PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

The Triplets of Helium

J. A. Gaunt

Phil. Trans. R. Soc. Lond. A 1929 **228**, 151-196
doi: 10.1098/rsta.1929.0004

IV. *The Triplets of Helium.*

By J. A. Gaunt, *Trinity College, Cambridge.*

(*Communicated by* R. H. Fowler, *F.R.S.*)

(Received November 6, 1928,—Read January 17, 1929.)

1. *Introduction.*

Heisenberg's theory* of the helium atom, following his famous principle of "resonance," accounted satisfactorily for the ortho- and para- states. His more detailed treatment of the triplets, besides giving ground for minor criticisms, necessarily had to be derived from Schrödinger's equation, with a somewhat incongruous electronic "spin" grafted upon it. The present work uses Dirac's recent theory,† in which the spin effects grow more naturally from the fundamental equations. Calculations which are independent of the spin, such as the approximate energy-levels and the ortho-para separations, are the same on either theory. We deal here with spin effects, such as the fine structure of the triplets and intercombinations between ortho- and para- states.

The fundamental equations, the perturbation theory which is used, and the perturbing spin energy, have been discussed fully elsewhere.‡ The present paper, after a short recapitulation of the general theory, gives in detail the calculations whose results alone were quoted in the other. §§ 4–7 work out the structure of the helium triplets with one excited election. The resulting spin separations are different from Heisenberg's, but in equally good agreement with experiment. At the same time, the correct first approximations to the wave-functions are found, and they are used in § 8 to verify the ordinary classification and selection rules.

§ 9 summarises the parallel work for the deepest triplet of O^{++}, some of whose intercombination lines appear strongly in the spectra of the nebulæ. Some estimates are made of the intensities of intercombination lines, but these are not favourable to the production of the nebular lines.

2. *The Basic Equation.*

The notation, with a few exceptions, is that of Dirac, and of Darwin's interpretation|| of Dirac's q-number theory in terms of wave-mechanics. We use h, not $2\pi h$,

* Heisenberg, 'Z. Physik,' vol. 39, p. 499 (1926).

† Dirac, 'Roy. Soc. Proc.,' A, vol. 117, p. 610 (1928); also *ibid.*, vol. 118, p. 351 (1928).

‡ Gaunt, 'Roy. Soc. Proc., A, vol. 122, p. 513 (1929).

|| Darwin, 'Roy. Soc. Proc.,' A, vol. 118, p. 654 (1928).

for PLANCK'S constant, and replace DIRAC'S $\sigma_1, \sigma_2, \sigma_3$, by the three components of the vector $\boldsymbol{\sigma}$, and ρ_1, ρ_2, ρ_3, by ρ', ρ'', ρ'''. The suffixes 1 and 2 are reserved to distinguish between the co-ordinates of the two electrons. Ze is the charge on the nucleus, r the distance between the electrons.

First neglect the interaction between the electrons. Each electron has a separate wave-function ψ_a or ψ_b with time-factor $\exp - (mc^2 + \mathrm{E}_a)\, it/h$ or $\exp - (mc^2 + \mathrm{E}_b)\, it/h$ and satisfying DIRAC'S equation

$$\left.\begin{aligned} \left[mc + \frac{\mathrm{E}_a + e\mathrm{V}}{c} + \rho'(\boldsymbol{\sigma}\,.\,\mathbf{p}) + \rho'''mc\right]\psi_a = 0 \\ \left[mc + \frac{\mathrm{E}_b + e\mathrm{V}}{c} + \rho'(\boldsymbol{\sigma}\,.\,\mathbf{p}) + \rho'''mc\right]\psi_b = 0 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.0)$$

Here V is the potential of the electrostatic field of the nucleus. The whole atom has an antisymmetrical wave-function

$$\Psi = \psi_a(1)\,\psi_b(2) - \psi_b(1)\,\psi_a(2), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.1)$$

with a time-factor $\exp - (2mc^2 + \mathrm{E})\, it/h$, where

$$\mathrm{E} = \mathrm{E}_a + \mathrm{E}_b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.2)$$

and this function satisfies the equation

$$\left[\mathrm{F} + \frac{\mathrm{E}}{c}\right]\Psi \equiv \left[2mc + \frac{\mathrm{E} + e\mathrm{V}(1) + e\mathrm{V}(2)}{c} + \rho_1'(\boldsymbol{\sigma}_1.\,\mathbf{p}_1) \right.$$
$$\left. + \rho_2'(\boldsymbol{\sigma}_2\,.\,\mathbf{p}_2) + \rho_1'''mc + \rho_2'''mc\right]\Psi = 0. \qquad (2.3)$$

Introducing an interaction energy, we assume that the accurate equation for the complete wave-function is

$$\left[\mathrm{F} + \frac{\mathrm{E} - \mathrm{P} - \mathrm{S}}{c}\right]\Psi = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.4)$$

P is that part of the interaction energy which is independent of spin. It consists of e^2/r and some negligible terms. In practice as much as possible of P is absorbed in V(1) and V(2). The best approximation (2·1) to Ψ is obtained by HARTREE'S method of self-consistent fields,* in which different potentials V_a, V_b are used in the equations (2.0), and

$$\mathrm{V}_a(1) = \frac{Ze}{r_1} - \frac{e\int |\psi_b(2)|^2/r}{\int |\psi_b(2)|^2}; \qquad \mathrm{V}_b(1) = \frac{Ze}{r_1} - \frac{e\int |\psi_a(2)|^2/r}{\int |\psi_a(2)|^2}. \quad . \quad . \quad . \quad (2.5)$$

The perturbation by P is then of the order of the ortho-para separations—say 1/10.

* HARTREE, 'Proc. Camb. Phil. Soc.,' vol. 24, p. 89 (1928); GAUNT, 'Proc. Camb. Phil. Soc.,' vol. 24, p. 382 (1928).

S is much smaller, of the order of the triplet separations—say 10^{-4}. It was shown in the other paper that an approximate form for S which is suitable to the calculations in hand is

$$S = T_1 + T_2 + U \quad \ldots \quad (2.6)$$

$$= -\frac{e^2h}{4\pi m^2c^2}\left\{\left[\frac{\mathbf{r}_2-\mathbf{r}_1}{r^3},\ \mathbf{p}_2\right]\cdot\boldsymbol{\sigma}_1+\left[\frac{\mathbf{r}_1-\mathbf{r}_2}{r^3},\ \mathbf{p}_1\right]\cdot\boldsymbol{\sigma}_2\right\}$$
$$+\left(\frac{eh}{4\pi mc}\right)^2\frac{(\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2)-3\,(\boldsymbol{\sigma}_1\cdot\mathbf{r}_0)\,(\boldsymbol{\sigma}_2\cdot\mathbf{r}_0)}{r^3}, \quad \ldots \quad (2.7)$$

where $\mathbf{r}_0$ is the direction of one electron from the other. T_1 may be interpreted as the energy of the first electron-magnet, of moment $-eh\boldsymbol{\sigma}/4\pi mc$, in the magnetic field due to the motion of the second charge; T_2 similarly; and U as the mutual energy of the two magnets.

The effect of the motion of the magnets in the electrostatic field is already included in (2.0). The characteristic energies of (2.0) occur in pairs, whose difference is small compared with P. It is therefore necessary to use a perturbation theory for nearly degenerate systems.

3. *Perturbation Theory.*

The equation (2.3) will have a number of antisymmetrical solutions Ψ_m whose energies are nearly equal to some value E

$$E_m = E + \delta E_m, \qquad \delta E_m = O\,(S). \quad \ldots \quad (3.0)$$

The remaining solutions Ψ_n have quite different energies.

It is convenient to use unnormalised wave-functions, and to write

$$\int |\Psi_m|^2 = C_m, \text{ etc.} \quad \ldots \quad (3.10)$$

where $\int$ denotes an integration over all space and a summation for the four values of each spin co-ordinate. Also let

$$\int \overline{\Psi}_{m'} P\, \Psi_m = P_{mm'}, \text{ etc.} \quad \ldots \quad (3.11)$$

Equation (2.4) has solutions with energies nearly equal to E

$$E^\mu = E + \Delta E^\mu + \delta E^\mu, \quad \ldots \quad (3.20)$$

where the last two terms arise from P and S respectively. The corresponding wave-function may be written

$$\Psi_\mu = \sum_m (a^\mu_m + \delta a^\mu_m)\,\Psi_m + \sum_n (a^\mu_n + \delta a^\mu_n)\,\Psi_n, \quad \ldots \quad (3.21)$$

where a^{μ}_{m}, a^{μ}_{n} are the coefficients in the absence of spin effects. As usual, a^{μ}_{m} is O (1), a^{μ}_{n} is O (P); and it is found that δa^{μ}_{m} is O (S/P) and δa^{μ}_{n} O (S).

An argument parallel to that of ordinary perturbation theory gives for a first approximation to the spin perturbation

$$(\delta E^{\mu} - \delta E_{m'}) C_{m'} a^{\mu}_{m'} - \sum_{m} S_{mm'} a^{\mu}_{m} + \Delta E^{\mu} C_{m'} \delta a^{\mu}_{m'} - \sum_{m} P_{mm'} \delta a^{\mu}_{m} = 0. \quad . \quad (3.3)$$

It is sufficient to use for the a^{μ}_{m} in this equation first approximations which satisfy the usual equation

$$\Delta E^{\mu} C_{m'} a^{\mu}_{m'} - \sum_{m} P_{mm'} a^{\mu}_{m} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.4)$$

The normal term, denoted by a suffix 0, is neither degenerate nor nearly so. Except for terms which are O (S), its wave-function is symmetrical in the position co-ordinates and antisymmetrical in the spins.

As a rule, the other terms appear in groups of four, involving four m's (1, 2, 3, 4) and are distinguished by four μ's (I, II, III, IV). Of these the first three have (to a first approximation) wave-functions antisymmetrical in the position co-ordinates, while the fourth wave-function is symmetrical in the positions. Also $\Delta E^{I} = \Delta E^{II} = \Delta E^{III} \neq \Delta E^{IV}$, so that there is still a double degeneracy after the perturbation by P alone. These are known results of HEISENBERG's theory.

Owing to the double degeneracy, the four equations (3.4) are all equivalent when $\Delta E^{\mu} = \Delta E^{I}$; and this one equation is the only one connecting the four $a_{m}{}^{I}$'s, which are triply indeterminate until the spin perturbation is used. Another form of this equation arises from considerations of symmetry. For if X is any symmetrical function of the positions of the two electrons (*e.g.*, the electric moment of the atom), the integral $X_{I\,0}$ vanishes to a first approximation. That is

$$\sum_{m} a_{m}{}^{I} X_{m\,0} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.50)$$

To the same order

$$X_{IV\,0} = \sum_{m} a_{m}{}^{IV} X_{m\,0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.51)$$

and to a second approximation

$$X_{I\,0} = \sum_{m} \delta a_{m}{}^{I} X_{m\,0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.52)$$

The coefficients of the a's in (3.4) and (3.50) must be proportional. Substitution for $X_{m\,0}$ in (3.51) and (3.52) and use of (3.3) in the latter, yield

$$(\delta E^{I} - \delta E_{m'}) C_{m'} a_{m'}{}^{I} - \sum_{m} S_{mm'} a_{m'}{}^{I} = \frac{X_{I\,0}}{X_{IV\,0}} (\Delta E^{IV} - \Delta E^{I}) C_{m'} a_{m'}{}^{IV}. \quad . \quad . \quad (3.6)$$

There are four such equations. The determinant of the coefficients on the left hand sides is denoted by Δ, and the cofactor of one of its terms by $\Delta_{mm'}$. Solving for $a_{m}{}^{I}$

$$\Delta \,.\, a_{m}{}^{I} = \frac{X_{I\,0}}{X_{IV\,0}} (\Delta E^{IV} - \Delta E^{I}) \sum_{m'} C_{m'} a_{m'}{}^{IV} \Delta_{mm'}. \quad . \quad . \quad . \quad . \quad . \quad (3.7)$$

We have also an equation expressing the fact that ψ_{I} and ψ_{IV} (the first approximations to Ψ_{I} and Ψ_{IV}) are orthogonal.

$$\sum_m C_m a_m^{\mathrm{IV}} a_m^{\mathrm{I}} = 0. \qquad (3.8)$$

This and the four equations like (3.7) give the determinant equation—a cubic in δE^{I}

$$\begin{vmatrix} 0 & C_m a_m^{\mathrm{IV}} \\ C_m a_m^{\mathrm{IV}} & \Delta \end{vmatrix} = 0. \qquad (3.9)$$

The three roots of this are δE^{I}, δE^{II}, δE^{III}.

Having found δE^{I} from (3.9), we have a_m^{I} in terms of $X_{\mathrm{I}\,0}/X_{\mathrm{IV}\,0}$ from (3.7), since a_m^{IV}, etc., are known from Heisenberg's theory. We can calculate C_{I} and C_{IV}, and so obtain the ratio $X_{\mathrm{I}\,0}^2/C_{\mathrm{I}} : X_{\mathrm{IV}\,0}^2/C_{\mathrm{IV}}$. This is roughly the ratio of the probabilities of transitions from the normal state to the ortho- and para- states respectively. It is of the order of $(S/P)^2$.

4. *The Wave-Functions with One Electron Excited.*

We shall use n, k, u for the three quantum numbers of a single orbit, and also Dirac's j ($= k$ or $-k-1$) to distinguish between the two possible spins. The quantum number n will often be omitted, when the orbit is sufficiently distinguished by its k. In Darwin's notation, the wave-functions corresponding to the two directions of spin have the components:

$$\left.\begin{aligned} \psi^u_{-k-1} &= -iP^u_{k+1}F_k, \quad -iP^{u+1}_{k+1}F_k, \quad (k+u+1)P^u_k G_k, \quad (-k+u)P^{u+1}_k G_k \\ \psi^u_k &= -iP^u_{k-1}F_{-k-1}, \quad -i(-k+u-1)P^{u+1}_{k-1}F_{-k-1}, \quad P^u_k G_{-k-1}, \quad P^{u+1}_k G_{-k-1} \end{aligned}\right\}. \qquad (4.00)$$

The suffixes to ψ give Dirac's j. It is a pity that Darwin's suffixes are the other way round.

The functions F are small, and the functions G differ little from each other, and from the radial part of the solution of Schrödinger's equation, which we will denote by g_{nk} (or g_k). To a sufficient approximation for our purpose

$$\left.\begin{aligned} \psi^u_{-k-1} &= 0, \quad 0, \quad (k+u+1)P^u_k g_{nk}, \quad (-k+u)P^{u+1}_k g_{nk} \\ \psi^u_k &= 0, \quad 0, \quad P^u_k g_{nk}, \quad P^{u+1}_k g_{nk} \end{aligned}\right\} \qquad (4.01)$$

Thus

$$\left.\begin{aligned} \psi^u_{-k-1} + (k-u)\,\psi^k_u &= 0, \quad 0, \quad (2k+1)P^u_k g_{nk}, \quad 0 = \phi^u_k \quad \chi_a \\ -\psi^u_{-k-1} + (k+u+1)\,\psi^u_k &= 0, \quad 0, \quad 0, \quad (2k+1)P^{u+1}_k g_{nk} = \phi^{u+1}_k \quad \chi_b \end{aligned}\right\} \qquad (4.02)$$

where

$$\phi^u_k = (2k+1)P^u_k g_{nk} \qquad (4.03)$$

and χ_a; χ_b are functions of the spin co-ordinate only, with components

$$\left.\begin{aligned} \chi_a &= 0, \quad 0, \quad 1, \quad 0 \\ \chi_b &= 0, \quad 0, \quad 0, \quad 1 \end{aligned}\right\} \qquad (4.04)$$

The first step is to disregard spin energies, and to perturb solutions of SCHRÖDINGER'S equation with P only. In this process ψ^u_k and ψ^u_{-k-1} have the same energy for all possible u, and may be replaced by the linear combinations $\phi^u_k\chi_a$, $\phi^u_k\chi_b$ (all u). The energy will not be independent of k, since the field is a non-Coulomb one. If one electron is in the normal state, the group of four wave-functions deduced by HEISENBERG as first approximations to the total wave-functions is

$$\left.\begin{aligned} \psi_\alpha &= [\phi^0_0(1)\,\phi^{u+1}_k(2) - \phi^0_0(2)\,\phi^{u+1}_k(1)]\,\chi_b(1)\,\chi_b(2) \\ \psi_\beta &= [\phi^0_0(1)\,\phi^{u-1}_k(2) - \phi^0_0(2)\,\phi^{u-1}_k(1)]\,\chi_a(1)\,\chi_a(2) \\ \psi_\gamma &= [\phi^0_0(1)\,\phi^u_k(2) - \phi^0_0(2)\,\phi^u_k(1)]\,[\chi_a(1)\,\chi_b(2) + \chi_b(1)\,\chi_a(2)] \\ \psi_{IV} &= [\phi^0_0(1)\,\phi^u_k(2) + \phi^0_0(2)\,\phi^u_k(1)]\,[\chi_a(1)\,\chi_b(2) - \chi_b(1)\,\chi_a(2)] \end{aligned}\right\} \qquad (4.10)$$

Of these the first three have the same energy, and linear combinations of them are determined by the spin to form ψ_I, ψ_{II}, ψ_{III}. In addition, all the energies are independent of u; but this degeneracy may be neglected, since it will appear that these groups of four remain separate when the spin perturbation is introduced.

We express (4.10) in terms of ψ^u_k, etc., by means of (4.02). We find that four approximate solutions of (2.3) are involved :—

$$\left.\begin{aligned} \psi_1 &= \psi^0_{-1}(1)\,\psi^{u-1}_{-k-1}(2) - \psi^0_{-1}(2)\,\psi^{u-1}_{-k-1}(1) \\ \psi_2 &= \psi^0_{-1}(1)\,\psi^{u-1}_k(2) - \psi^0_{-1}(2)\,\psi^{u-1}_k(1) \\ \psi_3 &= \psi^{-1}_{-1}(1)\,\psi^u_{-k-1}(2) - \psi^{-1}_{-1}(2)\,\psi^u_{-k-1}(1) \\ \psi_4 &= \psi^{-1}_{-1}(1)\,\psi^u_k(2) - \psi^{-1}_{-1}(2)\,\psi^u_k(1) \end{aligned}\right\} \qquad (4.11)$$

and that

$$\left.\begin{aligned} \psi_\alpha &= \psi_3 - (k+u+1)\,\psi_4 \\ \psi_\beta &= \psi_1 + (k-u+1)\,\psi_2 \\ \psi_\gamma &= -\psi_1 + (k+u)\,\psi_2 - \psi_3 - (k-u)\,\psi_4 \\ \psi_{IV} &= -\psi_1 + (k+u)\,\psi_2 + \psi_3 + (k-u)\,\psi_4 \end{aligned}\right\} \qquad (4.12)$$

The u, $u-1$, $u+1$ in (4.10) are arranged so that only the four functions (4.11) are involved. The sum of the third quantum numbers in these functions is the same, $u-1$ pairing with 0, and u with -1. This selection of a group of four functions (sometimes reducing to three or one) is justified *a posteriori* in § 7. The arrangement of (4.10) can be remembered by supposing that χ_a, χ_b, contribute $+\frac{1}{2}$ and $-\frac{1}{2}$ respectively to the third quantum number to give the total angular momentum about the z-axis. This corresponds to DIRAC's equation

$$\mathbf{M} = \mathbf{m} + \tfrac{1}{2} h \boldsymbol{\sigma} \qquad (4.13)$$

together with

$$\left.\begin{aligned} \tfrac{1}{2}\sigma_z\chi_a &= 0,\ 0,\ +\tfrac{1}{2},\ 0 \\ \tfrac{1}{2}\sigma_z\chi_b &= 0,\ 0,\ 0,\ -\tfrac{1}{2} \end{aligned}\right\} \qquad (4.14)$$

HEISENBERG assumes that functions like ψ_α, ψ_β, ψ_γ, remain separate when perturbed by the spin energy; that is, that they are identical with ψ_{I}, ψ_{II}, ψ_{III}. This is not so.

ψ_1, ψ_2, ψ_3, ψ_4 are the ψ_m's of § 3, but it is more convenient to calculate integrals by means of ψ_α, ψ_β, ψ_γ, ψ_{IV}. Thus

$$\mathrm{C}_\alpha = 2\int |\phi_0^0(1)|^2 |\phi_k^{u+1}(2)|^2 \, d\tau_1\, d\tau_2$$

$$= 2\,.\,(2k+1)^2\,.\,4\pi\,.\,\frac{4\pi}{2k+1}\,(k+u+1)!\,(k-u-1)!\int g_{10}(r_1)^2\, g_{nk}(r_2)^2\, r_1^2\, dr_1\, r_2^2\, dr_2,$$

and so on; or

$$\left.\begin{aligned} C_\alpha &= (2k+1)\,\frac{k+u+1}{k-u}\,\mathrm{C} \\ \mathrm{C}_\beta &= (2k+1)\,\frac{k-u+1}{k+u}\,\mathrm{C} \\ \mathrm{C}_\gamma &= \mathrm{C}_{\mathrm{IV}} = (2k+1)\,2\,\mathrm{C} \end{aligned}\right\} \qquad (4.20)$$

where $\mathrm{C} = 2\,(4\pi)^2\,(k+u)!\,(k-u)!\int_0^\infty g_{10}^2\, r^2\, dr \int_0^\infty g_{nk}^2\, r^2\, dr.$ (4.21)

From (4.12)

$$\left.\begin{aligned} \psi_1 &= \{2\,(k+u)\ \psi_\beta - (k-u+1)\ \psi_\gamma - (k-u+1)\ \psi_{\mathrm{IV}}\}/2\,(2k+1) \\ \psi_2 &= \{\quad 2\,\psi_\beta + \psi_\gamma + \psi_{\mathrm{IV}}\}/2\,(2k+1) \\ \psi_3 &= \{2\,(k-u)\ \psi_\alpha - (k+u+1)\ \psi_\gamma + (k+u+1)\ \psi_{\mathrm{IV}}\}/2\,(2k+1) \\ \psi_4 &= \{\quad -2\,\psi_\alpha - \psi_\gamma + \psi_{\mathrm{IV}}\}/2\,(2k+1) \end{aligned}\right\} \qquad (4.22)$$

On substituting from (4.22) in the integrals for C_1, C_2, C_3, C_4, and using (4.20), we easily obtain

$$\left.\begin{aligned} \mathrm{C}_1 &= (k-u+1)\,\mathrm{C} \qquad & \mathrm{C}_2 &= \mathrm{C}/(k+u) \\ \mathrm{C}_3 &= (k+u+1)\,\mathrm{C} \qquad & \mathrm{C}_4 &= \mathrm{C}/(k-u) \end{aligned}\right\} \qquad (4.23)$$

The a_m^{IV}'s can be read off from (4.12); and

$$\delta\mathrm{E}_1 = \delta\mathrm{E}_3, \qquad \delta\mathrm{E}_2 = \delta\mathrm{E}_4 \qquad (4.24)$$

since only the n's and j's of the two orbits are concerned.

5. *Calculation of Matrix-Components.*

We now calculate S_{aa}, etc., and from them and (4.22) deduce $S_{mm'}$. We require $\boldsymbol{\sigma}\chi_a$, $\boldsymbol{\sigma}\chi_b$. Using the matrices written out by DIRAC*

$$\left.\begin{array}{ll} \sigma_x\chi_a = 0,\,0,\,0,\,1 = \chi_b\,; & \chi_a = \sigma_x\chi_b \\ \sigma_y\chi_a = 0,\,0,\,0,\,i = i\chi_b\,; & \chi_a = i\sigma_y\chi_b \\ \sigma_z\chi_a = 0,\,0,\,1,\,0 = \chi_a & \\ \sigma_z\chi_b = 0,\,0,\,0,\,-1 = -\chi_b & \end{array}\right\} \qquad (5.00)$$

Thus

$$\left.\begin{array}{l} \boldsymbol{\sigma}\chi_a = (\chi_b,\, i\chi_b,\, \chi_a) \\ \boldsymbol{\sigma}\chi_b = (\chi_a,\, -i\chi_a,\, -\chi_b) \end{array}\right\} \qquad (5.01)$$

Let

$$\mathbf{r}_0 \equiv (l,\, m,\, n). \qquad (5.02)$$

$$\gamma = \frac{2\pi e^2}{ch}, \qquad a = \frac{h^2}{4\pi^2 m e^2}, \qquad (5.03)$$

$$\mathbf{t}_1 = +\tfrac{1}{2}i\gamma^2 a^2 e^2 \left[\frac{\mathbf{r}_0}{r^2},\, \nabla_1\right], \qquad \mathbf{t}_2 = -\tfrac{1}{2}i\gamma^2 a^2 e^2 \left[\frac{\mathbf{r}_0}{r^2},\, \nabla_2\right]. \qquad (5.04)$$

Then

$$\begin{aligned} S &= T_1 + T_2 + U \\ &= (\mathbf{t}_2\,\boldsymbol{\sigma}_1) + (\mathbf{t}_1\,\boldsymbol{\sigma}_2) + \tfrac{1}{4}\gamma^2 a^2 e^2 \{(\boldsymbol{\sigma}_1\,\boldsymbol{\sigma}_2) - 3\,(\boldsymbol{\sigma}_1\mathbf{r}_0)\,(\boldsymbol{\sigma}_2\mathbf{r}_0)\}/r^3. \end{aligned} \qquad (5.05)$$

Using (5.01)

$$\left.\begin{aligned} T_1\chi_a(1)\chi_a(2) &= [t_{2x} + it_{2y}]\,\chi_b(1)\chi_a(2) + t_{2z}\chi_a(1)\chi_a(2) \\ T_1\chi_b(1)\chi_b(2) &= [t_{2x} - it_{2y}]\,\chi_a(1)\chi_b(2) - t_{2z}\chi_b(1)\chi_b(2) \\ T_1[\chi_a(1)\chi_b(2) + \chi_b(1)\chi_a(2)] &= [t_{2x} + it_{2y}]\chi_b(1)\chi_b(2) \\ &\quad + [t_{2x} - it_{2y}]\chi_a(1)\chi_a(2) + t_{2z}[\chi_a(1)\chi_b(2) - \chi_b(1)\chi_a(2)] \\ T_1[\chi_a(1)\chi_b(2) - \chi_b(1)\chi_a(2)] &= [t_{2x} + it_{2y}]\chi_b(1)\chi_b(2) \\ &\quad - [t_{2x} - it_{2y}]\chi_a(1)\chi_a(2) + t_{2z}[\chi_a(1)\chi_b(2) + \chi_b(1)\chi_a(2)] \end{aligned}\right\}, \qquad (5.06)$$

$$\left.\begin{aligned} (\boldsymbol{\sigma}_1\,\boldsymbol{\sigma}_2)\,\chi_a(1)\chi_a(2) &= \chi_a(1)\chi_a(2) \\ (\boldsymbol{\sigma}_1\,\boldsymbol{\sigma}_2)\,\chi_b(1)\chi_b(2) &= \chi_b(1)\chi_b(2) \\ (\boldsymbol{\sigma}_1\,\boldsymbol{\sigma}_2)\,\chi_a(1)\chi_b(2) &= 2\chi_b(1)\chi_a(2) - \chi_a(1)\chi_b(2) \end{aligned}\right\}, \qquad (5.07)$$

$$\left.\begin{aligned} (\boldsymbol{\sigma}_1\mathbf{r}_0)(\boldsymbol{\sigma}_2\mathbf{r}_0)\,\chi_a(1)\chi_a(2) &= (l+im)^2\,\chi_b(1)\chi_b(2) \\ &\quad + (l+im)\,n\,[\chi_a(1)\chi_b(2) + \chi_b(1)\chi_a(2)] + n^2\chi_a(1)\chi_a(2) \\ (\boldsymbol{\sigma}_1\mathbf{r}_0)(\boldsymbol{\sigma}_2\mathbf{r}_0)\,\chi_b(1)\chi_b(2) &= (l-im)^2\,\chi_a(1)\chi_a(2) \\ &\quad - (l-im)\,n\,[\chi_a(1)\chi_b(2) + \chi_b(1)\chi_a(2)] + n^2\chi_b(1)\chi_b(2) \\ (\boldsymbol{\sigma}_1\mathbf{r}_0)(\boldsymbol{\sigma}_2\mathbf{r}_0)\,\chi_a(1)\chi_b(2) &= (l^2+m^2)\,\chi_b(1)\chi_a(2) - (l+im)\,n\chi_b(1)\chi_b(2) \\ &\quad + (l-im)\,n\chi_a(1)\chi_a(2) - n^2\chi_a(1)\chi_b(2) \end{aligned}\right\}, \qquad (5.08)$$

* *Loc. cit.*, p. 614.

whence

$$\left.\begin{aligned}
&U\chi_a(1)\chi_a(2) = \frac{\gamma^2a^2e^2}{4r^3}\{(1-3n^2)\chi_a(1)\chi_a(2) \\
&\qquad -3(l+im)n[\chi_a(1)\chi_b(2)+\chi_b(1)\chi_a(2)] - 3(l+im)^2\chi_b(1)\chi_b(2)\} \\
&U\chi_b(1)\chi_b(2) = \frac{\gamma^2a^2e^2}{4r^3}\{(1-3n^2)\chi_b(1)\chi_b(2) \\
&\qquad +3(l-im)n[\chi_a(1)\chi_b(2)+\chi_b(1)\chi_a(2)] - 3(l-im)^2\chi_a(1)\chi_a(2)\} \\
&U[\chi_a(1)\chi_b(2)+\chi_b(1)\chi_a(2)] = \frac{\gamma^2a^2e^2}{4r^3}\{(-2+6n^2)[\chi_a(1)\chi_b(2)+\chi_b(1)\chi_a(2)] \\
&\qquad -6(l-im)n\chi_a(1)\chi_a(2)+6(l+im)n\chi_b(1)\chi_b(2)\} \\
&U[\chi_a(1)\chi_b(2)-\chi_b(1)\chi_a(2)] = 0
\end{aligned}\right\}. \quad (5.09)$$

We can now deal with the summations over the spin co-ordinates, and express $S_{\alpha\alpha}$, etc., in terms of ordinary integrals. It is unnecessary to consider T_2, since by symmetry it gives the same results as T_1, and

$$S_{mm'} = 2\,T_{1\,mm'} + U_{mm'} \quad . \quad . \quad . \quad (5.10)$$

We shall use such symbols as

$$[F]'_{\alpha\beta} \equiv \int \overline{[\phi_0^0(1)\,\phi_k^{u-1}(2) - \phi_0^0(2)\,\phi_k^{u-1}(1)]}\,F\,.\,[\phi_0^0(1)\,\phi_k^{u+1}(2) - \phi_0^0(2)\,\phi_k^{u+1}(1)]\,d\tau_1\,d\tau_2. \quad (5.11)$$

That is, $[F]'_{\alpha\beta}$ is the same as $F_{\alpha\beta}$, except that the spin factors in the wave-functions are replaced by unity, and there is no summation.

Then by (5.06), (4.10),

$$\left.\begin{aligned}
&T_{1\,\alpha\beta} = 0, \quad T_{1\,\gamma\gamma} = 0, \quad T_{1\,IV\,IV} = 0, \quad T_{1\,\gamma\,IV} = 2\,[t_{2z}]'_{\gamma\,IV} \\
&T_{1\,\beta\gamma} = [t_{2x}+it_{2y}]'_{\beta\gamma}, \quad T_{1\,\beta\,IV} = -[t_{2x}+it_{2y}]'_{\beta\,IV}, \quad T_{1\,\alpha\alpha} = -[t_{2z}]'_{\alpha\alpha} \\
&T_{1\,\gamma\alpha} = [t_{2x}+it_{2y}]'_{\gamma\alpha}, \quad T_{1\,IV\,\alpha} = [t_{2x}+it_{2y}]'_{IV\,\alpha}, \quad T_{1\,\beta\beta} = [t_{2z}]'_{\beta\beta}
\end{aligned}\right\}. \quad (5.12)$$

and by (5.09):

$$\left.\begin{aligned}
&U_{\alpha\,IV} = U_{\beta\,IV} = U_{\gamma\,IV} = U_{IV\,IV} = 0. \\
&U_{\alpha\beta} = -3\,\frac{\gamma^2a^2e^2}{4}\left[\frac{(l-im)^2}{r^3}\right]'_{\alpha\beta} \qquad U_{\alpha\alpha} = \frac{\gamma^2a^2e^2}{4}\left[\frac{1-3n_2}{r^3}\right]'_{\alpha\alpha} \\
&U_{\beta\gamma} = -6\,\frac{\gamma^2a^2e^2}{4}\left[\frac{(l+im)n}{r^3}\right]'_{\beta\gamma} \qquad U_{\beta\beta} = \frac{\gamma^2a^2e^2}{4}\left[\frac{1-3n^2}{r^3}\right]'_{\beta\beta} \\
&U_{\gamma\alpha} = 6\,\frac{\gamma^2a^2e^2}{4}\left[\frac{(l+im)\,n}{r^3}\right]'_{\gamma\alpha} \qquad U_{\gamma\gamma} = -4\,\frac{\gamma^2a^2e^2}{4}\left[\frac{1-3n^2}{r^3}\right]'_{\gamma\gamma}
\end{aligned}\right\}. \quad (5.13)$$

By (5.04)

$$\left.\begin{aligned}
t_{2x} &= -i\,\frac{\gamma^2a^2e^2}{2r^2}\left(m\,\frac{\partial}{\partial z_2} - n\,\frac{\partial}{\partial y_2}\right) \\
t_{2y} &= -i\,\frac{\gamma^2a^2e^2}{2r^2}\left(n\,\frac{\partial}{\partial x_2} - l\,\frac{\partial}{\partial z_2}\right) \\
t_{2z} &= -i\,\frac{\gamma^2a^2e^2}{2r^2}\left(l\,\frac{\partial}{\partial y_2} - m\,\frac{\partial}{\partial x_2}\right)
\end{aligned}\right\} \quad . \quad . \quad . \quad (5.14)$$

so that

$$\left.\begin{aligned} t_{2x} + it_{2y} &= -\frac{\gamma^2 a^2 e^2}{2r^2}\left\{(l+im)\frac{\partial}{\partial z_2} - n\left(\frac{\partial}{\partial x_2} + i\frac{\partial}{\partial y_2}\right)\right\} \\ t_{2z} &= -\frac{\gamma^2 a^2 e^2}{4r^2}\left\{(l-im)\left(\frac{\partial}{\partial x_2} + i\frac{\partial}{\partial y_2}\right) - (l+im)\left(\frac{\partial}{\delta x_2} - i\frac{\partial}{\partial y_2}\right)\right\} \end{aligned}\right\} . \quad (5.15)$$

The evaluation of the integrals implicit in (5.12), (5.13) is somewhat tedious. (5.15) is arranged to match DARWIN's formulæ :

$$\left.\begin{aligned} \left(\frac{\partial}{\partial x} + i\frac{\partial}{\partial y}\right)\mathrm{P}_k^u f(r) &= \frac{1}{2k+1}\left\{\left(\frac{\partial}{\partial r} - \frac{k}{r}\right)\mathrm{P}_{k+1}^{u+1}\right. \\ &\qquad \left. - (k-u)(k-u-1)\left(\frac{\partial}{\partial r} + \frac{k+1}{r}\right)\mathrm{P}_{k-1}^{u+1}\right\} f(r) \\ \left(\frac{\partial}{\partial x} - i\frac{\partial}{\partial y}\right)\mathrm{P}_k^u f(r) &= \frac{1}{2k+1}\left\{-\left(\frac{\partial}{\partial r} - \frac{k}{r}\right)\mathrm{P}_{k+1}^{u-1}\right. \\ &\qquad \left. + (k+u)(k+u-1)\left(\frac{\partial}{\partial r} + \frac{k+1}{r}\right)\mathrm{P}_{k-1}^{u-1}\right\} f(r) \\ \frac{\partial}{\partial z}\mathrm{P}_k^u f(r) &= \frac{1}{2k+1}\left\{\left(\frac{\partial}{\partial r} - \frac{k}{r}\right)\mathrm{P}_{k+1}^{u}\right. \\ &\qquad \left. + (k+u)(k-u)\left(\frac{\partial}{\partial r} + \frac{k+1}{r}\right)\mathrm{P}_{k-1}^{u}\right\} f(r) \end{aligned}\right\} . \quad (5.20)$$

We expand $1/r^3$, $1/r^5$, in terms of Legendre polynomials. If γ be the angle between the vectors $\mathbf{r}_1$, $\mathbf{r}_2$,

$$\left.\begin{aligned} 1/r^3 &= (r_1^2 - 2r_1 r_2 \cos\gamma + r_2^2)^{-3/2} = \sum_{n=0}^{\infty} \mathrm{A}_n \mathrm{P}_n(\cos\gamma) \\ 1/r^5 &= (r_1^2 - 2r_1 r_2 \cos\gamma + r_2^2)^{-5/2} = \sum_{n=0}^{\infty} \mathrm{B}_n \mathrm{P}_n(\cos\gamma) \end{aligned}\right\} \quad . \; . \; . \quad (5.21)$$

where the functions A_n, B_n, depend on r_1, r_2, only. They have singularities at $r_1 = r_2$, which, however, occur in harmless combinations in our integrals.

We expand further

$$\begin{aligned} \mathrm{P}_n(\cos\gamma) &= \mathrm{P}_n(\cos\theta_1\cos\theta_2 + \sin\theta_1\sin\theta_2\cos\overline{\phi_1 - \phi_2}) \\ &= \sum_{u=-n}^{+n} \frac{\mathrm{P}_n^u(\theta_1\phi_1)\,\mathrm{P}_n^u(\theta_2\phi_2)}{(n-u)!\,(n+u)!} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5.22) \end{aligned}$$

Only a few terms of the expansions (5.21), (5.22) are relevant to each integral. The first selection is made by the integrals with respect to ϕ_1, ϕ_2. These two variables occur only in exponentials such as $e^{\iota u\phi_1}$, and all terms for which these exponentials do not cancel contribute nothing to the integral. Thus each term in the rest of the integrand selects one term of (5.22) with the appropriate u. It always turns out that the rest of the integrand involves ϕ_1 and ϕ_2 in the form $e^{\iota u(\phi_1-\phi_2)}$. Were the coefficients of ϕ_1 and ϕ_2 in the exponent not equal and opposite no selection from (5.22) could produce a non-vanishing integral. This is exactly what happens when we work out a matrix-component of S involving one of the group of four wave-functions (4.10) and a function from another group with a different u. The treatment by separate groups is thus justified.

Having adjusted the ϕ-integrations, we are left with integrations in θ_1, θ_2, of the forms

$$\int_0^\pi \dot{P}_k^u \dot{P}_n^u \sin\theta\, d\theta, \quad \begin{cases} \int_0^\pi \dot{P}_k^u \dot{P}_n^{u\pm1} \sin^2\theta\, d\theta, \\ \int_0^\pi \dot{P}_k^u \dot{P}_n^u \cos\theta \sin\theta\, d\theta, \end{cases} \quad \begin{cases} \int_0^\pi \dot{P}_k^u \dot{P}_n^{u\pm2} \sin^3\theta\, d\theta, \\ \int_0^\pi \dot{P}_k^u \dot{P}_n^{u\pm1} \cos\theta \sin^2\theta\, d\theta, \end{cases}$$

where the dots denote omission of the factor containing ϕ. These are special cases of the integral of the product of three tesseral harmonics, the upper suffix of one being the sum of the upper suffixes of the other two. Such integrals are studied in the appendix. In the first case quoted above, the integral vanishes unless $n = k$; in the next two we must have $n = k \pm 1$; and in the next two $n = k$ or $k \pm 2$. Thus only a few terms of (5.21) are relevant.

The integrations with respect to r_1, r_2, we leave for the moment, and use the notation

$$\left.\begin{aligned} (0\,k\,|\,\mathrm{F}\,|\,0\,k) &\equiv \int g_{10}(r_1)\, g_{nk}(r_2)\, \mathrm{F}\, g_{10}(r_1)\, g_{nk}(r_2)\,.\, r_1^2\, dr_1\, r_2^2\, dr_2 \\ (0\,k\,|\,\mathrm{F}\,|\,k\,0) &\equiv \int g_{nk}(r_1)\, g_{10}(r_2)\, \mathrm{F}\, g_{10}(r_1)\, g_{nk}(r_2)\,.\, r_1^2\, dr_1\, r_2^2\, dr_2 \end{aligned}\right\} \quad (5.23)$$

etc.

We give one example of the application of the rules set forth above to the integrations with respect to θ_1, θ_2, ϕ_1, ϕ_2. For the other integrals the result alone is quoted.

By (5.15), (5.20)

$$\begin{aligned}
(t_{2x} + it_{2y})\,\psi_\beta' = \\
-\frac{\gamma^2 a^2 e^2}{2r^3} \Big\{ & [r_1 \sin\theta_1\, e^{\iota\phi_1} - r_2 \sin\theta_2 e^{\iota\phi_2}] \Big[\left(\frac{\partial}{\partial r_2} - \frac{k}{r_2}\right) \mathrm{P}_{k+1}^{u-1}(2) \\
& \quad + (k+u-1)(k-u+1) \left(\frac{\partial}{\partial r_2} + \frac{k+1}{r_2}\right) \mathrm{P}_{k-1}^{u-1}(2) \Big] g_{nk}(2)\, \phi_0^0(1) \\
& - [r_1 \cos\theta_1 - r_2 \cos\theta_2] \Big[\left(\frac{\partial}{\partial r_2} - \frac{k}{r_2}\right) \mathrm{P}_{k+1}^{u}(2) \\
& \quad - (k-u+1)(k-u) \left(\frac{\partial}{\partial r_2} + \frac{k+1}{r_2}\right) \mathrm{P}_{k-1}^{u}(2) \Big] g_{nk}(2)\, \phi_0^0(1) \\
& - [r_1 \sin\theta_1 e^{\iota\phi_1}] \frac{\partial}{\partial r_2} \mathrm{P}_1^0(2)\, g_{10}(2)\, \phi_k^{u-1}(1) \\
& + [r_1 \cos\theta_1] \frac{\partial}{\partial r_2} \mathrm{P}_1^1(2)\, g_{10}(2)\, \phi_k^{u-1}(1) \Big\} \quad (5.30)
\end{aligned}$$

Multiply (5.30) by $\overline{\psi_\gamma'}$ and integrate, with due regard to the principles detailed above.

$$[t_{2x} + it_{2y}]'_{\beta\gamma} =$$

$$- \frac{\gamma^2 a^2 e^2}{2} (2k+1) \int g_{10}(1)\, \overline{\mathrm{P}_k^u(2)}\, g_{nk}(2) \Big\{ \Big[r_1 \sin\theta_1 e^{\iota\phi_1} \mathrm{P}_{k+1}^{u-1}(2) \frac{\mathrm{A}_1 \overline{\mathrm{P}_1^1(1)}\, \mathrm{P}_1^1(2)}{2\,!}$$

$$- r_2 \sin\theta_2 e^{\iota\phi_2} \mathrm{P}_{k+1}^{u-1}(2)\, \mathrm{A}_0 - r_1 \cos\theta_1 \mathrm{P}_{k+1}^u(2)\, \mathrm{A}_1 \mathrm{P}_1^0(1)\, \mathrm{P}_1^0(2)$$

$$+ r_2 \cos\theta_2 \mathrm{P}_{k+1}^u(2)\, \mathrm{A}_0 \Big] \left(\frac{\partial}{\partial r_2} - \frac{k}{r_2} \right)$$

$$+ \Big[r_1 \sin\theta_1 e^{\iota\phi_1} \mathrm{P}_{k-1}^{u-1}(2) \frac{\mathrm{A}_1 \overline{\mathrm{P}_1^1(1)}\, \mathrm{P}_1^1(2)}{2\,!} - r_2 \sin\theta_2 e^{\iota\phi_2} \mathrm{P}_{k-1}^{u-1} \mathrm{A}_0 \Big]$$

$$\times (k+u-1)(k-u+1) \left(\frac{\partial}{\partial r_2} + \frac{k+1}{r_2} \right)$$

$$+ [r_1 \cos\theta_1 \mathrm{P}_{k-1}^u(2)\, \mathrm{A}_1 \mathrm{P}_1^0(1)\, \mathrm{P}_1^0(2) - r_2 \cos\theta_2 \mathrm{P}_{k-1}^u(2)\, \mathrm{A}_0]$$

$$\times (k-u+1)(k-u) \left(\frac{\partial}{\partial r_2} + \frac{k+1}{r_2} \right) \Big\} g_{nk}(2)\, g_{10}(1)\, d\tau_1\, d\tau_2$$

$$- \frac{\gamma^2 a^2 e^2}{2} (2k+1)^2 \int g_{10}(1)\, \overline{\mathrm{P}_k^u(2)}\, g_{nk}(2) \Big\{ - r_1 \sin\theta_1 e^{\iota\phi_1} \mathrm{P}_1^0(2)\, \mathrm{P}_k^{u-1}(1)$$

$$\times \left[\frac{\mathrm{A}_{k-1} \overline{\mathrm{P}_{k-1}^u(1)}\, \mathrm{P}_{k-1}^u(2)}{(k+u-1)\,!\,(k-u-1)\,!} + \frac{\mathrm{A}_{k+1} \overline{\mathrm{P}_{k+1}^u(1)}\, \mathrm{P}_{k+1}^u(2)}{(k+u+1)\,!\,(k-u+1)\,!} \right]$$

$$+ r_1 \cos\theta_1 \mathrm{P}_1^1(2)\, \mathrm{P}_k^{u-1}(1) \left[\frac{\mathrm{A}_{k-1} \overline{\mathrm{P}_{k-1}^{u-1}(1)}\, \mathrm{P}_{k-1}^{u-1}(2)}{(k+u-2)\,!\,(k-u)\,!} \right.$$

$$\left. + \frac{\mathrm{A}_{k+1} \overline{\mathrm{P}_{k+1}^{u-1}(1)}\, \mathrm{P}_{k+1}^{u-1}(2)}{(k+u)\,!\,(k-u+2)\,!} \right] \Big\} \frac{\partial}{\partial r_2} g_{10}(2)\, g_{nk}(1)\, d\tau_1\, d\tau_2$$

$$+ \frac{\gamma^2 a^2 e^2}{2} (2k+1) \int g_{10}(2)\, \overline{\mathrm{P}_k^u(1)}\, g_{nk}(1) \Big\{ \Big[r_1 \sin\theta_1 e^{\iota\phi_1} \mathrm{P}_{k+1}^{u-1}(2) \frac{\mathrm{A}_{k+1} \mathrm{P}_{k+1}^{u-1}(1)\, \overline{\mathrm{P}_{k+1}^{u-1}(2)}}{(k+u)\,!\,(k-u+2)\,!}$$

$$- r_2 \sin\theta_2 e^{\iota\phi_2} \mathrm{P}_{k+1}^{u-1}(2) \frac{\mathrm{A}_k \mathrm{P}_k^u(1)\, \overline{\mathrm{P}_k^u(2)}}{(k+u)\,!\,(k-u)\,!} - r_1 \cos\theta_1 \mathrm{P}_{k+1}^{u-1}(2) \frac{\mathrm{A}_{k+1} \mathrm{P}_{k+1}^u(1)\, \overline{\mathrm{P}_{k+1}^u(2)}}{(k+u+1)\,!\,(k-u+1)\,!}$$

$$+ r_2 \cos\theta_2 \mathrm{P}_{k+1}^u(2) \frac{\mathrm{A}_k \mathrm{P}_k^u(1)\, \overline{\mathrm{P}_k^u(2)}}{(k+u)\,!\,(k-u)\,!} \Big] \left(\frac{\partial}{\partial r_2} - \frac{k}{r_2} \right)$$

$$+ \Big[r_1 \sin\theta_1 e^{\iota\phi_1} \mathrm{P}_{k-1}^{u-1}(2) \frac{\mathrm{A}_{k+1} \mathrm{P}_{k-1}^{u-1}(1)\, \overline{\mathrm{P}_{k+1}^{u-1}(2)}}{(k+u-2)\,!\,(k-u)\,!}$$

$$- r_2 \sin\theta_2 e^{\iota\phi_2} \mathrm{P}_{k-1}^{u-1}(2) \frac{\mathrm{A}_k \mathrm{P}_k^u(1)\, \overline{\mathrm{P}_k^u(2)}}{(k+u)\,!\,(k-u)\,!} \Big] (k+u-1)(k-u+1) \left(\frac{\partial}{\partial r_2} + \frac{k+1}{r_2} \right)$$

$$+ \Big[r_1 \cos\theta_1 \mathrm{P}_{k-1}^u(2) \frac{\mathrm{A}_{k-1} \mathrm{P}_{k-1}^u(1)\, \overline{\mathrm{P}_{k-1}^u(2)}}{(k+u-1)\,!\,(k-u-1)\,!}$$

$$- r_2 \cos\theta_2 \mathrm{P}_{k-1}^u(2) \frac{\mathrm{A}_k \mathrm{P}_k^u(1)\, \overline{\mathrm{P}_k^u(2)}}{(k+u)\,!\,(k-u)\,!} \Big] (k-u+1)(k-u) \left(\frac{\partial}{\partial r_2} + \frac{k+1}{r_2} \right) \Big\} g_{nk}(2)\, g_{10}(1)\, d\tau_1 d\tau_2$$

$$+\frac{\gamma^2 a^2 e^2}{2}(2k+1)^2\int g_{10}(2)\,\overline{P_k^u(1)}\,g_{nk}(1)\left\{-r_1\sin\theta_1 P_1^0(2)\,P_k^{u-1}(1)\,A_1 P_1^0(1)\,\overline{P_1^0(2)}\right.$$
$$\left.+r_1\cos\theta_1 P_1^1(2)\,P_k^{u-1}(1)\frac{A_1 P_1^1(1)\,\overline{P_1^1(2)}}{2\,!}\right\}\frac{\partial}{\partial r_2}g_{10}(2)\,g_{nk}(1)\,d\tau_1\,d\tau_2. \quad (5.31)$$

On carrying out the $\theta_1\ \phi_1$ integrations, (5.31) reduces to

$$[t_{2x}+it_{2y}]'_{\beta\gamma}=-\frac{\gamma^2a^2e^2}{2}(4\pi)^2\,(k+u)\,!\,(k-u+1)\,!\left\{(2k+1)\left(0\,k\left|\tfrac{1}{3}\frac{r_1}{r_2}A_1-A_0\right|0\,k\right)\right.$$
$$+\left(k\,0\left|\left\{\frac{A_{k-1}}{2k-1}-\frac{A_{k+1}}{2k+3}\right\}r_1\frac{\partial}{\partial r_2}\right|0\,k\right)-\left(0\,k\left|\left\{\frac{A_{k-1}}{2k-1}-\frac{A_{k+1}}{2k+3}\right\}r_1\frac{\partial}{\partial r_2}\right.\right.$$
$$\left.\left.+\frac{k+1}{2k-1}\frac{r_1}{r_2}A_{k-1}-A_k+\frac{k}{2k+3}\frac{r_1}{r_2}A_{k+1}\right|k\,0\right)\right\}. \quad (5.32)$$

The last integral in (5.31) vanishes.

$[t_{2x}+it_{2y}]'_{\beta\,\mathrm{IV}}$ is given by (5.31) with the signs of the last two integrals changed. This reduces to (5.32) with the sign of the last term changed. $[t_{2x}+it_{2y}]'_{\gamma\alpha}$ and $[t_{2x}+it_{2y}]'_{\mathrm{IV}\,\alpha}$ are obtained from $[t_{2x}+it_{2y}]'_{\beta\gamma}$ and $[t_{2x}+it_{2y}]'_{\beta\,\mathrm{IV}}$ respectively by replacing u by $u+1$.

$[t_{2z}]'_{\alpha\alpha}$ requires the calculation of an expression similar to (5.31), which reduces to

$$[t_{2z}]'_{\alpha\alpha}=\frac{\gamma^2a^2e^2}{2}(4\pi)^2\,(u+1)\,(k+u+1)!\,(k-u-1)!\left\{(2\,k+1)\left(0\,k\left|\tfrac{1}{3}\frac{r_1}{r_2}A_1-A_0\right|0\,k\right)\right.$$
$$+\left(k\,0\left|\left\{\frac{A_{k-1}}{2k-1}-\frac{A_{k+1}}{2k+3}\right\}r_1\frac{\partial}{\partial r_2}\right|0\,k\right)-\left(0\,k\left|\left\{\frac{A_{k-1}}{2k-1}-\frac{A_{k+1}}{2k+3}\right\}r_1\frac{\partial}{\partial r_2}\right.\right.$$
$$\left.\left.+\frac{k+1}{2k-1}\frac{r_1}{r_2}A_{k-1}-A_k+\frac{k}{2k+3}\frac{r_1}{r_2}A_{k+1}\right|k\,0\right)\right\}. \quad (5.33)$$

For $[t_{2z}]'_{\beta\beta}$ we replace $u+1$ by $u-1$; and for $[t_{2z}]'_{\gamma\,\mathrm{IV}}$ we replace $u+1$ by u and change the sign of the last term.

Thus by (5.12)

$$\left.\begin{array}{llll}
2T_{1\,\alpha\beta}=0 & 2T_{1\,\gamma\gamma}=0 & 2T_{1\,\mathrm{IV\,IV}}=0 & 2T_{1\,\gamma\,\mathrm{IV}}=2u\,\mathbf{T}' \\
2T_{1\,\beta\gamma}=-(k-u+1)\,\mathbf{T} & 2T_{1\,\beta\,\mathrm{IV}}=(k-u+1)\,\mathbf{T}' & 2T_{1\,\alpha\alpha}=-\dfrac{k+u+1}{k-u}(u+1)\,\mathbf{T} & \\
2T_{1\,\gamma\alpha}=-(k+u+1)\,\mathbf{T} & 2T_{1\,\mathrm{IV}\,\alpha}=-(k+u+1)\,\mathbf{T}' & 2T_{1\,\beta\beta}=\dfrac{k-u+1}{k+u}(u-1)\,\mathbf{T} &
\end{array}\right\}, \quad (5.34)$$

where

$$\left.\begin{aligned}\mathbf{T} = \gamma^2 a^2 e^2 (4\pi)^2 (k+u)!\,(k-u)!\,\Big\{ (2k+1)\Big(0\,k\Big|\tfrac{1}{3}\frac{r_1}{r_2}\mathrm{A}_1 - \mathrm{A}_0\Big|\,0\,k\Big) \\ + \Big(k\,0\Big|\Big\{\frac{\mathrm{A}_{k-1}}{2k-1} - \frac{\mathrm{A}_{k+1}}{2k+3}\Big\} r_1 \frac{\partial}{\partial r_2}\Big|\,0\,k\Big) - \Big(0\,k\Big|\Big\{\frac{\mathrm{A}_{k-1}}{2k-1} - \frac{\mathrm{A}_{k+1}}{2k+3}\Big\} r_1 \frac{\partial}{\partial r_2} \\ + \frac{k+1}{2k-1}\frac{r_1}{r_2}\mathrm{A}_{k-1} - \mathrm{A}_k + \frac{k}{2k+3}\frac{r_1}{r_2}\mathrm{A}_{k+1}\Big|\,k\,0\Big)\Big\} \\ \mathbf{T}' = \gamma^2 a^2 e^2 (4\pi)^2 (k+u)!\,(k-u)!\,\Big\{ (2k+1)\Big(0\,k\Big|\tfrac{1}{3}\frac{r_1}{r_2}\mathrm{A}_1 - \mathrm{A}_0\Big|\,0\,k\Big) \\ + \Big(k\,0\Big|\Big\{\frac{\mathrm{A}_{k-1}}{2k-1} - \frac{\mathrm{A}_{k+1}}{2k+3}\Big\} r_1 \frac{\partial}{\partial r_2}\Big|\,0\,k\Big) + \Big(0\,k\Big|\Big\{\frac{\mathrm{A}_{k-1}}{2k-1} - \frac{\mathrm{A}_{k+1}}{2k+3}\Big\} r_1 \frac{\partial}{\partial r_2} \\ + \frac{k+1}{2k-1}\frac{r_1}{r_2}\mathrm{A}_{k-1} - \mathrm{A}_k + \frac{k}{2k+3}\frac{r_1}{r_2}\mathrm{A}_{k+1}\Big|\,k\,0\Big)\Big\}\end{aligned}\right\}. \quad (5.35)$$

U is treated in the same way. (5.13) then becomes:

$$\mathrm{U}_{\alpha\,\mathrm{IV}} = \mathrm{U}_{\beta\,\mathrm{IV}} = \mathrm{U}_{\gamma\,\mathrm{IV}} = \mathrm{U}_{\mathrm{IV}\,\mathrm{IV}} = 0.$$

$$\left.\begin{aligned}\mathrm{U}_{\alpha\beta} &= (k+u+1)(k-u+1)\,\mathbf{U} \\ \mathrm{U}_{\beta\gamma} &= -(k-u+1)\,(2u-1)\,\mathbf{U} \\ \mathrm{U}_{\gamma\alpha} &= (k+u+1)\,(2u+1)\,\mathbf{U} \\ \mathrm{U}_{\alpha\alpha} &= -\frac{k+u+1}{k-u}\{\tfrac{1}{3}k(k+1) - (u+1)^2\}\,\mathbf{U} \\ \mathrm{U}_{\beta\beta} &= -\frac{k-u+1}{k+u}\{\tfrac{1}{3}k(k+1) - (u-1)^2\}\,\mathbf{U} \\ \mathrm{U}_{\gamma\gamma} &= 4\,\{\tfrac{1}{3}k(k+1) - u^2\}\,\mathbf{U}\end{aligned}\right\}, \quad \ldots \quad (5.40)$$

where

$$\mathbf{U} = 3\gamma^2 a^2 e^2 \frac{(k+u)!\,(k-u)!}{(2k-1)(2k+3)}\Big\{(2k+1)(0\,k\,|\,\tfrac{1}{5}\mathrm{B}_2 r_1^2 - \tfrac{2}{3}\mathrm{B}_1 r_1 r_2 + \mathrm{B}_0 r_2^2\,|\,0\,k) + \Big(0\,k\Big|\frac{2k+3}{2k-1}\mathrm{B}_{k-1} r_1 r_2 - \mathrm{B}_k(r_1^2 + r_2^2) + \frac{2k-1}{2k+3}\mathrm{B}_{k+1} r_1 r_2\Big|\,k\,0\Big)\Big\}. \quad (5.41)$$

We now make use of (4.22) to find $2\mathrm{T}_{1\,mm'}$ and $\mathrm{U}_{mm'}$. Thus:

$$2\mathrm{T}_{1\,11} = \frac{1}{(2k+1)^2}\{(k+u)^2\, 2\mathrm{T}_{1\,\beta\beta} - (k+u)(k-u+1)\, 2\mathrm{T}_{1\,\beta\gamma} - (k+u)(k-u+1)\, 2\mathrm{T}_{1\,\beta\,\mathrm{IV}} + \tfrac{1}{2}(k-u+1)^2\, 2\mathrm{T}_{1\,\gamma\,\mathrm{IV}}\}$$

(the other terms vanishing)

$$= \frac{1}{(2k+1)^2}\{(k+u)(k-u+1)(u-1)\,\mathbf{T} + (k+u)(k-u+1)^2\,\mathbf{T} - (k+u)(k-u+1)^2\,\mathbf{T}' + (k-u+1)^2\,u\mathbf{T}'\}$$

(by (5.34))

$$= \frac{(k-u+1)\,k}{(2k+1)^2}\{(k+u)\,\mathbf{T} - (k-u+1)\,\mathbf{T}'\}$$

Similarly

$$\left.\begin{array}{ll}
2\mathrm{T}_{1\,22} = \dfrac{k+1}{(2k+1)^2}\left\{-\dfrac{k-u+1}{k+u}\,\mathbf{T}+\mathbf{T}'\right\} & \\
2\mathrm{T}_{1\,33} = \dfrac{(k+u+1)\,k}{(2k+1)^2}\left\{(k-u)\,\mathbf{T}-(k+u+1)\,\mathbf{T}'\right\} & \\
2\mathrm{T}_{1\,44} = \dfrac{k+1}{(2k+1)^2}\left\{-\dfrac{k+u+1}{k-u}\,\mathbf{T}+\mathbf{T}'\right\} & \\
2\mathrm{T}_{1\,12} = \dfrac{k-u+1}{2\,(2k+1)^2}\left\{\mathbf{T}+\mathbf{T}'\right\} & 2\mathrm{T}_{1\,34} = \dfrac{k+u+1}{2\,(2k+1)^2}\left\{\mathbf{T}+\mathbf{T}'\right\} \\
2\mathrm{T}_{1\,13} = \dfrac{(k+u+1)\,(k-u+1)\,k}{(2k+1)^2}\left\{\mathbf{T}+\mathbf{T}'\right\} & 2\mathrm{T}_{1\,24} = \dfrac{k+1}{(2k+1)^2}\left\{\mathbf{T}+\mathbf{T}'\right\} \\
2\mathrm{T}_{1\,14} = -\dfrac{(k-u+1)}{2\,(2k+1)^2}\left\{\mathbf{T}+\mathbf{T}'\right\} & 2\mathrm{T}_{1\,23} = \dfrac{k+u+1}{2\,(2k+1)^2}\left\{\mathbf{T}+\mathbf{T}'\right\}
\end{array}\right\} \quad . \quad (5.50)$$

and in the same way

$$\left.\begin{array}{l}
\mathrm{U}_{11} = \tfrac{1}{3}\,\dfrac{(k-u+1)\,(2u-1)\,k\,(2k-1)}{(2k+1)^2}\,\mathbf{U}, \\
\mathrm{U}_{22} = -\tfrac{1}{3}\,\dfrac{(2u-1)\,(k+1)\,(2k+3)}{(k+u)\,(2k+1)^2}\,\mathbf{U}, \\
\mathrm{U}_{33} = -\tfrac{1}{3}\,\dfrac{(k+u+1)\,(2u+1)\,k\,(2k-1)}{(2k+1)^2}\,\mathbf{U}, \\
\mathrm{U}_{44} = \tfrac{1}{3}\,\dfrac{(2u+1)\,(k+1)\,(2k+3)}{(k-u)\,(2k+1)^2}\,\mathbf{U}, \\
\mathrm{U}_{12} = -\tfrac{1}{6}\,\dfrac{(k-u+1)\,(2k-1)\,(2k+3)}{(2k+1)^2}\,\mathbf{U}, \\
\mathrm{U}_{34} = -\tfrac{1}{6}\,\dfrac{(k+u+1)\,(2k-1)\,(2k+3)}{(2k+1)^2}\,\mathbf{U}, \\
\mathrm{U}_{13} = \tfrac{2}{3}\,\dfrac{(k+u+1)\,(k-u+1)\,k\,(2k-1)}{(2k+1)^2}\,\mathbf{U}, \\
\mathrm{U}_{24} = -\tfrac{2}{3}\,\dfrac{(k+1)\,(2k+3)}{(2k+1)^2}\,\mathbf{U}, \\
\mathrm{U}_{14} = -\tfrac{1}{6}\,\dfrac{(k-u+1)\,(2k-1)\,(2k+3)}{(2k+1)^2}\,\mathbf{U}, \\
\mathrm{U}_{23} = \tfrac{1}{6}\,\dfrac{(k+u+1)\,(2k-1)\,(2k+3)}{(2k+1)^2}\,\mathbf{U},
\end{array}\right\} \quad . \quad . \quad . \quad . \quad (5.51)$$

$\mathrm{S}_{mm'}$ can now be written down by (5.10).

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

6. *The Triplet Separations.*

$C_m a_m^{IV} \equiv$	$-(k-u+1)\,C$	C	$(k+u+1)\,C$	C
$\Delta \equiv$	$(k-u+1)\,C\,(\delta E^{\mu}-\delta E_1)$ $-(k-u+1)\,k\,\frac{(k+u)\,\mathbf{T}-(k-u+1)\,\mathbf{T}'}{(2k+1)^2}$ $-(k-u+1)(2u-1)\,2k\,(2k-1)\,\frac{\mathbf{U}}{6\,(2k+1)^2}$	$(k-u+1)\,\frac{\mathbf{T}+\mathbf{T}'}{2\,(2k+1)^2}$ $+(k-u+1)(2k-1)(2k+3)\,\frac{\mathbf{U}}{6\,(2k+1)^2}$	$-(k+u+1)(k-u+1)\,k\,\frac{\mathbf{T}+\mathbf{T}'}{(2k+1)^2}$ $-4\,(k+u+1)(k-u+1)\,k\,(2k-1)\,\frac{\mathbf{U}}{6\,(2k+1)^2}$	$(k-u+1)\,\frac{\mathbf{T}+\mathbf{T}'}{2\,(2k+1)^2}$ $+(k-u+1)(2k-1)(2k+3)\,\frac{\mathbf{U}}{6\,(2k+1)^2}$
	$(k-u+1)\,\frac{\mathbf{T}+\mathbf{T}'}{2\,(2k+1)^2}$ $+(k-u+1)(2k-1)(2k+3)\,\frac{\mathbf{U}}{6\,(2k+1)^2}$	$\frac{C}{k+u}\,(\delta E^{\mu}-\delta E_2)$ $+\frac{k+1}{k+u}\,\frac{(k-u+1)\,\mathbf{T}-(k+u)\,\mathbf{T}'}{(2k+1)^2}$ $+\frac{(2u-1)(2k+2)(2k+3)}{k+u}\,\frac{\mathbf{U}}{6\,(2k+1)^2}$	$-(k+u+1)\,\frac{\mathbf{T}+\mathbf{T}'}{2\,(2k+1)^2}$ $-(k+u+1)(2k-1)(2k+3)\,\frac{\mathbf{U}}{6\,(2k+1)^2}$	$-(k+1)\,\frac{\mathbf{T}+\mathbf{T}'}{(2k+1)^2}$ $+4\,(k+1)(2k+3)\,\frac{\mathbf{U}}{6\,(3k+1)^2}$
	$-(k+u+1)(k-u+1)\,k\,\frac{\mathbf{T}+\mathbf{T}'}{(2k+1)^2}$ $-4\,(k+u+1)(k-u+1)\,k\,(2k-1)\,\frac{\mathbf{U}}{6\,(2k+1)^2}$	$-(k+u+1)\,\frac{\mathbf{T}+\mathbf{T}'}{2\,(2k+1)^2}$ $-(k+u+1)(2k-1)(2k+3)\,\frac{\mathbf{U}}{6\,(2k+1)^2}$	$(k+u+1)\,C\,(\delta E^{\mu}-\delta E_1)$ $-(k+u+1)\,k\,\frac{(k-u)\,\mathbf{T}-(k+u+1)\,\mathbf{T}'}{(2k+1)^2}$ $+(k+u+1)(2u+1)\,2k\,(2k-1)\,\frac{\mathbf{U}}{6\,(2k+1)^2}$	$-(k+u+1)\,\frac{\mathbf{T}+\mathbf{T}'}{2\,(2k+1)^2}$ $-(k+u+1)(2k-1)(2k+3)\,\frac{\mathbf{U}}{6\,(2k+1)^2}$
	$(k-u+1)\,\frac{\mathbf{T}+\mathbf{T}'}{2\,(2k+1)^2}$ $+(k-u+1)(2k-1)(2k+3)\,\frac{\mathbf{U}}{6\,(2k+1)^2}$	$-(k+1)\,\frac{\mathbf{T}+\mathbf{T}'}{(2k+1)^2}$ $+4\,(k+1)(2k+3)\,\frac{\mathbf{U}}{6\,(2k+1)^2}$	$-(k+u+1)\,\frac{\mathbf{T}+\mathbf{T}'}{2\,(2k+1)^2}$ $-(k+u+1)(2k-1)(2k+3)\,\frac{\mathbf{U}}{6\,(2k+1)^2}$	$\frac{C}{k-u}\,(\delta E^{\mu}-\delta E_2)$ $+\frac{k+1}{k-u}\,\frac{(k+u+1)\,\mathbf{T}-(k-u)\,\mathbf{T}'}{(2k+1)^2}$ $-\frac{(2u+1)(2k+2)(2k+3)}{k-u}\,\frac{\mathbf{U}}{6\,(2k+1)^2}$ (6.00)

Above are given the values of $C_m \, a_m^{IV}$ ($m = 1, 2, 3, 4$), read off from (4.12) and (4.23), and the determinant Δ defined in § 3. The three values of δE^{μ} (μ = I, II, III) are the roots of the equation (3.9). It can be verified at once that the second and fourth columns of the determinant in this equation are proportional when

$$\delta E^{I} = \delta E_1 + \frac{k\,\mathbf{T}}{(2k+1)\,C} + \frac{k\,(2k-1)\,\mathbf{U}}{3\,(2k+1)\,C}. \quad \ldots \ldots \quad (6.10)$$

Similarly the third and fifth columns are equal when

$$\delta E^{III} = \delta E_2 - \frac{(k+1)\,\mathbf{T}}{(2k+1)\,C} + \frac{(k+1)\,(2k+3)\,\mathbf{U}}{3\,(2k+1)\,C}. \quad \ldots \ldots \quad (6.11)$$

It is now more convenient to write the determinant thus :

$$\Delta = \begin{vmatrix} (k-u+1)\,C\,(\delta E^{\mu} - \delta E^{I}) + (k-u+1)^2\,P & (k-u+1)\,Q & -(k-u+1)\,(k+u+1)\,P & (k-u+1)\,Q \\ (k-u+1)\,Q & \dfrac{C}{k+u}\,(\delta E^{\mu} - \delta E^{III}) + R & -(k+u+1)\,Q & R \\ -(k-u+1)\,(k+u+1)\,P & -(k+u+1)\,Q & (k+u+1)\,C\,(\delta E^{\mu} - \delta E^{I}) + (k+u+1)^2\,P & -(k+u+1)\,Q \\ (k-u+1)\,Q & R & -(k+u+1)\,Q & \dfrac{C}{k-u}\,(\delta E^{\mu} - \delta E^{III}) + R \end{vmatrix}$$

(6.12)

where

$$\left.\begin{aligned} P &\equiv k\,\frac{\mathbf{T}+\mathbf{T}'}{(2k+1)^2} + 4k\,(2k-1)\,\frac{\mathbf{U}}{6\,(2k+1)^2} \\ Q &\equiv \tfrac{1}{2}\,\frac{\mathbf{T}+\mathbf{T}'}{(2k+1)^2} + (2k-1)\,(2k+3)\,\frac{\mathbf{U}}{6\,(2k+1)^2} \\ R &\equiv -(k+1)\,\frac{\mathbf{T}+\mathbf{T}'}{(2k+1)^2} + 4\,(k+1)\,(2k+3)\,\frac{\mathbf{U}}{6\,(2k+1)^2} \end{aligned}\right\} \quad . \; . \quad (6.13)$$

The equation (3.9) reduces, by division of the first row and column by C, the second by $-(k-u+1)$, and the fourth by $(k+u+1)$, to :

$$\begin{vmatrix} 0 & 1 & 1 & 1 & 1 \\ 1 & \frac{C(\delta E^{\mu}-\delta E^{I})}{k-u+1}+P & -Q & P & -Q \\ 1 & -Q & \frac{C(\delta E^{\mu}-\delta E^{III})}{k+u}+R & -Q & R \\ 1 & P & -Q & \frac{C(\delta E^{\mu}-\delta E^{I})}{k+u+1}+P & -Q \\ 1 & -Q & R & -Q & \frac{C(\delta E^{\mu}-\delta E^{III})}{k-u}+R \end{vmatrix} = 0. \qquad (6.14)$$

The coefficient of $(\delta E^{\mu})^3$ is

$$-\frac{2(2k+1)C^3}{(k-u+1)(k+u)(k+u+1)(k-u)}. \qquad (6.15)$$

The coefficient of $(\delta E^{\mu})^2$ is

$$\frac{C^2\{C\delta E^{I}\,.\,2(3k+1)+C\delta E^{III}\,.\,2(3k+2)-(2Q+P+R)\,4k(k+1)\}}{(k-u+1)(k+u)(k+u+1)(k-u)}. \qquad (6.16)$$

Thus

$$\sum_{\mu=I,II,III} \delta E^{\mu} = \frac{3k+1}{2k+1}\delta E^{I} + \frac{3k+2}{2k+1}\delta E^{III} - \frac{2k(k+1)}{(2k+1)C}(2Q+P+R) \quad . \;.\; . \qquad (6.17)$$

and

$$\delta E^{II} = \frac{k}{2k+1}\delta E^{I} + \frac{k+1}{2k+1}\delta E^{III} - \frac{2k(k+1)}{(2k+1)C}\mathbf{U} \quad . \;.\; . \qquad (6.18)$$

$$= \frac{k}{2k+1}\delta E_1 + \frac{k+1}{2k+1}\delta E_2 - \frac{\mathbf{T}}{(2k+1)C} - \frac{(2k+1)(2k+3)}{3(2k+1)C}\mathbf{U}, \qquad (6.19)$$

(6.10), (6.11), (6.19) give the fine structure of the triplet.

We now consider combinations with the normal state. For terms I and III, Δ vanishes, having two rows proportional. Hence by (3.7)

$$X_{I\,0} = X_{III\,0} = 0, \quad . \;.\; . \qquad (6.20)$$

For μ = II, the following determinants are easily evaluated:

$$\Delta = (k-u+1)^2(k+u+1)^2 \begin{vmatrix} \frac{C(\delta E^{II}-\delta E^{I})}{k-u+1}+P & -Q & P & -Q \\ -Q & \frac{C(\delta E^{II}-\delta E^{III})}{k+u}+R & -Q & R \\ P & -Q & \frac{C(\delta E^{II}-\delta E^{I})}{k+u+1}+P & -Q \\ -Q & R & -Q & \frac{C(\delta E^{II}-\delta E^{III})}{k-u}+R \end{vmatrix}$$

$$= \frac{(k-u+1)(k+u+1)}{(k-u)(k+u)}(\delta E^{II}-\delta E^{I})(\delta E^{II}-\delta E^{III})C^2\{(\delta E^{II}-\delta E^{I})(\delta E^{II}-\delta E^{III})C^2$$
$$+(\delta E^{II}-\delta E^{I})CR\,.\,2k+(\delta E^{II}-\delta E^{III})CP\,.\,2(k+1)+(PR-Q^2)4k(k+1)\}$$

$$= \frac{(k-u+1)(k+u+1)}{(k-u)(k+u)}k(k+1)(\delta E^{II}-\delta E^{I})(\delta E^{II}-\delta E^{III})C^4$$
$$\times\left\{\left(\frac{\delta E^{II}-\delta E^{I}}{k+1}+2P/C\right)\left(\frac{\delta E^{II}-\delta E^{III}}{k}+2R/C\right)-4Q^2/C\right\}$$

$$= \frac{(k-u+1)(k+u+1)}{(k-u)(k+u)}k(k+1)(\delta E^{II}-\delta E^{I})(\delta E^{II}-\delta E^{III})C^4$$
$$\times\left\{\left(\frac{\delta E^{III}-\delta E^{I}}{2k+1}+\frac{2Q+2(k+1)P-2kR}{(2k+1)C}-2Q/C\right)\right.$$
$$\left.\times\left(\frac{\delta E^{I}-\delta E^{III}}{2k+1}-\frac{2Q+2(k+1)P-2kR}{(2k+1)C}-2Q/C\right)-4Q^2/C^2\right\}$$

$$= -\frac{(k-u+1)(k+u+1)}{(k-u)(k+u)}\frac{k(k+1)}{(2k+1)^2}(\delta E^{II}-\delta E^{I})(\delta E^{II}-\delta E^{III})C^4(\delta E_1-\delta E_2-\mathbf{T}'/C)^2. \quad \ldots\ldots (6.21)$$

$$\left.\begin{aligned} \Sigma C_{m'}a_{m'}^{IV}\Delta_{1m'} &= -\frac{(k-u+1)(k+u+1)}{(k-u)(k+u)}(\delta E^{II}-\delta E^{I})(\delta E^{II}-\delta E^{III})C^3 \\ &\qquad\times\{(\delta E^{II}-\delta E^{III})C+(R+Q)2k\} \\ &= -\frac{(k-u+1)(k+u+1)}{(k-u)(k+u)}\frac{k}{2k+1}(\delta E^{II}-\delta E^{I})(\delta E^{II}-\delta E^{III})C^4 \\ &\qquad\times\{\delta E_1-\delta E_2-\mathbf{T}'/C\} \\ \Sigma C_{m'}a_{m'}^{IV}\Delta_{3m'} &\text{ is the same but for sign.} \\ \Sigma C_{m'}a_{m'}^{IV}\Delta_{2m'} &= -\frac{(k-u+1)(k+u+1)}{k-u}\frac{k+1}{2k+1}(\delta E^{II}-\delta E^{I})(\delta E^{II}-\delta E^{III})C^4 \\ &\qquad\times\{\delta E_1-\delta E_2-\mathbf{T}'/C\} \\ \Sigma C_{m'}a_{m'}^{IV}\Delta_{4m'} &= -\frac{(k-u+1)(k+u+1)}{k+u}\frac{k+1}{2k+1}(\delta E^{II}-\delta E^{I})(\delta E^{II}-\delta E^{III})C^4 \\ &\qquad\times\{\delta E_1-\delta E_2-\mathbf{T}'/C\} \end{aligned}\right\} . \quad (6.22)$$

Hence by (3.7)

$$a_1^{\mathrm{II}} = ka^{\mathrm{II}};\; a_2^{\mathrm{II}} = (k+u)(k+1)\,a^{\mathrm{II}};\; a_3^{\mathrm{II}} = -ka^{\mathrm{II}};\; a_4^{\mathrm{II}} = (k-u)(k+1)\,a^{\mathrm{II}}, \quad (6.23)$$

where

$$a^{\mathrm{II}} \equiv \frac{2k+1}{k(k+1)} \frac{\mathrm{X}_{\mathrm{II}\,0}}{\mathrm{X}_{\mathrm{IV}\,0}} \frac{\Delta\mathrm{E}^{\mathrm{IV}} - \Delta\mathrm{E}^{\mathrm{II}}}{\delta\mathrm{E}_1 - \delta\mathrm{E}_2 - \mathbf{T}'/\mathrm{C}}. \quad (6.24)$$

The wave-function ψ_{II} is thus determined. The integral of its square is, by (6.23) and (4.23).

$$\mathrm{C}_{\mathrm{II}} = \{k^2(k-u+1)\,\mathrm{C} + (k+1)^2(k+u)\,\mathrm{C} + k^2(k+u+1)\,\mathrm{C} + (k+1)^2(k-u)\,\mathrm{C}\}\,a^{\mathrm{II}\,2}$$

$$= 2k(k+1)(2k+1)\,\mathrm{C}\,a^{\mathrm{II}\,2}$$

$$= \frac{2(2k+1)^3}{k(k+1)} \left[\frac{\mathrm{X}_{\mathrm{II}\,0}}{\mathrm{X}_{\mathrm{IV}\,0}} \frac{\Delta\mathrm{E}^{\mathrm{IV}} - \Delta\mathrm{E}^{\mathrm{II}}}{\delta\mathrm{E}_1 - \delta\mathrm{E}_2 - \mathbf{T}'/\mathrm{C}}\right]^2 \mathrm{C} \quad \ldots \quad (6.25)$$

By (4.12), (4.23)

$$\mathrm{C}_{\mathrm{IV}} = 2(2k+1)\,\mathrm{C} \quad \ldots \quad (6.26)$$

so that

$$\frac{\mathrm{X}^2_{\mathrm{II}\,0}}{\mathrm{C}_{\mathrm{II}}} : \frac{\mathrm{X}^2_{\mathrm{IV}\,0}}{\mathrm{C}_{\mathrm{IV}}} = \frac{k(k+1)}{(2k+1)^2} \left[\frac{\delta\mathrm{E}_1 - \delta\mathrm{E}_2 - \mathbf{T}'/\mathrm{C}}{\Delta\mathrm{E}^{\mathrm{IV}} - \Delta\mathrm{E}^{\mathrm{II}}}\right]^2. \quad \ldots \quad (6.27)$$

If there are an equal number of atoms in state II and state IV (6.27) should give approximately the ratio of the intensities of the lines II → 0 and IV → 0.

7. *Numerical Values.*

We now calculate $\mathbf{T}$, $\mathbf{T}'$, $\mathbf{U}$. It may be pointed out here that $\mathbf{T}/\mathrm{C}$, $\mathbf{T}'/\mathrm{C}$, $\mathbf{U}/\mathrm{C}$, are all independent of u; so that the results of the last section are independent of this quantum number, as might be expected. The first step is to evaluate the combinations of A's and B's which occur in (5.35), (5.41). We shall use μ for $\cos\gamma$, and $r_{\mathrm{max.}}$, $r_{\mathrm{min.}}$ for the greater and less of r_1, r_2.

Multiply the first equation (5.21) by $\frac{1}{2}[\mathrm{P}_{k-1}(\mu) - \mathrm{P}_{k+1}(\mu)]$ and integrate.

$$\frac{\mathrm{A}_{k-1}}{2k-1} - \frac{\mathrm{A}_{k+1}}{2k+3} = \frac{1}{2}\int_{-1}^{1} \frac{\mathrm{P}_{k-1}(\mu) - \mathrm{P}_{k+1}(\mu)}{(r_1^2 - 2r_1r_2\,\mu + r_2^2)^{3/2}}\,d\mu$$

$$= \frac{1}{2}\left[\frac{\mathrm{P}_{k-1}(\mu) - \mathrm{P}_{k+1}(\mu)}{r_1r_2\,(r_1^2 - 2r_1\,r_2\,\mu + r_2^2)^{1/2}}\right]_{-1}^{1} - \frac{1}{2r_1r_2}\int_{-1}^{1} \frac{\mathrm{P}'_{k-1}(\mu) - \mathrm{P}'_{k+1}(\mu)}{(r_1^2 - 2r_1r_2\,\mu + r_2^2)^{1/2}}\,d\mu$$

$$= \frac{1}{r_1r_2}\int_{-1}^{1} \frac{\frac{1}{2}(2k+1)\,\mathrm{P}_k(\mu)}{(r_1 - 2r_1r_2\,\mu + r_2^2)^{1/2}}\,d\mu = \frac{r_{\mathrm{min.}}^{k-1}}{r_{\mathrm{max.}}^{k+2}}. \quad \ldots \quad (7.00)$$

Similarly

$$\frac{k+1}{2k-1}\frac{r_1}{r_2}\mathrm{A}_{k-1}-\mathrm{A}_k+\frac{k}{2k+3}\frac{r_1}{r_2}\mathrm{A}_{k+1}$$

$$=\tfrac{1}{2}\int_{-1}^{1}\frac{(k+1)\frac{r_1}{r_2}\mathrm{P}_{k-1}(\mu)-(2k+1)\mathrm{P}_k(\mu)+k\frac{r_1}{r_2}\mathrm{P}_{k+1}(\mu)}{(r_1^2-2r_1r_2\,\mu+r_2^2)^{3/2}}d\mu$$

$$=\tfrac{1}{2}\int_{-1}^{1}\frac{\frac{r_1}{r_2}[\mathrm{P}_{k-1}(\mu)-\mathrm{P}_{k+1}(\mu)]+\left[\frac{r_1}{r_2}\mu-1\right](2k+1)\mathrm{P}_k(\mu)}{(r_1^2-2r_1r_2\,\mu+r_2^2)^{3/2}}d\mu$$

$$=\frac{r_1}{r_2}\frac{r_{\text{min.}}^{k-1}}{r_{\text{max.}}^{k+2}}+\frac{1}{r_2}\frac{\partial}{\partial r_2}\int_{-1}^{1}\frac{\tfrac{1}{2}(2k+1)\mathrm{P}_k(\mu)}{(r_1^2-2r_1r_2\,\mu+r_2^2)^{1/2}}d\mu$$

$$=\frac{1}{r_2^2}\frac{r_{\text{min.}}^{k}}{r_{\text{max.}}^{k+1}}+\frac{1}{r_2}\frac{\partial}{\partial r_2}\frac{r_{\text{min.}}^{k}}{r_{\text{max.}}^{k+1}} \quad \ldots \quad (7.01)$$

By an integration by parts:

$$\left(k\,0\left|\left\{\frac{\mathrm{A}_{k-1}}{2k-1}-\frac{\mathrm{A}_{k+1}}{2k+3}\right\}r_1\frac{\partial}{\partial r_2}\right|0\,k\right)+\left(0\,k\left|\left\{\frac{\mathrm{A}_{k-1}}{2k-1}-\frac{\mathrm{A}_{k+1}}{2k+3}\right\}r_1\frac{\partial}{\partial r_2}\right|k\,0\right)$$

$$=-\left(0\,k\left|\frac{r_1}{r_2^2}\frac{\partial}{\partial r_2}\left\{\frac{r_2^2\mathrm{A}_{k-1}}{2k-1}-\frac{r_2^2\mathrm{A}_{k+1}}{2k+3}\right\}\right|k\,0\right) \quad \ldots \quad (7.02)$$

and by (7.00)

$$\frac{r_1}{r_2^2}\frac{\partial}{\partial r_2}\left\{\frac{r_2^2\mathrm{A}_{k-1}}{2k-1}-\frac{r_2^2\mathrm{A}_{k+1}}{2k+3}\right\}=\frac{r_1}{r_2^2}\frac{\partial}{\partial r_2}\left(\frac{r_2}{r_1}\frac{r_{\text{min.}}^{k}}{r_{\text{max.}}^{k+1}}\right)=\frac{1}{r_2^2}\frac{r_{\text{min.}}^{k}}{r_{\text{max.}}^{k+1}}+\frac{1}{r_2}\frac{\partial}{\partial r_2}\frac{r_{\text{min.}}^{k}}{r_{\text{max.}}^{k+1}}. \quad (7.03)$$

Substituting the last four formulæ in (5.35),

$$\left.\begin{aligned}\mathbf{T}&=\gamma^2a^2e^2(4\pi)^2(k+u)!\,(k-u)!\left\{(2k+1)\left(0\,k\left|\tfrac{1}{3}\frac{r_1}{r_2}\mathrm{A}_1-\mathrm{A}_0\right|0\,k\right)\right.\\&\qquad\left.+2\left(k\,0\left|\frac{r_{\text{min.}}^{k}}{r_{\text{max.}}^{k+1}}\frac{1}{r_2}\frac{\partial}{\partial r_2}\right|0\,k\right)\right\}\\\mathbf{T}'&=\gamma^2a^2e^2(4\pi)^2(k+u)!\,(k-u)!\,(2k+1)\left(0\,k\left|\tfrac{1}{3}\frac{r_1}{r_2}\mathrm{A}_1-\mathrm{A}_0\right|0\,k\right)\end{aligned}\right\}. \quad (7.04)$$

Also

$$\tfrac{1}{3}\frac{r_1}{r_2}\mathrm{A}_1-\mathrm{A}_0=\tfrac{1}{2}\int_{-1}^{1}\frac{\frac{r_1}{r_2}\mathrm{P}_1(\mu)-\mathrm{P}_0(\mu)}{(r_1^2-2r_1r_2\mu+r_2^2)^{3/2}}d\mu$$

$$=\frac{1}{2r_2}\frac{\partial}{\partial r_2}\int_{-1}^{1}\frac{d\mu}{(r_1^2-2r_1r_2\mu+r_2^2)^{1/2}}$$

$$=\frac{1}{r_2}\frac{\partial}{\partial r_2}\frac{1}{r_{\text{max.}}}=\left\{\begin{array}{ll}0 & \text{if } r_1>r_2\\ -\dfrac{1}{r_2^3} & \text{if } r_1<r_2\end{array}\right\}. \quad \ldots \quad (7.05)$$

In the expression for $\mathbf{U}$ we have

$$\frac{2k+3}{2k-1} B_{k-1} r_1 r_2 - B_k (r_1^2 + r_2^2) + \frac{2k-1}{2k+3} B_{k+1} r_1 r_2$$

$$= \tfrac{1}{2} \int_{-1}^{1} \frac{(2k+3) P_{k-1}(\mu) r_1 r_2 - (2k+1) P_k(\mu)(r_1^2 + r_2^2) + (2k-1) P_{k+1}(\mu) r_1 r_2}{(r_1^2 - 2r_1 r_2 \mu + r_2^2)^{5/2}} d\mu$$

$$= \tfrac{1}{2} \int_{-1}^{1} \frac{3r_1 r_2 [P_{k-1}(\mu) - P_{k+1}(\mu)] - (2k+1) P_k(\mu)(r_1^2 - 2r_1 r_2 \mu + r_2^2)}{(r_1^2 - 2r_1 r_2 \mu + r_2^2)^{5/2}} d\mu$$

$$= \tfrac{1}{2} \left[\frac{P_{k-1}(\mu) - P_{k+1}(\mu)}{(r_1^2 - 2r_1 r_2 \mu + r_2^2)^{3/2}} \right]_{-1}^{1} - \tfrac{1}{2} \int_{-1}^{1} \frac{P'_{k-1}(\mu) - P'_{k+1}(\mu) + (2k+1) P_k(\mu)}{(r_1^2 - 2r_1 r_2 + r_2^2)^{3/2}} d\mu$$

$$= 0 \qquad (7.10)$$

so that

$$\mathbf{U} = 3\gamma^2 a^2 e^2 \frac{(k+u)!\,(k-u)!}{(2k-1)(2k+3)} (2k+1) (0\,k \,|\, \tfrac{1}{5} B_2 r_1^2 - \tfrac{2}{3} B_1 r_1 r_2 + B_0 r_2^2 \,|\, 0\,k), \qquad (7.11)$$

where

$$\tfrac{1}{5} B_2 r_1^2 - \tfrac{2}{3} B_1 r_1 r_2 + B_0 r_2^2$$

$$= \tfrac{1}{2} \int_{-1}^{1} \frac{P_2(\mu) r_1^2 - 2 P_1(\mu) r_1 r_2 + P_0(\mu) r_2^2}{(r_1^2 - 2r_1 r_2 \mu + r_2^2)^{5/2}} d\mu$$

$$= \tfrac{1}{2} r_1^2 \left[\frac{P_2(\mu) - P_0(\mu)}{3r_1 r_2 (r_1^2 - 2r_1 r_2 \mu + r_2^2)^{3/2}} \right]_{-1}^{1} - \tfrac{1}{2} \int_{-1}^{1} \frac{\frac{r_1}{r_2} P_1(\mu) - 1}{(r_1^2 - 2r_1 r_2 + r_2^2)^{3/2}} d\mu$$

$$= \begin{Bmatrix} 0 & \text{if } r_1 > r_2 \\ \dfrac{1}{r_2^3} & \text{if } r_1 < r_2 \end{Bmatrix} \qquad (7.12)$$

as in (7.05).

It will now be assumed that the orbits, (1, 0) and (n, k), are well separated; in other words that g_{10} is small where g_{nk} is large, and vice versa. Then the second term in $\mathbf{T}$ will be small compared with the first, and $\mathbf{T} = \mathbf{T}'$ nearly. Also since the (n, k) orbit is larger than the (1, 0) orbit, $g_{10}(1)^2 g_{nk}(2)^2$ is negligible for $r_1 > r_2$, so that with regard to (7.05), (7.12) we may put

$$-\left(0\,k \,\middle|\, \tfrac{1}{3} \frac{r_1}{r_2} A_1 - A_0 \,\middle|\, 0\,k\right) = (0\,k \,|\, \tfrac{1}{5} B_2 r_1^2 - \tfrac{2}{3} B_1 r_1 r_2 + B_0 r_2^2 \,|\, 0\,k)$$

$$\sim \int_0^\infty \frac{1}{r_2^3} g_{nk}(r_2)^2 r_2^2 \, dr_2 \int_0^\infty g_{10}(r_1)^2 r_1^2 \, dr_1. \qquad (7.20)$$

Strictly, the limits for r_1 should be 0 and r_2. Using (4.21), (7.04), (7.11):

$$-\mathbf{T}'/C = \frac{(2k-1)(2k+3)}{3C} \mathbf{U} \sim \frac{\gamma^2 a^2 e^2}{2} (2k+1) \int_0^\infty \frac{1}{r^3} g_{nk}(r)^2 r^2 \, dr \Big/ \int_0^\infty g_{nk}(r)^2 r^2 dr. \qquad (7.21)$$

We can get a fairly good estimate of (7.21) by taking g_{nk} to be the radial part of the wave-function in a Coulomb field $(Z-1)\,e/r$, where Ze is the charge on the nucleus. That is :

$$g_{nk}(r) \backsim r^k \exp\left(-\frac{Z-1}{na}r\right) L_{n+k}^{2k+1}\left(\frac{Z-1}{na}2r\right), \quad \ldots\ldots \quad (7.22)$$

so that

$$-\mathbf{T}'/C \simeq \frac{\gamma^2 a^2 e^2}{2}(2k+1)\left(\frac{Z-1}{na}2\right)^3 \int_0^\infty x^{2k-1} e^{-x} L_{n+k}^{2k+1}(x)^2\,dx \Big/ \int_0^\infty x^{2k+2} e^{-x} L_{n+k}^{2k+1}(x)^2\,dx. \quad (7.23)$$

The integrals in (7.23) are found by a method published by SCHRÖDINGER* and extended by WALLER.† The integral in the numerator is

$$\text{the coefficient of } \frac{(ts)^{n-k-1}}{(n+k)!^2} \text{ in } (2k-1)!\,\frac{(1-t)^{-2}(1-s)^{-2}}{(1-ts)^{2k}},$$

$$i.e.,\ (n+k)!^2\,(2k-1)! \times \text{the coefficient of } y^{n-k-1} \text{ in } \frac{\sum_{r=0}^{\infty}(r+1)^2 y^r}{(1-y)^{2k}}$$

$$\text{,,} \qquad \text{,,} \qquad \text{,,} \qquad \text{,,} \qquad \text{,,}\ (1-y)^{-2k}\frac{d}{dy}\frac{y}{(1-y)^2}$$

$$\text{,,} \qquad \text{,,} \qquad \text{,,} \qquad \text{,,} \qquad \text{,,}\ (1-y)^{-2k-2} + 2y(1-y)^{-2k-3}$$

$$= (n+k)!^2\,(2k-1)!\left\{\frac{(n+k)!}{(2k+1)!\,(n-k-1)!} + \frac{2\,.\,(n+k)!}{(2k+2)!\,(n-k-2)!}\right\}$$

$$= \frac{(n+k)!^3\,n}{(n-k-1)!\,2k\,(k+1)\,(2k+1)}. \quad (7.24)$$

Similarly the denominator of (7.23) is

$$\frac{(n+k)!^3\,2n}{(n-k-1)!}. \quad \ldots\ldots\ldots\ldots \quad (7.25)$$

Therefore

$$-\mathbf{T}'/C = \frac{(2k-1)(2k+3)}{3}\mathbf{U}/C \sim \left(\frac{Z-1}{n}\right)^3 \frac{\gamma^2 e^2}{a}\frac{1}{k(k+1)} = mc^2\frac{(Z-1)^3\gamma^4}{n^3 k(k+1)}. \quad (7.26)$$

The difference between δE_1 and δE_2 is the spin-doublet separation belonging to the (n, k) orbit. Their respective (DIRAC) j's are $-k-1$ and k, so that—again assuming a screened Coulomb field—

$$\left.\begin{aligned} \delta E_1 &= \delta\varepsilon - \tfrac{1}{2}mc^2\frac{(Z-1)^4\gamma^4}{n^3(k+1)} \\ \delta E_2 &= \delta\varepsilon - \tfrac{1}{2}mc^2\frac{(Z-1)^4\gamma^4}{n^3 k} \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (7.30)$$

We are not concerned with the value of $\delta\varepsilon$.

* SCHRÖDINGER, 'Ann. Physik,' vol. 80, p. 437 (1926).

† WALLER, 'Z. Physik,' vol. 38, p. 635 (1926).

Thus by (6.10), (6.19), (6.11), using **T**′ for **T**

$$\left.\begin{aligned}\delta E^{I} &= \delta\varepsilon - mc^2\frac{(Z-1)^3\gamma^4}{n^3k(k+1)}\left\{\frac{Z-1}{2}k+\frac{k}{2k+1}-\frac{k}{(2k+1)(2k+3)}\right\}\\ \delta E^{II} &= \delta\varepsilon - mc^2\frac{(Z-1)^3\gamma^4}{n^3k(k+1)}\left\{\frac{Z-1}{2}\,\frac{k^2+(k+1)^2}{2k+1}-\frac{1}{2k+1}+\frac{1}{2k+1}\right\}\\ \delta E^{III} &= \delta\varepsilon - mc^2\frac{(Z-1)^3\gamma^4}{n^3k(k+1)}\left\{\frac{Z-1}{2}(k+1)-\frac{k+1}{2k+1}-\frac{k+1}{(2k-1)(2k+1)}\right\}\end{aligned}\right\} . \quad (7.31)$$

The values of the brackets in (7.31) are given for $k=1$, and $Z=2$ and 3, and $Z\to\infty$

	$Z=2,\ k=1$	$Z=3,\ k=1$	$Z\to\infty,\ k=1$
I	$\frac{1}{2}+\frac{1}{3}-\frac{1}{15}=\frac{23}{30}$	$1+\frac{1}{3}-\frac{1}{15}=\frac{19}{15}$	$\frac{1}{2}Z$
II	$\frac{5}{6}-\frac{1}{3}+\frac{1}{3}=\frac{25}{30}$	$\frac{5}{3}-\frac{1}{3}+\frac{1}{3}=\frac{25}{15}$	$\frac{5}{6}Z$
III	$1-\frac{2}{3}-\frac{2}{3}=-\frac{10}{30}$	$2-\frac{2}{3}-\frac{2}{3}=\frac{10}{15}$	Z

(7.32)

The last column gives the "normal" structure of the triplet. The other two columns show that the P-terms of He and Li^+ are both partly inverted, and that in the former case two terms nearly coincide. These results are illustrated diagrammatically below. The heights of the lines indicate the weights of the terms. The figures give spin separations in arbitrary units.

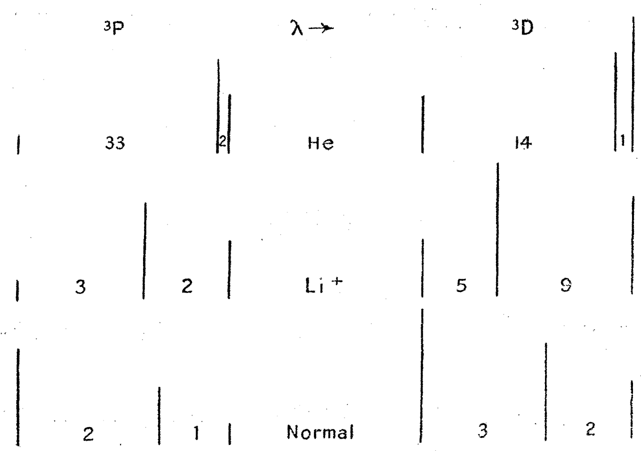

FIG. 1.

For $k=2$, the brackets in (7.31) are :—

		$Z=2$	$Z=3$
I	$\frac{Z-1}{2}\cdot 2+\frac{2}{5}-\frac{2}{35}$	$\frac{94}{70}$	$\frac{82}{35}$
II	$\frac{Z-1}{2}\cdot\frac{13}{5}-\frac{1}{5}+\frac{1}{5}$	$\frac{91}{70}$	$\frac{91}{35}$
III	$\frac{Z-1}{2}\cdot 3-\frac{3}{5}-\frac{1}{5}$	$\frac{49}{70}$	$\frac{77}{35}$

. . . (7.33)

Thus in He the D-terms are completely inverted, and spaced in the ratio 1 : 14; and in Li^+ they are partly inverted, and the spacing is 9 : 5.

The 2P-triplet of helium is the one for which the best observational data exist. It is well known that the two strongest $2\,^3P - 3\,^3S_1$ lines are scarcely resolvable, but their separation has recently been measured by HANSEN* and HOUSTON.† In this case the two orbits are too close to allow us to neglect the second term of $\mathbf{T}$ in (7.04). We make a rough calculation of $\mathbf{T}$ with wave-functions appropriate to Coulomb fields:

$$g_{10} = \exp(-2r/a), \qquad g_{21} = r\exp(-r/2a). \qquad (7.40)$$

The inner orbit is here supposed to lie in a Coulomb field with nuclear charge $2e$, while for the outer orbit the core charge is taken to be e. Then by (7.05):

$$\left(0\,k\left|\tfrac{1}{3}\frac{r_1}{r_2}A_1 - A_0\right|0\,k\right) = -\int_0^\infty\int_{r_1}^\infty \frac{1}{r_2}\exp\left(-\frac{4r_1}{a}-\frac{r_2}{a}\right) r_1^2\,dr_1\,r_2^2\,dr_2 = -\frac{16a^5}{5^4}, \qquad (7.41)$$

and

$$\left(k\,0\left|\frac{r_{\text{min.}}}{r^2_{\text{max.}}}\frac{1}{r_2}\frac{\partial}{\partial r_2}\right|0\,k\right) = \int_0^\infty\int_{r_1}^\infty \frac{r_1^2}{r_2^2}\exp\left(-\frac{5r_1}{2a}-\frac{r_2}{2a}\right)\frac{\partial}{\partial r_2}\exp\left(-\frac{2r_2}{a}\right) r_1^2\,dr_1\,r_2^2\,dr_2^2$$

$$+\int_0^\infty\int_{r_2}^\infty \frac{r_2}{r_1}\exp\left(-\frac{5r_1}{2a}-\frac{r_2}{2a}\right)\frac{\partial}{\partial r_2}\exp\left(-\frac{2r_2}{a}\right) r_2^2\,dr_2\,r_1^2\,dr_1$$

$$= -\frac{48a^5}{5^5} \qquad (7.42)$$

The integral in C is

$$\int_0^\infty \exp(-4r_1/a)\,r_1^2\,dr_1\int_0^\infty r_2^2\exp(-r/a)\,r_2^2\,dr_2 = \frac{3a^8}{4} \qquad (7.43)$$

Thus

$$\mathbf{T}/C = -\frac{\gamma^2 e^2}{a}\cdot\frac{32.7}{5^5} \qquad (7.44)$$

and using (7.41) in (7.11)

$$\mathbf{U}/C = \frac{\gamma^2 e^2}{a}\cdot\frac{32.3}{5^5}. \qquad (7.45)$$

We must make a corresponding estimate of $\delta E_1 - \delta E_2$. If V is the potential energy of the central field used for the (2, 1) orbit in an equation like (2.0), then $\delta E_1 - \delta E_2$ is the mean value over this orbit of ‡

$$-\frac{h^2 e}{16\pi^2 m^2 c^2}\frac{3}{r}\frac{\partial V}{\partial r} \qquad (7.46)$$

* HANSEN, 'Nature,' vol. 119, p. 237 (1927).

† HOUSTON, 'Proc. Nat. Acad. Sci.,' vol. 13, p. 91 (1927).

‡ DIRAC, 'Roy. Soc. Proc.,' A, vol. 117, p. 624 (1928).

If we use HARTREE's method, the best value of V for the outer orbit is (2.5)

$$V(2) = \frac{2e}{r_2} - \frac{e\int |\psi_{10}(1)|^2/r}{\int |\psi_{10}(1)|^2} = \frac{2e}{r_2} - \frac{e\int |\psi_{10}(1)|^2/r_{\max.}}{\int |\psi_{10}(1)|^2} \quad . \; . \; . \; . \quad (7.47)$$

since when we expand $1/r$ in terms of Legendre polynomials all terms but the first vanish on integration. Thus (7.46) is (with r_2 for r)

$$\frac{3\gamma^2 a^2 e^2}{4}\left\{\frac{2}{r_2^3} + \frac{1}{r_2}\frac{\partial}{\partial r_2}\frac{\int |\psi_{10}(1)|^2/r_{\max.}}{\int |\psi_{10}(1)|^2}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7.48)$$

The mean value of the first term is

$$2\int_0^\infty r_2 \exp(-r_2/a)\, dr_2 \Big/ \int_0^\infty r_2^4 \exp(-r_2/a)\, dr_2 = \frac{1}{12a^3}. \quad . \; . \; . \; . \quad (7.49)$$

The mean value of the second term is

$$-\int_0^\infty\int_0^{r_2}\frac{1}{r_2}\exp\left(-\frac{4r_1}{a}-\frac{r_2}{a}\right) r_2^2\, dr_2\, r_1^2\, dr_1 \Big/ \int_0^\infty \exp(-4r_1/a)\, r_1^2\, dr_1 \int_0^\infty r_2^4 \exp(-r_2/a)\, dr_2 = \frac{-64}{3.5^4 a^3}. \quad (7.50)$$

Therefore $$\delta E_1 - \delta E_2 = \frac{\gamma^2 e^2}{a}\left(\frac{1}{16} - \frac{16}{5^4}\right).$$

Thus from (6.10), (6.11), (6.19),

$$\left.\begin{aligned} \delta E^{I} - \delta E^{II} &= \tfrac{2}{3}(\delta E_1 - \delta E_2) + \tfrac{2}{3}\frac{\mathbf{T}}{c} + \tfrac{2}{3}\frac{\mathbf{U}}{c} = -\,0\cdot003\ \gamma^2 e^2/a \\ \delta E^{II} - \delta E^{III} &= \tfrac{1}{3}(\delta E_1 - \delta E_2) + \tfrac{1}{3}\frac{\mathbf{T}}{c} - \tfrac{5}{3}\frac{\mathbf{U}}{c} = -\,0\cdot063\ \gamma^2 e^2/a \end{aligned}\right\} \quad . \; . \quad (7.51)$$

This is an inverted triplet with two very close components.

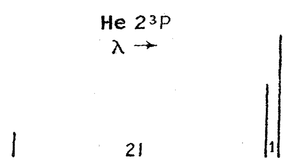

FIG. 2.

The experimental separations are :—

	$^3P_2 - {^3P_1}$	$^3P_1 - {^3P_0}$	Ratio	
HANSEN	$0\cdot075$ cm^{-1}	$0\cdot98$ cm^{-1}	13 : 1	(7.52)
HOUSTON	$0\cdot071$ cm^{-1}	$0\cdot992$ cm^{-1}	14 : 1	

The ratio of the separations in (7.51) is 21 : 1. It cannot be relied upon, for quite a small change in the relative values of the integrals involved—especially in $\delta E^{I} - \delta E^{II}$—might halve it or reverse its sign. The agreement is as good as can be expected.

HOUSTON gives a partly inverted 3D triplet, with separations 0·02 cm.$^{-1}$ and 0·06 cm.$^{-1}$. This agrees neither with the present theory nor with HEISENBERG'S.

The fine structure of the 2^3S—2^3P line of Li^+ has been investigated by SCHULER,* but as he finds no less than eleven components, comparison with the theory seems impossible.

The magnitude of the separation of the extreme components of the helium 2P triplet is given by (7.51) as 0·77 cm.$^{-1}$, as compared with HEISENBERG'S 0·62 cm.$^{-1}$, and the observed value of 1·06 cm.$^{-1}$. SUGIURA†, however, by calculating the mean value of $1/r^3$ with more accurate wave-functions, has raised HEISENBERG'S result to 0·86 cm.$^{-1}$. A similar correction would greatly improve our value.

For other Helium triplets (7.31) gives the following extreme separations.

	3P	3D	4D	
$\delta\nu$ (7.31) cm.$^{-1}$	0·25	0·046	0·02	(7.53)
$\delta\nu$ (HOUSTON)	0·286	0·08	0·04	

The calculated values are quite uncorrected, but no correction is likely to produce HOUSTON'S values for the D triplets.

For Li^+ 2P, (7.31) gives 5·8 cm.$^{-1}$, as compared with HEISENBERG'S 3·65 cm.$^{-1}$, corrected by SUGIURA to 4·25 cm.$^{-1}$. HEISENBERG gives 4·4 cm.$^{-1}$ as observed by S. WERNER (unpublished). The extreme width of SCHULER'S multiplet is 7·05 cm.$^{-1}$, but the meaning of this is doubtful.

We add an estimate of the intensity of ortho-para transitions. By (7.26), (7.30)

$$\delta E_1 - \delta E_2 - \mathbf{T}'/C = \tfrac{1}{2}mc^2 \frac{(Z-1)^3 (Z+1) \gamma^4}{n^3 k (k+1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.60)$$

If the separation between ortho- and para-terms be represented by a difference of quantum defect, $\Delta\delta$, then

$$\Delta E^{IV} - \Delta E^{II} = mc^2 \frac{(Z-1)^2 \gamma^2}{n^3} \Delta\delta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.61)$$

so that the ratio (6.27) of the probabilities of the transitions II — 0 and IV — 0 is

$$\frac{k(k+1)}{(2k+1)^2}\left[\frac{(Z^2-1)\gamma^2}{2k(k+1)\Delta\delta}\right]^2 = \frac{(Z^2-1)^2\gamma^4}{4k(k+1)(2k+1)^2\Delta\delta^2}. \quad . \quad . \quad . \quad (7.62)$$

Taking $\Delta\delta$ from HEISENBERG'S paper, we give examples of this ratio :—

	He, 2P → 1S	Li^+, 2P — 1S	
$\Delta\delta$	0·06	0·06	(7.63)
(7.62)	10^{-7}	7.10^{-7}	

Thus the line $2\,^3P_1 - 1\,^1S_0$ should be 10^{-7} as intense as the line $2\,^1P_1 - 1\,^1S_0$, and so on. Such lines are not observed.

* SCHULER, 'Ann. Physik,' vol. 76, p. 292 (1925).

† SUGIURA, 'Z. Physik,' vol. 44, p. 190 (1927).

8. *Classification and Selection Rules.*

The form of the spin-energies given by (7.31) for large Z suggests that the three terms I, II, III, have (ordinary) j's respectively equal to $k+1$, k, $k-1$. In this section we verify that the weights of the terms are $2k+3$, $2k+1$, $2k-1$, in accordance with the usual formula $2j+1$; and also that the selection rules $\Delta k = \pm 1$, $\Delta j = \pm 1, 0$, are valid to a first approximation.

The weights are governed by the fact that for certain values of u the four wave-functions in the group (4.10) reduce to three or one. In the preceding sections we have tacitly assumed that $k \geq 1$, $|u| < k$. If, however,

$$u = k + 1 \qquad (8.00)$$

we have

$$\psi_\beta = [\phi_0^0(1)\,\phi_k^k(2) - \phi_0^0(2)\,\phi_k^k(1)]\,\chi_a(1)\,\chi_a(2) = \psi_1, \qquad (8.01)$$

and the other three wave-functions of the group do not exist. The spin energy is evidently

$$\begin{aligned}\delta E &= \delta E_1 + S_{\beta\beta}/C_\beta \\ &= \delta E_1 + \frac{k}{2k+1}\frac{\mathbf{T}}{C} + \frac{k(2k-1)\,\mathbf{U}}{3(2k+1)\,C} = \delta E^{I}\end{aligned} \qquad (8.02)$$

by (4.20), (5.34), (5.40). (The factor $k-u+1$ belongs to a $0\,!$ The factor $(k-u)\,!$ must be omitted from $\mathbf{T}$, $\mathbf{U}$, C in (8.02).)

Similarly for

$$u = -k - 1 \qquad (8.10)$$

we have only

$$\psi_a = [\phi_0^0(1)\,\phi_k^{-k}(2) - \phi_0^0(2)\,\phi_k^{-k}(1)]\,\chi_b(1)\,\chi_b(2) = \psi_3 \qquad (8.11)$$

and

$$\delta E = \delta E_1 + S_{aa}/C_a = \delta E^{I} \qquad (8.12)$$

Again, with

$$u = k \qquad (k \geq 1) \qquad (8.20)$$

we have

$$\left.\begin{aligned}\psi_\beta &= [\phi_0^0(1)\,\phi_k^{k-1}(2) - \phi_0^0(2)\,\phi_k^{k-1}(1)]\,\chi_a(1)\,\chi_a(2) \\ \psi_\gamma &= [\phi_0^0(1)\,\phi_k^k(2) - \phi_0^0(2)\,\phi_k^k(1)]\,[\chi_a(1)\,\chi_b(2) + \chi_b(1)\,\chi_a(2)] \\ \psi_{IV} &= [\phi_0^0(1)\,\phi_k^k(2) + \phi_0^0(2)\,\phi_k^k(1)]\,[\chi_a(1)\,\chi_b(2) - \chi_b(1)\,\chi_a(2)]\end{aligned}\right\} \qquad (8.21)$$

but no ψ_a. (4.12) shows that these functions depend on ψ_1, ψ_2, ψ_3, alone; and, in fact, ψ_4 does not exist. The calculations of § 5 and § 7 are valid, with the omission of ψ_a and ψ_4.

The m's of § 3 are now three in number, and ΔE has a double instead of a triple root. The only modification is the omission of the last row and column from the determinants of § 6. If we multiply by $k-u$ the last column of the determinant in (6.14) and then put $u = k$, we are left with the modified determinant multiplied by the extra factor $C(\delta E^{\mu} - \delta E^{III})$. The roots of the equation with the modified determinant are thus the same as those of (6.14) with the omission of δE^{III}. That is,

$$\delta E^{\mu} = \delta E^{I} \text{ or } \delta E^{II}. \qquad (8.22)$$

The same is true for $u = -k$.

Thus the three terms arise from the following ranges of u.

$$\begin{array}{llll} \text{Term} & \text{Range of } u. & \text{Weight.} & j. \\ \text{I} \ldots\ldots & -k-1 \leq u \leq k+1 & 2k+3 & k+1 \\ \text{II} \ldots\ldots & -k \leq u \leq k & 2k+1 & k \\ \text{III} \ldots\ldots & -k+1 \leq u \leq k-1 & 2k-1 & k-1 \end{array} \qquad (8.30)$$

The multiplicities correspond with the values of j suggested.

For $k = 0$, $u = \pm 1$ gives $\delta E = \delta E_1$ as above. With $u = 0$ we have only

$$\left.\begin{aligned} \psi_{\gamma} &= [\phi^0_{10}(1)\,\phi^0_{n0}(2) - \phi^0_{10}(2)\,\phi^0_{n0}(1)]\,[\chi_a(1)\,\chi_b(2) + \chi_b(1)\,\chi_a(2)] \\ \psi_{IV} &= [\phi^0_{10}(1)\,\phi^0_{n0}(2) + \phi^0_{10}(2)\,\phi^0_{n0}(1)]\,[\chi_a(1)\,\chi_b(2) - \chi_b(1)\,\chi_a(2)] \end{aligned}\right\}, \qquad (8.31)$$

where the principal quantum numbers have been inserted to distinguish between the ϕ's. By (4.12)

$$\left.\begin{aligned} \psi_{\gamma} &= -\psi_1 - \psi_3 \\ \psi_{IV} &= -\psi_1 + \psi_3 \end{aligned}\right\}. \qquad (8.32)$$

By (5.34) (5.40)

$$S_{\gamma\gamma} = S_{\gamma\, IV} = S_{IV\, IV} = 0, \qquad (8.33)$$

so that evidently

$$\delta E = \delta E_1.$$

Thus the triplet has reduced to a single term of weight 3 — the well-known $^3S_1$. The para-term is a $^1S_0$.

In order to discuss the selection rules it is necessary to write down the wave-functions ψ_I, ψ_{II}, ψ_{III}, corresponding to the three terms of the triplet. The coefficients a^{μ}_m obey the five equations (3.6), (3.8). For I and III the right-hand side of (3.6) vanishes, by (6.20). We then have five homogeneous equations with the coefficients set out in (6.00). For I, the coefficients of $a_1{}^{I}$, $a_3{}^{I}$ in all these equations are in the ratio $-(k-u+1)$ to $(k+u+1)$; so the solution is

$$a_1{}^{I} : k+u+1 = a_3{}^{I} : k-u+1 ; \quad a_2{}^{I} = a_4{}^{I} = 0. \qquad (8.40)$$

For III, the coefficients of $a_2{}^{III}$, $a_4{}^{III}$, are equal in all the equations; so

$$a_2{}^{III} = -a_4{}^{III} ; \; a_1{}^{III} = a_3{}^{III} = 0, \qquad (8.41)$$

$a_m{}^{II}$ is given by (6.23).

In each wave-function there is an arbitrary multiplier which is chosen to suit our convenience.

$$\left.\begin{aligned} \psi_{\mathrm{I}} &= (k+u+1)(2k+1)\,\psi_1 + (k-u+1)(2k+1)\,\psi_3 \\ \psi_{\mathrm{II}} &= k\psi_1 + (k+u)(k+1)\,\psi_2 - k\psi_3 + (k-u)(k+1)\,\psi_4 \\ \psi_{\mathrm{III}} &= (2k+1)\,\psi_2 - (2k+1)\,\psi_4 \end{aligned}\right\} . \quad (8.42)$$

Using (4.22),

$$\left.\begin{aligned} \psi_{\mathrm{I}} &= (k-u+1)(k-u)\,\psi_\alpha + (k+u+1)(k+u)\,\psi_\beta - (k+u+1)(k-u+1)\,\psi_\gamma \\ \psi_{\mathrm{II}} &= -(k-u)\,\psi_\alpha + (k+u)\,\psi_\beta + u\,\psi_\gamma \\ \psi_{\mathrm{III}} &= \psi_\alpha + \psi_\beta + \psi_\gamma \end{aligned}\right\} . \quad (8.43)$$

As many of these equations as are relevant are true for the incomplete groups.

It is sufficient to consider radiation polarised parallel to the z-axis, for which we require the matrix-components of $z_1 + z_2$. We shall restrict ourselves to states in which only one electron is excited, the excited orbits in the two states being specified by n, k, u; n', k', u'. Dashes will be used throughout to distinguish the final state.

We write

$$Z_{\mathrm{I\,I'}} \equiv \int \bar{\psi}_{\mathrm{I'}} (z_1 + z_2)\, \psi_{\mathrm{I}}, \text{ etc.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.50)$$

The integrals most easy to calculate are $Z_{\alpha\alpha'}$, etc. Thus

$$Z_{\alpha\alpha'} = 2\int \overline{\phi_0^0(1)\,\phi_{k'}^{u'+1}(2)}\,(r_1\cos\theta_1 + r_2\cos\theta_2)\,\phi_0^0(1)\,\phi_k^{u+1}(2)\,d\tau_1\,d\tau_2$$

$$- 2\int \overline{\phi_0^0(1)\,\phi_{k'}^{u'+1}(2)}\,(r_1\cos\theta_1 + r_2\cos\theta_2)\,\phi_0^0(2)\,\phi_k^{u+1}(1)\,d\tau_1\,d\tau_2 . \quad . \quad . \quad (8.51)$$

The integrations with respect to ϕ_1, ϕ_2, vanish unless

$$u' = u. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.52)$$

The θ_1-, θ_2- integrations then vanish unless

$$k' = k \pm 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.53)$$

The second integral in (8.51) vanishes unless k or k' is 0, the other being 1. We shall leave aside the exceptional case involving $^3S_1$, and suppose $k' = k+1$, $k \geq 1$. Then

$$Z_{\alpha\alpha'} = 2(2k+1)(2k+3)\int g_{10}(1)\, g_{n'k+1}(2)\, \overline{P_{k+1}^{u+1}(2)}\,(r_1\cos\theta_1 + r_2\cos\theta_2)\; g_{10}(1)\, g_{nk}(2)\, P_k^{u+1}(2)\, d\tau_1\, d\tau_2$$

$$= 2(4\pi)^2 (k+u+2)!\,(k-u)!\int_0^\infty g_{10}^2 r^2\,dr \int_0^\infty g_{n'k+1} g_{nk} r \,.\, r^2\,dr. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.54)$$

$Z_{\beta\beta'}$, $Z_{\gamma\gamma'}$ require the same selection-rules, and are similarly calculated. $Z_{\alpha\beta'}$, etc., vanish owing to the spin factors. Thus

$$Z_{\alpha\alpha'} = (k+u+2)(k+u+1)\zeta\ ; \ Z_{\beta\beta'} = (k-u+2)(k-u+1)\zeta\ ;$$
$$Z_{\gamma\gamma'} = 2(k+u+1)(k-u+1)\zeta \quad . \ . \ . \ . \quad (8.55)$$

where

$$\zeta = 2(4\pi)^2 (k+u)!\ (k-u)! \int_0^\infty g_{10}^2 r^2\, dr \int_0^\infty g_{n'k+1} g_{nk} r \,.\, r^2\, dr. \quad . \ . \ . \quad (8.56)$$

Now (8.43) gives :

$$Z_{\mathrm{I\,I'}} = (k-u+1)(k-u)(k'-u'+1)(k'-u')Z_{\alpha\alpha'}$$
$$+ (k+u+1)(k+u)(k'+u'+1)(k'+u')Z_{\beta\beta'}$$
$$+ (k+u+1)(k-u+1)(k'+u'+1)(k'-u'+1)Z_{\gamma\gamma'}, \quad . \ . \quad (8.57)$$

and so on for other lines. Using $k' = k+1$, $u' = u$, and (8.55), such formulæ yield :—

$$\left.\begin{aligned}
Z_{\mathrm{I\,I'}} &= (k+u+2)(k+u+1)(k-u+2)(k-u+1)\,2(k+1)(2k+1)\zeta \\
Z_{\mathrm{II\,II'}} &= (k+u+1)(k-u+1)\,2k(k+2)\zeta \\
Z_{\mathrm{III\,III'}} &= 2(k+1)(2k+3)\zeta \\
Z_{\mathrm{I\,II'}} &= (k+u+1)(k-u+1)\,2u(2k+1)\zeta \\
Z_{\mathrm{II\,I'}} &= 0 \\
Z_{\mathrm{I\,III'}} &= -2(k+u+1)(k-u+1)\zeta \\
Z_{\mathrm{III\,I'}} &= 0 \\
Z_{\mathrm{II\,III'}} &= 2u(2k+3)\zeta \\
Z_{\mathrm{III\,II'}} &= 0
\end{aligned}\right\} . \quad (8.58)$$

It is seen that the non-vanishing lines follow the usual scheme :—

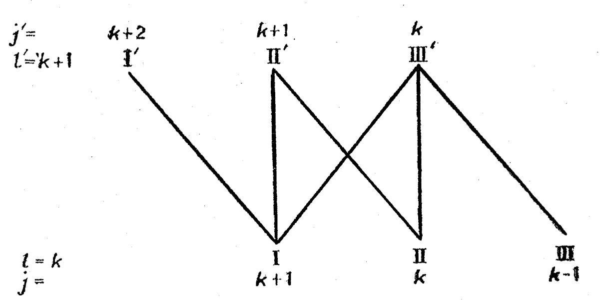

FIG. 3.

The selection rule is established

$$j' = j, j \pm 1. \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (8.59)$$

We can go on to verify the summation rule for the intensities. It is necessary to calculate the normalising factors. C_α, C_β, C_γ are given by (4.20). Using (8.43) we obtain

$$\left.\begin{aligned} C_{I} &= (k+u+1)(k-u+1)\,2(k+1)(2k+1)^2\,C \\ C_{II} &= 2k(k+1)(2k+1)\,C \\ C_{III} &= \frac{2k(2k+1)^2}{(k+u)(k-u)}\,C \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (8.60)$$

For $C_{I'}$, $C_{II'}$, $C_{III'}$, we replace k by $k+1$ and C by $(k+u+1)(k-u+1)\,C'$ where

$$C' = 2\,(4\pi)^2\,(k+u)!\,(k-u)!\int g_{10}{}^2 r^2\,dr\int g_{n'k+1}{}^2\,r^2\,dr \quad . \quad . \quad . \quad . \quad . \quad (8.61)$$

Then the intensities are proportional to :—

$$\left.\begin{aligned}
\frac{Z^2_{I\,I'}}{C_I C_{I'}} &= \frac{(k+u+2)(k-u+2)(k+1)}{(k+2)(2k+3)^2}\,\frac{\zeta^2}{CC'} & \sum_{-k-1}^{k+1} &= \tfrac{1}{3}\,\frac{(k+1)(2k+5)}{2k+3}\,\frac{\zeta^2}{CC'} \\
\frac{Z^2_{I\,II'}}{C_I C_{II'}} &= \frac{u^2}{(k+1)^2(k+2)(2k+3)}\,\frac{\zeta^2}{CC'} & \sum_{-k+1}^{k-1} &= \tfrac{1}{3}\,\frac{1}{k+1}\,\frac{\zeta^2}{CC'} \\
\frac{Z^2_{I\,III'}}{C_I C_{III'}} &= \frac{(k+u+1)(k-u+1)}{(k+1)^2(2k+1)^2(2k+3)^2}\,\frac{\zeta^2}{CC'} & \sum_{-k}^{k} &= \tfrac{1}{3}\,\frac{1}{(k+1)(2k+1)(2k+3)}\,\frac{\zeta^2}{CC'} \\
\frac{Z^2_{II\,II'}}{C_{II} C_{II'}} &= \frac{(k+u+1)(k-u+1)k(k+2)}{(k+1)^2(2k+1)(2k+3)}\,\frac{\zeta^2}{CC'} & \sum_{-k}^{k} &= \tfrac{1}{3}\,\frac{k(k+2)}{k+1}\,\frac{\zeta^2}{CC'} \\
\frac{Z^2_{II\,III'}}{C_{II} C_{III'}} &= \frac{u^2}{k(k+1)^2(2k+1)}\,\frac{\zeta^2}{CC'} & \sum_{-k}^{k} &= \tfrac{1}{3}\,\frac{1}{k+1}\,\frac{\zeta^2}{CC'} \\
\frac{Z^2_{III\,III'}}{C_{III} C_{III'}} &= \frac{(k+u)(k-u)(k+1)}{k(2k+1)^2}\,\frac{\zeta^2}{CC'} & \sum_{-k+1}^{k-1} &= \tfrac{1}{3}\,\frac{(k+1)(2k-1)}{2k+1}\,\frac{\zeta^2}{CC'}
\end{aligned}\right\} \quad (8.62)$$

The second column gives the sum of the first column over all u relevant to each line. ζ^2/CC' is independent of u. The sum of the coefficients of $\zeta^2/3CC'$ for the lines involving I, II, III, respectively are

$$\frac{(k+1)(2k+3)}{2k+1}, \quad k+1, \quad \frac{(k+1)(2k-1)}{2k+1}. \quad . \quad . \quad . \quad . \quad . \quad (8.63)$$

These have the correct ratio $2k+3 : 2k+1 : 2k-1$. Similarly the sums for I′, II′, III′, are respectively :

$$\frac{(k+1)(2k+5)}{2k+3}, \quad k+1, \quad \frac{(k+1)(2k+1)}{2k+3} \quad . \quad . \quad . \quad . \quad . \quad (8.64)$$

in the correct ratio $2k+5 : 2k+3 : 2k+1$.

It should be emphasised that the selection and summation rules of the second part of this section have been deduced only from a first approximation to the wave-functions.

Apart from radiation by quadripole and higher moments and the magnetic moment of the electron, there may be lines arising from the dipole moment through the smaller terms in the wave-functions which break the selection rules. The inter-combination between triplet terms and the normal term, for which intensities have been found, provides an extreme instance. This arises from the spin perturbations; but the perturbation by the interaction of the two electrons should give rise to stronger lines. The ratio of their intensities to the intensities of the lines which obey the selection rules might be expected to be of the order of the square of the ratio of the para-ortho separation to the total energy.

9. *A Triplet of Doubly Ionised Oxygen.*

So far, one electron has been confined to an orbit for which $k = 0$. In this section we consider the terms which arise when both electrons are in $(n, 1)$ orbits, as for the terms of O^{++} which give prominent lines in the nebular spectra. O^{++}, in the states under consideration, has a core of complete shells which may be represented by a central field, and two series electrons in (2, 1) orbits.

The result of the perturbation by P alone, the part independent of the spins, is not now quite so obvious as in § 4. There it is assumed that each wave-function corresponding to orbits with given n's and k's has one of two energies after perturbation by P alone. One of these energies is common to all the functions which are anti-symmetrical in the space-co-ordinates, and the other is common to all which are symmetrical, independently of the third quantum numbers u involved. This assumption will now be proved to a first approximation for the case when one $k = 0$, after which its modification for the case of this section will be examined.

It is convenient to distinguish the functions of (4.10) by an upper suffix u. We require to prove that

$$\int \overline{\psi_{\alpha}^{u'}}\, \mathrm{P}\, \psi_{\alpha}^{u} = \begin{cases} 0 & \text{if } u \neq u' \\ \mathrm{C}_{\alpha}^{u}\, \Delta \mathrm{E}^{\mathrm{I}} & \text{if } u = u' \end{cases} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.00)$$

with similar equations for β, γ, IV, ΔE^{I} being replaced by ΔE^{IV} in the last case. Now P is a function only of r_1, r_2, r, and can be expanded in the form:

$$\mathrm{P} \equiv \sum_{n=0}^{\infty} \mathrm{D}_n \mathrm{P}_n (\cos \gamma) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.01)$$

where D_n is a function of r_1 and r_2 only.

It follows that

$$\int \overline{\phi_{k}^{u}(1)\, \phi_{k'}^{u'}(2)}\, \mathrm{P}\, \phi_{k''}^{u''}(1)\, \phi_{k'''}^{u'''}(2)\, d\tau_1\, d\tau_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.02)$$

vanishes owing to the integrations with respect to ϕ_1, ϕ_2, unless

$$u + u' = u'' + u'''. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.03)$$

The first part of (9.00) is an immediate result.

For the second part

$$\int \overline{\psi_\alpha^u}\,\mathrm{P}\psi_\alpha^u = 2\int \overline{\phi_0^0(1)\,\phi_k^{u+1}(2)}\,\mathrm{P}\phi_0^0(1)\,\phi_k^{u+1}(2)\,d\tau_1\,d\tau_2 - 2\int \overline{\phi_0^0(1)\,\phi_k^{u+1}(2)}\,\mathrm{P}\,\phi_0^0(2)\,\phi_k^{u+1}(1)\,d\tau_1,\,d\tau_2$$

$$= 2\,(2k+1)^2 \int g_{10}(1)^2\, g_{nk}(2)^2\,\mathrm{D}_0\,\overline{\mathrm{P}_k^{u+1}(2)}\,\mathrm{P}_k^{u+1}(2)\,d\tau_1\,d\tau_2$$

$$-\,2\,(2k+1)^2 \int g_{10}(1)\,g_{nk}(1)\,g_{10}(2)\,g_{nk}(2)\,\mathrm{D}_k \times \frac{\overline{\mathrm{P}_k^{u+1}(1)}\,\mathrm{P}_k^{+1}(2)}{(k+u+1)!\,(k-u+1)!}\,\mathrm{P}_k^{u+1}(1)\,\overline{\mathrm{P}_k^{u+1}(2)}\,d\tau_1\,d\tau_2 \qquad (9.04)$$

by the rules laid down in § 5. Each term in (9.04) is $(k+u+1)!\,(k-u+1)!$ times a part independent of u, and the same factor occurs in C_α^u. Hence the second part of (9.00) is true, with $\Delta\mathrm{E}^{\mathrm{I}}$ independent of u. So for β, γ, IV; in the last case the second term of (9.04) has a $+$ sign, giving $\Delta\mathrm{E}^{\mathrm{IV}}$ instead of $\Delta\mathrm{E}^{\mathrm{I}}$.

In the case when both electrons are in $(n, 1)$ orbits, the total number of wave-functions consistent with Pauli's principle is 15. A wave-function of the form previously denoted by ψ_{IV} is now denoted by ψ_δ, since it may not be a first approximation to a perturbed wave-function owing to degeneracy. There is a new form of wave-function which involves two orbits differing only in their spin. Such a function is denoted by ψ_ϵ. We give a complete list of unperturbed wave-functions, grouped according to u.

$$\left.\begin{aligned}
\psi_\beta^2 &= [\phi_1^0(1)\,\phi_1^1(2) - \phi_1^0(2)\,\phi_1^1(1)]\,\chi_a(1)\,\chi_a(2)\\
\psi_\epsilon^2 &= \phi_1^1(1)\,\phi_1^1(2)\,[\chi_a(1)\,\chi_b(2) - \chi_b(1)\,\chi_a(2)]\\[4pt]
\psi_\beta^1 &= [\phi_1^{-1}(1)\,\phi_1^1(2) - \phi_1^{-1}(2)\,\phi_1^1(1)]\,\chi_a(1)\,\chi_a(2)\\
\psi_\gamma^1 &= [\phi_1^0(1)\,\phi_1^1(2) - \phi_1^0(2)\,\phi_1^1(1)]\,[\chi_a(1)\,\chi_b(2) + \chi_b(1)\,\chi_a(2)]\\
\psi_\delta^1 &= [\phi_1^0(1)\,\phi_1^1(2) + \phi_1^0(2)\,\phi_1^1(1)]\,[\chi_a(1)\,\chi_b(2) - \chi_b(1)\,\chi_a(2)]\\[4pt]
\psi_\alpha^0 &= [\phi_1^0(1)\,\phi_1^1(2) - \phi_1^0(2)\,\phi_1^1(1)]\,\chi_b(1)\,\chi_b(2)\\
\psi_\beta^0 &= [\phi_1^0(1)\,\phi_1^{-1}(2) - \phi_1^0(2)\,\phi_1^{-1}(1)]\,\chi_a(1)\,\chi_a(2)\\
\psi_\gamma^0 &= [\phi_1^{-1}(1)\,\phi_1^1(2) - \phi_1^{-1}(2)\,\phi_1^1(1)]\,[\chi_a(1)\,\chi_b(2) + \chi_b(1)\,\chi_a(2)]\\
\psi_\delta^0 &= [\phi_1^{-1}(1)\,\phi_1^1(2) + \phi_1^{-1}(2)\,\phi_1^1(1)]\,[\chi_a(1)\,\chi_b(2) - \chi_b(1)\,\chi_a(2)]\\
\psi_\epsilon^0 &= \phi_1^0(1)\,\phi_1^0(2)\,[\chi_a(1)\,\chi_b(2) - \chi_b(1)\,\chi_a(2)]\\[4pt]
\psi_\alpha^{-1} &= [\phi_1^{-1}(1)\,\phi_1^1(2) - \phi_1^{-1}(2)\,\phi_1^1(1)]\,\chi_b(1)\,\chi_b(2)\\
\psi_\gamma^{-1} &= [\phi_1^0(1)\,\phi_1^{-1}(2) - \phi_1^0(2)\,\phi_1^{-1}(1)]\,[\chi_a(1)\,\chi_b(2) + \chi_b(1)\,\chi_a(2)]\\
\psi_\delta^{-1} &= [\phi_1^0(1)\,\phi_1^{-1}(2) + \phi_1^0(2)\,\phi_1^{-1}(1)]\,[\chi_a(1)\,\chi_b(2) - \chi_b(1)\,\chi_a(2)]\\[4pt]
\psi_\alpha^{-2} &= [\phi_1^0(1)\,\phi_1^{-1}(2) - \phi_1^0(2)\,\phi_1^{-1}(1)]\,\chi_b(1)\,\chi_b(2)\\
\psi_\epsilon^{-2} &= \phi_1^{-1}(1)\,\phi_1^{-1}(2)\,[\chi_a(1)\,\chi_b(2) - \chi_b(1)\,\chi_a(2)]
\end{aligned}\right\} \qquad (9.10)$$

For any two of these wave-functions, say ψ, ψ', except ψ^0_δ and ψ^0_ϵ

$$\int \overline{\psi}' \, \mathrm{P} \, \psi = 0$$

either because the spin factors are different or because the u's do not satisfy (9.03). Hence as far as the perturbation by P is concerned, all the functions but the two excepted may be taken as first approximations to the perturbed wave-functions. In cases of degeneracy, of course, linear combinations may be formed by the spin perturbation.

In the excepted case

$$\int \overline{\psi}^0_\epsilon \mathrm{P} \psi^0_\delta = 4 \int \phi^0_1 (1) \, \phi^0_1 (2) \, \mathrm{P} \, \phi^{-1}_1 (1) \, \phi^1_1 (2) \, d\pi_1 \, d\pi_2$$

$$= 4.81 \int \mathrm{P}^0_1 (1) \, \mathrm{P}^0_1 (2) \, \mathrm{D}_2 \frac{\mathrm{P}^1_2 (1) \, \overline{\mathrm{P}^1_2 (2)}}{3\,!} \mathrm{P}^{-1}_1 (1) \, \mathrm{P}^1_1 (2) \, g_{n1} (1)^2 \, g_{n1} (2)^2 \, d\tau_1 \, d\tau_2$$

$$= - \tfrac{12}{25} \mathbf{D}_2 \qquad (9.11)$$

where

$$\mathbf{D}_2 = 18 \, (4\pi)^2 \int \mathrm{D}_2 \, g_{n1} (1)^2 \, g_{n1} (2)^2 \, r_1^2 \, dr_1 \, r_2^2 \, dr_2. \qquad (9.12)$$

By similar calculations

$$\int \overline{\psi}^0_\delta \, \mathrm{P} \psi^0_\delta = 8 \mathbf{D}_0 + \tfrac{56}{25} \mathbf{D}_2 \qquad (9.13)$$

$$\int \overline{\psi}^0_\epsilon \mathrm{P} \psi^0_\epsilon = \mathbf{D}_0 + \tfrac{4}{25} \mathbf{D}_2 \qquad (9.14)$$

where

$$\mathbf{D}_0 = 18 \, (4\pi)^2 \int \mathrm{D}_0 \, g_{n1} (1)^2 \, g_{n1} (2)^2 \, r_1^2 \, dr_1 \, r_2^2 \, dr_2 \qquad (9.15)$$

and

$$\mathrm{C}^0_\delta = 8\mathrm{C}, \qquad \mathrm{C}^0_\epsilon = \mathrm{C} \qquad (9.16)$$

where

$$\mathrm{C} = 18 \, (4\pi)^2 \int g_{n1} (1)^2 \, g_{n1} (2)^2 \, r_1^2 \, dr_1 \, r_2^2 \, dr_2 \qquad (9.17)$$

The perturbation by P replaces ψ^0_δ, ψ^0_ϵ to a first approximation by two linear combinations ψ^0_{IV}, ψ^0_{V}, whose extra energies $\Delta \mathrm{E}^{\mathrm{IV}}$, $\Delta \mathrm{E}^{\mathrm{V}}$, are the roots of the equation

$$\begin{vmatrix} 8\mathbf{D}_0 + \tfrac{56}{25} \mathbf{D}_2 - 8\mathrm{C}\Delta\mathrm{E} & - \tfrac{12}{25} \mathbf{D}_2 \\ - \tfrac{12}{25} \mathbf{D}_2 & \mathbf{D}_0 + \tfrac{4}{25} \mathbf{D}_2 - \mathrm{C}\Delta\mathrm{E} \end{vmatrix} = 0,$$

or

$$(\mathbf{D}_0 - \mathrm{C}\Delta\mathrm{E})^2 + 11 \frac{\mathbf{D}_2}{25} (\mathbf{D}_0 - \mathrm{C}\Delta\mathrm{E}) + 10 \left(\frac{\mathbf{D}_2}{25}\right)^2 = 0. \qquad (9.18)$$

Thus

$$\left.\begin{aligned} \Delta \mathrm{E}^{\mathrm{IV}} &= \frac{\mathbf{D}_0}{\mathrm{C}} + \frac{\mathbf{D}_2}{25\mathrm{C}} \\ \Delta \mathrm{E}^{\mathrm{V}} &= \frac{\mathbf{D}_0}{\mathrm{C}} + \frac{2\mathbf{D}_2}{5\mathrm{C}} \end{aligned}\right\} \qquad (9.19)$$

If we put

$$\left.\begin{aligned} \psi^0_{IV} &= a_\delta^{IV}\,\psi^0_\delta + a_\epsilon^{IV}\,\psi^0_\epsilon \\ \psi^0_V &= a_\delta^V\,\psi^0_\delta + a_\epsilon^V\,\psi^0_\epsilon \end{aligned}\right\}, \quad \ldots \quad (9.20)$$

then the coefficients satisfy the equations :

$$\left.\begin{aligned} \tfrac{48}{25}\,\mathbf{D}_2\,a_\delta^{IV} - \tfrac{12}{25}\,\mathbf{D}_2\,a_\epsilon^{IV} &= 0 \\ -\tfrac{24}{25}\,\mathbf{D}_2\,a_\delta^V - \tfrac{12}{25}\,\mathbf{D}_2\,a_\epsilon^V &= 0 \end{aligned}\right\} \quad \ldots \quad (9.21)$$

so that $a_\epsilon^{IV} = 4a_\delta^{IV}$, $a_\epsilon^V = -2a_\delta^V$, and we may take

$$\left.\begin{aligned} \psi^0_{IV} &= \psi^0_\delta + 4\psi^0_\epsilon \\ \psi^0_V &= \psi^0_\delta - 2\psi^0_\epsilon \end{aligned}\right\}. \quad \ldots \quad (9.22)$$

For any of the other wave-functions, ψ, the first approximation to ΔE is given by

$$\Delta E \int \bar{\psi}\,\psi = \int \bar{\psi}\,P\psi. \quad \ldots \quad (9.23)$$

On calculating the various integrals it is found that for

$$\psi^2_\epsilon,\ \psi^1_\delta,\ \psi^{-1}_\delta,\ \psi^{-2}_\epsilon, \qquad \Delta E = \frac{\mathbf{D}_0}{C} + \frac{\mathbf{D}_2}{25C} = \Delta E^{IV} \quad \ldots \quad (9.24)$$

and for the functions anti-symmetrical in the positional co-ordinates

$$\Delta E = \frac{\mathbf{D}_0}{C} - \frac{\mathbf{D}_2}{5C} = \Delta E^{I} = \Delta E^{II} = \Delta E^{III}\ \text{(say)}. \quad \ldots \quad (9.25)$$

Thus the term IV has weight 5, and may be classified as $^1D_2$; the term V has weight 1, and is a $^1S_0$; while the ortho-terms are grouped in the same manner as those of §§ 4-8, and will give rise to a P′-triplet. It is assumed that this arrangement holds to all orders of the perturbation by P.

In order to analyse the triplet, we consider the middle group of five wave-functions in (9.10). The upper suffix 0 will now be omitted. Using (4.02) we have

$$\left.\begin{aligned} \psi_\alpha &= \psi_2 - 2\psi_3 + \psi_4 + 2\psi_5 \\ \psi_\beta &= -\psi_2 - \psi_3 + 2\psi_4 - 2\psi_5 \\ \psi_\gamma &= -\psi_1 - \psi_2 + 2\psi_3 + 2\psi_4 + 4\psi_5 \\ \psi_\delta &= \psi_1 - \psi_2 + 2\psi_3 + 2\psi_4 + 4\psi_5 \\ \psi_\epsilon &= \psi_2 + \psi_3 + \psi_4 - \psi_5 \end{aligned}\right\}, \quad \ldots \quad (9.30)$$

where

$$\left.\begin{aligned} \psi_1 &= \psi^{-2}_{-2}(1)\,\psi^{1}_{-2}(2) - \psi^{-2}_{-2}(2)\,\psi^{1}_{-2}(1) \\ \psi_2 &= \psi^{-1}_{-2}(1)\,\psi^{0}_{-2}(2) - \psi^{-1}_{-2}(2)\,\psi^{0}_{-2}(1) \\ \psi_3 &= \psi^{-1}_{-2}(1)\,\psi^{0}_{1}(2) - \psi^{-1}_{-2}(2)\,\psi^{0}_{1}(1) \\ \psi_4 &= \psi^{0}_{-2}(1)\,\psi^{-1}_{1}(2) - \psi^{0}_{-2}(2)\,\psi^{-1}_{1}(1) \\ \psi_5 &= \psi^{-1}_{1}(1)\,\psi^{0}_{1}(2) - \psi^{-1}_{1}(2)\,\psi^{0}_{1}(1) \end{aligned}\right\}, \quad \ldots \quad (9.31)$$

and by (9.22),

$$\left.\begin{aligned} \psi_{IV} &= \psi_1 + 3\psi_2 + 6\psi_3 + 6\psi_4 \\ \psi_V &= \psi_1 - 3\psi_2 \qquad\qquad\qquad + 6\psi_5 \end{aligned}\right\} \quad \ldots \ldots \quad (9.32)$$

Inverting (9.30) :

$$\left.\begin{aligned} \psi_1 &= \tfrac{1}{2}(-\psi_\gamma + \psi_\delta) \\ \psi_2 &= \tfrac{1}{18}(4\psi_\alpha - 4\psi_\beta - \psi_\gamma - \psi_\delta + 8\psi_\epsilon) \\ \psi_3 &= \tfrac{1}{18}(-4\psi_\alpha - 2\psi_\beta + \psi_\gamma + \psi_\delta + 4\psi_\epsilon) \\ \psi_4 &= \tfrac{1}{18}(2\psi_\alpha + 4\psi_\beta + \psi_\gamma + \psi_\delta + 4\psi_\epsilon) \\ \psi_5 &= \tfrac{1}{18}(2\psi_\alpha - 2\psi_\beta + \psi_\gamma + \psi_\delta - 2\psi_\epsilon) \end{aligned}\right\} \quad \ldots \ldots \quad (9.33)$$

By a simple evaluation of integrals,

$$C_\alpha = 2C, \qquad C_\beta = 2C, \qquad C_\gamma = 8C, \qquad C_\delta = 8C, \qquad C_\epsilon = C, \quad \ldots \quad (9.34)$$

where

$$C = 18\,(4\pi)^2 \left[\int_0^\infty g_{n1}{}^2 r^2\,dr\right]^2, \quad \ldots \ldots \quad (9.35)$$

so that, by use of (9.33)

$$C_1 = 4C, \quad C_2 = \tfrac{4}{9}C, \quad C_3 = \tfrac{2}{9}C, \quad C_4 = \tfrac{2}{9}C, \quad C_5 = \tfrac{1}{9}C. \quad \ldots \ldots \quad (9.36)$$

Also (9.31) shows that if η_1, η_2 are the spin energies for a single $(n, 1)$ orbit with (DIRAC's) $j = -2$ and 1 respectively,

$$\delta E_1 = \delta E_2 = 2\eta_1, \quad \delta E_3 = \delta E_4 = \eta_1 + \eta_2, \quad \delta E_5 = 2\eta_2. \quad \ldots \ldots \quad (9.37)$$

In the theory of § 3 we now have five m's. ΔE^μ has a triple root ($\Delta E^I = \Delta E^{II} = \Delta E^{III}$) and two single roots ($\Delta E^{IV}$ and ΔE^V). For the triple root, the five equations (3.4) must reduce to two, which are the only independent equations connecting the five $a_m{}^I$'s so long as spin is neglected. We know, however, that ψ_I is orthogonal to ψ_{IV} and ψ_V, so that

$$\sum_m C_m a_m{}^{IV} a_m{}^I = 0, \qquad \sum_m C_m a_m{}^V a_m{}^I = 0. \quad \ldots \ldots \quad (9.40)$$

These equations are independent, and must be equivalent to (3.4). Thus

$$\left.\begin{aligned} P_{m'm'} - \Delta E^I C_{m'} &= \lambda C_{m'} a_{m'}{}^{IV} + \mu C_{m'} a_{m'}{}^V \\ P_{mm'} \qquad\qquad &= \lambda C_m a_m{}^{IV} + \mu C_m a_m{}^V \qquad (m \neq m') \end{aligned}\right\}, \quad \ldots \quad (9.41)$$

where λ, μ are unknown multipliers. λ is found by multiplying the equations (9.41) by $a_{m'}{}^{IV}$, $a_m{}^{IV}$, and adding for all m.

$$\sum_m P_{mm'} a_m{}^{IV} - \Delta E^I C_{m'} a_{m'}{}^{IV} = \lambda C_{IV},$$

since IV, V, are orthogonal. The left-hand side of this equation is transformed by means of (3.4) with μ = IV, giving

Similarly

$$\left.\begin{aligned}\lambda C_{IV} &= (\Delta E^{IV} - \Delta E^{I})\, C_{m'}\, a_{m'}^{IV} \\ \mu C_{V} &= (\Delta E^{V} - \Delta E^{I})\, C_{m'}\, a_{m'}^{V}\end{aligned}\right\} \quad \ldots \ldots \quad (9.42)$$

Substitute from (9.42) in (9.41), and thence in (3.3)

$$(\delta E^{I} - \delta E_{m'})\, C_{m'} a_{m'}^{I} - \sum_{m} S_{mm'} a_{m}^{I} = \frac{\Delta E^{IV} - \Delta E^{I}}{C_{IV}} \sum_{m} C_{m} a_{m}^{IV}\, \delta a_{m}^{I} \,.\, C_{m'} a_{m'}^{IV} + \frac{\Delta E^{V} - \Delta E^{I}}{C_{V}} \sum_{m} C_{m} a_{m}^{V}\, \delta a_{m}^{I} \,.\, C_{m'} a_{m'}^{V}. \quad (9.43)$$

We now have five equations (9.43) and two equations (9.40) connecting the seven unknowns

$$a_1^{I} \ldots a_5^{I}, \quad \frac{\Delta E^{IV} - \Delta E^{I}}{C_{IV}} \sum_{m} C_{m} a_{m}^{IV}\, \delta a_{m}^{I}, \quad \frac{\Delta E^{V} - \Delta E^{I}}{C_{V}} \sum_{m} C_{m} a_{m}^{V}\, \delta a_{m}^{I}.$$

Thus if Δ is the determinant of the coefficients of the left-hand side of (9.43), we have the cubic in δE^{I}:

$$\begin{vmatrix} 0, & 0, & C_m a_m^{IV} \\ 0, & 0, & C_m a_m^{V} \\ C_m a_m^{IV}, & C_m a_m^{V}, & \Delta \end{vmatrix} = 0. \quad \ldots \ldots \quad (9.44)$$

When this equation has been solved, the coefficients a_m^{I} can be determined from (9.40), (9.43).

The calculation of $S_{mm'}$ is parallel to § 5. Instead of ψ_{IV}, we now have the two functions ψ_δ, ψ_ϵ. (5.12), (5.13) can be taken over with a suitable alteration of suffixes.

$$\left.\begin{aligned}
&T_{1\,\alpha\beta} = T_{1\,\gamma\gamma} = T_{1\,\delta\delta} = T_{1\,\epsilon\epsilon} = T_{1\,\delta\epsilon} = 0 \\
&T_{1\,\beta\gamma} = [t_{2x} + it_{2y}]'_{\beta\gamma}, \quad T_{1\,\beta\delta} = -[t_{2x} + it_{2y}]'_{\beta\delta}, \quad T_{1\,\beta\epsilon} = -[t_{2x} + it_{2y}]'_{\beta\epsilon} \\
&T_{1\,\gamma\alpha} = [t_{2x} + it_{2y}]'_{\gamma\alpha}, \quad T_{1\,\delta\alpha} = [t_{2x} + it_{2y}]'_{\delta\alpha}, \quad T_{1\,\epsilon\alpha} = [t_{2x} + it_{2y}]'_{\epsilon\alpha} \\
&T_{1\,\alpha\alpha} = -[t_{2z}]'_{\alpha\alpha}, \quad T_{1\,\beta\beta} = [t_{2z}]'_{\beta\beta}, \quad T_{1\,\gamma\delta} = 2\,[t_{2z}]'_{\gamma\delta}, \quad T_{1\,\gamma\epsilon} = 2\,[t_{2z}]'_{\gamma\epsilon}
\end{aligned}\right\}. \quad (9.50)$$

$$\left.\begin{aligned}
&U_{\alpha\delta} = U_{\beta\delta} = U_{\gamma\delta} = U_{\alpha\epsilon} = U_{\beta\epsilon} = U_{\gamma\epsilon} = U_{\delta\delta} = U_{\epsilon\epsilon} = U_{\delta\epsilon} = 0 \\
&U_{\alpha\beta} = -3\,\frac{\gamma^2 a^2 e^2}{4}\left[\frac{(l - im)^2}{r^3}\right]'_{\alpha\beta} \qquad U_{\alpha\alpha} = \frac{\gamma^2 a^2 e^2}{4}\left[\frac{1 - 3n^2}{r^3}\right]'_{\alpha\alpha} \\
&U_{\beta\gamma} = -6\,\frac{\gamma^2 a^2 e^2}{4}\left[\frac{(l + im)\,n}{r^3}\right]'_{\beta\gamma} \qquad U_{\beta\beta} = \frac{\gamma^2 a^2 e^2}{4}\left[\frac{1 - 3n^2}{r^3}\right]'_{\beta\beta} \\
&U_{\gamma\alpha} = 6\,\frac{\gamma^2 a^2 e^2}{4}\left[\frac{(l + im)\,n}{r^3}\right]'_{\gamma\alpha} \qquad U_{\gamma\gamma} = -4\,\frac{\gamma^2 a^2 e^2}{4}\left[\frac{1 - 3n^2}{r^3}\right]'_{\gamma\gamma}
\end{aligned}\right\}. \quad (9.51)$$

The calculation of the integrals in (9.50), (9.51) is somewhat laborious. The results are

$$\left.\begin{array}{lll} 2T_{1\,\alpha\beta} = 2T_{1\,\gamma\gamma} = 2T_{1\,\delta\delta} = 2T_{1\,\epsilon\epsilon} = 2T_{1\,\delta\epsilon} = 2T_{1\,\gamma\epsilon} = 0 & & \\ 2T_{1\,\beta\gamma} = -10\mathbf{T} & 2T_{1\,\beta\delta} = \mathbf{T} & 2T_{1\,\beta\epsilon} = -2\mathbf{T} \\ 2T_{1\,\gamma\alpha} = 10\mathbf{T} & 2T_{1\,\delta\alpha} = -\mathbf{T} & 2T_{1\,\epsilon\alpha} = 2\mathbf{T} \\ 2T_{1\,\alpha\alpha} = 5\mathbf{T} & 2T_{1\,\beta\beta} = 5\mathbf{T} & 2T_{1\,\gamma\delta} = -16\mathbf{T} \end{array}\right\}, \quad (9.52)$$

where

$$\mathbf{T} = \gamma^2 a^2 e^2 \tfrac{36}{5} (4\pi)^2 \int_0^\infty \int_{r_1}^\infty g_{n1}(2)^2 \frac{1}{r_2^3} r_2^2\, dr_2\, g_{n1}(1)^2 r_1^2\, dr_1, \quad . \quad . \quad . \quad . \quad (9.53)$$

and

$$\left.\begin{array}{ll} U_{\alpha\delta} = U_{\beta\delta} = U_{\gamma\delta} = U_{\alpha\epsilon} = U_{\beta\epsilon} = U_{\gamma\epsilon} = U_{\delta\delta} = U_{\epsilon\epsilon} = U_{\delta\epsilon} = 0 & \\ U_{\alpha\beta} = 6\mathbf{U} & U_{\alpha\alpha} = -\mathbf{U} \\ U_{\beta\gamma} = 6\mathbf{U} & U_{\beta\beta} = -\mathbf{U} \\ U_{\gamma\alpha} = -6\mathbf{U} & U_{\gamma\gamma} = -16\mathbf{U} \end{array}\right\}. \quad (9.54)$$

where

$$\mathbf{U} = \gamma^2 a^2 e^2 \tfrac{18}{5} (4\pi)^2 (11\,|\,r_1^2 [B_0 - \tfrac{1}{5} B_2] - \tfrac{3}{5} r_1 r_2 [\tfrac{1}{3} B_1 - \tfrac{1}{7} B_3]\,|\,11) = \tfrac{1}{2}\mathbf{T} \quad (9.55)$$

Addition of (9.52), (9.54), gives $S_{\alpha\beta}$, etc., and then use of (9.33) gives $S_{mm'}$. The terms of Δ are tabulated in (9.60).

$$\begin{array}{llllll} C_m a_m^{\text{IV}} = & 4C & \tfrac{4}{3}C & \tfrac{4}{3}C & \tfrac{4}{3}C & 0 \\ C_m a_m^{\text{V}} = & 4C & -\tfrac{4}{3}C & 0 & 0 & \tfrac{2}{3}C \end{array}$$

$$\Delta = \begin{vmatrix} 4C(\delta E^\mu - 2\eta_1) - 6\mathbf{T} & 2\mathbf{T} & -\tfrac{2}{3}\mathbf{T} & -\tfrac{2}{3}\mathbf{T} & \tfrac{2}{3}\mathbf{T} \\ 2\mathbf{T} & \tfrac{4}{9}C(\delta E^\mu - 2\eta_1) - \tfrac{14}{27}\mathbf{T} & -\tfrac{10}{27}\mathbf{T} & -\tfrac{10}{27}\mathbf{T} & -\tfrac{10}{27}\mathbf{T} \\ -\tfrac{2}{3}\mathbf{T} & -\tfrac{10}{27}\mathbf{T} & \tfrac{2}{9}C(\delta E^\mu - \eta_1 - \eta_2) - \tfrac{7}{54}\mathbf{T} & \tfrac{19}{27}\mathbf{T} & -\tfrac{1}{54}\mathbf{T} \\ -\tfrac{2}{3}\mathbf{T} & -\tfrac{10}{27}\mathbf{T} & \tfrac{19}{27}\mathbf{T} & \tfrac{2}{9}C(\delta E^\mu - \eta_1 - \eta_2) - \tfrac{7}{54}\mathbf{T} & -\tfrac{1}{54}\mathbf{T} \\ \tfrac{2}{3}\mathbf{T} & -\tfrac{10}{27}\mathbf{T} & -\tfrac{1}{54}\mathbf{T} & -\tfrac{1}{54}\mathbf{T} & \tfrac{1}{9}C(\delta E^\mu - 2\eta_2) + \tfrac{1}{27}\mathbf{T} \end{vmatrix}. \quad (9.60)$$

One root of equation (9.44) is at once obvious, since it makes the fifth and sixth columns equal. The equation then reduces to a quadratic. It is simplest to take a hint from the wave-functions of (8.42), which are independent of the relative magnitudes of the δE_m's, and $\mathbf{T}$ and $\mathbf{U}$. If we first solve (9.44) and find the wave-functions ψ_{I}, ψ_{II}, ψ_{III}, with the simplification $\mathbf{T} = 0$, it is then easily verified that when $\mathbf{T} \neq 0$

the same $a_m^{\text{I}}, a_m^{\text{II}}, a_m^{\text{III}}$ will satisfy (9.40), (9.43), with suitable values for δE^μ. These are

$$\left.\begin{aligned} \delta E^{\text{I}} &= \tfrac{5}{3}\eta_1 + \tfrac{1}{3}\eta_2 - 11\mathbf{T}/4C \\ \delta E^{\text{II}} &= \eta_1 + \eta_2 + 15\mathbf{T}/4C \\ \delta E^{\text{III}} &= \tfrac{2}{3}\eta_1 + \tfrac{4}{3}\eta_2 + 5\mathbf{T}/2C \end{aligned}\right\}, \quad \ldots \quad (9.61)$$

with the corresponding wave-functions:

$$\left.\begin{aligned} \psi_{\text{I}} &= \psi_1 + 3\psi_2 - 3\psi_3 - 3\psi_4 \\ \psi_{\text{II}} &= \psi_3 - \psi_4 \\ \psi_{\text{III}} &= \psi_1 - 3\psi_2 - 12\psi_5 \end{aligned}\right\}. \quad \ldots \quad (9.62)$$

Alternatively, using (9.33), we may write the wave-functions:

$$\left.\begin{aligned} \psi_{\text{I}} &= \psi_\alpha - \psi_\beta - \psi_\gamma \\ \psi_{\text{II}} &= -\tfrac{1}{3}\psi_\alpha - \tfrac{1}{3}\psi_\beta \\ \psi_{\text{III}} &= -2\psi_\alpha + 2\psi_\beta - \psi_\gamma \end{aligned}\right\} \quad \ldots \quad (9.63)$$

As before, the terms I, II, III, are $^3P_2$, $^3P_1$, $^3P_0$, respectively. This classification agrees with the weights. For instance, the first group in (9.10) consists of only one ortho- and one para- term. These are

$$\psi_\beta^2 = \psi_6 + \psi_7, \qquad \psi_\epsilon^2 = \psi_6 - 2\psi_7 \quad \ldots \quad (9.70)$$

where

$$\left.\begin{aligned} \psi_6 &= \psi_{-2}^0(1)\,\psi_{-2}^1(2) - \psi_{-2}^0(2)\,\psi_{-2}^1(1) \\ \psi_7 &= \psi_1^0(1)\,\psi_{-2}^1(2) - \psi_1^0(2)\,\psi_{-2}^1(1) \end{aligned}\right\} \quad \ldots \quad (9.71)$$

so that

$$\delta E_6 = 2\eta_1, \qquad \delta E_7 = \eta_1 + \eta_2 \quad \ldots \quad (9.72)$$

$$\left.\begin{aligned} \psi_6 &= \tfrac{2}{3}\,\psi_\beta^2 + \tfrac{1}{3}\,\psi_\epsilon^2 \\ \psi_7 &= \tfrac{1}{3}\,\psi_\beta^2 - \tfrac{1}{3}\,\psi_\epsilon^2 \end{aligned}\right\} \quad \ldots \quad (9.73)$$

We easily find

$$C_\beta = 2C, \qquad C_\epsilon = 4C \quad \ldots \quad (9.74)$$

whence

$$C_6 = \tfrac{4}{3}C, \qquad C_7 = \tfrac{2}{3}C \quad \ldots \quad (9.75)$$

For the ortho- term there are only two equations (3.3), with $a_6 = a_7 = 1$. Adding, and using (3.4)

$$(\delta E - \delta E_6)\,C_6 + (\delta E - \delta E_7)\,C_7 - S_{\beta\beta} = 0 \quad \ldots \quad (9.76)$$

It is found that

$$S_{\beta\beta} = -5\mathbf{T} - \mathbf{U} = -\tfrac{11}{2}\mathbf{T} \quad \ldots \quad (9.77)$$

Substituting in (9.76)

$$\delta E = \tfrac{5}{3}\eta_1 + \tfrac{1}{3}\eta_2 - \frac{11\mathbf{T}}{4C} = \delta E^{\text{I}} \quad \ldots \quad (9.78)$$

Similarly for the last group in (9.10). The other two groups have two ortho- terms each, with spin energies δE^{I}, δE^{II}.

A rough calculation of (9.61) will serve to show why the triplets of doubly ionised oxygen, for instance, are nearly "normal," in contrast to those of helium. O^{++} has four electrons in the K and L_1 shells, and—for its lowest terms—two electrons in the incomplete L_2 shell. We shall treat these (2, 1) orbits as if they were in a Coulomb field Z^1e/r. Owing to fairly complete screening by the K-electrons, and very incomplete screening by the L-electrons, Z^1 should lie between 3 and 6.

We have

$$g_{21}(r) = r \exp(-Z^1 r/2a) \quad \ldots \quad (9.80)$$

so that

$$\int_0^\infty g_{21}{}^2 r^2 dr = \int_0^\infty r^4 \exp(-Z^1 r/a)\, dr = \left(\frac{a}{Z^1}\right)^5 4\,!. \quad \ldots \quad (9.81)$$

The difference between the two spin energies for the orbit is*

$$\eta_1 - \eta_2 = \frac{\gamma^2 a^2 Z^1 e^2}{4} \overline{\frac{1}{r^3}}.\, 3 = \tfrac{3}{4}\gamma^2 a^2 Z^1 e^2 \int_0^\infty r \exp(-Z^1 r/a)\, dr \bigg/ \left(\frac{a}{Z^1}\right)^5 4\,! = \frac{\gamma^2 Z^{14} e^2}{32a} \quad . \quad (9.82)$$

while by (9.17), (9.53),

$$\mathbf{T}/C = \gamma^2 a^2 e^2 \,.\, \tfrac{2}{5} \int_0^\infty \int_{r_1}^\infty r_2 \exp(-Z^1 r_2/a)\, dr_2 \,.\, r_1{}^4 \exp(-Z^1 r_1/a)\, dr_1 \bigg/ \left(\frac{a}{Z^1}\right)^{10} 4\,!^2$$

$$= \frac{2\gamma^2 Z^{13} e^2}{5a} \int_0^\infty (x+1)\, e^{-2x} x^4\, dx/4\,!^2 = \frac{7\gamma^2 Z^{13} e^2}{5\,.\,2^5\,.\,4\,!\,a}. \quad \ldots \quad (9.83)$$

Thus the ratio of the separations indicated by (9.61) is

$$\tfrac{2}{3}(\eta_1 - \eta_2) - \tfrac{13}{2}\,\mathbf{T}/C : \tfrac{1}{3}(\eta_1 - \eta_2) + \tfrac{5}{4}\,\mathbf{T}/C = 2Z^1 - \tfrac{91}{80} : Z^1 + \tfrac{7}{32}. \quad . \quad (9.84)$$

For example :

$$\left.\begin{array}{ll} Z^1 = 4, & \text{Ratio} = 1\cdot 63 \\ Z^1 = 5, & \text{Ratio} = 1\cdot 70 \end{array}\right\} \quad \ldots \quad (9.85)$$

The observed† value of the ratio for O^{++} is $193 : 116 = 1\cdot 66$, corresponding to a reasonable value of Z^1. It should be mentioned, however, that the sequence of similar ions O^{++}, N^{+}, C, presents a puzzling set of separation-ratios. Instead of approaching the normal ratio $2 : 1$ as the atomic number increases, the ratio is greater as the atomic number becomes less. Thus for N^{+} it is‡ $84 : 50 = 1\cdot 68$, and for C it is§ $27\cdot 5 : 14\cdot 8 = 1\cdot 86$. These values must be very sensitive to experimental error, and the anomaly may not be real.

* Dirac, 'Roy. Soc. Proc.,' vol. 117, p. 624 (1928).

† A. Fowler, 'Roy. Soc Proc.,' A, vol. 117, p. 321 (1927).

‡ Bowen, 'Phys. Rev.,' vol. 29, p. 231 (1927).

§ A. Fowler and Selwyn, 'Roy. Soc. Proc.,' A, vol. 118, p. 34 (1928).

It is probable that some of the lines in the spectra of gaseous nebulæ are due to transitions between the states of O^{++} discussed in this section.* The two green lines have the right frequency for $^3P'_2 - {^1D_2}$ and $^3P'_1 - {^1D_2}$, while another line agrees with $^1D_2 - {^1S_0}$. The first two are transitions between ortho- and para- states; the third is a "forbidden" transition because the k of neither electron alters. Other nebular lines are identified with similar transitions in N^+.

A formula for the intensity of an ortho-para transition is given in (6.27), and a similar formula could be constructed in the present case. It would give, however, the approximate probabilities of the transitions $^3P'_2 - {^1D_2}$, $^3P'_1 - {^1D_2}$, as fractions of the first approximation to the probabilities of transitions within $^3P'$; but these are themselves forbidden transitions. It would be necessary, therefore, to introduce at least the first order perturbation by P. This may make $^3P'_2 - {^3P'_1}$, etc., possible by adding to the approximate wave-functions small wave-functions with different k's; but the intensity would be of the order of $\left(\frac{\Delta E}{E}\right)^2$ as compared with a normal line. We should expect the green lines to be weaker still, in a ratio of the order of $\left(\frac{\delta E}{\Delta E}\right)^2$, as in (6.27). The strength of the nebular lines is therefore not explained by any new selection rule inherent in the new theory, and must be due to special conditions of the gas which emits them.

Appendix.

The Integral of a Product of Three Tesseral Harmonics.

1. In this appendix we denote by $P_k^u(\mu)$ DARWIN's form of the tesseral harmonic without the factor $e^{iu\phi}$.

$$P_k^u(\mu) \equiv (k-u)!\,(1-\mu^2)^{u/2}\left[\frac{d}{d\mu}\right]^{k+u}\frac{(\mu^2-1)^k}{2^k\,k!} \qquad (k \geq |u|) \quad . \quad . \quad . \quad . \quad (1)$$

Since

$$P_k^{-u}(\mu) = (-)^u\,P_k^u(\mu) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

we may assume without loss of generality that u is positive.

We require

$$\int_{-1}^{1} P_l^u\,P_m^v\,P_n^w\,d\mu \qquad (u \geq 0,\ v \geq 0,\ w \geq 0,\ u = v + w).$$

2. The following recurrence formula is given by DARWIN

$$(1-\mu^2)^{1/2}\,P_k^u = \frac{1}{2k+1}\{P_{k+1}^{u+1} - (k-u)(k-u-1)\,P_{k-1}^{u+1}\}. \quad . \quad . \quad . \quad (3)$$

* BOWEN, 'Nature,' vol. 120, p. 473 (1927).

We prove by induction that

$$(1-\mu^2)^{n/2}\,\mathrm{P}_k^u = \sum_{t=0}(-)^t\frac{(k-u)!\;(2k-2t-1)!!}{(k-u-2t)!\;(2k+2n-2t+1)!!}\times(2k+2n-4t+1)\binom{n}{t}\mathrm{P}_{k+n-2t}^{u+n} \quad (4)$$

where the upper limit of t is n or the integral part of $\frac{1}{2}(k-u)$ or k, whichever is least.* (4) reduces to (3) for $n=1$. If it is true for n, multiply by $(1-\mu^2)^{1/2}$ and use (3).

$$(1-\mu^2)^{\frac{n+1}{2}}\,\mathrm{P}_k^u = \sum_{t=0}(-)^t\frac{(k-u)!\;(2k-2t-1)!!}{(k-u-2t)!\;(2k+2n-2t+1)!!}\binom{n}{t}\times\{\mathrm{P}_{k+n+1-2t}^{u+n+1}-(k-u-2t)(k-u-2t-1)\,\mathrm{P}_{k+n-1-2t}^{u+n+1}\}$$

$$=\sum_{t=0}(-)^t\frac{(k-u)!\;(2k-2t-1)!!}{(k-u-2t)!\,(2k+2n+2-2t+1)!!}\,\mathrm{P}_{k+n+1-2t}^{u+n+1}\,\frac{n!}{t!\,(n-t+1)!}\times\{(2k+2n+2-2t+1)(n-t+1)+(2k-2t+1)\,t\},$$

which reduces to (4) with $n+1$ for n.

3. Multiply (4) by $\mathrm{P}_{k+n-2t}^{u+n}$ and integrate

$$\int_{-1}^{1}(1-\mu^2)^{n/2}\mathrm{P}_k^u\mathrm{P}_{k+n-2t}^{u+n}\,d\mu=(-)^t\,2\,\frac{(k+u+2n-2t)!\;(k-u)!\;(2k-2t-1)!!}{(2k+2n-2t+1)!!}\binom{n}{t}$$

$$(0\leq t\leq n,\quad 2t\leq k-u,\quad t\leq k).$$

Put

$$k=m,\quad k+n-2t=l,\quad u \text{ for } u+n,\quad v \text{ for } u,\quad \text{and}$$

$$l+m+n=2(k+n-t)=2s \quad \dots\dots\dots \quad (5)$$

$$\int_{-1}^{1}\mathrm{P}_l^u\mathrm{P}_m^v(1-\mu^2)^{n/2}\,d\mu=(-)^{s-l}\,2\,\frac{(l+u)!\;(m-v)!\;n!\;(2s-2n-1)!!}{(2s+1)!!\;(s-l)!\;(s-m)!}\quad(u=v+n),$$

(5) is a condition restricting $l+m+n$ to an even integer. The inequalities reduce to

$$m+n\geq l\geq m-n,\quad l\geq u,\quad l\geq n-m. \quad \dots\dots \quad (6)$$

In short, the integers l, m, n must be equal to the sides of a triangle of even perimeter. The expansion (4) shows that if these conditions are violated the above integral vanishes. Since

$$\mathrm{P}_n^n\equiv\frac{2n!}{2^n n!}(1-\mu^2)^{n/2},$$

we have

$$\int_{-1}^{1}\mathrm{P}_l^u\mathrm{P}_m^v\mathrm{P}_n^n\,d\mu=(-)^{s-l}\,2\,\frac{(l+u)!\;(m-v)!\;2n!\;(2s-2n)!\;s!}{(s-l)!\;(s-m)!\;(s-n)!\;(2s+1)!}\quad(u=v+n)\quad\dots\quad(7)$$

* $n!!\equiv n\,(n-2)(n-4)\dots 2$ or 1 $(n>0)$. $0!!=-1!!=1$.

under the conditions (5) and (6). The above proof holds for negative v, so that

$$\int_{-1}^{1} \mathrm{P}_l^l \mathrm{P}_m^v \mathrm{P}_n^w \, d\mu = (-)^w \int_{-1}^{1} \mathrm{P}_m^v \mathrm{P}_n^{-w} \mathrm{P}_l^l \, d\mu = (-)^{s-m-w} \, 2 \frac{2l!\,(m+v)!\,(n+w)!\,(2s-2l)!\,s!}{(s-l)!\,(s-m)!\,(s-n)!\,(2s+1)!}$$
$$(l = v + w). \quad . \quad . \quad . \quad (8)$$

4. Let $u = v + w$.

$$\int_{-1}^{1} \mathrm{P}_l^u \, \mathrm{P}_m^v \, \mathrm{P}_n^w \, d\mu = (-)^u \, (l-u)!\,(m+v)!\,(n+w)!$$
$$\int_{-1}^{1} \left(\frac{d}{d\mu}\right)^{l+u} \frac{(\mu^2-1)^l}{2^l\, l!} \left(\frac{d}{d\mu}\right)^{m-v} \frac{(\mu^2-1)^m}{2^m\, m!} \left(\frac{d}{d\mu}\right)^{n-w} \frac{(\mu^2-1)^n}{2^n\, n!} \, d\mu.$$

By $n - w$ partial integrations and the use of LEIBNITZ' theorem this becomes

$$(-)^{n+v} \, (l-u)!\,(m+v)!\,(n+w)! \sum_t \binom{n-w}{t}$$
$$\int_{-1}^{1} \left(\frac{d}{d\mu}\right)^{l+u+t} \frac{(\mu^2-1)^l}{2^l\, l!} \left(\frac{d}{d\mu}\right)^{m+n-u-t} \frac{(\mu^2-1)^m}{2^m\, m!} \cdot \frac{(\mu^2-1)^n}{2^n\, n!} \, d\mu.$$

The range of t is from the greater of 0 and $n - m - u$ to the least of $n - w$, $l - u$, $m + n - u$.

The above expression is equal to

$$(-)^{n+v} \, (l-u)!\,(m+v)!\,(n+w)! \sum_t \binom{n-w}{t} \int_{-1}^{1} \frac{(-)^n \, \mathrm{P}_l^{u+t} \, \mathrm{P}_m^{n+u-t} \, \mathrm{P}_n^n}{(l-u-t)!\,(m-n+u+t)!\,2n!} \, d\mu.$$

It therefore vanishes unless l, m, n satisfy the triangular conditions (5) and (6). If these conditions are satisfied, we have by (8)

$$\int_{-1}^{1} \mathrm{P}_l^u \, \mathrm{P}_m^v \, \mathrm{P}_n^w \, d\mu = (-)^{s-m-w} \, 2 \frac{(l-u)!\,(m+v)!\,(n+w)!\,(n-w)!\,(2s-2n)!\,s!}{(s-l)!\,(s-m)!\,(s-n)!\,(2s+1)!}$$
$$\times \sum_t (-)^t \frac{(l+u+t)!\,(m+n-u-t)!}{(l-u-t)!\,(m-n+u+t)!\,(n-w-t)!\,t!} \quad . \quad . \quad (9)$$

The range of t is sufficiently indicated by the factorials.

The triangular conditions are extremely useful.

The series in (9) can be summed only in special cases, of which a few are given. It is of the generalised hypergeometric type. Most of the formulæ used are taken from a paper by HARDY.*

5. (i) $l = u$. The series consists of a single term, and (9) reduces to (8).

(ii) $l = m + n$. The series in (9) reduces to

$$\sum_t (-)^t \frac{(m+n+u+t)!}{(m-n+u+t)!\,(n-w-t)!\,t!} = (-)^{n+w} \frac{(m+n+u)!\,2n!}{(n-w)!\,(n+w)!\,(m+v)!},$$

therefore

$$\int_{-1}^{1} \mathrm{P}_l^u \mathrm{P}_m^v \mathrm{P}_n^w \, d\mu = 2 \frac{(l+u)!\,(l-u)!\,l!\,2m!\,2n!}{(2l+1)!\,m!\,n!} \qquad (u = v + w, \ l = m + n). \quad . \quad (10)$$

* HARDY, 'Proc. Camb. Phil. Soc.,' vol. 21, p. 492 (1923).

(iii) $n = m + l$. The series consists of a single term with $t = l - u$

$$\int_{-1}^{1} \mathrm{P}_l^u \mathrm{P}_m^v \mathrm{P}_n^w \, d\mu = (-)^v \, 2 \, . \frac{(n+w)! \, (n-w)! \, n! \, 2l! \, 2m!}{(2n+1)! \, l! \, m!} \quad (u = v + w, \ l + m = n). \quad (11)$$

This is the same as (10) with $-v$ for v, and l, u, interchanged with n, w.

6. (i) $m = n$, $v = w$. Let $l = 2k$, $u = 2v$.

The series is

$$\sum_t (-)^t \frac{(2k+2v+t)! \, (2m-2v-t)!}{(2k-2v-t)! \, (2v+t)! \, (m-v-t)! \, t!}$$

$$= \frac{(2k+2v)! \, (2m-2v)!}{(2k-2v)! \, (m-v)! \, 2v!} \, {}_3\mathrm{F}_2 \begin{pmatrix} -2k+2v, & -m+v, & 2k+2v+1 \\ & -2m+2v, & 2v+1 \end{pmatrix}$$

$$= (-)^{m+v} \frac{(2k+2v)! \, 2m!}{(m-v)! \, (m+v)! \, (2k-m+v)!} \, {}_3\mathrm{F}_2 \begin{pmatrix} -m-v, & 2k+1, & -2m+2k \\ 2k-m+v+1, & -2m & \end{pmatrix}$$

$$= (-)^{k-v} \frac{(2k+2v)! \, (2m-2k)! \, (m+k)!}{(k+v)! \, (k-v)! \, (m+v)! \, (m-k)!},$$

therefore

$$\int_{-1}^{1} \mathrm{P}_{2k}^{2v} [\mathrm{P}_m^v]^2 \, d\mu = 2 \frac{(2k+2v)! \, 2k! \, (2k-2v)! \, (m+v)! \, (m-v)! \, (m+k)!^2 \, (2m-2k)!}{(k+v)! \, k!^2 \, (k-v)! \, (2m+2k+1)! \, (m-k)!^2}. \quad (12)$$

(ii) $u = m + n - 2l$, $v = 2m - n - l$, $w = 2n - m - l$. The series is

$$\frac{(m+n-l)! \, 2l!}{(3l-m-n)! \, (2m-2l)! \, (l+m-n)!} \, {}_3\mathrm{F}_2 \begin{pmatrix} m+n-l+1, & m+n-3l, & n-m-l \\ & -2l, & 2m-2l+1 \end{pmatrix}$$

$$= (-)^s \frac{(m+n-l)! \, (n+l-m)! \, s!}{(l+m-n)! \, (2l-s)! \, (2m-s)! \, (2n-s)!},$$

therefore

$$\int_{-1}^{1} \mathrm{P}_l^{m+n-2l} \mathrm{P}_m^{2m-n-l} \mathrm{P}_n^{2n-m-l} \, d\mu$$

$$= (-)^l \, 2 \frac{(3l-m-n)! \, (3m-n-l)! \, (3n-l-m)! \, (m+n-l)! \, (n+l-m)! \, (l+m-n)! \, s!^2}{(2l-s)! \, (2m-s)! \, (2n-s)! \, (s-l)! \, (s-m)! \, (s-n)! \, (2s+1)!}. \quad (13)$$

(iii) $u = v = w = 0$. The series is

$$\frac{(m+n)!}{(m-n)! \, n!} \, {}_3\mathrm{F}_2 \begin{pmatrix} l+1, & -l, & -n \\ m-n+1, & -m-n & \end{pmatrix}$$

$$= \frac{(l+n)! \, (m+n-l)!}{(m-n)! \, n!^2} \, {}_3\mathrm{F}_2 \begin{pmatrix} -n-l+m, & -l, & m+1 \\ m-n+1; & -n-l & \end{pmatrix}$$

$$= (-)^{s-m} \frac{(m+n-l)! \, (n+l-m)! \, s!}{(s-l)! \, (s-m)! \, (s-n)! \, n!},$$

therefore

$$\int_{-1}^{1} \mathrm{P}_l^0 \mathrm{P}_m^0 \mathrm{P}_n^0 \, d\mu = 2 \frac{l! \, m! \, n! \, s!^2 \, (m+n-l)! \, (n+l-m)! \, (l+m-n)!}{(2s+1)! \, (s-l)!^2 \, (s-m)!^2 \, (s-n)!^2}. \quad (14)$$

This agrees with the formula found by ADAMS* for the integral of the product of three Legendre polynomials, when due regard is paid to the extra factor $l\,!$ in P_l^0.

7. The above results are mainly curiosities. The integrals required in § 5 all have $P_1^0 (= \mu)$ or $P_1^1 (= \sqrt{1-\mu^2})$, or possibly P_2^0, P_2^1 or P_2^2 for one of the tesseral harmonics. Such integrals are easily found from the recurrence formula (3), or the similar formula

$$\mu P_k^u = \frac{1}{2k+1} \{P_{k+1}^u + (k+u)(k-u) P_{k-1}^u\}. \quad \ldots \ldots \quad (15)$$

Thus from (3)

$$\int_{-1}^{1} P_{k+1}^{u+1} P_k^u (1-\mu^2)^{\frac{1}{2}}\, d\mu = \frac{1}{2k+1} \int_{-1}^{1} P_{k+1}^{u+1} P_{k+1}^{u+1}\, d\mu = 2\,\frac{(k+u+2)!\,(k-u)!}{(2k+1)(2k+3)}, \qquad (16)$$

$$\int_{-1}^{1} P_{k-1}^{u+1} P_k^u (1-\mu^2)^{\frac{1}{2}}\, d\mu = \frac{-(k-u)(k-u-1)}{2k+1} \int_{-1}^{1} P_{k-1}^{u+1} P_{k-1}^{u+1}\, d\mu = -2\,\frac{(k+u)!\,(k-u)!}{(2k-1)(2k+1)}. \qquad (17)$$

And similarly from (15)

$$\int_{-1}^{1} P_{k+1}^u P_k^u \mu\, d\mu = \frac{1}{2k+1} \int_{-1}^{1} P_{k+1}^u P_{k+1}^u\, d\mu = 2\,\frac{(k+u+1)!\,(k-u+1)!}{(2k+1)(2k+3)}. \qquad (18)$$

Some other integrals require a further application of (3) or (15).

* ADAMS, 'Roy. Soc. Proc.,' vol. 27, p. 63 (1878).

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES