AAEC/TM382

AAEC/TM382

AUSTRALIAN ATOMIC ENERGY COMMISSION
RESEARCH ESTABLISHMENT
LUCAS HEIGHTS

SUM RULES IN THE GEMINAL EXPANSION OF MANY-ELECTRON WAVEFUNCTIONS

by

R.J.C. BROWN

April 1967

AUSTRALIAN ATOMIC ENERGY COMMISSION
RESEARCH ESTABLISHMENT
LUCAS HEIGHTS

SUM RULES IN THE GEMINAL EXPANSION OF MANY-ELECTRON WAVEFUNCTIONS

by

R. J. C. BROWN

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[*] that a useful approach to the wavefunction Ψ of an N-electron system is to expand it in terms of the geminal eigenfunctions Φ_n of a certain two-electron operator, the reduced Hamiltonian; the expansion:

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

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

$$< E > \ = \ \tfrac{1}{2}N \ \sum_n \ b_{nn}\ \epsilon_n \qquad , \qquad \ldots\ldots(1)$$

where ϵ_n are the eigenvalues of the reduced Hamiltonian and $b_{nn} = \ < F_n | F_n >$. If spin-orbit interactions are neglected, the eigenfunctions Φ_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:

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

$$\Sigma\ b_{nn}^{(1)} \ = \ \frac{3N(N-2)\ +\ 4S(S+1)}{4N(N-1)} \quad . \qquad \ldots\ldots(3)$$

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

Let $\underline{D}\ (N) = \underline{D}^{(\frac{1}{2})} \otimes \underline{D}^{(\frac{1}{2})} \otimes \ldots\ldots \otimes \underline{D}^{\ (\frac{1}{2})}$ 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:

$$\underline{D}\ (N) \ \simeq \ \sum_S \ a_N^{(S)}\ \underline{D}^{\ (S)} \qquad .$$

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

---

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

$$\left.\begin{aligned} a^{(0)}_{N+1} &= a^{(\frac{1}{2})}_{N} \\ \text{and} \\ a^{(S)}_{N+1} &= a^{(S-\frac{1}{2})}_{N} + a^{(S+\frac{1}{2})}_{N} \qquad (S \geqq \tfrac{1}{2}) \end{aligned}\right\} \quad .....(4)$$

are satisfied, together with the initial condition $a^{(\frac{1}{2})}_{1} = 1$. These relations allow construction of the accompanying table of values of $a^{(S)}_{N}$. As defined above, $a^{(S)}_{N}$ is the number of orthogonal spin states $|SM_s\lambda>$ which can be formed with N spins of $\frac{1}{2}$; alternatively, $a^{(S)}_{N}$ 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 $a^{(S)}_{N}$ is closely related to binomial coefficients, and can be expressed as:

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

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

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

and $a^{(S)}_{N} = 0$ in all other cases.

As a check, it is noted that:

$$\sum_{S} (2S+1)\, a^{(S)}_{N} = 2^{N} \quad , \quad .....(6)$$

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 $a^{(S)}_{N}$ and the sum rules is given by:

$$\sum_{n} b^{(0)}_{nn} = \frac{a^{(S)}_{N-2}}{a^{(S)}_{N}} \quad , \quad .....(7)$$

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 Ψ in terms of the geminals Φ_n . Thus:

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

$$\simeq \underline{D}\ (N-2) + \underline{D}^{(1)} \otimes \underline{D}\ (N-2) \quad .$$

Among the $a^{(S)}_{N}$ states $|SM_s\lambda>$ there are $a^{(S)}_{N-2}$ 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, $\Sigma\, b^{(0)}_{nn}$, is equal to the fraction of all the spin states which are formed from singlet geminal spin states.

REFERENCES

Bopp, F. (1959). - Z. Phys. 156 : 348.

Grimley, T. B. (1964). - Proc. Phys. Soc. 84 : 178.

Grimley, T. B., and Peat, F. D. (1965). - Proc. Phys. Soc. 86 : 249.

Messiah, A. (1962). - Quantum Mechanics, Appendix D. North-Holland, Amsterdam.

Patterson, J. D., and Anderson, R. K. (1965). - Proc. Soc. 85 : 41.

Peat, F. D., and Brown, R. J. C. (1966). - Can. J. Phys. 44 : 1349.

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

(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
N	1	2	3	4	5	6	7	8