i_2 \cdots i_n}$, and the $i_j$ are called indices of the tensor component and are often suppressed.

First it will be necessary to state the definition[5] of the $O_{rq}{}^{\mu}$. It will be convenient to discuss the seminormal units $e_{rq}{}^{\mu}$ rather than the orthogonal units $O_{rq}{}^{\mu}$. Since $e_{rq}{}^{\mu}$ is proportional to $O_{rq}{}^{\mu}$, where the proportionality constant is not zero, then $O_{rq}{}^{\mu}F=0$ if and only if $e_{rq}{}^{\mu}F=0$. Let $\mathfrak{N}_r{}^{\mu}$ be the group of all permutations for which no element of one column of $S_r{}^{\mu}$ is put into a different column. Let $\mathfrak{P}_r{}^{\mu}$ be the group of all permutations for which no element of one row of $S_r{}^{\mu}$ is put into a different row. Let

$$N_r{}^{\mu} \equiv \sum_{\tau \in \mathfrak{N}_r{}^{\mu}} \zeta_{\tau} \tau; \quad P_r{}^{\mu} \equiv \sum_{\tau \in \mathfrak{P}_r{}^{\mu}} \tau.$$

Define $E_{rs}{}^{\mu} \equiv P_r{}^{\mu} \sigma_{rs}{}^{\mu} N_s{}^{\mu}$. Denote as $S^*$ the tableau obtained from $S$ by removing $n$, and denote as $S^{**}=S^{2*}$ the tableau obtained from $S^*$ by removing $n-1$, etc. Let $e^{(n-1)*}=\epsilon$,

$$\begin{aligned} e_{rs}{}^{(n-2)*} &= \frac{1}{\Theta^{(n-2)*}} e_{rr}{}^{(n-1)*} E_{rs}{}^{(n-2)*} e_{ss}{}^{(n-1)*} \\ &\vdots \\ e_{rs}{}^{j*} &= \frac{1}{\Theta^{j*}} e_{rr}{}^{(j+1)*} E_{rs}{}^{j*} e_{ss}{}^{(j+1)*} \\ &\vdots \\ e_{rs} &= \frac{1}{\Theta} e_{rr}{}^{*} E_{rs} e_{ss}{}^{*}. \end{aligned}$$

*Theorem D1.* If for a given $F$ it is not possible to arrange the first $m$ indices of $F$ to obtain $F'$ such that when $F'$ is placed in $S_r{}^{\mu}$ to yield[16] $S_r{}^{\mu}(F')$, no two identical indices among the first $m+1$ indices of $F'$ occur in the same column of $S_r{}^{\mu}(F')$, then $O_{sr}F=0$ for all $s$.

*Proof.* Let $e_{sr}{}^{j*}$ operate on $F$. But, $E_{sr}{}^{j*}=P_s{}^{j*}\sigma_{sr}N_r{}^{j*}$ and $N_r{}^{j*}$ antisymmetrizes each column of $S_r{}^{j*}$; so, if $E_{sr}{}^{j*}$ operates on $F'$ and if two identical indices of the first $n-j$ indices of $F'$ are in the same column of $S_r{}^{j*}$, then $N_r{}^{j*}F'=0$. Now, $e_{rr}{}^{(j+1)*}F$ rearranges the first $n-j-1$ indices of $F$; so, if there is no way to rearrange the first $(n-j-1)$ indices of $F$ such that the first $n-j$ indices of $F'$ have all identical indices in different columns of $S_r{}^{j*}$, then $e_{sr}{}^{j*}F=0$ (for all $s$) and, thus, $e_{sr}F=0$ (for all $s$).

In particular, if the first $M$ indices of $F$ are the same then $e_{sr}F \neq 0$ only for $r$ with the first $M$ indices in the first row. Another corollary which follows immediately is: If $S_r{}^{\mu}$ has more rows than $F$ has different indices, then $O_{sr}{}^{\mu}F=0$. In particular, for an $n$-dimensional transformation space, if $\mu$ has more than $n$ rows, then $O_{sr}{}^{\mu}F=0$ for all possible $F$.

We want to be able to select a linearly independent set of $O_{rp}F_{ijk\ldots}$; the following theorem provides a method of accomplishing this.

*Theorem D2.* If $F$ is written with all identical indices adjacent, then:

(i) If the arrays $S_p(F)$ and $S_q(F)$ are identical, $O_{rp}F$ = constant (independent of $r$)$\times O_{rq}F$; (ii) if the array $S_p(F)$ has identical elements in the same column, then $O_{rp}F=0$.

*Proof.* (i) If $S_p(F)=S_q(F)$ and if $\sigma_{pq}$ is an elementary transposition, say, $(k, k+1)$, then

$$\begin{aligned} O_{rp}{}^{\mu}F &= O_{rp}{}^{\mu}(k, k+1)F \\ &= \sum_{\beta st} U_{st(k,\,k+1)}{}^{\beta} O_{rp}{}^{\mu} O_{st}{}^{\beta} F = \sum_{t} U_{pt(k,k+1)}{}^{\mu} O_{rt}{}^{\mu} F. \end{aligned}$$

But $U_{pt(k,k+1)}=0$ unless $t=p$ or $t=q$, since $\sigma_{pq}=(k, k+1)$ is an elementary transposition. Thus,

$$O_{rp}F = U_{pp(k,k+1)} O_{rp}F + U_{pq(k,k+1)} O_{rq}F.$$

But $U_{pp(k,k+1)} \neq 1$, since, if it were, then $k$ and $k+1$ would be in the same row of $S_p$, in which case $S_q=(k, k+1)S_p$ would not be a standard tableau. Thus, $O_{rp}F=$ constant $O_{rq}F$ if $\sigma_{iq}$ is an elementary transposition.

Now consider $S_F=\{e,\pi_2,\cdots,\pi_F\}$, the group of permutations which leaves $F$ invariant. If $S_p(F)$ is some array, then the arrays in $A_p=\{S_p(F),\pi_2 S_p(F),\cdots,\pi_F S_p(F)\}$ are all equal. Since the identical elements of $F$ are adjacent, the generators of $S_F$ are elementary transpositions; thus the previous proof allows us to conclude that $O_{rq}F=$ constant $O_{rq'}F$ for all $S_q$, $S_{q'} \in A_p$.

(ii) If $S_p$ has a pair of *adjacent* letters in the same column, say $k$ and $k+1$, and if the $k$th and $(k+1)$th indices of $F$ are identical, then

$$O_{rp}F = O_{rp}(k, k+1)F = \sum_{t} U_{pt(k,\,k+1)} O_{rt}F.$$

But, $U_{pt(k,k+1)}=-\delta_{pt}$. Thus, $O_{rp}F=-O_{rp}F$, and hence, $O_{rp}F=0$. If $S_p(F)$ has identical indices in the same column, but these positions in $S_p$ are not occupied by *adjacent* letters, then among the set of identical arrays there is an $S_q(F)$ with adjacent letters in these positions. Thus, using part (i) and the first part of (ii), we obtain $O_{rp}F=0$.

## APPENDIX E: SUMMARY

Denote as $\tau_a$ any permutation of the letters less than $n+1$ and as $\tau_b$ any permutation of the letters greater than $n$. Let $\tau_r$ be a product of $r$ disjoint transpositions where each transposition involves one letter of the $a$ set and one letter of the $b$ set. Then any permutation, $\tau$, can be written as $\tau=\tau_a\tau_b\tau_r$ for some $\tau_r$, $\tau_a$, and $\tau_b$.

[16] It is convenient in discussing such theorems to place the indices of $F$ in the tableau (say $S_p{}^{\mu}$) in place of the numbers $1\cdots N$; such an array we call an *array* and denote by $S_p{}^{\mu}(F)$.

We will consider $S_1^{[n,m]}$ as in Fig. 3(a) and show that

$$U_{11\tau}{}^{\alpha}=U_{11\tau_r}{}^{\alpha}=(-1)^r\Big/\binom{n}{r}. \tag{E1}$$

In addition we consider $S_f^{[2^m,1^{n-m}]}$ as in Fig. 3(b) and show that

$$U_{ff\tau}{}^{\beta}=\zeta_{\tau_a}\zeta_{\tau_b}U_{ff\tau_r}{}^{\beta}=\zeta_{\tau_a}\zeta_{\tau_b}\Big/\binom{n}{r}. \tag{E2}$$

*Evaluation of* $U_{11}{}^{\alpha}$: We have $U_{1i\sigma_a}{}^{\alpha}=\delta_{1i}$ and $U_{1i\sigma_b}{}^{\alpha}=\delta_{1i}$, where $\sigma$ is an elementary transposition, since the letters are adjacent and in the same row; hence, $U_{1i\tau_a}{}^{\alpha}=\delta_{1i}$ since $\tau_a$ can be constructed from the $\sigma_a$; similarly $U_{1i\tau_b}{}^{\alpha}=\delta_{1i}$. We may consider just $U_{11\tau_r}$ since $U_{11\tau}=U_{11\tau_a\tau_b\tau_r}=U_{11\tau_r}$. Since $\tau_a\tau_b\tau_r\tau_b^{-1}\tau_a^{-1}=\tau_r'$, then $U_{11\tau'_r}=U_{11\tau_a\tau_b\tau_r\tau_b^{-1}\tau_a^{-1}}=U_{11\tau_r}$, and we need only find the $m$ different elements $U_{11\tau_r}$ corresponding to $r=1, \cdots, m$. From the orthogonality theorem for unitary irreducible representations (e.g., Ref. 6, p. 102),

$$\sum_{\tau} U_{ij\tau}{}^{\alpha}U_{pq\tau}{}^{\beta}=\delta^{\alpha\beta}\delta_{ip}\delta_{jq}(N!/f^{\alpha})=\delta^{\alpha\beta}\delta_{ip}\delta_{jq}\Theta^{\alpha}. \tag{E3}$$

In particular let $\alpha=[n,m]$ and $\beta=[N]$. Since $U_{11\tau}{}^{[N]}=1$, then

$$0=\sum_{\tau} U_{11\tau}{}^{\alpha}=\sum_{\tau_a,\tau_b}\sum_{\tau_r} U_{11\tau_r}{}^{\alpha}$$

$$=n!m!\sum_{r=0}^{m}\binom{m}{r}\binom{n}{r}U_{11\tau_r}{}^{\alpha} \tag{E4}$$

$\left[\text{there are } \binom{m}{r}\binom{n}{r} \text{ different } \tau_r \text{ for a given } r\right]$. Since $U_{11\tau_r}{}^{\alpha}$ is the same for any $\tau$ with the same $r$, then $U_{11\tau_r}{}^{\alpha}$ is the same for all $\alpha$ with $m\geqslant r$ (since we can consider $\tau_r$ to just involve elements $\leqslant n+r$). Therefore, take $m=1$ in (E4):

$$0=1+\binom{n}{1}U_{11\tau_1}{}^{\alpha};$$

hence,

$$U_{11\tau_1}{}^{\alpha}=-1\Big/\binom{n}{1}.$$

We want to prove that

$$U_{11\tau_s}{}^{\alpha}=(-1)^r\Big/\binom{n}{s};$$

therefore, consider $m=s$ in (E4) and assume (E1) is true for $m\leqslant s-1$:

$$0=\sum_{r=0}^{s-1}\binom{s}{r}\binom{n}{r}U_{11\tau_r}{}^{\alpha}+\binom{n}{s}U_{11\tau_s}{}^{\alpha};$$

(a) $S_1^{[n,m]}$ =

| | | | |
|---|---|---|---|
| 1 | 2 | · · · | n |
| n+1 | n+2 | ... | N |

(b) $S^{[2^m,1^{n-m}]}$ =

| | |
|---|---|
| 1 | n+1 |
| 2 | n+2 |
| ⋮ | ⋮ |
| n | N |

FIG. 3. The tableaux used in Appendix E.

hence

$$-\binom{n}{s}U_{11\tau_s}{}^{\alpha}=\sum_{r=0}^{s-1}(-1)^r\binom{s}{r}.$$

Now consider

$$(1-x)^s=\sum_{r=0}^{s}(-1)^s\binom{s}{r}x^s$$

and let $x=1$; then

$$\sum_{r=0}^{s-1}(-1)^s\binom{s}{r}+(-1)^s=0.$$

Hence

$$U_{11\tau_s}{}^{\alpha}=(-1)^s\Big/\binom{n}{s}.$$

*Evaluation of* $U_{ff\tau}{}^{\beta}$: For any elementary transposition of the elements less than $n+1$ (the $a$ set), $U_{fi\sigma_a}{}^{\beta}=-\delta_{fi}$. Thus $U_{fi\tau_a}{}^{\beta}=\zeta_{\tau_a}\delta_{fi}$ and $U_{fi\tau_b}{}^{\beta}=\zeta_{\tau_b}\delta_{fi}$. Hence, if

$$\tau=\tau_a\tau_b\tau_r, \quad \text{then} \quad U_{ff\tau}{}^{\beta}=\zeta_{\tau_a}\zeta_{\tau_b}U_{ff\tau_r}.$$

We can now proceed to derive $U_{ff\tau_r}{}^{\beta}$ for $\beta=[2^m,1^{n-m}]$ just as we did for $\alpha=[n,m]$, except that now we consider the orthogonality relation

$$\sum_{\tau} U_{11\tau}{}^{[1^N]}U_{ff\tau}{}^{\beta}=0,$$

where

$$U_{11\tau}{}^{[1^N]}=\zeta_{\tau}=\zeta_{\tau_a}\zeta_{\tau_b}\zeta_{\tau_r}.$$

Hence, we obtain

$$0=\sum_{r=0}^{m}\binom{m}{r}\binom{n}{r}\zeta_{\tau_r}U_{ff\tau_r}{}^{\beta}$$

which we now know to have the solution

$$U_{ff\tau_r}{}^{\beta}=\zeta_{\tau_r}(-1)^r\Big/\binom{n}{r}=1\Big/\binom{n}{r}.$$