Hyperfine Structure Formulae for the Configuration p^3s

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Hfs interval factor formulae for the states of p^3s are derived by the method of Breit and Wills. The formulae for intermediate coupling are expressed in two forms: one involving the coefficients C's, the other the coefficients K's, corresponding to the representation of the functions of the states in intermediate coupling as a linear combination of the (jj) and the (LS) functions, respectively. The (jj)—(LS) transformation matrices as well as the interval factor formulae for (jj) and (LS) coupling are also given.

I. INTRODUCTION

BREIT and Wills[1] extended the relativistic theory of hyperfine structure to intermediate coupling and derived interval factor formulae for the configurations sx, $p\cdot p$, p^2, p^3, p^2s. Recently one of the writers[2] treated the d^2s configuration by the same method. p^3s, a configuration with an unpaired s electron, also merits consideration since it usually gives rise to measurable hyperfine separations. The formulae for this configuration are presented here.

II. WAVE FUNCTIONS AND INTERVAL FACTOR FORMULAE IN INTERMEDIATE COUPLING

The configuration p^3s gives rise to ten states: one with $J=3$, four with $J=2$, four with $J=1$, and one with $J=0$. As the relativistic treatment of hyperfine structure must be made via (jj) coupling, the configuration will be considered first in this coupling. The functions representing the states in (jj) coupling can be conveniently thought of as arising from the coupling of the states of p^3 with an s electron. The states of p^3 are given in Table I. They are designated by Greek letters with their J values indicated by superscripts.

TABLE I. *States of p^3.*

$(j_1, j_2, j_3) =$	$(3/2, 3/2, 3/2)$;		$(3/2, 3/2, 1/2)$;			$(3/2, 1/2, 1/2)$
Resultant $J =$	$3/2$	;	$5/2$	$3/2$	$1/2$;	$3/2$
Symbol	$\psi^{3/2}$		$\varphi^{5/2}$	$\varphi^{3/2}$	$\varphi^{1/2}$	$\chi^{3/2}$

The calculations can be made expediently by using eigenfunctions for a given magnetic quantum number. These functions of p^3 states will be represented by the state symbols with the magnetic quantum number, m, added as a subscript. It is necessary in the calculations to express the three-electron functions in terms of the one-electron functions, which for a given j and m will be represented by symbols of the type $(j)_m$. The three-electron functions for the states with $m=J$, expressed in terms of the one-electron functions, are given here. The functions for other values of m can readily be obtained from these by the method of Gray and Wills.[3] The signs of the p^3 functions and also those of the p^3s functions used in this calculation have been adjusted so as to give magnetic energy matrices identical with those published by Johnson.[4]

(3/2, 3/2, 3/2) Sub-group.

$$\psi_{3/2}{}^{3/2}=(1/\sqrt{6})[(3/2)_{3/2},\ (3/2)_{1/2},\ (3/2)_{-1/2}].$$

(3/2, 3/2, 1/2) Sub-group.

$$\varphi_{5/2}{}^{5/2}=(1/\sqrt{6})[(3/2)_{3/2},\ (3/2)_{1/2},\ (1/2)_{1/2}].$$

$$\varphi_{3/2}{}^{3/2}=(1/\sqrt{5})(1/\sqrt{6})[(3/2)_{3/2},\ (3/2)_{-1/2},\ (1/2)_{1/2}]-(2/\sqrt{5})(1/\sqrt{6})\times[(3/2)_{3/2},\ (3/2)_{1/2},\ (1/2)_{-1/2}].$$

$$\varphi_{1/2}{}^{1/2}=(1/\sqrt{2})(1/\sqrt{6})[(3/2)_{3/2},\ (3/2)_{-3/2},\ (1/2)_{1/2}]-(1/\sqrt{2})(1/\sqrt{6})\times[(3/2)_{1/2},\ (3/2)_{-1/2},\ (1/2)_{1/2}].$$

(3/2, 1/2, 1/2) Sub-group.

$$\chi_{3/2}{}^{3/2}=(1/\sqrt{6})[(3/2)_{3/2},\ (1/2)_{-1/2},\ (1/2)_{1/2}].$$

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[1] G. Breit and L. A. Wills, Phys. Rev. **44**, 470 (1933).
[2] M. F. Crawford, Phys. Rev. **47**, 768 (1935).
[3] N. Gray and L. A. Wills, Phys. Rev. **38**, 248 (1931).
[4] M. H. Johnson, Jr., Phys. Rev. **39**, 197 (1932).

Each square bracket in the preceding expressions is an abbreviation for the determinant representation of a three-electron function as a combination of products of three one-electron functions.

The states of p^3s will now be considered. The functions of the s electron will be symbolized by s_m. They can be combined with the functions of the p^3 states without paying attention to symmetry.

J=3. The function representing the state with $J=3$, $m=3$, which is independent of coupling, can be written

$$\mathrm{I}=s_{1/2}\varphi_{5/2}{}^{5/2}. \quad (1)$$

The interval factor formula obtained from this function by the procedure of Breit and Wills[1] is

$$A(J=3)=(1/6)a_s+(2/3)a'+(1/6)a''. \quad (2)$$

The a's represent the hyperfine structure interaction or coupling constants as in the paper of Breit and Wills.

J=2. The functions representing the four states with $J=2$, $m=2$ in (jj) coupling are

$$\mathrm{I}=s_{1/2}\psi_{3/2}{}^{3/2};$$
$$\mathrm{II}=(5/6)^{1/2}s_{-1/2}\varphi_{5/2}{}^{5/2}-(1/\sqrt{6})s_{1/2}\varphi_{3/2}{}^{5/2}; \quad (3)$$
$$\mathrm{III}=s_{1/2}\varphi_{3/2}{}^{3/2};\quad \mathrm{IV}=s_{1/2}\chi_{3/2}{}^{3/2}.$$

In intermediate coupling the general function for a state with $J=2$, $m=2$ is

$$(2)_2=C_1\mathrm{I}+C_2\mathrm{II}+C_3\mathrm{III}+C_4\mathrm{IV}. \quad (4)$$

From this we obtain

$$A(J=2)=a_s(1/4-(5/12)C_2^2)+a'((3/4)C_1^2+(14/15)C_2^2+(9/10)C_3^2+(3/4)C_4^2+(2/5\sqrt{6})C_2C_3)$$
$$+a''((7/30)C_2^2-(3/20)C_3^2-(2/5\sqrt{6})C_2C_3)+a'''(C_1-C_4)((1/\sqrt{15})C_2-3(2/5)^{1/2}C_3). \quad (5)$$

J=1. The functions representing the four states with $J=1$, $m=1$ in (jj) coupling are

$$\mathrm{I}=(\sqrt{3}/2)s_{-1/2}\psi_{3/2}{}^{3/2}-(1/2)s_{1/2}\psi_{1/2}{}^{3/2};\qquad \mathrm{II}=-(\sqrt{3}/2)s_{-1/2}\varphi_{3/2}{}^{3/2}+(1/2)s_{1/2}\varphi_{1/2}{}^{3/2};$$
$$\mathrm{III}=s_{1/2}\varphi_{1/2}{}^{1/2};\qquad \mathrm{IV}=(\sqrt{3}/2)s_{-1/2}\chi_{3/2}{}^{3/2}-(1/2)s_{1/2}\chi_{1/2}{}^{3/2}. \quad (6)$$

In intermediate coupling the general function is

$$(1)_1=C_1\mathrm{I}+C_2\mathrm{II}+C_3\mathrm{III}+C_4\mathrm{IV}. \quad (7)$$

From this we obtain

$$A(J=1)=a_s((3/4)C_3^2-1/4)+a'((5/4)C_1^2+(3/2)C_2^2+(5/4)C_4^2)+a''((1/2)C_3^2-(1/4)C_2^2)$$
$$+a'''[2(5/2)^{1/2}C_2(C_1-C_4)+C_3(C_4+C_1)]. \quad (8)$$

J=0. This state has no hyperfine structure and is independent of coupling.

III. Interval Factor Formulae in (jj) and (LS) Coupling, and the (jj)−(LS) Transformation Matrices

The interval factors of the states in (jj) coupling can be obtained directly from the preceding formulae. Consider the states with $J=2$. It is obvious that for one of these in (jj) coupling $C_1=1$, $C_2=C_3=C_4=0$; for another $C_2=1$, $C_1=C_3=C_4=0$; and so on for the others. The (jj) interval factors obtained in this manner are:

J=3. Sub-group.

$$s\varphi^{5/2}:\ A(J=3)=(1/6)a_s+(2/3)a'+(1/6)a''. \quad (9)$$

J=2. Sub-group.

$$s\psi^{3/2}:\ A(J=2)=(1/4)a_s+(3/4)a'.$$
$$s\varphi^{5/2}:\ A(J=2)=-(1/6)a_s+(14/15)a'+(7/30)a''.$$
$$s\varphi^{3/2}:\ A(J=2)=(1/4)a_s+(9/10)a'-(3/20)a''. \quad (10)$$
$$s\chi^{3/2}:\ A(J=2)=(1/4)a_s+(3/4)a'.$$

J = 1. Sub-group.

$$
\begin{aligned}
&s\psi^{3/2}:\ A(J=1)=-(1/4)a_s+(5/4)a'.\\
&s\varphi^{3/2}:\ A(J=1)=-(1/4)a_s+(3/2)a'-(1/4)a''.\\
&s\varphi^{1/2}:\ A(J=1)=(1/2)a_s+(1/2)a''.\\
&s\chi^{3/2}:\ A(J=1)=-(1/4)a_s+(5/4)a'.
\end{aligned}
\tag{11}
$$

The interval factors of the states in (LS) coupling can be obtained from Eqs. (6, 8) by using the (jj)—(LS) transformation matrices. These matrices are given in Table II.

The interval factors of the states in (LS) coupling, obtained by substituting the appropriate coefficients from the transformation matrices in the general equations, are

$$
\begin{aligned}
&A(^3D_3)=(1/6)a_s+(2/3)a'+(1/6)a''\triangleq(1/6)a_s+(4/5)a_p.\\
&A(^3D_2)=(1/12)a_s+(11/12)a'-(2/3)a'''\triangleq(1/12)a_s+(3/5)a_p.\\
&A(^5S_2)=(1/4)a_s+(5/6)a'-(1/12)a''+(4/3)a'''\triangleq(1/4)a_s.\\
&A(^3P_2)=(1/4)a_s+(3/4)a'\triangleq(1/4)a_s+(2/5)a_p.\\
&A(^1D_2)=(5/6)a'+(1/6)a''-(2/3)a'''\triangleq a_p.\\
&A(^3S_1)=-(1/4)a_s+(25/18)a'-(5/36)a''+(20/9)a'''\triangleq-(1/4)a_s.\\
&A(^3D_1)=-(1/4)a_s+(49/36)a'-(1/9)a''-(20/9)a'''\triangleq-(1/4)a_s+(4/5)a_p.\\
&A(^3P_1)=(1/4)a_s+(5/12)a'+(1/3)a''+(2/3)a'''\triangleq(1/4)a_s+a_p.\\
&A(^1P_1)=(5/6)a'+(1/6)a''-(2/3)a'''\triangleq a_p.
\end{aligned}
\tag{12}
$$

In the nonrelativistic approximation for the p electron a', a'', a''' can be expressed in terms of a_p as follows:

$$a'=(8/15)a_p,\qquad a''=(8/3)a_p,\qquad a'''=-(1/6)a_p, \tag{13}$$

where $a_p=2g\mu_0^2\overline{(r^{-3})}$. The second simplified expression given above for each interval factor is obtained by using these nonrelativistic approximations for the a's.

TABLE II. *Transformation matrices, $(jj)-(LS)$.*

$J=2$	$s\psi^{3/2}$	$s\varphi^{5/2}$	$s\varphi^{3/2}$	$s\chi^{3/2}$	$J=1$	$s\psi^{3/2}$	$s\varphi^{3/2}$	$s\varphi^{1/2}$	$s\chi^{3/2}$
$^5S_2$	$-\sqrt{2/3}$	0	$\sqrt{5/3}$	$\sqrt{2/3}$	$^3S_1$	$-\sqrt{2/3}$	$-\sqrt{5/3}$	0	$\sqrt{2/3}$
$^3D_2$	$1/\sqrt{6}$	$\sqrt{2}/\sqrt{5}$	$2/\sqrt{15}$	$-1/\sqrt{6}$	$^3D_1$	$5/3\sqrt{10}$	$-2/3$	0	$-5/3\sqrt{10}$
$^3P_2$	$-1/\sqrt{2}$	0	0	$-1/\sqrt{2}$	$^3P_1$	$-1/\sqrt{6}$	0	$-\sqrt{2}/\sqrt{3}$	$-1/\sqrt{6}$
$^1D_2$	$-1/3$	$\sqrt{3}/\sqrt{5}$	$-2\sqrt{2}/3\sqrt{5}$	$1/3$	$^1P_1$	$-1/\sqrt{3}$	0	$1/\sqrt{3}$	$-1/\sqrt{3}$

IV. Interval Factors in Intermediate Coupling Expressed in Terms of the Coefficients, K's, of the Transformation Relating the Intermediate to the (LS) States

When the coupling in a configuration tends towards (LS) it is convenient for the application of the theory to have the interval factors expressed in terms of the coefficients, K, that relate the intermediate states to the (LS) states. The interval factors can readily be converted into this form by means of the $(jj)-(LS)$ transformation matrices. In terms of the K's the interval factors are:

$$
\begin{aligned}
A(J=2)=\ &a_s(1/4-(1/6)K_2^2-(1/4)K_4^2-(\sqrt{2}/2\sqrt{3})K_2K_4)\\
&+a'((5/6)K_1^2+(11/12)K_2^2+(3/4)K_3^2+(5/6)K_4^2+(1/3\sqrt{3})K_1K_2+(1/3\sqrt{6})K_2K_4)\\
&+a''(-(1/12)K_1^2+(1/6)K_4^2-(1/3\sqrt{3})K_1K_2+(\sqrt{6}/9)K_2K_4)\\
&+a'''((4/3)K_1^2-(2/3)K_2^2-(2/3)K_4^2-(2/3\sqrt{3})K_1K_2+(10/3\sqrt{6})K_2K_4).
\end{aligned}
\tag{14}
$$

$$
\begin{aligned}
A(J=1)=a_s(&-(1/4)K_1^2-(1/4)K_2^2+(1/4)K_3^2-(1/\sqrt{2})K_3K_4)\\
&+a'((25/18)K_1^2+(49/36)K_2^2+(5/12)K_3^2+(5/6)K_4^2+(\sqrt{5}/9)K_1K_2+(5/3\sqrt{2})K_3K_4)\\
&+a''((-5/36)K_1^2-(1/9)K_2^2+(1/3)K_3^2+(1/6)K_4^2-(\sqrt{5}/9)K_1K_2-(\sqrt{2}/3)K_3K_4)\\
&+a'''((20/9)K_1^2-(20/9)K_2^2+(2/3)K_3^2-(2/3)K_4^2-(2\sqrt{5}/9)K_1K_2+(\sqrt{2}/3)K_3K_4). \quad (15)
\end{aligned}
$$

V. Energy Matrices in (LS) and (jj) Coupling

The coefficients, C, K, that appear in the interval factor formulae are obtainable from the empirical energies of the states of the configuration. To evaluate the coefficients from the energies the energy matrices are required, preferably for both (LS) and (jj) coupling to correspond to the two forms of the interval factor formulae. Johnson[4] has worked out the energy matrices in (LS) coupling. The energy matrices in (jj) coupling can readily be obtained from his results by means of the transformations given in Table II; they are presented in Table III. In the table the $J=3$ state is the energy datum level.

The coefficients determined from the empirical energies can be checked by computing the Landé g factors from the coefficients and comparing them with the empirical g's. The g's can be computed most easily via (LS) coupling since the matrices for the g's of the (LS) states are diagonal. Thus the g of a state with a given J in intermediate coupling is given by $\Sigma_i g_i K_i^2$ summed over all the (LS) states with the given J. The g_i's are the g factors of the (LS) states and the K_i's are the coefficients in the linear combination that expresses the function of the intermediate state in terms of the functions of the (LS) states.

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TABLE III. *Energy matrices, (jj) coupling.*

	$J=3$ $\mathrm{I}=s\varphi^{5/2}$	$J=2$ $\mathrm{I}=s\psi^{3/2}$	$J=2$ $\mathrm{II}=s\varphi^{5/2}$	$J=2$ $\mathrm{III}=s\varphi^{3/2}$	$J=2$ $\mathrm{IV}=s\chi^{3/2}$	$J=1$ $\mathrm{I}=s\psi^{3/2}$	$J=1$ $\mathrm{II}=s\varphi^{3/2}$	$J=1$ $\mathrm{III}=s\varphi^{1/2}$	$J=1$ $\mathrm{IV}=s\chi^{3/2}$	$J=0$ $\mathrm{I}=s\varphi^{1/2}$
$J=3$ I	0									
$J=2$ I		$\frac{1}{25}F_2+\frac{3}{2}\bar{a}$	$-\frac{2}{3\sqrt{15}}G_1$	$\sqrt{10}\left(\frac{F_2}{25}+\frac{G_1}{15}\right)$	$\frac{1}{5}F_2$					
II		$-\frac{2}{3\sqrt{15}}G_1$	$\frac{2}{5}G_1$	$-\frac{4\sqrt{2}}{15\sqrt{3}}G_1$	$\frac{2}{3\sqrt{15}}G_1$					
III		$\sqrt{10}\left(\frac{F_2}{25}+\frac{G_1}{15}\right)$	$-\frac{4\sqrt{2}}{15\sqrt{3}}G_1$	$-\frac{1}{5}F_2-\frac{1}{15}G_1$	$-\sqrt{10}\left(\frac{F_2}{25}+\frac{G_1}{15}\right)$					
IV		$\frac{1}{5}F_2$	$\frac{2}{3\sqrt{15}}G_1$	$-\sqrt{10}\left(\frac{F_2}{25}+\frac{G_1}{15}\right)$	$\frac{1}{25}F_2-\frac{3}{2}\bar{a}$					
$J=1$ I						$\frac{1}{25}F_2+\frac{4}{9}G_1+\frac{3}{2}$	$-\sqrt{10}\left(\frac{F_2}{25}-\frac{G_1}{9}\right)$	$-\frac{2}{9}G_1$	$\frac{1}{5}F_2$	
II						$-\sqrt{10}\left(\frac{F_2}{25}-\frac{G_1}{9}\right)$	$-\frac{1}{5}F_2+\frac{5}{9}G_1$	0	$\sqrt{10}\left(\frac{F_2}{25}-\frac{G_1}{9}\right)$	
III						$-\frac{2}{9}G_1$	0	$\frac{6}{25}F_2+\frac{2}{9}G_1$	$-\frac{2}{9}G_1$	
IV						$\frac{1}{5}F_2$	$\sqrt{10}\left(\frac{F_2}{25}-\frac{G_1}{9}\right)$	$-\frac{2}{9}G_1$	$\frac{1}{25}F_2+\frac{4}{9}G_1-\frac{3}{2}\bar{a}$	
$J=0$ I										$\frac{6}{25}F_2$