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THE THEORY OF COMPLEX SPECTRA

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Abstract

Part I. Calculation of the first order energies for configurations involving almost closed shells. A method is developed for calculating the electrostatic energy matrix for a configuration consisting of a closed shell minus ϵ electrons plus η other electrons with the same simplicity as for the corresponding configuration consisting of $\epsilon+\eta$ electrons. One classifies the states according to the quantum numbers of the "missing" and of the added electrons and calculates Slater's integral $(J-\delta K)$ for each pair of electrons in the usual way except that one attaches a negative sign to an integral connecting a "missing" with an added electron. It is then shown quite generally that the matrices of magnetic interaction are identical in LS coupling for the two configurations mentioned above except for a reversal of sign of the spin-orbit coupling parameter corresponding to the almost closed shell.

Part II. On two-electron spectra. It is shown that one is completely justified, when calculating the matrix of magnetic interaction in LS coupling by Johnson's method, in neglecting the equivalence of the two electrons of the atom. Similar results are shown to obtain for the addition of an electron to an ionic multiplet. The method of calculation of the matrix of magnetic interaction between configurations by this method is considered and it is shown that neglect of the equivalence of the electrons in case one of the configurations is composed of equivalent electrons leads to an error of a factor of $(2)^{1/2}$. One does not obtain a magnetic interaction between configurations which differ by more than the n value of one electron. This holds quite generally for any type of atom.

Part I. Calculation of the First Order Energies for Configurations Involving Almost Closed Shells

§1. Introduction

In 1929, Slater[1] gave a method of calculating the electrostatic interaction for any atom in terms of certain radial integrals (F's and G's). About a year ago Condon and the writer[2] extended Slater's tables to f electrons, and made a systematic comparison with this theory of all available data on two- and three-electron configurations. Johnson[3] has recently given a simple method of calculating the magnetic energy for any two-electron configuration, and he and others have made calculations of the magnetic energy for certain other configurations.[4] Finally, Condon and the writer[5] have made a

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

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

[3] M. H. Johnson, Phys. Rev. **38,** 1628 (1931); see also part II of this paper.

[4] M. Johnson, Phys. Rev. **39,** 197 (1932); Goudsmit, Phys. Rev. **35,** 1325 (1930); Inglis, Phys. Rev. **38,** 862 (1931); M. H. Johnson, Phys. Rev. **40,** 127 (1932); J. H. Bartlett, Phys. Rev. **35,** 229 (1930).

[5] E. U. Condon and G. H. Shortley, Phys. Rev. **35,** 1342 (1930).

detailed comparison of experimental data with theory for *sp*, *sd*, *sf* configurations, using the calculations of electrostatic and magnetic energy as first given by Houston.[6]

These calculations are all for atoms at the left of the periodic table, *i.e.*, atoms whose configurations involve just a very few electrons outside of closed shells. In calculating the electrostatic energy by Slater's method one classifies the different possible complete sets[7] for a given configuration according to the values of M_L and M_S. The electrostatic energy is diagonal with respect to these z-components of angular momenta, so one proceeds to use the diagonal sum rule to find the energies for the different multiplets. The process of calculating the diagonal element of the electrostatic energy for a given complete set involves the evaluation, from tables, of a certain integral $(J-\delta K)$ for all possible pairs of individual sets in the complete set. This is not difficult when the configuration consists of just a few electrons, but the amount of work becomes tremendous when one deals with a configuration which involves an *almost closed shell*, particularly a *d* shell. For this reason, practically no calculations of electrostatic interaction for configurations of this type have been made.[8] Laporte and Inglis,[9] and simultaneously Condon and the writer[5] recognized on somewhat empirical grounds that Houston's formulas would apply to configurations of the type p^5s and d^9s if one inverted the level scheme and took X negative. The agreement with experiment was found to be remarkable. Heisenberg[10] has considered in general those configurations consisting purely of an almost closed shell, with no additional electrons, by considering the relation between the equations satisfied by n electrons and by n "Löchern" under the Pauli exclusion principle.

We shall here give a method by which the electrostatic energy for a configuration which consists of a closed shell minus ϵ electrons plus η other electrons can be calculated with the same simplicity as for the corresponding configuration consisting of ϵ electrons of the type of the closed shell plus the η other electrons, and shall show that the matrices of magnetic interaction (in LS coupling) are exactly the same for these two configurations except for a reversal of sign of the spin-orbit coupling parameter applying to the almost closed shell.

§2. Formulation of the problem

One takes as the zero order approximation for the calculation of atomic energies a model in which each electron moves independently in a central force field of potential energy $U(r)$; and considers as a perturbation the potential energy

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[6] W. V. Houston, Phys. Rev. **33,** 297 (1929).

[7] A complete set of quantum numbers consists of N individual sets, each individual set specifying the nlm_lm_s of one of the N electrons of the configuration. These definitions are according to Condon, Phys. Rev. **36,** 1121 (1930).

[8] Slater gives partial results for p^5p; Ufford, in this laboratory, has calculated p^5p and d^9p.

[9] O. Laporte and D. R. Inglis, Phys. Rev. **35,** 1337 (1930).

[10] W. Heisenberg, Ann. d. Physik, **10,** 888, 1931.

$$V' = V - \sum_i U(r_i) = \sum_i \left[-\frac{Ze^2}{r_i} + \xi(r_i)\mathbf{L}_i\cdot\mathbf{S}_i - U(r_i) \right] + \sum_{i<j} \frac{e^2}{r_{ij}}, \tag{2.1}$$

where the first term represents the attraction between the electrons and the nucleus, the second the spin-orbit interaction, and the last the mutual repulsion of the electrons. In the central field $U(r)$, electron i with the individual set a^i of quantum numbers will have the eigenfunction[11]

$$u_i(a^i) = \frac{R_i(n^i l^i)}{r_i} \Theta_i(l^i m_l^i)\Phi_i(m_l^i)\delta(\sigma_i, m_s^i). \tag{2.2}$$

The zero order eigenfunction for the atom, going with the complete set $A = (a^1, a^2, \cdots, a^N)$ will be the antisymmetric combination

$$\psi(A) = \frac{1}{(N!)^{1/2}} \sum_P (-1)^p P u_1(a^1)u_2(a^2) \cdots u_N(a^N), \tag{2.3}$$

where P represents a permutation of quantum numbers relative to electron indices and p has the parity of P. (It is assumed that the Pauli exclusion principle is satisfied.) The zero order energy going with this ψ depends only on the *configuration*, i.e., on the set of $n^i l^i$ of A.

We are at the moment interested in the diagonal elements, in this representation, of the matrix of that part of V' which does not refer to the magnetic (spin-orbit) interaction. These terms fall into two classes: First we have

$$\sum_i \left[-\frac{Ze^2}{r_i} - U(r_i) \right], \tag{2.4}$$

which is of the form $\sum_i f(r_i)$. Slater has shown that for a given configuration the matrix of a quantity of this type is diagnoal, and that the value of the diagonal element depends only on the configuration; hence since at the present stage of the theory we are only interested in the disposition of the energy levels of a given configuration we need not consider these terms further. If it were of use, the calculation of the matrix of a quantity of this type is capable of a similar reduction to that which is made below for the quantity

$$G = \sum_{i<j} g(i,j) = \sum_{i<j} e^2/r_{ij}, \tag{2.5}$$

which is the second type of quantity occurring in V'.

The calculation of the relative electrostatic energies of the different multiplets in a configuration thus reduces to a calculation of the part of the matrix of G which refers to that configuration: in particular, it is necessary to calculate only the diagonal elements unless the configuration leads to more than one multiplet of a type. Slater has shown that the diagonal element of G for the state A is given by

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[11] The different factors of this function, also the F's and G's which occur later, are as in Slater's paper, with the corrections suggested in reference 2, p. 1026.

$$
\begin{aligned}
A\,|\,G\,|\,A) = \sum_{k>t=1}^{N} \Big[& \iint \bar{v}_1(a^k)\bar{v}_2(a^t)g(1,\,2)v_1(a^k)v_2(a^t)\,d\tau_1 d\tau_2 \\
& - \delta(\overset{k}{m_s},\,\overset{t}{m_s}) \iint \bar{v}_1(a^k)\bar{v}_2(a^t)g(1,\,2)\,v_1(a^t)\,\bar{v}_2(a^k)\,d\tau_1 d\tau_2 \Big] \\
= \sum_{k>t} & [J(k;\,t) - \delta(\overset{k}{m_s}\overset{t}{m_s})K(k,\,t)], \qquad (2.6)
\end{aligned}
$$

where $v(a)$ is the spin-free eigenfunction $u(a)/\delta(\sigma,\,m_s)$. The first integral here is known as the direct integral, the second as the exchange integral. J and K are of course symmetric in k and t and independent of $m_s{}^k$ and $m_s{}^t$.

§3. A summation over a closed shell

We shall need to consider a sum of terms like the summand of (2.6), in which a^t runs over the individual sets of the $n'l'$ closed shell, and in which a^k has the fixed value nlm_lm_s. We do not assume that all the sets a^t are different from a^k, as is the case in (2.6). This sum is, in detail

$$
\begin{aligned}
\sum_{m_s'} \sum_{m_l'=-l'}^{l'} \Big[& \iint g(1,\,2)R_1^2(nl)R_2^2(n'l')\Theta_1^2(lm_l)\Theta_2^2(l'm_l')(2\pi)^{-2}d\tau_1 d\tau_2 \\
& - \delta(m_s,\,m_s') \iint g(1,\,2)R_1(nl)R_1(n'l')R_2(nl)R_2(n'l')\Theta_1(lm_l)\bar{\Phi}_1(m_l) \qquad (3.1) \\
& \cdot \Theta_1(l'm_l')\Phi_1(m_l')\Theta_2(lm_l)\Phi_2(m_l)\Theta_2(l'm_l')\bar{\Phi}_2(m_l')\,d\tau_1 d\tau_2 \Big].
\end{aligned}
$$

Now the summation over m_s' gives a factor two in the first term and a factor one in the second. The summation over m_l' may be carried out by the use of the spherical harmonic addition theorem in the form

$$
\sum_{m_l'=-l'}^{l'} \Theta_1(l'm_l')\Theta_2(l'm_l')\Phi_1(m_l')\bar{\Phi}_2(m_l') = \frac{2l'+1}{4\pi} P_{l'}(\cos\omega), \qquad (3.2)
$$

where ω is the angle between the radii vectores 1 and 2 from the origin; in particular if 1 and 2 are identical, $P_{l'}(\cos\omega) = 1$. This gives for our sum

$$
\begin{aligned}
& 2\iint g(1,\,2)R_1^2(nl)R_2^2(n'l')\Theta_1^2(lm_l)\left(\frac{2l'+1}{4\pi}\right)\left(\frac{1}{2\pi}\right)d\tau_1 d\tau_2 \\
& - \iint g(1,\,2)R_1(nl)R_1(n'l')R_2(nl)R_2(n'l')\Theta_1(lm_l)\bar{\Phi}_1(m_l) \\
& \cdot \Theta_2(lm_l)\Phi_2(m_l)\left(\frac{2l'+1}{4\pi}\right)P_{l'}(\cos\omega)\,d\tau_1 d\tau_2. \qquad (3.3)
\end{aligned}
$$

Now writing

$$
g(1,\,2) = \frac{e^2}{r_{12}} = e^2 \sum_{\kappa=0}^{\infty} \frac{r_<^{\kappa}}{r_>^{\kappa+1}} P_\kappa(\cos\omega),
$$

where $r_<$ is the lesser and $r_>$ the greater of r_1 and r_2, each of these integrals can be written as a sum over κ of integrals involving $e^2 r_<^\kappa / r_>^{\kappa+1} \cdot P_\kappa(\cos\omega)$ in place of $g(1, 2)$.

In the direct integral one may choose a new coordinate system for the variables θ_2, ϕ_2 with the direction θ_1, ϕ_1 as pole, in which case $\omega = \theta_2$. Then all terms vanish except for $\kappa = 0$, in which case the integration over θ_2, ϕ_2 gives a factor 4π. The integration over θ_1, ϕ_1 may then be performed directly, giving for the value of the direct integral

$$2(2l' + 1) \int_0^\infty \int_0^\infty \frac{e^2}{r_>} R_1^2(nl) R_2^2(n'l') dr_1 dr_2 = 2(2l' + 1) F^0(nl;\, n'l') \quad (3.4)$$

or just the number of electrons in the closed shell times $F^0(nl;\, n'l')$.[11] This result is seen to be quite independent of m_l and m_s.

The exchange integral, on using the same expansion, becomes

$$- \sum_\kappa e^2 \iint \frac{r_<^\kappa}{r^{\kappa+1}} R_1(nl) R_1(n'l') R_2(nl) R_2(n'l') \Theta_1(lm_l) \bar{\Phi}_1(m_l)$$

$$\cdot \Theta_2(lm_l) \Phi_2(m_l) \left(\frac{2l' + 1}{4\pi} \right) P_{l'}(\cos\omega) P_\kappa(\cos\omega) d\tau_1 d\tau_2$$

To evaluate this we expand the product $P_{l'}(\cos\omega)\, P_\kappa(\cos\omega)$ in a series of Legendre polynomials $P_\lambda(\cos\omega)$. This we may do since the $P_\lambda(\cos\omega)$ form a complete set of functions in the interval 0 to π. The coefficient of $P_\lambda(\cos\omega)$ in this expansion is given by

$$\begin{aligned} C^\lambda_{l'\kappa} &= \frac{2\lambda + 1}{2} \int_0^\pi P_\lambda(\cos\omega) P_{l'}(\cos\omega) P_\kappa(\cos\omega) \sin\omega d\omega \\ &= \frac{2\lambda + 1}{(2l' + 1)^{1/2} (2\kappa + 1)^{1/2}} \{ b^\lambda(l'0;\, \kappa 0) \}^{1/2} \end{aligned}$$

where the last factor is the positive square root of b^λ as given in the tables of Slater and of Condon and Shortley.[12]

When we substitute the relation

$$P_{l'}(\cos\omega) P_\kappa(\cos\omega) = \sum_\lambda C^\lambda_{l'\kappa} P_\lambda(\cos\omega),$$

the above exchange integral becomes a double sum over κ and λ. In each summand the dependence on θ_2, ϕ_2 is through the factor

$$\Theta_2(lm_l) \Phi_2(m_l) P_\lambda(\cos\omega).$$

The integral of this over the whole range of θ_2 and ϕ_2 vanishes unless $\lambda = l$, in which case it becomes[13]

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[12] A closed expression for the integral of the product of three ordinary Legendre polynomials in known. See Hobson, *Spherical Harmonics*, p. 87, or Gaunt, Phil. Trans. Roy. Soc. **A228**, 195 (1929).

[13] This is a well known integral in the theory of spherical harmonics, see, *e.g.*, Mac Robert, *Spherical Harmonics*, p. 137.

$$\frac{4\pi}{2l+1}\Theta_1(lm_l)\Phi_1(m_l).$$

The integration over θ_1, ϕ_1 can now be performed to give simply a constant factor. Thus we are left with

$$-\frac{2l'+1}{2l+1}\sum_{\kappa}C^{l}_{l'\kappa}e^2\int_0^\infty\int_0^\infty\frac{r_<^{\kappa}}{r_>^{\kappa+1}}R_1(nl)R_1(n'l')R_2(nl)R_2(n'l')dr_1dr_2$$

$$=-\frac{2l'+1}{2l+1}\sum_{\kappa}C^{l}_{l'\kappa}G^{\kappa}(nl;\,n'l')$$

for the value of the exchange integral. Note that this result is also independent of m_l and m_s. The values of κ which can occur in the summation are those which satisfy the triangular conditions

$$\kappa+l+l'=2g\quad(g\text{ integral})$$
$$|l-l'|\leqq\kappa\leqq l+l'.$$

This calculation, incidentally, furnishes a formal direct proof of the fact that the electrostatic interaction of any electron with a closed shell is independent of the m_l, m_s of that electron.

§4. Calculation of the matrix of electrostatic energy

Consider the state A of a configuration which consists of a closed shell minus ϵ electrons plus η other electrons in addition to any number of completely closed shells. Denote the individual sets of the closed shell by a^1, a^2, $\cdots$, a^ϵ, $a^{\epsilon+1}$, $\cdots$, a^n, where $a^{\epsilon+1}$, $\cdots$, a^n are the sets occurring in A and $a^1\cdots a^\epsilon$ are the "missing" sets. Denote the rest of the sets occurring in A by b^1, b^2, $\cdots$, b^η. In the diagonal element (2.6) of G we will have first a sum over all pairs of electrons belonging to the closed shells present plus a sum of terms between each of the other electrons and all electrons in closed shells. These are just as in Slater's calculations—dependent only on the configuration—and may be given in terms of simple expressions involving radial integrals. In particular we have found in the last section the expression for a sum of the latter type. The remainder of the diagonal element is given by

$$\left.\begin{aligned}&\sum_{i>j=\epsilon+1}^{n}\left[J(a^ia^j)-\delta(\overset{i}{m_s},\overset{j}{m_s})K(a^ia^j)\right] && (\alpha)\\ +&\sum_{i=\epsilon+1}^{n}\sum_{j=1}^{\eta}\left[J(a^ib^j)-\delta(\overset{i}{m_s},\overset{j}{m_s})K(a^ib^j)\right] && (\beta)\\ +&\sum_{i>j=1}^{\eta}\left[J(b^ib^j)-\delta(\overset{i}{m_s},\overset{j}{m_s})K(b^ib^j)\right]. && (\gamma)\end{aligned}\right\}\quad(4.1)$$

Call these three terms (α), (β), (γ) respectively. We wish now to reduce the inconvenient summations over the range $\epsilon+1$ to n to the more convenient summations over the range 1 to ϵ.

Consider first the term (α). We may write

$$
\begin{aligned}
(\alpha) &= \sum_{i>j=\epsilon+1}^{n} [J(a^ia^j) - \delta(\overset{i}{m_s}, \overset{j}{m_s})K(a^ia^j)] \\
&= \sum_{i>j=1}^{n} [\cdots] - \sum_{i=\epsilon+1}^{n} \sum_{j=1}^{\epsilon} [\cdots] - \sum_{i>j=1}^{\epsilon} [\cdots] \\
&= \sum_{i>j=1}^{n} [\cdots] - \sum_{i=1}^{n} \sum_{j=1}^{\epsilon} [\cdots] + \sum_{i=1}^{\epsilon} \sum_{j=1}^{\epsilon} [\cdots] - \sum_{i>j=1}^{\epsilon} [\cdots] \\
&= \sum_{i>j=1}^{n} [J(a^ia^j) - \delta(\overset{i}{m_s}, \overset{j}{m_s})K(a^ia^j)] \\
&\quad - \sum_{i=1}^{n} \sum_{j=1}^{\epsilon} [J(a^ia^j) - \delta(\overset{i}{m_s}, \overset{j}{m_s})K(a^ia^j)] \qquad (4.2) \\
&\quad + \sum_{j>i=1}^{\epsilon} [J(a^ia^j) - \delta(\overset{i}{m_s}, \overset{j}{m_s})K(a^ia^j)] + \sum_{i=1}^{\epsilon} [J(a^ia^i) - K(a^ia^i)].
\end{aligned}
$$

Now since $J(a^ia^i) \equiv K(a^ia^i)$ the last term vanishes identically. The first term is a summation over the closed shell and so depends only on the configuration. The second term is of the form of the sum of terms like (3.1) in which nlm_lm_s takes on the values 1 to ϵ. Since (3.1) was shown to be independent of m_l and m_s, this term depends only on the configuration. Hence the only term of (α) which may vary within the configuration is

$$
\sum_{i>j=1}^{\epsilon} [J(a^ia^j) - \delta(\overset{i}{m_s}, \overset{j}{m_s})K(a^ia^j)], \qquad (4.3)
$$

which has the required simple summation.

The term (β) becomes similarly

$$
\begin{aligned}
(\beta) &= \sum_{i=\epsilon+1}^{n} \sum_{j=1}^{\eta} [J(a^ib^j) - \delta(\overset{i}{m_s}, \overset{j}{m_s})K(a^ib^j)] \\
&= \sum_{i=1}^{n} \sum_{j=1}^{\eta} [J(a^ib^j) - \delta(\overset{i}{m_s}, \overset{j}{m_s})K(a^ib^j)] \qquad (4.4) \\
&\quad - \sum_{i=1}^{\epsilon} \sum_{j=1}^{\eta} [J(a^ib^j) - \delta(\overset{i}{m_s}, \overset{j}{m_s})K(a^ib^j)]
\end{aligned}
$$

of which the first term depends only on the configuration.

Since the term (γ) is already in its simplest form we find for *that part of* $(A\,|G\,|A)$ *which may vary within the configuration*, the value

$$
\left.
\begin{aligned}
&\sum_{i>j=1}^{\epsilon} [J(a^ia^j) - \delta(\overset{i}{m_s}, \overset{j}{m_s})K(a^ia^j)] && (\alpha) \\
- &\sum_{i=1}^{\epsilon} \sum_{j=1}^{\eta} [J(a^ib^j) - \delta(\overset{i}{m_s}, \overset{j}{m_s})K(a^ib^j)] && (\beta) \\
+ &\sum_{i>j=1}^{\eta} [J(b^ib^j) - \delta(\overset{i}{m_s}, \overset{j}{m_s})K(b^ib^j)]. && (\gamma)
\end{aligned}
\right\} \quad (4.5)
$$

This gives a perfectly simple and definite procedure for calculating the electrostatic energies for such a configuration. Since $\sum m_l$ and $\sum m_s$ over a closed shell is zero one can proceed as follows:

Calculation of the electrostatic energy for a configuration consisting of a closed shell minus ϵ electrons plus η other electrons (call the group of ϵ missing electrons group a, the group of η other electrons group b):

I. Make a table of all allowed complete sets of quantum numbers for the configuration consisting of groups a and b. Call this Table I, and label the different complete sets $A, B, C, \cdots$. This table lists all possible complete sets for the configuration in question, each labelled by the quantum numbers of the "missing" electrons and the additional electrons.

II. Make a second table which is identical with the first except that the signs of m_l and m_s for the electrons of group a are reversed. Denote the entries which correspond to $A, B, C \cdots$ by $A_0, B_0, C_0 \cdots$. The values of $\sum m_l$ and $\sum m_s$ as obtained from *this table* will be the true values for the states $A, B, C \cdots$ of the configuration we are calculating. Call this Table II.

III. Combine the values of M_L and M_S *from Table II* into a double entry table as in Slater, determine the multiplets, and arrange for their calculation by the diagonal sum method.

IV. Calculate the $\sum [J-\delta K]$ for each complete set as outlined in Slater, *using the quantum numbers of Table I, and assigning a plus sign if both electrons lie in group* a *or group* b, *but a minus sign if one electron lies in each group*, in accordance with (4.5).

This procedure involves exactly the same amount of calculation as for the corresponding configuration with ϵ electrons *toward* a closed shell.[14] However, because of the various reversals of sign that occur the results will in general be quite different in appearance from the corresponding results for the analogous simple configurations.

As an illustration we will sketch the calculation of the electrostatic energy matrix for p^5p. The missing electron a then belongs to the shell n^ap, the added electron b to the shell n^bp. There are nine possible assignments of m_l values and going with each of these there are four possible assignments of m_s values. These are listed below along with the *true values* of M_L and M_S.

$\overset{a}{m_l}$	$\overset{b}{m_l}$	M_L	$\overset{a}{m_s}$	$\overset{b}{m_s}$	M_S
-1	1	2 (α)	$-$	$+$	1 (1)
	0	1 (β)	$-$	$-$	0 (2)
	-1	0 (γ)	$+$	$+$	0 (3)
0	1	1 (δ)	$+$	$-$	-1 (4)
	0	0 (ζ)			
	-1	-1 (θ)			
1	1	0 (ι)			
	0	-1 (κ)			
	-1	-2 (λ)			

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[14] Table II is not actually constructed: one simply calculates the true M_L and M_S from Table I by reversing the signs of the electrons of group a. Table II will be useful in the considerations of §5.

For the calculation of the electrostatic interaction sets with M_L, $M_S \geqq 0$ are arranged in the following double-entry table.

M_L	$M_S = 0$	$M_S = 1$
2	$\alpha_2\alpha_3$	α_1
1	$\beta_2\beta_3$ $\delta_2\delta_3$	β_1 δ_1
0	$\gamma_2\gamma_3$ $\zeta_2\zeta_3$ $\iota_2\iota_3$	γ_1 ζ_1 ι_1

Using Slater's table of *a*'s and *b*'s and the signs as directed above, we obtain the electrostatic energies[15] as follows

$$\begin{aligned}
{}^3D &= (\alpha_1) = -F_0 - F_2 & {}^3D &= -F_0 - F_2 \\
{}^1D + {}^3D &= (\alpha_2) + (\alpha_3) = -F_0 - F_2 + 6G_2 & {}^1D &= -F_0 - F_2 + 12G_2 \\
{}^3D + {}^3P &= (\beta_1) + (\delta_1) = -2F_0 + 4F_2 & {}^3P &= -F_0 + 5F_2 \\
{}^3P + {}^3D + {}^1D + {}^1P &= (\beta_2) + (\beta_3) + (\delta_2) + (\delta_3) & & \\
&= -4F_0 + 8F_2 + 12G_2 & {}^1P &= - - F_0 + 5F_2 \\
{}^3S + {}^3P + {}^3D &= (\gamma_1) + (\zeta_1) + (\iota_1) & & \\
&= -3F_0 - 6F_2 & {}^3S &= -F_0 - 10F_2 \\
{}^3S + {}^3P + {}^3D + {}^1S + {}^1P + {}^1D &= (\gamma_2) + (\gamma_3) + (\zeta_2) + (\zeta_3) + (\iota_2) + (\iota_3) & & \\
&= -6F_0 - 12F_2 + 6G_0 + 12G_2 & {}^1S &= -F_0 - 10F_2 + 6G_0
\end{aligned}$$

where

$$\begin{aligned}
F_0 &= F^0(n^a p;\, n^b p) \\
F_2 &= (1/25)F^2(n^a p;\, n^b p) \\
G_0 &= G^0(n^a p;\, n^b p) \\
G_2 &= (1/25)G^2(n^a p;\, n^b p).
\end{aligned}$$

These energies are seen to be quite different from those for the corresponding configuration *pp* as on p. 1029, reference 2, especially in regard to the singlet-triplet separations.

One can generalize this scheme to include configurations which involve two or more almost closed shells.* The procedure is essentially the same as above with the additional direction that one assign a plus sign to the integral $J - \delta K$ connecting electrons "missing" from two different shells.

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[15] These energies check with those calculated by Ufford (unpublished) for the same configuration by the straightforward method. The F's and G's with subscripts are defined as on p. 1026, reference 2, to be Slater's F's and G's divided by the denominator of a^k or b^k as it occurs in the tables.

* This case is not completely uninteresting from the spectroscopic point of view: it furnishes the most pleasing way of inferring that the electrostatic energies for the configurations p^5s and d^9s are given by the same formulas as for the configurations ps and ds.

§5. The matrix of magnetic energy

In this section we shall show quite generally that the matrix of the spin orbit interaction

$$V^1 = \sum_i V_i^1 = \sum_i \xi(r_i) \boldsymbol{L}_i \cdot \boldsymbol{S}_i \tag{5.1}$$

is the same, in *LS* coupling,[16] for the configuration consisting of a closed $n^a l^a$ shell *minus* ϵ electrons plus η other electrons as for the configuration consisting of ϵ electrons $n^a l^a$ plus the η other electrons, except for a reversal of the sign of the spin orbit coupling parameter

$$\zeta_{n^a l^a} = (n^a l^a \,|\, \xi(r) \,|\, n^a l^a). \tag{5.2}$$

For convenience we shall speak of these two configurations as "configuration $\mathcal{R}$" and "configuration $\mathcal{L}$" (right and left in the periodic table). Our procedure will be as follows: To each of the zero order eigenfunctions of configuration $\mathcal{R}$ with a definitely chosen phase, we correlate a zero order eigenfunction of configuration $\mathcal{L}$ in a definite way. We shall then see that the matrix of V^1 in these two configurations differs only in the sign of $\zeta_{n^a l^a}$, while the matrices of $\boldsymbol{L}^2$, $\boldsymbol{S}^2$, and $\boldsymbol{L} \cdot \boldsymbol{S}$ are identical. The latter fact shows that the transformation to *LS* coupling will be the same for the two configurations; and the former, that the matrices of V^1, when so transformed, will differ only in the sign of $\zeta_{n^a l^a}$. Now the matrices of magnetic interaction have been calculated[4] in *LS* coupling for various configurations of the type $\mathcal{L}$; in particular for all two electron configurations,[17] which correspond to the important cases of the type p^5x, d^9x, etc. Hence this calculation, which is in general rather complicated, will not have to be made independently for configurations of the type $\mathcal{R}$.

According to this program, we will first adopt a standard order of listing quantum numbers in the eigenfunction (2.3). The individual sets will be listed first in increasing order of the n values; the individual sets with a particular n will be arranged in increasing order of the l values; those with particular n and l will be listed in decreasing order of the m_l values; and the set with $m_s = +\frac{1}{2}$ will be listed before that with $m_s = -\frac{1}{2}$ in case the two sets agree in regard to n, l, and m_l. With the individual sets arranged in this order in (2.3) we obtain what we shall call $\psi(A)$. We shall now wish to choose the phase of the zero order eigenfunctions of configuration $\mathcal{R}$ in a particular way. For the complete set A we shall take $+\psi(A)$ if the sum of the m_l values of the electrons in the almost completed shell is even, $-\psi(A)$ if this sum is odd. We shall correlate to each complete set A of configuration $\mathcal{R}$ in Table I the complete set A_0 of configuration $\mathcal{L}$ as given in Table II, the eigenfunction

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[16] The fact that we determine this matrix in *LS* coupling does not mean that the energy calculation is in any way limited to the Russell-Saunders case. The energy matrix will not be *diagonal* in *LS* coupling, and the transformation necessary to diagonalize it will represent the socalled *breakdown* of the coupling.

[17] M. H. Johnson, reference 3; this method needs a justification, however, which is given in Part II of this paper.

being taken with the + phase when the set is in the standard order. These two complete sets have the same M_L and M_S values.

We must now verify our assertions regarding the matrices of V^1, $\boldsymbol{L}^2$, $\boldsymbol{S}^2$, and $\boldsymbol{L}\cdot\boldsymbol{S}$. Formulas for the matrix elements of such quantities have been obtained by Johnson[4] using the general formulas given by Condon.[7] These formulas will have to be supplemented by an exact determination of the sign of the non-diagonal elements. A general rule may be stated as follows.[18] To the matrix component between two states, $\psi(A)$ and $\psi(A')$, differing in regard to one or two individual sets, one prefixes + or − according to the parity of the permutation which changes the set A' from its standard order to the order in which equal elements in A and A' occupy the same places.

We will use the following notation for the matrix components of angular momentum for one electron.

$$\begin{aligned}(c\,|\,L_x\,|\,d) &= (n^c l^c \overset{c}{m}_l \overset{c}{m}_s\,|\,L_x\,|\,n^d l^d \overset{d}{m}_l \overset{d}{m}_s) \\ &= \delta(n^c l^c \overset{c}{m}_s;\, n^d l^d \overset{d}{m}_s)\delta(\overset{c}{m}_l \pm 1, \overset{d}{m}_l)\tfrac{1}{2}\hbar[(l_d \pm \overset{d}{m}_l)(l^d \mp \overset{d}{m}_l + 1)]^{1/2};\end{aligned} \tag{5.3}$$

$$(c\,|\,S_x\,|\,d) = \delta(n^c l^c \overset{c}{m}_l;\, n^d l^d \overset{d}{m}_l)\delta(\overset{c}{m}_s \pm 1, \overset{d}{m}_s)\tfrac{1}{2}\hbar; \tag{5.4}$$

$$\begin{aligned}(c\,|\,\boldsymbol{L}\cdot\boldsymbol{S}\,|\,d) &= \hbar^2\delta(n^c l^c \overset{c}{m}_j;\, n^d l^d \overset{d}{m}_j)\{\delta(c, d)\overset{c}{m}_l \overset{c}{m}_s + \tfrac{1}{2}\delta(\overset{c}{m}_s, \overset{d}{m}_s \pm 1) \\ &\quad \cdot [(l_c - \overset{c}{m}_j + \tfrac{1}{2})(l_c + \overset{c}{m}_j + \tfrac{1}{2})]^{1/2}\};\end{aligned} \tag{5.5}$$

where $m_j = m_l + m_s$. One fact we shall need particularly is that the matrix component of any of these quantities between the states $m_l^c m_s^c$ and $m_l^d m_s^d$ is the same as that between $-m_l^c$, $-m_s^c$ and $-m_l^d$, $-m_s^d$.

Matrix of V^1. One obtains a non-diagonal element of V^1 only between states differing in regard to one individual set, say that c occurs in A while c' occurs in A'. The value of this component is

$$\pm\, \zeta_{n^c l^c}(c\,|\,\boldsymbol{L}\cdot\boldsymbol{S}\,|\,c'), \tag{5.6}$$

where the sign is determined in accordance with the above convention. If the element c occurs in the group b of additional electrons one obtains the same value for configuration $\mathcal{R}$ and configuration $\mathcal{L}$. If c is in the almost closed shell c and c' must be of the form $(m_l)^-$ and $(m_l - 1)^+$ respectively. A and A' are already in the same order, as are A_0 and A_0'. But $\psi(A)$ and $\psi(A')$ are taken with opposite signs by our rule for choosing the phase. Hence in the matrix components

$$\begin{aligned}(A\,|\,V^1\,|\,A') &= -\,\zeta_{n^a l^a}(m_l, -\,|\,\boldsymbol{L}\cdot\boldsymbol{S}\,|\,m_l - 1, +), \\ (A_0\,|\,V^1\,|\,A_0') &= \zeta_{n^a l^a}(-\,m_l + 1, -\,|\,\boldsymbol{L}\cdot\boldsymbol{S}\,|\,-\,m_l, +) = -\,(A\,|\,V^1\,|\,A'),\end{aligned}$$

$\zeta_{n^a l^a}$ occurs with opposite sign. For the diagonal element of V^1 one has

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[18] Communicated by Professor Condon.

$$\begin{aligned}(A \mid V^1 \mid A) &= \zeta_{n^a l^a} \sum_{i=\epsilon+1}^{n} m_l^i m_s^i + \sum_{i=1}^{\eta} (b^i \mid V_i^1 \mid b^i) \\ &= \zeta_{n^a l^a} \sum_{i=1}^{n} m_l^i m_s^i - \zeta_{n^a l^a} \sum_{i=1}^{\epsilon} m_l^i m_s^i + \sum_{i=1}^{\eta} (b^i \mid V_i^1 \mid b^i),\end{aligned}$$

where the first sum is zero. For the configuration $\mathcal{L}$ one obtains

$$(A_0 \mid V^1 \mid A_0) = \zeta_{n^a l^a} \sum_{i=1}^{\epsilon} m_l^i m_s^i + \sum_{i=1}^{\eta} (b^i \mid V_i^1 \mid b^i)$$

since the product $m_l^i m_s^i$ is the same for a missing electron as for the corresponding electron in A_0. These two elements are seen to be the same except for the sign of $\zeta_{n^a l^a}$. This completes the proof of our assertion concerning the matrices of V^1.

Matrix of $\boldsymbol{L}^2$. We get non-diagonal matrix components of $\boldsymbol{L}^2$ only between states differing in regard to two individual sets, say c and d. This component has the value

$$(A \mid \boldsymbol{L}^2 \mid A') = \pm 4 \{ (c \mid L_x \mid c')(d \mid L_x \mid d') - (c \mid L_x \mid d')(d \mid L_x \mid c') \}.$$

Now if both c and c' are in group b the value is obviously the same for $\mathcal{R}$ and $\mathcal{L}$. If c is in shell a, d in group b, one obtains no value from the second term. In order to obtain a value for the first term c and c' must be of the form $(m_l)^{\pm}$, $(m_l - 1)^{\mp}$. If the element lying between these two is present in $\mathcal{R}$, so far as the shell a is concerned A and A' differ by an odd permutation, while A_0 and A_0' do not differ in order. The converse is true if this element is missing. This introduces one difference of sign between $(A \mid \boldsymbol{L}^2 \mid A')$ and $(A_0 \mid \boldsymbol{L}^2 \mid A_0')$; however we get a second difference of sign from the different choice of phase of $\psi(A)$ and $\psi(A')$, which makes these two elements just equal. In a similar way one demonstrates the equality in case c and c' are both in shell a.

The diagonal element of $\boldsymbol{L}^2$ is

$$(A \mid \boldsymbol{L}^2 \mid A) = \hbar^2 M_L^2 + \hbar \sum_{c} \{ l^c (l^c + 1) - (m_l^c)^2 \} - 4 \sum_{c<d} (c \mid L_x \mid d)^2,$$

where c and d run over all the individual sets of A. The first term is the same for A and A_0, as are also the parts of the second and third terms arising from group b. The part of these terms which arises from group a is the same if calculated for A_0 as for the group of *missing* electrons. The equivalence of this to the calculation for $\mathcal{L}$ is a direct consequence of the following interesting relation: If one takes the integers $l, \cdots, 0, \cdots, -l$ and arranges them into two groups α and β, then the following sum has the same value for groups α and β (the individual integers are denoted by m_l):

$$\sum_{m_l} [l(l+1) - m_l^2] + \sum [-l(l+1) + m_l^2 - m_l],$$

where the second sum is taken over those m_l's for which $m_l - 1$ is also in the group.

This completes the proof that the matrix of $\boldsymbol{L}^2$ is the same for $\mathcal{R}$ and $\mathcal{L}$. The calculation for $\boldsymbol{S}^2$ is very similar and will not be discussed in detail.

Matrix of $\boldsymbol{L}\cdot\boldsymbol{S}$. If A' differs from A in two electrons, the calculation is much the same as for $\boldsymbol{L}^2$ and $\boldsymbol{S}^2$. If A differs from A' in regard to one electron, c, one obtains[19]

$$(A\,|\,\boldsymbol{L}\cdot\boldsymbol{S}\,|\,A') = \pm\,\Big\{(c\,|\,\boldsymbol{L}\cdot\boldsymbol{S}\,|\,c') - 2\sum_{d}(c\,|\,L_x\,|\,d)(d\,|\,S_x\,|\,c') - 2\sum_{d'}(c'\,|\,L_x\,|\,d')(d'\,|\,S_x\,|\,c)\Big\},$$

where d and d' run over all the individual sets common to A and A'. If c is in group b we obviously get the same result for $\mathcal{L}$ and $\mathcal{R}$. If c is in shell a, we get no value unless c, c' are of the form $(m_l)^-$, $(m_l-1)^+$. Then to obtain a value for the second term d must be $(m_l-1)^-$, for the third term d' must be $(m_l)^+$. With these values for d and d', the second and third terms each become $-(c\,|\boldsymbol{L}\cdot\boldsymbol{S}|\,c')$. One may easily verify that A and A', A_0 and A_0' always differ by the same permutation. One obtains a minus sign in the element $(A\,|\boldsymbol{L}\cdot\boldsymbol{S}|\,A')$ due to the difference in phase in the eigenfunctions. Then if neither d nor d' is in configuration $\mathcal{L}$, they must both be in $\mathcal{R}$, hence in this case

$$(A\,|\,\boldsymbol{L}\cdot\boldsymbol{S}\,|\,A') = -\,(c\,|\,\boldsymbol{L}\cdot\boldsymbol{S}\,|\,c')$$

$$(A_0\,|\,\boldsymbol{L}\cdot\boldsymbol{S}\,|\,A_0') = (c\,|\,\boldsymbol{L}\cdot\boldsymbol{S}\,|\,c') - 2(c\,|\,\boldsymbol{L}\cdot\boldsymbol{S}\,|\,c') = (A\,|\,\boldsymbol{L}\cdot\boldsymbol{S}\,|\,A').$$

Similar considerations hold for the other two possibilities.

The diagonal element of $\boldsymbol{L}\cdot\boldsymbol{S}$ is given by

$$(A\,|\,\boldsymbol{L}\cdot\boldsymbol{S}\,|\,A') = M_L M_S \hbar^2,$$

which obviously equals $(A_0\,|\boldsymbol{L}\cdot\boldsymbol{S}|\,A_0')$. This completes the proof as outlined at the beginning of the section.

We will not at this time go further into detail concerning calculations of special cases for configurations of this type. The writer is preparing a sequel to this paper which will consider all the special cases of interest and their comparison with experiment.

PART II. ON TWO-ELECTRON SPECTRA

§6. The direct calculation of the magnetic interaction in *LS* coupling

In a recent paper M. H. Johnson[3] gave a clever method for the calculation of the matrix of magnetic interaction directly in *LS* coupling for any two-electron configuration. This method, which was based on the work of Güttinger and Pauli[20] on the calculation of angular momentum matrices, at once disposed of the whole of the two-electron problem which previously had been attacked configuration by configuration, by Houston,[6] Bartlett,[4] and Goudsmit.[4] However, in making this calculation, Johnson assumes without

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[19] This formula is alternative to, and somewhat simpler than, that given on p. 199 of Johnson's paper, reference 4.

[20] P. Güttinger and W. Pauli, Zeits. f. Physik **67**, 754 (1931).

proof[21] that one will obtain correct results by calculating the matrix of $\xi(r_1)\boldsymbol{L}_1\cdot\boldsymbol{S}_1+\xi(r_2)\boldsymbol{L}_2\cdot\boldsymbol{S}_2$ in the system of states characterized by definite values nls of the quantum numbers of electron 1, definite values $n'l's'$ of the quantum numbers of electron 2, and the values $LSJM_J$ of the resultant momenta; of course calculating nothing at all for states known to be ruled out by the exclusion principle. This complete neglect of the equivalence of the two electrons, which is usually taken care of by antisymmetrization, needs justification; and since our calculations of magnetic interaction for configurations of the type p^5x, d^9x, etc. depend on the use of Johnson's matrices, it was thought appropriate to include a justification of this point at this place.

We are interested in the matrix components of $\xi(r_1)\boldsymbol{L}_1\cdot\boldsymbol{S}_1+\xi(r_2)\boldsymbol{L}_2\cdot\boldsymbol{S}_2$ joining antisymmetric states characterized by $LSJM_J$ for a given two-electron configuration. Each such state is a definite known[22] linear combination of states characterized by LSM_LM_S, or say γ for short. Now our basic states are characterized by $n_1l_1m_{l1}s_1m_{s1}$; $n_2'l_2'm_{l2}'s_2{}^4m_{s2}'$. Call the eigenfunction going with this state $\phi(n_1\cdots m_{s2}')$. We can build up a state characterized by $n_1l_1s_1$; $n_2'l_2's_2'$; LSM_LM_S by taking definite known linear combinations of these states ϕ. Call the state so obtained $\psi(\alpha_1, \beta_2, \gamma)$. Now this state will be neither symmetric nor antisymmetric in 1 and 2 if $\beta\not\equiv\alpha$, since if it were it would be an eigenstate for both quantum numbers α and quantum numbers β for each electron, and this is of course impossible. However, to have a physical significance we must make this state antisymmetric in 1 and 2. Now since the state $\psi(\alpha_2, \beta_1, \gamma)$ is also an eigenstate of γ, the antisymmetric combination

$$\Psi(\gamma) = \frac{1}{(2)^{1/2}}[\psi(\alpha_1, \beta_2, \gamma) - \psi(\alpha_2, \beta_1, \gamma)] \tag{6.1}$$

will be an eigenstate of γ and will be the only one that satisfies the antisymmetry condition. We can then consider the state $LSJM_J$ in which we are interested as built up of linear combinations, in the known way, of these antisymmetric states. The general matrix component joining two states $LSJM_J$; $L'S'J'M_J'$ of the same configuration will be the sum of matrix components between these antisymmetric functions, with a constant α and β. The most general term will be

$$\tfrac{1}{2}[\bar{\psi}(\alpha_1,\beta_2,\gamma)-\bar{\psi}(\alpha_2,\beta_1,\gamma)][\{1\}+\{2\}][\psi(\alpha_1,\beta_2,\gamma')-\psi(\alpha_2,\beta_1,\gamma')]$$

where $\{1\}=\xi(r_1)\boldsymbol{L}_1\cdot\boldsymbol{S}_1$, etc. Expanded, this becomes

$$\begin{aligned}&\tfrac{1}{2}\bar{\psi}(\alpha_1, \beta_2, \gamma)\{1\}\psi(\alpha_1, \beta_2, \gamma') + \tfrac{1}{2}\bar{\psi}(\alpha_2, \beta_1, \gamma)\{1\}\psi(\alpha_2, \beta_1, \gamma')\\ &+ \tfrac{1}{2}\bar{\psi}(\alpha_1, \beta_2, \gamma)\{2\}\psi(\alpha_1, \beta_2, \gamma') + \tfrac{1}{2}\bar{\psi}(\alpha_2, \beta_1, \gamma)\{2\}\psi(\alpha_2, \beta_1, \gamma')\\ &- \tfrac{1}{2}\bar{\psi}(\alpha_1, \beta_2, \gamma)\{1\}\psi(\alpha_2, \beta_1, \gamma') - \tfrac{1}{2}\bar{\psi}(\alpha_2, \beta_1, \gamma)\{1\}\psi(\alpha_1, \beta_2, \gamma')\\ &- \tfrac{1}{2}\bar{\psi}(\alpha_1, \beta_2, \gamma)\{2\}\psi(\alpha_2, \beta_1, \gamma') - \tfrac{1}{2}\bar{\psi}(\alpha_2, \beta_1, \gamma)\{2\}\psi(\alpha_1, \beta_2, \gamma').\end{aligned} \tag{6.2}$$

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[21] I am indebted to Mr. Johnson for calling my attention to this point.

[22] The matrix of this transformation was first given in general by E. P. Wigner, *Gruppentheorie*, p. 206.

Now of this the first term equals the fourth and the second the third, since the interchange of the electron indices 1 and 2 in a matrix component does not affect its value. Together these first four terms give

$$\bar{\psi}(\alpha_1, \beta_2, \gamma)[\{1\} + \{2\}]\psi(\alpha_1, \beta_2, \gamma'). \qquad (6.3)$$

Now as to the last four terms; certainly none of these will have any value unless $\beta \equiv \alpha$, *i.e., unless the electrons are equivalent,* since any function of electron 1 is diagonal with respect to the quantum numbers of electron 2 and *vice versa*. If the electrons are equivalent, $\psi(\alpha_1, \alpha_2, \gamma)$ will be either symmetric or antisymmetric. To show this we note that $\psi(\alpha_1, \alpha_2, \gamma)$ is the product of an orbital function[23] $\psi_r(n_1l_1, n_2l_2, LM_L)$ and a spin function $\psi_\sigma(s_1, s_2, SM_S)$. We express this ψ_r in terms of the fundamental ϕ_r's by the transformation

$$\psi_r(n_1l_1n_2l_2LM_L) = \sum_{m_l, m_l'} \phi_r(n_1l_1m_{l1}n_2l_2m_{l2}')(n_1l_1m_{l1}n_2l_2m_{l2}' | n_1l_1n_2l_2LM_L). \qquad (6.4)$$

Now from page 206 of Wigner we have the relation

$$(n_1l_1m_{l1}'n_1l_1m_{l2} | n_1l_1n_2l_2LM_L) = (-1)^{2l-L}(n_1l_1m_{l1}n_2l_2m_{l2}' | n_1l_1n_2l_2LM_L). \qquad (6.5)$$

In the summation (6.4) m_l and m_l' run over the same range $-l \cdot \cdot \cdot l$. Hence we may rewrite our summation, using (6.5), as follows:

$$\begin{aligned} \psi_r(n_1l_1n_2l_2LM_L) = & \sum_{m_l < m_l'} [\phi_r(n_1l_1m_{l1}n_2l_2m_{l2}') + (-1)^{2l-L}\phi_r(n_1l_1m_{l1}'n_2l_2m_{l2})] \\ & \cdot (n_1l_1m_{l1}n_2l_2m_{l2}' | n_1l_1n_2l_2LM_L) \\ & + \sum_{m_l} \phi_r(n_1l_1m_{l1}n_2l_2m_{l2})(n_1l_1m_{l1}n_2l_2m_{l2} | n_1l_1n_2l_2LM_L), \end{aligned}$$

and this, since ϕ_r is merely a product of a function of electron 1 with one of electron 2, is symmetric if $2l-L$ is even and antisymmetric if $2l-L$ is odd. Similarly ψ_σ is symmetric if $2s-S$ is even, antisymmetric if it is odd. Hence $\psi(\alpha_1, \alpha_2, \gamma)$, the product of ψ_r and ψ_σ, will be either symmetric or antisymmetric depending on whether $2(l+s)-(L+S)$ is even or odd.

If either $\psi(\alpha_1, \alpha_2, \gamma)$ or $\psi(\alpha_1, \alpha_2, \gamma')$ is symmetric we get zero for our matrix component. (Either $\Psi(\gamma)$ or $\Psi(\gamma')$ vanishes identically; the last four terms of (6.2) cancel the first four.) If both are antisymmetric the last four terms of (6.2) are exactly equal to the first four. But in this case our normalization of Ψ is wrong by a factor $1/(2)^{1/2}$ so again we get just the result (6.3).

Hence, for any case in which states γ and γ' are permitted by the exclusion principle we have the result

$$\bar{\Psi}(\gamma)[\{1\} + \{2\}]\Psi(\gamma') = \bar{\psi}(\alpha_1, \beta_2, \gamma)[\{1\} + \{2\}]\psi(\alpha_1, \beta_2, \gamma') \qquad (6.6)$$

which justifies the assignment of the quantum numbers α to electron 1 and β to electron 2 in calculating the matrix of any function of the type $\{1\} + \{2\}$ in LS coupling.

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[23] Note that according to the convention we are using $n_1l_1n_2l_2$ indicates that electrons 1 and 2 have the *same* quantum numbers nl. A difference in quantum numbers is indicated by a prime or a superscript.

§7. The addition of an electron to an ionic multiplet

We can treat, by this same method, the problem of calculating the magnetic energy matrix for the system of states resulting from the addition of an electron to a Russell-Saunders multiplet of the next ion. The consideration of such a set of levels as thus arising from a certain "parent" multiplet is justified only in case the spread of the resulting set of levels (a triad for an added p electron, a pentad for a d) is small compared to the distances between the sets arising from different parents; otherwise we should have an "interaction between parents". The special case ${}^3P+s$ was considered by Goudsmit,[4] and the general calculation was given by Johnson[3] in his paper on two-electron systems for the case in which one adds an electron which is not equivalent to any electron in the ion. Johnson's calculation was made with the same assumptions as in the case of two-electron spectra, and requires for justification the considerations we shall now give.

Consider a Russell-Saunders multiplet of an ion. In this case the magnetic interaction in the ion is so weak that it can be considered as a small perturbation applied to the degenerate l^i, s^i energy level resulting from the electrostatic interaction. (We will use the letter i to designate resultant momenta for the ion and e to designate the quantum numbers of the added electron.) The magnetic interaction energy $V^1=\sum\xi(r_k)\boldsymbol{L}_k\cdot\boldsymbol{S}_k$ for the ion is diagonal with respect to j^i and m_j^i, and the dependence on j^i and m_j^i of each term may be obtained from Johnson's formulas (p. 1635):

$$(l^is^ij^im_j^i|\,\boldsymbol{L}_k\cdot\boldsymbol{S}_k\,|\,l^is^ij^im_j^i)$$
$$= (l^i|\,L_k\,|\,l^i)(s^i|\,S_k\,|\,s^i)\left\{\frac{j^i(j^i+1)-l^i(l^i+1)-s^i(s^i+1)}{2}\right\}.$$

Here the first two factors are quite independent of j^i and m_i^j. Since the matrix of $\xi(r_k)$ does not depend on j^i or m_j^i the whole dependence of the matrix of V^1 on j^i, m_j^i is given by[24]

$$(l^is^ij^im_j^i|\,V^1\,|\,l^is^ij^im_j^i) = \zeta\hbar^2\left\{\frac{j^i(j^i+1)-l^i(l^i+1)-s^i(s^i+1)}{2}\right\}$$
$$= \zeta(l^is^ij^im_j^i|\,\boldsymbol{L}_i\cdot\boldsymbol{S}_i\,|\,l^is^ij^im_j^i).$$

Hence our combination of ionic multiplet and electron is effectively a configuration l^is^i, l^es^e with a magnetic interaction energy $\zeta\boldsymbol{L}_i\cdot\boldsymbol{S}_i+\xi(r_e)\boldsymbol{L}_e\cdot\boldsymbol{S}_e$.

Now our resultant states for the atom, characterized by $LSJM_J$, are known linear combinations of states characterized by LSM_LM_S. Denote this last set of quantum numbers by γ and the eigenstate by $\Psi(\gamma)$. This latter state must be properly antisymmetrized in all electrons. Now from the functions $\phi(l^im_l^is^im_s^i;\ l^em_l^es^em_s^e)$ we can build up uniquely the state $\phi(l^is^i;\ l^es^e;\ \gamma)$ or, for short, $\psi(\alpha_{1\ldots n}, \beta_e, \gamma)$ where in place of i we write the names

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[24] This is, of course, just the Landé interval rule. Note that the numerical value of ζ can be obtained directly from the multiplet splitting of the ion.

of the electrons $1 \cdots n$ in the ion. This state is antisymmetric in all the ion electrons, but unless the quantum numbers nls of one of the ion electrons agree with those of the added electron, it can be neither symmetric nor antisymmetric with respect to interchange of the added electron with any of the ion electrons. In this non-equivalent case, we build up an antisymmetric $\Psi(\gamma)$ by taking the following linear combination

$$\Psi(\gamma) = \frac{1}{(n+1)^{1/2}}\left[\psi(\alpha_{1\cdots n}, \beta_e, \gamma) - \sum_{k=1}^{n}\psi(\alpha_{1\cdots e\cdots n}, \beta_k, \gamma)\right], \tag{7.2}$$

where e replaces k in the subscript of α under the summation sign. Now a general term in our interaction matrix is

$$\bar{\Psi}(\gamma)\left\{\zeta \mathbf{L}_i \cdot \mathbf{S}_i + \xi(r_a)\mathbf{L}_a \cdot \mathbf{S}_a\right\}\Psi(\gamma'), \tag{7.3}$$

where $\zeta \mathbf{L}_i \cdot \mathbf{S}_i$ acts on the ion electrons and $\xi(r_a)\mathbf{L}_a \cdot \mathbf{S}_a$ acts on the added electron.[25] Now in our case of no ion electrons equivalent to the added electron, this matrix component will vanish between states having different ion electrons, and hence a different added electron. The $(n+1)$ terms which remain will all be equal, hence (7.3) becomes simply

$$\psi(\alpha_{1\cdots n}, \beta_e, \gamma)\left\{\zeta \mathbf{L}_i \cdot \mathbf{S}_i + \xi(r_e)\mathbf{L}_e \cdot \mathbf{S}_e\right\}\psi(\alpha_{1\cdots n}, \beta_e, \gamma') \tag{7.4}$$

which is the expression used by Johnson.

The special cases p^5x or d^9x of configurations of the type $\mathcal{L}$ may be considered as the addition of electron x to the ^2P or ^2D multiplet of the p^5 or d^9 ion. In this case since this doublet is the only multiplet of the ionic configuration the "parentage" of our states is unquestioned to the accuracy of the first order perturbation theory of Part I. The remark of footnote 24 enables us to obtain an estimate of the value of $\zeta_{n^a l^a}$ for these configurations from the doublet splitting of the ion, since the ζ of equation (7.1) equals $-\zeta_{n^a l^a}$ in this case to the approximation in which we use the same central field for the two cases.

§8. The matrix of magnetic interaction between configurations for two electrons

We will now extend the results of §6 to show how one calculates the matrix of magnetic interaction between two two-electron configurations by using the very convenient formulas of Johnson which give directly the matrix component of magnetic interaction between any two states with precise values of $l_1 l_2' s_1 s_2' LSJM_J$. This matrix is diagonal with respect to JM_J, so let us consider the matrix component joining state $SLJM_J$ of configuration $x(=\alpha\beta)$ and state $S'L'JM_J$ of configuration $y(=\gamma\delta)$.

The state $SLJM_J$ will be a linear combination of states SLM_LM_S, or say λ, while the state $S'L'JM_J$ will be a linear combination of states $S'L'M_L'M_S'$, or say λ'. The antisymmetric $\Psi(\lambda)$ will be of the form

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[25] i. e., $\zeta \mathbf{L}_i \cdot \mathbf{S}_i$ acts on the electrons belonging to α, $\xi(r_a)\mathbf{L}_a \cdot \mathbf{S}_a$ on the electron belonging to β in ψ.

$$\Psi(\lambda) = \frac{1}{(2)^{1/2}}[\psi(\alpha_1, \beta_2, \lambda) - \psi(\alpha_2, \beta_1, \lambda)],$$

when we take $\alpha \not\equiv \beta$. Similarly

$$\Psi(\lambda') = \frac{1}{(2)^{1/2}}[\psi(\gamma_1, \delta_2, \lambda') - \psi(\gamma_2, \delta_1, \lambda')],$$

when we take $\gamma \not\equiv \delta$. The general term in the interaction matrix will be

$$\tfrac{1}{2}[\bar{\psi}(\alpha_1, \beta_2, \lambda) - \bar{\psi}(\alpha_2, \beta_1, \lambda)][\{1\} + \{2\}][\psi(\gamma_1, \delta_2, \lambda') - \psi(\gamma_2, \delta_1, \lambda')].$$

From this we easily see that we get no value for this interaction unless one of the electrons retains the same quantum numbers, say $\alpha \equiv \gamma$. In this case the remaining terms reduce to

$$\bar{\psi}(\alpha_1, \beta_2, \lambda)\{2\}\psi(\alpha_1, \delta_2, \lambda').$$

Hence we have the result that

$$\begin{aligned}\bar{\Psi}(\alpha\beta SLJM_J)[\xi(r_1)\mathbf{L}_1\cdot\mathbf{S}_1 + \xi(r_2)\mathbf{L}_2\cdot\mathbf{S}_2]\Psi(\alpha\delta S'L'JM_J)& \\ = \bar{\psi}(\alpha_1\beta_2 SLJM_J)[\xi(r_2)\mathbf{L}_2\cdot\mathbf{S}_2]\psi(\alpha_1\delta_2 S'L'JM_J),&\end{aligned}$$

which becomes, if $\alpha = nl$; $\beta = n'l'$; $\delta = n''l''$,

$$= (n_2' l_2' \mid \xi(r_2) \mid n_2'' l_2')(l_1 l_2' SLJM_J \mid \mathbf{L}_2\cdot\mathbf{S}_2 \mid l_1 l_2' S'L'JM_J) \qquad (8.1)$$

The value of the last factor here is given by Johnson, and in particular it is seen from his formulas to be diagonal with respect to l_2. This means that we may have a magnetic interaction only between configurations differing just in the n of one electron, the matrix being given then by (8.1).

This was for the case in which neither of the configurations was composed of equivalent electrons. We have now to consider the case in which the two electrons of configuration x are equivalent. (If both configurations are composed of equivalent electrons we get no interaction unless the states are identical, which case has already been treated.) If λ is an allowed level, $\psi(\alpha_1, \alpha_2, \lambda)$ will already be antisymmetric. The general term in the interaction matrix will then be

$$\begin{aligned}&\frac{1}{(2)^{1/2}}\bar{\psi}(\alpha_1, \alpha_2, \lambda)[\{1\} + \{2\}][\psi(\alpha_1, \delta_2, \lambda') - \psi(\alpha_2, \delta_1, \lambda')] \\ &\quad = \frac{1}{(2)^{1/2}}\bar{\psi}(\alpha_1, \alpha_2, \lambda)\{2\}\psi(\alpha_1, \delta_2, \lambda') - \frac{1}{(2)^{1/2}}\bar{\psi}(\alpha_1, \alpha_2, \lambda)\{1\}\psi(\alpha_1, \delta_2, \lambda') \\ &\quad = (2)^{1/2}\bar{\psi}(\alpha_1, \alpha_2, \lambda)\{2\}\psi(\alpha_1, \delta_2, \lambda'). \qquad (8.2)\end{aligned}$$

The balance of the computation is as above. Hence if one configuration is composed of equivalent electrons we obtain a factor of $(2)^{1/2}$ which is not obtained in the case of non-equivalent electrons. In this particular case then, one does not obtain the correct result by simply assigning definite quantum numbers to the individual electrons.

The result, that we obtain a magnetic interaction only between configurations which differ just in the n of one electron, holds quite generally for any configurations of any number of electrons. This can be readily seen from (5.5) and (5.6). Such configurations can be considered as two members of the same series, and in general lie far apart in the spectrum. The type of series perturbation found by Shenstone and Russell[26] cannot be due to magnetic interaction, but must be purely electrostatic.

The writer intends, in the near future, to consider more in detail the question of the interaction of configurations, especially in connection with the interesting work of Shenstone and Russell on perturbed series and in an attempt to explain some of the poor agreements found by Condon and himself, references 2 and 5.

I wish to take this opportunity to express to Professor E. U. Condon my sincere appreciation of his friendly and stimulating guidance in the study of quantum mechanics in general and atomic spectra in particular.

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[26] A. G. Shenstone and H. N. Russell, Phys. Rev. **39**, 415 (1932).