

NOTE ON THE CALCULATION OF ZERO ORDER EIGENFUNCTIONS

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ABSTRACT

An elementary procedure is outlined for obtaining zero approximation eigenfunctions of many electron problems. The procedure allows a calculation of these functions as linear combinations of products of functions, each involving one electron only. The proper combination of products for one of the terms of highest multiplicity may, as a rule, be obtained by inspection; the remaining functions are obtained from this by the use of angular momentum operators. The "strong field" eigenfunctions for equivalent and non-equivalent electrons are obtained first, and from these are found the "weak field" eigenfunctions. The usual solution of the secular equation is unnecessary wherever the resultant states may be interpreted as having a definite and known kind of vector coupling (e.g. Russell-Saunders, or (jj)).

THE solution of quantum mechanical problems involving many electrons is usually carried out by means of a perturbation calculation. In the case of degenerate systems the direct method of performing the calculation involves the solution of the secular determinant. This step is frequently awkward. In some cases it may be avoided by the use of the method of sums. In other cases it is possible to use general theorems about the form of angular momentum matrices, as for instance in the derivation of the Landé g factor. The method of sums is however not always sufficient to solve a given problem, and the use of matrices is often difficult. We describe below a systematic and elementary way of automatically solving the secular equation, i.e. removing the degeneracy, for any case in which the angular momenta of the resultant states are known. For such cases the "zero approximation functions," which are linear combinations of the complete set of functions describing the degenerate problem, may be formed directly by a simple application of certain angular momentum operators. Having the "zero approximation" eigenfunctions the perturbation energies are obtainable by direct integration. Needless to say, this method is applicable only for cases of definite and known vector coupling, such as Russell Saunders or (jj) , and not for unknown intermediate couplings.

The general method can be explained by considering a single p electron which gives rise to 2P states. If the coupling between the orbital motion and the spin is weak, the following "strong field" eigenfunctions may be constructed: ${}^2P_{1,\frac{1}{2}}, {}^2P_{0,\frac{1}{2}}, {}^2P_{-1,\frac{1}{2}}, {}^2P_{1,-\frac{1}{2}}, {}^2P_{0,-\frac{1}{2}}, {}^2P_{-1,-\frac{1}{2}}$ where the first subscript gives the value of the orbital magnetic quantum number m_l , and the second gives the spin quantum number m_s . If the possible orbital functions are denoted by u_1, u_0, u_{-1} , and the two spin functions by s_+ and s_- , the ${}^2P_{1,\frac{1}{2}}$ term must be

represented by $e^{i\theta} u_1 s_+$ where θ is a real number. For simplicity we let $\theta = 0$. In order to form the other functions we use the formulas:¹

$$\begin{aligned}(J_x + iJ_y)\psi(j, m) &= (j + m)^{1/2}(j - m + 1)^{1/2}\psi(j, m - 1) \\ (L_x + iL_y)u(l, m_l) &= (l + m_l)^{1/2}(l - m_l + 1)^{1/2}u(l, m_l - 1) \\ (S_x + iS_y)s(s, m_s) &= (s + m_s)^{1/2}(s - m_s + 1)^{1/2}s(s, m_s - 1) \\ (J_x - iJ_y)\psi(j, m) &= (j - m)^{1/2}(j + m + 1)^{1/2}\psi(j, m + 1) \\ (L_x - iL_y)u(l, m_l) &= (l - m_l)^{1/2}(l + m_l + 1)^{1/2}u(l, m_l + 1) \\ (S_x - iS_y)s(s, m_s) &= (s - m_s)^{1/2}(s + m_s + 1)^{1/2}s(s, m_s + 1).\end{aligned}$$

Here $\psi(j, m)$ denotes the "weak field" eigenfunction containing both spatial and spin coordinates, (the symbols j, m are here suffixes), and represents a state of total angular momentum j , and total magnetic quantum number m . The function $u(l, m_l)$ contains only spatial coordinates and represents a state of total orbital angular momentum l , and orbital magnetic quantum number m_l . Similarly $s(s, m_s)$ contains only spin coordinates and represents a state of total spin s , and spin magnetic quantum number m_s . Again l, m_l, s, m_s are suffixes.

$$(J_x, J_y, J_z) = (L_x + S_x, L_y + S_y, L_z + S_z)$$

where by definition the components of the total angular momentum operator J are the sums of the components of orbital and spin operators L and S .

Successive applications of the operators $L_x + iL_y$ and $S_x + iS_y$ starting with ${}^2P_{1, \frac{1}{2}}$, will give immediately all the "strong field" functions, but in this simple case the "strong field" functions can be written down at once without use of the operators.

The "weak field" function ${}^2P_{3/2} (m = 3/2)$ must be equal to the "strong field" function ${}^2P_{1, \frac{1}{2}}$ since a stationary state in which the value of m is a maximum can arise only when m_l and m_s have their maximum values. The ${}^2P_{3/2} (m = \frac{1}{2})$ eigenfunction will be a linear combination of the "strong field" eigenfunctions ${}^2P_{1, -\frac{1}{2}}$ and ${}^2P_{0, \frac{1}{2}}$. Applying the operator $(J_x + iJ_y)$ to the term ${}^2P_{3/2} (m = 3/2)$ gives the proper combination of these terms and automatically the proper normalization factor. Further applications of the operator lead to the remaining "weak field" functions for the ${}^2P_{3/2}$ term. The ${}^2P_{\frac{1}{2}} (m = \frac{1}{2})$ term may be obtained by constructing a combination of ${}^2P_{0, \frac{1}{2}}$ and ${}^2P_{1, -\frac{1}{2}}$ which is normal, and orthogonal to ${}^2P_{3/2} (m = \frac{1}{2})$. The ${}^2P_{\frac{1}{2}} (m = -\frac{1}{2})$ term may be obtained from this by operating with $(J_x + iJ_y)$ or by constructing a function orthogonal to ${}^2P_{3/2} (m = -\frac{1}{2})$ in a way similar to the above. All the 2P eigenfunctions are listed in Table I. In this and the following tables the symbol representing the term stands for the corresponding eigenfunction also.

When dealing with states arising from two or more non-equivalent electrons, different orbital functions must be used. Thus for the combination of a p and a d electron which gives rise to singlet and triplet P, D and F terms, there appear the orbital functions u_1, u_0, u_{-1} for the p electron and v_2, v_1, v_0 ,

¹ H. Weyl, Gruppentheorie und Quantenmechanik, Kapitel IV.

TABLE I. 2P eigenfunctions arising from a p electron.

"Strong field"		"Weak field"
${}^2P_{1, \frac{1}{2}} = u_1 s_+$	${}^2P_{3/2}(m=3/2) = {}^2P_{1, \frac{1}{2}}$	$= u_1 s_+$
${}^2P_{0, \frac{1}{2}} = u_0 s_+$	${}^2P_{3/2}(m=\frac{1}{2}) = 1/3^{1/2}({}^2P_{0, \frac{1}{2}} + {}^2P_{1, -\frac{1}{2}})$	$= 1/3^{1/2}({}^2P_{0, \frac{1}{2}} + u_1 s_-)$
${}^2P_{-1, \frac{1}{2}} = u_{-1} s_+$	${}^2P_{3/2}(m=-\frac{1}{2}) = 1/3^{1/2}({}^2P_{-1, \frac{1}{2}} + {}^2P_{0, -\frac{1}{2}})$	$= 1/3^{1/2}(u_{-1} s_+ + {}^2P_{0, -\frac{1}{2}})$
${}^2P_{1, -\frac{1}{2}} = u_1 s_-$	${}^2P_{3/2}(m=-3/2) = {}^2P_{-1, -\frac{1}{2}}$	$= u_{-1} s_-$
${}^2P_{0, -\frac{1}{2}} = u_0 s_-$	${}^2P_{\frac{1}{2}}(m=\frac{1}{2}) = 1/3^{1/2}({}^2P_{0, \frac{1}{2}} - {}^2P_{1, -\frac{1}{2}})$	$= 1/3^{1/2}(u_0 s_+ - {}^2P_{1, -\frac{1}{2}})$
${}^2P_{-1, -\frac{1}{2}} = u_{-1} s_-$	${}^2P_{\frac{1}{2}}(m=-\frac{1}{2}) = 1/3^{1/2}({}^2P_{-1, \frac{1}{2}} - {}^2P_{0, -\frac{1}{2}})$	$= 1/3^{1/2}({}^2P_{-1, \frac{1}{2}} - u_0 s_-)$

v_{-1}, v_{-2} for the d electron. To satisfy the exclusion principle, the total eigenfunction must be made antisymmetric, and since the only combination of spin functions giving $m=1$ is $s_+^I s_+^{II}$, the antisymmetric orbital combination $1/2^{1/2}(u_1^I v_2^{II} - u_1^{II} v_2^I)$ must be used to obtain ${}^3F_{3,1}$

$${}^3F_{3,1} = \frac{1}{2^{1/2}} \begin{vmatrix} u_1^I s_+^I & u_1^{II} s_+^{II} \\ v_2^I s_+^I & v_2^{II} s_+^{II} \end{vmatrix}.$$

The superscripts refer to the number of the electron. Operating on ${}^3F_{3,1}$ with $\sum_{I,II}(L_x + iL_y)$ gives

$$\begin{aligned} \sum_{I,II}(L_x + iL_y){}^3F_{3,1} &= 6^{1/2}{}^3F_{2,1} \\ &= \frac{1}{2^{1/2}} \begin{vmatrix} 2^{1/2}u_0^I s_+^I & u_1^{II} s_+^{II} \\ v_2^I s_+^I & v_2^{II} s_+^{II} \end{vmatrix} + \frac{1}{2^{1/2}} \begin{vmatrix} u_1^I s_+^I & 2^{1/2}u_0^{II} s_+^{II} \\ v_2^I s_+^I & 2v_1^{II} s_+^{II} \end{vmatrix} \end{aligned}$$

The sum of these two determinants is equal to the sum of two other determinants

$$\frac{1}{2^{1/2}} \begin{vmatrix} 2^{1/2}u_0^I s_+^I & 2^{1/2}u_0^{II} s_+^{II} \\ v_2^I s_+^I & v_2^{II} s_+^{II} \end{vmatrix} + \frac{1}{2^{1/2}} \begin{vmatrix} u_1^I s_+^I & u_1^{II} s_+^{II} \\ 2v_1^I s_+^I & 2v_1^{II} s_+^{II} \end{vmatrix}$$

These new determinants are obtained by expanding each of the former by the column changed by the operator and then recombining by rows. The result of this expansion and recombination is directly obtained by applying the operators to the rows instead of to the columns. It is seen that this is applicable to all the cases considered. The advantage of the second form is that the columns of any one determinant are all the same except for the electron index. Thus the notation can be abridged by writing only one column of each determinant. For example:

$${}^3F_{3,1} = \frac{1}{2^{1/2}} \begin{vmatrix} u_1 s_+ \\ v_2 s_+ \end{vmatrix}; \quad \sum_{I,II}(L_x + iL_y){}^3F_{3,1} = \begin{vmatrix} u_0 s_+ \\ v_2 s_+ \end{vmatrix} + 2^{1/2} \begin{vmatrix} u_1 s_+ \\ v_1 s_+ \end{vmatrix} \text{ etc.}$$

All the 3F terms can be obtained from ${}^3F_{3,1}$ by operating with $\sum_{I,II}(L_x + iL_y)$ and $\sum_{I,II}(S_x + iS_y)$.

The procedure outlined above applies in general with the obvious generalization of using three kinds of orbital functions in the case of three electrons, etc. Two electron eigenfunctions may be separated into products of spin and orbital functions. For triplet states there are three symmetric spin

functions $s_1 = s_+^I s_+^{II}$, $s_0 = 1/2^{1/2}(s_+^I s_-^{II} + s_-^I s_+^{II})$, $s_{-1} = s_-^I s_-^{II}$, and for singlet states there is only one antisymmetric function

$$\hat{s}_0 = \frac{1}{2^{1/2}}(s_+^{\text{I}}s_-^{\text{II}} - s_-^{\text{I}}s_+^{\text{II}}).$$

To satisfy the exclusion principle, the orbital eigenfunctions for triplet states must be antisymmetric, and may be represented by determinants. For singlet states the orbital functions must be symmetric and may be written as “permanents” thus:

$$\begin{pmatrix} u_1 \\ v_2 \end{pmatrix} = u_1^{\text{I}} v_2^{\text{II}} + u_1^{\text{II}} v_2^{\text{I}}.$$

The 3F eigenfunctions arising from the combination of a p and a d electron are listed in Table II.

TABLE II. "Strong field" 3F eigenfunctions arising from the combination of a p and a d electron. The subscript i can take the values 1, 0, -1 , where s_1 , s_0 and s_{-1} have the values given above.

[illegible]

${}^1F_{3,0}$ may be found by making a normal function which is orthogonal to ${}^3F_{3,0}$. This amounts merely to changing the sign between the two determinants representing the ${}^3F_{3,0}$ term. An easy consideration shows that the 1F functions are obtained from the 3F functions by substituting for each determinant the corresponding "permanent" e.g., by substituting for $|u_i^{u_i}|$ the expression $(u_i^{u_i}) \equiv u_1^I v_2^{II} + u_1^{II} v_2^I$, and by substituting $\hat{s}_0$ for s_i . The same connection between singlet and triplet functions exists for all two-electron configurations.

TABLE III. ³D "strong field" eigenfunctions arising from the combination of a p and a d electron. The omitted functions are easily constructed.

$$\begin{aligned} {}^3D_{2,\mathfrak{i}} &= 1/6^{1/2} \left\{ \left| \begin{matrix} u_1 \\ v_1 \end{matrix} \right| - 2^{1/2} \left| \begin{matrix} u_0 \\ v_2 \end{matrix} \right| \right\} s_{\mathfrak{i}} \\ {}^3D_{1,\mathfrak{i}} &= 1/(12)^{1/2} \left\{ 3^{1/2} \left| \begin{matrix} u_1 \\ v_0 \end{matrix} \right| - 2^{1/2} \left| \begin{matrix} u_{-1} \\ v_2 \end{matrix} \right| - \left| \begin{matrix} u_0 \\ v_1 \end{matrix} \right| \right\} s_{\mathfrak{i}} \\ {}^3D_{0,\mathfrak{i}} &= 1/2^{1/2} \left\{ \left| \begin{matrix} u_1 \\ v_{-1} \end{matrix} \right| - \left| \begin{matrix} u_{-1} \\ v_1 \end{matrix} \right| \right\} s_{\mathfrak{i}} \\ &\vdots \\ {}^3D_{-2,\mathfrak{i}} &= 1/6^{1/2} \left\{ (2)^{1/2} \left| \begin{matrix} u_0 \\ v_{-2} \end{matrix} \right| - \left| \begin{matrix} u_{-1} \\ v_{-1} \end{matrix} \right| \right\} s_{\mathfrak{i}} \end{aligned}$$

${}^3D_{2,1}$ is orthogonal to ${}^3F_{2,1}$ and is obtained from it by changing the sign between the determinants. The other 3D functions are obtained from ${}^3D_{2,1}$ by use of the operators, and are listed in Table III.

For two non-equivalent p electrons the procedure is exactly like the above except that now there are orbital functions u_1, u_0, u_{-1} and v_1, v_0, v_{-1} . If, however, the two p electrons are equivalent, simplifications occur since the orbital functions for the two electrons are the same. Consider first the 1D state arising from this configuration. For the ${}^1D_{2,0}$ state only the combinations $u_1^I s_+^I u_1^{II} s_-^{II}$ and $u_1^I s_-^I u_1^{II} s_+^{II}$ may be used, and their antisymmetric combination, written in the abbreviated notation is

$${}^1D_{2,0} = \frac{1}{2^{1/2}} \begin{vmatrix} u_1 s_+ \\ u_1 s_- \end{vmatrix}.$$

All the 1D eigenfunctions may be obtained from ${}^1D_{2,0}$ by successive applications of the operator $\sum_{I,II}(L_x + iL_y)$ or from ${}^1D_{-2,0}$ by use of $\sum_{I,II}(L_x - iL_y)$. The 1D eigenfunctions are found to be:

$$\begin{aligned} {}^1D_{1,0} &= \frac{1}{2} \left\{ \begin{vmatrix} u_0 s_+ \\ u_1 s_- \end{vmatrix} + \begin{vmatrix} u_1 s_+ \\ u_0 s_- \end{vmatrix} \right\}, \\ {}^1D_{0,0} &= \frac{1}{12^{1/2}} \left\{ \begin{vmatrix} u_{-1} s_+ \\ u_1 s_- \end{vmatrix} + 2 \begin{vmatrix} u_0 s_+ \\ u_0 s_- \end{vmatrix} + \begin{vmatrix} u_1 s_+ \\ u_{-1} s_- \end{vmatrix} \right\} \dots \end{aligned}$$

The 3P eigenfunctions may be obtained from either ${}^3P_{1,1}$ or ${}^3P_{-1,1}$. Either one of these can be constructed by inspection as was done for ${}^1D_{2,0}$. Having either of them the remaining 3P eigenfunctions are obtained by using $\sum_{I,II}(L_x + iL_y)$ and $\sum_{I,II}(S_x + iS_y)$ or $\sum_{I,II}(L_x - iL_y)$ and $\sum_{I,II}(S_x - iS_y)$. These eigenfunctions are found to be:

$${}^3P_{1,i} = \frac{1}{2^{1/2}} \begin{vmatrix} u_1 \\ u_0 \end{vmatrix} s_i, \quad {}^3P_{0,i} = \frac{1}{2^{1/2}} \begin{vmatrix} u_1 \\ u_{-1} \end{vmatrix} s_i, \quad {}^3P_{-1,i} = \frac{1}{2^{1/2}} \begin{vmatrix} u_0 \\ u_1 \end{vmatrix} s_i.$$

${}^1S_{0,0}$ must be a linear combination of the three eigenfunctions having a resultant m_l and m_s equal to zero, so

$${}^1S_{0,0} = A \begin{vmatrix} u_1 s_+ \\ u_{-1} s_- \end{vmatrix} + B \begin{vmatrix} u_{-1} s_+ \\ u_1 s_- \end{vmatrix} + C \begin{vmatrix} u_0 s_+ \\ u_0 s_- \end{vmatrix}.$$

Since ${}^1S_{0,0}$ must be orthogonal to ${}^1D_{0,0}$ and ${}^3P_{0,0}$ and must be normalized there are three conditions for determining the coefficients A , B , and C , namely:

$$\begin{aligned} \int ({}^1S_{0,0})^* ({}^1D_{0,0}) dv &= 0; & \int ({}^1S_{0,0})^* ({}^3P_{0,0}) dv &= 0; \\ \int ({}^1S_{0,0})^* ({}^1S_{0,0}) dv &= 1. \end{aligned}$$

These conditions determine ${}^1S_{0,0}$ to within a factor of absolute magnitude one, and it is found that

$$^1S_{0,0} = \frac{1}{6^{1/2}} \left\{ \begin{vmatrix} u_1 & s_+ \\ u_{-1} & s_- \end{vmatrix} - \begin{vmatrix} u_0 & s_+ \\ u_0 & s_- \end{vmatrix} + \begin{vmatrix} u_{-1} & s_+ \\ u_1 & s_- \end{vmatrix} \right\}.$$

The method outlined above can be very simply extended to a combination of three or more electrons. For n electrons the determinants are of order n .

If the electrons are non-equivalent, a different orbital function must be used for each, and the calculation may become clumsy. It is always definite however, and if the electrons are equivalent, the calculation is very much abridged. Eigenfunctions for three equivalent p electrons, calculated by this method, are listed in Table IV.

TABLE IV. 2P and 2D "strong field" eigenfunctions arising from the combination of three equivalent p electrons.

$^2D_{2, \frac{1}{2}} = 1/6^{1/2} \begin{vmatrix} u_1 s_+ \\ u_1 s_- \\ u_0 s_+ \end{vmatrix}$	$^2D_{2, -\frac{1}{2}} = 1/6^{1/2} \begin{vmatrix} u_1 s_+ \\ u_1 s_- \\ u_0 s_- \end{vmatrix}$
$^2D_{1, \frac{1}{2}} = 1/12^{1/2} \left\{ \begin{vmatrix} u_1 s_+ \\ u_0 s_- \\ u_0 s_+ \end{vmatrix} + \begin{vmatrix} u_1 s_+ \\ u_1 s_- \\ u_{-1} s_+ \end{vmatrix} \right\}$	$^2D_{1, -\frac{1}{2}} = 1/12^{1/2} \left\{ \begin{vmatrix} u_0 s_+ \\ u_1 s_- \\ u_0 s_- \end{vmatrix} + \begin{vmatrix} u_1 s_+ \\ u_1 s_- \\ u_{-1} s_- \end{vmatrix} \right\}$
$^2D_{0, \frac{1}{2}} = 1/6 \left\{ \begin{vmatrix} u_1 s_+ \\ u_{-1} s_- \\ u_0 s_+ \end{vmatrix} + 2 \begin{vmatrix} u_1 s_+ \\ u_0 s_- \\ u_{-1} s_+ \end{vmatrix} + \begin{vmatrix} u_0 s_+ \\ u_1 s_- \\ u_{-1} s_- \end{vmatrix} \right\}$	$^2D_{0, -\frac{1}{2}} = 1/6 \left\{ \begin{vmatrix} u_{-1} s_+ \\ u_1 s_- \\ u_0 s_- \end{vmatrix} + 2 \begin{vmatrix} u_0 s_+ \\ u_1 s_- \\ u_{-1} s_- \end{vmatrix} + \begin{vmatrix} u_1 s_+ \\ u_0 s_- \\ u_{-1} s_- \end{vmatrix} \right\}$
$^2D_{-1, \frac{1}{2}} = 1/12^{1/2} \left\{ \begin{vmatrix} u_0 s_+ \\ u_0 s_- \\ u_{-1} s_+ \end{vmatrix} + \begin{vmatrix} u_1 s_+ \\ u_{-1} s_- \\ u_{-1} s_+ \end{vmatrix} \right\}$	$^2D_{-1, -\frac{1}{2}} = 1/12^{1/2} \left\{ \begin{vmatrix} u_{-1} s_+ \\ u_1 s_- \\ u_{-1} s_- \end{vmatrix} + \begin{vmatrix} u_0 s_+ \\ u_0 s_- \\ u_{-1} s_- \end{vmatrix} \right\}$
$^2D_{-2, \frac{1}{2}} = 1/6^{1/2} \begin{vmatrix} u_0 s_+ \\ u_{-1} s_- \\ u_{-1} s_+ \end{vmatrix}$	$^2D_{-2, -\frac{1}{2}} = 1/6^{1/2} \begin{vmatrix} u_{-1} s_+ \\ u_0 s_- \\ u_{-1} s_- \end{vmatrix}$
$^2P_{1, \frac{1}{2}} = 1/12^{1/2} \left\{ \begin{vmatrix} u_1 s_+ \\ u_0 s_- \\ u_0 s_+ \end{vmatrix} + \begin{vmatrix} u_1 s_+ \\ u_{-1} s_- \\ u_1 s_- \end{vmatrix} \right\}$	$^2P_{1, -\frac{1}{2}} = 1/12^{1/2} \left\{ \begin{vmatrix} u_1 s_- \\ u_0 s_- \\ u_0 s_+ \end{vmatrix} + \begin{vmatrix} u_1 s_+ \\ u_{-1} s_- \\ u_1 s_- \end{vmatrix} \right\}$
$^2P_{0, \frac{1}{2}} = 1/12^{1/2} \left\{ \begin{vmatrix} u_1 s_+ \\ u_{-1} s_- \\ u_0 s_+ \end{vmatrix} + \begin{vmatrix} u_0 s_+ \\ u_{-1} s_+ \\ u_1 s_- \end{vmatrix} \right\}$	$^2P_{0, -\frac{1}{2}} = 1/12^{1/2} \left\{ \begin{vmatrix} u_1 s_- \\ u_0 s_- \\ u_{-1} s_+ \end{vmatrix} + \begin{vmatrix} u_1 s_+ \\ u_{-1} s_- \\ u_0 s_- \end{vmatrix} \right\}$
$^2P_{-1, \frac{1}{2}} = 1/12^{1/2} \left\{ \begin{vmatrix} u_1 s_+ \\ u_{-1} s_- \\ u_{-1} s_+ \end{vmatrix} + \begin{vmatrix} u_0 s_+ \\ u_{-1} s_+ \\ u_0 s_- \end{vmatrix} \right\}$	$^2P_{-1, -\frac{1}{2}} = 1/12^{1/2} \left\{ \begin{vmatrix} u_1 s_- \\ u_{-1} s_- \\ u_{-1} s_+ \end{vmatrix} + \begin{vmatrix} u_0 s_+ \\ u_{-1} s_- \\ u_0 s_- \end{vmatrix} \right\}$

The "weak field" eigenfunctions for a particular state can be obtained from the "strong field" eigenfunctions of that state by forming linear combinations in the proper way. Since the weak and strong field levels are the same for singlet states, the weak and strong field eigenfunctions are the same for singlet states. For states of multiplicity higher than one the procedure is as follows: the "weak field" eigenfunction having the largest value of j and the maximum value of the corresponding m is the same as the "strong field" eigenfunction with the maximum values of m_l and m_s , i.e. $^3P_2(m=2) = ^3P_{1,1}$. The 3P_2 eigenfunctions for the other values of m may be obtained from the $^3P_2(m=2)$ eigenfunction by applying the operator $\sum(J_x + iJ_y)$. The $^3P_2(m=-2)$ eigenfunction might have been obtained by inspection and the re-

maining eigenfunctions calculated by means of the operator $\sum(J_x - iJ_y)$. This affords a check on the work. It is seen that the use of the $\sum(J_x + iJ_y)$ or $\sum(J_x - iJ_y)$ operators is equivalent to making linear combinations of the "strong field" eigenfunctions. These operators give the proper linear combinations and normalization factors automatically as well as checking each other. The ${}^3P_1(m=1)$ eigenfunction must be a linear combination of the two "strong field" eigenfunctions for which $m_l + m_s = 1$, that is of ${}^3P_{1,0}$ and ${}^3P_{0,1}$. Since the ${}^3P_1(m=1)$ eigenfunction must be orthogonal to ${}^3P_2(m=1)$ and is to be normalized, it can be determined to within a factor of absolute magnitude one. Successive applications of $\sum(J_x + iJ_y)$ will give all the 3P_1 eigenfunctions. It will be found that there will be just enough conditions to determine the ${}^3P_{0,0}$ eigenfunction. It is easy to see that this procedure is applicable in general. This "weak field" eigenfunction for 3P states arising from the combination of two equivalent p electrons are:

$$\begin{aligned} {}^3P_2(m=2) &= {}^3P_{1,1}, \\ {}^3P_2(m=1) &= \frac{1}{2^{1/2}} \{ {}^3P_{1,0} + {}^3P_{0,1} \} \cdots {}^3P_2(m=-2) = {}^3P_{-1,-1}; \\ {}^3P_1(m=1) &= \frac{1}{2^{1/2}} \{ {}^3P_{0,1} - {}^3P_{1,0} \} \\ {}^3P_0(m=0) &= \frac{1}{3^{1/2}} \{ {}^3P_{1,-1} + {}^3P_{0,0} - {}^3P_{-1,1} \} \end{aligned}$$

It is to be observed that the proper linear combination of "strong field" eigenfunctions to form "weak field" eigenfunctions for a given state is independent of the electron configuration giving rise to that state. In the calculation of "weak field" functions it is also not necessary to write out the "strong field" functions explicitly, but it is sufficient to apply the operators to a "strong field" function $\phi(m_l, m_s)$, the operators $L_x + iL_y$ and $L_x - iL_y$ applying to the first index m_l , $S_x + iS_y$, $S_x - iS_y$ applying to the second, m_s .

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