JANUARY 15, 1932 *PHYSICAL REVIEW* *VOLUME 39*

THE THEORY OF COMPLEX SPECTRA. PART I. ENERGY LEVELS

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(Received November 17, 1931)

Abstract

A general method of finding the wave function for *LS* coupling which is similar to that of Gray and Wills is described. The successive transformations which carry the angular momentum matrices, S^2, L^2 and J^2 to a diagonal form, are determined by writing down these matrices in terms of the unperturbed wave functions and solving the resulting linear equations for the transformation coefficients. This yields the wave functions appropriate for *LS* coupling. The method is applied to give the wave functions for all the states of *LS* coupling with the smallest value of $|M_J|$ in the following electronic configurations: p^2, d^2, p^3, p^2s and p^3s. The matrix of the spin-orbit interaction is calculated with these wave functions and is factored according to J values because J^2 is an integral of the motion. By adding the electrostatic energies as computed by Slater's method to the diagonal elements (the electrostatic energy is known to be a diagonal matrix in *LS* coupling), the complete energy matrix is obtained. Setting the determinant of the matrix equal to zero, the secular equation for each J value is found for the above electronic configurations. These equations determine the position of the energy levels in intermediate coupling provided that second order perturbations may be neglected and provided magnetic effects other than the spin-orbit interaction do not contribute appreciably to the Hamiltonian.

Introduction

In a previous paper[1] the calculation of the matrix elements of the spin-orbit interaction in *LS* coupling has been made for any two-electron configuration from the commutation relations which angular momentum vectors satisfy in matrix mechanics. This makes it possible to obtain in a simple manner the secular equations for any two-electron configuration. Although the method can probably be employed for more complex configurations, there are difficulties connected with the necessary extension. Furthermore, if the precise form of the magnetic interaction terms in the Hamiltonian is not correct, other calculations which it may not be possible to carry out by this method, must be made. For these reasons it is profitable to consider a quite different approach to the whole problem.

It was remarked in the above mentioned paper that difficulties with the unperturbed wave functions used by Slater[2] arose because these functions were not written for definite values of the total angular momentum, J^2. In this paper we propose to find the transformation to functions which make J^2 a diagonal matrix. Now such a transformation is by no means uniquely determined and, in fact, wave functions correct for any coupling scheme in an isolated atomic system have this property. For in any such coupling scheme

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[1] M. H. Johnson, Jr. Phys. Rev. **38,** 1628 (1931).

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

J^2 is always an integral of the motion so that the proper wave functions must be written for definite values of J^2. For several reasons it is preferable to find the wave functions for LS coupling rather than those for jj coupling (say). In the first place we know that in LS coupling the electrostatic energy is a diagonal matrix. We can then avail ourselves of the calculation of electrostatic energies by Slater's method in the cases where such calculations have been made. By his method we can always obtain the electrostatic energies if there are no two multiplets of the same kind in the group of states considered. In any other coupling scheme we should have to compute the whole matrix of the electrostatic energy, a task which it is profitable to avoid if possible. In the second place it is often very easy in LS coupling to find the matrices of other quantities such as the electric moment, the energy in a magnetic field etc., directly from matrix relations. This may obviate the necessity of using the wave functions, which are rather awkward sums of determinants, in finding such matrices.

From our present point of view the situation is greatly simplified by the existence of spatial degeneracy and the fact that Slater's functions are written for definite values of J_z. J_z is an integral of the motion so that in the transformations we contemplate it is a diagonal invariant. It is therefore only necessary in making these transformations to use linear combinations of functions with the same value of M_J. Because of the spatial degeneracy we know that all the states of distinct energy will be represented among the functions for the smallest value of $|M_J|$. Hence for the energy level problem it is only necessary to consider functions for the smallest value of $|M_J|$. This will still be true no matter how the Hamiltonian is modified (for an isolated atom) for no internal interaction can affect the spatial degeneracy or the fact that J_z is an integral of motion. Then if the actual Hamiltonian differs from the one which we shall employ, the transformations we determine can still be used to advantage.

THE METHOD OF FINDING WAVE FUNCTIONS FOR *LS* COUPLING

Our method of obtaining the wave functions for LS coupling is perfectly straight-forward. We compute the matrices of L^2, S^2 and J^2 with the unperturbed functions and then find the transformations to make these matrices diagonal. We know that the wave functions for LS coupling must be written for definite values of L^2, S^2, J^2, and J_z so that this is an obvious procedure. The matrix components in which we are interested may be calculated from the following formulas which can be obtained by an application of the equations that Condon[3] has given for matrix elements calculated with Slater's

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[3] E. U. Condon, Phys. Rev. **36**, 1121 (1930). The notation used here is very similar to Condon's. The single electron wave functions are written as $u_\alpha(1)$. The 1 stands for all the coordinates (including spin) of electron 1 and the subscript α stands for the set of single electron quantum numbers $n_\alpha\ l_\alpha\ m_{l\alpha}$ and $m_{s\alpha}$. The antisymmetric wave functions are

$$\psi_A = (N!)^{-1/2} \quad \Sigma(-1)^P P u_\alpha(1) u_\beta(2) \cdots u_\xi(N)$$

where the sum is extended over all the permutations, P. Matrix components are written in the Dirac notation wave functions. Rather than use J^2, we use $\boldsymbol{L.S}$ which must also be diagonal if L^2, S^2 and J^2 are diagonal.

$$(A \mid L^2 \mid A') = 4\{(\alpha \mid l_x \mid \alpha')(\beta \mid l_x \mid \beta') - (\alpha \mid l_x \mid \beta')(\beta \mid l_x \mid \alpha')\} \text{ if } A' \text{ differs from } A \text{ in } \alpha \text{ and } \beta$$

$$\begin{aligned}(A \mid L^2 \mid A) = {} & M_L{}^2 + \sum_{\alpha} \{l_\alpha(l_\alpha + 1) - m_{l\alpha}{}^2\} \\ & - \sum_{\substack{\text{all pairs} \\ \alpha,\beta}} \{l_\alpha(l_\alpha+1) - m_{l\alpha}(m_{l\alpha} \pm 1)\} (n_\alpha l_\alpha m_{l\alpha} \pm 1 m_{s\alpha} \mid 1 \mid n_\beta l_\beta m_{l\beta} m_{s\beta})\end{aligned}$$

$$(A \mid L^2 \mid A') = 0 \text{ otherwise}$$

$$(A \mid S^2 \mid A') = 4\{(\alpha \mid s_x \mid \alpha')(\beta \mid s_x \mid \beta') - (\alpha \mid s_x \mid \beta')(\beta \mid s_x \mid \alpha')\} \text{ if } A' \text{ differs from } A \text{ in } \alpha \text{ and } \beta$$

$$\begin{aligned}(A \mid S^2 \mid A) = {} & M_S{}^2 + \tfrac{1}{2}N - N' \text{ where } N = \text{number of electrons} \\ & N' = \text{number of pairs } \alpha, \beta \text{ with the same } n, l, \text{ and } m_l\end{aligned}$$

$$(A \mid S^2 \mid A') = 0 \text{ otherwise}$$

$$\begin{aligned}(A \mid \boldsymbol{L \cdot S} \mid A') = {} & 2\{(\alpha \mid l_x \mid \alpha')(\beta \mid s_x \mid \beta') + (\beta \mid l_x \mid \beta')(\alpha \mid s_x \mid \alpha') \\ & - (\alpha \mid l_x \mid \beta')(\beta \mid s_x \mid \alpha') - (\beta \mid l_x \mid \alpha')(\alpha \mid s_x \mid \beta')\} \text{ if } A' \text{ differs from } A \text{ in } \alpha \text{ and } \beta.\end{aligned}$$

$$(A \mid \boldsymbol{L \cdot S} \mid A') = 2\left\{\sum_{\alpha''}(\alpha \mid \overset{**}{l_x} \mid \alpha'')(\alpha'' \mid s_x \mid \alpha') - \sum_{\beta}(\beta \mid l_x \mid \alpha')(\alpha \mid s_x \mid \beta)\right\} \text{ if } A' \text{ differs from } A \text{ in } \alpha$$

$$(A \mid \boldsymbol{L \cdot S} \mid A) = M_L M_S$$

$$(A \mid \boldsymbol{L \cdot S} \mid A') = 0 \text{ otherwise.}$$

In these formulas

$$(\alpha \mid l_x \mid \beta) = \tfrac{1}{2}\{l_\alpha(l_\alpha + 1) - m_{l\alpha}(m_{l\alpha} \pm 1)\}^{1/2}(n_\alpha l_\alpha m_{l\alpha} \pm 1 m_{s\alpha} \mid 1 \mid n_\beta l_\beta m_{l\beta} m_{s\beta})$$

$$(\alpha \mid s_x \mid \beta) = \tfrac{1}{2}(n_\alpha l_\alpha m_{l\alpha} m_{s\alpha} \pm 1 \mid 1 \mid n_\beta l_\beta m_{l\beta} m_{s\beta})$$

$$(A \mid H \mid A') = \int \bar{\psi}_A H \psi_{A'}$$

where the integration implies a summation over the spin coordinates. The abbreviation

$$(\alpha \mid f \mid \beta) = \int \bar{u}_\alpha(k) f(k) u_\beta(k)$$

which is consistent with the above notation, is also introduced. Thus, for example, formula (b) on page 1129 of Condon's paper is, in this notation

$$(A \mid F \mid A') = (\alpha \mid f \mid \alpha')$$

if A' differs from A only in the individual set of quantum numbers α.

** In carrying out this summation it must be remembered that the exclusion principle operates to eliminate the terms for which α'' is equal to any of the other quantum numbers $\beta \cdots \xi$.

$$M_L = \sum_\alpha m_{l\alpha}$$

$$M_S = \sum_\alpha m_{s\alpha}.$$

All the diagonal elements of the unit matrix are unity and all the nondiagonal elements are zero. The signs must always be so chosen that $M_J = M_J'$. We see that L^2 and S^2 have no components between states of different M_L and M_S values as is required by the fact that both these matrices commute with L_z and S_z. Although the furmulas appear formidable, they are actually very easy to use when one has become familiar with the notation.

The required transformations are easy to obtain because the matrices L^2, S^2 and $\mathbf{L}.\mathbf{S}$ commute with one another. The matrix $\mathbf{S}^2$ is usually the simplest so that we first find the transformation, $\mathbf{R}$, which carries it to a diagonal form.[4]

$$RS^2R^{-1} = (S^2)'$$

$$RL^2R^{-1} = (L^2)'$$

$$R(\mathbf{L}\cdot\mathbf{S})R^{-1} = (\mathbf{L}\cdot\mathbf{S})'$$

where $(S^2)'$ is diagonal and commutes with $(L^2)'$ and $(\mathbf{L}.\mathbf{S})'$. The last two matrices can therefore have components only between the degenerate states of $(S^2)'$. Thus $\mathbf{R}$ tends to simplify the matrices L^2 and $\mathbf{L}.\mathbf{S}$. Let T carry $(L^2)'$ to a diagonal form, leaving $(S^2)'$ invariant.

$$T(L^2)'T^{-1} = (L^2)''$$

$$T(S^2)'T^{-1} = (S^2)'' = (S^2)'$$

$$T(\mathbf{L}\cdot\mathbf{S})'T^{-1} = (\mathbf{L}\cdot\mathbf{S})''$$

where $(L^2)''$ is diagonal. Now $(\mathbf{L}.\mathbf{S})''$ can only have components between states which are degenerate in both $(L^2)''$ and $(S^2)''$, and so is further simplified. As L^2 and S^2 had no components between states of different M_L and M_S values, the transformations R and T have no components between states of different M_L and different M_S. Hence $L_z'' = L_z$ and $S_z'' = S_z$. The transformation TR carries us to a representation in which L^2, S^2, L_z and S_z are diagonal matrices. Finally let U carry $(\mathbf{L}.\mathbf{S})''$ to a diagonal form, leaving $(L^2)''$ and $(S^2)''$ invariant.

$$U(\mathbf{L}\cdot\mathbf{S})''U^{-1} = (\mathbf{L}\cdot\mathbf{S})'''$$

$$U(L^2)''U^{-1} = (L^2)''' = (L^2)''$$

$$U(S^2)''U^{-1} = (S^2)''' = (S^2)'$$

Where $(\mathbf{L}.\mathbf{S})'''$ is diagonal. This transformation involves together the states of a single multiplet. After it the wave functions will be correct for LS coup-

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[4] R is determined in the manner in which any principle axis transformation is found. The determinant of the matrix S^2 is set equal to zero in order to obtain its characteristic values. (It is not actually necessary to do this as the characteristic values of S^2 are known from the commutation rules which the components of $\mathbf{S}$ obey.) The set of homogeneous linear equations $RS^2 = (S^2)'R$ together with the normalization condition determine the transformation coefficients.

ling as we still then have secured that L^2, S^2, J^2 and J_z be diagonal matrices. We can combine the three transformations into a single one, *UTR*, which will enable us to pass directly from the unperturbed functions to the functions correct for *LS* coupling. It is apparent one advantage of treating L^2, S^2 and $\mathbf{L.S}$ separately, instead of attempting to make J^2 diagonal directly, is that we factor the transformation into relatively simple parts.

The spin-orbit interaction is

$$H_2 = \sum_k f(r_k) \mathbf{l}_k \cdot \mathbf{s}_k .$$

Its matrix components in the initial representation are easily found from the formulas Condon[3] has given. They are

$$\begin{aligned}(A \mid H_2 \mid A') &= \tfrac{1}{2}(n_\alpha l_\alpha \mid f \mid n_\alpha' l_\alpha')\left[l_\alpha(l_\alpha + 1) - m_{l\alpha}(m_{l\alpha} \pm 1)\right]^{1/2} \\ &\qquad (m_{l\alpha} \pm 1 m_{s\alpha} \pm 1 \mid 1 \mid m_{l\alpha'} m_{s\alpha'}) \text{ if } A' \text{ differs from } A \text{ in } \alpha \\ (A \mid H_2 \mid A) &= \sum_\alpha (n_\alpha l_\alpha \mid f \mid n_\alpha l_\alpha) m_{l\alpha} m_{s\alpha} \\ (A \mid H_2 \mid A') &= 0 \text{ otherwise}\end{aligned}$$

where $(n_\alpha l_\alpha \mid f \mid n_{\alpha'} l_{\alpha'}) = \displaystyle\int R_{n_\alpha l_\alpha}(r) f(r) R_{n_{\alpha'} l_{\alpha'}}(r) dr .$

Then the matrix of the spin-orbit interaction in *LS* coupling is given by

$$H_2''' = (UTR) H_2 (UTR)^{-1}.$$

H_2''' should be factored according to J values since J^2 is an integral of the motion and is diagonal in this representation. We observe that the energy matrix will always factor according to J values after the transformation *UTR* though the form of the interaction terms be quite different than the above. For no matter what the internal interactions in the atom may be, J^2 will always be an integral of the motion.

As we remarked before, we can obtain the whole energy matrix by adding the electrostatic energies to the diagonal elements of H_2'''. It is easily shown that the diagonal element of the whole energy matrix are the energies of the states of the atom if *LS* coupling is physically realized (that is if L^2 and S^2 are also integrals of the motion). The secular equations in any case are found in the usual way by setting the determinant of the energy matrix equal to zero. As the matrix is factored according to J values, we obtain a separate algebraic equation for each J value which is of the same order as the number of states with this J value.

The procedure we have followed is closely related to the method used by Gray and Wills[5] to find the wave functions for *LS* coupling. If we examine the meaning underlying their manipulation with the operators $L_x \pm iL_y$ and $S_x \pm iS_y$, we see that they determine linear combinations of the unperturbed wave functions which make L^2, S^2, L_z and S_z diagonal (strong field functions). Thus the result of their first process is just the transformation *TR* with the

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

difference that they determine all the strong field functions whereas we determine only those for the smallest value of $|M_J|$. Similarly their second process with the operators $J_x \pm iJ_y$ gives the transformation U, again for all the wave functions. Our method is essentially the same as theirs, the only difference being in the manner in which the transformations are determined. The possible advantages of the present method are in the first place the compactness furnished by the matrix notation and in the second place the fact that it is only necessary to use the wave functions for the smallest value of $|M_J|$.

To illustrate our procedure in detail the complete calculation is given below for the configuration p^2. Only the results, that is the transformation UTR, the energy matrix in LS coupling and the secular equations are given for the configurations d^2, p^3, p^2s and p^3s .

APPLICATIONS

The configuration p^2

From Slater's notation[6] the wave functions for the smallest value of $|M_J|$, $M_J = 0$, are

	p^2	M_L	M_S
I	(0 ½) (−1 ½)	−1	1
II	(1 ½) (−1 −½)	0	0
III	(0 ½) (0 −½)	0	0
IV	(−1 ½) (1 −½)	0	0
V	(1 −½) (0 −½)	1	−1

The angular momentum matrices determined by our formulas are

$$L^2 = \begin{array}{c|c|ccc|c}
 & \mathrm{I} & \mathrm{II} & \mathrm{III} & \mathrm{IV} & \mathrm{V} \\
\hline
\mathrm{I} & 2 & & 0 & & 0 \\
\hline
\mathrm{II} & & 2 & 2 & 0 & \\
\mathrm{III} & 0 & 2 & 4 & 2 & 0 \\
\mathrm{IV} & & 0 & 2 & 2 & \\
\hline
\mathrm{V} & 0 & & 0 & & 2
\end{array}
\qquad
\mathbf{L}\cdot\mathbf{S} = \begin{array}{|c|ccc|c}
\hline
-1 & \sqrt{1/2} & 0 & -\sqrt{1/2} & 0 \\
\hline
\sqrt{1/2} & & & & \sqrt{1/2} \\
0 & & 0 & & 0 \\
-\sqrt{1/2} & & & & -\sqrt{1/2} \\
\hline
0 & \sqrt{1/2} & 0 & -\sqrt{1/2} & -1
\end{array}
\qquad
S^2 = \begin{array}{|c|ccc|c}
\hline
2 & & 0 & & 0 \\
\hline
 & 1 & 0 & -1 & \\
0 & 0 & 0 & 0 & 0 \\
 & -1 & 0 & 1 & \\
\hline
0 & & 0 & & 2
\end{array}$$

The transformation R is very easy to obtain and is

$$R = \begin{array}{|c|ccc|c}
\hline
1 & & 0 & & 0 \\
\hline
 & \sqrt{1/2} & 0 & \sqrt{1/2} & \\
0 & 0 & 1 & 0 & 0 \\
 & \sqrt{1/2} & 0 & -\sqrt{1/2} & \\
\hline
0 & & 0 & & 1
\end{array} = R^{-1}\,{}^{***}$$

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[6] Reference 2. In each bracket is placed the set of quantum numbers α for one of the electrons. The quantum numbers n_α, l_α, n_β, $l_\beta \cdots n_\xi$, l_ξ are omitted from the brackets as these quantum numbers do not change in the set of wave functions for one electronic configuration.

*** The reciprocals of any of our transformations are easily obtained because of their unitary character. Thus $R^{-1} = R^*$. As all our transformations are real, it is only necessary to interchange the rows and columns of a transformation matrix to obtain its reciprocal.

$$(S^2)' = \left|\begin{array}{c|ccc|c} 2 & & 0 & & 0 \\ \hline & 0 & 0 & 0 & \\ 0 & 0 & 0 & 0 & 0 \\ & 0 & 0 & 2 & \\ \hline 0 & & 0 & & 2 \end{array}\right. \qquad (L^2)' = \left|\begin{array}{c|ccc|c} 2 & & 0 & & 0 \\ \hline & 2 & 2\sqrt{2} & 0 & \\ 0 & 2\sqrt{2} & 4 & 0 & 0 \\ & 0 & 0 & 2 & \\ \hline 0 & & 0 & & 2 \end{array}\right. \qquad (L\cdot S)' = \left|\begin{array}{c|ccc|c} -1 & 0 & 0 & 1 & 0 \\ \hline 0 & & & & 0 \\ 0 & & 0 & & 0 \\ 1 & & & & 1 \\ \hline 0 & 0 & 0 & 1 & -1 \end{array}\right.$$

We observe that in fact $(L^2)'$ and $(\boldsymbol{L}.\boldsymbol{S})'$ have components only between the degenerate states of $(S^2)'$. The transformation T is equally simple.

$$T = \left|\begin{array}{c|ccc|c} 1 & & 0 & & 0 \\ \hline & \sqrt{1/3} & \sqrt{2/3} & 0 & \\ 0 & \sqrt{2/3} & -\sqrt{1/3} & 0 & 0 \\ & 0 & 0 & 1 & \\ \hline 0 & & 0 & & 1 \end{array}\right. = T^{-1}$$

$$(S^2)'' = (S^2)' \qquad (L^2)'' = \left|\begin{array}{c|ccc|c} 2 & & 0 & & 0 \\ \hline & 6 & 0 & 0 & \\ 0 & 0 & 0 & 0 & 0 \\ & 0 & 0 & 2 & \\ \hline 0 & & 0 & & 2 \end{array}\right. \qquad (L\cdot S)'' = (L\cdot S)'$$

The invariance of $(\boldsymbol{L}.\boldsymbol{S})'$ to T is peculiar to this case and does not represent the general situation. The product TR

$$TR = \left|\begin{array}{c|ccc|c} 1 & & 0 & & 0 \\ \hline & \sqrt{1/6} & \sqrt{2/3} & \sqrt{1/6} & \\ 0 & \sqrt{1/3} & -\sqrt{1/3} & \sqrt{1/3} & 0 \\ & \sqrt{1/2} & 0 & -\sqrt{1/2} & \\ \hline 0 & & 0 & & 1 \end{array}\right.$$

is the transformation from the initial to the strong field functions. Finally for U we have

$$U = \left|\begin{array}{c|ccc|c} \sqrt{1/6} & 0 & 0 & 2\sqrt{1/6} & \sqrt{1/6} \\ \hline 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ \sqrt{1/2} & 0 & 0 & 0 & -\sqrt{1/2} \\ \hline \sqrt{1/3} & 0 & 0 & -\sqrt{1/3} & \sqrt{1/3} \end{array}\right.$$

$$(S^2)''' = (S^2)' \qquad (L^2)''' = L^2)'' \qquad (L\cdot S)''' = \left|\begin{array}{c|ccc|c} 1 & & 0 & & 0 \\ \hline & 0 & 0 & 0 & \\ 0 & 0 & 0 & 0 & 0 \\ & 0 & 0 & -1 & \\ \hline 0 & & 0 & & -2 \end{array}\right.$$

The transformation to *LS* coupling is then

$$
\begin{array}{r|c|ccc|c}
 & \mathrm{I} & \mathrm{II} & \mathrm{III} & \mathrm{IV} & \mathrm{V} \\
\hline
{}^3P_2 & \sqrt{1/6} & \sqrt{1/3} & 0 & -\sqrt{1/3} & \sqrt{1/6} \\
\hline
{}^1D_2 & 0 & \sqrt{1/6} & \sqrt{2/3} & \sqrt{1/6} & 0 \\
UTR = {}^1S_0 & 0 & \sqrt{1/3} & -\sqrt{1/3} & \sqrt{1/3} & 0 \\
{}^3P_1 & \sqrt{1/2} & 0 & 0 & 0 & -\sqrt{1/2} \\
\hline
{}^3P_0 & \sqrt{1/3} & -\sqrt{1/6} & 0 & \sqrt{1/6} & \sqrt{1/3}
\end{array}
$$

$$
(S^2)''' = \begin{array}{|c|ccc|c}
\hline
1\cdot2 & & 0 & & 0 \\
\hline
 & 0 & 0 & 0 & \\
0 & 0 & 0 & 0 & 0 \\
 & 0 & 0 & 1\cdot2 & \\
\hline
0 & & 0 & & 1\cdot2
\end{array}
\qquad
(L^2)''' = \begin{array}{|c|ccc|c}
\hline
1\cdot2 & & 0 & & 0 \\
\hline
 & 2\cdot3 & 0 & 0 & \\
0 & 0 & 0 & 0 & 0 \\
 & 0 & 0 & 1\cdot2 & \\
\hline
0 & & 0 & & 1\cdot2
\end{array}
\qquad
(J^2)''' = \begin{array}{|c|ccc|c}
\hline
2\cdot3 & & 0 & & 0 \\
\hline
 & 2\cdot3 & 0 & 0 & \\
0 & 0 & 0 & 0 & 0 \\
 & 0 & 0 & 1\cdot2 & \\
\hline
0 & & 0 & & 0
\end{array}
$$

The connection between the Roman numerals and the ordinary multiplet notation as shown by the labelling of *UTR*, is evident when we remember that the characteristic values of the angular momenta are of the form $1(1+1)$. These characteristic values are the basis of the usual multiplet notation.

The matrix of H_2 calculated with the initial wave functions,* is

$$
H_2 = \begin{array}{|c|ccc|c}
\hline
-a/2 & 0 & a\sqrt{1/2} & -a\sqrt{1/2} & 0 \\
\hline
0 & a & 0 & 0 & 0 \\
a\sqrt{1/2} & 0 & 0 & 0 & a\sqrt{1/2} \\
-a\sqrt{1/2} & 0 & 0 & -a & -a\sqrt{1/2} \\
\hline
0 & 0 & a\sqrt{1/2} & -a\sqrt{1/2} & -a/2
\end{array}
$$

Applying *UTR*, we obtain for the spin-orbit interaction in *LS* coupling

$$
\begin{array}{r|c|ccc|c}
 & {}^3P_2 & {}^1D_2 & {}^1S_0 & {}^3P_1 & {}^3P_0 \\
\hline
{}^3P_2 & a/2 & a\sqrt{1/2} & 0 & 0 & 0 \\
\hline
{}^1D_2 & a\sqrt{1/2} & 0 & 0 & 0 & 0 \\
H_2''' = {}^1S_0 & 0 & 0 & 0 & 0 & -a\sqrt{2} \\
{}^3P_1 & 0 & 0 & 0 & -a/2 & 0 \\
\hline
{}^3P_0 & 0 & 0 & -a\sqrt{2} & 0 & -a
\end{array}
$$

This is in agreement with the result previously found for this configuration.[1] As the secular equations, determined from the above matrix, have already been given, we will not write them down again.

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* In this matrix and following matrices of the spin-orbit interaction, a is an abbreviation for $(nl\,|f|\,nl)$.

The configuration d^2

The wave functions for $M_J = 0$ are

	d^2	M_L	M_S
I	(2 -½) (-1 -½)	1	-1
II	(1 -½) (0 -½)	1	-1
III	(2 ½) (-2 -½)	0	0
IV	(1 ½) (-1 -½)	0	0
V	(0 ½) (0 -½)	0	0
VI	(2 -½) (-2 ½)	0	0
VII	(1 -½) (-1 ½)	0	0
VIII	(1 ½) (-2 ½)	-1	1
IX	(-1 ½) (0 ½)	-1	1

The transformation into LS coupling is

	I	II	III	IV	V	VI	VII	VIII	IX
$^3F_4$	$3\sqrt{1/70}$	$\sqrt{3/35}$	$\sqrt{2/35}$	$2\sqrt{2/35}$	0	$\sqrt{2/35}$	$2\sqrt{2/35}$	$3\sqrt{1/70}$	$-\sqrt{3/35}$
$^3P_2$	$\sqrt{1/15}$	$-\sqrt{1/10}$	$2\sqrt{1/15}$	$-\sqrt{1/15}$	0	$2\sqrt{1/15}$	$-\sqrt{1/15}$	$\sqrt{1/15}$	$\sqrt{1/10}$
$^3F_3$	$\sqrt{3/10}$	$\sqrt{1/5}$	0	0	0	0	0	$-\sqrt{3/10}$	$\sqrt{1/5}$
$^3P_1$	$\sqrt{1/5}$	$-\sqrt{3/10}$	0	0	0	0	0	$-\sqrt{1/5}$	$-\sqrt{3/10}$
UTR $= {}^1S_0$	0	0	$\sqrt{1/5}$	$-\sqrt{1/5}$	$\sqrt{1/5}$	$-\sqrt{1/5}$	$\sqrt{1/5}$	0	0
$^1D_2$	0	0	$-\sqrt{2/7}$	$-\sqrt{1/14}$	$\sqrt{2/7}$	$\sqrt{2/7}$	$\sqrt{1/14}$	0	0
$^1G_4$	0	0	$\sqrt{1/70}$	$4\sqrt{1/70}$	$3\sqrt{2/35}$	$-\sqrt{1/70}$	$-4\sqrt{1/70}$	0	0
$^3P_0$	$\sqrt{2/15}$	$-\sqrt{1/5}$	$-2\sqrt{1/30}$	$\sqrt{1/30}$	0	$-2\sqrt{1/30}$	$\sqrt{1/30}$	$\sqrt{2/15}$	$\sqrt{1/5}$
$^3F_2$	$\sqrt{6/35}$	$2\sqrt{1/35}$	$-\sqrt{3/70}$	$-2\sqrt{3/70}$	0	$-\sqrt{3/70}$	$-2\sqrt{3/70}$	$\sqrt{6/35}$	$-2\sqrt{1/35}$

If we transform the matrix of the spin-orbit interaction into LS coupling, we obtain a result which has already been given.[1] For this reason we do not write down the matrix of the spin-orbit interaction and the secular equations.

The configuration p^3

The wave functions for $M_J = \frac{1}{2}$ are

	p^3	M_L	M_S
I	(1 -½) (0 ½) (0 -½)	1	-½
II	(1 -½) (1 ½) (-1 -½)	1	-½
III	(1 ½) (0 ½) (-1 -½)	0	½
IV	(1 ½) (0 -½) (-1 ½)	0	½
V	(1 -½) (0 ½) (-1 ½)	0	½

The transformation into LS coupling is

$$\mathrm{UTR} = \begin{array}{c|cc|ccc} & \mathrm{I} & \mathrm{II} & \mathrm{III} & \mathrm{IV} & \mathrm{V} \\ \hline {}^3D_{5/2} & \sqrt{1/5} & \sqrt{1/5} & \sqrt{1/10} & -2\sqrt{1/10} & \sqrt{1/10} \\ {}^2P_{3/2} & \sqrt{1/6} & -\sqrt{1/6} & \sqrt{1/3} & 0 & -\sqrt{1/3} \\ \hline {}^2P_{1/2} & \sqrt{1/3} & -\sqrt{1/3} & -\sqrt{1/6} & 0 & \sqrt{1/6} \\ {}^4S_{3/2} & 0 & 0 & \sqrt{1/3} & \sqrt{1/3} & \sqrt{1/3} \\ {}^2D_{3/2} & \sqrt{3/10} & \sqrt{3/10} & -\sqrt{1/15} & 2\sqrt{1/15} & -\sqrt{1/15} \end{array}$$

The matrix of the spin-orbit interaction in LS coupling is

$$J = 5/2 \qquad \begin{array}{c|c} & {}^2D_{5/2} \\ \hline {}^2D_{5/2} & 0 \end{array}$$

$$J = 3/2 \qquad \begin{array}{c|ccc} & {}^2P_{3/2} & {}^4S_{3/2} & {}^2D_{3/2} \\ \hline {}^2P_{3/2} & 0 & a & -a/2\sqrt{5} \\ {}^4S_{3/2} & a & 0 & 0 \\ {}^2D_{3/2} & -a/2\sqrt{5} & 0 & 0 \end{array}$$

$$J = 1/2 \qquad \begin{array}{c|c} & {}^2P_{1/2} \\ \hline {}^2P_{1/2} & 0 \end{array}$$

The electrostatic energies calculated by Slater's method when referred to the ${}^2D$ multiplet are[2]

$$\begin{aligned} {}^2D&: \quad 0 \\ {}^2P&: \quad 6/25F^2 = 2X \\ {}^4S&: -9/25F^2 = -3X. \end{aligned}$$

Taking ${}^2D_{5/2}$ as the reference level the secular equations are

$$\begin{aligned} J &= 5/2 \quad -W = 0 \\ J &= 3/2 \quad -W^3 - W^2X + W(9a^2/4 + 6X^2) + 15/4Xa^2 = 0 \\ J &= \tfrac{1}{2} \quad -W + 2X = 0. \end{aligned}$$

The secular equations are in agreement with those obtained by Inglis[7] for this configuration.

The configuration p^2s

The wave functions for $M_J = \frac{1}{2}$ are

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[7] D. R. Inglis, Phys. Rev. **38**, 862 (1931). This calculation also confirms the results obtained by D. R. Inglis and M. H. Johnson, Jr. (Phys. Rev. **38**, 1642 (1931)) who found the matrix of the spin-orbit interaction in LS coupling for this configuration by working backwards from the secular equations.

	P^2		S	M_L	M_S
I	$(1\ -\frac{1}{2})$	$(0\ \frac{1}{2})$	$(0\ -\frac{1}{2})$	1	$-\frac{1}{2}$
II	$(1\ \frac{1}{2})$	$(0\ -\frac{1}{2})$	$(0\ -\frac{1}{2})$	1	$-\frac{1}{2}$
III	$(1\ -\frac{1}{2})$	$(0\ -\frac{1}{2})$	$(0\ \frac{1}{2})$	1	$-\frac{1}{2}$
IV	$(1\ \frac{1}{2})$	$(-1\ \frac{1}{2})$	$(0\ -\frac{1}{2})$	0	$\frac{1}{2}$
V	$(1\ \frac{1}{2})$	$(-1\ -\frac{1}{2})$	$(0\ \frac{1}{2})$	0	$\frac{1}{2}$
VI	$(0\ \frac{1}{2})$	$(0\ -\frac{1}{2})$	$(0\ \frac{1}{2})$	0	$\frac{1}{2}$
VII	$(-1\ \frac{1}{2})$	$(1\ -\frac{1}{2})$	$(0\ \frac{1}{2})$	0	$\frac{1}{2}$
VIII	$(0\ \frac{1}{2})$	$(-1\ \frac{1}{2})$	$(0\ \frac{1}{2})$	-1	$\frac{3}{2}$

The transformation into LS coupling is

$$UTR=\begin{array}{c|ccc|cccc|c}
 & \mathrm{I} & \mathrm{II} & \mathrm{III} & \mathrm{IV} & \mathrm{V} & \mathrm{VII} & \mathrm{VI} & \mathrm{VIII} \\
\hline
{}^2P_{3/2} & \frac{1}{3}\sqrt{\frac{1}{2}} & \frac{1}{3}\sqrt{\frac{1}{2}} & -\frac{1}{3}\sqrt{2} & \frac{2}{3} & -\frac{1}{3} & 0 & \frac{1}{3} & 0 \\
{}^4P_{5/2} & \sqrt{\frac{1}{10}} & \sqrt{\frac{1}{10}} & \sqrt{\frac{1}{10}} & \sqrt{\frac{1}{5}} & \sqrt{\frac{1}{5}} & 0 & -\sqrt{\frac{1}{5}} & \sqrt{\frac{1}{10}} \\
{}^2D_{5/2} & \sqrt{\frac{1}{5}} & -\sqrt{\frac{1}{5}} & 0 & 0 & -\sqrt{\frac{1}{10}} & -\sqrt{\frac{2}{5}} & -\sqrt{\frac{1}{10}} & 0 \\
\hline
{}^2S_{1/2} & 0 & 0 & 0 & 0 & \sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{3}} & \sqrt{\frac{1}{3}} & 0 \\
{}^4P_{3/2} & \frac{2}{3}\sqrt{\frac{2}{5}} & \frac{2}{3}\sqrt{\frac{2}{5}} & \frac{2}{3}\sqrt{\frac{2}{5}} & -\frac{1}{3}\sqrt{\frac{1}{5}} & -\frac{1}{3}\sqrt{\frac{1}{5}} & 0 & \frac{1}{3}\sqrt{\frac{1}{5}} & -\sqrt{\frac{2}{5}} \\
{}^2P_{1/2} & \frac{1}{3} & \frac{1}{3} & -\frac{2}{3} & -\frac{1}{3}\sqrt{2} & \frac{1}{3}\sqrt{\frac{1}{2}} & 0 & -\frac{1}{3}\sqrt{\frac{1}{2}} & 0 \\
{}^2D_{3/2} & -\sqrt{\frac{3}{10}} & \sqrt{\frac{3}{10}} & 0 & 0 & -\sqrt{\frac{1}{15}} & -2\sqrt{\frac{1}{15}} & -\sqrt{\frac{1}{15}} & 0 \\
\hline
{}^4P_{1/2} & \frac{1}{3}\sqrt{\frac{1}{2}} & \frac{1}{3}\sqrt{\frac{1}{2}} & \frac{1}{3}\sqrt{\frac{1}{2}} & -\frac{1}{3} & -\frac{1}{3} & 0 & \frac{1}{3} & \sqrt{\frac{1}{2}}
\end{array}$$

The matrix of the spin-orbit interaction transformed into LS coupling is

$$J = 5/2 \qquad \begin{array}{c|cc}
 & {}^2D_{5/2} & {}^4P_{5/2} \\
\hline
{}^2D_{5/2} & 0 & -a\sqrt{\frac{1}{2}} \\
{}^4P_{5/2} & -a\sqrt{\frac{1}{2}} & a/2
\end{array}$$

$$J = 3/2 \qquad \begin{array}{c|ccc}
 & {}^2D_{3/2} & {}^4P_{3/2} & {}^2P_{3/2} \\
\hline
{}^2D_{3/2} & 0 & a/2\sqrt{\frac{1}{3}} & a/2\sqrt{\frac{5}{3}} \\
{}^4P_{3/2} & a/2\sqrt{\frac{1}{3}} & -a/3 & a/6\sqrt{5} \\
{}^2P_{3/2} & a/2\sqrt{\frac{5}{3}} & a/6\sqrt{5} & a/3
\end{array}$$

$$J = 1/2 \qquad \begin{array}{c|ccc}
 & {}^4P_{1/2} & {}^2P_{1/2} & {}^2S_{1/2} \\
\hline
{}^4P_{1/2} & -5a/6 & a/3\sqrt{\frac{1}{2}} & -2a\sqrt{\frac{1}{3}} \\
{}^2P_{1/2} & a/3\sqrt{\frac{1}{2}} & -2a/3 & a\sqrt{\frac{2}{3}} \\
{}^2S_{1/2} & -2a\sqrt{\frac{1}{3}} & a\sqrt{\frac{2}{3}} & 0
\end{array}$$

The electrostatic energies calculated by Slater's method, are[8]

$${}^2D\colon 2F^0(Ps) + F^0(P^2) + 1/25E^2 - \tfrac{1}{3}G^1$$

$${}^4P\colon 2F^0(Ps) + F^0(P^2) - 5/25F^2 - \tfrac{2}{3}G^1$$

$${}^2P\colon 2F^0(Ps) + F^0(P^2) - 5/25F^2 + \tfrac{1}{3}G^1$$

$${}^2S\colon 2F^0(Ps) + F^0(P^2) + 10/25F^2 - \tfrac{1}{3}G^1.$$

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

It is convenient to use the midpoint between the ${}^2D_{5/2}$ and the ${}^4P_{5/2}$ levels as a reference point from which to measure energies. The electrostatic energies become

$$\begin{aligned} {}^2D:&\quad 3/25F^2 + \tfrac{1}{6}G^1 = \alpha \\ {}^4P:&\ -\ 3/25F^2 - \tfrac{1}{6}G^1 = -\alpha \\ {}^2P:&\ -\ 3/25F^2 + \tfrac{5}{6}G^1 = \beta \\ {}^2S:&\quad 12/25F^2 + \tfrac{1}{6}G^1 = \gamma. \end{aligned}$$

The secular equations are

$$J = 5/2 \qquad W^2 - (\alpha - a/4)^2 - a^2/2 = 0$$

$$\begin{aligned} J = 3/2 \qquad & -W^3 + W^2(\beta - \tfrac{3}{4}a) + W\{\alpha^2 + a/6(2\alpha + 5\beta) + (\tfrac{3}{4}a)^2\} \\ & - \alpha^2\beta - 1/12a\alpha(\alpha + 4\beta) + 1/16a^2(4\alpha + \beta) + (\tfrac{3}{4}a)^3 = 0 \end{aligned}$$

$$\begin{aligned} J = \tfrac{1}{2} \qquad & -W^3 + W^2\{-\alpha + \beta + \gamma - 9/4a\} - W\{-\alpha(\beta + \gamma) + \beta\gamma \\ & \quad + a/6(7\alpha - 12\gamma - 8\beta) - (3a/4)^2\} - \alpha\beta\gamma \\ & + a/12(11\alpha\gamma + 3\alpha\beta - 13\beta\gamma) + a^2/16(7\alpha - 17\beta + 15\gamma) + 3(3a/4)^3 = 0. \end{aligned}$$

The configuration p^3s

The wave functions for $M_J = 0$ are

	p^3			s	M_L	M_S
I	(1 -½)	(0½)	(0 -½)	(0 -½)	1	-1
II	(1 -½)	(1½)	(-1 -½)	(0 -½)	1	-1
III	(1½)	(0½)	(-1 -½)	(0 -½)	0	0
IV	(1½)	(0 -½)	(-1½)	(0 -½)	0	0
V	(1 -½)	(0½)	(-1½)	(0 -½)	0	0
VI	(1 -½)	(0 -½)	(-1½)	(0½)	0	0
VII	(1 -½)	(0½)	(-1 -½)	(0½)	0	0
VIII	(1½)	(0 -½)	(-1 -½)	(0½)	0	0
IX	(-1½)	(0 -½)	(0½)	(0½)	-1	1
X	(-1½)	(-1 -½)	(1½)	(0½)	-1	1

The transformation into LS coupling is

$$\mathrm{UTR} = \begin{array}{c|cc|cccccc|cc} & \mathrm{I} & \mathrm{II} & \mathrm{III} & \mathrm{IV} & \mathrm{V} & \mathrm{VI} & \mathrm{VII} & \mathrm{VIII} & \mathrm{IX} & \mathrm{X} \\ \hline {}^3D_3 & \sqrt{1/10} & \sqrt{1/10} & \tfrac{1}{2}\sqrt{1/5} & -\sqrt{1/5} & \tfrac{1}{2}\sqrt{1/5} & -\tfrac{1}{2}\sqrt{1/5} & \sqrt{1/5} & -\tfrac{1}{2}\sqrt{1/5} & \sqrt{1/10} & \sqrt{1/10} \\ {}^3P_2 & \tfrac{1}{2}\sqrt{1/3} & -\tfrac{1}{2}\sqrt{1/3} & \sqrt{1/6} & 0 & -\sqrt{1/6} & -\sqrt{1/6} & 0 & \sqrt{1/6} & -\tfrac{1}{2}\sqrt{1/3} & \tfrac{1}{2}\sqrt{1/3} \\ \hline {}^1P_1 & 0 & 0 & \tfrac{1}{2} & 0 & -\tfrac{1}{2} & \tfrac{1}{2} & 0 & -\tfrac{1}{2} & 0 & 0 \\ {}^5S_2 & 0 & 0 & \sqrt{1/6} & \sqrt{1/6} & \sqrt{1/6} & \sqrt{1/6} & \sqrt{1/6} & \sqrt{1/6} & 0 & 0 \\ {}^1D_2 & 0 & 0 & \tfrac{1}{2}\sqrt{1/3} & -\sqrt{1/3} & \tfrac{1}{2}\sqrt{1/3} & \tfrac{1}{2}\sqrt{1/3} & -\sqrt{1/3} & \tfrac{1}{2}\sqrt{1/3} & 0 & 0 \\ {}^3P_1 & \tfrac{1}{2} & -\tfrac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & \tfrac{1}{2} & -\tfrac{1}{2} \\ {}^3S_1 & 0 & 0 & \sqrt{1/6} & \sqrt{1/6} & \sqrt{1/6} & -\sqrt{1/6} & -\sqrt{1/6} & -\sqrt{1/6} & 0 & 0 \\ {}^3D_2 & \tfrac{1}{2} & \tfrac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & -\tfrac{1}{2} & -\tfrac{1}{2} \\ \hline {}^3D_1 & \tfrac{1}{2}\sqrt{3/5} & \tfrac{1}{2}\sqrt{3/5} & -\tfrac{1}{2}\sqrt{2/15} & \sqrt{2/15} & -\tfrac{1}{2}\sqrt{2/15} & \tfrac{1}{2}\sqrt{2/15} & -\sqrt{2/15} & \tfrac{1}{2}\sqrt{2/15} & \tfrac{1}{2}\sqrt{3/5} & \tfrac{1}{2}\sqrt{3/5} \\ {}^3P_0 & \sqrt{1/6} & -\sqrt{1/6} & -\tfrac{1}{2}\sqrt{1/3} & 0 & \tfrac{1}{2}\sqrt{1/3} & \tfrac{1}{2}\sqrt{1/3} & 0 & -\tfrac{1}{2}\sqrt{1/3} & -\sqrt{1/6} & \sqrt{1/6} \end{array}$$

The matrix of the spin-orbit interaction in *LS* coupling is

$$J = 3 \qquad \begin{array}{c|c} & {}^3D_3 \\ \hline {}^3D_3 & 0 \end{array}$$

$$J = 2 \qquad \begin{array}{c|cccc} & {}^3P_2 & {}^5S_2 & {}^1D_2 & {}^3D_2 \\ \hline {}^3P_2 & 0 & a & a\sqrt{1/2} & -a/2\sqrt{3} \\ {}^5S_2 & a & 0 & 0 & 0 \\ {}^1D_2 & a\sqrt{1/2} & 0 & 0 & 0 \\ {}^3D_2 & -a/2\sqrt{3} & 0 & 0 & 0 \end{array}$$

$$J = 1 \qquad \begin{array}{c|cccc} & {}^1P_1 & {}^3P_1 & {}^3S_1 & {}^3D_1 \\ \hline {}^1P_1 & 0 & 0 & a\sqrt{2/3} & -a\sqrt{5/6} \\ {}^3P_1 & 0 & 0 & a\sqrt{1/3} & -a/2\sqrt{5/3} \\ {}^3S_1 & a\sqrt{2/3} & a\sqrt{1/3} & 0 & 0 \\ {}^3D_1 & -a\sqrt{5/6} & -a/2\sqrt{5/3} & 0 & 0 \end{array}$$

$$J = 0 \qquad \begin{array}{c|c} & {}^3P_0 \\ \hline {}^3P_0 & 0 \end{array}$$

The electrostatic energies calculated by Slater's method are, when referred to the ${}^3D$ multiplet,

$$\begin{array}{lll} {}^3D: & 0 & \\ {}^1D: & \tfrac{2}{3}G^1 & = \alpha \\ {}^3P: & 6/25F^2 & = \beta \\ {}^1P: & 6/25F^2 + \tfrac{2}{3}G^1 & = \gamma \\ {}^5S: & -\,9/25F^2 - \tfrac{1}{3}G^1 & = \delta \\ {}^3S: & -\,9/25F^2 + G^1 & = \mu . \end{array}$$

We find the following secular equations with the ${}^3D_3$ as the reference level.

$$J = 3 \qquad -W = 0$$

$$J = 2 \quad W^4 - W^3(\alpha + \beta + \delta) + W^2\{\alpha(\beta + \delta) + \beta\delta - 9/4a^2\}$$
$$- W\{\alpha\beta\delta - a^2/4(7\alpha + 5\delta)\} - \tfrac{3}{4}\alpha\delta a^2 = 0$$

$$J = 1 \quad W^4 - W^3(\beta + \gamma + \mu) + W^2\{\beta(\gamma + \mu) + \gamma\mu - 9/4a^2\}$$
$$- W\{\beta\gamma\mu - a^2/4(6\beta + 3\gamma + 5\mu)\} - 5/12a^2\mu(2\beta + \gamma) = 0$$

$$J = 0 \qquad -W + \beta = 0.$$

In conclusion it is the writer's pleasant duty to acknowledge his indebtedness to the counsel of Professor J. C. Slater under whose direction this work was done, to the discussions and criticisms of Professor E. C. Kemble and Dr. L. A. Young, and finally to Harvard University for the award of a Whiting Fellowship which made the completion of this work possible.