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Eigenfunctions of S^2 by a Spin Operator Method*

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An operator is derived which is a function of step-up and step-down operators pertaining to spin angular momentum, and which creates a state of definite multiplicity when operating on a single determinant of spatial and spin orbitals. This paper is concerned with the problem of finding all of the orthogonal singlets for a $2N$-electron system in terms of the spin operator. The five orthogonal singlets corresponding to the six-electron spin degeneracy problem are studied in detail by means of the branching diagram. The fourteen orthogonal singlets corresponding to the eight-electron problem and the forty-two orthogonal singlets corresponding to the ten-electron problem are written down. Some remarks are made concerning the application of this method to a configuration interaction investigation.

INTRODUCTION

In the investigation of molecules by configuration interaction, one is faced with the problem of setting up the states of definite multiplicity for the various configurations and of taking the matrix components of the energy between the different configurations. The following paper deals primarily with the singlet states, as they are usually of greatest interest in these problems. A simple and direct method of constructing all of the orthogonal singlets for a $2N$-electron system is presented. A brief discussion is given of the application of the operator techniques developed to the problem of configuration interaction. The reader is referred to Condon and Shortley[1] and the work of Racah[2] for a more general treatment of these problems.

For a set of $2N$ electrons occupying $2N$ distinct orbitals, it is possible to form many states of a given multiplicity by associating either α or β spin with the collection of orbitals in a variety of ways. In fact, one can construct

$$(2N)!/N!(N+1)!$$

orthogonal singlet states. One means of setting up all of the singlets is the valence-bond method which leads to the correct number of linearly independent singlets, but the states so obtained are not orthogonal.[3] Another method of constructing all of the singlets is by using the branching diagram,[4] a pictorial description of adding the spin angular momentum of electrons one by one. This scheme shows, for any number of electrons, how many states of various multiplicities there are, and what the parentage of each state is. The method of the branching diagram will be used in the following discussion.

A spin operator method is given here for setting up all of the orthogonal singlets. The five orthogonal singlets corresponding to a six-electron system are analyzed in some detail, and from this analysis a spin operator O is derived which when operating on a single determinant creates an eigenfunction of S^2. All of the orthogonal singlets for the six-, eight-, and ten-electron systems are written down in terms of the operator O.

THE SIX-ELECTRON PROBLEM

In Fig. 1 the branching diagram for a six-electron system is given. This diagram not only shows how many states of a given multiplicity there are for n electrons, but by applying the methods of vector addition of angular momentum, the branching diagram also shows how the states are actually constructed. In Figs. 1(b) through 1(e) the five possible ways of obtaining a singlet state for the six-electron problem are illustrated. Let us consider in some detail the state described in Fig. 1(b). The branching diagram tells us that this state results from the combination of two three-electron systems, say A and B, each of which are in a state of $S=\frac{3}{2}$. Let us order the six orbitals for this problem φ_1, φ_2, φ_3, φ_4, φ_5, and φ_6. These orbitals are assumed to be orthonormal and distinct. Let φ_1, φ_2, and φ_3 and three electrons make up set A and φ_4, φ_5, and φ_6 and three electrons comprise set B. The singlet in Fig. 1(b) can be expressed as

$$\begin{aligned}\Psi_1(S=0)=&C_0\varphi_A(S=\tfrac{3}{2}, M_S=\tfrac{3}{2})\cdot\varphi_B(S=\tfrac{3}{2}, M_S=-\tfrac{3}{2})\\&+C_1\varphi_A(S=\tfrac{3}{2}, M_S=\tfrac{1}{2})\cdot\varphi_B(S=\tfrac{3}{2}, M_S=-\tfrac{1}{2})\\&+C_2\varphi_A(S=\tfrac{3}{2}, M_S=-\tfrac{1}{2})\cdot\varphi_B(S=\tfrac{3}{2}, M_S=+\tfrac{1}{2})\\&+C_3\varphi_A(S=\tfrac{3}{2}, M_S=-\tfrac{3}{2})\cdot\varphi_B(S=\tfrac{3}{2}, M_S=+\tfrac{3}{2}).\end{aligned}\tag{1}$$

The states representing by $\varphi_A(S, M_S)$ and $\varphi_B(S, M_S)$ are

$$\varphi_A(S=\tfrac{3}{2}, M_S=\tfrac{3}{2})=\begin{vmatrix}\varphi_1(1)\alpha(1)\varphi_1(2)\alpha(2)\varphi_1(3)\alpha(3)\\\varphi_2(1)\alpha(1)\varphi_2(2)\alpha(2)\varphi_2(3)\alpha(3)\\\varphi_3(1)\alpha(1)\varphi_3(2)\alpha(2)\varphi_3(3)\alpha(3)\end{vmatrix}\equiv|\alpha\alpha\alpha|,\tag{2}$$

$$\varphi_B(S=\tfrac{3}{2}, M_S=-\tfrac{3}{2})=\begin{vmatrix}\varphi_4(4)\beta(4)\varphi_4(5)\beta(5)\varphi_4(6)\beta(6)\\\varphi_5(4)\beta(4)\varphi_5(5)\beta(5)\varphi_5(6)\beta(6)\\\varphi_6(4)\beta(4)\varphi_6(5)\beta(5)\varphi_6(6)\beta(6)\end{vmatrix}\equiv|\beta\beta\beta|,\tag{3}$$

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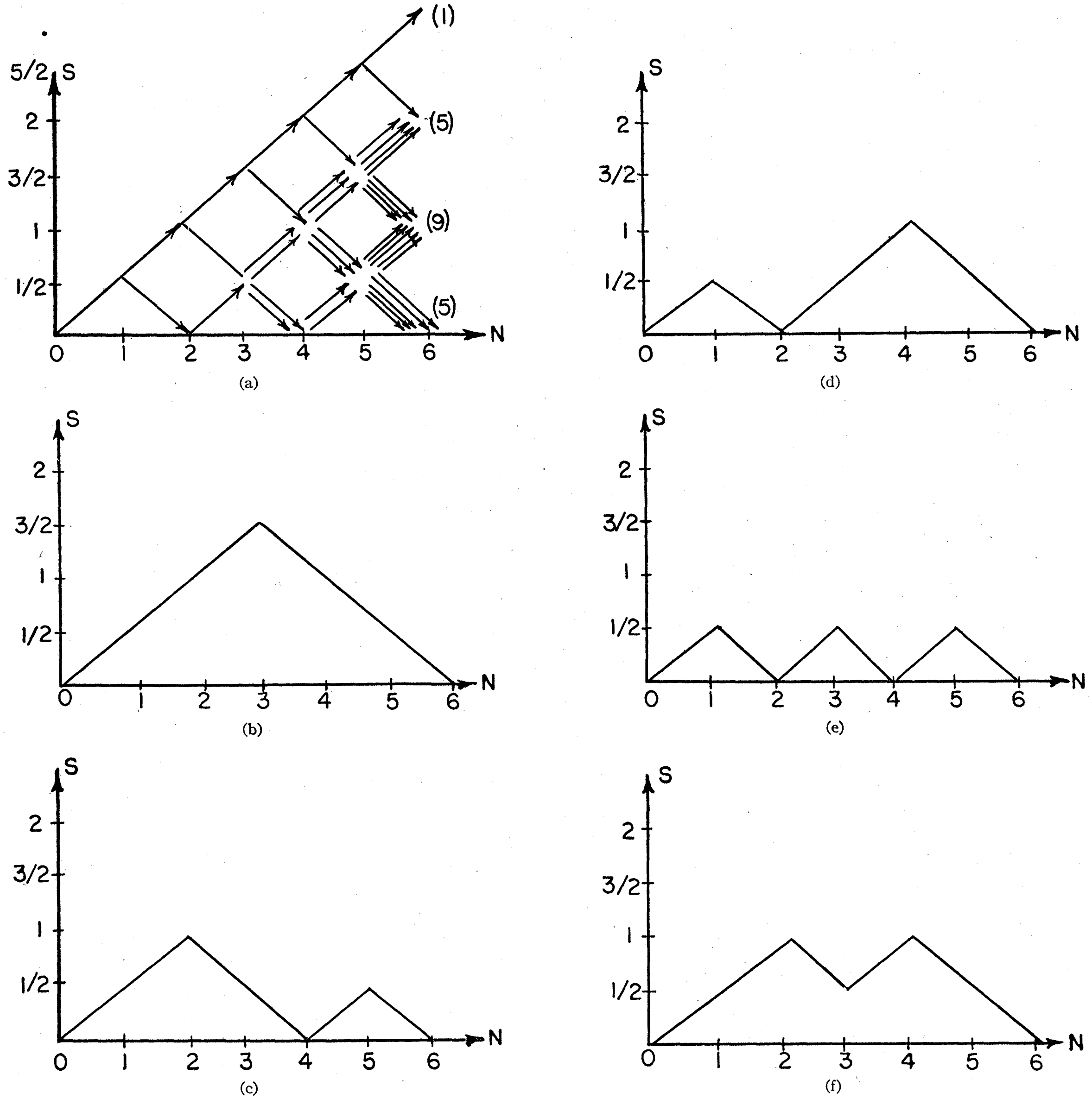

(a) (d) (b) (e) (c) (f)

FIG. 1. (a) Branching diagram for a six-electron system; (b) first path; (c) second path; (d) third path; (e) fourth path; and (f) fifth path.

$$\varphi_A(S=\tfrac{3}{2},\ M_S=\tfrac{1}{2})=[|\beta\alpha\alpha|+|\alpha\beta\alpha|+|\alpha\alpha\beta|]/\sqrt{3},\quad (4)$$

$$\varphi_B(S=\tfrac{3}{2},\ M_S=-\tfrac{1}{2})=[|\beta\beta\alpha|+|\beta\alpha\beta|+|\alpha\beta\beta|]/\sqrt{3},\quad (5)$$

$$\varphi_A(S=\tfrac{3}{2},\ M_S=-\tfrac{1}{2})=[|\alpha\beta\beta|+|\beta\alpha\beta|+|\beta\beta\alpha|]/\sqrt{3},\quad (6)$$

$$\varphi_B(S=\tfrac{3}{2},\ M_S=+\tfrac{1}{2})=[|\alpha\alpha\beta|+|\beta\alpha\alpha|+|\alpha\beta\alpha|]/\sqrt{3},\quad (7)$$

$$\varphi_A(S=\tfrac{3}{2},\ M_S=-\tfrac{3}{2})=|\beta\beta\beta|,\quad (8)$$

$$\varphi_B(S=\tfrac{3}{2},\ M_S=+\tfrac{3}{2})=|\alpha\alpha\alpha|.\quad (9)$$

All determinants are assumed to be normalized.

The expression $\varphi_A(S=\frac{3}{2},\ M_S)\cdot\varphi_B(S=\frac{3}{2},\ -M_S)$ involves the combination of the determinants which make up the states. The "product" of two determinants is taken to mean

$$|\alpha\beta\alpha|\cdot|\beta\beta\alpha|=\begin{vmatrix}\varphi_1(1)\alpha(1) & \cdot & \cdot & \cdot & \varphi_1(6)\alpha(6)\\ \varphi_2(1)\beta(1) & \cdot & \cdot & \cdot & \varphi_2(6)\beta(6)\\ \varphi_3(1)\alpha(1) & \cdot & \cdot & \cdot & \varphi_3(6)\alpha(6)\\ \varphi_4(1)\beta(1) & \cdot & \cdot & \cdot & \varphi_4(6)\beta(6)\\ \varphi_5(1)\beta(1) & \cdot & \cdot & \cdot & \varphi_5(6)\beta(6)\\ \varphi_6(1)\alpha(1) & \cdot & \cdot & \cdot & \varphi_6(6)\alpha(6)\end{vmatrix}.\quad (10)$$

In general the "product" of an $n\times n$ determinant and an $m\times m$ determinant is an $(m+n)\times(m+n)$ determinant. We also note that the order must be preserved, i.e., $|\alpha\beta\alpha|\cdot|\beta\beta\alpha|$ is not equal to $|\beta\beta\alpha|\cdot|\alpha\beta\alpha|$. It is to be borne in mind that the $\varphi_{A,B}(S,M_S)$ are normalized states of definite multiplicity. The coefficients C_i in (1) are the transformation amplitudes for the vector addition of angular momentum, and sometimes called the Clebsch-Gordon coefficients. They may be obtained in this case from the general expression for combining two systems of spin S to form a resultant singlet. This is

$$\Psi(S=0)=\sum_{M_S=-S}^{+S}(-1)^{S-M_S}\varphi_A(S,M_S)\cdot\varphi_B(S,-M_S). \quad (11)$$

Let us now look into the question of forming the various $\varphi_{A,B}(S,M_S)$ states. $\varphi_A(S=\frac{3}{2}, M_S=+\frac{1}{2})$ is obtained by the step-down operator acting on $\varphi_A(S=\frac{3}{2}, M_S=+\frac{3}{2})$, and $\varphi_B(S=\frac{3}{2}, M_S=-\frac{1}{2})$ is gotten by the step-up operator acting on $\varphi_B(S=\frac{3}{2}, M_S=-\frac{3}{2})$. Thus except for a constant we have

$$\varphi_A(S=\tfrac{3}{2}, M_S=+\tfrac{1}{2})=S_A^-\varphi_A(S=\tfrac{3}{2}, M_S=+\tfrac{3}{2}),$$
$$\varphi_B(S=\tfrac{3}{2}, M_S=-\tfrac{1}{2})=S_B^+\varphi_B(S=\tfrac{3}{2}, M_S=-\tfrac{3}{2}),$$

where $S_A^-=S_1^-+S_2^-+S_3^-$ and $S_B^+=S_4^++S_5^++S_6^+$. Writing this out, we get

$$S_A^-|\alpha\alpha\alpha|=[|\beta\alpha\alpha|+|\alpha\beta\alpha|+|\alpha\alpha\beta|]. \quad (12)$$

$$S_B^+|\beta\beta\beta|=[|\alpha\beta\beta|+|\beta\alpha\beta|+|\beta\beta\alpha|]. \quad (13)$$

In order to have normalized states, we must multiply the right-hand side of both (12) and (13) by $(3)^{-\frac{1}{2}}$, which is the number of ways of reversing one spin in set A or B taken to the $-\frac{1}{2}$ power. We can write the second term in (1), except for the factor of -1, as

$$[(S_A^-S_B^+)/3]\varphi_A(S=\tfrac{3}{2}, M_S=\tfrac{3}{2})\cdot\varphi_B(S=\tfrac{3}{2}, M_S=-\tfrac{3}{2}). \quad (14)$$

The third term in (1) may be written as

$$[(S_A^-S_B^+)^2/3\times4]\varphi_A(S=\tfrac{3}{2}, M_S=\tfrac{3}{2})\cdot\varphi_B(S=\tfrac{3}{2}, M_S=-\tfrac{3}{2}). \quad (15)$$

The factor of 3 in the denominator is the product of the number of ways of reversing two spins in set A taken to the $\frac{1}{2}$ power and the number of ways of reversing two spins in B taken to the $\frac{1}{2}$ power. The factor of 4 in the denominator arises because in the expansion of $(S_A^-S_B^+)^2$ we encounter equivalent terms of the type $S_1^-S_2^-S_4^+S_5^++S_1^-S_2^-S_5^+S_4^++S_2^-S_1^-S_4^+S_5^++S_2^-S_1^-S_5^+S_4^+$. Thus if there are M spin reversals in set A and in set B, we must divide out the permutations among set A and set B as in the case above.

The fourth term in (1) may be written

$$[(S_A^-S_B^+)^3/36]\varphi_A(S=\tfrac{3}{2}, M_S=\tfrac{3}{2})\cdot\varphi_B(S=\tfrac{3}{2}, M_S=-\tfrac{3}{2}). \quad (16)$$

Here there is just one way of reversing all the spins in A and in B. The factor of 36 in the denominator is necessary because there are 3! ways of expressing the reversals in A, i.e., $S_1^-S_2^-S_3^-$, $S_2^-S_1^-S_3^-$, etc., and 3! ways in B.

We can combine (14), (15), and (16) and write the singlet (1) as

$$\Psi_1(S=0)=\{(S_A^-S_B^+)^0-\tfrac{1}{3}(S_A^-S_B^+)^1+(1/12)(S_A^-S_B^+)^2-(1/36)(S_A^-S_B^+)^3\}\times\varphi_A(S=\tfrac{3}{2}, M_S=\tfrac{3}{2})\cdot\varphi_B(S=\tfrac{3}{2}, M_S=-\tfrac{3}{2}). \quad (17)$$

We must multiply the right-hand side of (17) by $\frac{1}{2}$ in order that the final state will be normalized.

We have now expressed the singlet shown in Fig. 1(a) as the result of an operator acting on the "product" of $\varphi_A(S=\frac{3}{2}, M_S=\frac{3}{2})$ and $\varphi_B(S=\frac{3}{2}, M_S=-\frac{3}{2})$. We seek now to generalize this operator to the $2N$-electron case. That is, given a $2N$-electron system, a collection of N electrons and N orbitals will be terms as set A, and the remaining N electrons and N orbitals denoted by set B. We wish to form the $2N$-electron-orbital singlet state by combining sets A and B, each of which is to be in a state of maximum multiplicity, i.e., $S_{A,B}=N/2$. Our composite state will be

$$\Psi(S=0)=O_1[\varphi_A(S=N/2, M_S=+N/2)\cdot\varphi_B(S=N/2), M_S=-N/2)]. \quad (18)$$

Denoting the number of spin reversals in A or B by M, the general form of the operator, which will be represented by O_1, is

$$O_1=\sum_{M=0}^{N}(-1)^M[(N-M)!/(N!M!(N+1)^{\frac{1}{2}})]\times(S_A^-S_B^+)^M, \quad (19)$$

where

$$\begin{aligned}S_A^-&=S_{1A}^-+S_{2A}^-+S_{3A}^-+\cdots+S_{NA}^-.\\S_B^+&=S_{1B}^++S_{2B}^++S_{3B}^++\cdots+S_{NB}^+.\end{aligned} \quad (20)$$

The $(-1)^M$ is the Clebsch-Gordon coefficient. The factor $(N-M)!/N!M!$ is

$$[(N-M)!M!/N!]^{\frac{1}{2}}\cdot[(N-M)!M!/N!]^{\frac{1}{2}}\cdot1/M!\cdot1/M!. \quad (21)$$

The first factor in (21) is the number of ways of making M reversals in set A, which contains N elements, taken to the $-\frac{1}{2}$ power. The second factor is the number of ways of making M reversals of spin in set B taken to the $-\frac{1}{2}$ power. The third factor divides out equivalent permutations in set A, as explained above. The fourth factor does the same in set B.

Therefore, we have found an operator O_1 which, when acting on the "product" of two N-electron systems, each in a state of maximum S and one with $M_S=S$ and the other with $M_S=-S$, produces a composite state of $2N$-electrons which is a singlet. It turns out that the present operator O_1 is not general enough to be a really powerful tool. In the course of events a number of modifications will suggest themselves.

Let us now investigate the creation of the remaining singlets for the six-electron problem. The reader is referred to Figs. 1(c), 1(d), 1(e), and 1(f) for a pictorial description of the structure of these states. In Fig. 1(c) our resultant singlet is the "product" of a singlet state made up of the first four orbitals and four electrons, and the singlet made from the last two orbitals and electrons. Equation (11) shows that if we combine two systems each of which is in a singlet state to form a resultant singlet, that the composite state is merely the "product" of $\varphi_1(s=0)$ and $\varphi_2(S=0)$. Our plan is, therefore, to generate the two singlets inferred from Fig. 1(b) and to take their "product" to get the final state: The singlet formed from the first four orbitals and four electrons is the result of combining two states $\varphi_A(S=1, M_S=1)$ and $\varphi_B(S=1, M_S=-1)$. The singlet formed from the last two orbitals and two electrons is the result of combining two states $\varphi_A'(S=\frac{1}{2}, M_S=\frac{1}{2})$ and $\varphi_B'(S=\frac{1}{2}, M_S=-\frac{1}{2})$. Thus the six-electron singlet for Fig. 1(b) is simply

$$\Psi_2(S=0)=O_1|\alpha\alpha\beta\beta|\cdot O_1'|\alpha\beta|, \tag{22}$$

which when expanded is

$$\Psi_2(S=0)=(1/\sqrt{6})[|\alpha\alpha\beta\beta|-\tfrac{1}{2}\{|\alpha\beta\alpha\beta|+|\alpha\beta\beta\alpha| +|\beta\alpha\alpha\beta|+|\beta\alpha\beta\alpha|\}+|\beta\beta\alpha\alpha|]\cdot[|\alpha\beta|-|\beta\alpha|]. \tag{23}$$

For the purpose of illustration let us write out O_1 and O_1'. For O_1, $N=2$; and for O_1', $N=1$. Thus from (19) we get

$$O_1=(1/\sqrt{3})[1-\tfrac{1}{2}\{S_1^-S_3^++S_1^-S_4^++S_2^-S_3^++S_2^-S_4^+\} +\tfrac{1}{4}\{S_1^-S_2^-S_3^+S_4^++S_2^-S_1^-S_3^+S_1^+ +S_1^-S_2^-S_4^+S_3^++S_2^-S_1^-S_4^+S_3^+\}].$$

Since $S_i^-S_j^+$ commute for $i\neq j$,

$$O_1=[1-\tfrac{1}{2}\{S_1^-S_3^++S_1^-S_4^++S_2^-S_3^++S_2^-S_4^+\} +S_1^-S_2^-S_3^+S_4^+]/\sqrt{3}, \tag{24}$$

and O_1' is

$$O_1'=[1-S_5^-S_6^+]/\sqrt{2}. \tag{25}$$

The singlet in Fig. 1(d) is constructed in the same manner as $\Psi_2(S=0)$, only now the first two orbitals and two electrons are combined to form a singlet, and the last four orbitals and four electrons are combined to form a singlet. The composite singlet is just the "product" of these singlets. Hence

$$\Psi_3(S=0)=O_1'|\alpha\beta|\cdot O_1|\alpha\alpha\beta\beta|, \tag{26}$$

$$\Psi_3(S=0)=(1/\sqrt{6})[|\alpha\beta|-|\beta\alpha|] \cdot[|\alpha\alpha\beta\beta|-\tfrac{1}{2}\{|\alpha\beta\alpha\beta|+|\alpha\beta\beta\alpha|+|\beta\alpha\alpha\beta| +|\beta\alpha\beta\alpha|\}+|\beta\beta\alpha\alpha|]. \tag{27}$$

Theorem I, which is proved in Appendix I, and which states that different paths on the branching diagram terminating at the same destination lead to orthogonal states, shows us that Ψ_2 and Ψ_3 are indeed orthogonal.

The singlet formed in Fig. 1(e) is obtained by taking the "product" of three singlets, each made up of two orbitals and two electrons. Thus

$$\Psi_4(S=0)=O_1^{(1)}|\alpha\beta|\cdot O_1^{(3)}|\alpha\beta|\cdot O_1^{(5)}|\alpha\beta|, \tag{28}$$

where $O_1^{(i)}$ is

$$O_1^{(i)}=[1-S_i^-S_{i+1}^+]/\sqrt{2}. \tag{29}$$

It is of interest to note that this state is one of the familiar valence-bond singlets. In valence-bond language one would describe the state as having a bond between φ_1 and φ_2, a bond between φ_3 and φ_4, and a bond between φ_5 and φ_6. The expanded form of this state is

$$\Psi_4(S=0)=[(|\alpha\beta|-|\beta\alpha|)\cdot(|\alpha\beta|-|\beta\alpha|) \cdot(|\alpha\beta|-|\beta\alpha|)]/\sqrt{8}. \tag{30}$$

Let us now consider the last singlet, that shown in Fig. 1(f). The singlets formed so far have been either the "product" of subsidiary singlets formed by the application of O_1, or in the case of Fig. 1(b), a total singlet formed directly by the use of O_1. The state shown in Fig. 1(f) is the result of combining two states each made up of three orbitals and three electrons and both in a state of $S=\frac{1}{2}$. Our plan is now to find out how to use O_1 so that it can operate on a determinant made up of an odd number of electrons; therefore, not in a state of $M_S=0$. We want the result of operating with O_1 on, for example, $|\alpha\alpha\beta|$ to be a state of $\Psi(S=\frac{1}{2})$. The formation of a state of $\Psi(S=\frac{1}{2})$ from three electrons may be accomplished in two different ways as indicated by the branching diagram, Fig. 1. The two possible states are shown in Figs. 2(a) and 2(b). The state illustrated in Fig. 2(a) is the result of the combination of a singlet formed by the first two orbitals and two electrons and a state $\varphi(S=\frac{1}{2})$ formed from the third orbital and an electron. That is

$$\begin{aligned}\Psi_{2a}&=[|\alpha\beta|-|\beta\alpha|]\cdot|\alpha|/\sqrt{2},\\ \Psi_{2a}&=\{O_1|\alpha\beta|\}\cdot|\alpha|.\end{aligned} \tag{31}$$

The state shown in Fig. 2(b) is the result of the combination of a state $\varphi(S=1)$ formed from the first two electrons, and a state $\varphi(S=\frac{1}{2})$ formed from the third orbital and an electron. The method of creating such a state by the vector addition of angular momentum is well known, and the result is

$$\Psi(S=\tfrac{1}{2}, M_S=\tfrac{1}{2})=(2/\sqrt{6})|\alpha\alpha|\cdot|\beta| -(1/\sqrt{6})[|\alpha\beta|+|\beta\alpha|]\cdot|\alpha|. \tag{32}$$

We can factor this state as follows:

$$\Psi(S=\tfrac{1}{2}, M_S=\tfrac{1}{2})=(1/\sqrt{6})\{|\alpha|\cdot(|\alpha\beta|-|\beta\alpha|) +(|\alpha\cdot|\alpha|\cdot\beta|-|\beta\cdot|\alpha|\cdot\alpha|)\}. \tag{33}$$

This defines a new way of writing a "product"; for example,

$$|\alpha\beta\cdot\{|\alpha\beta|-|\beta\alpha|\}\cdot\beta\beta|=|\alpha\beta\alpha\beta\beta\beta|-|\alpha\beta\beta\alpha\beta\beta|. \tag{34}$$

We can generate the state $\Psi(S=\frac{1}{2}, M_S=\frac{1}{2})$ by the application of an operator,

$$(1-S_2^-S_3^+)+(1-S_1^-S_3^+), \tag{35}$$

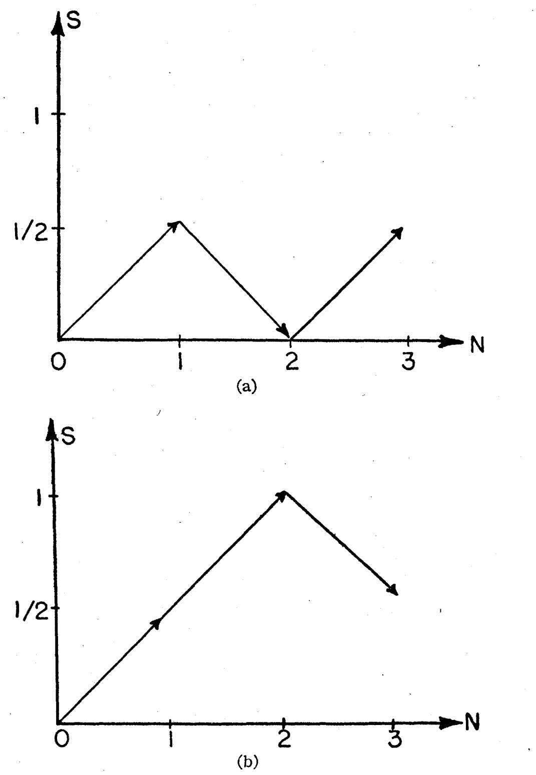

FIG. 2. (a) and (b) Three-electron system of $S=\frac{1}{2}$, $M_S=\frac{1}{2}$.

which operates on $|\alpha\alpha\beta|$. We have

$$(1-S_2^-S_3^+)|\alpha\alpha\beta|=|\alpha\alpha\beta|-|\alpha\beta\alpha|,$$
$$(1-S_1^-S_3^+)|\alpha\alpha\beta|=|\alpha\alpha\beta|-|\beta\alpha\alpha|.$$

Therefore, except for the proper normalization constant

$$[(1-S_2^-S_3^+)+(1-S_1^-S_3^+)]|\alpha\alpha\beta| \\ =2|\alpha\alpha\beta|-|\alpha\beta\alpha|-|\beta\alpha\alpha|. \quad (36)$$

Thus the state $\Psi(S=\frac{1}{2}, M_S=\frac{1}{2})$ can be created by use of O_1, since (36) can be written

$$\Psi(S=\tfrac{1}{2}, M_S=\tfrac{1}{2})=[O_1{}^{(2,3)}+O_1{}^{(1,3)}]|\alpha\alpha\beta|\sqrt{3} \\ =[2|\alpha\alpha\beta|-|\alpha\beta\alpha|-|\beta\alpha\alpha|]/\sqrt{6}. \quad (37)$$

Similarly,

$$\Psi(S=\tfrac{1}{2}, M_S=-\tfrac{1}{2})=[O_1{}^{(4,5)}+O_1{}^{(4,6)}]|\alpha\beta\beta|/\sqrt{3} \\ =[2|\alpha\beta\beta|-|\beta\alpha\beta|-|\beta\alpha\alpha|]/\sqrt{6}. \quad (38)$$

Since we have found the two states $\Psi(S=\frac{1}{2}, M_S=\pm\frac{1}{2})$ corresponding to those involved in the formation of the singlet in $\Psi_5(S=0)$, Fig. 1(e), we can create the composite six-electron singlet as

$$\Psi_5(S=0)=O_1[\Psi(S=\tfrac{1}{2}, M_S=\tfrac{1}{2})\cdot\Psi(S=\tfrac{1}{2}, M_S=-\tfrac{1}{2})]. \quad (39)$$

When written out, this is

$$\Psi_5(S=0)=\tfrac{1}{6}O_1[4|\alpha\alpha\beta\alpha\beta\beta|-2|\alpha\alpha\beta\beta\alpha\beta| \\ -2|\alpha\alpha\beta\beta\beta\alpha|-2|\alpha\beta\alpha\alpha\beta\beta|+|\alpha\beta\alpha\beta\alpha\beta|+|\alpha\beta\alpha\beta\beta\alpha| \\ -2|\beta\alpha\alpha\alpha\beta\beta|+|\beta\alpha\alpha\beta\alpha\beta|+|\beta\alpha\alpha\beta\beta\alpha|], \quad (40)$$

where the orbitals associated with spin α comprise set A and the orbitals associated with spin β comprise set B. For example, the first determinant in (40) has φ_1, φ_2, and φ_4 in A and φ_3, φ_5, and φ_6 in B.

With expression (40) we have completed the task of writing down all of the orthogonal singlets for the six electron case with the help of the operator O_1. Now we wish to generalize this operator so that it can be used for a wider variety of situations. Equations (37), (38), and (40) show that it is sometimes necessary to use more than one definition of sets A and B. It would be much more convenient to have a form of O_1 which would automatically operate on all possible choices for sets A and B. We can easily modify O_1 to do this, and the generalized form of O_1 will be written as O. It is

$$O=\frac{1}{(N+1)^{\frac{1}{2}}}\sum_i\Bigg[1+\sum_{M=1}^{N}\frac{(-1)^M(N-M)!}{N!M!} \\ \times\{(S_{A_i}^-S_{B_i}^+)^M+(S_{A_i}^+S_{B_i}^-)^M\} \\ \times\prod_{jA_ikB_i}^{N}(S_{jA_i}^+S_{jA_i}^-S_{kB_i}^-S_{kB_i}^+ \\ +S_{jA_i}^-S_{jA_i}^+S_{kB_i}^+S_{kB_i}^-)\Bigg], \quad (41)$$

where the sum over i is the sum over all different divisions of the orbitals φ_1 to φ_{2N} into two groups of N orbitals. O is to operate on a determinant with total M_S equal to zero. The rules for applying O to determinants with total M_S not zero will be given in a later section. The properties of O will now be written down and the proofs of these statements is given in the various appendices.

I. O is hermitian.
II. O commutes with S^2.
III. O commutes with the Hamiltonian H.
IV. O^2 equals $(N+1)^{\frac{1}{2}}\{n[1+(n-1)/(N+1)]\}^{\frac{1}{2}}O$.[5]
V. O commutes with the antisymmetrizing operator A.

We are now in a position to illustrate how O operates on a determinant. Consider for example O operating on $|\alpha\beta\alpha\beta|$. First, since O commutes with the antisymmetrizing operator, we can write $O|\alpha\beta\alpha\beta|$ as $AO\varphi_1(1)\alpha(1)\varphi_2(2)\times\beta(2)\varphi_3(3)\alpha(3)\varphi_4(4)\beta(4)$, where O now operates on a spin-product function. We can divide our four orbitals φ_1, φ_2, φ_3, and φ_4 into two groups in three different ways $\varphi_1, \varphi_2-\varphi_3, \varphi_4$; $\varphi_1, \varphi_3-\varphi_2, \varphi_4$; $\varphi_1, \varphi_4-\varphi_2, \varphi_3$. Let us first consider the

$$\prod_{jA_i,kB_i}^{N}(S_{jA_i}^+S_{jA_i}^-S_{kB_i}^-S_{kB_i}^+ + S_{jA_i}^-S_{jA_i}^+S_{kB_i}^+S_{kB_i}^-)$$

part of O operating on

$$\varphi_1(1)\alpha(1)\varphi_2(2)\beta(2)\varphi_3(3)\alpha(3)\varphi_4(4)\beta(4).$$

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[5] See Eq. (49) for the definition of n.

Suppose we take the division φ_1, $\varphi_2-\varphi_3$, φ_4 and let φ_1 and φ_2 comprise set A, and φ_3 and φ_4 make up set B. Then we have

$$\begin{aligned}&[S_1^+S_1^-S_2^+S_2^-S_3^-S_3^+S_4^-S_4^+\\&\qquad+S_1^-S_1^+S_2^-S_2^+S_3^+S_3^-S_4^+S_4^-]\\&\qquad\times\varphi_1(1)\alpha(1)\varphi_2(2)\beta(2)\varphi_3(3)\alpha(3)\varphi_4(4)\beta(4).\end{aligned}\tag{42}$$

This is clearly zero. Hence this choice of dividing our four orbitals into two groups yields nothing. Similarly the choice φ_1, $\varphi_4-\varphi_2$, φ_3 gives nothing. For the selection φ_1, $\varphi_3-\varphi_2$, φ_4 we have

$$\begin{aligned}&[S_1^+S_1^-S_3^+S_3^-S_2^-S_2^+S_4^-S_4^+\\&\quad+S_1^-S_1^+S_3^-S_3^+S_2^+S_2^-S_4^+S_4^-]\\&\quad\times\varphi_1(1)\alpha(1)\varphi_2(2)\beta(2)\varphi_3(3)\alpha(3)\varphi_4(4)\beta(4)\\&\qquad=\varphi_1(1)\alpha(1)\varphi_2(2)\beta(2)\varphi_3(3)\alpha(3)\varphi_4(4)\beta(4).\end{aligned}\tag{43}$$

Thus when operating on a spin product function with the $\prod_i$ operator, we get zero for all choices of i except one, which leaves the spin product function invariant. Let us now examine the factor

$$[(S_{Ai}^-S_{Bi}^+)^M+(S_{Ai}^+S_{Bi}^-)^M].$$

The term $(S_{Ai}^+S_{Bi}^-)^M$ gives zero for all M, since in this example we have associated α spin with all orbitals in set A. Thus we see that O effectively reduces to

$$\begin{aligned}O=[1-\tfrac{1}{2}(S_1^-S_2^++S_1^-S_4^++S_3^-S_2^++S_3^-S_4^+)\\+S_1^-S_3^-S_2^+S_4^+]/\sqrt{3},\end{aligned}$$

which is the same as (24) if we interchange the 2's and 3's in that expression. One should note that we would have obtained the same result had we associated β spin with all orbitals in A. This is as it should be, for the assignment of spin to set A or B is entirely arbitrary.

Using our new operator O, let us look back at the five singlets we have set up for the six-electron problem. $\Psi_1(S=0)$, originally given in (17), is just

$$\Psi_1(S=0)=O|\alpha\alpha\alpha\beta\beta\beta|.\tag{44}$$

Here O reduces to just the original operator. $\Psi_2(S=0)$, given in (22), is

$$\Psi_2(S=0)=O|\alpha\alpha\beta\beta|\cdot O|\alpha\beta|.\tag{45}$$

$\Psi_3(S=0)$, given in (26), is

$$\Psi_3(S=0)=O|\alpha\beta|\cdot O|\alpha\alpha\beta\beta|.\tag{46}$$

$\Psi_4(S=0)$, given in (28), is

$$\Psi_4(S=0)=O|\alpha\beta|\cdot O|\alpha\beta|\cdot O|\alpha\beta|.\tag{47}$$

In the case of $\Psi_5(S=0)$ we encounter operands, i.e. $|\alpha\alpha\beta|$ or $|\alpha\beta\beta|$, with $M_S\neq 0$ as in (37) and (38). If we operate on $|\alpha\alpha\beta|$ with O, taking N to be 1 and letting the sum over i range over all possibilities of dividing the three orbitals into two groups with one orbital per group and excluding the remaining orbital, then the expanded form of O is

$$\begin{aligned}O=(1-\{&S_1^-S_2^++S_1^+S_2^-\})\\&\times(S_1^+S_1^-S_2^-S_2^++S_1^-S_1^+S_2^+S_2^-)/\sqrt{2}\\&+(1-\{S_1^-S_3^++S_1^+S_3^-\})\\&\times(S_1^+S_1^-S_3^-S_3^++S_1^-S_1^+S_3^+S_3^-)/\sqrt{2}\\&+(1-\{S_2^-S_3^++S_2^+S_3^-\})\\&\qquad\times(S_2^+S_2^-S_3^-S_3^++S_2^-S_2^+S_3^+S_3^-)/\sqrt{2}.\end{aligned}\tag{48}$$

As a result of operating on $|\alpha\alpha\beta|$, this gives

$$O|\alpha\alpha\beta|=[2|\alpha\alpha\beta|-|\alpha\beta\alpha|-|\beta\alpha\alpha|]/\sqrt{2}.$$

This is indeed a state of $S=\frac{1}{2}$, $M_S=\frac{1}{2}$; however, it is not properly normalized. We must multiply by $3^{-\frac{1}{2}}$ to effect normalization. Let us derive this extra coefficient and set down the rules for the operation of O on any spin-product function with $M_S\neq 0$.

Suppose O operates on a spin-product function with $x\alpha$ spins and $y\beta$ spins, let us assume x is greater than y. First, the constant N in O is to be taken as equal to y. We have $x-y$ excess α spins, hence $M_S=(x-y)/2$. In the sum over i in the operator O, the number of choices of i that will give a nonvanishing result in the number of ways of choosing y electrons out of the collection of x electrons, i.e.,

$$n=x!/(x-y)!y!.\tag{49}$$

Operation with O on this spin-product function will produce n states with $S=(x-y)/2$ and $M_S=(x-y)/2$. Thus

$$O\cdot\text{spin-product}=\psi_1+\psi_2+\cdots+\psi_n=\Phi,$$

each of the ψ_i being normalized. We have $(\psi_i,\psi_i)=1$, $(\psi_i,\psi_j)=1/(N+1)$. Thus

$$\begin{aligned}(\Phi,\Phi)=\textstyle\sum_i(\psi_i,\psi_i)+2\sum_{i>j}(\psi_i,\psi_j)\\=n[1+(n-1)/(N+1)].\end{aligned}$$

Therefore, if we multiply O by $\{n[1+(n-1)/N+1)]\}^{-\frac{1}{2}}$, we will produce a normalized resultant state. We can modify the form of O given in (41) so that it can operate on any spin product function. That is,

$$\begin{aligned}O=&\frac{1}{(N+1)^{\frac{1}{2}}\{n[1+(n-1)/(N+1)]\}^{\frac{1}{2}}}\\&\times\sum_i\Bigg[1+\sum_{M=1}^{N}\frac{(-1)^M(N-M)!}{N!M!}\\&\times\{(S_{Ai}^-S_{Bi}^+)^M+(S_{Ai}^+S_{Bi}^-)^M\}\\&\prod_{jAi,kBi}^{N}(S_{jAi}^+S_{jAi}^-S_{kBi}^-S_{kBi}^+\\&\qquad\qquad+S_{jAi}^-S_{jAi}^+S_{kBi}^+S_{kBi}^-)\Bigg].\end{aligned}\tag{50}$$

This will be taken to be the final form of the operator O. We can now write down $\Psi_5(S=0)$ directly as

$$\Psi_5(S=0)=O[O|\alpha\alpha\beta|\cdot O|\alpha\beta\beta|].\tag{51}$$

THE EIGHT-ELECTRON PROBLEM

Before passing on to applications of the operator O other than the creation of the orthogonal singlets for an n-electron problem, the use of this operator may be further illustrated by writing down the fourteen orthogonal singlets for the eight-electron problem. It is to be recalled that the singlets for the six-electron problem were found by partitioning the six orbitals in the various ways suggested by the branching diagram. The construction of this diagram is not necessary in general, and we shall write down the singlets for the eight-electron case without recourse to it. The fourteen orthonormal singlets for the eight-electron problem are:

$$\Psi_1(S=0)=O|\alpha\beta|\cdot O|\alpha\beta|\cdot O|\alpha\beta|\cdot O|\alpha\beta|, \tag{52}$$

$$\Psi_2(S=0)=O|\alpha\beta|\cdot O|\alpha\alpha\alpha\beta\beta\beta|, \tag{53}$$

$$\Psi_3(S=0)=O|\alpha\alpha\alpha\beta\beta\beta|\cdot O|\alpha\beta|, \tag{54}$$

$$\Psi_4(S=0)=O|\alpha\alpha\alpha\alpha\beta\beta\beta\beta|, \tag{55}$$

$$\Psi_5(S=0)=O|\alpha\beta|\cdot O|\alpha\alpha\beta\beta|\cdot O|\alpha\beta|, \tag{56}$$

$$\Psi_6(S=0)=O|\alpha\beta|\cdot O|\alpha\beta|\cdot O|\alpha\alpha\beta\beta|, \tag{57}$$

$$\Psi_7(S=0)=O|\alpha\alpha\beta\beta|\cdot O|\alpha\beta|\cdot O|\alpha\beta|, \tag{58}$$

$$\Psi_8(S=0)=O|\alpha\alpha\beta\beta|\cdot O|\alpha\alpha\beta\beta|, \tag{59}$$

$$\Psi_9(S=0)=O[O|\alpha\alpha\alpha\beta\beta|\cdot O|\alpha\beta\beta|], \tag{60}$$

$$\Psi_{10}(S=0)=O[O|\alpha\alpha\beta|\cdot O|\alpha\alpha\beta\beta\beta|], \tag{61}$$

$$\Psi_{11}(S=0)=O[O|\alpha\alpha\beta\alpha|\cdot O|\beta\alpha\beta\beta|], \tag{62}$$

$$\Psi_{12}(S=0)=O[O|\alpha\alpha\alpha\beta|\cdot O|\alpha\beta\beta\beta|], \tag{63}$$

$$\Psi_{13}(S=0)=O[O|\alpha\alpha\beta|\cdot O|\alpha\beta\beta|]\cdot O|\alpha\beta|, \tag{64}$$

$$\Psi_{14}(S=0)=O|\alpha\beta|\cdot O[O|\alpha\alpha\beta|\cdot O|\alpha\beta\beta|], \tag{65}$$

THE TEN-ELECTRON PROBLEM

The forty-two orthogonal singlets for a ten-electron system are:

$$\Psi_1=O|\alpha\beta|\cdot O|\alpha\beta|\cdot O|\alpha\beta|\cdot O|\alpha\beta|\cdot O|\alpha\beta|, \tag{66}$$

$$\Psi_2=O|\alpha\alpha\beta\beta|\cdot O|\alpha\beta|\cdot O|\alpha\beta|\cdot O|\alpha\beta|, \tag{67}$$

$$\Psi_3=O|\alpha\beta|\cdot O|\alpha\alpha\beta\beta|\cdot O|\alpha\beta|\cdot O|\alpha\beta|, \tag{68}$$

$$\Psi_4=O|\alpha\beta|\cdot O|\alpha\beta|\cdot O|\alpha\alpha\beta\beta|\cdot O|\alpha\beta|, \tag{69}$$

$$\Psi_5=O|\alpha\beta|\cdot O|\alpha\beta|\cdot O|\alpha\beta|\cdot O|\alpha\alpha\beta\beta|, \tag{70}$$

$$\Psi_6=O|\alpha\alpha\beta\beta|\cdot O|\alpha\beta|\cdot O|\alpha\alpha\beta\beta|, \tag{71}$$

$$\Psi_7=O|\alpha\beta|\cdot O|\alpha\alpha\alpha\beta\beta\beta|\cdot O|\alpha\beta|, \tag{72}$$

$$\Psi_8=O|\alpha\alpha\beta\beta|\cdot O|\alpha\alpha\alpha\beta\beta\beta|, \tag{73}$$

$$\Psi_9=O|\alpha\alpha\alpha\beta\beta\beta|\cdot O|\alpha\alpha\beta\beta|, \tag{74}$$

$$\Psi_{10}=O[O|\alpha\alpha\beta|\cdot O|\alpha\beta\beta|]\cdot O|\alpha\beta|\cdot O|\alpha\beta|, \tag{75}$$

$$\Psi_{11}=O|\alpha\beta|\cdot O[O|\alpha\alpha\beta|\cdot O|\alpha\beta\beta|]\cdot O|\alpha\beta|, \tag{76}$$

$$\Psi_{12}=O|\alpha\beta|\cdot O|\alpha\beta|\cdot O[O|\alpha\alpha\beta|\cdot O|\alpha\beta\beta|], \tag{77}$$

$$\Psi_{13}=O|\alpha\alpha\beta\beta|\cdot O|\alpha\alpha\beta\beta|\cdot O|\alpha\beta|, \tag{78}$$

$$\Psi_{14}=O|\alpha\beta|\cdot O|\alpha\alpha\beta\beta|\cdot O|\alpha\alpha\beta\beta|, \tag{79}$$

$$\Psi_{15}=O|\alpha\alpha\alpha\alpha\beta\beta\beta\beta|\cdot O|\alpha\beta|, \tag{80}$$

$$\Psi_{16}=O|\alpha\beta|\cdot O|\alpha\alpha\alpha\alpha\beta\beta\beta\beta|, \tag{81}$$

$$\Psi_{17}=O|\alpha\alpha\alpha\beta\beta\beta|\cdot O|\alpha\beta|\cdot O|\alpha\beta|, \tag{82}$$

$$\Psi_{18}=O|\alpha\beta|\cdot O|\alpha\beta|\cdot O|\alpha\alpha\alpha\beta\beta\beta|, \tag{83}$$

$$\Psi_{19}=O|\alpha\alpha\beta\beta|\cdot O[O|\alpha\alpha\beta|\cdot O|\alpha\beta\beta|], \tag{84}$$

$$\Psi_{20}=O[O|\alpha\alpha\beta|\cdot O|\alpha\beta\beta|]\cdot O|\alpha\alpha\beta\beta|, \tag{85}$$

$$\Psi_{21}=O[O|\alpha\alpha\alpha\beta|\cdot O|\alpha\beta\beta\beta|]\cdot O|\alpha\beta|, \tag{86}$$

$$\Psi_{22}=O|\alpha\beta|\cdot O[O|\alpha\alpha\alpha\beta|\cdot O|\alpha\beta\beta\beta|], \tag{87}$$

$$\Psi_{23}=O[O|\alpha\alpha\beta|\cdot O|\alpha\alpha\beta\beta\beta|]\cdot O|\alpha\beta|, \tag{88}$$

$$\Psi_{24}=O|\alpha\beta|\cdot O[O|\alpha\alpha\beta|\cdot O|\alpha\alpha\beta\beta\beta|], \tag{89}$$

$$\Psi_{25}=O[O|\alpha\alpha\alpha\beta\beta|\cdot O|\alpha\beta\beta|]\cdot O|\alpha\beta|, \tag{90}$$

$$\Psi_{26}=O|\alpha\beta|\cdot O[O|\alpha\alpha\alpha\beta\beta|\cdot O|\alpha\beta\beta|], \tag{91}$$

$$\Psi_{27}=O|\alpha\beta|\cdot O[O|\alpha\alpha\beta\alpha|\cdot O|\beta\alpha\beta\beta|], \tag{92}$$

$$\Psi_{28}=O[O|\alpha\alpha\beta\alpha|\cdot O|\beta\alpha\beta\beta|]\cdot O|\alpha\beta|, \tag{93}$$

$$\Psi_{29}=O|\alpha\alpha\alpha\alpha\alpha\beta\beta\beta\beta\beta|, \tag{94}$$

$$\Psi_{30}=O[O|\alpha\alpha\alpha\alpha\beta|\cdot O|\alpha\beta\beta\beta\beta|], \tag{95}$$

$$\Psi_{31}=O[O|\alpha\alpha\alpha\beta|\cdot O|\alpha\alpha\beta\beta\beta\beta|], \tag{96}$$

$$\Psi_{32}=O[O|\alpha\alpha\alpha\alpha\beta\beta|\cdot O|\alpha\beta\beta\beta|], \tag{97}$$

$$\Psi_{33}=O[O|\alpha\alpha\alpha\beta\beta|\cdot O|\alpha\alpha\beta\beta\beta|], \tag{98}$$

$$\Psi_{34}=O[O|\alpha\alpha\beta|\cdot O|\alpha\alpha\alpha\beta\beta\beta\beta|], \tag{99}$$

$$\Psi_{35}=O[O|\alpha\alpha\alpha\alpha\beta\beta\beta|\cdot O|\alpha\beta\beta|], \tag{100}$$

$$\Psi_{36}=O[O|\alpha\alpha\beta\alpha\alpha|\cdot O|\beta\beta\alpha\beta\beta|], \tag{101}$$

$$\Psi_{37}=O[O|\alpha\alpha\alpha\beta\alpha\beta\beta|\cdot O|\alpha\beta\beta|], \tag{102}$$

$$\Psi_{38}=O[O|\alpha\alpha\beta|\cdot O|\alpha\alpha\beta\alpha\beta\beta\beta|], \tag{103}$$

$$\Psi_{39}=O[O|\alpha\alpha\beta\alpha\beta|\cdot O|\alpha\alpha\beta\beta\beta|], \tag{104}$$

$$\Psi_{40}=O[O|\alpha\alpha\alpha\beta\beta|\cdot O|\alpha\beta\alpha\beta\beta|], \tag{105}$$

$$\Psi_{41}=O[O|\alpha\alpha\beta\alpha\beta|\cdot O|\alpha\beta\alpha\beta\beta|], \tag{106}$$

$$\Psi_{42}=O[O|\alpha\alpha\alpha\beta\alpha|\cdot O|\beta\alpha\beta\beta\beta|]. \tag{107}$$

APPLICATIONS TO CONFIGURATION INTERACTION

Let us now turn from the consideration of how to set up the orthogonal singlets and very briefly investigate some of the aspects of a configuration interaction calculation. The determination of the expectation value of the Hamiltonian H with respect to a particular state will be considered as an example of how the spin operator O can be used. Suppose we wish to find the expectation value of H with respect to the six electron singlet given in (44), i.e., $O|\alpha\alpha\alpha\beta\beta\beta|$.

$$\begin{aligned}(\psi|H|\psi)&=[O|\alpha\alpha\alpha\beta\beta\beta|\cdot|H|\cdot O|\alpha\alpha\alpha\beta\beta\beta|]\\&=[OA(\alpha\alpha\alpha\beta\beta\beta)|H|OA(\alpha\alpha\alpha\beta\beta\beta)]\\&=[AO^2A(\alpha\alpha\alpha\beta\beta\beta)|H|(\alpha\alpha\alpha\beta\beta\beta)]\\&=(N+1)^{\frac{1}{2}}[AO(\alpha\alpha\alpha\beta\beta\beta)|H|(\alpha\alpha\alpha\beta\beta\beta)],\\(\psi|H|\psi)&=2AO(\alpha\alpha\alpha\beta\beta\beta)|H|(\alpha\alpha\alpha\beta\beta\beta).\end{aligned}\tag{108}$$

The spatial orbitals in the spin-product function $(\alpha\alpha\alpha\beta\beta\beta)$ are assumed to be orthonormal. In the expansion of $AO(\alpha\alpha\alpha\beta\beta\beta)$ the only terms which will make nonzero contributions to the matrix element are those for which a given electron is assigned the same spin on both sides of the matrix element. Therefore, we need only consider those terms in the expansion which lead to $\alpha(1)\alpha(2)\alpha(3)\beta(4)\beta(5)\beta(6)$. Let us write the antisymmetrizing operator as

$$A=\sum_P(-1)^P P^q P^\sigma.\tag{109}$$

Because of the orthogonality of the spatial orbitals in the spin-product function, the only spatial coordinate permutations in A that will give rise to nonvanishing integrals are the P^q's which effect a single interchange. When O operates on $(\alpha\alpha\alpha\beta\beta\beta)$, all those values of M in O greater than one cause two or more spin interchanges between sets A and B. Therefore, in order to match spins on both sides of H, we will need a permutation from A which is the product of at least two interchanges of spin and space coordinates. This will, therefore, lead to a zero contribution due to the spatial orthogonality. Hence the only terms that give contributions from the operator O are those from M values of zero or one. For $M=0$, we will get nonvanishing integrals from all possible interchanges of a single pair of spatial coordinates within set A or within set B. For $M=1$ in O the terms arising from the operation of O on the spin-product are all the possible single spin interchanges between sets A and B. Therefore, in order to match spins for a nonzero integral, we will need those permutations in A which put the spins back in place. But these permutations involve the interchange of a single pair of spatial coordinates between sets A and B, and will therefore give rise to exchange integrals. Let us now write down $(\psi|H|\psi)$.

$$\begin{aligned}(\psi|H|\psi)=\Bigg\{\Bigg[1-\sum_{j_A=1\neq k_A=1}^{3}\sum^{3}P_{j_Ak_A}{}^q-\sum_{j_B=4\neq k_B=4}^{6}\sum^{6}P_{j_Bk_B}{}^q\\+\frac{1}{3}\sum_{j_A=1}^{3}\sum_{k_B=4}^{6}P_{j_Ak_B}{}^q\Bigg]\varphi_1(1)\alpha(1)\varphi_2(2)\alpha(2)\varphi_3(3)\\\times\alpha(3)\varphi_4(4)\beta(4)\varphi_5(5)\beta(5)\varphi_6(6)\beta(6)\\\times|H|\varphi_1(1)\alpha(1)\varphi_2(2)\alpha(2)\cdots\varphi_6(6)\beta(6)\Bigg\}.\end{aligned}\tag{110}$$

This expression may seem complicated, but the reader will also note that this matrix element is taken with respect to a singlet state which is a linear combination of twenty determinants. This leads to the direct product of twenty determinants and contributions from 180 nonzero cross products.

This general procedure for treating matrix elements can be extended to nondiagonal matrix elements and can be generalized to systems with a rather large number of electrons.

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APPENDIX I

Theorem I

Different paths on the branching diagram terminating at the same destination lead to orthogonal states.

Proof

It is assumed that all spatial orbitals are orthonormal. A one to one correspondence exists between a determinant D and spin-product function p, and it is $D=Ap$ where A is the antisymmetrizing operator. If two spin-product functions composed of the same set of spatial orbitals differ in the assignment of spin to these spatial orbitals, then the spin-product functions, or the determinants corresponding to them, are orthogonal. It is understood that if two states of the same multiplicity are orthogonal, then the orthogonality is independent of the M_S quantum number of the states. Having made these preliminary remarks, let us proceed.

The first case in the branching diagram where one encounters two different paths leading to the same end point is for three electrons as shown in Figs. 2(a) and 2(b). The two states are

$$\Psi_{2a}=(1/\sqrt{2})\{|\alpha\beta\alpha|-|\beta\alpha\alpha|\}=(A/\sqrt{2})[(\alpha\beta\alpha)-(\beta\alpha\alpha)],$$

$$\begin{aligned}\Psi_{2b}=(1/\sqrt{6})\{2|\alpha\alpha\beta|-|\alpha\beta\alpha|-|\beta\alpha\alpha|\}\\=(A/\sqrt{6})[2(\alpha\alpha\beta)-(\alpha\beta\alpha)-(\beta\alpha\alpha)],\end{aligned}$$

where $(\alpha\beta\alpha\alpha\beta\cdots)$ will in general denote a spin-product function. Ψ_{2a} and Ψ_{2b} are orthogonal.

Let us now consider an arbitrary x-electron terminal point on the branching diagram corresponding to an arbitrary multiplicity, say S. We shall assume that all of the different paths leading to this terminal point correspond to orthogonal states of multiplicity S. It will be shown that all of the states arising from the combination of an additional electron with the various states corresponding to a given terminal point are orthogonal. It will also be shown that any two $(x+1)$-electron states of the same multiplicity which arise from the combination of the $(x+1)$st electron with x-electron states of different multiplicities are orthogonal.

Consider the addition of the $(x+1)$st electron to the ith state corresponding to the x-electron terminal point of multiplicity S which results in an $(x+1)$-electron state of $S+\frac{1}{2}$ and $M_S=S+\frac{1}{2}$. The composite state is

$$\psi_i(S+\tfrac{1}{2}, M_S=S+\tfrac{1}{2})=\varphi_i(S, M_S=S)\cdot\varphi(S=\tfrac{1}{2}, M_S=\tfrac{1}{2}),$$

where $\varphi(s=\frac{1}{2}, M_S=\frac{1}{2})$ is just $\varphi_{x+1}(x+1)\alpha(x+1)$. Now φ_i is equal to A_x operating on some linear combination of x-electron spin-product functions, where A_x antisymmetrizes a function of x coordinates. $\psi_i(S+\frac{1}{2}, S+\frac{1}{2})$ is equal to A_{x+1} operating on that same linear combination of spin-product functions each spin-product being multiplied by $\varphi_{x+1}(x+1)\alpha(x+1)$. Consider any $\psi_j(S+\frac{1}{2}, S+\frac{1}{2})$ for $j\neq i$. This is A_{x+1} operating on the linear combination of spin-product functions corresponding to $\varphi_j(S, S)$, each spin-product being multiplied by $\varphi_{x+1}(x+1)\alpha(x+1)$. $\varphi_i(S, S)$ has been assumed orthogonal to $\varphi_j(S, S)$. Therefore, $\psi_i(S+\frac{1}{2}, S+\frac{1}{2})$ is orthogonal to $\psi_j(S+\frac{1}{2}, S+\frac{1}{2})$, for the orthogonality of two linear combinations of x-electron spin-product functions is not changed when it is multiplied by $\varphi_{x+1}(x+1)\alpha(x+1)$ and operated on by A_{x+1}.

Now consider the addition of the $(x+1)$st electron to the ith state which corresponds to the x-electron terminal point at multiplicity S and which results in an $(x+1)$-electron state $\psi_i(S-\frac{1}{2}, M_S=S-\frac{1}{2})$. We have

$$\psi_i(S-\tfrac{1}{2}, M_S=S-\tfrac{1}{2})=C_1\varphi_i(S, S)\varphi(\tfrac{1}{2}, -\tfrac{1}{2})\\ +C_2\varphi_i(S, S-1)\varphi(\tfrac{1}{2}, +\tfrac{1}{2}).$$

Consider any other $\psi_j(S-\frac{1}{2}, S-\frac{1}{2})$ obtained by adding the $(x+1)$st electron to $\varphi_j(S, M_S)$. We have

$$\psi_j(S-\tfrac{1}{2}, S-\tfrac{1}{2})=C_1\varphi_j(S, S)\varphi(\tfrac{1}{2}, -\tfrac{1}{2})\\ +C_2\varphi_j(S, S-1)\varphi(\tfrac{1}{2}, +\tfrac{1}{2}).$$

Since $\varphi_j(S, S)$ is orthogonal to $\varphi_i(S, S)$ and $\varphi_j(S, S-1)$ is orthogonal to $\varphi_i(S, S-1)$, we have that $\psi_i(S-\frac{1}{2}, S-\frac{1}{2})$ is orthogonal to $\psi_j(S-\frac{1}{2}, S-\frac{1}{2})$ by the same arguments given above.

Therefore, it has been shown that all of the states arising from the combination of an additional electron with the various states corresponding to a given terminal point are orthogonal.

Suppose now that we have two $(x+1)$-electron states of the same multiplicity which arise from the combination of the $(x+1)$st electron with x-electron states of different multiplicities. Two x-electron states of different multiplicity are orthogonal. Therefore, by proceeding in the same manner as above. it is easily shown that the two $(x+1)$-electron states are orthogonal.

Therefore, the theorem is proved.

APPENDIX II

Theorem II

The spin operator O given in (49) commutes with S^2.

Proof

The operator S^2 may be expressed as

$$S^2=\text{const}+\sum_{i>j} P_{ij}^{\sigma}. \tag{A-1}$$

The commutation of S^2 and O is clearly a question of the commutation of $\sum_{i>j} P_{ij}^{\sigma}$ and O. It will be established that P_{st}^{σ} commutes with O for arbitrary s and t and therefore, that S^2 commutes with O. It has been shown that the following properties hold for P_{st}^{σ}.[6]

$$S_s^{+}P_{st}^{\sigma}=P_{st}^{\sigma}S_t^{+}, \tag{A-2}$$

$$S_s^{-}P_{st}^{\sigma}=P_{st}^{\sigma}S_t^{-}, \tag{A-3}$$

$$(S_s^{-}S_k^{+})^{M}P_{st}^{\sigma}=P_{st}^{\sigma}(S_t^{-}S_k^{+})^{M}, \tag{A-4}$$

$$(S_t^{+}S_t^{-}S_s^{+}S_s^{-})P_{st}^{\sigma}=P_{st}^{\sigma}(S_t^{+}S_t^{-}S_s^{+}S_s^{-}), \tag{A-5}$$

$$(S_t^{+}S_t^{-}S_k^{+}S_k^{-})P_{st}^{\sigma}=P_{st}^{\sigma}(S_s^{+}S_s^{-}S_k^{+}S_k^{-}). \tag{A-6}$$

We will speak here about the operation of O on a spin-product function, as this allows one to treat the electrons as being distinguishable, which is convenient. We can break down the sum over i in the operator O into two cases:

1. All choices of i for which both s and t are in the same group, i.e., A or B.
2. All of those choices of i for which s and t are in different groups, i.e. s in A and t in B.

Let us consider case 1. For (5), we have

$$(S_{sA}^{+}S_{sA}^{-}S_{tA}^{+}S_{tA}^{-})P_{st}^{\sigma}=P_{st}^{\sigma}(S_{sA}^{+}S_{sA}^{-}S_{tA}^{+}S_{tA}^{-}).$$

The expression $(S_{A_i}^{-}S_{B_i}^{+})^{M}$ consists of all possible M tuples, i.e.,

$$S_{x1A_i}^{-}S_{x2A_i}^{-}\cdots S_{xMA_i}^{-}S_{y1B_i}^{+}S_{y2B_i}^{+}\cdots S_{yMB_i}^{+}.$$

If neither S_{sA}^{-} nor S_{tA}^{-} appear in a given M tuple, then that M tuple commutes with P_{st}^{σ}. If just $S_{sA_i}^{-}$ appears, then

$$(S_{x1A_i}^{-}\cdots S_{sA_i}^{-}\cdots S_{xMA_i}^{-}S_{y1B_i}^{+}\cdots S_{yMB_i}^{+})P_{st}^{\sigma}\\ =P_{st}^{\sigma}(S_{x1A_i}^{-}\cdots S_{tA_i}^{-}\cdots S_{xMA_i}^{-}S_{y1B_i}^{+}\cdots S_{yMB_i}^{+}).$$

Therefore, the sum of the two M tuples, one with just $S_{sA_i}^{-}$ and the other with $S_{tA_i}^{-}$ in place of $S_{sA_i}^{-}$ but otherwise identical, commutes with P_{st}^{σ}. Hence P_{st}^{σ} commutes with the sum of all possible M tuples which contain either $S_{sA_i}^{-}$ or $S_{tA_i}^{-}$ but not both at the same time. If both $S_{sA_i}^{-}$ and $S_{tA_i}^{-}$ appear in an M tuple, then P_{st}^{σ} commutes with that M tuple. Therefore, it follows that P_{st}^{σ} commutes with all O_i in which both s and t are in the same group.

Let us now consider case 2. We can easily show that

$$(S_{sA}^{+}S_{sA}^{-}S_{tB}^{-}S_{tB}^{+})P_{st}^{\sigma}=P_{st}^{\sigma}(S_{tA}^{+}S_{tA}^{-}S_{sB}^{-}S_{sB}^{+}).$$

Therefore,

$$(S_{sA}^{+}S_{sA}^{-}S_{tB}^{-}S_{tB}^{+}+S_{tA}^{+}S_{tA}^{-}S_{sB}^{-}S_{sB}^{+})P_{st}^{\sigma}\\ =P_{st}^{\sigma}(S_{sA}^{+}S_{sA}^{-}S_{tB}^{-}S_{tB}^{+}+S_{tA}^{+}S_{tA}^{-}S_{sB}^{-}S_{sB}^{+}).$$

As in case 1, we can examine all of the M tuples which

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[6] P. Dirac, *Quantum Mechanics* (Oxford University Press, London, 1947), p. 222.

appear in the expansion of O, those where neither s nor t occur, those where one or the other occur, and those where both s and t appear. In quite the same way as in case 1, it can be shown that $P_{st}{}^{\sigma}$ commutes with the collection of all possible M tuples.

Therefore, in this fashion one can show that $P_{st}{}^{\sigma}$ commutes with O, which implies that S^2 commutes with O.

APPENDIX III

Theorem III

The spin operator O is Hermitian.

Proof

Every term in O appears symmetrically with its hermitian conjugate. Therefore, O is Hermitian.

Theorem IV

The spin operator O commutes with the Hamiltonian H.

Proof

This is a matter of restricting ourselves to spin-free Hamiltonians.

Theorem V

The spin operator O squared is

$$(N+1)^{\frac{1}{2}}\{n[1+(n-1)/(n+1)]\}^{\frac{1}{2}}O.$$

Proof

It will be shown first that $O^2=\text{const}\cdot O$. The value of the constant will be determined later. We shall consider an N-electron problem and the effect of O^2 operating on a single $N\times N$ determinant D_0, the generalization of O^2 operating on any linear combination of $N\times N$ determinants being trivial.

Let OD_0 be written as

$$\begin{aligned}OD_0=C_0D_0+C_1\{D_1{}^{(1)}+D_2{}^{(1)}+\cdots+D_{X^2}{}^{(1)}\}\\ +C_2\{D_1{}^{(2)}+D_2{}^{(2)}+D_3{}^{(2)}+\cdots D_{X(X-1)/2}{}^{(2)}\\ +\cdots+C_XD_1{}^{(X)}.\end{aligned}$$

where, in $D_k{}^{(j)}$, j refers to the number of reversals in set A or B and k denotes the kth determinant with j reversals. Let us now order these determinants such that

$$D_1{}^{(1)}=P_{1A1B}{}^{\sigma}D_0\cdots D_{X^2}{}^{(1)}=P_{XAXB}{}^{\sigma}D_0,$$
$$D_1{}^{(2)}=P_{1A1B}{}^{\sigma}P_{2A2B}{}^{\sigma}D_0,\ D_2{}^{(2)}=P_{1A1B}{}^{\sigma}P_{2A3B}{}^{\sigma}D_0,\ \cdots,$$

and so forth.

Let us consider O^2D_0 term by term. The first term is just C_0OD_0. The second term may be written

$$C_1O\{P_{1A1B}{}^{\sigma}+P_{1A2B}{}^{\sigma}+\cdots+P_{XAXB}{}^{\sigma}\}D_0.$$

In Appendix II it was shown that any $P_{st}{}^{\sigma}$ commutes with O. Therefore, the second term can be expressed as

$$C_1\{P_{1A1B}{}^{\sigma}+P_{1A2B}{}^{\sigma}+\cdots+P_{XAXB}{}^{\sigma}\}OD_0.$$

We know that OD_0 is an eigenfunction of S^2 which is

$$S^2=\text{const}+\sum_{i>j}P_{ij}{}^{\sigma}.$$

Thus

$$\sum_{i>j}P_{ij}{}^{\sigma}(OD_0)=\text{const}OD_0.$$

We can write $\sum_{i>j}P_{ij}{}^{\sigma}$ as

$$\sum_{i>j}P_{ij}{}^{\sigma}=\sum_{j_A>k_A}P_{j_Ak_A}{}^{\sigma}+\sum_{j_B>k_B}P_{j_Bk_B}{}^{\sigma}+\sum_{j_Ak_B}P_{j_Ak_B}{}^{\sigma}.$$

Since $P_{j_Ak_A}{}^{\sigma}$ and $P_{j_Bk_B}{}^{\sigma}$ commute with O and since they leave D_0 invariant, we have

$$\sum_{j_Ak_B}P_{j_Ak_B}{}^{\sigma}(OD_0)=\text{const}OD_0.$$

However, the second term in O^2D_0 is just

$$C_1[\sum_{j_Ak_B}P_{j_Ak_B}{}^{\sigma}]OD_0,$$

and is, therefore, a constant times OD_0.

The third term can be written as

$$C_2[\sum_{j_Ak_B}\sum_{s_At_B}P_{j_Ak_B}{}^{\sigma}P_{s_At_B}{}^{\sigma}]OD_0.$$

However, we see from

$$[\sum_{j_Ak_B}P_{j_Ak_B}{}^{\sigma}]OD_0=\text{const}OD_0,$$

that

$$[\sum_{j_Ak_B}P_{j_Ak_B}{}^{\sigma}]^2OD_0=[\sum_{j_Ak_B}P_{j_Ak_B}{}^{\sigma}\sum_{s_At_B}P_{s_At_B}{}^{\sigma}]OD_0.$$

Hence, the third term in O^2D_0 is just a constant times OD_0. Proceeding in this manner it is clear that

$$O^2D_0=\text{const}OD_0.$$

Now let

$$OD_i=\psi_i.$$

We have

$$(\psi_i,\psi_i)=(OD_i,OD_i)=(O^2D_i,D_i)=\text{const}(OD_i,D_i)=1.$$

However,

$$OD_i=\frac{1}{(N+1)^{\frac{1}{2}}\{n[1+(n-1)/(N+1)]\}^{\frac{1}{2}}}D_i$$
$$+\text{orthogonal } D_j\text{'s}.$$

Therefore,

$$\text{const}\left[(N+1)^{-\frac{1}{2}}\left\{n\left(1+\frac{n-1}{N+1}\right)\right\}^{-\frac{1}{2}}\right](D_i,D_i)=1,$$

and

$$\mathrm{const}=\left[(N+1)^{\frac{1}{2}}\left\{n\left(1+\frac{n-1}{N+1}\right)\right\}^{\frac{1}{2}}\right];$$

so

$$O^2=\left[(N+1)^{\frac{1}{2}}\left\{n\left(1+\frac{n-1}{N+1}\right)\right\}^{\frac{1}{2}}\right]O.$$

APPENDIX IV

Theorem VI

The spin operator O commutes with the antisymmetrizing operator A.

Proof

The antisymmetrizing operator A can be written as

$$A=\sum_P(-1)^P P^q P^\sigma,$$

where P^q is a permutation of the spatial coordinates and P^σ is a permutation of the spin coordinates. Any spatial permutation operator clearly commutes with O. Any spin permutation operator can be written as a product of $P_{ij}{}^\sigma$'s. But, any $P_{ij}{}^\sigma$ commutes with O. Therefore, any spin permutation operator commutes with O. Hence every permutation in A commutes with O, which implies that A commutes with O.

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The 1.25-Minute Rb^{82m} Daughter of 27-Day Sr^{82}

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The 3.15-Mev positron associated with the decay of the 27-day Sr^{82} has been found to arise from the decay of a 1.25-minute metastable Rb^{82} isomer by an allowed transition to the Kr^{82} ground state. No isomeric transition to the 6.3-hour Rb^{82} ground state was observed. A tentative decay scheme and spin and parity assignments are discussed.

INTRODUCTION

The 27-day Sr^{82} was observed to have a positron radiation of 3.15 Mev.[1,2] Castner and Templeton suggested this radiation was due to a short-lived Rb daughter because of its high energy. However, they were unable to find this Rb isotope because of the time required for the chemical separation used. Also, they established that the 6.3-hour Rb^{82} was not the daughter of the 27-day Sr^{82}.

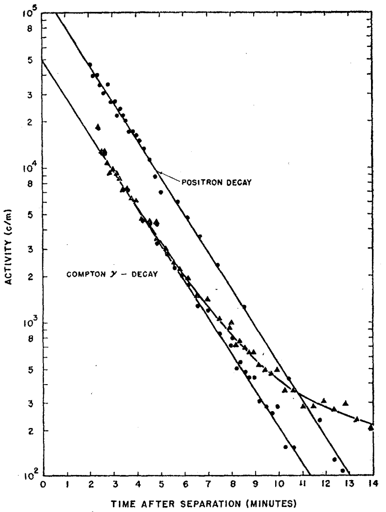

FIG. 1. Positron and Compton γ decay of Rb^{82m}.

It was the purpose of this work to clarify the decay scheme. The pertinent results have been published in Hollander, Perlman, and Seaborg's revised Table of Isotopes.[3]

PROCEDURE

Chemical Separation

Purified strontium fractions containing the 27-day Sr^{82} were prepared from target materials containing either strontium or zirconium which had been bombarded with 350-Mev protons or 190-Mev deuterons on the University of California's 184-in. cyclotron. Fuming nitric acid precipitations of $\mathrm{Sr(NO_3)_2}$ followed by cation resin adsorption and elution of the strontium fraction was used for this purification. Holdback agents were used to keep the preparation free of the other spallation products.

The purified strontium fraction was allowed to stand to insure adequate growth of any daughter activity of several hours half-life. Perchloric acid, strontium, and rubidium carrier were added and the solution boiled to fuming. After cooling to ice temperature, the rubidium perchlorate was precipitated by rapid addition of chilled

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[1] S. V. Castner and D. H. Templeton, Phys. Rev. 88, 1126 (1952); S. V. Castner, M.S. thesis, University of California Radiation Laboratory Unclassified Report UCRL-942, October, 1950 (unpublished).

[2] K. C. Maclure, Ph.D. thesis, McGill University, September, 1952 (unpublished).

[3] Hollander, Perlman, and Seaborg, Revs. Modern Phys. 25, 469 (1953).