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Gordon A. Gallup
UNL, ggallup1@unl.edu

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Projected Hartree Product Wavefunctions. II. General Considerations of Young Operators*

G. A. GALLUP†

Quantum Theory Project, University of Florida, Gainesville, Florida 32601

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A discussion is given of the forms of two specific and one general Young operator for the irreducible representations of S_n important for fermion space functions. Comparisons are made of the projected Hartree product version of Löwdin's projected Hartree-Fock method with CI calculations.

I. INTRODUCTION

Although the connections between the symmetric groups and antisymmetric eigenfunctions of the total spin have been known many years,¹⁻⁵ it is only in recent times that investigations using these methods have been applied to spin-free problems^{6,7} and computation of matrix elements.⁵ In a previous article⁸ hereafter called I, the author has given a discussion of the use of Young operators in a spin-free version of the projected Hartree-Fock problem.⁹ Goddard has recently given a discussion of this problem using methods of the symmetric groups,¹⁰ and Poshusta and Kramling¹¹ have given a discussion based on the concept of immanents.¹²

The interest in the independent-particle model arises from the feeling that wavefunctions constructed from single-particle orbitals will be of the simplest type as far as physical interpretations are concerned. In spite of the differences in the details of the computations, all independent-particle model wavefunctions consist of what is essentially a projected Hartree product of spatial orbitals. In I it was shown that use of just one Young operator from the symmetric group S_n can guarantee that the function represent a state of pure

multiplicity for a system of n electrons, and these functions can be used to compute matrix elements of spin-free operators. A self-consistent field computation based on these Young operators was also discussed with some applications to simple systems.

In this article we give some detailed properties of the Young operators needed for calculations of the type given in I and indeed for any computations of matrix elements of spin-free operators with respect to antisymmetric eigenfunctions of the spin. We also discuss the relationship among some of the methods for writing antisymmetric eigenfunctions of the spin, some comparisons of projected Hartree product wavefunctions and CI computations, and the some effects of assumed orthogonality between various spatial orbitals.

II. SPECIFIC YOUNG OPERATORS

In this section we shall examine two specific forms for a Young operator corresponding to the irreducible representations of the symmetric group for eigenfunctions of the total spin angular momentum. We are interested, of course, in the idempotents appropriate for the spatial part of the wavefunction but we may analyze either the two-row tableaux (partitions) or the two-column tableaux, since these cases are merely conjugate. We shall choose as the basis for this article the tableaux corresponding to $(2^{(n/2)-S}, 1^{2S})$, for spatial functions appropriate to the spin quantum number S .

Littlewood¹² shows that the idempotents P and N each have an intersection of rank 1 with the $(2^{n/2-S}, 1^{2S})$ subalgebra and no other parts in common. Hence PNP and NPN are each proportional to a Hermitian primitive characteristic unit of $(2^{(n/2)-S}, 1^{2S})$ as was pointed out in I. It was also shown in I that a primitive characteristic unit can be factored, and we wish to calculate the factored form of θNPN and $\theta' PNP$,

$$e^{(\omega)} = \frac{f(\omega)}{|G|} E \sum_{i=1}^k a(X_i) X_i. \quad (1)$$

We will call the subgroup with elements in E the base subgroup and denote it by G_B . From Eq. (1) we obtain immediately

$$\sum_{i=1}^k |a(X_i)|^2 = \frac{|G|}{|G_B| f(\omega)}. \quad (2)$$

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† On leave during academic year 1967-1968 from Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68508.

¹ H. Weyl, *Theory of Groups and Quantum Mechanics* (Dover Publications, Inc., New York, 1928).

² E. P. Wigner, *Group Theory* (Academic Press Inc., New York, 1959).

³ R. Serber, *Phys. Rev.* **45**, 461 (1934).

⁴ T. Yamanouchi, *Proc. Phys.-Math. Soc. Japan* **20**, 547 (1938).

⁵ M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, *Table of Molecular Integrals* (Maruzen, Tokyo, 1955).

⁶ F. A. Matsen, in *Advances in Quantum Chemistry* (Academic Press Inc. New York 1964), Vol. 1; *J. Phys. Chem.* **68**, 3282 (1964); **70**, 1568 (1966).

⁷ F. A. Matsen, A. A. Cantu, and R. D. Poshusta, *J. Phys. Chem.* **70**, 1558 (1966).

⁸ G. A. Gallup, *J. Chem. Phys.* **48**, 1752 (1968).

⁹ P.-O. Löwdin, *Phys. Rev.* **97**, 1509 (1955), see also, article in *Quantum Theory of Atoms Molecules and the Solid State*, P.-O. Löwdin, Ed. (Academic Press Inc., New York, 1966), p. 601.

¹⁰ W. A. Goddard, *Phys. Rev.* **157**, 73, 81, 93 (1967), *J. Chem. Phys.* **48**, 450, 1008 (1968).

¹¹ R. D. Poshusta and R. W. Kramling, *Phys. Rev.* **167**, 139 (1968).

¹² D. E. Littlewood, *Theory of Group Characters* (Oxford University Press, London, 1950), 2nd ed.

We may also make the general statement that the necessary and sufficient condition that an element of G be in G_B is that it commutes with $e^{(\omega)}$. We take up the computation of θNPN first since it is a little simpler.

The factorization of a characteristic unit as in Eq. (1) is very important, since it provides easy access of some other results as we shall see later.

The coefficients of the permutations in the operators NPN and PNP are very important for the computation of matrix elements and also for the determination of the general idempotent discussed in Sec. IV. Matsen⁶ has also discussed the operators NPN and PNP from a somewhat different point of view.

A. The Operator θNPN

For purposes of discussion we assume we have a tableau for $(2^{n/2-S}, 1^{2S})$ with numbers inserted as shown in Fig. 1.¹³ It is evident that all elements of N commute with NPN and are part of G_B . If $S \neq 0$ then no other element of S_n commutes with NPN and $G_N = G_B$. When $S = 0$, n is an even integer, and one element from P will commute with NPN . This element is $(1, n/2+1)(2, (n/2+2) \cdots (n/2, n))$ which we may denote p and $G_B = \{G_N, pG_N\}$. Thus we obtain

$$|G_B| = [(n/2) + S]! [(n/2) - S]!; \quad S \neq 0,$$

$$= 2[(n/2)!]^2; \quad S = 0,$$

and Eq. (2) becomes

$$\sum_{i=1}^k |a(X_i)|^2 = \frac{n+2S+2}{4S+2}; \quad S \neq 0$$

$$= (n+2)/4; \quad S = 0, \quad (3)$$

where

$$k = \binom{n}{(n/2) + S}$$

or

$$\frac{1}{2} \binom{n}{n/2}.$$

If N and P are each normalized so that the coefficient of I in each is 1, then

$$\theta = f^{(\omega)} / |G| |G_N|$$

and $a(X_i)$ is the number of times X_i appears in the

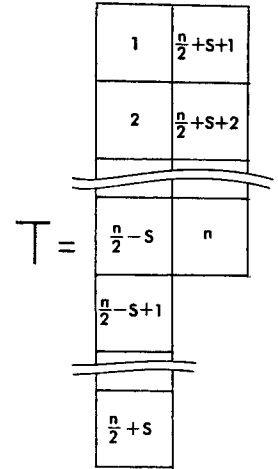


FIG. 1. Numbering for the general tableau T .

product NPN divided by $|G_N|$ with the appropriate sign affixed.

Consider an element of the class $(1^{n-2l}, 2^l)$ of S_n with $l \leq (n/2) - S$. Such a permutation may have each interchange (e, f) such that e is from the first column and f is from the second column of the tableau T . We shall see that a complete set of right coset generators may be obtained from the type of permutation under consideration. For definiteness let $i_1, i_2, i_3, \dots, i_l = (i)$ be a set of l different entries from the first column of T , such that $i_1 < i_2 < \dots < i_l$. Let $j_1, j_2, \dots, j_l = (j)$ be a set from the second column similarly ordered. These $2l$ numbers determine a permutation from the class $(1^{n-2l}, 2^l)$,

$$[(i)(j)] = (i_1 j_1)(i_2 j_2) \cdots (i_l j_l). \quad (4)$$

It is easily seen that $[(i)(j)]$ appears

$$l! [(n/2) + S - l]! [(n/2) - S]!$$

times in NPN , hence

$$a([(i)(j)]) = \binom{(n/2) + S}{l}^{-1}. \quad (5)$$

This result is true regardless of the value of S . There are in all $l!$ permutations of $(1^{n-2l}, 2^l)$ connecting the set (i) with the set (j) . However, it may be shown that these all are in the same coset, hence the specific permutation defined by Eq. (4) is the only one needed. We may put these results together and obtain

$$e^{(\omega)} = \frac{2S+1}{(n+1)!} \binom{n+1}{(n/2) - S} N \left\{ I + \sum_{i=1}^{(n/2)-S} \sum_{(i)} \sum_{(j)} \binom{(n/2) + S}{l}^{-1} [(i)(j)] \right\}; \quad S \neq 0,$$

$$= [(n+1)!]^{-1} \binom{n+1}{n/2} N \{ I + p \} \left\{ I + \sum_{i=1}^k \sum_{(i)} \sum_{(j)} \binom{(n/2)}{l}^{-1} [(i)(j)] \right\}; \quad S = 0, \quad (6)$$

¹³ D. E. Rutherford, *Substitutional Analysis* (Edinburgh University Press, London, 1948).

1	7
2	8
3	9
4	10
5	
6	

FIG. 2. Tableau for the triplet case of ten electrons.

where k is $n/4$ or $(n-2)/4$, whichever is integral. It is not difficult to see that we have found all the coset generators and that Eq. (2) is satisfied.

As we shall see later θNPN is a rather special form for $e^{(\omega)}$.

B. The Operator $\theta'PNP$

In this case it is seen that G_B contains all elements of P , but it also contains all elements of N which commute with P . Considering the same tableau T as before, all permutations of the numbers $(n/2) - S + 1, (n/2) - S + 2, \dots, (n/2) + S$ do not involve any numbers in the elements of P , hence these are part of G_B . There are $(2S)!$ such permutations. The other permutations of N which are in G_B are products of the same permutation of $1, 2, \dots, (n/2) - S$ and $(n/2) + S + 1, (n/2) + S + 2, \dots, n$. Thus in this case we have

$$|G_B| = 2^{(n/2)-S} [(n/2) - S]! (2S)!$$

The coset generators are somewhat more difficult to characterize in this case although we still need only elements from the class $(1^{n-2l}, 2^l)$ for the singlet case. To make the description simpler we define a few terms: Let us call the first $(n/2) - S$ rows of T the *body* and the other part the *tail*. We shall call an element of $(1^{n-2l}, 2^l)$ a *simple chain* if it may be written $(i_1 j_1) (i_2 j_2) \dots (i_l j_l)$ and each of the pairs of numbers $j_1, i_2; j_2, i_3; \dots; j_{l-1}, i_l$ is taken from the same row of the body. For example in the tableau in Fig. 2, (72)(89)(35) and (91)(72)(84)(10, 6) are simple chains. If i_l and j_l are also in the same row we have a loop. It is evident that a loop can contain no entries

TABLE I. Right coset generators and coefficients for two-column partitions of S_4 .^a

(2 1 ²)		(2 ²)	
X	$a(X)$	X	$a(X)$
I	1	I	1
(12)	$-\frac{1}{2}$	(12)	$-\frac{1}{2}$
(13)	$-\frac{1}{2}$	(14)	$-\frac{1}{2}$
(24)	$-\frac{1}{2}$		
(34)	$-\frac{1}{2}$		
(12)(34)	0		

^a These results are based on the numbering of Fig. 1.

from the tail and a simple chain can contain no more than two entries from the tail. A *composite chain* is made up of two or more disconnected simple chains. We shall consider only the singlet case ($S=0$) here.

We use the normalization of P and N as before and again $a(X_i)$ is the number of times X_i appears in PNP divided by $2^{(n/2)-S}$ with the appropriate sign. It is not too difficult to see that for $S=0$, any composite or simple chain in the class $(1^{n-2l}, 2^l)$ has a coefficient $(-2)^{-l}$. If a composite chain K_l is made up of simple chains of lengths l_1, \dots, l_i , we denote it $K_l(l_1 l_2 \dots l_i)$; $l_1 + l_2 + \dots + l_i = l$. In each coset there

TABLE II. Right coset generators and coefficients for two-column partitions of S_6 .^a

(2 1 ³)		(2 ² 1)	
X	$a(X)$	X	$a(X)$
I	1	I	1
(12)	$-\frac{1}{2}$	(12)	$-\frac{1}{2}$
(13)	$-\frac{1}{2}$	(15)	$-\frac{1}{2}$
(14)	$-\frac{1}{2}$	(13)	$-\frac{1}{2}$
(25)	$-\frac{1}{2}$	(23)	$-\frac{1}{2}$
(35)	$-\frac{1}{2}$	(34)	$-\frac{1}{2}$
(45)	$-\frac{1}{2}$	(35)	$-\frac{1}{2}$
(12)(35)	0	(12)(34)	$\frac{1}{2}$
(12)(45)	0	(12)(35)	$\frac{1}{2}$
(13)(45)	0	(13)(45)	$\frac{1}{2}$
		(23)(45)	$\frac{1}{2}$
		(15)(23)	$\frac{1}{2}$
		(15)(34)	$\frac{1}{2}$
		(13)(24)	$\frac{1}{2}$
		(24)(35)	$\frac{1}{2}$

^a These results are based on the numbering of Fig. 1.

are $(l_1+1)(l_2+1)\dots(l_i+1)$ such chains. We obtain for $S=0$

$$e^{(\omega)} = [(n+1)!]^{-1} \binom{n+1}{n/2} G_B \times \{I + \sum_{l=1}^{(n/2)-1} [(-1)^l / 2^l] \sum_{l_1 \dots l_i} K_l(l_1 \dots l_i)\}, \quad (7)$$

where the \sum' indicates the sum is over only the chains generating distinct cosets. Tables I-III give the coefficients and right coset generators of $\theta'PNP$ for two column partitions of S_4, S_6 , and S_8 .

III. THE PROJECTED SLATER DETERMINANT

The primitive characteristic unit in the form θNPN has a rather special form which is connected with the

TABLE III. Right coset generators and coefficients for two-column partitions of S_6 .^a

(2 1 ⁴)		(2 ² 1 ²)		(2 ³)	
X	a(X)	X	a(X)	X	a(X)
I	1	I	1	I	1
(12)	-1/2	(13)	-1/2	(12)	-1/2
(13)	-1/2	(14)	-1/2	(13)	-1/2
(14)	-1/2	(23)	-1/2	(23)	-1/2
(15)	-1/2	(24)	-1/2	(15)	-1/2
(26)	-1/2	(35)	-1/2	(26)	-1/2
(36)	-1/2	(45)	-1/2	(34)	-1/2
(46)	-1/2	(36)	-1/2	(12) (46)	-1/2
(56)	-1/2	(46)	-1/2	(12) (34)	-1/2
(12) (36)	0	(12)	-1/2	(15) (46)	-1/2
(12) (46)	0	(16)	-1/2	(16) (24)	-1/2
(12) (56)	0	(12) (35)	-1/2	(13) (45)	-1/2
(13) (46)	0	(12) (45)	-1/2	(16) (45)	-1/2
(13) (56)	0	(12) (36)	-1/2	(13) (24)	-1/2
(14) (56)	0	(12) (46)	-1/2	(15) (34)	-1/2
		(16) (23)	-1/2		
		(16) (24)	-1/2		
		(16) (35)	-1/2		
		(16) (45)	-1/2		
		(25) (13)	-1/2		
		(25) (14)	-1/2		
		(25) (36)	-1/2		
		(25) (46)	-1/2		
		(56) (13)	-1/2		
		(56) (14)	-1/2		
		(56) (23)	-1/2		
		(56) (24)	-1/2		
		(13) (46)	-1/2		
		(14) (36)	-1/2		
		(23) (45)	-1/2		
		(24) (35)	-1/2		
		(13) (24)	-1/2		
		(14) (23)	-1/2		
		(35) (46)	-1/2		
		(36) (45)	-1/2		
		(13) (45)	0		
		(13) (245)	0		
		(13) (456)	0		
		(123) (45)	0		
		(163) (45)	0		
		(23) (46)	0		
		(23) (146)	0		
		(23) (465)	0		
		(132) (46)	0		
		(253) (46)	0		

^a These results are based on the numbering of Fig. 1.

irreducible representations of S_n obtained from the spin basis functions produced by any spin projection operators which commutes with all permutations. Let us assume that we have a product spin function

$$\psi(n, S) = \alpha(1)\alpha(2)\cdots\alpha[(n/2)+S] \times \beta[(n/2)+S+1]\cdots\beta(n).$$

If we have a projection operator Θ_S which satisfies $[\Theta_S, \pi]=0$ for every permutation of S_n we may construct a spin function for the principle case $M=S$ ¹⁴

$$\varphi_1(S, S) = C\Theta_S\psi(n, S). \tag{8}$$

We label the function defined by Eq. (8) 1. It is well

known that

$$\frac{2S+1}{n+1} \binom{n+1}{(n/2)-S} - 1$$

other spin functions may be constructed orthogonal to $\varphi_1(S, S)$ and to each other, $\varphi_2(S, S), \dots, \varphi_f(S, S)$. We assume that the functions are all normalized. The f functions form a basis for an irreducible representation of S_n ;

$$\pi\varphi_i(S, S) = \sum_j D^{(S)}(\pi)_{ij}\varphi_j(S, S),$$

and we want to obtain

$$e_{11}^{(S)} = (f/g) \sum_{\pi} D^{(S)}(\pi)_{11}\pi, \tag{9}$$

¹⁴ P.-O. Löwdin, Rev. Mod. Phys. **36**, 966 (1964).

where

$$D^{(S)}(\pi)_{11} = \langle \varphi_1(S, S) | \pi | \varphi_1(S, S) \rangle.$$

The product function $\psi(n, S)$ determines a two-row tableau which may be taken as the conjugate of T, \bar{T} . We see that the elements of P of \bar{T} are such that $\pi_P \psi(n, S) = \psi(n, S)$ and hence $D^{(S)}(\pi_P)_{11} = 1$, and G_B for $e_{11}^{(S)}$ is at least P of \bar{T} . But this is sufficient to prove that $e_{11}^{(S)} = \theta PNP$ for \bar{T} . Taking the conjugate we obtain exactly

$$e^{(\mu)} = e_{11}^{(S)} = \theta NPN$$

or Eq. (1). For this reason use of the projector θNPN for T is equivalent to using a spin projection operator on a single Slater determinant with $M = S$. McIntosh¹⁵ has obtained an essentially equivalent result by a different method. The operator $\theta'PNP$ gives no such simple result, of course. It may be observed also that $\theta'PNP$ and θNPN correspond to Goddard's $G1$ and GF methods, respectively.¹⁰

The operator θNPN is interesting in another light, since the result of its application to a product of spatial functions is closely connected with a form of determinantal wavefunction originated by Hartree¹⁶ and used by Wigner.¹⁷ The function

$$\Psi = Nu_1(1)u_2(2) \cdots u_n(n)$$

is just Hartree's double determinantal function and it is interesting that the further application of P gives a function appropriate for a given spin.

IV. A GENERAL CHARACTERISTIC UNIT

In I it was mentioned that the most general function of the correct symmetry that can be obtained from a single product function is

$$\Psi = e^{(\mu)} \sum_i \gamma_i X_i | (\lambda) \rangle, \quad (10)$$

where X_i are certain selected permutations from the right coset generators of the G_B for $e^{(\mu)}$. There are a number of ways the X_i in Eq. (10) may be chosen but one of the simplest is by considering the various standard tableaux [with or without repeated elements, depending on (λ)] and the permutation changing T into the others. We may assume without loss of generality that if $(\lambda) \neq (\mu)$ the repeated functions are in the first rows of T , then we have $k = t_{(\mu)}^{(\lambda)}$ standard tableaux $T_1 (= T), T_2, \dots, T_k$ and the permutations σ_{ij} such that

$$T_1 \sigma_{1j} = \sigma_{1j} T_j.$$

If the tableaux are ordered in the standard fashion (12), the relation

$$\theta NPN \sum_{j=1}^k \gamma_j \sigma_{1j} = 0 \quad (11)$$

implies $\gamma_j = 0$. This result is shown in Appendix C. Similar considerations apply to $\theta'PNP$. We may construct an equivalence relation between the σ_{1j} and certain of the right coset generators, since σ_{1j} is in some coset of G_B and

$$G_B \sigma_{1j} = \epsilon G_B X_k; \quad | \epsilon | = 1,$$

and it is evident that the X_k may be used in Eq. (11) in place of the σ_{1j} .

The primitive characteristic unit $e^{(\mu)}$ has a rank 1. This implies that any element of the algebra of the form

$$y = e^{(\mu)} \sum_{j=1}^{f(\mu)} \gamma_j X_j,$$

is essentially idempotent, i.e.,

$$y^2 = \lambda y,$$

in which $y \neq y^\dagger$, in general. We may construct a form for the most general Hermitian, primitive, characteristic unit as $y^\dagger y / S(\gamma)$, where $f_{(\mu)} S(\gamma) / |G|$ is the coefficient of the identity in

$$\sum_{j=1}^{f(\mu)} \sum_{k=1}^{f(\mu)} \gamma_j^* \gamma_k X_j^\dagger e^{(\mu)} X_k.$$

$S(\gamma)$ can be written in matrix notation as

$$S(\gamma) = \boldsymbol{\gamma}^\dagger \mathbf{S} \boldsymbol{\gamma},$$

and it is easily shown that \mathbf{S} is a positive definite matrix since the $e^{(\mu)} X_j$ are linearly independent. We shall denote $y^\dagger y / S(\gamma)$ as $E^{(\mu)}(\gamma)$, and examine more closely its form. In general,

$$E^{(\mu)}(\gamma) = (f_{(\mu)} / |G|) \sum_{\pi} P(\gamma, \pi) \pi, \quad (12)$$

where $P(\gamma, \pi)$ is a rational expression involving polynomials in $\boldsymbol{\gamma}$ in the numerator and $S(\gamma)$ in the denominator. If we return to the our original idempotent $e^{(\mu)}$,

$$e^{(\mu)} = (f_{(\mu)} / |G|) \sum_{\pi} a(\pi) \pi,$$

TABLE IV. $P(\gamma, \pi)$ coefficients for general idempotent for (2, 1) of S_3 .

π	$P(\gamma, \pi)$
I	1
(12)	$(-\gamma_1^2 - \gamma_1 \gamma_2 + \frac{1}{2} \gamma_2^2) / S(\gamma)$
(13)	$(\frac{1}{2} \gamma_1^2 + 2 \gamma_1 \gamma_2 + \frac{1}{2} \gamma_2^2) / S(\gamma)$
(23)	$(\frac{1}{2} \gamma_1^2 - \gamma_1 \gamma_2 - \gamma_2^2) / S(\gamma)$
(123)	$-\frac{1}{2}$
(132)	$-\frac{1}{2}$
	$S(\gamma) = \gamma_1^2 + \gamma_1 \gamma_2 + \gamma_2^2$

¹⁵ H. V. McIntosh, J. Math. Phys. 1, 453 (1960).

¹⁶ D. R. Hartree, Proc. Cambridge Phil. Soc. 24, 89 (1928).

¹⁷ E. P. Wigner, Phys. Rev. 46, 1002 (1934).

we may write $P(\gamma, \pi)$ in terms of the a 's as

$$P(\gamma, \pi) = \left[\sum_{j,k} \gamma_j^* \gamma_k a(X_k^{-1} \pi^{-1} X_j) \right] / \sum_{j,k} \gamma_j^* \gamma_k a(X_k^{-1} X_j). \quad (13)$$

Table IV give an example of $E^{(\omega)}(\gamma)$ for the (2, 1) representation of S_3 . Appendix A gives a method for evaluating $a(\pi)$ for θNPN . Equation (13) is more general than our purposes require, since we have chosen our coset generators from the class $(1^{n-2i}, 2^i)$. Thus, these elements are involuntary, and the inverses are unnecessary.

It is evident from the foregoing that the four common ways in which the spin-degeneracy problem may be handled are completely equivalent. For purposes of illustration let us assume we have a set of n one-electron, spatial orbitals. As was shown by Löwdin¹⁴ the Slater determinantal functions constructed from these orbitals and the spin functions and corresponding to points in the upper half of a "path diagram" yield linearly independent functions after being subjected to a spin projection operator. Thus, if the determinants are denoted D_1, D_2, \dots, D_k ,

$$\Theta_S \sum_{i=1}^k \gamma_i'' D_i = \Psi_S, \quad (14)$$

is most general spin eigenfunction that can be formed from the spatial orbitals given.

Larsson¹⁸ has used another procedure. Let $\Theta_1, \Theta_2, \dots, \Theta_k$ be the k pure spin eigenfunctions for n fermions and spin S , and $\Phi(1, 2, \dots, n)$ be the product of our n spatial orbitals. The function

$$\Psi_S = \mathcal{A} \Phi(1, 2, \dots, n) \sum_{i=1}^k \gamma_i' \Theta_i, \quad (15)$$

is the same as that given by Eq. (14), where \mathcal{A} is the antisymmetrizer. The numbers γ_i'' and γ_i' are related by a linear transformation, of course.

Pauncz¹⁹ and Harris²⁰ have pointed out that sums of various permutations of the Φ in Eq. (15) multiplied by just one Θ will when antisymmetrized give Ψ_S , viz.,

$$\Psi_S = \mathcal{A} \Theta \sum_{i=1}^k \gamma_i''' \pi_i \Phi(1, 2, \dots, n), \quad (19)$$

and the γ_i''' are linearly related to γ_i'' and γ_i' .

The fourth method here under discussion for spin-free operator yields

$$\Psi^{(\omega)} = E^{(\omega)}(\gamma) \Phi(1, 2, \dots, n), \quad (17)$$

which for a set γ_i linearly related to $\gamma_i', \gamma_i'',$ or γ_i''' will give an energy equal to that calculated from Ψ_S in Eqs. (14), (15), or (16) for $(\mu) = (2^{(n/2)-S}, 1^{2S})$.

¹⁸ S. Larsson, "Calculations on the 2S Ground State of the Lithium Atom Using Wavefunctions of the Hylleraas Type," Uppsala Quantum Chemistry Group Tech. Note No. 197 (1967).

¹⁹ R. Pauncz, J. Chem. Phys. **43**, S69 (1965).

²⁰ F. E. Harris, Advan. Quantum Chem. **3**, 61 (1966).

The forms given in Eqs. (15)–(17) are more easily generalized to nonproduct functions for Φ , of course. We may say that for a given $\Phi(1, 2, \dots, n)$ there is a best spin function $\sum_i \gamma_i' \Theta_i$ for form (15) or a best $E^{(\omega)}(\gamma)$ for form (17) to give the lowest calculated value of the ground-state energy. As an example it is seen from I that the $E^{(2,1)}(\gamma)$ giving the "full" configuration function for the allyl radical is

$$E^{(2,1)}(\gamma) = \frac{1}{3} \{ I + 0.901(12) - 0.074(13) - 0.826(23) - \frac{1}{2}(123) - \frac{1}{2}(132) \}. \quad (18)$$

V. COMPARISON TO CI CALCULATIONS

Under certain circumstances it is advantageous to look upon projected Hartree product (PHP) methods as restricted CI calculations, when a fixed basis is used for expanding the orbitals. The question arises: When, if ever, is the projected SCF wavefunction equivalent to a full CI wavefunction? As was seen in I, there is equivalence for the π system of the allyl radical when the calculation is based on three p orbitals. We can make considerable progress toward answering this question by noting that a sufficient condition for non-equivalence is that the effective number of adjustable parameters in the PHP scheme be less than the number of independent functions constructable from the fixed basis. For a calculation involving n electrons, m basis functions in the fixed basis, a spin of S , and no spatial symmetry the number of independent parameters N_p in $E^{(\omega)}(\gamma) u_1(1) u_2(2) \dots u_n(n)$ is

$$N_p = n(m-1) + \frac{2S+1}{n+1} \binom{n+1}{(n/2)-S}. \quad (19)$$

The second term on the right of (19) is just the dimension of the vector γ . The number of independent functions N_F is given in Appendix B as

$$N_F = \frac{2S+1}{m+1} \binom{m+1}{(n/2)+S+1} \binom{m+1}{(n/2)-S}. \quad (20)$$

The smallest number of functions is had when $m=n$ and

$$N_p - N_F = n(n-1) + \frac{2S+1}{n+1} \binom{n+1}{(n/2)-S} \times \left[1 - \binom{n+1}{(n/2)+S+1} \right],$$

$$= n(n-1); \quad S = n/2,$$

$$= 0; \quad S = (n/2) - 1,$$

$$< 0; \quad S < (n/2) - 1.$$

Thus there can never be equivalence if $m=n$ and the system is not in one of the two highest multiplicities. Therefore, the result for allyl is somewhat exceptional, since the lowest multiplicity is the next from the highest in any three-electron system.

In considering PHP methods using a fixed basis for the orbitals it is possible to view the trial function as a sum of configurations with coefficients which are restricted by various relations among them.²¹ As can be seen from Eq. (20) the number of independent eigenfunctions of the spin increases rapidly with n and m . It is necessary to choose configurations in the CI method in some manner, and the real test of the PHP methods will be their comparison with such CI computations and with multiconfigurational SCF methods.^{22,23} Such a computation is underway on H_2 .

VI. ORTHOGONALITY PATTERNS

For $n \geq 5$ the number of terms in $E^{(\omega)}(\gamma)$ is very large, and it seems necessary with present day computing equipment to make some assumptions which will have a simplifying effect on the energy expression. One way of doing this is to require that certain of the spatial orbitals are orthogonal to one another. There seems to be no *a priori* method based on energy values for deciding which pattern is best since any such requirement is a restriction which except for one case will in general raise the calculated energy. Therefore, the *desideratum* is simplification of the energy expression. Let us assume our n spatial orbitals are divided into p subsets the i th containing l_i orbitals. One has the equation

$$\sum_i l_i = n. \quad (21)$$

We denote the k th member of the i th subset u_{ik} ; $i=1, 2, \dots, p$; $k=1, 2, \dots, l_i$ and it is assumed that

$$\langle u_{ik} | u_{i'k'} \rangle = \delta_{ii'} \Delta(i)_{kk'}, \quad (22)$$

that is, each function is orthogonal to every function not in the same subset.

Functions with the property (22) can be used to determine a certain set of conjugate subgroups of S_n and we will proceed to define one of these. Let us arrange the u_{ik} in dictionary order

$$u_{11}, u_{12}, \dots, u_{1l_1}; u_{21}, u_{22}, \dots, u_{2l_2};$$

$$\times \dots; u_{p1}, u_{p2}, \dots, u_{pl_p},$$

and let the j th one be a function of spatial coordinates j and form a single-product function by multiplying all of these together,

$$\phi_a(1, 2, \dots, n) = u_{11}(1) u_{12}(2) \dots u_{pl_p}(n). \quad (23)$$

An element of S_n denoted π may operate on ϕ_a and we may compute the inner product $\langle \phi_a | \pi \phi_a \rangle = \langle \pi \rangle_a$. If none of the $\Delta(i)_{kk'}$ are zero then the set of π such that $\langle \pi \rangle_a \neq 0$ form a subgroup of S_n , in fact, just $S_{l_1} \times S_{l_2} \times \dots \times S_{l_p}$, or at least one conjugate to it.

In the following we shall use π_S to denote an element of $S_{l_1} \times \dots \times S_{l_p}$ and π, σ, ν etc., for any elements of S_n .

We wish to evaluate the energy expression for a Hartree product function as given by (23), that is

$$\mathcal{E} = \langle \phi_a | H E^{(\omega)}(\gamma) | \phi_a \rangle / \langle \phi_a | E^{(\omega)}(\gamma) | \phi_a \rangle. \quad (24)$$

We shall look at the normalization integral first. Using Eqs. (12) and (22) it is seen that

$$\langle \phi_a | E^{(\omega)}(\gamma) \phi_a \rangle = (f^{(\omega)} / |G|) \sum_{\pi_S} P(\gamma, \pi_S) \langle \phi_a | \pi_S | \phi_a \rangle, \quad (25)$$

with only $l_1! l_2! \dots l_p!$ terms. The spin-free Hamiltonian H will be assumed to have only one- and two-particle operators,

$$\begin{aligned} H &= F + G \\ &= \sum_m f_m + \sum_{m < n} g_{mn}, \end{aligned} \quad (26)$$

and we have immediately that

$$\begin{aligned} \langle \phi_a | F E^{(\omega)}(\gamma) | \phi_a \rangle &= (f^{(\omega)} / |G|) \sum_{\pi_S} P(\gamma, \pi_S) \langle \phi_a | F \pi_S | \phi_a \rangle, \end{aligned} \quad (27)$$

since only the same permutations are non zero as in Eq. (25). The two-electron operator G is only a slightly more complicated. It is observed that the terms of G are of two kinds, those for which m and n in g_{mn} refer to coordinates within the same subset in ϕ_a and those for which m and n are in different subsets. We will symbolize the sum of all g_{mn} totally within the i th subset as $G(i)$ and we let $g(m_i, m_j)$; $m_i=1, 2, \dots, l_i$; $m_j=1, 2, \dots, l_j$; be a particular term of the second kind. We then have

$$\begin{aligned} \langle \phi_a | G E^{(\omega)}(\gamma) | \phi_a \rangle &= \frac{f^{(\omega)}}{|G|} \sum_{i=1}^p \sum_{\pi_S} P(\gamma, \pi_S) \langle \phi_a | G(i) \pi_S | \phi_a \rangle + \frac{f^{(\omega)}}{|G|} \sum_{i,j} \sum_{\pi_S} \{ P(\gamma, \pi_S) \langle \phi_a | g(m_i, m_j) \pi_S | \phi_a \rangle \\ &\quad + P[\gamma, (m_i m_j) \pi_S] \langle \phi_a | g(m_i, m_j) (m_i, m_j) \pi_S | \phi_a \rangle \}, \end{aligned}$$

²¹ The same can be said for the restricted Hartree-Fock treatment, but with even greater restrictions of the coefficients.

²² T. L. Gilbert, J. Chem. Phys. **43**, 5248 (1965).

²³ G. Das and A. C. Wahl, J. Chem. Phys. **44**, 87 (1966).

where (m_i, m_j) is the permutation interchanging coordinates m_i and m_j . We now have

$$\frac{1}{2}l_1!l_2!\cdots l_p!(n^2+2-l_1^2-l_2^2-\cdots-l_p^2)$$

different permutations yielding nonzero integrals in (28). This is less than $n!$ in most cases of interest and so the energy expression has been simplified as compared to the general case.

The one case mentioned above for which assumed orthogonality is not a restriction is for the operator θNPN . The orthogonality pattern of the pairing theorem^{24,25} may be assumed here with no effect on the energy. For all other $E^{(w)}(\gamma)$, assumed orthogonality will effect the calculated energy.

APPENDIX A: EVALUATION OF $a(\pi)$

In this appendix we derive a formula for $a(\pi)$ in the idempotent θNPN , based on the cycle structure of π . It is fairly evident that each cycle in π makes its own contribution to the determination of $a(\pi)$ independent of the others, so we assume that π contains at least one cycle of length l . We observe that $a(\pi)$ is present in the equation

$$\theta NPN\pi NPN = a(\pi)NPN, \tag{A1}$$

and $a(\pi) = a(\nu^{-1}\pi\nu)$ where ν is any element of N . The cycle $\kappa = (i_1, i_2, \dots, i_l)$ has one invariant under transformations by ν . We have the equation

$$\kappa = (i_1 i_2) (i_2 i_3) \cdots (i_{l-1} i_l), \tag{A2}$$

and it is observed that some of the interchanges may contain entries from different columns of T . We call such an interchange a *crossing*, and it is obvious the number of crossings is invariant to transformation by ν . We denote this number by $n_c(\kappa)$. Some of the interchanges in (A2) may not be crossings so these are elements of N . These may be permuted all to the left (or right), and together form another element of N . There exists an element of N , ν_0 , which will bring κ to the form

$$\nu_0 \kappa \nu_0^{-1} = \nu [1, (n/2) + S + 1] [(n/2) + S + 1, 2] \times [2, (n/2) + S + 2] \cdots, \tag{A3}$$

where number of interchanges after ν is $n_c(\kappa)$ and ν is an element of N . Because of the formula

$$(ij)(jk) = (ik)(ij),$$

Eq. (A3) becomes

$$\nu_0 \kappa \nu_0^{-1} = \nu (1, 2) (2, 3) \cdots [1, (n/2) + S + 1] \times [2, (n/2) + S + 2] \cdots, \tag{A4}$$

and κ is equivalent to an element of N times one of the

²⁴ A. T. Amos and G. G. Hall, Proc. Roy. Soc. (London) **A263**, 483 (1961).

²⁵ P.-O. Löwdin, J. Appl. Phys. Suppl. **33**, 251 (1962).

1	12
2	13
3	14
4	15
5	16
6	17
7	18
8	19
9	20
10	
11	

FIG. 3. Tableau for the triplet case of 20 electrons.

right coset generators. It is evident that the number of independent crossings in κ is $\frac{1}{2}n_c(\kappa)$ or $\frac{1}{2}[n_c(\kappa)H]$ whichever is an integer, and this we denote by $\varphi_c(\kappa)$ and let $\varphi(\pi)$ be the sum of φ_c for all cycles in π . If π has the cycle structure $(1^{\alpha_1}, 2^{\alpha_2}, 3^{\alpha_3}, \dots)$, then

$$a(\pi) = (-1)^{n-\alpha_1-\alpha_2-\cdots-\varphi(\pi)} \binom{(n/2)+S}{\varphi(\pi)}^{-1}. \tag{A5}$$

As an example let us take the case where $n=20$, $S=1$,

$$\pi = (1, 12, 2) (18, 19, 20) (3, 4, 16, 17, 11) \times (5, 13, 6, 14, 7, 15),$$

and one has the tableau in Fig. 3. We need merely count the number of times numbers for different columns are adjacent in each cycle. Thus

$$\varphi(\pi) = \frac{2}{2} + \frac{0}{2} + \frac{2}{2} + \frac{5+1}{2} = 5,$$

$$\alpha_1 + \alpha_2 + \cdots = 3 + 2 + 1 + 1 = 7,$$

$$a(\pi) = + \binom{11}{5}^{-1} = + \frac{1}{462}.$$

APPENDIX B: NUMBER OF INDEPENDENT FUNCTIONS FROM A FIXED BASIS

We give here a derivation of the formula for the number of independent functions which can be constructed for n electrons from a fixed basis of m functions which was used in Sec. V.

If the multiplicity is $2S+1$ then all product functions must contain at least $(n/2)+S$ different spatial orbitals since otherwise the tableaux with repeated elements vanish. Let us choose k of the m functions with $(n/2)+S \leq k \leq n$. There is a k -part partition of n , $(2^{n-k}, 1^{2k-n})$ which shows that $n-k$ functions must be repeated when placed in the tableau $(2^{(n/2)-S}, 1^{2S})$. There are $\binom{n}{n-k}$ ways the pairing may be done for each of the $\binom{m}{k}$ ways the k functions may be chosen

from the m . The number of standard tableaux is just $j=1, 2, \dots, j'-1$ columns for the i' th row and then

$$\frac{2S+1}{2k-n+1} \binom{2k-n+1}{k-S-(n/2)},$$

so we must multiply these three numbers together and sum over k from $(n/2)+S$ to n . Thus the total number of independent functions N_F is

$$\begin{aligned} N_F &= \sum_{k=(n/2)+S}^n \frac{2S+1}{2k-n+1} \binom{m}{k} \binom{k}{n-k} \binom{2k-n+1}{k-S-(n/2)} \\ &= \frac{(2S+1)}{(m+1)} \binom{m+1}{(n/2)+S+1} \binom{m+1}{(n/2)-S}. \end{aligned}$$

APPENDIX C: LINEAR INDEPENDENCE OF $\theta NPN_{\sigma_{1k}}$

We here prove the theorem merely stated in Sec. IV of the article that the quantities

$$\theta NPN_{\sigma_{1k}}; \quad k=1, 2, \dots, f(\omega) \quad (C1)$$

are linearly independent in the group algebra. We here again define the σ_{ik} . Let T_1, T_2, \dots, T_f be standard tableaux for which the k th one has the symbol $\alpha(k)_{ij}$ in the i th row and j th column. The tableaux T_k are assumed ordered as follows:

$$\alpha(k)_{ij} = \alpha(k')_{ij}$$

for the rows $i=1, 2, \dots, i'-1$, all columns, and for the

$$\alpha(k)_{i'j'} < \alpha(k')_{i'j'} \quad \text{if } k < k'.$$

Also we let P_i and N_i ; $i=1, \dots, f$ be the positive and negative projectors corresponding to T_i . It is easily seen that if $\alpha(k')_{i'j'} > \alpha(k)_{i'j'}$, then $\alpha(k)_{i''j''} = \alpha(k')_{i'j'}$, where necessarily $i'' > i'$ and $j'' < j'$, i.e., this element appears in a later row and earlier column of T_k . It is also easily seen because of this that (see also Ref. 12)

$$N_i P_j = P_j N_i = 0; \quad j > i. \quad (C2)$$

Equation (C2) is the basis of our proof. Thus we examine

$$\sum_{k=1}^f \gamma_k \theta N_1 P_1 N_1 \sigma_{1k} = 0, \quad (C3)$$

where σ_{1k} is the permutation $\sigma_{1k}^{-1} T_1 \sigma_{1k} = T_k$. Multiplying each term in (C3) on the right by I in the form $\sigma_{1k}(\sigma_{1k})^{-1}$ and on the left by $P_l N_l$ we get

$$\begin{aligned} 0 &= \theta \sum_k \gamma_k \sigma_{1k} N_k P_k N_k P_l N_l \\ &= \theta' \gamma_l \sigma_{1l} N_l P_l N_l + \theta \sum_{k=l+1}^f \gamma_k \sigma_{1k} N_k P_k N_k P_l N_l \\ &= \theta' \gamma_f \sigma_{1f} N_f P_f N_f; \quad l=f. \end{aligned} \quad (C4)$$

As we let $l=f, f-1, f-2, \dots, 1$ in turn we see that $\gamma_f, \gamma_{f-1}, \dots, \gamma_1$ are each zero since $\sigma_{1k} N_k P_k N_k \neq 0$. Thus the quantities are linearly independent.

Projected Hartree Product Wavefunctions. III. Comparison with the CI Method for H_2^*

R. C. MORRISON† AND G. A. GALLUP

Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68508

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Calculations of the energy of H_2 have been performed using both the projected Hartree-Fock (PHF) method and a full CI method in the same basis for comparison of the two methods. It is discovered that PHF can account for 86% of the correlation energy, whereas CI will account for 88% of the correlation energy.

I. INTRODUCTION

In two recent articles^{1,2} Gallup has given a spin-free version^{3,4} of the projected Hartree-Fock (PHF)

method originally suggested by Löwdin.⁵ This is an extension of the independent-particle model in which optimization of the orbital functions in a different orbitals for different spins (DODS) trial function is done after the application of all projections necessary to insure the correct symmetry. Thus it has been emphasized by Goddard⁶ and in the first paper of this series, hereinafter denoted as (I)¹ that the use of single-particle orbitals with spatial dissymmetry and what might be called identity dissymmetry can

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† NASA Trainee 1966-1968.

¹ G. A. Gallup, J. Chem. Phys. **48**, 1752 (1968).

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⁴ R. D. Poshusta and R. W. Kramling, Phys. Rev. **167**, 139 (1968).

⁵ P.-O. Löwdin, Phys. Rev. **97**, 1509 (1955).

⁶ W. A. Goddard, Phys. Rev. **157**, 73, 81 (1967).