

Atomic Energy Levels and Zeeman Effect

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The present theory of complex spectra, neglecting magnetic interactions *between* electrons, has been successful enough in interpreting the data for certain simple configurations that it is of interest to discuss the extent to which this procedure can be applied to the energy levels and Zeeman effect of other configurations. The theory is

extended to include p^5p and comparison is made with experimental data. Greater discrepancies appear here than in simpler cases. This is an example of the greater importance of the neglected interactions in more complex configurations.

THE theory of complex spectra, in the approximation which has as yet been most useful in correlating energy differences and g -values in simple configurations, accounts for the electrostatic and the largest electromagnetic energies. It makes use of angular integrations, leaving radial integrals as parameters to be determined by fitting part of the experimental data, some other data to be "predicted" thereby. The theory might be perfected by including all interactions,¹ but that must encumber it with more parameters and require more of the data for their determination, so is not desirable except where the simple approximation fails. We wish here to suggest that the neglected inter-electronic magnetic interactions become of greater importance with increasing complexity of configuration, and to show that even in the case p^5p the present approximation is only partially satisfactory.

I. SECULAR EQUATIONS FOR p^5p

The secular equations are very similar to those for the configuration pp' given by Johnson.² They are, however, slightly simpler, involving one less parameter, because of the fact that application of the Slater³ method, as carried out

¹The first step in this direction has been made by H. C. Wolfe (Phys. Rev. **41**, 443 (1932)) who accounts for the interaction of the type (spin of one electron)—(orbit of other) in the simplest configurations. The still-neglected spin-spin interaction is smaller but of the same order of magnitude in the helium triplet. See also H. C. Brinkman, *Zeits. f. Physik, in print*.

²M. H. Johnson, Jr., Phys. Rev. **38**, 185 (1931).

³J. C. Slater, Phys. Rev. **34**, 1293 (1929).

by one of us and Shortley,⁴ here gives two relations between the multiplet energies of (LS) coupling, rather than one relation as in pp' . To obtain the equations for p^5p we substitute γ for β in the secular equations* for pp' . Then the parameters for p^5p may be expressed in terms of Slater's radial integrals³ ($F^2/25 = F_2$) and represent the extreme-coupling multiplets as follows:

$$\begin{aligned} {}^3D: & 0, & {}^1D: & \alpha = 12G_2, \\ {}^3P: & \gamma, & {}^1P: & \gamma = 6F_2, \\ {}^3S: & -\frac{3}{2}\gamma, & {}^1S: & \delta = -9F_2 + 6G_0. \end{aligned}$$

The matrices of spin-orbit interaction remain the same in p^5p , as Shortley⁴ has shown, but we now expect to find the sign of the larger parameter (for p^5) negative.

⁴G. H. Shortley, Phys. Rev. **40**, 185 (1932). To visualize the here-pertinent result, we may derive it in the following abbreviated manner, similar to the well-known explanation of the inverted multiplet of an almost-closed shell. A closed shell has electrons $a^1 \cdots a^6$, say, and we consider electrostatic interaction between them and, for example, one other electron b . The sum of these interactions is a constant. To calculate (within a constant) the interaction of $a^1 \cdots a^5$ with b , consider a representation in which the sums $m_1^1 + \cdots + m_1^5 = m_l$ and $m_s^1 \cdots m_s^5 = m_s$ are diagonal; then removal of a^6 , which has quantum numbers $-m_s$, $-m_s$, decreases the interaction by an amount calculated by Slater³ for the quantum numbers $-m_l$, $-m_s$, m_l^b , m_s^b . (The interaction of a^6 with the other a 's is independent of m_l , m_s .)

* In Johnson's paper,² in the nondiagonal terms of the energy matrix for $J=0$, $a_1 + a_2$ should appear in place of $a_1 - a_2$, as has been kindly called to our attention by Dr. Brinkman and may be verified by reckoning the energies for (jj) coupling, e.g. The consequent *small* change in the energies for $J=0$ has been made in Table I.

II. DETERMINATION OF THE PARAMETERS

The five parameters were so evaluated as to make satisfactory agreement with the following experimental energies: the three levels with $J=2$, the two levels with $J=0$, and the sum of the energies for $J=1$; the $J=3$ state having been chosen as the zero level. The values so selected are: $a_1=40$, $a_2=-403$, $\alpha=537$, $\gamma=946$, $\delta=3084$. The solutions of the secular equation for $J=1$, with these parameters, are given in Table I, together with the g -values calculated with the help of formulas to be developed in §3.

That determination of the parameters is an obvious extension of previous applications of the

TABLE I. Energy levels and g -values for Ne, $2p^53p$.

J	W (cm $^{-1}$)		g'	
	obs. ⁵	calc.	obs. ⁵	calc.
0	3313.7	3292	0/0	0/0
1	1381.4	1376	1.340	1.402
0	1260.4	1282	0/0	0/0
2	1201.5	1201.5	1.301	1.378
1	1115.1	1151	0.999	1.046
2	658.8	729	1.229	1.142
1	464.6	370	0.6695	0.627
2	167.2	128	1.137	1.148
3	0	0	1.329	(1.333)
1	-1399.2	-1328	1.984	1.907

theory. It is not, however, an adequate test of the subordination of the neglected magnetic interactions, since we cannot be sure that a parameter so determined really represents only the interaction it is intended to represent. A more severe indication of the importance of the neglected interactions is the fact that the magnetic parameters calculated for this configura-

tion from the spectra of quite similar atoms⁶ differ from those determined above, and lead to much worse disagreements of energy levels (though the g -values are about as good). Otherwise such calculation would constitute a more practicable determination of the parameters, leaving more data to be predicted.

III. CALCULATION OF THE ZEEMAN EFFECT

We apply the method given by Inglis and Johnson⁷ to the configuration pp' , using energy matrices given by Johnson.² We give the resulting formulas in the form for pp' so that they may be applied, if desired, to that configuration as well. They are to be modified for p^5p by substituting γ for β as in §1. For $J=2$ the coefficients of the transformation from (LS) to intermediate coupling (*vide* references 2 and 6) are:

$$R(k1) = \frac{1}{3^{1/2}} \left\{ \frac{\alpha - 2\zeta - W_k}{2^{1/2}\theta} \rho_k + \frac{\zeta}{\theta} \right\} R(k3),$$

$$R(k2) = \rho_k R(k3),$$

$$R(k3) = \left\{ \frac{1}{3} \left(\frac{\alpha - 2\zeta - W_k}{2^{1/2}\theta} \rho_k + \frac{\zeta}{\theta} \right)^2 + \rho_k^2 + 1 \right\}^{-1/2},$$

where $\rho_k = (1/2^{1/2})(\beta - W_k)/(\alpha - 4\zeta - W_k)$;

$$\zeta = \frac{1}{4}(a_1 + a_2); \quad \theta = \frac{1}{4}(a_1 - a_2).$$

In terms of these, the g -values for intermediate coupling are

$$g_k' = (7/6) \{R(k1)\}^2 + \{R(k2)\}^2 + (3/2) \{R(k3)\}^2.$$

For the four states with $J=1$, the coefficients are more involved than heretofore:

$$S(k1) = \tau_k S(k4); \quad S(k2) = -(3^{1/2}/4\theta)(\sigma_k - 3\gamma/2 - 2\zeta - W_k)S(k4); \quad S(k3) = \sigma_k S(k4);$$

$$S(k4) = \{ \tau_k^2 + (3/16\theta^2)(\sigma_k - 3\gamma/2 - 2\zeta - W_k)^2 + \sigma_k^2 + 1 \}^{-1/2}$$

where

$$\sigma_k = \frac{1}{2(6)^{1/2}} \frac{(5\zeta + W_k) \{ 3(3\gamma/2 + 2\zeta + W_k) - 8\zeta \} + 5(3\gamma/2 + 2\zeta + W_k)\zeta}{5\zeta^2 + (5\zeta + W_k)(\beta - \zeta - W_k)}$$

$$\tau_k = [1/(5\zeta + W_k)] \{ (10/3)^{1/2} \zeta \sigma_k + (3^{1/2}/4\theta)(\sigma_k - 3\gamma/2 - 2\zeta - W_k) \}.$$

The Zeeman effect for the states with $J=1$ is then given by

$$g_k' = \frac{1}{2} \{ S(k1) \}^2 + (3/2) \{ S(k2) \}^2 + \{ S(k3) \}^2 + 2 \{ S(k4) \}^2.$$

⁵ E. Back, Ann. d. Physik 76, 317 (1925).

Here (as also in other applications of this method) the g -values are best calculated by

⁶ By estimating slight alterations in effective nuclear charge, we have with sufficient accuracy $a_2 = -520$ from $\text{Ne}^+ 2p^5 2P$ or from $\text{Ne} 2p^5 ns$, and $a_1 = 8.6$ from $\text{Na} 3p 2P$.

⁷ Inglis and Johnson, Phys. Rev. 38, 1642 (1931).

substituting in the formulas energy values, W_k , calculated from the parameters, rather than observed energies. Otherwise a single energy discrepancy may play havoc with a g -value, and with the g -sum. The formulas give g -values obeying the sum rule if "calculated" energies be used, as is easily proved.

IV. LIMITATIONS OF THE PRESENT APPROXIMATION

Application of the theory to configurations having an s electron and an almost-closed shell (p^5s and d^9s) leads to experimental agreements ranging around 1 percent whereas the deviations in the two-electron configurations ps and ds average more than ten times as great.⁸ This fact suggests⁶ that the disagreements are due largely to neglected magnetic interactions between the electrons, since the usual magnetic (spin-orbit) energy should be relatively larger in p^5s than in ps , because of the larger nuclear charge effective in p^5s for the electrons having an orbital angular momentum. The excellent agreement⁹ in cases involving almost-closed shells suggests that extension of the application should be most fruitful in the case of p^5p . Here one should indeed find a distinct superiority over the configurations pp' , pd , etc. The situation is, however, not so favorable as in p^5s . The largest interactions and

the over-all separation remain of the same order of magnitude, as do the neglected magnetic inter-electronic interactions. But here we have many more levels crowded into the same range, and we take into account an additional spin-orbit interaction which is probably of the same order of magnitude as the neglected interactions. The energy deviations bear about the same relation to the over-all separation as in p^5s , but the accuracy relative to the separation of adjacent lines becomes here much less.

For Zeeman effect, the orientation of the angular momenta is all-important. In p^5p in intermediate coupling, the spin and orbit of each electron are oriented by electrostatic forces—in general fairly large—and by magnetic forces. For the outer electron the neglected magnetic forces may be as large as the reckoned magnetic force. The orientations of the spin and orbit of the outer electron might thus behave quite otherwise than calculated, making a considerable error in the Zeeman effect. In the g -values of p^5d , etc., the outer electron plays an even more important rôle, and the neglected interactions should become even less negligible.

In all but the simplest configurations, in intermediate coupling, no exact results may be expected from the present approximation. (The same is true of (LS) coupling (Slater's case³), where overlapping of configurations is more common, but there the remedy is quite different.) Even with rough results, there remains the possible utility of deciding between uncertain identifications of spectral lines, and the satisfaction that the theory fulfills our expectations.

⁸ W. V. Houston, Phys. Rev. 33, 297 (1929); Laporte and Inglis, Phys. Rev. 35, 1337 (1930); Condon and Shortley, Phys. Rev. 35, 1342 (1930).

⁹ The inconsistency of Pt and K^+ is directly attributable to interference of nearby configurations.