The Energy Levels of the Rare-Gas Configurations*

GEORGE H. SHORTLEY, *Palmer Physical Laboratory, Princeton University*

(Received August 4, 1933)

The secular equations expressing the electrostatic and spin-orbit interactions of the configurations p^5p and p^5d are found to be very conveniently handled if one neglects the interaction between levels which have different levels of the ionic doublet as parents, an approximation significant for all but the lowest p^5p's of neon and argon. The 10 levels of p^5p and the 12 of p^5d are each expressed in terms of six parameters, one of which corresponds directly to the ionic doublet splitting. It is found that the higher members of the p^5p series in neon and argon, the lowest configurations of this type in krypton and xenon, and all eight members of the neon p^5d series agree with these formulas to within the magnitude of the above-mentioned neglected interaction (which becomes relatively very small for the higher series members) in all cases where two configurations do not obviously strongly perturb each other. Because of the generally very weak interaction between configurations in these spectra, better agreement between theory and observed data is found than has been the case for any other atoms. This calculation gives the eigenstates for these configurations exact specification in the jj-coupling scheme.

THE structure of the rare-gas spectra is recalled by Fig. 1, which is a plot of the energy levels of neon I, the most completely analyzed of these spectra, as given by Bacher and Goudsmit. All known levels of the rare gases are included in the systems $n'p^5nl$ where $n'=2, 3, \cdots$ for neon, argon, $\cdots$. This makes these spectra remarkably clean, almost as clean as one-electron doublet spectra. As seen in Fig. 1, the configurations of each series rapidly divide, with increasing n, into two groups of levels. The upper of these groups approaches the $^2P_{1/2}$ limit of the ion, the lower the $^2P_{3/2}$ limit. For p^5s the upper and lower groups each consist of two levels, and for neon this configuration is completely known up to $2p^511s$. For p^5p the upper group consists of four levels and the lower of six; this configuration is completely known in neon up to $2p^57p$. For $l>1$, the upper group consists of four levels and the lower of eight; the $2p^5nd$ of neon are completely analyzed up to $n=10$, while only two levels of the lowest p^5f are found.

The configuration p^5s has been considered in detail by Laporte and Inglis and by Condon and Shortley,[1] who used the formulas[2] derived by Houston for the configuration sp. We shall here consider the configurations p^5p and p^5d.

The configuration $n'p^5np$

The configuration p^5p contains 1 level with $J=3$, 3 with $J=2$, 4 with $J=1$, and 2 with $J=0$. Hence the diagonalization of the Hamiltonian for this configuration involves the solution of a linear, a quadratic, a cubic, and a quartic equation. These equations contain as parameters six radial integrals. Given the values of these parameters, the solution of these equations is rather complicated; to obtain the values of these parameters from the observed energies and then check the self-consistency of the equations, as we propose to do, is much more complicated. A simplification valid in many cases can, however, be made. Just as our consideration of one configuration at a time is an approximation in which we neglect the interaction between configurations, so we may use an approximation in which we also neglect the interaction between the groups of levels of the same configuration which

* Presented at the Washington Meeting of the American Physical Society, April 28, 1933.

[1] Laporte and Inglis, Phys. Rev. **35**, 1337 (1930); Condon and Shortley, Phys. Rev. **35**, 1342 (1930).

[2] That these formulas are applicable with change of sign of the spin-orbit parameter and hence of Houston's X is readily shown from previous results [Shortley, Phys. Rev. **40**, 185 (1932)]. That X was found to be negative in these comparisons then shows that the electrostatic integral $G_0(sp)$ is positive, as is perhaps to be expected [cf. Bacher, Phys. Rev. **43**, 264 (1933)].

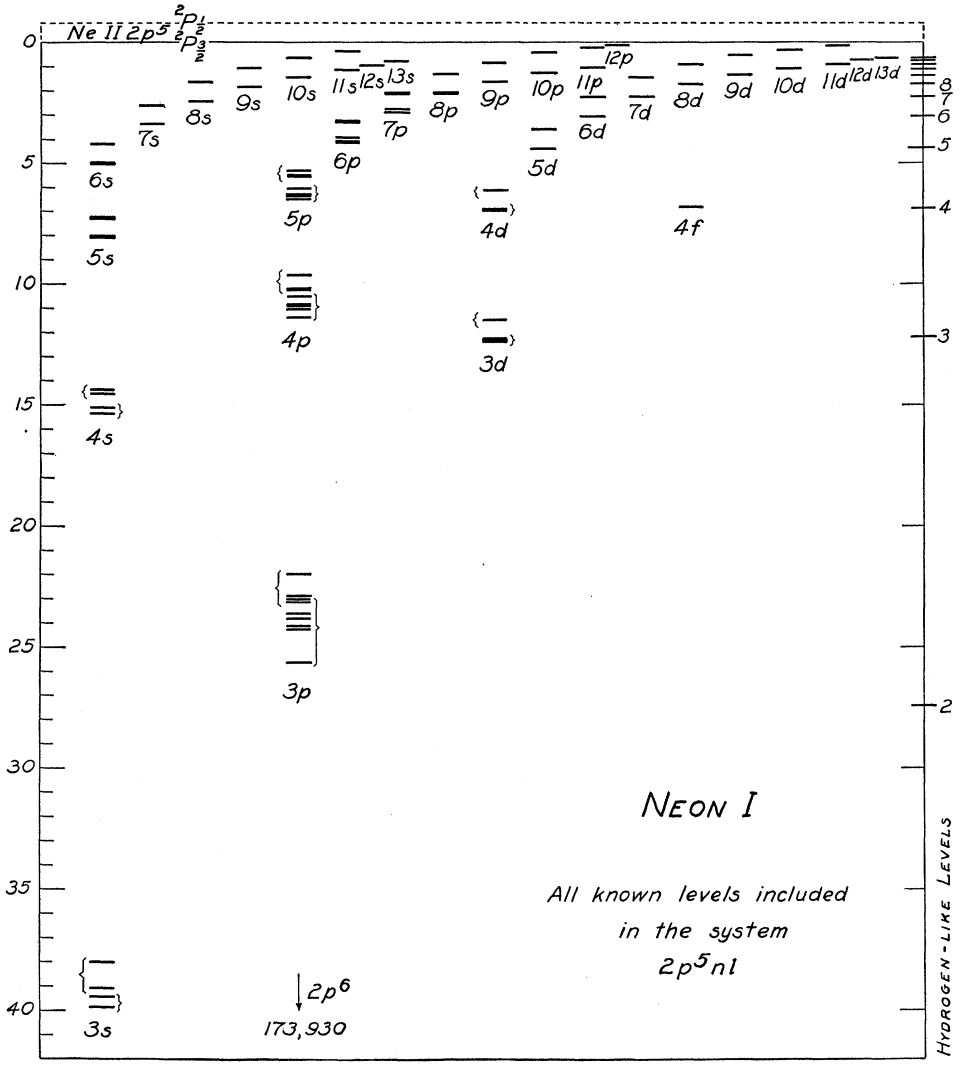

FIG. 1. Scale in thousands of cm^{-1}. Each line represents in general a group of observed levels not "resolved" on this scale.

have different levels of the ionic doublet as parents. This latter approximation is expected (cf. Fig. 1) to be increasingly good as we go up the series of configurations.

Now the quantum number which distinguishes levels belonging to one parent from those belonging to the other is the j value of the p^5 group, which is also the j value of the missing electron.[3] Hence in order to split the secular equation according to parentage, it is necessary to obtain the matrix of the Hamiltonian in the jj-coupling scheme.

The matrix of spin-orbit interaction is diagonal in jj coupling, the diagonal element having the

[3] Cf. §2 of Shortley, Phys. Rev. **43**, 451 (1933).

value

$$(A\,|\,V^1\,|\,A)=\sum_i \zeta_{nl^i}\cdot\tfrac{1}{2}\{j^i(j^i+1)-l^i(l^i+1)-s^i(s^i+1)\},\quad(1)$$

where the summation is taken over all electrons in the configuration.[4] This element is independent of the J and M_J values of the state A. The matrix for $n'p^5np$ is the same as that for $n'pnp$ with reversed sign of $\zeta'=\zeta_{n'p}$. The values of the elements are

$$\begin{array}{lll} & n'p^5np & \\ a & (\tfrac{3}{2},\tfrac{3}{2}): & -\tfrac{1}{2}\zeta'+\tfrac{1}{2}\zeta \\ b & (\tfrac{3}{2},\tfrac{1}{2}): & -\tfrac{1}{2}\zeta'-\ \zeta \\ c & (\tfrac{1}{2},\tfrac{3}{2}): & \zeta'+\tfrac{1}{2}\zeta \\ d & (\tfrac{1}{2},\tfrac{1}{2}): & \zeta'-\ \zeta. \end{array}\quad(2)$$

In the parentheses are given the j values first of the p^5 core and then of the added p electron. The letters a, b, c, d are introduced as a convenient abbreviation for the four possible combinations of j values. States labeled by a and b belong to the lower doublet level, states labeled by c and d to the higher doublet level of the ion.

The matrix of electrostatic interaction is diagonal in LS coupling; the diagonal elements are given on page 193 of reference 4. With the transformation of reference 3 this matrix is found in jj coupling to have the value

$-F_0+$ | $3a$ | $-F_2$

	$2a$	$2b$	$2c$
$2a$	$3F_2+4G_2$	$-2F_2+4G_2$	$2F_2-4G_2$
$2b$	$-2F_2+4G_2$	$4G_2$	$-F_2-4G_2$
$2c$	$2F_2-4G_2$	$-F_2-4G_2$	$4G_2$

	$1a$	$1b$	$1c$	$1d$
$1a$	$-F_2$	$2\cdot5^{\frac{1}{2}}F_2$	$-2\cdot5^{\frac{1}{2}}F_2$	$10^{\frac{1}{2}}F_2$
$1b$	$2\cdot5^{\frac{1}{2}}F_2$	0	$5F_2$	0
$1c$	$-2\cdot5^{\frac{1}{2}}F_2$	$5F_2$	0	0
$1d$	$10^{\frac{1}{2}}F_2$	0	0	0

	$0a$	$0d$
$0a$	$-5F_2+4G_0$	$-5\cdot2^{\frac{1}{2}}F_2+2\cdot2^{\frac{1}{2}}G_0$
$0d$	$-5\cdot2^{\frac{1}{2}}F_2+2\cdot2^{\frac{1}{2}}G_0$	$2G_0$

. . . . . (3)

In the notation here used the J value is given as an arabic numeral, followed by a letter which specifies the electronic j values according to the scheme (2). The matrices are independent of the value of M_J.

Adding the spin-orbit interaction (2) and splitting these matrices according to the parent j values as indicated by the broken lines, we obtain the following equations for the energy levels:

Upper levels

$$\begin{array}{lll} (2c)=-F_0+ & \zeta'+\tfrac{1}{2}\zeta & +4G_2 \\ (1c)=-F_0+ & \zeta'+\tfrac{1}{2}\zeta & \\ (1d)=-F_0+ & \zeta'-\ \zeta & \\ (0d)=-F_0+ & \zeta'-\ \zeta & +2G_0 \end{array}\quad(4)$$

[4] Notation as in §5 of Shortley, Phys. Rev. **40**, 185 (1932).

Lower levels

$$
\begin{aligned}
(3a) &= -F_0-\tfrac{1}{2}\zeta'+\tfrac{1}{2}\zeta- \quad F_2 \\
\left.\begin{matrix}2a'\\2b'\end{matrix}\right\} &= -F_0-\tfrac{1}{2}\zeta'-\tfrac{1}{4}\zeta+\tfrac{3}{2}F_2 \qquad +4G_2\pm[(\tfrac{3}{4}\zeta+\tfrac{3}{2}F_2)^2+(2F_2-4G_2)^2]^{\frac{1}{2}} \\
\left.\begin{matrix}1a'\\1b'\end{matrix}\right\} &= -F_0-\tfrac{1}{2}\zeta'-\tfrac{1}{4}\zeta-\tfrac{1}{2}F_2 \qquad \pm[(\tfrac{3}{4}\zeta-\tfrac{1}{2}F_2)^2+20F_2^2]^{\frac{1}{2}} \\
(0a) &= -F_0-\tfrac{1}{2}\zeta'+\tfrac{1}{2}\zeta- 5F_2 \qquad +4G_0.
\end{aligned}
\qquad (4)\ \textit{cont.}
$$

The six unprimed levels of this group belong in our approximation rigorously to the quantum numbers assigned to them. The eigenstates for the primed levels are linear combinations of those for the corresponding unprimed levels. We arbitrarily denote the higher of the two levels by a' and the lower by b' since the level a would lie above the level b if the electrostatic interaction vanished.

Now the value of one of the parameters, ζ', should in all cases in which our approximation is good be obtainable from the splitting of the parent doublet, which is just $\frac{3}{2}\zeta'$. But this splitting is known from the spectra of the ions only to an accuracy of one wave number. Hence we prefer to determine this parameter, along with the rest, from the data for each configuration, and then to check it against the doublet splitting of the ion later.

The six linear expressions in (4) should determine the six parameters. From the values of the parameters we could then predict absolute positions of the other four levels. However, in order to make the values of the parameters less sensitive to the small perturbations which must exist both between the two parts of one configuration and between neighboring configurations, we prefer to fit by least squares the eight quantities obtained by adding to the above six levels the means of $2a'$ and $2b'$ and of $1a'$ and $1b'$. *This leaves the separations* $2a'-2b'$ *and* $1a'-1b'$ *to be absolutely predicted.*

The results of such a calculation are shown in Fig. 2 for neon, Fig. 3 for argon, and Fig. 4 for krypton and xenon. In these figures the empirical value for $1b'$ has been taken as the zero for each configuration; a break in the wave-number scale indicates the separation between the two groups of levels.

The first question one asks concerns the validity of the neglect of interaction between the two groups of levels. If the parameters we have obtained are approximately correct, the magnitude of this interaction may be found by using the interaction elements of the matrices (3) according to the second-order perturbation theory. In this way the *largest* interaction was found to have approximately the value represented by the length of the short black bar drawn underneath each configuration. This gives an idea of the agreement to be expected in the comparison.

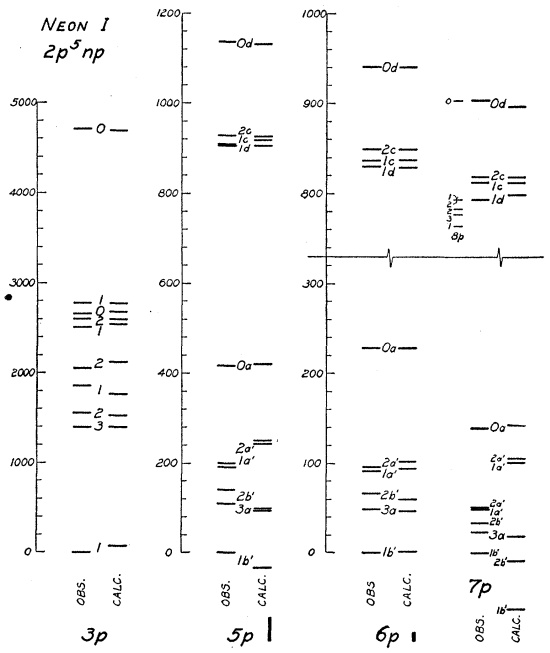

FIG. 2. (The lengths of the black bars represent the maximum interaction between the two groups of levels in each configuration.)

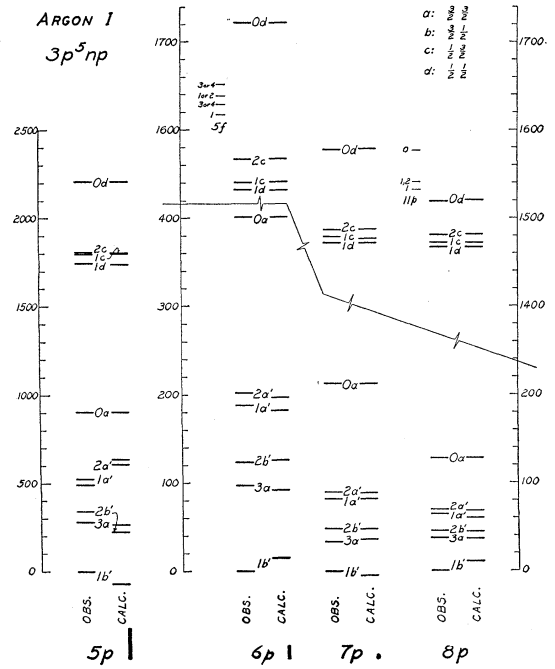

FIG. 3. (The lengths of the black bars represent the maximum interaction between the two groups of levels in each configuration.)

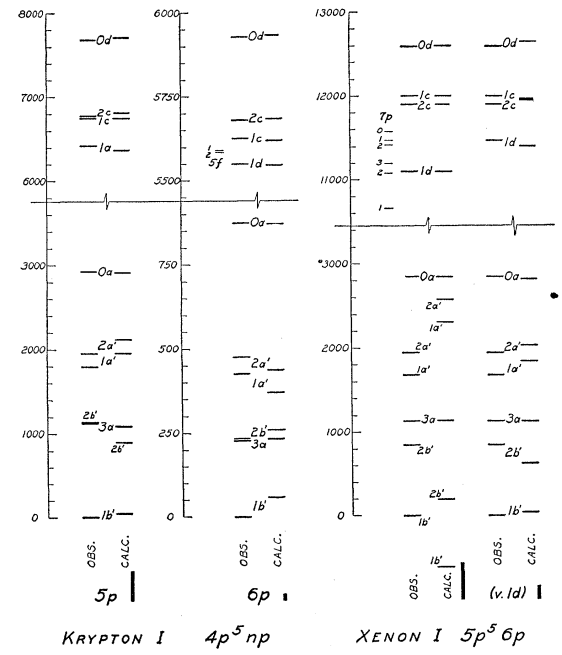

FIG. 4. (See text for explanation of xenon rearrangement.)

Having obtained the values of the parameters, one can readily find the coefficients in the expansion

$$\psi(Ja')=\psi(Ja)(Ja|Ja')+\psi(Jb)(Jb|Ja'),$$
$$\psi(Jb')=\psi(Ja)(Ja|Jb')+\psi(Jb)(Jb|Jb'). \quad (5)$$

Since $|(a|a')|^2=|(b|b')|^2$, $|(a|b')|^2=|(b|a')|^2$, and $|(a|a')|^2+|(b|a')|^2=1$; one may call $|(Ja|Ja')|^2$ the purity of the levels Ja' and Jb'. It is, so far as this work is concerned, purely accidental that the electrostatic interaction between $1c$ and $1d$ vanishes identically and hence that these levels are to our approximation 100 percent pure. To the same approximation the separation between these two levels represents just the doublet splitting of the np electron in the central field due to the core.

NEON I (CF. FIG. 2)

The $2p^53p$ is taken from the work of Inglis and Ginsburg,[5] who solved the complete secular equation in LS coupling using the levels of $J=0$, 2, 3, and the mean of the four levels with $J=1$ to obtain the parameters, leaving otherwise the $J=1$ levels to be absolutely predicted.

The $2p^55p$ is the first of the series to which our approximation is at all applicable. These levels agree to within the rather large maximum interaction between the groups.

For $2p^56p$, the interaction is much smaller and the agreement correspondingly better.

TABLE I. *Neon I* $2p^5np$.

	$3p$	$5p$	$6p$	$7p$
F_0	−1737	−385.8	−314.7	−291.9
F_2	157.7	31.0	10.4	18.3
G_0	750.5	112.6	55.8	49.0
G_2	44.8	1.9	3.0	−1.7
ζ'	403	528.6	520.2	521.0
ζ	40	8.1	5.4	13.2
$(2a\|2a')$		0.921	0.977	
$(2b\|2a')$		−0.390	−0.208	
$(1a\|1a')$		0.683	0.697	
$(1b\|1a')$		0.730	0.716	
% Purity $2a'b'$		84.8	95.5	
% Purity $1a'b'$		46.6	48.6	

[5] Inglis and Ginsburg, Phys. Rev. **43**, 194 (1933). With regard to this configuration see also St. Rozental, Zeits. f. Physik **83**, 534 (1933).

$2p^5 7p$ is found to agree not at all; the reason is that the lower $8p$ group exactly overlaps the upper $7p$ and is therefore expected to interact strongly with it.

The values of the parameters and the coefficients in (5) are given by Table I. The significance to be attached to these values must be judged by comparison with Fig. 2. The value of ζ' is to be compared with the value 521 obtained from the parent doublet splitting of 782 cm^{-1}.

Argon I (cf. Fig. 3)

The p^5p configurations of argon remain rather well separated from each other up to $3p^5 8p$, the last of the series which is completely known. $8p\ 0a$ falls about 200 cm^{-1} below $7p\ 1d$ and the lower group of $11p$ falls close to the upper group of $8p$ as indicated in the figure. There is definite evidence of perturbation on $8p$. The $5f$ group overlapping $6p$ does not have a pronounced effect.

Table II. *Argon I* $3p^5np$.

	$5p$	$6p$	$7p$	$8p$
F_0	−805.8	−585.6	−521.4	−515.7
F_2	75.7	18.7	9.8	5.5
G_0	235.6	95.5	53.6	28.3
G_2	2.0	6.4	2.5	2.5
ζ'	977.2	952.3	953.5	953.3
ζ	44.1	7.1	3.6	5.0
$(2a\|2a')$	0.927	0.986	0.968	0.999
$(2b\|2a')$	−0.378	−0.168	−0.254	−0.045
$(1a\|1a')$	0.702	0.690	0.690	0.723
$(1b\|1a')$	0.712	0.724	0.725	0.692
% Purity $2a'b'$	85.9	97.2	93.7	99.8
% Purity $1a'b'$	49.3	47.6	47.6	52.3

The constants are given in Table II. The value of ζ' is to be compared with the 954 obtained from the ionic doublet splitting of 1431 cm^{-1}.

Krypton I and Xenon I (cf. Fig. 4)

Even the lowest p^5p's of krypton and xenon are amenable to treatment with our approximation. For krypton the $2p^5 5p$ and $6p$ are completely known. The $2p^5 5p$ agrees to within the error of the approximation. The $6p$ shows definite evidence of outside perturbation which is undoubtedly mainly due to the lower group of $7p$ which lies at only 6200 on the $6p$ scale, rather than to the $5f$ levels plotted.

In xenon only the $5p^5 6p$ is complete. This in the first plot agrees very poorly with the calculations. It is definitely perturbed by the lower $7p$ group which overlaps as indicated. Although one cannot make a rigorous assignment of these overlapping levels to configurations one suspects on comparing this figure with the others that the highest $J=1$ of $7p$ might belong more exactly to $6p$ than the $1d$ assigned to it. If one makes this rearrangement one obtains the plot on the right which shows a decidedly better agreement.

The constants for these spectra have the values given in Table III. ζ' for krypton is to be compared with the 3581 obtained from the ion. The doublet splitting for the xenon ion is not known.

Table III.

	Krypton I $4p^5np$		*Xenon I* $5p^56p$	
	$5p$	$6p$	Given	Rearranged
F_0	−2984	−2028.4	−4764	−4682
F_2	213	34.8	321	198
G_0	671	194.1	748	622
G_2	20	16.3	−25	−2
ζ'	3632	3567.6	7028	7094
ζ	246	49.0	599	374
$(2a\|2a')$	0.955	0.999		0.954
$(2b\|2a')$	−0.297	−0.022		−0.299
$(1a\|1a')$	0.736	0.750		0.775
$(1b\|1a')$	0.678	0.662		0.632
% Purity $2a'b'$	91.2	99.9		91.0
% Purity $1a'b'$	54.2	56.2		60.1

The configuration $n'p^5nd$

The diagonal elements of spin-orbit interaction for p^5d in jj coupling are

$$\begin{array}{lll} & n'p^5nd & \\ a & (\tfrac{3}{2},\tfrac{5}{2}): & -\tfrac{1}{2}\zeta_p + \zeta_d \\ b & (\tfrac{3}{2},\tfrac{3}{2}): & -\tfrac{1}{2}\zeta_p - \tfrac{3}{2}\zeta_d \\ c & (\tfrac{1}{2},\tfrac{5}{2}): & \zeta_p + \zeta_d \\ d & (\tfrac{1}{2},\tfrac{3}{2}): & \zeta_p - \tfrac{3}{2}\zeta_d, \end{array} \qquad (6)$$

where we have introduced a notation a, b, c, d similar to that used for p^5p. Here the parameter ζ_p, which is the same as the former ζ', accomplishes the splitting of the configuration into two

groups, states characterized by a and b lying in the upper group, those characterized by c and d in the lower.

The electrostatic energies in LS coupling have the values

$$\begin{aligned} &{}^3F = -F_0 - 2F_2 && {}^1F = -F_0 - 2F_2 + 90G_3 && {}^3D = -F_0 + 7F_2 \\ &{}^1D = -F_0 + 7F_2 && {}^3P = -F_0 - 7F_2 && {}^1P = -F_0 - 7F_2 + 20G_1. \end{aligned} \tag{7}$$

Transforming to jj coupling gives the electrostatic matrices

$-F_0+$

	$4a$
$4a$	$-2F_2$

	$3a$	$3b$	$3c$
$3a$	$2\frac{2}{5}F_2+24G_3$	$-\frac{4}{5}\cdot 6\frac{1}{2}F_2+12\cdot 6\frac{1}{2}G_3$	$\frac{8}{5}\cdot 5\frac{1}{2}F_2-12\cdot 5\frac{1}{2}G_3$
$3b$	$-\frac{4}{5}\cdot 6\frac{1}{2}F_2+12\cdot 6\frac{1}{2}G_3$	$-\frac{7}{5}F_2+36G_3$	$-\frac{1}{5}\cdot 30\frac{1}{2}F_2-6\cdot 30\frac{1}{2}G_3$
$3c$	$\frac{8}{5}\cdot 5\frac{1}{2}F_2-12\cdot 5\frac{1}{2}G_3$	$-\frac{1}{5}\cdot 30\frac{1}{2}F_2-6\cdot 30\frac{1}{2}G_3$	$30G_3$

	$2a$	$2b$	$2c$	$2d$
$2a$	$\frac{4}{5}F_2$	$\frac{2}{5}\cdot 21\frac{1}{2}F_2$	$-\frac{8}{5}\cdot 14\frac{1}{2}F_2$	$\frac{3}{5}\cdot 21\frac{1}{2}F_2$
$2b$	$\frac{2}{5}\cdot 21\frac{1}{2}F_2$	$21\frac{1}{5}F_2$	$\frac{7}{5}\cdot 6\frac{1}{2}F_2$	$14\frac{1}{5}F_2$
$2c$	$-\frac{8}{5}\cdot 14\frac{1}{2}F_2$	$\frac{7}{5}\cdot 6\frac{1}{2}F_2$	0	0
$2d$	$\frac{3}{5}\cdot 21\frac{1}{2}F_2$	$14\frac{1}{5}F_2$	0	0

	$1a$	$1b$	$1d$
$1a$	$-28\frac{4}{5}F_2+12G_1$	$14\frac{1}{5}F_2+4G_1$	$-\frac{7}{5}\cdot 5\frac{1}{2}F_2+4\cdot 5\frac{1}{2}G_1$
$1b$	$14\frac{1}{5}F_2+4G_1$	$-\frac{7}{5}F_2+\frac{4}{3}G_1$	$-14\frac{1}{5}\cdot 5\frac{1}{2}F_2+\frac{4}{3}\cdot 5\frac{1}{2}G_1$
$1d$	$-\frac{7}{5}\cdot 5\frac{1}{2}F_2+4\cdot 5\frac{1}{2}G_1$	$-14\frac{1}{5}\cdot 5\frac{1}{2}F_2+\frac{4}{3}\cdot 5\frac{1}{2}G_1$	$20\frac{2}{3}G_1$

	$0b$
$0b$	$-7F_2$

(8)

Just as in the case of p^5p we find if we neglect the interaction between levels belonging to different parents the following formulas to express the twelve levels in terms of six parameters:

$$\begin{aligned} (3c) &= -F_0 + \zeta_p + \zeta_d && +30G_3 \\ (2c) &= -F_0 + \zeta_p + \zeta_d \\ (2d) &= -F_0 + \zeta_p - \tfrac{3}{2}\zeta_d \\ (1d) &= -F_0 + \zeta_p - \tfrac{3}{2}\zeta_d && +20\tfrac{2}{3}G_1 \\ (4a) &= -F_0 - \tfrac{1}{2}\zeta_p + \zeta_d - 2F_2 \end{aligned} \tag{9}$$

$$\left.\begin{matrix}3a'\\3b'\end{matrix}\right\} = -F_0-\tfrac{1}{2}\zeta_p-\tfrac{1}{4}\zeta_d+\tfrac{3}{2}F_2+30G_3 \pm[(29\tfrac{1}{10}F_2-6G_3+\tfrac{5}{4}\zeta_d)^2+96(3G_3-\tfrac{1}{5}F_2)^2]^{\frac{1}{2}}$$

$$\left.\begin{matrix}2a'\\2b'\end{matrix}\right\} = -F_0-\tfrac{1}{2}\zeta_p-\tfrac{1}{4}\zeta_d+\tfrac{5}{2}F_2 \qquad \pm[(\tfrac{5}{4}\zeta_d-17\tfrac{1}{10}F_2)^2+8\tfrac{4}{25}F_2^2]^{\frac{1}{2}} \qquad (9)\ cont.$$

$$\left.\begin{matrix}1a'\\1b'\end{matrix}\right\} = -F_0-\tfrac{1}{2}\zeta_p-\tfrac{1}{4}\zeta_d-\tfrac{7}{2}F_2+20\tfrac{2}{3}G_1\pm[(\tfrac{5}{4}\zeta_d-21\tfrac{1}{10}F_2+16\tfrac{2}{3}G_1)^2+(4G_1+14\tfrac{4}{5}F_2)^2]^{\frac{1}{2}}$$

$$(0b) = -F_0-\tfrac{1}{2}\zeta_p-\tfrac{3}{2}\zeta_d-7\ F_2.$$

We take the six levels given by linear expressions and the means of $3a'$, $3b'$; $2a'$, $2b'$; and $1a'$, $1b'$; fitting the six parameters to these nine quantities by least squares. *This leaves the 3a'-3b', 2a'-2b', 1a'-1b' separations to be absolutely predicted.*

From Fig. 1 we see that our approximation should be applicable to all the p^5d's of neon I. Since these are known completely from $3d$. through $10d$ we obtain the long series of configurations plotted in Fig. 5. These all agree within the accuracy of the calculation[6] except $6d$ and $7d$, which are clearly perturbed. The most of this perturbation is due to the fact that the upper group of $6d$ lies only 26 cm^{-1} below the lower of

[6] The extreme coarseness of the wave-number scale for the right half of the plot is to be noted.

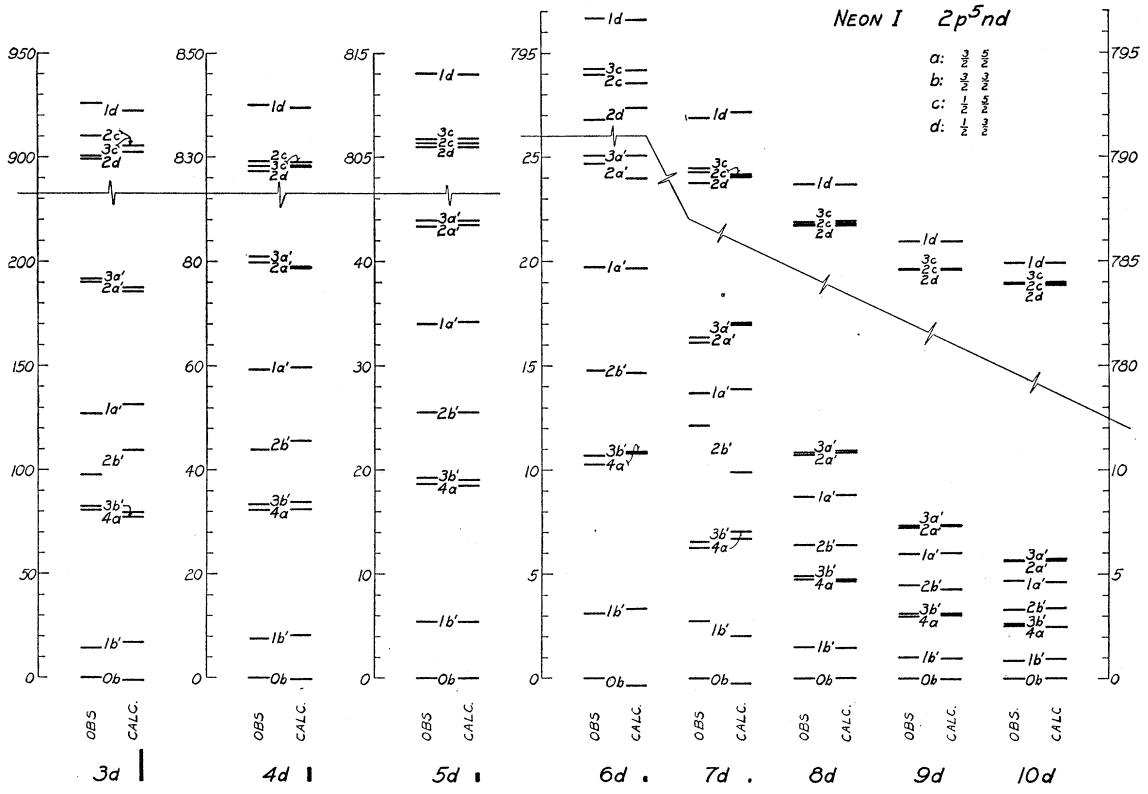

FIG. 5. Except for $6d$ and $7d$, which perturb each other, the agreement is within the accuracy, indicated by the lengths of the black bars, of the neglect of interaction between levels belonging to different parents; in the cases $8d$, $9d$, $10d$, where the maximum discrepancy is only 0.20 cm^{-1}, this agreement is within the accuracy of the calculation.

TABLE IV. *Neon I* $2p^5nd$.

	$3d$	$4d$	$5d$	$6d$	$7d$	$8d$	$9d$	$10d$
F_0	−374.23	−306.59	−285.78	−273.97	−269.61	−266.52	−264.38	−263.55
F_2	15.507	6.595	3.620	2.008	1.433	0.900	0.615	0.467
G_1	2.98	1.70	1.04	0.64	0.47	0.29	0.20	0.16
G_3	0.002	0.026	0.016	0.020	−0.004	0.004	0.001	0.002
ζ_p	530.11	521.62	520.40	519.10	519.49	520.24	520.20	520.35
ζ_d	1.178	0.002	0.141	0.476	0.064	0.043	0.000	0.044
$(3a\|3a')$	0.957	0.959	0.961	0.970	0.955	0.962	0.96	0.96
$(3b\|3a')$	−0.285	−0.281	−0.276	−0.241	−0.297	−0.276	−0.29	−0.27
$(2a\|2a')$	0.413	0.399	0.406	0.444	0.41	0.41	0.40	0.41
$(2b\|2a')$	0.911	0.917	0.914	0.898	0.91	0.92	0.91	0.91
$(1a\|1a')$	0.615	0.638	0.659	0.697	0.682	0.677	0.678	0.67
$(1b\|1a')$	0.789	0.770	0.751	0.718	0.733	0.736	0.735	0.74
% Purity $3a'b'$	91.6	92.0	92.4	94.1	91.2	92.5	92	92
% Purity $2a'b'$	17.1	15.9	16.5	19.7	17	16	16	17
% Purity $1a'b'$	37.8	40.7	43.4	48.6	46.5	45.8	46.0	45

$7d$. That there is further perturbation on the *upper group* of $7d$ is shown by the abnormally large $2c$-$2d$ separation, which should be just the $7d$ electron doublet splitting. This further perturbation may be attributed to the fact that the lower part of $9d$ lies 100 cm^{-1} above the upper of $7d$ and perhaps to the $2p^5 10s$ which lies about 20 cm^{-1} above $7d$.

The constants used in these calculations are given by Table IV. The value of ζ_p is to be compared with the 521 obtained from the ionic doublet splitting. We should from the values here given predict a doublet splitting of 780.4 ± 0.2 cm^{-1} in comparison with the observed 782 cm^{-1}.

Thus the present theory accounts very satisfactorily for the observed structure of these rare-gas configurations. The perturbations which occur seem to be small except when two configurations of the same series overlap. Since there can be no spin-orbit perturbation corresponding to the interaction which splits the configuration into two groups, in estimating the mutual perturbation of two configurations we should compare the distance of the nearest levels not to the overall configuration size but to the much smaller spread of each group of levels. This requires that two configurations lie very close in order appreciably to affect each other.

In those cases in which our approximations are valid we have obtained the actual eigenfunctions for each level in terms of the jj-coupling scheme.[7] From these eigenfunctions we shall calculate the Zeeman effect, Stark effect, and line strengths for these configurations.

[7] The phases in this scheme are chosen in the following definite way (cf. reference 3). By use of Wigner's formula (*Gruppentheorie*, p. 206) for the addition of l and $\bar{l}$ to obtain L, l^i and s^i are added to obtain j^i, l^e and s^e to obtain j^e, and j^i and j^e to obtain J, each addition being made with the correlation to l and $\bar{l}$ in the order specified. Here i refers to the p^5 core, e to the added p or d electron.