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Analysis of the First Short Period and Its Isoelectronic Sequences

F. Rohrlich
Department of Physics, State University of Iowa, Iowa City, Iowa

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The configurations $2p^n$, $2s2p^{n-1}$, and $2s^22p^{n-2}$ are analyzed for all observed spectra of the respective isoelectronic sequences. The semiempirical Slater method is amended to include the polarization correction and, wherever possible, configuration interaction. The polarization parameter Λ is found to be approximately linear in the degree of ionization, q. The Slater parameters characteristic of the term separations of $2s^m2p^n$ and of configuration interaction are found to be linear functions of m, n, and q, partly corresponding to the Bacher-Goudsmit theory in second approximation. A comparison with self-consistent field calculations is made. Other consequences of the analysis are discussed.

1. INTRODUCTION

There are two different levels on which the energies of the electronic structure of atoms are usually calculated. One is the completely theoretical approach in which one tries to solve the many-body problem by some suitable approximation, e.g., the Hartree self-consistent field approximation. There are no arbitrary parameters to adjust and the accuracy of the final result depends in principle only on the precision with which a well-defined mathematical problem can be solved.

The other level is a semiempirical one. Following Slater's method of the central field approximation one expresses the energies in terms of certain radial integrals, F^k and G^k. The difficult mathematical problem of finding the radial dependence of the wave functions is now circumvented by treating these radial integrals as adjustable parameters. They are determined by fitting the theoretical energy levels to the observed ones, usually by the methods of least squares. This latter approach is much easier and quicker than, for example, the Hartree calculation, and is actually the only one that is practical for very complex atoms.

The accuracy of the semiempirical method can be improved by going beyond first-order perturbation theory (Slater method) and including configuration interaction. Also, one is not restricted to Russell-Saunders coupling, but can include spin-orbit as well as spin-spin and spin-other-orbit interactions. All these refinements introduce additional parameters, which, of course, lead to an improved agreement between calculated and observed energies.

There are two difficulties with this method.

(a) The first is the lack of any check on the values of the parameters. Only in the few cases where calculations on the purely theoretical level have been made can one compare with such results. A check on the internal consistency of the semiempirical method is possible to a limited degree, when analyses of neighboring elements are available and the corresponding parameters are "about the same."

(b) The second difficulty is in certain cases the lack of sufficient experimental data to determine all the necessary parameters. A typical example is the problem of classifying stellar spectra which cannot be produced in the laboratory, as, for example, the emission lines of the solar corona. The calculation of the associated energy levels requires an extrapolation of the parameters (e.g., along isoelectronic sequences) which involves considerable uncertainty and arbitrariness.

The various parameters are all functions of the configuration and the net charge of the (ionized) atom (the *degree of ionization*, q). If it were possible to show certain regularities of the parameters as functions of the configuration and q, both difficulties would be alleviated appreciably. But such results cannot come from the analysis of individual atoms, but must come from a simultaneous, systematic analysis of all atoms associated with certain configurations and degrees of ionization. It is the purpose of this paper to advocate such analyses, and to show in a relatively simple case, that one is indeed led to regularities of the parameters which are in fact much more striking than anticipated.

One cannot expect such regularities to appear unless the method which one adopts permits the calculation of the levels within quite high accuracy. It will be necessary to include configuration interaction as well as a recently discovered interaction which describes certain higher order processes effectively in first order, thereby improving considerably the agreement with experiments that can be obtained by a "linear" theory. Following Trees we shall refer to this interaction—for lack of a better name—as the *polarization effect*.[1]

At this point one must recall a method proposed by Bacher and Goudsmit[2] which enables one to calculate the energies of an atom from those of its ions. The success of this method clearly indicates regularities of the Slater F^k and G^k integrals as functions of q. Recently, a more detailed analysis of the Bacher-Goudsmit

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[1] D. Layzer, Ph.D. thesis, Harvard University, 1950 (unpublished) was the first to point out that in the analysis of spectra in the iron group considerably improved agreement can be obtained by a term proportional to $L(L+1)$. This was confirmed independently by R. E. Trees, Phys. Rev. **83**, 756 (1951) and **84**, 1089 (1951). A first step towards an understanding of the physical effects underlying this correction term was made by G. Racah, Phys. Rev. **85**, 381 (1952).

[2] R. F. Bacher and S. Goudsmit, Phys. Rev. **46**, 948 (1934).

TABLE I. Polarization energy E_P of p^n.

$n \backslash L$	0	1	2
1	...	0	...
2	$-4\alpha+3\beta$	-2α	2α
3	-6α	$-4\alpha+2\beta$	0
4	$-8\alpha+4\beta$	$-6\alpha+\beta$	$-2\alpha+\beta$
5	...	$-8\alpha+2\beta$	...

approach[3] showed in fact that a linear dependence of certain Slater parameters on the number of equivalent electrons in a configuration would be sufficient to satisfy the basic assumptions of this method.

A linear dependence on the degree of ionization was obtained by Catalan, Rohrlich, and Shenstone[4] in an analysis of the low configurations in the long periods. But these results were relatively crude, since q ranged from 0 to 5 only, and configuration interaction and the polarization effect were completely ignored.

The first period is ideally suited for the purpose of this investigation. Spectra exceeding the tenth have been observed[5] for many elements in this period, and the configurations are simple enough to permit good accuracy without calculations of forbidding complexity.

Following a discussion of the polarization effect (Sec. 2) and configuration interaction (Sec. 3) in which all necessary formulas are derived, we give in Secs. 4 and 5 the equations for the term values for the configurations $s^m p^n$ from which the parameters are calculated. Section 6 deals with the polarization parameter Λ and Sec. 7 gives the results for the Slater parameters. A comparison with the meager data available from Hartree calculations is attempted in Sec. 8. The final section gives a summary of the results obtained by the above outlined program.

2. POLARIZATION

As was shown by Racah,[1] the effective first-order interaction that accounts for the distortion of the wave functions due to various higher order effects is given by the operator

$$\sum_{i<j}(2\alpha \mathbf{l}_i\cdot\mathbf{l}_j+\beta q_{ij}) \tag{2.1}$$

for the configuration l^n. The operator q_{ij} is defined by[6]

$$(l^2LM|q_{ij}|l^2LM)=(2l+1)\delta(L,0).$$

The polarization energy in a state of definite orbital angular momentum L and seniority v is therefore[7]

$$E_P(l^nvL)=\alpha[L(L+1)-nl(l+1)]+\beta Q_l(n,v), \tag{2.2}$$

where[6]

$$Q_l(n,v)=\tfrac{1}{4}(n-v)(4l+4-n-v). \tag{2.3}$$

For the configuration s^n

$$E_P(s^nvL)=\begin{matrix} 0 & (n=1,\ {}_1{}^2S \text{ state}) \\ \beta & (n=2,\ {}_0{}^1S \text{ state}). \end{matrix} \tag{2.4}$$

For the configuration p^n, we find easily the results listed in Table I. The seniority numbers are omitted in that table, because for each n and L there is only one value of v.

We see from Table I that the E_P of conjugate configurations differ by constants from each other, independent of v and L:

$$E_P(p^4)-E_P(p^2)=-4\alpha+\beta \tag{2.5}$$

$$E_P(p^5)-E_P(p)=-8\alpha+2\beta. \tag{2.6}$$

3. CONFIGURATION INTERACTION $l^n-s^2l^{n-2}$

In this section, we want to derive the formula which expresses the off-diagonal matrix element of electrostatic repulsion between the configurations l^n and s^2l^{n-2}, in terms of the associated radial integral $G_l(s,l)$. This formula is

$$\left(l^n\alpha vSL\left|\sum_{i<j}\frac{e^2}{r_{ij}}\right|l^{n-2}s^2\alpha'v'SL\right)$$
$$=(-1)^l\epsilon\delta(v,v')\delta(\alpha,\alpha')[Q_l(n,v)]^{\frac{1}{2}}G_l(s,l), \tag{3.1}$$

where Q_l is given by (2.3) and

$$\epsilon=-1 \text{ for}\begin{cases} n=2l+2 \text{ and } \tfrac{1}{2}v \text{ odd} \\ n=2l+3 \text{ and } \tfrac{1}{2}(v-1) \text{ odd}, \end{cases} \tag{3.2}$$
$$\epsilon=+1 \text{ otherwise.}$$

Here, v denotes the seniority number, defined in RIII, and α is any set of quantum numbers which is necessary in addition to v, S, and L, in order to specify the states.

To prove this relation, we first note that Eqs. (33c) and (49′) of RIII can be combined to give

$$\left(l^n\alpha vSL\left|\sum_{i<j}\frac{e^2}{r_{ij}}\right|l^{n-2}s^2\alpha'v'SL\right)$$
$$=\frac{\epsilon}{(2l+1)^{\frac{1}{2}}}\cdot\delta(\alpha,\alpha')\delta(v,v')[Q_l(n,v)]^{\frac{1}{2}}$$
$$\times\left(l^2\,{}^1S\left|\frac{e^2}{r}\right|s^2\,{}^1S\right).$$

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[3] R. E. Trees, J. Research Natl. Bur. Standards **53**, 35 (1954). The Bacher-Goudsmit method was extended by S. Meshkov and C. W. Ufford, Phys. Rev. **94**, 75 (1954).

[4] Catalan, Rohrlich, and Shenstone, Proc. Roy. Soc. (London) **A221**, 421 (1954), esp. Figs. 4, 5, and 6. In an earlier paper [F. Rohrlich, Phys. Rev. **74**, 1381 (1948), especially Fig. 4], this author pointed out that deviations from a smooth variation of term differences as a function of n in $d^{n-2}sp$ and $d^{n-1}p$ seems to be an indication of wrong classification.

[5] C. E. Moore, *Atomic Energy Levels* (U. S. Department of Commerce, National Bureau of Standards, Washington, D. C., 1949), Vol. I. We have taken all the experimental material for the present work from these tables.

[6] G. Racah, Phys. Rev. **63**, 367 (1943), in the following quoted as (RIII).

[7] Alternatively, lacking a deeper understanding of this interaction, Eq. (2.2) may be regarded as a definition based on semi-empirical evidence.

But

$$\left(l^2\,{}^1S\left|\frac{e^2}{r}\right|s^2\,{}^1S\right)=(l^2\,{}^1S\,|\,P_l(\cos\omega)\,|\,s^2\,{}^1S)R^l(ll,ss)$$

$$=(l^2\,{}^1S\,|\,C_1{}^{(l)}\cdot C_2{}^{(l)}\,|\,s^2\,{}^1S)R^l(ls,sl)$$

$$=\frac{(-1)^l}{(2l+1)^{\frac{1}{2}}}G^l(s,l).$$

The result (3.1) follows from the last two equations if we observe that

$$G^l(s,l)=(2l+1)G_l(s,l). \qquad (3.3)$$

by definition.

Equation (3.1) is a generalization of Eq. (75) in RIII, the latter being the case $l=2$.

In the following, we shall be concerned with p-electrons so that it will be useful to list the matrix elements of the $p^n-p^{n-2}s^2$ interaction explicitly. The coefficient $g_1(s,p)$ by which $G_1(s,p)$ must be multiplied to give the matrix element, is listed in Table II.

TABLE II. Coefficient $g_1(s,p)$ for configuration interaction $p^n-p^{n-2}\,s^2$.

n	Term	$g_1(s,p)$
2,6	${}_0{}^1S$	$-\sqrt{3}$
3,5	${}_1{}^2P$	$-\sqrt{2}$
4	${}_0{}^1S$	2
	${}_2{}^1D$	1
	${}_2{}^3P$	1

4. ANALYSIS OF $2s2p^n$

The configurations $2s2p^n$ are less disturbed by other configurations than are $2p^n$ and $2s^22p^{n-2}$. Typical configurations with which $2s2p^n$ can interact are $2p^n3s$, $2s^22p^{n-2}3s$, and $2s2p^{n-1}3p$. These are all associated with very high excitation, so that their effect on $2s2p^n$ can be assumed to be negligible.

A. $2s2p$ and $2s2p^5$

These simple configurations contain only the two terms ${}^3P$ and ${}^1P$ whose spacing is determined by the parameter $G_1\equiv G_1(2s,2p)$. However, since spin-orbit interaction may be appreciable in some cases, we chose that particular combination of levels which is independent of the coupling,

$$G_1=\tfrac{1}{2}({}^1P_1+{}^3P_1-{}^3P_2-{}^3P_0). \qquad (4.1)$$

There is no polarization effect and the Slater parameter F_2 does not appear.

B. $2s2p^3$

This configuration has the terms ${}^{3,5}S$, ${}^{1,3}P$, and ${}^{1,3}D$. In order to eliminate any effects due to deviations from Russell-Saunders coupling, we form the four coupling independent combinations[8]

$$\begin{aligned}a&={}^3D_3,\\ b&={}^3P_0,\\ c&={}^3D_2+{}^1D_2+{}^3P_2+{}^5S_2,\\ d&={}^3D_1+{}^3P_1+{}^1P_1+{}^3S_1,\end{aligned} \qquad (4.2)$$

whose energies can easily be expressed in terms of the Slater parameters and the polarization parameters α and β of Sec. 2. We define

$$\lambda=4\alpha-\beta, \qquad (4.3)$$

$$f=3F_2+2\alpha, \qquad (4.4)$$

$$A=F_0-3G_1-5f+\lambda+\beta, \qquad (4.5)$$

and find for p^3s:

$$\begin{aligned}{}^5S&=A,\\ {}^3S&=A+4G_1,\\ {}^3D&=A+3f+G_1,\\ {}^1D&=A+3f+3G_1,\\ {}^3P&=A+5f+G_1-2\lambda,\\ {}^1P&=A+5f+3G_1-2\lambda.\end{aligned} \qquad (4.6)$$

It is important to note that these expressions involve only the 4 parameters A, f, G_1, and λ, even though we have originally 5 parameters, F_0, F_2, G_1, α and β. The above coupling independent combinations become

$$\begin{aligned}a&=A+3f+G_1,\\ b&=A+5f+G_1-2\lambda,\\ c&=4A+11f+5G_1-2\lambda,\\ d&=4A+13f+9G_1-4\lambda.\end{aligned} \qquad (4.7)$$

The solution of these equations is

$$\begin{aligned}G_1&=\tfrac{1}{4}(a+d-b-c),\\ \lambda&=\tfrac{1}{6}(2G_1+9a-b-2c),\\ f&=\frac{b-a}{2(1-\lambda/f)}=\tfrac{1}{3}(G_1+3a+b-c),\\ A&=a-3f-G_1.\end{aligned} \qquad (4.8)$$

C. $2s2p^2$ and $2s2p^4$

These configurations have the terms ${}^2S$, ${}^{2,4}P$, and ${}^2D$. But in this case the spin-orbit interaction cannot be eliminated in a simple way without losing the number of equations necessary for the determination of the remaining parameters. We must therefore be satisfied with the center of each multiplet as a sufficiently good approximation to the term value. As in the case of $2s2p^3$ there occur in $2s2p^2$ only four parameters,

$$A=F_0-5F_2-2G_1-2\alpha,$$

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[8] E. U. Condon and G. W. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1951).

f and λ, as defined in Eqs. (4.4) and (4.3), and G_1. The terms are

$$\begin{aligned} {}^4P &= A, \\ {}^2P &= A+3G_1, \\ {}^2D &= A+2f+G_1, \\ {}^2S &= A+5f-3\lambda+G_1. \end{aligned} \tag{4.9}$$

The solution of these equations is

$$\begin{aligned} A &= {}^4P, \\ G_1 &= \tfrac{1}{3}({}^2P-{}^4P), \\ f &= \tfrac{1}{2}({}^2D-P), \\ P &\equiv \tfrac{1}{3}(2\,{}^4P+{}^2P) \\ \Lambda &\equiv \frac{\lambda}{f} = 1-\tfrac{2}{3}\left(\frac{{}^2S-{}^2D}{{}^2D-P}\right). \end{aligned} \tag{4.10}$$

For p^4s the same equations hold except that A must be redefined according to the remarks at the end of Sec. 2,

$$\begin{aligned} A &= F_0-5F_2-2G_1-6\alpha+\beta, \\ &= F_0-\tfrac{1}{3}(5f+2\lambda-\beta)-2G_1. \end{aligned} \tag{4.11}$$

5. ANALYSIS OF $2p^n$ AND $2s^22p^{n-2}$

In the analysis of these configurations, it is essential that their mutual interaction be included, since they are quite close in energy and even overlap for the lowest elements of the isoelectronic sequence. The matrix element of this configuration interaction is a multiple of $G_1(2s,2p)$, as was derived in Sec. 3. This is the only way in which G_1 affects the term separations in these configurations.

A. $2p^2$ and $2s^2$

Here, as in $2s2p^2$, we must be satisfied with the multiplet centers and ignore the spin-orbit interaction. The terms of p^2 are then given by

$$\begin{aligned} {}^3P &= A, \\ {}^1D &= A+2f, \\ {}^1S &= A+5f-3\lambda, \end{aligned} \tag{5.1}$$

whereas s^2 has only the one term ${}^1S=A'$. The configuration interaction $-\sqrt{3}G_1$ therefore affects only the ${}^1S$ terms and yields a quadratic equation. We thus have four terms and the five parameters A', A, f, λ, and G_1.

We shall now assume that the polarization parameter $\Lambda\equiv\lambda/f$ of $2s2p^2$ is the same as that of $2p^2$. This seems to be plausible from the derivation and interpretation of the polarization interaction and will also be borne out in the numerical results.

Thus, we are left with four equations for four parameters which can easily be solved. The solution need not be given here.

B. $2p^3$ and $2s^22p$

The $2s^22p$ configuration gives rise to only one term, ${}^2P=A'$, which interacts via configuration interaction with the ${}^2P$ term of $2p^3$. The other terms of p^3, ${}^2D$, and ${}^4S$ are thereby affected only via the spin-orbit interaction terms. When these are taken into account too, there results a 2×2 matrix for $J=\frac{1}{2}$, a 4×4 matrix for $J=\frac{3}{2}$, and a single equation for ${}^2D_{\frac{5}{2}}$, yielding 7 equations in all. We have the 7 parameters A', A, f, λ, G_1, $\zeta(p^3)$, and $\zeta'(p^2s)$, so that these are uniquely determined. However, since the spin-orbit interaction parameters ζ and ζ' are relatively small, and an exact solution in terms of the 7 parameters is obviously quite complicated, we take again the multiplet centers and calculate the terms only. For $2p^3$, we have in our notation

$$\begin{aligned} {}^4S &= A, \\ {}^2D &= A+3f, \\ {}^2P &= A+5f-2\lambda, \end{aligned} \tag{5.2}$$

where

$$\begin{aligned} A &= F_0-15F_2-6\alpha \\ &= F_0-5f+\lambda+\beta. \end{aligned} \tag{5.3}$$

Including the interaction ${}^2P(p^3)-{}^2P(ps^2)$ which is $-\sqrt{2}G_1$ we have again 4 equations for the 4 parameters A', A, f, G_1, provided we take Λ from the $2s2p^n$ analysis.

C. $2p^4$ and $2s^22p^2$

Unfortunately, the configuration $2p$ lies so high that there is no case in the whole isoelectronic sequence of C *I* in which all its terms have been observed.[9] If, in first approximation we neglect the interaction of $2s^22p^2$ with $2p^4$ and restrict ourselves to an analysis of $2s^22p^2$, we can refer to the work by Garstang[10] who analyzed $2s^22p^2$ with great accuracy, including spin-orbit, spin-other-orbit, and spin-spin interaction. We shall use his results in the following.

D. $2p^5$ and $2s^22p^3$

As in the case of $2p^3$ and $2s^22p$, only the ${}^2P$ terms are affected by configuration interaction. The procedure is in every respect the same as in that case, p^5 and p being conjugate to each other. Following Eq. (2.4), $A(2s^22p^3)$ is however different from $A(2p^3)$,

$$A(2s^22p^3)=F_0-5f+\lambda+\beta(p^3)+\beta(s^2) \tag{5.4}$$

and F_0 now refers to $2s^22p^3$.

E. $2p^6$ and $2s^22p^4$

The configuration $2p^6$ is not observed, so that we must be content with an analysis of $2s^22p^4$ without

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[9] More precisely, the ${}^3P$ term is known in O III to Na VI, the ${}^1D$ term is known in O III and Na VI, and the ${}^1S$ term is known in O III only, and with some uncertainty (see reference 5).

[10] R. H. Garstang, Monthly Notices Roy. Astron. Soc. **111**, 114 (1951).

configuration interaction. We can here again take over the results of Garstang,[10] but the neglect of configuration interaction will make the over-all agreement relatively worse than for the other configurations, especially for large q.

6. RATIO PROBLEM AND THE PARAMETER Λ

Consider the following ratios of term differences:

$$\begin{aligned}
&R_2=({}^1S-{}^1D)/({}^1D-{}^3P) \text{ for } p^2,\ p^4,\ s^2p^2, \text{ and } s^2p^4,\\
&R_2'=({}^2S-{}^2D)/({}^2D-P),\ [P=\tfrac{1}{3}(2\,{}^4P+{}^2P)],\\
&\qquad\qquad \text{for } sp^2 \text{ and } sp^4,\\
&R_3=({}^4S-{}^2D)/({}^2D-{}^2P) \text{ for } p^3 \text{ and } s^2p^3,\\
&R_3'=(S-D)/(D-P),\ [P=\tfrac{1}{4}(3\,{}^3P+{}^1P),\\
&\qquad D=\tfrac{1}{4}(3\,{}^3D+{}^1D),\ S=\tfrac{1}{8}(5\,{}^5S+3\,{}^3S)], \text{ for } sp^3.
\end{aligned} \tag{6.1}$$

According to the Slater theory, all these ratios should be

$$R=\tfrac{3}{2}. \tag{6.2}$$

The problem is that the experimental values of R deviate appreciably from $\frac{3}{2}$, the deviations being towards larger values for R_3 and R_3', and towards smaller values for R_2 and R_2'.

Examples of these discrepancies were given, e.g., by Condon and Shortley (reference 7, p. 198 ff.) and very recently by Racah.[11] He was also the first to point out that the deviations from $\frac{3}{2}$ are almost independent of the degree of ionization q, and that the polarization correction, Λ, could account for the difference, simply because there is one more parameter available.[1]

In the theory given above, where in addition to the polarization correction also configuration interaction plays an important role, this "explanation" cannot be applied so simply, since R will in general depend on both, Λ and G_1. In those cases, however, where configuration interaction is not important, i.e., in the sp^{n-1} configurations, R does indeed depend on Λ only, even though G_1 occurs explicitly in the expression for the term energies.

Consider first R_2'. From Eq. (4.10), we see that

$$R_2'=\tfrac{3}{2}(1-\Lambda). \tag{6.3}$$

The polarization effect alone is thus responsible for the deviations from $\frac{3}{2}$. Similarly, from Sec. 4B when spin-orbit interaction is ignored, we find from Eq. (4.6) and the definitions (4.3) and (4.4),

$$\begin{aligned}
S&=A+\tfrac{3}{2}G_1,\\
D&=A+\tfrac{3}{2}G_1+3f,\\
P&=A+\tfrac{3}{2}G_1+5f-2\lambda,
\end{aligned}$$

and, therefore,

$$R_3'=\tfrac{3}{2}\cdot\frac{1}{1-\Lambda}. \tag{6.4}$$

R_2' and R_3' are thus seen to depend on Λ only and the reason for the deviations in opposite directions is now quite clear.

For R_2 and R_3 the situation is more complicated, since they depend on Λ and G_1. However, there is no more problem regarding the agreement between theory and experiment, since the terms are fitted *exactly* by as many parameters as there are terms in the configuration (see Sec. 5).

At this point the reader may question the wisdom of this "solution" of the ratio problem, since Λ is an arbitrary parameter which can always be so chosen as to reproduce the experimental value of R. Indeed, nothing seems to be gained by finding a set of Λ's from the observed ratios R.

It is the purpose of the remaining part of this section to show that the Λ's are more fundamental than the R's, and that they have a number of properties which put them in one class with the Slater parameters F and G.

In general, to each configuration and to each degree of ionization, q, there corresponds a different set of Slater parameters and a different polarization parameter Λ. For example, for the configurations $2s^m2p^n$, Λ will depend on m, n, and q. The experiments now seem to show that, to a very good approximation, Λ *is independent of m and n, and that it is a linear and slowly varying function of q.*

We were able to verify this assertion only for the configurations $2s2p^n$, since the importance of spin-orbit interaction together with configuration interaction prevents a detailed calculation on $2p^n$ and $2s^22p^{n-2}$ without a prohibitive amount of labor. However, reasonable results for f, which depend on Λ, were obtained by assuming the same Λ for these configurations as for $2s2p^n$, though, unfortunately, these results are not very sensitive to the value of Λ.

Consider now the configurations $2s2p^n$, where configuration interaction can be neglected, as was pointed out in Sec. 4. But spin-orbit interaction, described by the parameter ζ, can easily be eliminated for $n=3$ only (Sec. 4B). (The cases $n=1$ and 5 do not involve Λ.) The values of Λ obtained from this configuration will therefore be the most reliable. For $n=2$ and $n=4$, we can take the "centers of gravity" of the multiplets as a first approximation to term values. Since the Landé interval rule is not very well satisfied, the resultant Λ are not as reliable as those for $n=3$. The result of this calculation is given in Table III and plotted in Fig. 1.

In this figure, a straight line was fitted by least squares to the most reliable points, i.e., $\Lambda(2s2p^3)$ for $q\geq 3$. The points for the first few values of q are very poor, because configuration mixing is very large for these stages of ionization. The situation improves markedly with increasing q. The points for $\Lambda(2s2p^2)$

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[11] G. Racah, International Conference on Spectroscopy, Lund, Summer, 1954 (unpublished). I am grateful to Dr. Trees for showing me a copy of this paper.

TABLE III. The parameter Λ. The results for $2s2p^3$ are ζ-independent; for $2s2p^2$ and $2s2p^4$ the terms are approximated by the multiplet centers, except in the last column ($2s2p^4$) where the levels of highest J were used instead of the centers. The degree of polarization, q, is the number of electrons missing from the neutral atom.

q	$2s2p^2$	$2s2p^3$	$2s2p^4$	$2s2p^4$
0	−1.343	0.031		
1	−0.535	−0.185	−0.301	−0.311
2	−0.407	−0.237	−0.260	−0.273
3	−0.300	−0.229	−0.232	−0.256
4	−0.261	−0.211	−0.206	−0.241
5	−0.209	−0.188	−0.180	−0.237
6	−0.183	−0.187	−0.154	−0.215
7	−0.165	−0.141	−0.129	−0.207
8	−0.147	−0.140	−0.093	−0.185
9	−0.125	−0.133		
10	−0.082			

are seen to be in very good agreement with the straight line for large enough q. For $\Lambda(2s2p^4)$, the points lie below the line even for large q. In order to see how significant this deviation is, we recalculated $\Lambda(2s2p^4)$ using the levels of largest J instead of the centers of these inverted multiplets. The points for larger q's now lie *above* the straight line, indicating that the deviations from the straight line are not significant.[12] Within this approximation we conclude, therefore, that $\Lambda(2s2p^n)$ is independent of n and is a linear function of q. The q-dependence is[13]

$$\Lambda(2s2p^n)=0.0170q-0.2777$$

which is obtained by a least square calculation of 7 points of $2s2p^3$ and has a standard deviation of

$$\Delta=\pm0.0080. \tag{6.6}$$

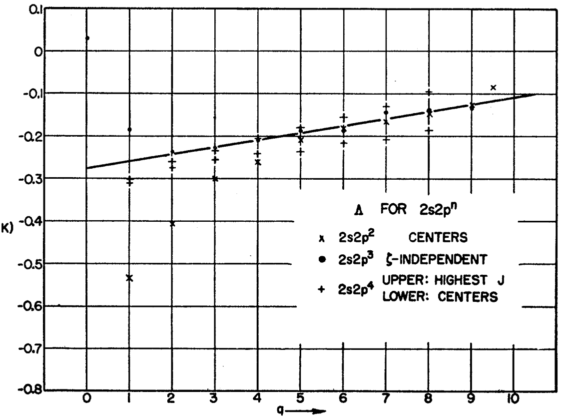

FIG. 1. The polarization parameter Λ as a function of the degree of ionization, q, calculated from the configurations $2s2p^n$. The straight line is the best fit to $2s2p^3$.

7. THE PARAMETERS G_1 AND f

The analysis of $2s2p^n$ according to Sec. 4 leads not only to $\Lambda(2s2p^n)$ which we discussed in the previous section, but also to $G_1(2s,2p)$ and $f(2p,2p)$. These results are given in Tables IV and V, and are plotted in Figs. 2, 3, and 4.

These figures show the linear variation of G_1 with q, for q not too small. As remarked previously, for small q the configurations overlap so strongly that good results cannot be expected from this simple analysis.

The linear dependence of G_1 on q for fixed n is surprisingly accurate for $q\geq 2$. In fact, in a number of cases relatively small deviations from linearity can be traced back to uncertain experimental data, as is the case for $n=2$ and $q=5$ (see below). It is therefore justified to take the well established points for which the overlap of configurations is not expected to be important, and to fit straight lines to them with least square methods. The results with their standard deviations Δ are as follows:

$$\begin{aligned}
&2s2p\colon && q=2\text{–}5,\ 7\text{–}11, && G_1=6.575q+11.864, && \Delta=\pm0.160,\\
&2s2p^2\colon && q=2\text{–}4,\ 6\text{–}10, && G_1=6.636q+16.359, && \Delta=\pm0.093,\\
&2s2p^3\colon && q=2\text{–}9, && G_1=6.636q+21.275, && \Delta=\pm0.074,\\
&2s2p^4\colon && q=3\text{–}8, && G_1=6.628q+25.491, && \Delta=\pm0.054,\\
&2s2p^5\colon && q=3\text{–}7, && G_1=6.685q+29.915, && \Delta=\pm0.146.
\end{aligned} \tag{7.1}$$

Since the magnitude of G_1 ranges from about 25 to 85 kK, these mean deviations correspond to a few tenth of one percent. A surprising accuracy indeed.

The above mentioned point $n=2$, $q=5$ is now seen to be the largest deviation from the straight line (for $q\geq 2$ or 3) it stems from the $2s2p^2$ configuration in the spectrum of Ne VI. This spectrum was observed by Paul and Polster[14] who did not find any intersystem combinations. They were therefore forced to estimate the position of the quartet levels and gave a value of

$$2s2p^2\,{}^4P=99.3\pm0.5\text{ kK}. \tag{7.2}$$

Since the calculation of G_1 is based on the difference between the ${}^2P$ and the ${}^4P$ term [see Eq. (4.10)] an error in this estimate will affect the value of G_1. On the other hand, our above analysis leads to a value of

$$2s2p^2\ G_1=49.55\pm0.09\text{ kK},$$

From this result, one obtains with Eq. (4.10) a theoretical estimate

$$2s2p^2\,{}^4P=101.22\pm0.19\text{ kK}. \tag{7.3}$$

We believe that this is a more reliable estimate than (7.2).

The straight lines (7.1) are also shown in Fig. 2. It is clearly apparent that these lines are very nearly parallel and very nearly equidistant. This implies that

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[12] These points actually give better agreement with $2s2p^3$ than do the points calculated from the centers. We have therefore used the levels with highest J consistently for all inverted multiplets.

[13] Since Λ is dimensionless the labeling "*kK*" of the ordinate in Fig. 1 should be omitted.

[14] F. W. Paul and H. D. Polster Phys. Rev. **59**, 429 (1941).

TABLE IV. The parameter $G_1(2s,2p)$. All values are in units of $\mathrm{kK}=10^3\mathrm{K}=10^3\ \mathrm{cm}^{-1}$.

q	$2s2p$	$2s2p^2$	$2s2p^3$	$2s2p^4$	$2s2p^5$	$2s^2-2p^2$	$2s^22p-2p^3$	$2s^22p^3-2p^5$
0	10.292	14.578	20.724					
1	18.023	22.544	28.388	30.918	37.317	26.12	29.68	
2	24.990	29.566	34.455	38.220	42.431	33.54	38.70	47.46
3	31.707	36.445	41.217	45.297	49.870	39.59	44.32	53.51
4	38.185	42.968	47.859	52.036	56.907	45.96	50.72	59.52
5	44.832	(50.180)	54.478	58.679	63.743	51.46		
6		56.139	61.059	65.297	70.465		62.61	
7	57.783	62.772	67.850	71.917	77.026	64.19	69.46	
8	64.215	69.32	74.398	78.440		71.35	77.99	77.324
9	70.945	76.03	80.878			78.01	82.79	
10	77.505	82.80				85.99		
11	84.525							

$G_1(2s,2p)$ as calculated from $2s2p^n$ is in good approximation a linear function of q as well as n. Again, a family of equidistant parallels can be fitted to the calculated points by a least square computation and one finds for the 36 points considered in (7.1) for $2s2p^n$,

$$G_1=6.6098q+4.7002n+7.0533, \tag{7.4}$$

with a standard deviation of

$$\Delta=\pm 0.239. \tag{7.5}$$

The parameter G_1 does not enter into the formulas for the term values of the configurations p^n and s^2p^{n-2}, but enters only in the interaction between these configurations,[15] according to the results of Sec. 3. Though configuration interaction occurs only between terms of the same S, L, and parity, other terms will also be affected, because of the deviations from pure Russell-Saunders coupling, which is appreciable in some cases. It is therefore not a very good approximation to neglect spin-orbit interaction. This is done here only to simplify the otherwise rather complicated calculations. The following results must therefore be judged accordingly and are subject to improvement by a better approximation.

With the aid of Secs. 3 and 5, we find the values for G_1 shown in Table IV and in Fig. 3 where the five parallels from the $2s2p^n$ analysis are plotted for comparison [see Eq. (7.4)]. We observe that the experimental data are much more incomplete than in the $2s2p^n$ case, which is understandable, since the $2p^n$ configuration is never among the lowest configurations. Specifically, neither the $2p^4$ nor the $2p^6$ configuration was observed with all its terms for any atom or ion.[5] However, even the relatively incomplete data show the main characteristics observed previously for the $2s2p^n$ configuration: G_1 is a linear function of both, q and n. The q dependence seems to have very nearly the same slope as for the $2s2p^n$ configuration. Ignoring the lower q values the line for G_1 from the $2s^2-2p^2$ interactions lies just about half-way between the parallels for $2s2p^2$ and $2s2p^3$. The distance between the parallels which would fit the $2s^2-2p^2$ and the $2s^22p-2p^3$ interaction is within our accuracy the same as the distance between the $2s2p^{n-1}$ and $2s2p^n$ lines. Similarly, the $2s^22p^3-2p^5$ line is about twice that distance away from the $2s^22p-2s^22p^3$ line, the difference in the configurations being *two* p-electrons. Using Eq. (7.4), we can therefore give an approximate formula for $G_1(2s,2p)$ when it occurs as configuration interaction between $2s^22p^{n-2}$ and $2p^n$,

$$G_1=6.61q+4.70n+9.40. \tag{7.6}$$

TABLE V. The parameter $f(2p,2p)$.

q	$2s2p^2$	$2s2p^3$	$2s2p^4$	$2s^22p^2$	$2s^22p^3$	$2s^22p^4$	$2p^2$	$2p^3$
0	2.235	5.762	···	5.082	···	7.899	···	···
1	4.684	7.166	7.616	7.613	···	10.350	1.718	2.814
2	7.104	9.043	10.061	10.031	11.40	12.755	4.225	5.425
3	9.595	11.156	12.325	12.409	13.95	15.271	6.644	7.965
4	11.816	13.360	14.610	14.762	15.86	17.703	8.866	10.196
5	14.766	15.661	16.964	17.025	18.05	20.061	11.355	···
6	16.617	17.716	19.382	19.677		22.385	···	14.955
7	18.878	20.569	21.857	21.715		25.085	15.93	17.09
8	21.20	22.75	24.38	24.065		26.66	18.10	19.24
9	23.66	25.10		26.43			20.51	21.42
10	26.54						22.64	

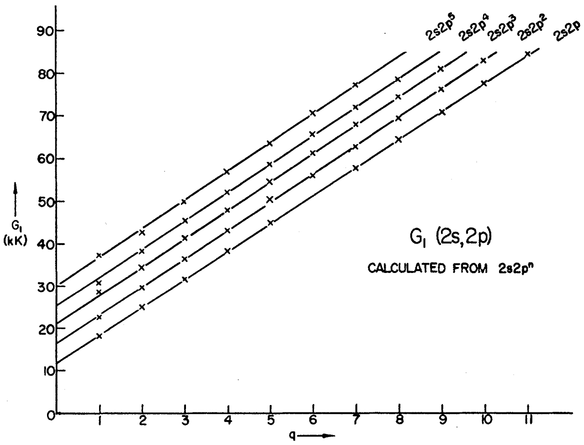

FIG. 2. The Slater parameter $G_1(2s,2p)$ as a function of q, calculated from $2s2p^n$. The straight lines are the best fit for each value of n.

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[15] The interaction of the p-electrons with the closed subshell $2s^2$ is not analyzed here. It would also involve G_1, but it does not contribute to the term separations.

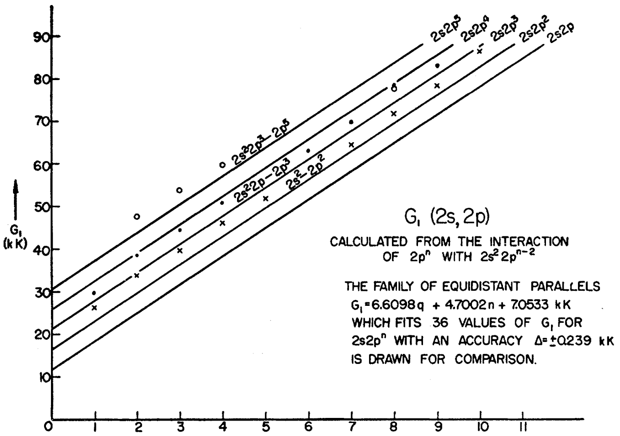

FIG. 3. The Slater parameter $G_1(2s,2p)$ as a function of q, calculated from the configuration interaction of $2p^n$ with $2s^22p^{n-2}$. The set of parallels is the best overall fit of G_1 for $2s2p^{n-1}$ and is drawn for the purpose of comparison.

We note that G_1 for $2s^22p^3-2p^5$ with $q=8$ (P IX) is the only very large discrepancy with this formula. No explanation is offered for this one case.

Since the calculations involve poorer approximations than those for $2s2p^n$, little weight should be put on the absolute value of G_1 in (7.6). In fact, if one computes G_1 for the $2s^22p^3-2p^5$ interaction using the centers instead of the highest J levels in the inverted multiplets (see footnote 11), the results fall on the $2s2p^5$ line. This indicates that a better calculation may well shift the set of parallels (7.6) towards lower values, decreasing the constant 9.40 by perhaps as much as 2.35. In that case the G_1 values for the $s^2p^n-p^{n+2}$ interaction would coincide with those of sp^{n+2}. It is then suggestive to argue that the parameter G_1 of the $2s^22p^n$ configuration (which we did not include explicitly in our energy formulae, because it does not contribute to the term separations) should be equal to the parameter G_1 which determines the configuration interaction of $2s^22p^n$ with $2p^{n+2}$. In that case, the above coincidences lead to the approximate equality

$$G_1(2s^22p^n)=G_1(2s2p^{n+2}). \tag{7.7}$$

When this equation is valid, Eq. (7.4) can be generalized to the configuration $2s^m2p^n$,

$$G_1=6.6098q+4.7002N-2.3471, \quad (N=2m+n). \tag{7.8}$$

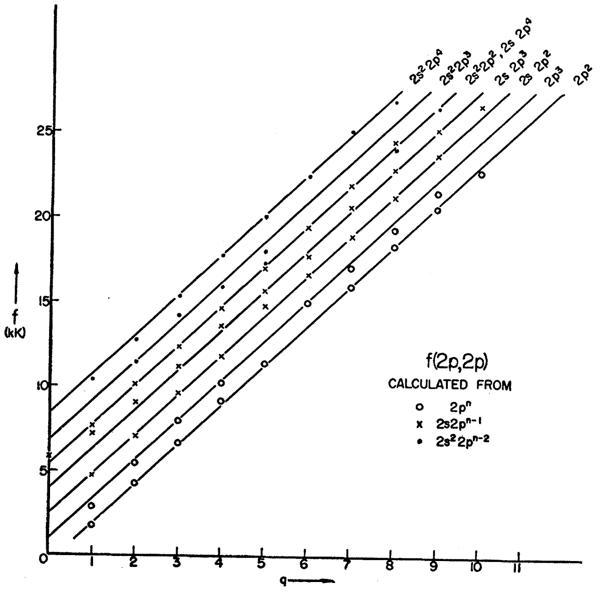

FIG. 4. The parameter $f(2p,2p)$ as a function of q, calculated from the configurations $2s^m2p^n$. The set of parallel straight lines constitutes the best over-all fit to all the points with $q>2$.

An experimental check on Eq. (7.7) can only be made simultaneously with an analysis of the parameters A of Secs. 4 and 5.

The results for the parameter $f(2p,2p)$ are given in Table V. A plot (Fig. 4) shows that the configuration $2s2p^n$ gives again a linear dependence on q,

$$\begin{aligned} 2s2p^2\colon q=3,\ 4,\ 6\text{–}9,\ f&=2.343q+2.510\ \text{kK}, \\ \Delta&=\pm0.055\ \text{kK}, \\ 2s2p^3\colon q=3\text{–}9,\ f&=2.340q+4.005\ \text{kK}, \\ \Delta&=\pm0.153\ \text{kK}, \\ 2s2p^4\colon q=3\text{–}8,\ f&=2.412q+4.985\ \text{kK}, \\ \Delta&=\pm0.075\ \text{kK}. \end{aligned} \tag{7.9}$$

The standard deviations are of the same order as those for G_1 [Eq. (7.1)], but since f ranges from about 10 to 25, this corresponds to a somewhat larger relative error, about $\frac{1}{3}$ to 1 percent.

As in the case of G_1, the $2s2p^2$ configuration of Ne VI gives a poor result and was not included in the least square analysis (7.9). Using Eq. (4.10), we find from the above semiempirical value of f for the ${}^4P$ term of $2s2p^2$ in Ne VI,

$${}^4P=100.91\pm0.17\ \text{kK}, \tag{7.10}$$

in good agreement with Eq. (7.3).

The straight lines (7.7) are almost parallel and equidistant, though a set of three such lines would not give as good overall agreement as for G_1. However, when we add the f values calculated from $2p^n$ and $2s^22p^{n-2}$ to those for $2s2p^{n-1}$, we notice that also these data are well represented by parallels with the same distances as those for $2s2p^{n-1}$.

One of the most important results of Fig. 4 is the fact that $f(2s2p^4)$ and $f(2s^22p^2)$ coincide. This means that, if the parameter f for $2s^m2p^n$ and any q can be approximated by

$$f=\alpha q+\beta m+\gamma n+\delta,$$

the constants β and γ satisfy the relation

$$\beta=2\gamma. \tag{7.11}$$

TABLE VI. Comparison of Slater parameters obtained semiempirically and by self-consistent field calculations for $2s^22p^n$.

	Oxygen			Nitrogen			Carbon		
q	G_1	$G_1^{(H)}$	ΔG	G_1	$G_1^{(H)}$	ΔG	G_1	$G_1^{(H)}$	ΔG
−1	33.345	30.800	2.545	28.645	25.532	3.113			
0	35.255	34.275	0.980	30.554	29.666	0.888	25.854	24.449	1.405
1	37.164	37.523	−0.359						
2	39.074	39.798	−0.724						
3	40.983	42.358	−1.375						
	$F_2^{(0)}$	$F_2^{(H)}$	ΔF	$F_2^{(0)}$	$F_2^{(H)}$	ΔF	$F_2^{(0)}$	$F_2^{(H)}$	ΔF
−1	2.862	2.441	0.421	2.299	1.966	0.333			
0	3.169	2.901	0.268	2.609	2.520	0.089	2.049	2.039	0.010
1	3.470	3.368	0.102						
2	3.767	3.718	0.049						
3	4.059	4.152	−0.093						

This is exactly the relation which for G_1 leads to Eq. (7.7), but which could not be obtained from the experimental evidence in that case. Also here, because of the incomplete experimental data, this assertion cannot be checked for all cases, but for the ones available it is indeed very well satisfied. We can thus write

$$f=\alpha q+\gamma N+\delta, \quad (N=2m+n) \qquad (7.12)$$

and try to fit this family of parallels to the data of Fig. 4. The results for the 50 best points is

$$f=2.3374q+1.4743N-3.4470 \text{ kK}, \qquad (7.13)$$

with a standard deviation

$$\Delta=\pm 0.164 \text{ kK}. \qquad (7.14)$$

8. COMPARISON WITH HARTREE CALCULATIONS

Unfortunately, there are only very few self-consistent field calculations with exchange which involve the configurations of interest here, and for which the two Slater integrals $F_2(2p,2p)$ and $G_1(2s,2p)$ have been calculated. Furthermore, practically all these calculations involve very low q for which our results cannot be expected to be very good, so that the following comparison cannot be regarded as definitive in any sense. Its main purpose is to show that the main relations for f and G_1 which we have obtained are within the expected errors consistent with a calculation "on the purely theoretical level." At the same time, this comparison will give us a very rough estimate of the order of magnitude of the parameter β.

There exists one example of a $2s2p^n$ configuration. That is the $2s2p$ Be I term system.[16] Since the one-electron Hartree wave functions depend slightly on S and L, the Slater parameters differ somewhat for different terms of each configurations. With few exceptions these variations are of the order of one percent. We have taken the average of these values. There is also a conversion factor from atomic units to kK, a factor $\frac{1}{3}$ for Hartree's G_1, and a factor 1/25 for Hartree's F_2, to convert these parameters into G_1 and F_2 as defined here. We thus obtain the self-consistent field value

$$2s2p: G_1(2s,2p)=11.41 \text{ kK} \quad (q=0). \qquad (8.1)$$

Our formula (7.4) yields the result

$$2s2p: G_1(2s,2p)=11.75 \text{ kK} \quad (q=0). \qquad (8.2)$$

The agreement between Eqs. (8.1) and (8.2) must be considered very good, since we are dealing here with $q=0$ for which (7.4) is certainly not very accurate.

For the configurations $2s^22p^n$, calculations for the elements carbon[17] (C I), nitrogen[18] (N^- and N I), and oxygen[19] (O^-, O I, O II, O III, and O IV) are available. The best we can do here is to use the somewhat hypothetical formula (7.8) for G_1. For F_2, we find from (4.3) and (4.4)

$$F_2=F_2^{(0)}-\tfrac{1}{6}\beta, \qquad (8.3)$$

where

$$F_2^{(0)}\equiv\tfrac{1}{3}f(1-\tfrac{1}{2}\Lambda). \qquad (8.4)$$

Thus, a direct comparison of F_2 can only be made if we know the parameter β. We shall therefore compare $F_2^{(0)}$ with the Hartree values, hoping that a consistent difference between the two quantities will give some indications of the presence of β.

The comparison of G_1 and $F_2^{(0)}$ is conveniently carried out by expressing first G and f in terms of q and Z. The linear relation between the number of equivalent $2s$ and $2p$ electrons, q, and Z is

$$Z=2+m+n+q, \qquad (8.5)$$

so that Eq. (7.8) becomes

$$2s^m2p^n: G_1(2s,2p)=1.910q +4.700(Z+m)-11.748, \qquad (8.6)$$

and Eq. (7.13) becomes

$$2s^m2p^n: f(2p,2p)=0.863q +1.474(Z+m)-6.396. \qquad (8.7)$$

These relations and Eqs. (8.3) and (8.4) permit the construction of Table VI where our idealized semi-

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[16] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **154**, 588 (1936).

[17] A. Jucy, Proc. Roy. Soc. (London) **173**, 59 (1939).

[18] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **193**, 299 (1948).

[19] Hartree, Hartree, and Swirles, Trans. Roy. Soc. (London) **A238**, 229 (1940).

empirical values of G_1 and F_2 are compared with those from the Hartree calculations. Since the latter include negative ions, we have extrapolated our formulas accordingly.

A study of Table VI reveals the following. First of all, it confirms qualitatively the increase of G_1 and F_2 with q and with Z. The values of G_1 agree generally within a few percent, except for the negative ions ($q=-1$) where the Hartree values, $G_1^{(H)}$ are about 10 percent lower. This agreement is satisfactory, since the table lists low q values. As can be seen from Figs. 1, 2, and 4 the parameters approach their linear behavior with increasing q, the deviation being all to one side. On this basis, one would suspect that G_1 should perhaps be larger by about 1.5 to 2, so that ΔG is positive throughout and approaches zero for $q>3$. In that case, $G_1(2s^22p^n)$ would be closer to the configuration interaction values $G_1(2s^22p^n-2p^{n+2})$, Eq. (7.6), than to the idealized Eq. (7.8). It is very unfortunate that $G_1^{(H)}$ values for $q>3$ are not known.

In the case of F_2 one might be inclined to detect a linear behavior in ΔF, and conclude from (8.3) that β varies like $-0.9q+1.8$. But the tendency of approaching the linear behavior from one side, as for G_1, may invalidate such a conclusion. In fact, within the errors of this comparison, β may actually be zero.

Finally, one should not take the Hartree values as the perfect basis of comparison, because the self-consistent field calculations do not give complete agreement with experiment. In particular, the ratio problem of Sec. 6 is not resolved within that approximation: An attempt to include configuration interaction did not improve the situation.[19] In this respect our semi-empirical analysis teaches us that it is primarily the polarization parameter Λ which is responsible for the deviations from $R=\frac{3}{2}$. The versatility of the semiempirical approach shows here definite superiority.

9. SUMMARY

As was stated in the introduction, the purpose of this work is primarily to show by a relatively simple example how a systematic analysis of certain configurations leads to a study of the dependence of the semiempirical parameters on the number of equivalent electrons, the degree of ionization, etc. In particular, it was found that the *linear theory* (Slater theory amended by polarization terms) together with configuration interaction leads to parameters $G_1(2s,2p)$ and $f(2p,2p)$ which are in good approximation linear functions of m, n, and q for the configurations $2s^m2p^n$ [see Eqs. (7.8) and (7.13)], and that the polarization parameter Λ is linear in q and independent of m and n. These statements are valid for large enough q. The polarization parameter β is probably small, and there are some indications that it decreases with increasing q.

The possiblity of an analysis of this type is of interest in itself from a practical standpoint: It eliminates the arbitrariness of the parameters associated with the analysis of a single spectrum, and it allows extrapolations to unknown cases in a far more satisfactory manner than was hitherto possible. As an application and illustration of this point we carried out an extrapolation leading to the identification of the famous yellow coronal emission line λ 5694. This work will be published elsewhere.

However, an analysis of the above type also has theoretical interest; it was for this purpose that the first steps towards a similar analysis were carried out by Trees[3] for the case of $4s$ and $3d$ electrons.

In order to discuss the theoretical aspects, let us first observe that we could take the idealized linear equations for Λ, G_1, and f, and compute the terms of the various configurations in the isoelectronic sequences of the first period. If we restrict ourselves to values of q not less than 2 or 3, the over-all agreement will be given by a standard deviation of the order of, or slightly larger than, Δ in Eqs. (7.5) and (7.14). This means a very good agreement indeed.

The most extensive previous analysis of configurations in the first short period is that by Bacher and Goudsmit.[2] Their agreement is not as good as the present one for several reasons. Their method was mentioned in the introduction and seems to be very different from the Slater method. However, Trees[3] was able to show that the linear theory in which the parameters are allowed to vary linearly with m, n, and q (strictly, the Slater theory requires the *same* F^k and G^k for all m, n, and q) is essentially equivalent to the Bacher-Goudsmit method in second approximation: Trees' arguments for s and d electrons is valid for s and p electrons with only trivial modifications. Higher approximations of the methods by Bacher and Goudsmit correspond to higher powers of m, n, and q in the expressions for the radial integrals. It follows that, had we neglected configuration interaction, our agreement with experiment should be about the same as obtained by them. (They used their second approximation in their numerical work.) This is probably the case. A large part of our improved agreement is due to the restriction to spectra with $q\geq 2$ or 3. Bacher and Goudsmit at the time did not have available the experimental material of all the highly ionized elements. But at least a small part of the improved agreement must be due to our taking account of configuration interaction. The latter, however, has little effect on f, as can be seen from Fig. 4 where $2s^22p^2$ and $2s^22p^4$ are calculated without configuration interaction, whereas $2s^22p^3$ and $2p^n$ include it. The self-consistent field calculations bear this out too: The Slater parameters change only very slightly when configuration interaction is included.

Our results, however, seem to show additional features, not expected from a comparison of the linear theory with the Bacher-Goudsmit theory. In particular, we mention the following:

(a) The relation (7.11) which says that each s-electron contributes to the parameters just twice as much as each p-electron, arises naturally from a study of Fig. 4 for f. It is somewhat suggested for G_1 too, but it has no good experimental basis for that parameter.

(b) $G_1(2s,2p)$ calculated from the interaction of the configurations $2p^n$ and $2s^2 2p^{n-2}$ is not very different from, and has the same n and q dependence as the $G_1(2s,2p)$ expected from $2s^2 2p^{n-2}$ (though it does not enter into the multiplet separations), provided Eq. (7.8) is assumed. The latter can be regarded as constructed in analogy to Eq. (7.13) for f.

(c) The linearity with q and the approximate independence from m and n of the polarization parameter Λ is unexpected. Λ is negative, indicating an effectively attractive interaction.

These are some of the points that are raised by the present investigation and which need to be understood and clarified. To what extent some of these results are of an accidental nature can perhaps be learned from further analyses of this type, e.g., by a study of the second short period. Also, the parameters A will have to be investigated and their dependence on m, n, and q will have to be checked. The more difficult problem of the long periods will probably be easier to attack, once the problems of s and p electrons are resolved.

ACKNOWLEDGMENTS

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Hfs Separations and Hfs Anomalies in the $^2P_{\frac{1}{2}}$ State of Ga^{69}, Ga^{71}, Tl^{203}, and Tl^{205}†*

A. Lurio‡ and A. G. Prodell
Columbia University, New York, New York

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By use of the method of atomic beam magnetic resonance, the ground-state hyperfine structure splittings in the two common gallium and thallium isotopes have been measured. The measured values are: $\Delta\nu(\mathrm{Ga}^{69}) = (2677.9875 \pm 0.0010) \times 10^6$ sec^{-1}, $\Delta\nu(\mathrm{Ga}^{71}) = (3402.6946 \pm 0.0013) \times 10^6$ sec^{-1}, $\Delta\nu(\mathrm{Tl}^{203}) = (21\,105.447 \pm 0.005) \times 10^6$ sec^{-1}, and $\Delta\nu(\mathrm{Tl}^{205}) = (21\,310.835 \pm 0.005) \times 10^6$ sec^{-1}. A comparison of the ratio of the dipole coupling constants in the ground state of the two isotopes with the ratio of the nuclear g_I factors yields the hfs anomaly. Theoretical and experimental values of the anomaly are compared.

INTRODUCTION

Considerable success has been achieved in explaining the hfs anomaly in atoms whose ground states are in an $S_{\frac{1}{2}}$ configuration. Bohr and Weisskopf[1] have explained the observed anomalies as a consequence of the penetration of the external unpaired electron into the nucleus. The theory of Bohr and Weisskopf predicts an anomaly for a $P_{\frac{1}{2}}$ configuration which, however, is considerably smaller than the anomaly for a $S_{\frac{1}{2}}$ configuration, since the amplitude of the unpaired electron wave function at the nucleus is much less for P than for S states. Up to the present time no critical measurements have been made of the hfs anomaly for atoms in a $P_{\frac{1}{2}}$ state. In order to test the applicability of the theory to such atoms, the hfs of the stable isotopes of gallium and thallium has been measured. A comparison of the ratio of the magnetic interaction constants as observed for two isotopic atoms in the same state with the known ratio of the nuclear gyromagnetic constants gives the hfs anomaly. Both gallium and thallium have two commonly occuring isotopes and are, therefore, suitable for a measurement of the anomaly; for gallium the spin of both isotopes is $\frac{3}{2}$ and for thallium it is $\frac{1}{2}$.

In both gallium and thallium the atomic ground state arises from a single P electron outside of a closed $(2s)^2$ subshell. This leads to a fine structure doublet of which the $P_{\frac{1}{2}}$ is the lower-lying level. To an excellent approximation the energy levels of gallium and thallium in this state in a magnetic field are given by the Breit-Rabi formula. They are shown in Figs. 1 and 2. Small second-order corrections have been given by Clendenin[2] who has shown that the zero-field hfs splitting $\Delta\nu$ may be written as follows:

$$\Delta\nu = (I+\tfrac{1}{2})[a'' - 2(a''')^2/\delta], \tag{1}$$

where the (a''') term is the correction term arising from the perturbation by the $^2P_{\frac{3}{2}}$ state, separated from the $^2P_{\frac{1}{2}}$ state by δ.

This correction term is of interest here in that $\Delta\nu$ does not arise solely from the magnetic dipole interaction constant a'' in the $P_{\frac{1}{2}}$ state. From Clendenin's expression for the (a''') term it is found that a'' is increased by 0.49 kc/sec and 0.79 kc/sec for Ga^{69} and Ga^{71} respec-

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‡ Present address is Department of Physics, Yale University, New Haven, Connecticut.

[1] A. Bohr and V. F. Weisskopf, Phys. Rev. 77, 94 (1950).

[2] W. W. Clendenin, Phys. Rev. 94, 1590 (1954).