is added. The difference is[9]

$$N^{(+)}-N^{(-)}=Z/\Omega_0. \tag{1}$$

Further, Jones has shown that, if one assumes complete circular symmetry about [111] (actually it is trigonal) then the conductivity perpendicular to the principal axis (our case) is given by

$$\sigma_\perp=\sigma_\perp^{(-)}+\sigma_\perp^{(+)}, \tag{2}$$

where

$$\sigma_\perp^{(-)}=\frac{e^2}{c^2}\frac{\tau^{(-)}N^{(-)}}{m^{(-)}},$$

$$\sigma_\perp^{(+)}=\frac{e^2}{c^2}\frac{\tau^{(+)}N^{(+)}}{m^{(+)}}.$$

[9] H. Jones, Proc. Roy. Soc. **A155**, 653 (1936).

Here τ is the relaxation time and m the reduced mass.

It appears from (1) combined with (2) that the effect of reducing the overlap would be to add an additional term to ρ_0 over and above the linear term due to the random atomic scattering. The experimental results, however, indicate just the opposite effect. It appears, therefore, that one must suppose that the low temperature conductivity is due mainly to positive holes, and further that as the overlap is reduced the density of such holes sharply increases.

In conclusion we should like to express our thanks to Dr. S. H. Browne for providing some of the crystals used in this experiment. This work was supported, in part, by a grant from the George Sheffield Fund.

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Theory of Complex Spectra. I

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This paper gives a closed formula which entirely replaces for the two-electron spectra the previous lengthy calculations with the diagonal-sum method. Applications are also made to some configurations with three or more electrons and to the p'' configurations of the nuclei.

§1. INTRODUCTION

THE first-order perturbation energy for the terms of a given configuration was calculated at first by Slater.[1] In his classical paper he showed that the electrostatic interaction between two electrons depends on a very few integrals F^k and G^k, and he developed the diagonal-sum procedure for calculating the coefficients of these integrals; with this procedure he obtained numerical tables of coefficients for the two-electron configurations involving s, p, or d electrons. These tables were extended by several authors[2] to f electrons and to some configurations with three or more electrons.

But the diagonal-sum procedure has some deficiencies. Firstly, when two terms of a kind occur in a given configuration, this procedure will determine only the sum of their energies, and they can be separated only by other methods. Secondly, this method does not give general formulas, but only numerical tables; it is therefore impossible to make generalizations, and one must begin again for each new case with new and more complex calculations.[3]

It is the purpose of this paper to substitute for the numerical methods of Chapters VI and VII of TAS more general methods and more conformable to Chapter III of the same book.

[1] J. C. Slater, Phys. Rev. **34**, 1293 (1929).
[2] See E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge 1935), (which we shall denote by TAS) Chapters VI and VII, for definitions, notations and bibliographical indications.
[3] G. H. Shortley and B. Fried, Phys. Rev. **54**, 739 (1938).

§2. TWO-ELECTRON CONFIGURATIONS

If ω is the angle between the radii vectors of the two electrons, the coefficients f_k of F^k are[4] the eigenvalues of the matrix

$$(l_1 l_2 m_1 m_2 | P_k(\cos\omega) | l_1 l_2 m_1' m_2'); \tag{1}$$

here P_k is the Legendre polynomial of the order k. The transformation which diagonalizes this matrix is $(l_1 l_2 LM | l_1 l_2 m_1 m_2)$, and therefore

$$f_k(l_1 l_2 L) = \sum_{m_1 m_2 m_1' m_2'} (l_1 l_2 LM | l_1 l_2 m_1 m_2)(l_1 l_2 m_1 m_2 | P_k(\cos\omega) | l_1 l_2 m_1' m_2')(l_1 l_2 m_1' m_2' | l_1 l_2 LM), \tag{2}$$

or

$$f_k(l_1 l_2 L) = (l_1 l_2 LM | P_k(\cos\omega) | l_1 l_2 LM). \tag{3}$$

In the same way, if $\pm g_k$ are the coefficients of G^k for the singlet and for the triplet terms, we have

$$g_k(l_1 l_2 L) = \sum_{m_1 m_2 m'_1 m'_2} (l_1 l_2 LM | l_1 l_2 m_1 m_2)(l_1 l_2 m_1 m_2 | P_k(\cos\omega) | l_2 l_1 m'_2 m'_1)(l_1 l_2 m'_1 m'_2 | l_1 l_2 LM), \tag{4}$$

and in view of[5]

$$(l_1 l_2 m'_1 m'_2 | l_1 l_2 LM) = (-1)^{l_1+l_2-L}(l_2 l_1 m'_2 m'_1 | l_2 l_1 LM), \tag{5}$$

this becomes

$$g_k(l_1 l_2 L) = (-1)^{l_1+l_2-L}(l_1 l_2 LM | P_k(\cos\omega) | l_2 l_1 LM). \tag{6}$$

Slater calculated the matrix elements of P_k $(\cos\omega)$ in the $l_1 l_2 m_1 m_2$ scheme, and then obtained the eigenvalues of this operator by means of the diagonal-sum procedure; we will calculate the matrix elements of $\cos\omega$ directly in the $l_1 l_2 LM$ scheme by the method of Güttinger and Pauli,[6] and then calculate f_k and g_k with the ordinary methods of matrix calculations.

If $\mathbf{u}_i$ is the unit vector in the direction from the origin to the electron i, by comparing TAS $4^3 21$ with TAS $9^3 11$, we have

$$(l_i \vdots u_i \vdots l_i) = 0, \quad (l_i \vdots u_i \vdots l_i - 1) = (l_i - 1 \vdots u_i \vdots l_i) = \frac{1}{[(2l_i-1)(2l_i+1)]^{\frac{1}{2}}}; \tag{7}$$

and since

$$\cos\omega = (\mathbf{u}_1 \cdot \mathbf{u}_2), \tag{8}$$

introducing (7) in TAS $12^3 2$ we find that the only non-vanishing elements of $(l_1 l_2 LM | \cos\omega | l_1' l_2' LM)$ are

$$\begin{aligned}
(l_1 l_2 LM | \cos\omega | l_1-1\ l_2-1\ LM) &= -\frac{[(l_1+l_2+L+1)(l_1+l_2+L)(l_1+l_2-L)(l_1+l_2-L-1)]^{\frac{1}{2}}}{2[(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)]^{\frac{1}{2}}},\\
(l_1 l_2 LM | \cos\omega | l_1+1\ l_2-1\ LM) &= \frac{[(L+l_1-l_2+2)(L+l_1-l_2+1)(L+l_2-l_1)(L+l_2-l_1-1)]^{\frac{1}{2}}}{2[(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)]^{\frac{1}{2}}},\\
(l_1 l_2 LM | \cos\omega | l_1-1\ l_2+1\ LM) &= \frac{[(L+l_1-l_2)(L+l_1-l_2-1)(L+l_2-l_1+2)(L+l_2-l_1+1)]^{\frac{1}{2}}}{2[(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)]^{\frac{1}{2}}},\\
(l_1 l_2 LM | \cos\omega | l_1+1\ l_2+1\ LM) &= -\frac{[(l_1+l_2+L+3)(l_1+l_2+L+2)(l_1+l_2-L+2)(l_1+l_2-L+1)]^{\frac{1}{2}}}{2[(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)]^{\frac{1}{2}}}.
\end{aligned} \tag{9}$$

From these formulas it is possible to calculate the matrix elements of P_k $(\cos\omega)$ with the ordinary methods of matrix calculations; in order that these elements may have a value different from zero, k must satisfy the conditions

$$k + l_1 + l'_1 = 2g_1, \quad k + l_2 + l'_2 = 2g_2 \tag{10}$$

[4] TAS §8[6].
[5] TAS 14^3 7.
[6] Güttinger and Pauli, Zeits. f. Physik **67**, 743 (1931); TAS §10^3 *et seq.*

(g_1 and g_2 are integers), and the so-called triangular conditions

$$|l_1-l'_1| \leqslant k \leqslant l_1+l'_1, \quad |l_2-l'_2| \leqslant k \leqslant l_2+l'_2; \tag{11}$$

if these conditions are satisfied, the final result is

$$(l_1l_2LM|P_k(\cos\omega)|l'_1l'_2LM) = \frac{(-1)^{g_1+g_2-k}(2g_1-2l_1)!(2g_2-2l'_2)!g_1!g_2!}{(g_1-k)!(g_1-l_1)!(g_1-l'_1)!(g_2-k)!(g_2-l_2)!(g_2-l'_2)!(2g_1+1)!(2g_2+1)!}$$

$$\cdot\left[\frac{(2l_1+1)(2l'_1+1)(2l_2+1)(2l'_2+1)(l_1+l_2+L+1)!(l'_1+l'_2+L+1)!}{\times(l_1+l_2-L)!(l'_1+l'_2-L)!(L+l_1-l_2)!(L+l'_2-l'_1)!}\right]^{\frac{1}{2}}$$

$$\cdot\sum_u(-1)^u\frac{(u+l'_1-l'_2)!(u+l_2-l_1)!(k+l_1+l'_2-u)!}{(u+L+1)!(u-L)!(l_1+l_2-u)!(l'_1+l'_2-u)!(k-l_1-l'_2+u)!}, \tag{12}$$

where, in the summation, u takes on all integral values consistent with the factorial notation, the factorial of a negative number being meaningless.

In order to demonstrate this formula, it suffices to verify that (12) reduces to $\delta(l_1l'_1)\delta(l_2l'_2)$ for $k=0$ and to (9) for $k=1$ and that, introducing (12) for $k=n-1$ and $k=n-2$ in the formula[7]

$$P_n(\cos\omega) = \frac{2n-1}{n}\cos\omega P_{n-1}(\cos\omega) - \frac{n-1}{n}P_{n-2}(\cos\omega) \tag{13}$$

written in matrix form, we obtain again (12) for $k=n$. These verifications are somewhat long, but they are not difficult and will be omitted for brevity.

It is remarkable that (12) has an unsymmetrical aspect: it is however possible (as is shown in the appendix) to transform this formula by means of algebraic identities and to replace it with[8]

$$(l_1l_2LM|P_k(\cos\omega)|l'_1l'_2LM)$$

$$= \frac{(-1)^{g_1+g_2-k-L}(l_1+l'_1-k-1)!!(k+l_1-l'_1-1)!!(k+l'_1-l_1-1)!!}{\times(l_2+l'_2-k-1)!!(k+l_2-l'_2-1)!!(k+l'_2-l_2-1)!!}{(k+l_1+l'_1+1)!!(k+l_2+l'_2+1)!!}$$

$$\cdot\left[\frac{(2l_1+1)(2l_2+1)(2l'_1+1)(2l'_2+1)(l_1+l_2-L)!(l'_1+l'_2-L)!}{\times(L+l_1-l_2)!(L+l'_1-l'_2)!(L+l_2-l_1)!(L+l'_2-l'_1)!}\right]^{\frac{1}{2}}$$

$$\cdot\sum_v(-1)^v\frac{(l_1+l_2+l'_1+l'_2+1-v)!}{(l_1+l_2-L-v)!(l'_1+l'_2-L-v)!(l_1+l'_1-k-v)!(l_2+l'_2-k-v)!v!}$$

$$\times(k+L-l_1-l'_2+v)!(k+L-l'_1-l_2+v)! \tag{12'}$$

Introducing (12′) in (3) and (6), and putting

$$v = l_1+l_2-L-w,$$

[7] Courant and Hilbert, *Methoden der Mathematischen Physik* (Springer, 1931), p. 73, Eq. (19).

[8] With the symbol $n!!$ we indicate the *semifactorial* of n, that is the product 1.3.5 . . . n if n is odd, and the product 2.4.6 . . . n if n is even.

we obtain

$$f_k(l_1l_2L)=\frac{(k-1)!!^4(2l_1-k-1)!!(2l_2-k-1)!!(2l_1+1)(2l_2+1)}{(2l_1+k+1)!!(2l_2+k+1)!!}$$
$$\times\sum_w(-1)^w\binom{l_1+l_2+L+1+w}{w}\binom{l_1+l_2-L}{w}\binom{L+l_1-l_2}{k-w}\binom{L+l_2-l_1}{k-w} \quad (14)$$

and

$$g_k(l_1l_2L)=(-1)^{l_1+l_2-L}\frac{(k+l_1-l_2-1)!!^2(k+l_2-l_1-1)!!^2(l_1+l_2-k-1)!!^2(2l_1+1)(2l_2+1)}{(l_1+l_2+k+1)!!^2}$$
$$\times\sum_w(-1)^w\binom{l_1+l_2+L+1+w}{w}\binom{l_1+l_2-L}{w}\binom{L+l_1-l_2}{k+l_1-l_2-w}\binom{L+l_2-l_1}{k+l_2-l_1-w}. \quad (15)$$

The dependence on L of such formulas was already given by Kramers[9] for f_k and by Brinkman[10] for g_k by means of a group-theoretical procedure, but it was impossible, by such a general method, to give the first factor.

Putting

$$p=l_1(l_1+1)l_2(l_2+1),\quad s=l_1(l_1+1)+l_2(l_2+1),\quad \Lambda=L(L+1),\quad \lambda=\frac{\Lambda-s}{2}=(l_1\cdot l_2),\quad q=(l_1+l_2+1)^2, \quad (16)$$

we obtain, for the most common and important cases:

$$f_0=1,$$
$$f_2=\frac{6\lambda^2+3\lambda-2p}{(2l_1-1)(2l_1+3)(2l_2-1)(2l_2+3)}, \quad (17)$$
$$f_4=9\frac{70\lambda^4+350\lambda^3-10(6p-5s-39)\lambda^2-10(17p-6s-9)\lambda+3p(2p-4s-27)}{4(2l_1-3)(2l_1-1)(2l_1+3)(2l_1+5)(2l_2-3)(2l_2-1)(2l_2+3)(2l_2+5)},$$

and

$$g_{l_1-l_2}(l_1l_2L)=\frac{(-1)^{l_1+l_2-L}}{2^{2k}}\binom{2k}{k}\frac{\Lambda(\Lambda-2)(\Lambda-6)\cdots[\Lambda-(k-1)k]}{(2l_2+1)(2l_2+3)^2(2l_2+5)^2\cdots(2l_1-1)^2(2l_1+1)},$$

$$g_{l_1-l_2+2}(l_1l_2L)=\frac{(-1)^{l_1+l_2-L}}{2^{2k-1}}\binom{2k-2}{k-1}\Lambda(\Lambda-2)(\Lambda-6)\cdots[\Lambda-(k-3)(k-2)]. \quad (18)$$
$$\cdot\frac{k(2k-1)\Lambda^2-2(k-1)(2k-1)(q-k)\Lambda+(k-1)[(2k-3)q^2-(4k^2-6k-1)q+(k-1)k^2]}{(2l_2-1)^2(2l_2+1)(2l_2+3)^2(2l_2+5)^2\cdots(2l_1-1)^2(2l_1+1)(2l_1+3)^2}.$$

By means of these formulas all results of TAS and of Shortley and Fried[3] were checked, and a sole mistake was found: the coefficient of F_2 and of G_2 in the F terms of the configuration ff is not $+10$, as reported in TAS (p. 207), but -10, as given in the original paper of Condon and Shortley.[11]

§3. CONFIGURATIONS WITH THREE OR MORE ELECTRONS

The expression of the electrostatic interaction of two electrons as function of λ is not only important for a more rapid calculation of the two-electron terms: in the case of three or more electrons the methods of Chapter III of TAS give us the possibility of calculating the matrix elements of

[9] Kramers, Proc. Amst. Acad. **34**, 965 (1931).
[10] Brinkman, Zeits. f. Physik **79**, 753 (1932).
[11] Condon and Shortley, Phys. Rev. **37**, 1030 (1931).

$\lambda_{ij}=(\mathbf{l}_i\cdot\mathbf{l}_j)$ in every complex case of vector coupling; and it is therefore possible to calculate the terms of more complex configurations, even if two or more terms of the same kind occur.

We will at first pay attention to some particular applications to atomic and nuclear spectra, that can be treated without matrix calculations; then we shall treat in detail the p^2p configuration, and give the results for the p^2l configuration. For other important configurations and for the cases of (jj) coupling the calculations are more complex, and a new general procedure for this purpose will therefore be developed in a later paper.

The first application was already made to the p^n configurations by Van Vleck,[12] who found empirically the formula of f_2 for p electrons, and expressed λ^2_{ij} as a linear function of λ_{ij} and of $(\mathbf{s}_i\mathbf{s}_j)$ by means of Dirac's vector model; but, as Van Vleck himself pointed out, such a procedure is not generally sufficient for d^n configurations.

This procedure suffices however for the terms of d^n with higher multiplicity. In these states all spins are parallel, and it follows therefore from the principle of antisymmetry that the possible values of each λ are 0 or -5 (F or P resultant); from this we have that

$$\lambda^2+5\lambda=0; \tag{19}$$

introducing this relation into the expressions

$$f_2(dd)=\frac{2\lambda^2+\lambda-24}{147}, \quad f_4(dd)=\frac{35\lambda^4+175\lambda^3-585\lambda^2-2655\lambda-162}{7938}, \tag{20}$$

we obtain

$$f_2=-(3\lambda+8)/49, \quad f_4=(15\lambda-9)/441, \tag{21}$$

and therefore

$$E=\sum_{i<j}\left(F^0-\frac{3\lambda_{ij}+8}{49}F^2+\frac{15\lambda_{ij}-9}{441}F^4\right);$$

since for a d^n term

$$L(L+1)=6n+2\sum_{i<j}\lambda_{ij}, \tag{22}$$

we obtain that for all d^n configurations with $S=n/2$

$$E=\frac{n(n-1)}{2}F^0-\frac{\frac{3}{2}L(L+1)+n(4n-13)}{49}F^2+\frac{1\frac{5}{2}L(L+1)-\frac{9}{2}n(n+9)}{441}F^4. \tag{23}$$

§4. THE NUCLEAR CONFIGURATIONS p^n

The calculation of the energy levels of a nuclear configuration p^n with symmetrical forces was made by Hund[13] with the diagonal-sum procedure. After very long calculations he obtained a numerical table for the energies of such configurations, and from this table he deduced empirical formulas for the interactions of Wigner and of Majorana. The direct calculation of such formulas is a remarkable application of the above developed methods.

Putting, as customary in order to avoid fractional coefficients,

$$F_0=F^0, \quad F_2=F^2/25, \tag{24}$$

we obtain from (17) that the normal (Wigner) interaction between two particles is

$$V_{ij}=F_0+(6\lambda_{ij}^2+3\lambda_{ij}-8)F_2; \tag{25}$$

[12] J. H. Van Vleck, Phys. Rev. **45**, 412 (1934).
[13] Hund, Zeits. f. Physik **105**, 202 (1937).

hence the Wigner interaction between all particles of the configuration is

$$V_W=\frac{n(n-1)}{2}F_0+\sum_{i<j}(6\lambda_{ij}^2+3\lambda_{ij}-8)F_2. \tag{26}$$

In order to calculate this sum, we cannot use Dirac's vector model, because the exclusion principle does not hold for a proton and a neutron; but we can observe that for p particles the operator

$$M_{ij}=\lambda_{ij}^2+\lambda_{ij}-1 \tag{27}$$

is Majorana's operator of position exchange, since it has the eigenvalue 1 for the symmetrical states S and D, and the eigenvalue -1 for the antisymmetrical state P: from (26) and (27) we obtain

$$V_W=\frac{n(n-1)}{2}F_0+\sum_{i<j}(6M_{ij}-3\lambda_{ij}-2)F_2. \tag{28}$$

The sum

$$\mathfrak{M}=\sum_{i<j}M_{ij} \tag{29}$$

is Hund's $(\alpha-\beta)$ and depends only from the symmetry character of the positional eigenfunction of the level: it is the difference between the number of symmetrically connected couples and the number of antisymmetrically connected couples. From (29) and from

$$\sum_{i<j}\lambda_{ij}=\tfrac{1}{2}L(L+1)-n, \tag{30}$$

we obtain

$$V_W=\frac{n(n-1)}{2}F_0+[6\mathfrak{M}-\tfrac{3}{2}L(L+1)-n(n-4)]F_2. \tag{31}$$

The Majorana interaction is

$$V_M=\sum_{i<j}M_{ij}V_{ij}=\mathfrak{M}F_0+\sum_{i<j}(\lambda_{ij}^2+\lambda_{ij}-1)(6\lambda_{ij}^2+3\lambda_{ij}-8)F_2 \tag{32}$$

and reduces to

$$V_M=\mathfrak{M}F_0+\sum_{i<j}(M_{ij}-3\lambda_{ij}+3)F_2 \tag{33}$$

in virtue of

$$\lambda_{ij}^3+2\lambda_{ij}^2-\lambda_{ij}-2=0 \tag{34}$$

(which expresses the fact that λ_{ij} has only the eigenvalues 1, -1, and -2) and of (27). In view of (29) and (30), (33) becomes

$$V_M=\mathfrak{M}F_0+[\mathfrak{M}-\tfrac{3}{2}L(L+1)+\tfrac{3}{2}n(n+1)]F_2. \tag{35}$$

Putting

$$F_0=A-\tfrac{1}{3}B \quad \text{and} \quad F_2=\tfrac{1}{3}B$$

in (31) and (35), we obtain Hund's formulas.

When two terms with the same L, R, S and $\mathfrak{M}$ occur, Hund could only calculate their sum, and said that his formulas hold for their mean values; since our method gives the energies of all terms separately, we can say that in the later case the first-order energies are the same, and that Hund's formulas hold for each term separately.

§5. THE CONFIGURATION p^2p

It follows from §2 that the interaction between two non-equivalent p electrons is

$$W_{pp}=F^0(np,n'p)+\frac{6\lambda^2+3\lambda-8}{25}F^2(np,n'p)\pm(-1)^L\left[G^0(np,n'p)+\frac{6\lambda^2+3\lambda-8}{25}G^2(np,n'p)\right], \tag{36}$$

where the upper sign holds when the spins are antiparallel, and the lower sign when the spins are parallel.

Following Dirac's vector model[14] we can substitute the operator

$$-\frac{1+4(\mathbf{s}\cdot\mathbf{s}')}{2}=-\frac{1+\mu}{2} \tag{37}$$

for the double sign. For $(-1)^L$ we can substitute the operator (27).

Considering that λ satisfies the Eq. (34), we have that

$$W_{pp}=F^0(np,n'p)+\frac{6\lambda^2+3\lambda-8}{25}F^2(np,n'p) \\ -\frac{1+\mu}{2}\left[(\lambda^2+\lambda-1)G^0(np,n'p)+\frac{\lambda^2-2\lambda+2}{25}G^2(np,n'p)\right]. \tag{38}$$

Putting

$$F_0=F^0(np,np)+2F^0(np,n'p),\quad F_2=\tfrac{1}{25}F^2(np,np),\quad F'_2=\tfrac{1}{25}F^2(np,n'p),$$
$$G_0=G^0(np,n'p),\quad G_2=\tfrac{1}{25}G^2(np,n'p),$$

and marking by 1 and 2 the two np electrons, and by 3 the $n'p$ electron, we obtain for the electrostatic interaction of the $np^2n'p$ configuration:

$$E=F_0+(6\lambda_{12}^2+3\lambda_{12}-8)F_2+\sum_1^2{}_i(6\lambda_{i3}^2+3\lambda_{i3}-8)F'_2 \\ -\sum_1^2{}_i\frac{1+\mu_{i3}}{2}[(\lambda_{i3}^2+\lambda_{i3}-1)G_0+(\lambda_{i3}^2-2\lambda_{i3}+2)G_2]. \tag{39}$$

The most convenient scheme for calculating this energy operator is the LS scheme of the parent ion np^2. In this scheme λ_{12} is diagonal, and the coefficient of F_2 is therefore the diagonal matrix

$$\|(\mathrm{L}\,|\,6\lambda_{12}^2+3\lambda_{12}-8\,|\,\mathrm{L}')\|=\begin{array}{c|ccc} & \mathrm{D} & \mathrm{P} & \mathrm{S} \\ \mathrm{D} & 1 & 0 & 0 \\ \mathrm{P} & 0 & -5 & 0 \\ \mathrm{S} & 0 & 0 & 10 \end{array} \tag{40}$$

In order to calculate the coefficients of F'_2, G_0 and G_2 we must at first calculate the matrices of λ_{i3}. From TAS 10^32 we have

$$\|(\mathrm{L}\,|\,l_i\,|\,\mathrm{L}')\|=\begin{array}{c|ccc} & \mathrm{D} & \mathrm{P} & \mathrm{S} \\ \mathrm{D} & \frac{1}{2} & \pm\frac{1}{2\sqrt{3}} & 0 \\ \mathrm{P} & \pm\frac{1}{2\sqrt{3}} & \frac{1}{2} & \pm\left(\frac{2}{3}\right)^{\frac{1}{2}} \\ \mathrm{S} & 0 & \pm\left(\frac{2}{3}\right)^{\frac{1}{2}} & \frac{1}{2} \end{array}, \tag{41}$$

[14] Dirac, Proc. Roy. Soc. **A123**, 714 (1929) and *Quantum Mechanics* (Oxford, 1930), Chapter 11.

the upper sign holding for $i=1$ and the lower for $i=2$; from this table and from TAS 12^32 we obtain

$$\left\|(\mathrm{L}L\,|\,\lambda_{i3}\,|\,\mathrm{L}'L)\right\| = \begin{array}{c|ccc} & \mathrm{D} & \mathrm{P} & \mathrm{S} \\ \mathrm{D} & \dfrac{\Lambda-8}{4} & \mp\dfrac{[\Lambda(12-\Lambda)]^{\frac{1}{2}}}{4\sqrt{3}} & 0 \\ \mathrm{P} & \mp\dfrac{[\Lambda(12-\Lambda)]^{\frac{1}{2}}}{4\sqrt{3}} & \dfrac{\Lambda-4}{4} & \mp\dfrac{[\Lambda(6-\Lambda)]^{\frac{1}{2}}}{\sqrt{6}} \\ \mathrm{S} & 0 & \mp\dfrac{[\Lambda(6-\Lambda)]^{\frac{1}{2}}}{\sqrt{6}} & \dfrac{\Lambda-2}{4} \end{array}, \tag{42}$$

Λ having the meaning of (16); and this matrix gives us easily the coefficient of F'_2:

$$\left\|(\mathrm{L}L\,|\,\sum_1^2{}_i\,(6\lambda_{i3}{}^2+3\lambda_{i3}-8)\,|\,\mathrm{L}'L)\right\| = \begin{array}{c|ccc} & \mathrm{D} & \mathrm{P} & \mathrm{S} \\ \mathrm{D} & \dfrac{\Lambda^2-15\Lambda+40}{2} & 0 & \dfrac{\Lambda[(12-\Lambda)(6-\Lambda)]^{\frac{1}{2}}}{\sqrt{2}} \\ \mathrm{P} & 0 & \dfrac{-3\Lambda^2+21\Lambda-20}{2} & 0 \\ \mathrm{S} & \dfrac{\Lambda[(12-\Lambda)(6-\Lambda)]^{\frac{1}{2}}}{\sqrt{2}} & 0 & \dfrac{-5\Lambda^2+42\Lambda-64}{4} \end{array}. \tag{43}$$

In order to calculate the coefficients of G_0 and G_2 we must also calculate the matrices of $\mu_{i3}=4(\mathbf{s}_i\cdot\mathbf{s}_3)$. From TAS 10^32 and 12^32 we obtain in the same way

$$\left\|(\mathrm{s}S\,|\,\mu_{i3}\,|\,\mathrm{s}'S)\right\| = \begin{array}{c|cc} & \mathrm{s}=1 & \mathrm{s}=0 \\ \mathrm{s}=1 & S(S+1)-1\tfrac{1}{4} & \mp[[S(S+1)+\tfrac{1}{4}][1\tfrac{5}{4}-S(S+1)]]^{\frac{1}{2}} \\ \mathrm{s}=0 & \mp[[S(S+1)+\tfrac{1}{4}][1\tfrac{5}{4}-S(S+1)]]^{\frac{1}{2}} & S(S+1)-\tfrac{3}{4} \end{array} \tag{44}$$

and therefore

$$\left\|\left({}_m\mathrm{L}\ {}^2L\left|\frac{1+\mu_{i3}}{2}\right|{}_{m'}\mathrm{L}\ {}^2L\right)\right\| = \begin{array}{c|cc} & {}^3\mathrm{L} & {}^1\mathrm{L} \\ {}^3\mathrm{L} & -\dfrac{1}{2} & \mp\dfrac{\sqrt{3}}{2} \\ {}^1\mathrm{L} & \mp\dfrac{\sqrt{3}}{2} & \dfrac{1}{2} \end{array} \tag{45}$$

and

$$\left({}_{\mathrm{L}}\,{}^4L\left|\frac{1+\mu_{i3}}{2}\right|{}_{\mathrm{L}}\,{}^4L\right)=1. \tag{45'}$$

TABLE I.

Atom	Configuration	$(^4P-{}^4D)/(^4D-{}^2S)$
Theory	$np^2n'p$	0.667
N I	$2p^23p$	0.521
N I	$2p^24p$	0.504
O II	$2p^23p$	0.520
S II	$3p^24p$	0.604

From (42) and (45) we get

$$\left\|\left({}_{m}\mathrm{L}\ {}^2L\left|\sum_1^2{}_i\frac{1+\mu_{i3}}{2}(\lambda_{i3}{}^2+\lambda_{i3}-1)\right|{}_{m'}\mathrm{L}'\ {}^2L\right)\right\|$$

$$= \begin{array}{c|ccc} & {}^1\mathrm{D} & {}^3\mathrm{P} & {}^1\mathrm{S} \\ {}^1\mathrm{D} & \dfrac{\Lambda^2-12\Lambda+24}{24} & \dfrac{(\Lambda-4)[\Lambda(12-\Lambda)]^{\frac{1}{2}}}{8} & \dfrac{\Lambda[(12-\Lambda)(6-\Lambda)]^{\frac{1}{2}}}{12\sqrt{2}} \\ {}^3\mathrm{P} & \dfrac{(\Lambda-4)[\Lambda(12-\Lambda)]^{\frac{1}{2}}}{8} & \dfrac{\Lambda^2-8\Lambda+8}{8} & \dfrac{(\Lambda-1)[\Lambda(6-\Lambda)]^{\frac{1}{2}}}{2\sqrt{2}} \\ {}^1\mathrm{S} & \dfrac{\Lambda[(12-\Lambda)(6-\Lambda)]^{\frac{1}{2}}}{12\sqrt{2}} & \dfrac{(\Lambda-1)[\Lambda(6-\Lambda)]^{\frac{1}{2}}}{2\sqrt{2}} & \dfrac{-5\Lambda^2+48\Lambda-60}{48} \end{array} \tag{46}$$

and

$$\left\|\left({}_{m}\mathrm{L}\ {}^2L\left|\sum_1^2{}_i\frac{1+\mu_{i3}}{2}(\lambda_{i3}{}^2-2\lambda_{i3}+2)\right|{}_{m'}\mathrm{L}'\ {}^2L\right)\right\|$$

$$= \begin{array}{c|ccc} & {}^1\mathrm{D} & {}^3\mathrm{P} & {}^1\mathrm{S} \\ {}^1\mathrm{D} & \dfrac{\Lambda^2-30\Lambda+240}{24} & \dfrac{(\Lambda-10)[\Lambda(12-\Lambda)]^{\frac{1}{2}}}{8} & \dfrac{\Lambda[(12-\Lambda)(6-\Lambda)]^{\frac{1}{2}}}{12\sqrt{2}} \\ {}^3\mathrm{P} & \dfrac{(\Lambda-10)[\Lambda(12-\Lambda)]^{\frac{1}{2}}}{8} & \dfrac{\Lambda^2-2\Lambda-40}{8} & \dfrac{(\Lambda-7)[\Lambda(6-\Lambda)]^{\frac{1}{2}}}{2\sqrt{2}} \\ {}^1\mathrm{S} & \dfrac{\Lambda[(12-\Lambda)(6-\Lambda)]^{\frac{1}{2}}}{12\sqrt{2}} & \dfrac{(\Lambda-7)[\Lambda(6-\Lambda)]^{\frac{1}{2}}}{2\sqrt{2}} & \dfrac{-5\Lambda^2+12\Lambda+156}{48} \end{array}. \tag{47}$$

From (42) and (45′) we get

$$\left({}^3\mathrm{P}\ {}^4L\left|\sum_1^2{}_i\frac{1+\mu_{i3}}{2}(\lambda_{i3}{}^2+\lambda_{i3}-1)\right|{}^3\mathrm{P}\ {}^4L\right)=-\frac{\Lambda^2-8\Lambda+8}{4} \tag{46′}$$

and

$$\left({}^3\mathrm{P}\ {}^4L\left|\sum_1^2{}_i\frac{1+\mu_{i3}}{2}(\lambda_{i3}{}^2-2\lambda_{i3}+2)\right|{}^3\mathrm{P}\ {}^4L\right)=-\frac{\Lambda^2-2\Lambda-40}{4}. \tag{47′}$$

Introducing our results into (39) we obtain

$$^4D=F_0-5F_2-F'_2-G_0-4G_2,$$

$$^4P=F_0-5F_2+5F'_2-G_0-10G_2,$$

$$^4S=F_0-5F_2-10F'_2+2G_0-10G_2,$$

$$^2S = F_0 - 5F_2 - 10F'_2 - G_0 + 5G_2,$$
$$^2F = F_0 + F_2 + 2F'_2 - G_0 - G_2.$$

The energy matrix for the ^2D terms is

	^1D	^3P
^1D	$F_0+F_2-7F'_2+\frac{1}{2}G_0-4G_2$	$-\frac{3}{2}G_0+3G_2$
^3P	$-\frac{3}{2}G_0+3G_2$	$F_0-5F_2-F'_2+\frac{1}{2}G_0+2G_2$

and has the eigenvalues

$$^2D = F_0 - 2F_2 - 4F'_2 + \tfrac{1}{2}G_0 - G_2 \pm 3[(F_2 - F'_2 - G_2)^2 + \tfrac{1}{4}(G_0 - 2G_2)^2]^{\frac{1}{2}}.$$

The energy matrix for the ^2P terms is

	^1D	^3P	^1S
^1D	$F_0+F_2+7F'_2-\frac{1}{16}G_0-2\frac{3}{3}\frac{3}{5}G_2$	$(-G_0+2G_2)\sqrt{5}$	$(4F'_2-\frac{1}{3}\frac{3}{5}G_0-\frac{1}{3}\frac{3}{5}G_2)\sqrt{5}$
^3P	$(-G_0+2G_2)\sqrt{5}$	$F_0-5F_2+5F'_2+\frac{1}{2}G_0+5G_2$	$-G_0+5G_2$
^1S	$(4F'_2-\frac{1}{3}\frac{3}{5}G_0-\frac{1}{3}\frac{3}{5}G_2)\sqrt{5}$	$-G_0+5G_2$	$F_0+10F_2-\frac{1}{3}\frac{9}{5}G_0-1\frac{9}{3}\frac{3}{5}G_2$

It follows from our results that the ratio $(^4P-{}^4D)/(^4D-{}^2S)$ has the theoretical value of $\frac{2}{3}$. The comparison with the experimental ratios[15] is given in Table I.

The deviations are of the same order as those of the np^3 configurations of the same elements.[16]

§6. THE CONFIGURATION p^2l

The terms of the configuration $np^2n'l$ can be calculated in the same way as those of $np^2n'p$. The only difference is that the coefficients of G^{l-1} and G^{l+2} in W_{pl} are polynomials of higher degree in λ, and must be reduced to the second degree by means of the equation

$$\lambda^3 + 2\lambda^2 - (l^2+l-1)\lambda - l(l+1) = 0, \tag{48}$$

which corresponds to the Eq. (34) of the pp case. This reduction cannot be carried out without specifying the value of l; it is possible however to avoid such direct reduction, by calculating at first the single values of $g_{l-1}(l1L)$ and $g_{l+1}(l1L)$ for the three possible values of L by means of (15), and then determining the polynomials of the second degree which assume these values for the values l, -1, and $-(l+1)$ of the variable λ. By this procedure we find that the electrostatic interaction between a p and a l electron can be expressed by means of the formula

$$W_{pl} = F^0(np, n'l) + [6\lambda^2+3\lambda-4l(l+1)]F'_2 - \frac{1+\mu}{2}[(\lambda^2+l\lambda-l)G_{l-1} + (\lambda^2-(l+1)\lambda+l+1)G_{l+1}], \tag{49}$$

where[17]

$$F'_2 = \frac{F^2(np, n'l)}{5(2l-1)(2l+3)}, \quad G_{l-1} = \frac{3G^{l-1}(np, n'l)}{(2l+1)(2l-1)^2}, \quad G_{l+1} = \frac{3G^{l+1}(np, n'l)}{(2l+1)(2l+3)^2}. \tag{50}$$

From this point the calculations were carried out exactly in the same way as for p^2p, and give the following results

[15] See Bacher and Goudsmit, *Atomic Energy States* (McGraw-Hill, 1932).
[16] TAS, p. 198.
[17] Our definitions (50) differ in some cases by a factor 3 from the definitions of TAS, p. 177.

Quartets:

$$L=l+1: \quad F_0-5F_2-l(2l-1)F'_2-l(2l-1)G_{l-1}-2(l+1)G_{l+1},$$
$$L=l: \quad F_0-5F_2+(2l-1)(2l+3)F'_2-l(2l-1)G_{l-1}-(l+1)(2l+3)G_{l+1},$$
$$L=l-1: \quad F_0-5F_2-(l+1)(2l+3)F'_2+2lG_{l-1}-(l+1)(2l+3)G_{l+1}.$$

Doublets:

$$L=l+2: \quad F_0+F_2+2l(2l-1)F'_2-l(2l-1)G_{l-1}-G_{l+1},$$
$$L=l-2: \quad F_0+F_2+2(l+1)(2l+3)F'_2-G_{l-1}-(l+1)(2l+3)G_{l+1},$$
$$L=l+1: \quad F_0-2F_2-(l+3)(2l-1)F'_2+\tfrac{1}{2}(2l-1)G_{l-1}-G_{l+1}$$
$$\pm[[3F_2-3(2l-1)F'_2-\tfrac{1}{2}(l-1)(2l-1)G_{l-1}-(l+2)G_{l+1}]^2+3l(l+2)[\tfrac{1}{2}(2l-1)G_{l-1}-G_{l+1}]^2]^{\frac{1}{2}},$$
$$L=l-1: \quad F_0-2F_2-(l-2)(2l+3)F'_2-G_{l-1}-\tfrac{1}{2}(2l+3)G_{l+1}$$
$$\pm[[3F_2+3(2l+3)F'_2+(l-1)G_{l-1}-\tfrac{1}{2}(l+2)(2l+3)G_{l+1}]^2+3(l^2-1)[G_{l-1}+\tfrac{1}{2}(2l+3)G_{l+1}]^2]^{\frac{1}{2}}.$$

The energy matrix for the doublets with $L=l$ is of the third order and has the elements:

$$(^1\mathrm{D}\,|E|\,^1\mathrm{D})=F_0+F_2-(2l-3)(2l+5)F'_2-\frac{2l^2-13l+12}{6}G_{l-1}-\frac{2l^2+17l+27}{6}G_{l+1},$$
$$(^3\mathrm{P}\,|E|\,^3\mathrm{P})=F_0-5F_2+(2l-1)(2l+3)F'_2+\tfrac{1}{2}l(2l-1)G_{l-1}+\tfrac{1}{2}(l+1)(2l+3)G_{l+1},$$
$$(^1\mathrm{S}\,|E|\,^1\mathrm{S})=F_0+10F_2-\tfrac{1}{3}l(2l-1)G_{l-1}-\tfrac{1}{3}(l+1)(2l+3)G_{l+1},$$
$$(^1\mathrm{D}\,|E|\,^3\mathrm{P})=\tfrac{1}{2}[(2-l)G_{l-1}+(l+3)G_{l+1}][(2l-1)(2l+3)]^{\frac{1}{2}},$$
$$(^3\mathrm{P}\,|E|\,^1\mathrm{S})=\tfrac{1}{2}[-(2l-1)G_{l-1}+(2l+3)G_{l+1}][2l(l+1)]^{\frac{1}{2}},$$
$$(^1\mathrm{D}\,|E|\,^1\mathrm{S})=(2F'_2-\tfrac{1}{6}G_{l-1}-\tfrac{1}{6}G_{l+1})[2l(l+1)(2l-1)(2l+3)]^{\frac{1}{2}}.$$

APPENDIX

From the addition theorem for binomial coefficients

$$\sum_s \binom{x}{s}\binom{y}{z-s}=\binom{x+y}{z}, \tag{51}$$

putting $x=a-b$, $y=b$, $z=a-c$, we have

$$\frac{a!}{b!c!}=\sum_s \frac{(a-b)!(a-c)!}{(a-b-s)!(a-c-s)!(b+c-a+s)!s!}. \tag{52}$$

If y is negative, we can transform (51) by means of

$$\binom{y}{z-s}=(-1)^{z-s}\binom{z-s-y-1}{z-s} \tag{53}$$

and obtain

$$\textstyle\sum_s (-1)^s\binom{x}{s}\binom{z-s-y-1}{z-s}=(-1)^z\binom{x+y}{z} \tag{54}$$

or

$$\textstyle\sum_s (-1)^s\binom{x}{s}\binom{z-s-y-1}{z-s}=\binom{z-x-y-1}{z}; \tag{54'}$$

putting $y=z-t-1$ we have from (54)

$$\sum_s (-1)^s \frac{(t-s)!}{s!(x-s)!(z-s)!} = (-1)^z \frac{(t-z)!(x+z-t-1)!}{x!z!(x-t-1)!} \quad \text{if} \quad x>t\geqq z\geqq 0, \tag{55}$$

and from (54′)

$$\sum_s (-1)^s \frac{(t-s)!}{s!(x-s)!(z-s)!} = \frac{(t-x)!(t-z)!}{x!z!(t-x-z)!} \quad \text{if} \quad t\geqq x\geqq 0,\ t\geqq z\geqq 0. \tag{55′}$$

Using repeatedly (52), and also (55) and (55′), we can transform the sum in (12) as follows:

$$\begin{aligned}
&\sum_u (-1)^u \frac{(u+l'_1-l'_2)!}{(u+L+1)!}\cdot\frac{(u+l_2-l_1)!}{(u-L)!(k-l_1-l'_2+u)!}\cdot\frac{(k+l_1+l'_2-u)!}{(l_1+l_2-u)!(l_1'+l'_2-u)!}\\
&\quad=\sum_{\alpha\beta u}(-1)^u\frac{(u+l'_1-l'_2)!}{(u+L+1)!}\cdot\frac{(L+l_2-l_1)!(l_2+l'_2-k)!}{(L+l_2-l_1-\alpha)!(l_2+l_2'-k-\alpha)!(k-l_2-l'_2-L+u+\alpha)!\alpha!}\\
&\qquad\cdot\frac{(k+l'_2-l_2)!(k+l_1-l'_1)!}{(k+l'_2-l_2-\beta)!(k+l_1-l'_1-\beta)!(l'_1+l_2-k-u+\beta)!\beta!}\\
&\quad=\sum_{\alpha\beta}(-1)^{k-l_2-l'_2-L+\alpha}\frac{(L+l_2-l_1)!(l_2+l'_2-k)!(k+l'_2-l_2)!(k+l_1-l'_1)!}{(L+l_2-l_1-\alpha)!(l_2+l'_2-k-\alpha)!(k+l'_2-l_2-\beta)!(k+l_1-l'_1-\beta)!}\\
&\qquad\cdot\frac{(l'_1+l_2+L-k-\alpha)!}{(l'_1+l_2+L+1-k+\beta)!}\cdot\frac{(\alpha+\beta)!}{(l'_1-l'_2-L+\alpha+\beta)!(L+l'_2-l'_1)!\alpha!\beta!}\\
&\quad=\sum_{\alpha\beta\gamma}(-1)^{k-l_2-l'_2-L+\alpha}\frac{(L+l_2-l_1)!(l_2+l'_2-k)!(k+l'_2-l_2)!(k+l_1-l'_1)!(l'_1+l_2+L-k-\alpha)!}{(L+l_2-l_1-\alpha)!(l_2+l'_2-k-\alpha)!(k+l'_2-l_2-\beta)!}\\
&\qquad\times(k+l_1-l'_1-\beta)!(l'_1+l_2+L+1-k+\beta)!\\
&\qquad\cdot\frac{1}{(L+l'_2-l'_1-\gamma)!(\alpha-\gamma)!(l'_1-l'_2-L+\beta+\gamma)!\gamma!}\\
&\quad=\sum_\gamma(-1)^{k-l_2-l'_2-L+\gamma}\frac{(L+l_2-l_1)!(l_2+l'_2-k)!(k+l'_2-l_2)!(k+l_1-l'_1)!}{(L+l'_2-l'_1-\gamma)!\gamma!}\\
&\qquad\cdot\frac{(l_1+l'_1-k)!(L+l'_1-l'_2)!}{(L+l_2-l_1-\gamma)!(l_2+l'_2-k-\gamma)!(l_1+l'_1-l_2-l'_2+\gamma)!}\\
&\qquad\cdot\frac{(k+l_1+l'_1+1+\gamma)!}{(l'_1+l'_2+L+1)!(l_1+l_2+L+1)!(k+l_1-l'_2-L+\gamma)!(k+l'_1-l_2-L+\gamma)!}.
\end{aligned}$$

Putting $\gamma=l_2+l'_2-k-v$, this expression becomes

$$\begin{aligned}
&\sum_v(-1)^{v-L}\frac{(L+l_2-l_1)!(l_2+l'_2-k)!(k+l'_2-l_2)!(k+l_1-l'_1)!}{(k+L-l'_1-l_2+v)!(l_2+l'_2-k-v)!(k+L-l_1-l'_2+v)!v!(l_1+l'_1-k-v)!}\\
&\qquad\times(l_1+l'_1-k)!(L+l'_1-l'_2)!(l_1+l_2+l'_1+l'_2+1-v)!\\
&\qquad\times(l_1+l_2-L-v)!(l'_1+l'_2-L-v)!(l'_1+l'_2+L+1)!(l_1+l_2+L+1)!;
\end{aligned}$$

introducing this result into (12) we obtain (12′).