SPECTRA OF TWO ELECTRON SYSTEMS

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Abstract

Following the method of Güttinger and Pauli[1] four angular momentum vectors are treated in matrix mechanics. Analytic formulas are obtained for the matrix components of the spin-orbit interaction of two electrons in LS coupling. Since the electrostatic energy in LS coupling is a diagonal matrix whose elements may be calculated by Slater's method, this gives the complete energy matrix. Then for any two electron configuration one easily obtains the secular equations whose roots give the energy levels in intermediate coupling. In this manner the secular equations are worked out for the configurations p^2, $p\cdot p$, d^2, $d\cdot d$, and $d\cdot p$.

Introduction

In THE theory of complex spectra the effect of the electrostatic repulsion of the electrons on the energy levels of an atom has been reduced in many cases to the calculation of a few radial integrals.[2] By this method it is always possible to calculate the multiplet separations for two electron configurations with such accuracy as is afforded by a first order perturbation theory. In order to obtain more detailed information about the energy levels it is necessary to include in the perturbation problem the interaction of the spin each electron with its own orbital motion. This has been done for two electrons when one is in an s state.[3] Also partial information (in some simple cases complete) about the secular equations has been obtained by Goudsmit.[4]

It is easy to see why the spin-orbit interaction has not been dealt with by Slater's method. In this method it is not necessary to find the wave function for a given state of the atom. For due to the high degree of degeneracy remaining in the problem after the application of the perturbation, it is possible to find all the energy levels from the invariance of diagonal sums. When the spin-orbit interaction is included, much of this degeneracy is removed so the diagonal sum method loses its effectiveness.

The essential difficulty with Slater's wave functions is that the square of the total angular momentum, J^2, which is an integral of the equations of motion, is not diagonal when these wave functions are used. Consequently the secular determinant when computed with these functions, is not factored according to J values as it should be. The proper linear combination of Slater's functions to make J^2 diagonal may be found by studying the angular momentum operators.[5] With these proper functions as a basis the matrix of the spin-

[1] Güttinger and Pauli, Zeits. f. Physik **67**, 743 (1931). This will be referred to as 1.

[2] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[3] Houston, Phys. Rev. **33**, 297 (1929).

[4] Goudsmit, Phys. Rev. **35**, 1325 (1930). This method has recently been extended by D.R Inglis, Phys. Rev. **38**, 862 (1931).

[5] Gray and Wills, Phys. Rev. **38**, 248 (1931).

orbit interaction would be factored according to J values. However for the general two electron configuration this appears to be a lengthy process. So in this paper we attempt to calculate the spin-orbit interaction in LS coupling directly from the matrix equations.[6]

Elimination of the Quantum Number M_J

If $\boldsymbol{L}$ is the total orbital angular momentum, $\boldsymbol{S}$ is the total spin angular momentum and $\boldsymbol{J}$ their resultant, then

$$\begin{aligned} \boldsymbol{J} &= \boldsymbol{L} + \boldsymbol{S} \\ \boldsymbol{L} &= \boldsymbol{l}_1 + \boldsymbol{l}_2 \\ \boldsymbol{S} &= \boldsymbol{s}_1 + \boldsymbol{s}_2 \end{aligned} \tag{1}$$

where $\boldsymbol{l}_1$ and $\boldsymbol{l}_2$ are the orbital and $\boldsymbol{s}_1$ and $\boldsymbol{s}_2$ are the spin angular momenta of electrons 1 and 2 respectively. Then the following commutation relations are valid

$$\begin{aligned} [J_x, A_x] &= 0 \\ [J_x, A_y] &= [A_x, J_y] = iA_z \\ [J_x, B] &= 0 \end{aligned} \tag{2}$$

where $\boldsymbol{A}$ is any vector which is a function of the spin and orbital momentum vectors and B is any scalar formed from these vectors. In these equations angular momentum is measured in units of $h/2\pi$. In particular Eqs. (2) hold for $\boldsymbol{l}_1$, $\boldsymbol{l}_2$, $\boldsymbol{s}_1$ and $\boldsymbol{s}_2$. Now we suppose that J^2 is diagonal with the characteristic values $J(J+I)$ and J_z is a diagonal with the characteristic values M_J, $|M_J| \leqq J$. Then from reference 1 we find that the solutions of Eqs. (2) are

$$\begin{aligned} (A_x \pm iA_y)^{JM_J}_{JM_J\mp1} &= A^J_J\{(J \pm M_J)(J \mp M_J + 1)\}^{1/2} \\ A^{JM_J}_{zJM_J} &= A^J_J M_J \\ (A_x \pm iA_y)^{J\ M_J}_{J+1M_J\mp1} &= A^J_{J+1}(\pm 1)\{(J \mp M_J + 1)(J \mp M_J + 2)\}^{1/2} \\ A^{J\ M_J}_{zJ+1M_J} &= A^J_{J+1}\{(J+1)^2 - M_J{}^2\}^{1/2} \\ (A_x \pm iA_y)^{J\ M_J}_{J-1M_J\mp1} &= A^J_{J-1}(\mp 1)\{(J \pm M_J)(J \pm M_J - 1)\}^{1/2} \\ A^{J\ MJ}_{zJ+1M_J} &= A^J_{J-1}(J^2 - M_J{}^2)^{1/2}. \end{aligned} \tag{3}$$

In particular if $\boldsymbol{A} = \boldsymbol{J}$, then $A^J_J = 1$ and $A^J_{J+1} = 0$.

Calculation of $\boldsymbol{L}$ and $\boldsymbol{S}$

The calculation of $\boldsymbol{S}$ is exactly the same as in reference 1. We now suppose that L^2 and S^2 are also diagonal with the characteristic values $L(L+I)$ and

[6] We should also note another possible method of obtaining the matrix of the spin-orbit interaction by those famous ξ's and η's, which may be simple for one experienced in their peculiarities. H. Weyl, Gruppentheorie und Quantenmechanick Kap. III; H. A. Kramers, Amst. Akad. **33**, 953 (1930).

$S(S+I)$. This is possible since the matrices L^2, S^2, J^2 and J_z all commute with one another. Then from reference 1 we find for **S**

$$
\begin{aligned}
S_J^J &= \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \\
S_{J-1}^J &= \left(\frac{(L+S+1-J)(L+S+1+J)(J-L+S)(J-S+L)}{4J^2(2J-1)(2J+1)}\right)^{1/2} \qquad (4)\\
S_{J-1}^J &= S_J^{J-1}.
\end{aligned}
$$

The last equation follows from the Hermitean character of the components of **S**.

The results for **L** may be obtained from the above by interchanging L and S. This gives

$$
\begin{aligned}
L_J^J &= \frac{J(J+1)+L(L+1)-S(S+1)}{2J(J+1)} \\
L_{J-1}^J &= -\left(\frac{(S+L+1-J)(S+L+1+J)(J-S+L)(J-L+S)}{4J^2(2J-1)(2J+1)}\right)^{1/2} \qquad (5)\\
L_{J-1}^J &= L_J^{J-1}.
\end{aligned}
$$

The minus sign before the component nondiagonal in J occurs in extracting a square root. The minus sign must be used in order that $(L_x+S_x)_{LSJ\pm1M_J}^{LSJ\ M_J}=0$ as is required by the fact that J^2 commutes with all components of $\boldsymbol{J}$. Of course all components of **L** and **S** are diagonal in L and S as all components of both **L** and **S** commute with L^2 and S^2.

Dependence of $\boldsymbol{l}_1$, $\boldsymbol{l}_2$, $\mathbf{s}_1$ and $\mathbf{s}_2$ on the Quantum Number J

In the following formulas we use l for l_1 and l_2 and s for s_1 and s_2 whenever the formulas apply for both subscripts. We find the dependence of $\boldsymbol{l}$ on J from the equation

$$[S_x - iS_y, l_z]_{L'SJ''M_J+1}^{L\ SJ'\ M_J} = 0.$$

The calculation is exactly the same as the calculation of the coordinate matrix in reference 1. Hence we have the result

$$
\begin{aligned}
l_{LSJ}^{LSJ} &= l_{LS}^{LS}\frac{J(J+1)+L(L+1)-S(S+1)}{2J(J+1)} \\
l_{LSJ+1}^{LSJ} &= -l_{LS}^{LS}\left(\frac{(L+S+J+2)(L+S-J)(J+1+L-S)(J+1-L+S)}{4(J+1)^2(2J+1)(2J+3)}\right)^{1/2} \\
l_{L-1SJ+1}^{L\ SJ} &= -l_{L-1S}^{L\ S}\left(\frac{(J-L+S+2)(J-L+S+1)(L+S-1-J)(L+S-J)}{4(J+1)^2(2J+1)(2J+3)}\right)^{1/2} \qquad (6)\\
l_{L-1SJ}^{L\ SJ} &= l_{L-1S}^{L\ S}\left(\frac{(J+L-S)(J-L+S+1)(L+S+1+J)(L+S-J)}{4J^2(J+1)^2}\right)^{1/2} \\
l_{L-1SJ-1}^{L\ SJ} &= l_{L-1S}^{L\ S}\left(\frac{(J+L-S-1)(J+L-S)(L+S+1+J)(L+S+J)}{4J^2(2J-1)(2J+1)}\right)^{1/2}.
\end{aligned}
$$

The remaining terms may be obtained by interchanging the upper and lower indices.

For the dependence of s on J we use the equation

$$[L_x - iL_y, s_z]^{LS\,J'\,M_J}_{LS'J''M_J+1} = 0.$$

With $J'=J-1$ and $J''=J+1$ we have

$$L^{LSJ-1}_{LSJ}\; s^{LS\;J}_{LS'J+1} = s^{LSJ-1}_{LS'J}\, L^{LS'J}_{LS'J+1}. \tag{7}$$

With $J'=J$, $J''=J+1$ and with $J'=J$, $J''=J-1$ we obtain the following two equations in exactly the same manner as Eqs. (15′) and (16′) are obtained in reference 1.

$$\{(J+1)L^{LSJ}_{LSJ} - (J+2)L^{LS'J+1}_{LS'J+1}\}s^{LS\;J}_{LS'J+1} - L^{LS'J}_{LS'J+1}s^{LS\;J}_{LS'J} = 0 \tag{8}$$

$$\{JL^{LSJ}_{LSJ} - (J-1)L^{LS'J-1}_{LS'J-1}\}s^{LS\;J}_{LS'J-1} + L^{LS'J}_{LS'J-1}s^{LS\;J}_{LS'J} = 0. \tag{9}$$

With $S'=S$ in Eq. (7) we obtain

$$\begin{aligned} s^{LSJ}_{LSJ+1} &= -\, s^{LS}_{LS}L^{LSJ}_{LSJ+1} \\ &= s^{LS}_{LS}\left(\frac{(L+S-J)(L+S+J+2)(J+1+L-S)(J+1+S-L)}{4(J+1)^2(2J-1)(2J+1)}\right)^{1/2} \end{aligned} \tag{10a}$$

From Eq. (8) with $S'=S$ we have

$$s^{LSJ}_{LSJ}L^{LSJ}_{LSJ+1} = s^{LSJ}_{LSJ+1}\{(J+1)L^{LSJ}_{LSJ} - (J+2)L^{LSJ+1}_{LSJ+1}\}$$

$$s^{LSJ}_{LSJ} = s^{LS}_{LS}\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}. \tag{10b}$$

From Eq. (7) with $S'=S-1$ we have

$$L^{LSJ-1}_{LSJ}\; s^{LS\;\;J}_{LS-1J+1} = s^{LS\;\;J-1}_{LS-1J}\quad L^{LS-1J}_{LS-1J+1}$$

or

$$\left(\frac{(L+S+1-J)(J-S+L)}{4J^2(2J-1)(2J+1)}\right)^{1/2}\,{}^{LS\;\;J}_{LS-1J+1}$$

$$= \left(\frac{(L+S-J-1)(J-S+L+2)}{4(J+1)^2(2J+1)(2J+3)}\right)^{1/2} s^{LS\;\;J-1}_{LS-1J}$$

$$s^{LS\;\;J}_{LS-1J+1} = -\, s^{LS}_{LS-1}\left(\frac{(L+S-J-1)(L+S-J)(J-S+L+2)(J-S+L+1)}{4(J+1)^2(2J+1)(2J+3)}\right)^{1/2} \tag{10c}$$

From Eq. (8) with $S'=S-1$ we have

$$s^{LS\;\;J}_{LS-1J}\, L^{LS-1J}_{LS-1J+1} = s^{LS\;\;J}_{LS-1J+1}\{(J+1)L^{LSJ}_{LSJ} - (J+2)L^{LS-1J+1}_{LS-1J+1}\}$$

$$s^{LS\;\;J}_{LS-1J} = -\, s^{LS}_{LS-1}\left(\frac{(L+S-J)(J-S+L+1)(J+S-L)(L+S+J+1)}{4J^2(J+1)^2}\right)^{1/2} \tag{10d}$$

Finally from Eq. (9) with $S'=S-1$ we obtain

$$s_{LS-1\,J-1}^{LS\;\;J} = s_{LS-1}^{LS}\left(\frac{(L+S+J)(J-L+S-1)(J+S-L)(L+S+J+1)}{4J^2(2J-1)(2J+1)}\right)^{1/2}. \quad (10e)$$

The remaining components may be obtained by interchanging the upper and lower indices. Formulas (10a) to (10e) can, except for sign, be obtained from Eqs. (6) by interchanging L and S.

Determination of l_{LS}^{LS} etc.

If we suppose that L^2, S^2, L_z and S_z are diagonal, then $\mathbf{L}$, $\mathbf{l}_1$ and $\mathbf{l}_2$ will be related to each other in the same manner as $\mathbf{J}$, $\mathbf{L}$ and $\mathbf{S}$ in the above calculation. $\mathbf{S}$, $\mathbf{s}_1$, and $\mathbf{s}_2$ will also be related in this manner. Then we can obtain the components of $\mathbf{l}_1$ and $\mathbf{l}_2$ and of $\mathbf{s}_1$ and $\mathbf{s}_2$ in this representation by a substitution of the appropriate quantum numbers in Eqs. (4) and (5). Now suppose we make a unitary transformation to a representation in which J^2, L^2, S^2 and J_z are diagonal. Such a transformation leaves L^2, S^2 and J_z invariant and so can only have components between states of the same L, S and M_J values. Between two sets of L, S and M_J values, the matrix components of $\mathbf{l}$ and $\mathbf{s}$ will have a constant factor $l_{L'S}^{L\,S}$ and $s_{LS'}^{LS}$. This factor which is determined by the substitution of the appropriate quantum numbers in Eqs. (4) and (5), will not depend on J and will remain after the transformation. The other factor will depend on J and is just the factor we have determined above. Hence we have

$$l_{1LS}^{LS} = \frac{L(L+1)+l_1(l_1+1)-l_2(l_2+1)}{2L(L+1)}$$

$$l_{2LS}^{LS} = \frac{L(L+1)+l_2(l_2+1)-l_1(l_1+1)}{2L(L+1)} \quad (11)$$

$$l_{1L-1S}^{L\;\;S} = \left(\frac{(l_1+l_2-L+1)(l_1+l_2+L+1)(L-l_1+l_2)(L-l_2+l_1)}{4L^2(2L-1)(2L+1)}\right)^{1/2} = -\,l_{2L-1S}^{L\;\;S}$$

$$s_{1LS}^{LS} = \frac{S(S+1)+s_1(s_1+1)-s_2(s_2+1)}{2S(S+1)}$$

$$s_{2LS}^{LS} = \frac{S(S+1)+s_2(s_2+1)-s_1(s_1+1)}{2S(S+1)}$$

$$s_{1LS-1}^{LS} = \left(\frac{(s_1+s_2-S+1)(s_1+s_2+S+1)(S-s_1+s_2)(S-s_2+s_1)}{4S^2(2S-1)(2S+1)}\right)^{1/2} = -\,s_{2LS-1}^{LS}.$$

Remembering that in our case $s_1=s_2=\frac{1}{2}$, the formulas for s_1 and s_2 reduce to

$$s_{1LS}^{LS} = s_{2LS}^{LS} = \tfrac{1}{2}$$

$$s_{1LS-1}^{LS} = -\,s_{2LS-1}^{IS} = \tfrac{1}{2}\left(\frac{(2+S)(2-S)}{(2S-1)(2S+1)}\right)^{1/2}.$$

Summary of Formulas

$$(l_x \pm il_y)^{L\,S\,JM_J}_{L'S'JM_J\mp1}/l^{L\,S\,J}_{L'S'J} = (s_x \pm is_y)^{L\,S\,JM_J}_{L'S'JM_J\mp1}/s^{L\,S\,J}_{L'S'J} = \left\{(J \pm M_J)(J \mp M_J + 1)\right\}^{1/2}$$

$$l^{L\,S\,JM_J}_{zL'S'JM_J}/l^{L\,S\,J}_{L'S'J} = s^{L\,SJM_J}_{zL'S'JM_J}/s^{L\,S\,J}_{L'S'J} = M_J$$

$$(l_x \pm il_y)^{L\,S\,J\,\,M_J}_{L'S'J+1M_J\mp1}/l^{L\,S\,J}_{L'S'J+1} = (s_x \pm is_y)^{L\,S\,J\,\,M_J}_{L'S'J+1M_J\mp1}/s^{L\,S\,J}_{L'S'J+1} = \pm\left\{(J \mp M_J + 1)(J \mp M_J + 2)\right\}^{1/2}$$

$$l^{LSJ\,\,M_J}_{zL'S'J+1M_J}/l^{L\,S\,J}_{L'S'J+1} = s^{L\,S\,J\,\,M_J}_{zL'S'J+1M_J}/s^{L\,S\,J}_{L'S'J+1} = \left\{(J+1)^2 - M_J^2\right\}^{1/2}$$

$$(l_x \pm il_y)^{LSJ\,\,M_J}_{L'S'J-1M_J\mp1}/l^{L\,S\,J}_{L'S'J-1} = (s_x \pm is_y)^{L\,S\,J\,\,M_J}_{L'S'J-1M_J\mp1}/s^{L\,S\,J}_{L'S'J-1} = \mp\left\{(J \pm M_J)(J \pm M_J - 1)\right\}^{1/2}$$

$$l^{L\,S\,J\,\,M_J}_{zL'S'J-1M_J}/l^{L\,S\,J}_{L'S'J-1} = s^{L\,S\,J\,\,M_J}_{zL'S'J-1M_J}/s^{L\,S\,J}_{L'S'J-1} = (J^2 - M_J^2)^{1/2}$$

$$l^{LSJ}_{LSJ+1}/l^{LS}_{LS} = -\left(\frac{(L+S+J+2)(L+S-J)(J+1+L-S)(J+1+S-L)}{4(J+1)^2(2J+1)(2J+3)}\right)^{1/2}$$

$$l^{LSJ}_{LSJ}/l^{LS}_{LS} = \frac{J(J+1) - S(S+1) + L(L+1)}{2J(J+1)}$$

$$l^{LSJ}_{LSJ-1}/l^{LS}_{LS} = -\left(\frac{(L+S+J+1)(L+S+1-J)(J+L-S)(J+S-L)}{4J^2(2J-1)(2J+1)}\right)^{1/2}$$

$$l^{L\,\,SJ}_{L-1SJ+1}/l^{L\,\,S}_{L-1S} = -\left(\frac{(L+S-J-1)(L+S-J)(J-L+S+2)(J-L+S+1)}{4(J+1)^2(2J+1)(2J+3)}\right)^{1/2}$$

$$l^{L\,\,SJ}_{L-1SJ}/l^{L\,\,S}_{L-1S} = \left(\frac{(L+S-J)(J-L+S+1)(J+L-S)(L+S+J+1)}{4J^2(J+1)^2}\right)^{1/2}$$

$$l^{L\,\,SJ}_{L-1SJ-1}/l^{L\,\,S}_{L-1S} = \left(\frac{(L+S+J)(J+L-S-1)(J+L-S)(L+S+J+1)}{4J^2(2J-1)(2J+1)}\right)^{1/2}$$

$$l^{L\,\,SJ}_{L+1SJ+1}/l^{L\,\,S}_{L+1S} = \left(\frac{(L+S+J+2)(J+L-S+1)(J+L-S+2)(L+S+J+3)}{4(J+1)^2(2J+1)(2J+3)}\right)^{1/2}$$

$$l^{L\,\,SJ}_{L+1SJ}/l^{L\,\,S}_{L+1S} = \left(\frac{(L+S-J+1)(J-L+S)(J+L-S+1)(L+S+J+2)}{4J^2(J+1)^2}\right)^{1/2}$$

$$l^{L\,\,SJ}_{L+1SJ-1}/l^{L\,\,S}_{L+1S} = -\left(\frac{(L+S-J+1)(L+S-J+2)(J-L+S)(J-L+S-1)}{4J^2(2J-1)(2J+1)}\right)^{1/2}$$

$$s^{LSJ}_{LSJ+1}/s^{LS}_{LS} = \left(\frac{(L+S-J)(L+S+J+2)(J+1+L-S)(J+1-L+S)}{4(J+1)^2(2J+1)(2J+3)}\right)^{1/2}$$

$$s^{LSJ}_{LSJ}/s^{LS}_{LS} = \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

$$s^{LSJ}_{LSJ-1}/s^{LS}_{LS}=\left(\frac{(L+S-J+1)(L+S+J+1)(J+L-S)(J-L+S)}{4J^2(2J-1)(2J+1)}\right)^{1/2}$$

$$s^{LS\ J}_{LS-1J+1}/s^{LS}_{LS-1}=-\left(\frac{(L+S-J-1)(L+S-J)(J-S+L+2)(J-S+L+1)}{4(J+1)^2(2J+1)(2J+3)}\right)^{1/2}$$

$$s^{LS\ J}_{LS-1J}/s^{LS}_{LS-1}=-\left(\frac{(L+S-J)(J-S+L+1)(J+S-L)(L+S+J+1)}{4J^2(J+1)^2}\right)^{1/2}$$

$$s^{LS\ J}_{LS-1J-1}/s^{LS}_{LS-1}=\left(\frac{(L+S+J)(J-L+S-1)(J+S-L)(L+S+J+1)}{4J^2(2J-1)(2J+1)}\right)^{1/2}$$

$$s^{LS\ J}_{LS+1J+1}/s^{LS}_{LS+1}=\left(\frac{(L+S+J+2)(J-L+S+1)(J+S-L+2)(L+S+J+3)}{4(J+1)^2(2J+1)(2J+3)}\right)^{1/2}$$

$$s^{LS\ J}_{LS+1J}/s^{LS}_{LS+1}=-\left(\frac{(L+S-J+1)(J-S+L)(J+S-L+1)(L+S+J+2)}{4J^2(J+1)^2}\right)^{1/2}$$

$$s^{LS\ J}_{LS+1J-1}/s^{LS}_{LS+1}=-\left(\frac{(L+S-J+1)(L+S-J+2)(J-S+L)(J-S+L-1)}{4J^2(2J-1)(2J+1)}\right)^{1/2}$$

$$l^{LS}_{1LS}=\frac{L(L+1)+l_1(l_1+1)-l_2(l_2+1)}{2L(L+1)}\qquad l^{LS}_{2LS}=\frac{L(L+1)+l_2(l_2+1)-l_1(l_1+1)}{2L(L+1)}$$

$$l^{L\ S}_{1L-1S}=-l^{L\ S}_{2L-1S}=\left(\frac{(l_1+l_2-L+1)(l_1+l_2+L+1)(L-l_1+l_2)(L-l_2+l_1)}{4L^2(2L-1)(2L+1)}\right)^{1/2}$$

$$l^{L\ S}_{1L+1S}=-l^{L\ S}_{2L+1S}=\left(\frac{(l_1+l_2-L)(l_1+l_2+L+2)(L+1-l_1+l_2)(L+1-l_2+l_1)}{4(L+1)^2(2L+1)(2L+3)}\right)^{1/2}$$

$$s^{LS}_{1LS}\quad s^{LS}_{2LS}=\tfrac{1}{2}$$

$$s^{LS}_{1LS-1}=-s^{LS}_{2LS-1}=\tfrac{1}{2}\left(\frac{(2-S)(2+S)}{(2S-1)(2S+1)}\right)^{1/2}$$

$$s^{LS}_{1LS+1}=-s^{LS}_{2LS+1}=\tfrac{1}{2}\left(\frac{(1-S)(3+S)}{(2S+1)(2S+3)}\right)^{1/2}$$

The Matrix of the Spin-Orbit Interaction

We wish to obtain the matrix of $a_1(l_1\cdot s_1)+a_2(l_2\cdot s_2)$. From Eqs. (2) we know that this expression commutes with J^2 and J_z. It will therefore be diagonal with respect to the quantum numbers J and M_J. By matrix multiplication we have

$$\begin{aligned}(l\cdot s)^{L\ S\ JM_J}_{L'S'JM_J}=&\sum_{J''}\tfrac{1}{2}(l_x-il_y)^{L\ SJ\ \ M_J}_{L'SJ''M_J+1}(s_x+is_y)^{L'S\ J''M_J+1}_{L'S'J\ \ M_J}\\&+\tfrac{1}{2}(l_x+il_y)^{LSJ\ \ M_J}_{L'SJ''M_J-1}(s_x-is_y)^{I'S\ J''M_J-1}_{L'S'J\ \ M_J}+l_z{}^{L\ S\ J\ \ M_J}_{L'SJ''M_J}s_z{}^{L'S\ J''M_J}_{L'S'J\ \ M_J}\\=&(J+1)(2J+3)l^{L\ SJ}_{L'SJ+1}s^{L'S\ J+1}_{L'S'J}+J(J+1)l^{L\ SJ}_{L'SJ}s^{L'S\ J}_{L'S'J}\end{aligned}$$

$$+ J(2J - 1) l^{L\,SJ}_{L'SJ-1} s^{L'S\,J-1}_{L'S'J} \,.$$

Substitution from our previous formulas into the above equation yields the following result for the matrix components of the spin-orbit interaction.

$$(l\cdot s)^{L\quad S\quad JM_J}_{L-1S-1JM_J} = -\tfrac{1}{2}(l^{L\ \ S}_{L-1S})(s^{L-1S}_{L-1S-1})\{(L+S-J)(L+S-J-1)(L+S+J)(L+S+J+1)\}^{1/2}$$

$$(l\cdot s)^{L\quad SJM_J}_{L-1SJM_J} = \tfrac{1}{2}(l^{L\ \ S}_{L-1S})(s^{L-1S}_{L-1S})\{(L+S-J)(J-L+S+1)(J+L-S)(L+S+J+1)\}^{1/2}$$

$$(l\cdot s)^{L\quad S\quad JM_J}_{L-1S+1JM_J} = \tfrac{1}{2}(l^{L\ \ S}_{L-1S})(s^{L-1S}_{L-1S+1})\{(J-L+S+2)(J-L+S+1)(J-S+L)(J-S+L-1)\}^{1/2}$$

$$(l\cdot s)^{LS\quad JM_J}_{LS-1JM_J} = -\tfrac{1}{2}(l^{LS}_{LS})(s^{LS}_{LS-1})\{(L+S-J)(J+L-S+1)(L+S+J+1)(J-L+S)\}^{1/2}$$

$$(l\cdot s)^{LSJM_J}_{LSJM_J} = \tfrac{1}{2}(l^{LS}_{LS})(s^{LS}_{LS})\{J(J+1)-L(L+1)-S(S+1)\}$$

$$(l\cdot s)^{LS\quad JM_J}_{LS+1JM_J} = -\tfrac{1}{2}(l^{LS}_{LS})(s^{LS}_{LS+1})\{(L+S-J+1)(J+L-S)(L+S+J+2)(J-L+S+1)\}^{1/2}$$

$$(l\cdot s)^{L\quad S\quad JM_J}_{L+1S-1JM_J} = \tfrac{1}{2}(l^{L\ \ S}_{L+1S})(s^{L+1S}_{L+1S-1})\{(J-L+S)(J-L+S-1)(J+L-S+1)(J+L-S+2)\}^{1/2}$$

$$(l\cdot s)^{L\quad SJM_J}_{L+1SJM_J} = \tfrac{1}{2}(l^{L\ \ S}_{L+1S})(s^{L+1S}_{L+1S})\{(L+S-J+1)(J-L+S)(J+L-S+1)(L+S+J+2)\}^{1/2}$$

$$(l\cdot s)^{L\quad S\quad JM_J}_{L+1S+1JM_J} = -\tfrac{1}{2}(l^{L\ \ S}_{L+1S})(s^{L+1S}_{L+1S+1})\{(L+S-J+1)(L+S-J+2)(L+S+J+2)(L+S+J+3)\}^{1/2}$$

These formulas apply for both electrons. In conjunction with the expressions given above for $l^{LS}_{L'S}$ and $s^{LS}_{LS'}$ they completely determine the matrix of the spin-orbit interaction.

The Configuration p^2

In this case $l_1 = l_2 = 1$ and $a_1 = a_2 = a$. The multiplets are ^1D, ^3P and ^1S. The energy matrix calculated from the above formulas is given below. It is sufficient to give separate matrices for each J value as there are no components between states of different J value.

$J = 2$

	$^1D_2$	$^3P_2$
$^1D_2$	0	$(\frac{1}{2})^{1/2}a$
$^3P_2$	$(\frac{1}{2})^{1/2}a$	$a/2$

$J = 1$

	$^3P_1$
$^3P_1$	$-a/2$

$J = 0$

	$^3P_0$	$^1S_0$
$^3P_0$	$-a$	$-(2)^{1/2}a$
$^1S_0$	$-(2)^{1/2}a$	0

From Slater's paper we find for the electrostatic energies in terms of his radial integrals

$$^1D: \quad F^0 + 1/25F^2$$
$$^3P: \quad F^0 - 5/25F^2$$
$$^1S: \quad F^0 + 10/25F^2.$$

We now measure energies from the $^3P_1$ level. Then adding the electrostatic energies to the diagonal terms and setting the determinant of the energy matrix equal to zero, we obtain the following secular equations.

$$J = 2 \quad W^2 - W(3/2a + 6/25F^2) + 6/25F^2a = 0$$
$$J = 1 \quad W = 0$$
$$J = 0 \quad W^2 - W(15/25F^2) - 9/4a^2 - 15/50F^2a = 0.$$

These equations determine the energy levels in intermediate coupling in terms of the coupling parameters a and F^2. They have been previously obtained and discussed by Goudsmit.[7]

The Configuration $p \cdot p$

In this case also $l_1 = l_2$ but now $a_1 \neq a_2$. The multiplets are singlet and triplet D, P and S. From our formulas, the energy matrix is

$J = 3$

	$^3D_3$
$^3D_3$	$\frac{1}{2}(a_1 + a_2)$

$J = 2$

	$^3D_2$	$^1D_2$	$^3P_2$
$^3D_2$	$-\frac{1}{4}(a_1 + a_2)$	$-\frac{1}{2}(3/2)^{1/2}(a_1 - a_2)$	$\frac{1}{4}(3)^{1/2}(a_1 - a_2)$
$^1D_2$	$-\frac{1}{2}(3/2)^{1/2}(a_1 - a_2)$	0	$\frac{1}{4}(2)^{1/2}(a_1 + a_2)$
$^3P_2$	$\frac{1}{4}(3)^{1/2}(a_1 - a_2)$	$\frac{1}{4}(2)^{1/2}(a_1 + a_2)$	$\frac{1}{4}(a_1 + a_2)$

$J = 1$

	$^3D_1$	$^3P_1$	$^1P_1$	$^3S_1$
$^3D_1$	$-\frac{3}{4}(a_1+a_2)$	$\frac{1}{4}(5/3)^{1/2}(a_1-a_2)$	$-\frac{1}{4}(10/3)^{1/2}(a_1+a_2)$	0
$^3P_1$	$\frac{1}{4}(5/3)^{1/2}(a_1 - a_2)$	$-\frac{1}{4}(a_1+a_2)$	$-\frac{1}{4}(2)^{1/2}(a_1-a_2)$	$(\frac{1}{3})^{1/2}(a_1-a_2)$
$^1P_1$	$-\frac{1}{4}(10/3)^{1/2}(a_1+a_2)$	$-\frac{1}{4}(2)^{1/2}(a_1-a_2)$	0	$\frac{1}{2}(\frac{2}{3})^{1/2}(a_1+a_2)$
$^3S_1$	0	$(\frac{1}{3})^{1/2}(a_1-a_2)$	$\frac{1}{2}(\frac{2}{3})^{1/2}(a_1 + a_2)$	0

[7] Reference 4. To agree with Goudsmit's results we must set $a/2 = A$ and $3/25\ F^2 = X$ in the above equations.

* In the secular equations the parameters never appear in the denominators of fractions. An expression such as 6/25 F^2 must always be taken to mean (6/25) F^2.

$J=0$		$^3P_0$	$^1S_0$
	$^3P_0$	$-\frac{1}{2}(a_1+a_2)$	$-\frac{1}{2}(2)^{1/2}(a_1-a_2)$
	$^1S_0$	$-\frac{1}{2}(2)^{1/2}(a_1-a_2)$	0

For the electrostatic energies referred to the ^3D multiplet we find by Slater's method[8]

$$^3D:\quad 0$$
$$^1D:\quad 2G^0 + 2/25G^2 = \alpha$$
$$^3P:\quad -6/25F^2 + 2G^0 - 4/25G^2 = \beta$$
$$^1P:\quad -6/25F^2 + 6/25G^2 = \gamma$$
$$^3S:\quad 9/25F^2 - 9/25G^2 = -3/2\gamma$$
$$^1S:\quad 9/25F^2 + 2G^0 + 11/25G^2 = \delta.$$

Measuring the energy levels from the $^3D_3$ we obtain the following secular equations

$$J = 3\quad W = 0$$

$$J = 2\quad -W^3 + W^2\{\alpha + \beta - 3/2(a_1 + a_2)\} - W\{\alpha\beta - \tfrac{1}{4}(a_1 + a_2)(4\alpha + 5\beta) + 9/4a_1a_2\} - 3/4(a_1 + a_2)\alpha\beta + \tfrac{3}{4}a_1a_2(\alpha + 2\beta) = 0$$

$$J = 1\quad W^4 - W^3\{\beta - \tfrac{1}{2}\gamma - 3(a_1 + a_2)\} + W^2\{-\tfrac{1}{2}\gamma(\beta + 3\gamma) + \tfrac{1}{4}(a_1 + a_2)(-9\beta + 5\gamma) + 9/4(a_1{}^2 + a_2{}^2 + 3a_1a_2)\}$$
$$- W\{-3/2\beta\gamma^2 + \tfrac{1}{8}(a_1 + a_2)(7\beta + 24\gamma) + 3/32(a_1 + a_2)^2(12\beta - 7\gamma) - 3/32(a_1 - a_2^2)\gamma - 27/8a_1a_2(a_1 + a_2)\} + 15/8(a_1 + a_2)\beta\gamma^2 - 5/8(2a_1^2 + 29_2^2 + 5a_1a_2)\gamma^2 = 0$$

$$J = 0\quad W^2 - W\{\beta + \delta - 3/2(a_1 + a_2)\} + \beta\delta - \tfrac{1}{2}(a_1 + a_2)(\beta + 2\delta) + 2a_1a_2 = 0.$$

The Configuration d^2

In this case $l_1 = l_2 = 2$ and $a_1 = a_2 = a$. The multiplets are ^1G, ^3F, ^1D, ^3P and ^1S. From our formulas the magnetic energy matrix is

$J = 4$		$^1G_4$	$^3F_4$
	$^1G_4$	0	a
	$^3F_4$	a	$3/2a$

$J = 3$		$^3F_3$
	$^3F_3$	$-\frac{1}{2}a$

$J = 2$		$^3F_2$	$^1D_2$	$^3P_2$
	$^3F_2$	$-2a$	$-2(3/5)^{1/2}a$	0
	$^1D_2$	$-2(3/5)^{1/2}a$	0	$(21/10)^{1/2}a$
	$^3P_2$	0	$(21/10)^{1/2}a$	$\frac{1}{2}a$

[8] E. U. Condon and G. H. Shortley, Phys. Rev. **37**, 1025 (1931).

$J = 1$		$^3P_1$
	$^3P_1$	$-\frac{1}{2}a$

$J = 0$		$^3P_0$	$^1S_0$
	$^3P_0$	$-a$	$-(6)^{1/2}a$.
	$^1S_0$	$-(6)^{1/2}a$	0

By Slater's method[8] we find for the electrostatic energies referred to the ^3F multiplet

$$
\begin{aligned}
^1G&: \quad 12/49F^2 + 10/441F^4 = \alpha \\
^3F&: \quad 0 \\
^1D&: \quad 5/49F^2 + 45/441F^4 = \beta \\
^3P&: \quad 15/49F^2 - 75/441F^4 = \gamma \\
^1S&: \quad 22/49F^2 + 135/441F^4 = \delta.
\end{aligned}
$$

Measuring energies from the $^3F_3$ level, we find the following secular equations.

$$
\begin{aligned}
J &= 4 \quad W^2 - W(\alpha + 5/2a) + 2a\alpha = 0 \\
J &= 3 \quad -W = 0 \\
J &= 2 \quad -W^3 + W^2(\beta + \gamma) - W\{\beta\gamma - \tfrac{1}{2}a(\beta + 2\gamma) - 25/4a^2\} - 3/2a\beta\gamma \\
&\qquad - 3/20a^2(10\beta + 21\gamma) = 0 \\
J &= 1 \quad -W + \gamma = 0 \\
J &= 0 \quad W^2 - W(\gamma + \delta) + \gamma\delta + \tfrac{1}{2}a(\gamma - \delta) - 25/4a^2 = 0.
\end{aligned}
$$

THE CONFIGURATION $d \cdot d$

In this case $l_1 = l_2 = 2$ but $a_1 \neq a_2$. The multiplets are singlet and triplet S, P, D, F and G. From our formulas the magnetic energy matrix is

$J = 5$		$^3G_5$
	$^3G_5$	$a_1 + a_2$

$J = 4$		$^3G_4$	$^1G_4$	$^3F_4$
	$^3G_4$	$-\frac{1}{4}(a_1 + a_2)$	$-\frac{1}{2}(5)^{1/2}(a_1 - a_2)$	$\frac{1}{4}(5)^{1/2}(a_1 - a_2)$
	$^1G_4$	$-\frac{1}{2}(5)^{1/2}(a_1 - a_2)$	0	$\frac{1}{2}(a_1 + a_2)$
	$^3F_4$	$\frac{1}{4}(5)^{1/2}(a_1 - a_2)$	$\frac{1}{2}(a_1 + a_2)$	$\frac{3}{4}(a_1 + a_2)$

$J = 3$		$^3G_3$	$^3F_3$	$^1F_3$	$^3D_3$
	$^3G_3$	$-5/4(a_1 + a_2)$	$\frac{1}{4}(3/7)^{1/2}(a_1 - a_2)$	$-3/2(1/7)^{1/2}(a_1 + a_2)$	0
	$^3F_3$	$\frac{3}{4}(3/7)^{1/2}(a_1 - a_2)$	$-\frac{1}{4}(a_1 + a_2)$	$-\frac{1}{2}(3)^{1/2}(a_1 - a_2)$	$2(1/7)^{1/2}(a_1 - a_2)$
	$^1F_3$	$-3/2(1/7)^{1/2}(a_1 + a_2)$	$-\frac{1}{2}(3)^{1/2}(a_1 - a_2)$	0	$(3/7)^{1/2}(a_1 + a_2)$
	$^3D_3$	0	$2(1/7)^{1/2}(a_1 - a_2)$	$(3/7)^{1/2}(a_1 + a_2)$	$\frac{1}{2}(a_1 + a_2)$

$J = 2$		$^3F_2$	$^3D_2$	$^1D_2$	$^3P_2$
	$^3F_2$	$-(a_1 + a_2)$	$(2/5)^{1/2}(a_1 - a_2)$	$-(3/5)^{1/2}(a_1 + a_2)$	0
	$^3D_2$	$(2/5)^{1/2}(a_1 - a_2)$	$-\frac{1}{4}(a_1 + a_2)$	$-\frac{1}{4}(6)^{1/2}(a_1 - a_2)$	$\frac{3}{4}(7/5)^{1/2}(a_1 - a_2)$
	$^1D_2$	$-(3/5)^{1/2}(a_1 + a_2)$	$-\frac{1}{4}(6)^{1/2}(a_1 - a_2)$	0	$\frac{1}{2}(21/10)^{1/2}(a_1 + a_2)$
	$^3P_2$	0	$\frac{3}{4}(7/5)^{1/2}(a_1 - a_2)$	$\frac{1}{2}(21/10)^{1/2}(a_1 + a_2)$	$\frac{1}{4}(a_1 + a_2)$

		$^3D_1$	$^3P_1$	$^1P_1$	$^3S_1$
$J=1$	$^3D_1$	$-\frac{3}{4}(a_1+a_2)$	$\frac{1}{4}(7)^{1/2}(a_1-a_2)$	$-\frac{1}{4}(14)^{1/2}(a_1+a_2)$	0
	$^3P_1$	$\frac{1}{4}(7)^{1/2}(a_1-a_2)$	$-\frac{1}{4}(a_1+a_2)$	$-\frac{1}{4}(2)^{1/2}(a_1-a_2)$	a_1-a_2
	$^1P_1$	$-\frac{1}{4}(14)^{1/2}(a_1+a_2)$	$-\frac{1}{4}(2)^{1/2}(a_1-a_2)$	0	$\frac{1}{2}(2)^{1/2}(a_1+a_2)$
	$^3S_1$	0	a_1-a_2	$\frac{1}{2}(2)^{1/2}(a_1+a_2)$	0

		$^3P_0$	$^1S_0$
$J=0$	$^3P_0$	$-\frac{1}{2}(a_1+a_2)$	$-\frac{1}{2}(6)^{1/2}(a_1+a_2)$
	$^1S_0$	$-\frac{1}{2}(6)^{1/2}(a_1+a_2)$	0

Now we could proceed as before, that is add the electrostatic energies to the diagonal terms of the above matrix and then expand the determinant of the matrix in order to obtain the secular equations. But in this case the expanded fourth order equations are so complicated that it seems preferable to leave them in the form of fourth order determinants, as the determinants are probably easier than the expanded form to handle numerically. For this reason we do not give the expanded form for the secular equations.

The Configuration $d \cdot p$

In this case we have $l_1=2$ and $l_2=1$. The multiplets are singlet and triplet P, D and F. From our formulas the magnetic energy matrix is

		$^3F_4$
$J=4$	$^3F_4$	$\frac{1}{2}(2a_1+a_2)$

		$^3F_3$	$^1F_3$	$^3D_3$
$J=3$	$^3F_3$	$-1/6(2a_1+a_2)$	$-(\frac{1}{3})^{1/2}(2a_1-a_2)$	$\frac{1}{3}(2)^{1/2}(a_1-a_2)$
	$^1F_3$	$-(\frac{1}{3})^{1/2}(2a_1-a_2)$	0	$(1/6)^{1/2}(a_1+a_2)$
	$^3D_3$	$\frac{1}{3}(2)^{1/2}(a_1-a_2)$	$(1/6)^{1/2}(a_1+a_2)$	$1/6(5a_1+a_2)$

		$^3F_2$	$^3D_2$	$^1D_2$	$^3P_2$
$J=2$	$^3F_2$	$-\frac{2}{3}(2a_1+a_2)$	$\frac{1}{3}(7/5)^{1/2}(a_1-a_2)$	$-\frac{1}{3}(21/10)^{1/2}(a_1+a_2)$	0
	$^3D_2$	$\frac{1}{3}(7/5)^{1/2}(a_1-a_2)$	$-1/12(5a_1+a_2)$	$-\frac{1}{2}(1/6)^{1/2}(5a_1-a_2)$	$\frac{3}{4}(3/5)^{1/2}(a_1-a_2)$
	$^1D_2$	$-\frac{1}{3}(21/10)^{1/2}(a_1+a_2)$	$-\frac{1}{2}(1/6)^{1/2}(5a_1-a_2)$	0	$\frac{3}{4}(2/5)^{1/2}(a_1+a_2)$
	$^3P_2$	0	$\frac{3}{4}(3/5)^{1/2}(a_1-a_2)$	$\frac{3}{4}(2/5)^{1/2}(a_1+a_2)$	$\frac{1}{4}(3a_1-a_2)$

		$^3D_1$	$^3P_1$	$^1P_1$
$J=1$	$^3D_1$	$-\frac{1}{4}(5a_1+a_2)$	$\frac{1}{4}(3)^{1/2}(a_1-a_2)$	$-\frac{1}{4}(6)^{1/2}(a_1+a_2)$
	$^3P_1$	$\frac{1}{4}(3)^{1/2}(a_1-a_2)$	$-\frac{1}{4}(3a_1-a_2)$	$-\frac{1}{4}(2)^{1/2}(3a_1+a_2)$
	$^1P_1$	$-\frac{1}{4}(6)^{1/2}(a_1+a_2)$	$-\frac{1}{4}(2)^{1/2}(3a_1+a_2)$	0

		$^3P_0$
$J=0$	$^3P_0$	$-\frac{1}{2}(3a_1-a_2)$.

For the same reason as the previous case we do not give the expanded form of the secular equations.

Many Electron Configurations

Our formulas for four vectors may be applied to give the secular equations relating the levels arising from a common parent term. We take l_1 and s_1 for the orbital and spin momentum of the ion and l_2 and s_2 for the orbital and spin momentum of the added electron. Then the formulas for the matrix of the spin-orbit interaction apply directly when we remember that s_1 is no longer restricted to the value 1/2. We must use Eqs. (11) for $s_{1LS'}^{LS}$.

We consider first the addition of an s electron to a ^3P multiplet, a case already treated by Goudsmit.[4] The multiplets are ^4P and ^2P. Remembering that $l_1=l=L$, $s_1=l$, $l_2=0$ and $s_2=1/2$ we have from Eqs. (11)

$$l_{1LS}^{LS} = 1$$

$$l_{2LS}^{LS} = 0$$

$$s_{1LS}^{LS} = \frac{S(S+1)+5/4}{2S(S+1)} = \begin{cases} 2/3 \text{ for } ^4P \\ 4/3 \text{ for } ^2P \end{cases}$$

$$s_{1LS-1}^{LS} = \left(\frac{(25/4-S^2)(S^2-\frac{1}{4})}{4S^2(4S^2-1)}\right)^{1/2}.$$

Our formulas for the matrix of the spin-orbit interaction give

$$J = 5/2 \qquad \begin{array}{c|c} & ^4P_{5/2} \\ \hline ^4P_{5/2} & a_1 \end{array}$$

$$J = 3/2 \qquad \begin{array}{c|cc} & ^4P_{3/2} & ^2P_{3/2} \\ \hline ^4P_{3/2} & -\frac{2}{3}a_1 & -\frac{1}{3}(5)^{1/2}a_1 \\ ^2P_{3/2} & -\frac{1}{3}(5)^{1/2}a_1 & \frac{2}{3}a_1 \end{array}$$

$$J = \tfrac{1}{2} \qquad \begin{array}{c|cc} & ^4P_{1/2} & ^2P_{1/2} \\ \hline ^4P_{1/2} & -5/3a_1 & -\frac{1}{3}(2)^{1/2}a_1 \\ ^2P_{1/2} & -\frac{1}{3}(2)^{1/2}a_1 & -\frac{4}{3}a_1 \end{array}.$$

Let α be the electrostatic energy of the ^2P multiplet referred to the ^4P. Then measuring energies from the $^4P_{5/2}$ level we obtain the following secular equations

$$J = 5/2 \qquad -W = 0$$

$$J = 3/2 \qquad W^2 - (\alpha - 2a_1)W - 5/3\alpha a_1 = 0$$

$$J = \tfrac{1}{2} \qquad W^2 - (\alpha - 5a_1)W - 8/3\alpha a_1 + 6a_1^2 = 0.$$

As another example we consider the addition of a p electron to a ^1P multiplet. The multiplets are ^2S, ^2P and ^2D. From Eqs. (11), remembering that $l_1=1$, $s_1=0$, $l_2=1$, $s_2=1/2=S$, we have

$$s_{1LS}^{LS} = 0$$

$$s_{2LS}^{LS} = 1$$

$$l_{2LS}^{LS} = \tfrac{1}{2}$$

$$l_{2L-1S}^{L\ S} = \tfrac{1}{2}\left(\frac{9-L^2}{4L^2-1}\right)^{1/2}.$$

Then we find for the matrix of the spin-orbit interaction

$$J = 5/2 \quad \begin{array}{c|c} & {}^2D_{5/2} \\ \hline {}^2D_{5/2} & \tfrac{1}{2}a_2 \end{array}$$

$$J = 3/2 \quad \begin{array}{c|cc} & {}^2D_{3/2} & {}^2P_{3/2} \\ \hline {}^2D_{3/2} & -\tfrac{3}{4}a_2 & \tfrac{1}{4}(5)^{1/2}a_2 \\ {}^2P_{3/2} & \tfrac{1}{4}(5)^{1/2}a_2 & \tfrac{1}{4}a_2 \end{array}$$

$$J = \tfrac{1}{2} \quad \begin{array}{c|cc} & {}^2P_{1/2} & {}^2S_{1/2} \\ \hline {}^2P_{1/2} & -\tfrac{1}{2}a_2 & \tfrac{1}{2}(2/5)^{1/2}a_2 \\ {}^2S_{1/2} & \tfrac{1}{2}(2/5)^{1/2}a_2 & 0 \end{array} .$$

Let α be the electrostatic energy of the ${}^2P$ multiplet referred to the ${}^2D$ and β be the electrostatic energy of the ${}^2S$ referred to the ${}^2D$. Measuring energies from the ${}^2D_{5/2}$ level we obtain the following secular equations.

$$J = 5/2 \qquad -W = 0$$

$$J = 3/2 \qquad W^2 - (\alpha - 2a_2)W + 5/8a_2(a_2 - 2\alpha) = 0$$

$$J = \tfrac{1}{2} \qquad W^2 - (\alpha + \beta - 3/2a_2)W + \alpha\beta - \tfrac{1}{2}a_2(\alpha + 2\beta) + 2/5a_2^2 = 0$$

The Adjustment of the Parameters

In the secular equations that we have given the coefficients are functions of the radial integrals F^k, G^k and a_1 and a_2. Until these integrals can be calculated they must be treated as parameters which may be adjusted to fit the experimental data. In simple cases this may be accomplished easily by using the sums of energies for each J value. These sums are always linear in the parameters so that if we set the various sums equal to their experimental values, we obtain a linear set of equations for the parameters. In more complicated cases we will not obtain enough equations to determine the parameters in this way and more laborious calculations will have to be made. However these calculations will be useful for other quantities besides the energy levels may be found in terms of the same parameters. Thus in the following paper the g values for intermediate coupling are calculated in terms of these parameters and in a later paper the writer will treat the question of intensities in intermediate coupling.

In conclusion the writer wishes to thank Professor Pauli for suggesting the method of treating this problem.