

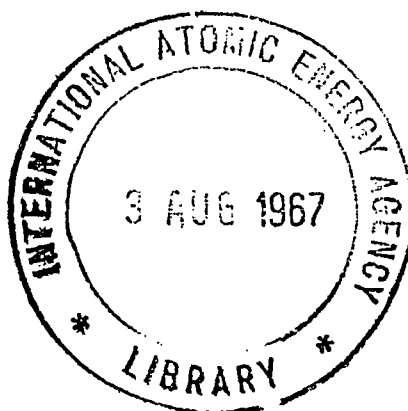


**AUSTRALIAN ATOMIC ENERGY COMMISSION**  
**RESEARCH ESTABLISHMENT**  
**LUCAS HEIGHTS**

**SUM RULES IN THE GEMINAL EXPANSION OF  
MANY-ELECTRON WAVEFUNCTIONS**

by

**R.J.C. BROWN**



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ABSTRACT

An interpretation of certain sum rules in the method of Bopp is given in terms of the irreducible representations of the rotation group. It is accompanied by a simple numerical table, from which the sum rules may be obtained by inspection.

It has been shown<sup>\*</sup> that a useful approach to the wavefunction  $\Psi$  of an  $N$ -electron system is to expand it in terms of the geminal eigenfunctions  $\Phi_n$  of a certain two-electron operator, the reduced Hamiltonian; the expansion:

$$\Psi (123\dots N) = \sum_n \Phi_n (12) F_n (3\dots N)$$

leads to a simple result for the expectation value of the energy:

$$\langle E \rangle = \frac{1}{2}N \sum_n b_{nn} \epsilon_n, \quad \dots(1)$$

where  $\epsilon_n$  are the eigenvalues of the reduced Hamiltonian and  $b_{nn} = \langle F_n | F_n \rangle$ . If spin-orbit interactions are neglected, the eigenfunctions  $\Phi_n$  may be classified as singlets or triplets and the corresponding  $b_{nn}$  are written  $b_{nn}^{(0)}$  or  $b_{nn}^{(1)}$  respectively. Grimley and Peat (1965) used the reduced spin operator to show that the following sum rules are obeyed for an antisymmetric  $N$ -electron wavefunction of total spin  $S$ :

$$\sum_n b_{nn}^{(0)} = \frac{N(N+2) - 4S(S+1)}{4N(N-1)} \quad \dots(2)$$

$$\sum_n b_{nn}^{(1)} = \frac{3N(N-2) + 4S(S+1)}{4N(N-1)} \quad \dots(3)$$

These sum rules have a close relationship with the group theoretical description of the spin angular momentum. The present note demonstrates this relationship.

Let  $\underline{D}(N) = \underline{D}^{(\frac{1}{2})} \otimes \underline{D}^{(\frac{1}{2})} \otimes \dots \otimes \underline{D}^{(\frac{1}{2})}$  be the reducible representation (Messiah 1962) of the rotation group formed by taking the tensor product of  $N$  irreducible representations  $\underline{D}^{(\frac{1}{2})}$ . Denote by  $a_N^{(S)}$  the number of times the irreducible representation  $\underline{D}^{(S)}$  occurs in  $\underline{D}(N)$  so that:

$$\underline{D}(N) \approx \sum_S a_N^{(S)} \underline{D}^{(S)}$$

The numbers  $a_N^{(S)}$  are obtained in the following way. Since  $\underline{D}(N+1) = \underline{D}(N) \otimes \underline{D}^{(\frac{1}{2})}$  the recursion relations:

\* Bopp 1959, Grimley 1964, Patterson and Anderson 1965, Grimley and Peat 1965, Peat and Brown 1966.

$$a_{N+1}^{(0)} = a_N^{(\frac{1}{2})}$$

and

$$a_{N+1}^{(S)} = a_N^{(S-\frac{1}{2})} + a_N^{(S+\frac{1}{2})}$$

$$(S \geq \frac{1}{2})$$

.....(4)

are satisfied, together with the initial condition  $a_1^{(\frac{1}{2})} = 1$ . These relations allow construction of the accompanying table of values of  $a_N^{(S)}$ . As defined above,  $a_N^{(S)}$  is the number of orthogonal spin states  $|SM_S \lambda\rangle$  which can be formed with  $N$  spins of  $\frac{1}{2}$ ; alternatively,  $a_N^{(S)}$  is the number of distinct ways of proceeding from the entry  $(1, \frac{1}{2})$  to the entry  $(N, S)$  in the table by diagonal steps to the right. Inspection of the table shows that  $a_N^{(S)}$  is closely related to binomial coefficients, and can be expressed as:

$$a_N^{(S)} = \binom{N-1}{\frac{1}{2}N-S} - \binom{N-1}{\frac{1}{2}N-S-2}$$

$$= \frac{N! (2S+1)}{(\frac{1}{2}N-S)! (\frac{1}{2}N+S+1)!} \quad \text{.....(5)}$$

for  $S = \frac{1}{2}N, \frac{1}{2}N-1, \frac{1}{2}N-2, \dots, (\frac{1}{2} \text{ or } 0)$ ,

and  $a_N^{(S)} = 0$  in all other cases.

As a check, it is noted that:

$$\sum_S (2S+1) a_N^{(S)} = 2^N, \quad \text{.....(6)}$$

which may be proved by induction using the recursion relations (4). Hence the listing of states provided by the Table exhausts the spin states which may be formed from  $N$  spins of  $\frac{1}{2}$ .

The connection between the  $a_N^{(S)}$  and the sum rules is given by:

$$\sum_n b_{nn}^{(0)} = \frac{a_{N-2}^{(S)}}{a_N^{(S)}}, \quad \text{.....(7)}$$

which may be verified using Equations 2 and 5. This purely algebraic result can be interpreted by partial reduction of  $\underline{D}(N)$ , corresponding to the expansion of the total wavefunction  $\Psi$  in terms of the geminals  $\Phi_n$ . Thus:

$$\underline{D}(N) \approx (\underline{D}^{(0)} + \underline{D}^{(1)}) \otimes \underline{D}(N-2)$$

$$\approx \underline{D}(N-2) + \underline{D}^{(1)} \otimes \underline{D}(N-2)$$

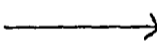
Among the  $a_N^{(S)}$  states  $|SM_S \lambda\rangle$  there are  $a_{N-2}^{(S)}$  states which are obtained by coupling a singlet geminal with the states of the remaining  $N-2$  electrons. The total weight of the singlet geminal states in Equation 1,  $\sum b_{nn}^{(0)}$ , is equal to the fraction of all the spin states which are formed from singlet geminal spin states.

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TABLE 1. VALUES OF  $a_N^{(s)}$

4	.	.	.	.	.	.	.	1
7/2	.	.	.	.	.	.	1	.
3	.	.	.	.	.	1	.	7
5/2	.	.	.	.	1	.	6	.
2	.	.	.	1	.	5	.	20
3/2	.	.	1	.	4	.	14	.
1	.	1	.	3	.	9	.	28
1/2	1	.	2	.	5	.	14	.
0	.	1	.	2	.	5	.	14
	1	2	3	4	5	6	7	8

  
 N