only possibilities allowed, assuming $f_1=0$ at higher energy than $d_1'=0$. The possibilities for the opposite case follow in an analogous manner. It must be noted that results obtained here for degeneracies, the various bands which may stick together etc. are not dependent on our approximation. In an exact treatment (i.e., fitting boundary conditions over the whole surface of the cell) while the numerical values would be shifted, the spherical harmonics would still be classified according to representations, the compatibility relations would still hold and all the

above results would follow. Thus, for example, the bands arising from a d atomic level would still have the same symmetry properties as above (determined essentially by the transformation properties of the various d functions). All the information we have obtained about these bands from their symmetry properties would still be valid in an exact treatment, or in any other method of approximation.

We wish to thank Professor Slater who suggested this problem and Dr. Shockley for many useful suggestions.

OCTOBER 1, 1937

PHYSICAL REVIEW

VOLUME 52

The Zeeman Effect of the Rare Gases

I. B. GREEN

Mendenhall Laboratory of Physics, Ohio State University, Columbus, Ohio (Received August 4, 1937)

The g values of the neutral rare gases have been calculated from the atomic coupling factors for the $np^{s}n'p$ configurations, and excellent agreement is shown to exist between theory and experiment in most cases. From curves of the g values, interesting conclusions regarding the the genealogy of the terms in these configurations are noted.

HE Zeeman effect of the neutral rare gases has been studied by a number of investigators, first among them Back¹ who showed, by means of his work on neon, the first discrepancies of the simple Landé theory and its failure to explain the anomalous g values that he had observed. At the same time, he gave the first evidence of the g sum rule.

A theoretical investigation by Houston² led the way to the interpretation of these g values and the possibility of their calculation from atomic coupling parameters. Pogany's1(d), 1(e) work on the rare gases has shown that excellent agreement exists between theory and experiment for the first excited state of these atoms, the configuration $np^{5}(n+1)s$, the type of configuration studied by Houston and Condon and Shortley,³ and Jacquinot⁴ has extended the work of Pogany to include the higher series members of this type of configuration in neon, namely the $2p^{5}3s$, $2p^{5}4s$, $2p^{5}5s$, and $2p^{5}6s$ configurations. Although a comparatively large amount of experimental evidence exists, there seem to have been no other calculations made for any other configurations of the rare gases except the $2p^{5}3p$ configuration of neon, where the agreement between theory and experiment is extremely poor.

It is the purpose of the present paper to give a comparison between the observed g values and the g values calculated from the parameters determined by Bartberger⁵ from a least-squares solution of the problem as set up by Shortley⁶ for the $np^{5}n'p$ configurations of the rare gases. Bartberger's parameters were determined from the matrix of the energy set up in JJ coupling as the zero-order approximation, but such a zero-order scheme is not suitable for the calculation of g values, since the weak-field magnetic interaction terms are not diagonal in *jj* coupling. They are, however, in LS coupling, and Bart-

¹(a) Back, (neon), Ann. d. Physik **76**, 329 (1925); (b) Terrien and Dykstra, (argon), J. de phys. **5**, 439 (1934); (c) Bakker, (argon, krypton, xenon), Diss. Amsterdam, 1931; (d) Pogany (krypton) Zeits. f. Physik **86**, 729 (1933); (e) Pogany (argon, krypton, xenon) Zeits. f. Physik 93, 364 (1935).

² Houston, Phys. Rev. **33**, 297 (1929). ³ Condon and Shortley, Phys. Rev. **35**, 1342 (1930); see also Laporte and Inglis, Phys. Rev. **35**, 1337 (1930).

⁴ Jacquinot, Comptes rendus 202, 1578 (1936).

⁵ Bartberger, Phys. Rev. 48, 682 (1935).

⁶ Shortley, Phys. Rev. 44, 666 (1933).

berger's parameters were used in the matrices set up in the LS scheme. The electrostatic coupling parameters are given on page 298 and the electromagnetic interaction terms on page 268 of Condon and Shortley's Atomic Spectra,7 to which the reader is referred. The only change to be noted is that the sign of the parameter ζ' as given by Bartberger is to be changed before introduction into the matrix.

The calculation of the g factor of a particular term is then comparatively simple. It has been outlined by Marvin,8 but perhaps a brief resumé would not be out of place here. The value of the term is subtracted from the diagonal terms of the matrix. The determinant thus formed would then be equal to zero. If $M_1, M_2, M_3 \cdots$ represent the minors of the diagonal terms of this determinant and $g_1, g_2, g_3 \cdots$ the *LS* g values of the terms designating the rows and columns of the original matrix; then the g value in intermediate coupling of the particular term under consideration is given by

$$g = \frac{g_1 M_1 + g_2 M_2 + g_3 M_3 + \cdots}{M_1 + M_2 + M_3 + \cdots}.$$

This method is very much simpler of application and identical in result with the method which diagonalizes the matrix and which may be written

$$g(\alpha j) = \sum_{\gamma s l} g(slj) | (\gamma slj | \alpha j) |^2$$

In fact, it may be shown that the square of the

TABLE I. e values of Ne 2p⁵np.

J	LEVEL	$2p^{5}3p$ (obs.) ^{1(a)}	2p53p (calc.)(9)	2p ⁵ 4p (obs.)*	2∳ ⁵ 4∲ (calc.)		
1	$\begin{array}{c} p_2\\ p_5\\ p_7\\ p_{10}\\ \Sigma g \end{array}$	$ \begin{array}{r} 1.340 \\ .999 \\ .669 \\ \underline{1.984} \\ \overline{4.992} \end{array} $	$ \begin{array}{r} 1.339 \\ 1.105 \\ .561 \\ 1.993 \\ \overline{5.000} \end{array} $	$ \begin{array}{r} 1.397 \\ .685 \\ .981 \\ \underline{1.934} \\ \overline{4.997} \end{array} $	$ \begin{array}{r} 1.411 \\ .695 \\ .964 \\ \underline{1.930} \\ \overline{5.000} \end{array} $		
2	φ 4 φ6 φ8 Σg	$ \begin{array}{r} 1.301 \\ 1.229 \\ 1.137 \\ \overline{3.667} \end{array} $	$ \begin{array}{r} 1.415 \\ 1.106 \\ 1.146 \\ \overline{3.667} \end{array} $	$ \begin{array}{r} 1.178 \\ 1.376 \\ 1.116 \\ \overline{3.670} \end{array} $	$ \begin{array}{r} 1.190 \\ 1.363 \\ 1.114 \\ \overline{3.667} \end{array} $		

^{*} Unpublished results of Green and Peoples, reported at Washington meeting of the American Physical Society, 1937.

TABLE II. g values of A $3p^{5}np$.

-					
J	LEVEL	$3p^{5}4p$ (obs.) ^{1(e)}	3p ⁵ 4p (calc.)	3p ⁵ 5p (obs.) ^{1(b)}	3p55p (calc.)
1	Р2 Р4 Р7	1.379 .819 .840	1.363 .887 .774	1.45 .61 1.01	1.466 .643 1.001
992) 93 - 2 	Σg		$\frac{1.976}{5.000}$	$\frac{1.90}{4.97}$	$\frac{1.890}{5.000}$
2	Рз Р6 Р8	$1.248 \\ 1.302 \\ 1.121 \\ \hline 2.651$	$ \begin{array}{c c} 1.280 \\ 1.271 \\ 1.116 \\ \hline 1.67 \end{array} $	$ \begin{array}{r} 1.18 \\ 1.42 \\ \underline{1.09} \\ \overline{1.09} \end{array} $	$ \begin{array}{r} 1.179 \\ 1.378 \\ 1.110 \\ \hline \end{array} $
	Σg	3.671	3.667	3.69	3.667

TABLE III. g values of Kr and Xe.

Yenon

	11.5 5001			renon			
J	LEVEL	$4p^{5}5p$ (obs.) ^{1(e)}	4p ⁵ 5p (calc.)	LEVEL	5 <i>p</i> ⁵ 6 <i>p</i> (obs.) ^{1(e)}	5p ⁵ 6p (calc.)	
1	$p_{3} \\ p_{4} \\ p_{7} \\ p_{10} \\ \Sigma g$	$ \begin{array}{r} 1.425 \\ .631 \\ 1.028 \\ 1.891 \\ \overline{4.975} \end{array} $	$ \begin{array}{r} 1.461 \\ .653 \\ 1.002 \\ \underline{1.884} \\ \overline{5.000} \end{array} $	$ \begin{array}{c} p_2 \\ p_4 \\ p_7 \\ p_{10} \\ \Sigma g \end{array} $	 	$ \begin{array}{r} 1.494 \\ .639 \\ 1.029 \\ 1.838 \\ \overline{5.000} \end{array} $	
2	$\begin{array}{c} p_2 \\ p_6 \\ p_8 \\ \Sigma g \end{array}$	$ \begin{array}{r} 1.163 \\ 1.400 \\ 1.116 \\ \overline{3.679} \end{array} $	$ \begin{array}{r} 1.179 \\ 1.365 \\ 1.123 \\ \overline{3.667} \end{array} $	рз р6 р9 Σg	$ \begin{array}{r} 1.183 \\ 1.402 \\ 1.113 \\ \overline{3.698} \end{array} $	$ \begin{array}{r} 1.178 \\ 1.391 \\ 1.098 \\ \overline{3.667} \end{array} $	

transformation coefficient

Krypton

$$(\gamma slj | \alpha j) |^2 = M_{\alpha} / \sum M_{\alpha}$$

The calculations are summarized in Table I. II and III. The calculations for Ne $2p^{5}3p$ are Shortley's.9

In addition to the configurations in the tables the 4p⁵6p of Kr has been determined experimentally,1(e) but the coupling parameters have not yet been calculated accurately. In addition, a serious discrepancy exists in the g sum of the terms for j=1.

In general, except for the lowest levels of argon and neon, the agreement between theory and experiment is very satisfactory. In all cases where there is a disagreement in the g value, there is also a disagreement between the observed and calculated positions of the levels.

But a much more significant result is found when we plot the observed g values against the ratio of electromagnetic to electrostatic coupling parameters. This is shown in Figs. 1 and 2. In order to show the complete transition from LS

⁷ Condon and Shortley, Theory of Atomic Spectra (Cambridge University Press, 1935). ⁸ Marvin, Phys. Rev. 44, 818 (1933).

⁹ Shortley, Phys. Rev. 47, 295 (1935).



FIG. 1. g values of $np^{\delta}n'p$ of rare gases plotted against ratio of electromagnetic to electrostatic coupling parameter J=1. The g sum rule is indicated by the sum of the ordinates of the four curves being equal to 5.



FIG. 2. g values of $np^5n'p$ of rare gases plotted against ratio of electromagnetic to electrostatic coupling parameter J=2. The g sum rule is indicated by the sum of the ordinnates of the three curves being equal to 11/3.

coupling to JJ coupling on one graph, the g values of the levels have been plotted as ordinates, and $\chi/5+\chi$ as abscissae, where $\chi = \zeta'/5F_2$, ζ' being the electromagnetic and F_2 the electrostatic coupling parameter. Thus the abscissa is 0 for LS coupling and 1 for jj coupling.

All of the known g values have been plotted and members of the same series within each element joined together. Smooth curves were then drawn among the points so determined and all the elements joined together and extrapolated at both ends to the g values for LS coupling and jj coupling.

These curves bring out very clearly the genealogy of the levels of the rare gas configurations and show definitely the futility cf the assignment of L and S values to the levels in these cases of intermediate coupling.

Thus, we see in the spectrum of neon that the levels p_5 and p_7 , called 1P_1 and 3D_1 respectively in the $2p^53p$ configuration, have actually interchanged g values in the $2p^54p$ configuration and to be consistent, should now be called 3D_1 and 1P_1 , respectively. It seems meaningless to designate members of the same series by different LS designations. A similar situation holds with respect to the levels p_4 and p_6 which also seem to interchange roles in going from the $2p^53p$ to the $2p^54p$ configurations.

It is also striking to note the sensitivity of the g values with respect to changes in the coupling. The ${}^{3}S_{1}$ changes very slowly until jj coupling is almost reached, and then changes very rapidly. ${}^{3}D_{1}$ changes rapidly at each end and very slowly at intermediate values and has a point of inflection. ${}^{3}P_{1}$ and ${}^{3}P_{2}$ drop very rapidly and then assume an almost steady value. ${}^{1}P_{1}$ rises rapidly at first, and then very gradually. ${}^{3}D_{2}$ drops very slowly and rises again near jj coupling. ${}^{1}D_{2}$ behaves almost oppositely.

In conclusion, the author wishes to express his thanks to Professor C. W. Ufford of Allegheny College, for supplying him with important data, and for some very valuable discussions.