

## MANY-ELECTRON WAVE FUNCTIONS

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## ABSTRACT

If it is possible to describe the state of an atom by the addition of several vectors, and if one assumes the wave function for any state of a configuration to be a linear combination of product functions for that configuration, then one can determine the coefficients in the linear combination by a simple method. Examples are given. The usual interval formula is not applicable for  $2p^3$ , where nonsplitting is the case.

## INTRODUCTION

IN A previous paper,<sup>1</sup> the writer has investigated, for two equivalent  $2p$  electrons, the stages between ( $ls$ ), or Russell-Saunders, coupling and ( $jj$ ) coupling. As a zeroth approximation, the wave functions for the intermediate case were assumed to be linear combinations of product functions associated with  $2p^2$ . The secular equation could be solved rather readily when the functions used to determine its matrix elements were those linear combinations associated with the various terms (such as  ${}^3P_2$ ) of Russell-Saunders coupling. Such linear combinations were found by solving an appropriate secular equation. The purpose of the present paper is to call attention to an apparently little-known method which enables one to write down these linear combinations directly.

1. If there exist two independent states  $\psi_{m_A}^A$  and  $\psi_{m_B}^B$ , which may be represented by vectors  $A$  and  $B$  with projections  $m_A$  and  $m_B$  respectively, then the total system may be written as  $\psi_{m_A}^A \psi_{m_B}^B$ . If the two vectors combine to form a resultant vector  $C$  with projection  $m_C$ , then this state will have the form  $\psi_{m_C}^C = \sum_{m_A m_B} S_{C m_A m_B}^{A B} \psi_{m_A}^A \psi_{m_B}^B$ , where  $m_A + m_B = m_C$ . The coefficients  $S_{C m_A m_B}^{A B}$  are known,<sup>2</sup> at least if we restrict the quantum numbers to integral and half-integral values. If  $\psi_{m_A}^A$  refer to electrons 1 and 2, and  $\psi_{m_B}^B$  to electron 3, the resulting function will not be antisymmetric with respect to interchange of any two electrons, in general, and determinant wave functions must be constructed.

For convenience, the coefficients for  $B = \frac{1}{2}$  and  $B = 1$  are listed.

TABLE I.  $S_{C m_A m_B}^{A \frac{1}{2}}$ 

$C$	$m_B = -\frac{1}{2}$	$m_B = \frac{1}{2}$
$A - \frac{1}{2}$	$\left(\frac{A + m_C + \frac{1}{2}}{2A + 1}\right)^{1/2}$	$-\left(\frac{A - m_C + \frac{1}{2}}{2A + 1}\right)^{1/2}$
$A + \frac{1}{2}$	$\left(\frac{A - m_C + \frac{1}{2}}{2A + 1}\right)^{1/2}$	$\left(\frac{A + m_C + \frac{1}{2}}{2A + 1}\right)^{1/2}$

<sup>1</sup> J. H. Bartlett, Jr., Phys. Rev. **34**, 1252 (1929). See also Phys. Rev. **35**, 229 (1930).

<sup>2</sup> E. Wigner, Gruppentheorie (Vieweg, 1931) S. 206.

TABLE II.  $S_{C m_A m_B}^{A_1}$ 

$C$	$m_B = -1$	$m_B = 0$	$m_B = 1$
$A-1$	$\left[ \frac{(A+m_C)(A+m_C+1)}{2A(2A+1)} \right]^{1/2}$	$-\left[ \frac{(A+m_C)(A-m_C)}{A(2A+1)} \right]^{1/2}$	$\left[ \frac{(A-m_C+1)(A-m_C)}{2A(2A+1)} \right]^{1/2}$
$A$	$\left[ \frac{(A-m_C)(A+m_C+1)}{2A(A+1)} \right]^{1/2}$	$\frac{m_C}{[A(A+1)]^{1/2}}$	$-\left[ \frac{(A-m_C+1)(A+m_C)}{2A(A+1)} \right]^{1/2}$
$A+1$	$\left[ \frac{(A-m_C)(A-m_C+1)}{(2A+1)(2A+2)} \right]^{1/2}$	$\left[ \frac{(A+m_C+1)(A-m_C+1)}{(2A+1)(A+1)} \right]^{1/2}$	$\left[ \frac{(A+m_C+1)(A+m_C)}{(2A+1)(2A+2)} \right]^{1/2}$

Table II has been given in a different form by Wigner.<sup>3</sup> The form above seems to be handier and more symmetrical.

2. A simple example is that of two equivalent  $p$  electrons. Let the wave function  $\psi_{m_A}^{(1)}\psi_{m_B}^{(2)}$  be denoted by  $(m_A, m_B)$ . We shall determine the space function by combining the  $l$ -vectors, and the spin function by combining the  $s$ -vectors. The product of these two functions will then be represented by a vector  $L$  and a vector  $S$ , together with their projections  $m_L$  and  $m_S$ . It will be a linear combination of individual product functions and need not have the required antisymmetry property. If, however, we replace each individual product function by the corresponding determinant, the linear combination of these determinants will be our required function. In the case of two electrons,  $S_1 = \frac{1}{2}$  and  $S_2 = \frac{1}{2}$ , resulting in wave functions symmetric or antisymmetric in the spins. The space factor turns out likewise, and so we do not need to introduce determinant functions. This is only a special case, however.

The space factors for  $2p^2$ ,  $m_l = 0$  follow:<sup>4</sup>

$$S: \left(\frac{1}{3}\right)^{1/2} \{ (1, -1) - (0, 0) + (-1, 1) \}$$

$$D: \left(\frac{1}{6}\right)^{1/2} \{ (1, -1) + 2(0, 0) + (-1, 1) \}$$

$$P: \left(\frac{1}{2}\right)^{1/2} \{ (1, -1) - (-1, 1) \}.$$

Since these are either symmetric or antisymmetric in the two electrons, it is only necessary to multiply by the appropriate spin factor to obtain a wave function which is antisymmetric.

$$\text{For } m_l = 1, \quad P: \left(\frac{1}{2}\right)^{1/2} \{ (1, 0) - (0, 1) \}$$

$$D: \left(\frac{1}{2}\right)^{1/2} \{ (1, 0) + (0, 1) \}.$$

$$\text{For } m_l = -1, \quad P: \left(\frac{1}{2}\right)^{1/2} \{ (0, -1) - (-1, 0) \}$$

$$D: \left(\frac{1}{2}\right)^{1/2} \{ (0, -1) + (-1, 0) \}.$$

The spin functions are:

$$s = 0 : \left(\frac{1}{2}\right)^{1/2} \{ \alpha(1)\beta(2) - \alpha(2)\beta(1) \}$$

<sup>3</sup> E. Wigner, Gruppentheorie, p. 208.

<sup>4</sup> These functions agree with those in the previous paper, reference 1.

$$s = 1 \begin{cases} m_s = 1: \alpha(1)\alpha(2) \\ m_s = 0: (\frac{1}{2})^{1/2} \{ \alpha(1)\beta(2) + \alpha(2)\beta(1) \} \\ m_s = -1: \beta(1)\beta(2). \end{cases}$$

$\alpha(1)$  denotes that function of electron 1 corresponding to  $m_s = \frac{1}{2}$ , and  $\beta(1)$  corresponds to  $m_s = -\frac{1}{2}$ .

If now, we wish the functions for  ${}^3P, j=0, 1, \text{ and } 2$ , then the coefficients  $S^1_{j^1 m_l m_s}$  are what are required. For  $m=0$  (and for the other values of  $m$  also) the form of the wave function is the same as for  $m_l=0$  above,<sup>4</sup> i.e.:

$${}^3P_0: (\frac{1}{3})^{1/2} \{ (1, -1) - (0, 0) + (-1, 1) \}.$$

The parentheses refer here to  $m_l$  and  $m_s$  however, instead of to  $m_{l_1}$  and  $m_{l_2}$ .

3. A more complicated example is furnished by the configuration  $2p^3$  which has for terms  ${}^2P, {}^2D, \text{ and } {}^4S$ . When there are three electrons described by vectors  $l_1, l_2, l_3$  and  $s_1, s_2, s_3$  then we may suppose the resultant of  $l_1$  and  $l_2$  to be  $\bar{l}$  and that of  $s_1$  and  $s_2$  to be  $\bar{s}$ . The total wave function characteristic of a state  $(l, s, m_l, m_s)$  may be written as

$$\sum_p (-)^{i_p} P \psi_{m_l}^l \psi_{m_s}^s = \sum s_l(\bar{l} l_3; \bar{m}_l m_{l_3}) s_s(\bar{s} s_3; \bar{m}_s m_{s_3}) \sum (-)^{i_p} P [s_l(l_1 l_2; m_{l_1} m_{l_2}) s_s(s_1 s_2; m_{s_1} m_{s_2}) \psi(l_1 s_1; m_{l_1} m_{s_1}/1) \psi(l_2 s_2; m_{l_2} m_{s_2}/2) \psi(l_3 s_3; m_{l_3} m_{s_3}/3)]$$

where  $P$  is a permutation of (123) and  $i_p$  its order. Thus we may proceed from determinant wave functions for two electrons, if it proves to be convenient. If we try to build up the  ${}^2D_{5/2}, m_l=2$  from  $2p^2 {}^1D_2$  and  $2p$  then the functions for  ${}^1D$  are:

$$\begin{aligned} m_l = 2 & \quad (\frac{1}{2})^{1/2} | \alpha^1(1)\beta^1(2) | \\ m_l = 1 & \quad (\frac{1}{2}) \{ | \alpha^1(1)\beta^0(2) | - | \alpha^0(1)\beta^1(2) | \}. \end{aligned}$$

For  $2p$ ,

$$\begin{aligned} m_l = 0 & \quad \alpha^0(3) \\ m_l = 1 & \quad \alpha^1(3) \end{aligned}$$

(where the superscripts now denote the magnetic quantum number).

The only possible function for  ${}^2D_{5/2}, m_l=2$  is then  $(1/6)^{1/2} | \alpha^1(1)\beta^1(2)\alpha^0(3) |$ . One does not need to resort to the vector addition method to deduce this result.

For  $j=3/2, m=3/2$  there are three possible states, namely  ${}^2D, {}^2P, \text{ and } {}^4S$ . The  ${}^2D$  may be considered as arising from  $2p {}^3P$  and  $2p$ , or else from  $2p^2 {}^1D$  and  $2p$ . The same wave function is obtained in either case, which seems at first surprising because the  ${}^1D$  and  ${}^3P$  terms have not the same energy. But if we consider that the added electron is equivalent to the other two, the reason is apparent. If a nonequivalent  $p$  electron should be added, then we should obtain two  ${}^2D$  terms with different energies.

For  $2p^3$  some of the wave functions follow:

$${}^2D: m_l = 1, m_s = \frac{1}{2}: (1/12)^{1/2} \{ |\beta^1(1)\alpha^{-1}(2)\alpha'(3)| - |\beta^0(1)\alpha^1(2)\alpha^0(3)| \}$$

$$m_l = 0, m_s = \frac{1}{2}: (1/6) \{ |\beta^1(1)\alpha^{-1}(2)\alpha^0(3)| + 2 |\beta^0(1)\alpha^{-1}(2)\alpha^1(3)|$$

$$+ |\beta^{-1}(1)\alpha^0(2)\alpha^1(3)| \}$$

$${}^2P: m_l = 1, m_s = \frac{1}{2}: (1/12)^{1/2} \{ |\beta^1(1)\alpha^{-1}(2)\alpha^1(3)| + |\beta^0(1)\alpha^1(2)\alpha^0(3)| \}$$

$$m_l = 0, m_s = \frac{1}{2}: (1/12)^{1/2} \{ |\beta^1(1)\alpha^{-1}(2)\alpha^0(3)| + |\beta^{-1}(1)\alpha^1(2)\alpha^0(3)| \}$$

$${}^4S: m_l = 0, m_s = 3/2: (1/6)^{1/2} |\alpha^1(1)\alpha^0(2)\alpha^{-1}(3)|$$

$$m_l = 0, m_s = \frac{1}{2}: (1/18)^{1/2} \{ |\beta^{-1}(1)\alpha^1(2)\alpha^0(3)| + |\beta^0(1)\alpha^{-1}(2)\alpha^1(3)|$$

$$+ |\beta^1(1)\alpha^0(2)\alpha^{-1}(3)| \}$$

$${}^2D_{3/2}, m = 3/2: (1/6)^{1/2} \{ (4/5)^{1/2} |\alpha^1(1)\beta^1(2)\beta^0(3)| - (1/10)^{1/2} |\alpha^1(1)\beta^1(2)\alpha^{-1}(3)|$$

$$+ (1/10)^{1/2} |\beta^0(1)\alpha^1(2)\alpha^0(3)| \}$$

$${}^2P_{3/2}, m = 3/2: (1/12)^{1/2} \{ |\alpha^1(1)\beta^1(2)\alpha^{-1}(3)| + |\alpha^0(1)\beta^0(2)\alpha^1(3)| \}.$$

4. Suppose now, to verify the correctness of the linear combinations, that we calculate the energy levels of  $2p^3$ ,  $j=3/2$ , for ( $jj$ ) coupling. This necessitates finding the matrix elements of  $(l \cdot s)_1 + (l \cdot s)_2 + (l \cdot s)_3$ . Given two determinantal wave functions  $|n_1(1) n_2(2) n_3(3)|$  and  $|n_1'(1) n_2'(2) n_3'(3)|$ , then the matrix elements will not vanish only when not more than one of the  $n$ 's is different from an  $n'$ . If  $n_1 = n_1'$ ,  $n_2 = n_2'$  and  $n_3 \neq n_3'$ , the matrix element is  $(n_3 | l \cdot s | n_3')$ . If  $n_3 = n_3'$ , the matrix element is  $(n_1 | l \cdot s | n_1') + (n_2 | l \cdot s | n_2') + (n_3 | l \cdot s | n_3')$ .

The matrix elements of  $(l \cdot s)$  are:<sup>5</sup>

$$(m_s, m_l | l \cdot s | m_s, m_l) = \lambda m_s m_l$$

$$(\alpha, m_l | l \cdot s | \beta, m_l + 1) = (\lambda/2) [l(l+1) - m_l(m_l + 1)]^{1/2}$$

$$(\beta, m_l | l \cdot s | \alpha, m_l - 1) = (\lambda/2) [l(l+1) - m_l(m_l - 1)]^{1/2}.$$

The secular equation is then:

$$\begin{vmatrix} -\epsilon & (5/4)^{1/2} & 0 \\ (5/4)^{1/2} & -\epsilon & 1 \\ 0 & 1 & -\epsilon \end{vmatrix} = 0.$$

The roots are  $\epsilon=0$  and  $\pm 3/2$ , agreeing with what one would expect from elementary considerations. When the electrostatic interaction is not negligible, then one must solve the cubic equation by applying the well-known formulae.

It is seen that the diagonal terms in the matrix of  $(l \cdot s)$  are zero, which means that the  ${}^2P$  and  ${}^2D$  of  $2p^3$  do not split up, as is the case<sup>1</sup> with  $2s2p^3$ . This is not what one should expect from the formula  $\Delta E = \text{const.} [j(j+1) - l(l+1) - s(s+1)]$ , showing that the range of applicability of this formula is limited. One can verify the fact that no splitting occurs by a consideration of  ${}^2D_{5/2}$  and  ${}^2P_{1/2}$ . The displacement must be the same for  $(ls)$  coupling as for  $(jj)$

<sup>5</sup> W. Heisenberg u. P. Jordan, Zeits. f. Physik 37, 268 (1926).

coupling, where it is zero, a result that one can obtain without using wave functions.

#### DISCUSSION

The vectorial method of finding correct linear combinations seems to be quite general, but does not, of course, apply when the resulting state cannot be represented as a vector which is the sum of several component vectors. For instance, the transition from (*ls*) to (*jj*) coupling involves a disturbance of symmetry so that one cannot find the wave functions for the intermediate cases by the above method. But it becomes much easier to find these functions if one knows the proper functions for (*ls*) coupling. The problem reduces to that of solving a secular equation for a given *j* and *m*, the degree of this equation being the only practical limitation, instead of the number of electrons.

*Note added Sept. 8, 1931:* The correct linear combinations can also be found by a method due to N. M. Gray and N. A. Wills (Phys. Rev. **38**, 248, 1931). The present writer believes, however, that the vectorial method, due to Wigner, is the simpler.