THE RELATIVE INTENSITIES OF NEBULAR LINES

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Abstract

It is proved rigorously for multipole radiation that the transition $j=0 \rightarrow j=0$ cannot occur. The relative intensities of the lines of the multiplet ${}^{2}P \rightarrow {}^{2}D$ are calculated. They are in the ratio $3/2 \rightarrow 5/2:1/2 \rightarrow 3/2:3/2 \rightarrow 3/2:1/2 \rightarrow 5/2 = 10:5:2:1$, approximately. This is not in agreement with experiment in that the weaker lines are not observed. The relative intensities of the intercombination lines comprising the multiplet ${}^{1}D \rightarrow {}^{3}P$ are calculated, using in part the Darwin-Pauli theory of the spinning election as applied by Houston to the study of intercombination lines. The line ${}^{1}D_{2} \rightarrow {}^{3}P_{2}$ always is strongest according to the calculations, and the experiments confirm this. The line ${}^{1}D_{2} \rightarrow {}^{3}P_{1}$ is about half as strong, which also checks experiment. The intensity of ${}^{1}D_{2} \rightarrow {}^{3}P_{0}$ varies, however, from zero to a value of the same order of magnitude as that of ${}^{1}D_{2} \rightarrow {}^{3}P_{1}$. This is in disagreement with experiment in that the line is not observed. This is the same sort of disagreement as for the multiplet $^{2}P\rightarrow^{2}D$. It is concluded that Bowen's hypothesis, attributing the emission of the "forbidden" nebular lines to quadrupole radiation, is substantiated to some extent, but not fully. The discrepancies between theory and experiment may arise from the simplifying assumptions introduced.

CERTAIN lines in nebular spectra have been interpreted¹ as due to transitions in O III, N II, O II and S II,² occurring in violation of Laporte's rule. According to theory,³ these lines can only be emitted either when an electric field (or an inhomogeneous magnetic field) is present, or when the atom is left undisturbed for a time long enough that quadrupole radiation⁴ can become effective. The first possibility has been considered¹ and found to be improbable, due to the non-observation of a broadening of the Balmer lines such as would be expected. Accordingly, the other alternative (corresponding to the hypothesis of Bowen) is treated in the present paper. The rigorous handling of this problem would require calculations of a complication hardly justifiable, but it is hoped that the work here presented is sufficient to warrant a qualitative conclusion. In particular, we cannot give the relative transition probabilities from the normal state to excited states corresponding to different electronic configurations (such as $(2s)^22p3s$ and $2s2p^3$ in O III). It should be remarked in passing that the emission

¹ For a full discussion, see F. Becker u. W. Gotrian, Ergebnisse der exakten Naturwissen schaften, Bd. 7, 8 ff. (1928).

² I. S. Bowen, Nature 123, 450 (1929).

⁸ E. Wigner, Zeits. f. Physik **43**, 624 (1927) and **45**, 601 (1927). Also J. v. Neumann and E. wigner, Zeits f. Physik **49**, 91 (1928).

⁴ For the development of the theory, see I. I. Placinteanu, Zeits. f. Physik **39**, 276 (1926) and J. Frenkel, Elektrodynamik (1926) Bd. I, p. 93. Also see A. Rubinowicz. Zeits. f. Physik **53**, 267 (1929). This will be referred to as l.c.

of forbidden lines, in the optical region, under conditions that subsist in the laboratory, must have another cause than quadrupole radiation, for to talk of an undisturbed atom in this case would be absurd. On the other hand, it may be possible to ascribe the emission of forbidden x-ray lines to quadrupole radiation, since the action of external disturbances for the inner electrons is much smaller and since the quadrupole radiation is much greater because the wave-length is comparable with the atomic radius.⁵

It was possible for Rubinowicz⁴ to show that the radiation in any given direction from a multipole has, at large distances, the properties of a plane wave. The intensity of radiation in the z direction is determined by the time mean of the z component of the Poynting vector S, so that if A is the vector potential, and A^* its complex conjugate, we have:

$$(\bar{z}S) = \frac{ck^2}{8\pi} [\bar{z}A^*] [\bar{z}A^*] = \frac{ck^2}{8\pi} (A_x A_x^* + A_y A_y^*)$$
$$= \frac{ck^2}{8\pi} \cdot \frac{1}{2} [(A_x + iA_y)(A_x + iA_y)^* + (A_x - iA_y)(A_x - iA_y)^*]$$

where c = velocity of light, $\nu =$ frequency of emitted light, $k = 2\pi\nu/c$, and \bar{z} denotes a unit vector in the z direction. From formula (2) of Rubinowicz,⁴

$$A_x = \frac{1}{c} \int \frac{e^{-ikR}}{R} i_x d\tau$$

where the time factor $e^{2\pi i rt}$ is omitted, i_x signifies the component of current in the x direction, and R is the distance from the source of radiation to the point under consideration. Let r be the distance from the center of the atom to this same point.

Then

$$A_x \cong \frac{1}{c} \ \frac{e^{-ikr}}{r} \int i_x e^{ikz} d\tau$$

Expanding in series, and letting i = ep/m, where p is the momentum,

$$A_{x} = \frac{e}{mc} \frac{e^{-ikr}}{r} \left[\int p_{x} d\tau + \int ik(zp_{x}) d\tau + \cdots \right]$$

The first term gives the part due to dipole radiation (Rubinowicz⁴ p. 272) the second that due to quadrupole radiation (l.c., formula (14), p=1), and so on. Thus, we shall deal with matrix elements of the types p, zp, z^2p , etc. For quadrupole radiation, therefore,

$$A_x + iA_y \sim z(p_x + ip_y)$$
; $A_x - iA_y \sim z(p_x - ip_y)$.

The problem then essentially reduces to calculating the matrix amplitudes of $z(p_x+ip_y)$ with aid of the relation

$$\left[z(p_{x}+ip_{y})\right]_{n,l',j',m-1}^{n,l,j,m} = \sum_{n'l'',j'',m'} \sum_{m,l',j'',m'} \sum_{m',l'',j'',m'} p_{x}+ip_{y})_{n,l',j',m-1}^{n',l'',j'',m}$$

⁵ I owe this suggestion to Professor W. Pauli, Jr.

where the summation is to be taken over all such intermediate states as are accessible both from the end state (n, l', j', m-1) as well as from the initial state(n, l, j, m).

I. QUADRUPOLE RADIATION BETWEEN STATES OF THE SAME MULTIPLICITY

The following formulae⁶ are necessary for our calculation:

a. Zeeman Lines.

$$\begin{split} A^{m,i}_{m\pm 1,j} &= \frac{A^{i}_{j}}{j(j+1)} \frac{1}{2} (j\mp m) (j\pm m+1) \ ; \ A^{m,i}_{m,j} &= \frac{A^{i}_{j}}{j(j+1)} m^{2} \\ A^{m,i}_{m\pm 1,j+1} &= \frac{A^{i}_{j+1}}{(j+1)(2j+3)} \frac{1}{2} (j\pm m+2) (j\pm m+1) \ ; \\ A^{m,i}_{m,j+1} &= \frac{A^{i}_{j+1}}{(j+1)(2j+3)} [(j+1)^{2} - m^{2}] \\ A^{m,i}_{m\pm 1,j-1} &= \frac{A^{i}_{j-1}}{j(2j-1)} \frac{1}{2} (j\mp m) (j\mp m-1) \ ; \\ A^{m,i}_{m,j-1} &= \frac{A^{i}_{j-1}}{j(2j-1)} (j^{2} - m^{2}) \end{split}$$

b. Multiplet Lines.

$$\begin{split} \Delta l &= -1 \ \begin{cases} J_{-1} = G_{i} \quad A_{i,l-1}^{i,l} = \frac{C}{4jl} P(j,l) P(j-1,l) \\ J_{0} = G_{i} \quad A_{i,l-1}^{i,l} = C \frac{2j+1}{4jl(j+1)} P(j,l) Q(j,l) \\ J_{+1} = G_{j-1} A_{j,l-1}^{i-1,l} = \frac{C}{4jl} Q(j,l) Q(j-1,l) \end{cases} \\ \Delta l &= 0 \ \begin{cases} J_{0} = G_{i} \quad A_{i,l}^{j,l} = \frac{C}{4jl} \frac{2l+1}{l+1} \frac{2j+1}{j+1} R^{2}(j,l) \\ J_{\pm 1} = G_{i} \quad A_{j-1,l}^{j,l} = G_{j-1} A_{j,l}^{j-1,l} = \frac{C}{4jl} \frac{2l+1}{l+1} P(j,l) Q(j-1,l) \end{cases} \\ \Delta l &= +1 \ \begin{cases} J_{-1} = G_{i} \quad A_{j-1,l+1}^{j,l} = \frac{C}{4j(l+1)} Q(j,l+1) Q(j-1,l+1) \\ J_{0} = G_{i} \quad A_{j,l+1}^{j,l} = \frac{C}{4j(l+1)} \frac{2j+1}{j+1} P(j,l+1) Q(j,l+1) \\ J_{+1} = G_{j-1} A_{j,l+1}^{j-1,l} = \frac{C}{4j(l+1)} P(j,l+1) P(j-1,l+1) . \end{cases} \end{cases} \end{split}$$

 6 See W. Pauli, Handbuch der Physik, Bd. XXIII, p. 67 and p. 243 in particular, and the accompanying text, for a thoroughgoing discussion.

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Here are made the following abbreviations:

$$P(j,l) = (j+l)(j+l+1) - s(s+1)$$

-Q(j,l) = (j-l)(j-l+1) - s(s+1)
$$R(j,l) = j(j+1) + l(l+1) - s(s+1)$$

where s = 0 for singlets, $\frac{1}{2}$ for doublets, etc. One verifies readily that

$$P(j,l) = R(j,l) + 2jl -Q(j,l) = R(j,l) - 2(j+1)l.$$

The *A*'s above are squares of matrix amplitudes.

Now let v = x + iy, $p_v = p_x + ip_y$, w = x - iy, $p_w = p_x - ip_y$. In the calculations, products of the form $AB = z_b^a v_c^b z_e^d v_f^e$ occur, where the letters a to f denote values which the inner quantum number takes on. Such products are listed in Table I. (AB = BA)

TABLE I. Products AB.							
B A	$z_{j\rightarrow1}^{i}v_{j}^{j\rightarrow1}$.	$\left \begin{array}{c} z_{j}^{j} v_{j}^{j} \\ j \end{array} \right $	$z_{j+1}^{j}v_{j}^{j+1}$				
$z_{j-1}^{j} v_{j}^{j-1}$	$\frac{(j^2-m^2)(j-m+1)(j-m)}{j^2(2j-1)(2j+1)}$						
zj ^j vj	$\frac{(j^2-m^2)(j-m+1)m}{j^2(j+1)[(2j-1)(2j+1)]^{1/2}}$	$\frac{\frac{m^2(j+m)(j-m+1)}{[j(j+1)]^2}}{[j(j+1)]^2}$					
$z_{j+1}^{j} v_{j}^{i+1}$	$\frac{(j^2-m^2)(j-m+1)(j+m+1)}{j(j+1)(2j+1)[(2j-1)(2j+3)]^{1/2}}$	$\frac{m(j+m)(j-m+1)(j+m+1)}{j(j+1)^2[(2j+1)(2j+3)]^{1/2}}$	$\frac{(j+m)(j-m+1)(j+m+1)^2}{(2j+3)(2j+1)(j+1)^2}$				
A B	$z^i_{j j+1}$		$B \xrightarrow{A} \frac{z_{j+1}^{i} z_{j+1}^{i+1}}{z_{j+1}^{i+1} z_{j+2}^{i+1}}$				
$z_{j v j}^{j v j}$	$\frac{m^2(j-m+2)(j-m+1)}{j(j+1)^2(2j+3)}$		$\begin{bmatrix} i & j+1 \\ j^2 j+1^2 j+2^2 \end{bmatrix} (j-m+1)(j+m+1)(j-m+1)(j-m+2)(j-m+$				
$z_{j+1}^{j} v_{j+1}^{j+1}$	$\frac{m(j-m+1)(j-m+2)(j+m+1)}{(j+1)^2(2j+3)[j(j+2)]^{1/2}}$	$\frac{(j-m+1)(j+m+1)^2(j-m+2)}{(2j+3)(j+1)^2(j+2)}$	$\sum_{j=1}^{j+1} \sum_{j=1}^{j+1} (j+1)(j+3)(2j+3)(2j+5)$				

The procedure is to determine $[(zp_v)_{n,l',j',m-1}^{n,l,j}]^2$ and then to sum over m to eliminate the effect of spacial degeneracy. Natural excitation is assumed to be the case.

Let

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$$\tau(j) = \frac{3j^2 + 3j - 1}{5}$$

The products AB given above are dependent on m. We sum them over all possible values of m. The results are given in Table II

In the case of the multiplet ${}^{2}P \rightarrow {}^{2}D$, the intermediate state can be either a P-state or a D-state. We shall calculate the relative intensities of the

$t_i^{j}a_i^{j}z$.		i i. 1
	26	$z_{j+1}v_{j}^{*} =$
$\frac{1}{3(2j+1)} \left[3j^2 + 2j + 1 - \frac{j-1}{j}\tau(j-1) \right]$		
$\frac{1}{3} \frac{j(j-1)}{j+1} \left[\frac{2-1j}{2j+1} \right]^{1/2} \left[1 - \frac{\tau(j-1)}{j^2} \right] \frac{2j^2 + \frac{3}{2}(j-1)(2j-1)[j(j+1) - \tau(j-1)]}{j(j+1)^2}$	$[j(j+1)-\tau(j-1)]$ +1) ²	
$\frac{-1}{(j+1)(2j+1)} \left[r(j-1) - j^2 \right]$	$\frac{3(j-1)(2^{j}-1)[(j+1)^{2}-\tau(j-1)]+2j(2j+1)}{(j+1)^{2}[(2j+1)(2j+3)]^{l/2}}$	$\frac{1}{2}j(j-1)(2j-1)[(j+1)^{n}-r(j-1)] + 2j(2j+1)^{n}+j(2j-1)(j+1)^{n}}{(j+1)^{n}(2j+1)(2j+3)}$
$z_i^{j}v_{i+1}^{j+1}$	$\frac{i}{z_{j+1}v_{j+1}}$	
$\frac{1}{3} \frac{2j+1}{(j+1)(2j+3)} [(j+1)(j+2)+\tau(j)]$		
	$\frac{1}{3} \frac{2j+1}{(2j+3)(j+1)(j+2)} [(j+1)(j^2+j6+6)+jr(j)]$	
$i_{j+1}^{j} i_{j+2}^{j+1}$		
$\frac{-\frac{1}{3}j(2j+1)[r(j)+3j+5]+(j+1)(j+2)(j+3)}{(j+2)(2j+3)(2j+3)(2j+3)}$		

TABLE II. $\Sigma_m[AB]^2(m)$

lines of this multiplet assuming (1) that there is one intermediate P-state effective and (2) that there is one intermediate D-state effective.

A sample calculation for the line ${}^{2}P_{1/2} \rightarrow {}^{2}D_{3/2}$ follows.

Case (I).

$$(zp_{v})_{n,2,3/2,m-1}^{n,1,1/2,m} = \sum_{n',1,1/2,m}^{n,1,1/2,m} p_{vn,2,3/2,m-1}^{n',1,1/2,m} + \sum_{n',1,3/2,m}^{n,1,1/2,m} p_{vn,2,1/2,m-1}^{n',1,3/2,m}$$

Using the relation

$$p_{vn,2}^{n',1} = 2\pi i m \nu_{n,2}^{n',1} v_{n,2}^{n',1}$$

we calculate that

$$\sum [zp_{v}]^{2}(m) \sim (\nu_{n,2}^{n',1})^{2} \left\{ \frac{4}{9} A_{n',1,1/2}^{n,1,1/2} A_{n,2,3/2}^{n',1,1/2} + \frac{28}{45} A_{n',1,3/2}^{n,1,1/2} A_{n,2,3/2}^{n',1,3/2} - \frac{4}{9(5)^{1/2}} \left(A_{n',1,1/2}^{n,1,1/2} A_{n,1,3/2}^{n',1,1/2} A_{n,2,3/2}^{n',1,1/2} A_{n,2,3/2}^{n',1,3/2} \right)^{1/2} \right\}$$
$$= (\nu_{n,2}^{n',1})^{2} A_{n',1}^{n,1} A_{n,2}^{n',1} \left(\frac{40}{9} + \frac{14}{45} - \frac{4}{9} \right) = 4 \cdot 3(\nu_{n,2}^{n',1})^{2} A_{n',1}^{n,1} A_{n,2}^{n',1} \right)^{1/2}$$

The relative intensities are then as follows:

$$3/2 \rightarrow 5/2: 1/2 \rightarrow 3/2: 3/2 \rightarrow 3/2: 1/2 \rightarrow 5/2 = 10.8:4.3:2.8:1.8$$

Case (2).

The relative intensities when a D-state is intermediate are

$$3/2 \rightarrow 5/2: 1/2 \rightarrow 3/2: 3/2 \rightarrow 3/2: 1/2 \rightarrow 5/2 = 23.8: 14: 4:1$$

Only the line ${}^{2}P_{1_{\frac{1}{2}}} \rightarrow {}^{2}D_{2_{\frac{1}{2}}}$ is observed experimentally. It is to be noted that the transition $j = \frac{1}{2} \rightarrow j = 2\frac{1}{2}$ is especially weak, as one would expect. This calculation is in error insofar as it leaves out of account the effect of the possible intermediate state $2s2p^{4}$ ${}^{4}P$, which lies so low that it may have some influence. Transitions to and from this state would, however, be intercombinations, and so it is believed that its effect is quite negligible.

Since *m* must change⁷ by ± 1 , it is a trivial conclusion that the transition $j=0 \rightarrow j=0$ cannot occur for multipole radiation. A corresponding rule,⁸ which is not exact in that it neglects the interaction of angular momenta of spin and orbit, states that the transition $l=0 \rightarrow l=0$ cannot occur. The rule for the inner quantum number, is however, perfectly rigorous (for multipole radiation). When, however, electric fields or similar influences are present, then both of the above rules will be violated.

II. DIPOLE RADIATION FOR INTERCOMBINATIONS BETWEEN STATES OF DIFFERENT MULTIPLICITIES

1. The Secular Equations and Perturbed Wave Functions. To calculate quadrupole radiation for intercombination lines, we must first know the

⁷ This follows from the fact that the matrix elements are of the type $z^n p$, as already stated.

⁸ A. Rubinowicz, Phys. Zeits. 29, 823 (1928).

dipole radiation to or from the intermediate state. It is simplest to treat as intermediate states those arising from the 2p3s configuration. The 2p3dconfiguration can probably be neglected, since the combinations with the ground state are rather weak. As to 2s2p,³ a straightforward method of attact such as employed for 2p3s is much too complicated to be worthwhile. For this reason, the present paper deals only with 2p3s. A short discussion of $2s2p^3$ is given later.

To calculate the dipole radiation, we make use of the method developed by Houston⁹ for determining the wave functions which result from the disturbance of symmetry coming from the mutual interaction between the angular momenta of spin and orbit. The function of the co-ordinates of one electron may be written as $R_{ln}^{(r)} P_l^{ml}$, where l is the azimuthal quantum number, and m_l its projection on a prefered axis. Also,

$$P_{l}^{m_{l}} = (l - m_{l})! \sin^{m_{l}} \theta \left(\frac{d}{d\cos\theta}\right)^{l+m_{l}} \frac{(-\sin^{2}\theta)^{l}}{2^{l}l!} e^{im_{l}\phi}$$

The two possible values of the spin variable are denoted by S_{α} and S_{β} , respectively. The perturbing energy arises (1) from the electrostatic interaction of the two electrons and (2) from two magnetic interactions, namely between the spin of each electron and its orbit. As unperturbed wave functions of $(2p)^2$, we take the following¹⁰:

$$\begin{split} \psi_{\alpha}^{2} &= \left(\frac{1}{2}\right)^{1/2} \left\{ P_{1}^{0}(1) P_{1}^{1}(2) - P_{1}^{0}(2) P_{1}^{1}(1) \right\} S_{\alpha}(1) S_{\alpha}(2) \\ \psi_{\epsilon}^{2} &= \left(\frac{1}{2}\right)^{1/2} P_{1}^{-1}(1) P_{1}^{-1}(2) \left\{ S_{\alpha}(1) S_{\beta}(2) - S_{\beta}(1) S_{\alpha}(2) \right\} \\ \psi_{\alpha}^{1} &= \left(\frac{1}{2}\right)^{1/2} \left\{ P_{1}^{-1}(1) P_{1}^{-1}(2) - P_{1}^{-1}(2) P_{1}^{-1}(1) \right\} S_{\alpha}(1) S_{\alpha}(2) \\ \psi_{\gamma}^{1} &= \frac{1}{2} \left\{ P_{1}^{0}(1) P_{1}^{-1}(2) - P_{1}^{0}(2) P_{1}^{-1}(1) \right\} \left\{ S_{\alpha}(1) S_{\beta}(2) + S_{\beta}(1) S_{\alpha}(2) \right\} \\ \psi_{\delta}^{1} &= \frac{1}{2} \left\{ P_{1}^{0}(1) P_{1}^{-1}(2) + P_{1}^{0}(2) P_{1}^{-1}(1) \right\} S_{\beta}(1) S_{\beta}(2) \\ \psi_{\alpha}^{0} &= \left(\frac{1}{2}\right)^{1/2} \left\{ P_{1}^{0}(1) P_{1}^{-1}(2) - P_{1}^{0}(2) P_{1}^{-1}(1) \right\} S_{\alpha}(1) S_{\beta}(2) \\ \psi_{\gamma}^{0} &= \frac{1}{2} \left\{ P_{1}^{-1}(1) P_{1}^{-1}(2) - P_{1}^{-1}(2) P_{1}^{-1}(1) \right\} S_{\alpha}(1) S_{\beta}(2) - S_{\beta}(1) S_{\alpha}(2) \right\} \\ \psi_{\delta}^{0} &= \frac{1}{2} \left\{ P_{1}^{-1}(1) P_{1}^{0}(2) \left\{ S_{\alpha}(1) S_{\beta}(2) - S_{\beta}(1) S_{\alpha}(2) \right\} \\ \psi_{\epsilon}^{0} &= \left(\frac{1}{2}\right)^{1/2} \left\{ P_{1}^{-1}(1) P_{1}^{-1}(2) - P_{1}^{-1}(2) P_{1}^{-1}(1) \right\} S_{\beta}(1) S_{\beta}(2) \\ \psi_{\gamma}^{-1} &= \frac{1}{2} \left\{ P_{1}^{0}(1) P_{1}^{-1}(2) - P_{1}^{0}(2) P_{1}^{-1}(1) \right\} \left\{ S_{\alpha}(2) S_{\beta}(2) + S_{\beta}(1) S_{\alpha}(2) \right\} \\ \psi_{\delta}^{-1} &= \frac{1}{2} \left\{ P_{1}^{0}(1) P_{1}^{-1}(2) - P_{1}^{0}(2) P_{1}^{-1}(1) \right\} \left\{ S_{\alpha}(1) S_{\beta}(2) - S_{\beta}(1) S_{\alpha}(2) \right\} \end{split}$$

$$\begin{aligned} \psi_{\alpha}^{-2} &= (\frac{1}{2})^{1/2} \Big\{ P_1^{0}(1) P_1^{-1}(2) - P_1^{0}(2) P_1^{-1}(1) \Big\} S_{\beta}(1) S_{\beta}(2) \\ \psi_{\epsilon}^{-2} &= (\frac{1}{2})^{1/2} P_1^{-1}(1) P_1^{-1}(2) \Big\{ S_{\alpha}(1) S_{\beta}(2) - S_{\beta}(1) S_{\alpha}(2) \Big\} \,. \end{aligned}$$

⁹ W. V. Houston, Phys. Rev. 33, 297 (1929).

¹⁰ See J. A. Gaunt, Phil. Trans. A228, 184 (1929) for similar functions.

The common radial function is not written. The superscript of ψ specifies $m = \sum m_1 + m_s$, the quantum number corresponding to the projection of the angular momentum in a fixed direction, which is a constant of the motion when the atom is not subject to an external field. The subscript of ψ serves to distinguish between functions with the same m. Since, for an undisturbed atom, terms with different m cannot combine, the original fifteen-rowed secular equation may be broken up into (1) two equivalent two-rowed equations, (2), two equivalent three-rowed equations, and (3) one five-rowed equation. From (1), one solves for the energy levels which are consistent with m = 2 and these are 1D_2 and 3P_2 . One also has a possibility of m = 1 for these, and so from (2) we obtain them and 3P_1 in addition. From (3), we obtain all the energy levels, namely 1D_2 , ${}^3P_{0,1,2}$, and 1S_0 .

The procedure adopted here is to start out with wave functions which are correct zeroth approximations if only the electrostatic interaction of the electrons is considered. Of these functions written above, ψ_{δ^0} and ψ_{ϵ^0} are not such. Applying a perturbation calculation,¹¹ the perturbation being the electrostatic interaction, we find for the proper wave functions,

$${}^{1}D_{2}: \psi_{\mathrm{IV}}{}^{0} = (\frac{1}{3})^{1/2}\psi_{\delta}{}^{0} + (\frac{2}{3})^{1/2}\psi_{\epsilon}{}^{0}$$
$${}^{1}S_{0}: \psi_{\mathrm{V}}{}^{0} = -(\frac{2}{3})^{1/2}\psi_{\delta}{}^{0} + (\frac{1}{3})^{1/2}\psi_{\epsilon}{}^{0}$$

The problem is then to find linear combinations which are correct zeroth approximations when the magnetic interaction resulting in the splitting-up of the multiplet is taken into account.

If we define

$$\gamma_{12} = \frac{h^2}{16\pi^2} \frac{ze^2}{m_0^2 c^2} \int R_{12}^2 \frac{1}{r^3} d\tau$$

and

$$Y_1 = \frac{\Delta E_1}{\gamma_{12}}$$
; $Y_2 = \frac{\Delta E_2}{\gamma_{12}}$; $\epsilon = \frac{\Delta E}{\gamma_{12}}$

where ΔE_1 and ΔE_2 are the excitation energies of 1D_2 and 1S_0 , respectively, then it is possible to write the secular equation for m = 0 as follows:

	$-1-\epsilon$	0	1	$-(1/3)^{1/2}$	$-(8/3)^{1/2}$	
	0	$-1-\epsilon$	-1	$(1/3)^{1/2}$	$(8/3)^{1/2}$	
	1	-1	— ε	$-(4/3)^{1/2}$	$(8/3)^{1/2}$	
	$-(1/3)^{1/2}$	$(1/3)^{1/2}$	$-(4/3)^{1/2}$	$Y_1 - \epsilon$	0	= 0
	$-(8/3)^{1/2}$	$(8/3)^{1/2}$	$(8/3)^{1/2}$	0	$Y_2 - \epsilon$	

The energies are measured from a zero between the two outer triplet terms, which would be the energy of the unresolved triplet.

 11 This is in every respect the same as that of Gaunt (ref. 10) except that we use normalized functions.

The calculation may be simplified¹² by considering the triplet by itself and finding the wave functions for the various values of j (in zeroth approximation). Thus, for m = 0, we solve the secular equation:

$-1-\epsilon$	0	1	
0	$-1-\epsilon$	-1	=0
1	-1	e	

obtaining as roots $\epsilon_1 = -2$, $\epsilon_2 = -1$, $\epsilon_3 = 1$ and as wave functions

$$\begin{split} \epsilon_{3} : {}^{3}P_{2} : \psi_{\mu}{}^{0} &= \left(\frac{1}{6}\right)^{1/2} (\psi_{\alpha}{}^{0} - \psi_{\beta}{}^{0} + 2\psi_{\gamma}{}^{0}) \\ \epsilon_{2} : {}^{3}P_{1} : \psi_{\lambda}{}^{0} &= \left(\frac{1}{2}\right)^{1/2} (\psi_{\alpha}{}^{0} + \psi_{\beta}{}^{0}) \\ \epsilon_{1} : {}^{3}P_{0} : \psi_{\kappa}{}^{0} &= \left(\frac{1}{3}\right)^{1/2} (\psi_{\alpha}{}^{0} - \psi_{\beta}{}^{0} - \psi_{\gamma}{}^{0}) \,. \end{split}$$

Then, for j = 2

$$\begin{array}{c|c} & \psi_{\mu}^{0} & \psi_{\mathrm{IV}}^{0} \\ \psi_{\mu}^{0} & 1 - \epsilon & -2^{1/2} \\ \psi_{\mathrm{IV}}^{0} & -2^{1/2} & Y_{1} - \epsilon \end{array} = 0$$

and for j=0

$$\begin{array}{c|c} \psi_{\kappa}^{0} & \psi_{V}^{0} \\ \psi_{\kappa}^{0} & -2 - \epsilon & -2(2)^{1/2} \\ \psi_{V}^{0} & -2(2)^{1/2} & Y_{2} - \epsilon \end{array} \right| = 0$$

The roots become:

$${}^{1}S_{0}:\epsilon_{5} = (\frac{1}{2}) \left[Y_{2} - 2 + \left\{ (Y_{2} + 2)^{2} + 32 \right\}^{1/2} \right] \\ {}^{1}D_{2}:\epsilon_{4} = (\frac{1}{2}) \left[Y_{1} + 1 + \left\{ (Y_{1} - 1)^{2} - 8 \right\}^{1/2} \right] \\ {}^{3}P_{2}:\epsilon_{3} = (\frac{1}{2}) \left[Y_{1} + 1 - \left\{ (Y_{1} - 1)^{2} - 8 \right\}^{1/2} \right] \\ {}^{3}P_{1}:\epsilon_{2} = -1 \\ {}^{3}P_{0}:\epsilon_{1} = (\frac{1}{2}) \left[Y_{2} - 2 - \left\{ (Y_{2} + 2)^{2} + 32 \right\}^{1/2} \right] \right]$$

The wave functions are:

$$m = 2$$

$$1D_{2}: (1/c_{4}\Delta_{2})^{1/2}(-2^{1/2}\psi_{\alpha}^{2} + c_{4}\psi_{\epsilon}^{2})$$

$$^{3}P_{2}: (1/c_{3}\Delta_{2})^{1/2}(2^{1/2}\psi_{\alpha}^{2} + c_{3}\psi_{\epsilon}^{2})$$

$$m = 1$$

$$1D_{2}: (1/c_{4}\Delta_{2})^{1/2}(-\psi_{\alpha}^{1} - \psi_{\gamma}^{1} + c_{4}\psi_{\delta}^{1})$$

$$^{3}P_{2}: (1/c_{3}\Delta_{2})^{1/2}(\psi_{\alpha}^{1} + \psi_{\gamma}^{1} + c_{3}\psi_{\delta}^{1})$$

$$^{3}P_{1}: (1/2)^{1/2}(-\psi_{\alpha}^{1} + \psi_{\gamma}^{1})$$

 12 This became apparent during a discussion of the matter with Dr. L. L. Rosenfeld whom ${\bf I}$ wish to thank for his helpfulness.

$$m = 0 \qquad {}^{1}S_{0}: (1/c_{5}\Delta_{0})^{1/2}(2 \cdot 2^{1/2}\psi_{\kappa}^{0} + c_{5}\psi_{V}^{0}) \\ {}^{1}D_{2}: (1/c_{4}\Delta_{2})^{1/2}(-2^{1/2}\psi_{\mu}^{0} + c_{4}\psi_{IV}^{0}) \\ {}^{3}P_{2}: (1/c_{3}\Delta_{2})^{1/2}(2^{1/2}\psi_{\mu}^{0} + c_{3}\psi_{IV}^{0}) \\ {}^{3}P_{1}: (1/2)^{1/2}(\psi_{\alpha}^{0} + \psi_{\beta}^{0}) \\ {}^{3}P_{0}: (1/c_{1}\Delta_{0})^{1/2}(2 \cdot 2^{1/2}\psi_{\kappa}^{0} - c_{1}\psi_{V}^{0}) \\ m = -1 \qquad {}^{1}D_{2}: (1/c_{4}\Delta_{2})^{1/2}(-\psi_{\alpha}^{-1} + \psi_{\gamma}^{-1} + c_{4}\psi_{\delta}^{-1}) \\ {}^{3}P_{1}: (1/2)^{1/2}(\psi_{\alpha}^{-1} - \psi_{\gamma}^{-1} + c_{3}\psi_{\delta}^{-1}) \\ {}^{3}P_{1}: (1/2)^{1/2}(\psi_{\alpha}^{-1} + \psi_{\gamma}^{-1}) \\ m = -2 \qquad {}^{1}D_{2}: (1/c_{4}\Delta_{2})^{1/2}(2^{1/2}\psi_{\alpha}^{-2} + c_{4}\psi_{\epsilon}^{-2}) \\ {}^{3}P_{3}: (1/c_{3}\Delta_{2})^{1/2}(-2^{1/2}\psi_{\alpha}^{-2} + c_{3}\psi_{\epsilon}^{-2}). \end{cases}$$

In these formulae, Δ_j means the separation, in terms of ϵ , of the two levels with the same j. Thus: $\Delta_0 = |\epsilon_5 - \epsilon_1|$. For brevity we have written

 $c_1 = |2 + \epsilon_1|$, $c_5 = |2 + \epsilon_5|$, $c_3 = |1 - \epsilon_3|$, and $c_4 = |1 - \epsilon_4|$ One finds that

 $c_1c_5 = 8$ and $c_3c_4 = 2$. When Y_1 and Y_2 are large, $c_5 \cong \Delta_0$, $c_4 \cong \Delta_2$.

For the case where interaction between spin and orbit is negligible, the triplet has the 2:1 ratio of separations. When the interaction between the electrons is zero, (that is, $Y_1 = Y_2 = 0$), $\epsilon_1 = -4$, $\epsilon_2 = \epsilon_3 = -1$, $\epsilon_4 = \epsilon_5 = 2$, or the ${}^{1}S_0$ and ${}^{1}D_2$ levels merge 13 together, as do the ${}^{3}P_2$ and ${}^{3}P_1$ levels. The quintet degenerates into a triplet with separation ratio 1:1. In the case treated by Houston, neighboring levels such as ${}^{1}P_1$ and ${}^{3}P_2$ and ${}^{3}P_1$ and ${}^{3}P_0$ merged together likewise.

Following Houston, let

$$\gamma_{ln} = \frac{h^2}{16\pi^2} \frac{Ze^2}{m_0^2 c^2} \int R_{ln}^2 \frac{1}{r^3} d\tau$$

and $X = \Delta E_3 / \gamma_{ln}$, $\epsilon = \Delta E / \gamma_{ln}$, where ΔE_3 is the singlet-triplet separation.

¹³ For details as to the reason for this, see S. Goudsmit, Phys. Rev. **31**, 956 (1928). For the case of (jj) coupling in the singlet-triplet case, see W. Pauli, Handbuch der Physik, vol. XXIII, pp. 254-257. The two pairs of levels (${}^{1}P_{1}$ and ${}^{3}P_{2}$, ${}^{3}P_{1}$ and ${}^{3}P_{0}$) are expected to form a relativistic doublet.

We may note that the splitting-up of the multiplets ${}^{3}P$ and ${}^{3}D$ of the configuration $2s2p^{3}$ is, according to the approximation of Goudsmit, zero. One finds for the (*ii*) coupling case (1) for $j_{1}=1/2$, $j_{2}=1/2$, $j_{3}=1/2$, $j_{4}=3/2$ one state with j=2 and one with j=1, (2) for $j_{1}=1/2$, $j_{2}=1/2$, $j_{3}=3/2$, $j_{4}=3/2$ one state with j=3, one with j=0, and two each with j=3 and j=1, and (3) for $j_{1}=1/2$, $j_{2}=3/2$, $j_{3}=3/2$, $j_{4}=3/2$ one state with j=2 and one with j=1. The Γ value for j=3 is 0; for j=2, $\Sigma\Gamma=0$; for j=1, $\Sigma\Gamma=0$; and for j=0, $\Gamma=0$. This gives immediately the result of non-splitting. Actually, one observes a small splitting-up in O III, both triplets being resolved into two lines each. This is no doubt due to the presence of the other terms arising from the same electronic configuration. In C I, N II, and F IV, on the other hand, the triplets appear unresolved.

Also, choose as the functions of the unperturbed system the following:

$$\begin{split} \phi_{1} &= \left(\frac{1}{2}\right) \left\{ P_{0}^{0}(1) P_{l}^{m}(2) + P_{0}^{0}(2) P_{l}^{m}(1) \right\} \left\{ S_{\alpha}(1) S_{\beta}(2) - S_{\alpha}(2) S_{\beta}(1) \right\} \\ \phi_{2} &= \left(\frac{1}{2}\right)^{1/2} \left\{ P_{0}^{0}(1) P_{l}^{m-1}(2) - P_{0}^{0}(2) P_{l}^{m-1}(1) \right\} S_{\alpha}(1) S_{\alpha}(2) \\ \phi_{3} &= \left(\frac{1}{2}\right) \left\{ P_{0}^{0}(1) P_{l}^{m}(2) - P_{0}^{0}(2) P_{l}^{m}(1) \right\} \left\{ S_{\alpha}(1) S_{\beta}(2) + S_{\alpha}(2) S_{\beta}(1) \right\} \\ \phi_{4} &= \left(\frac{1}{2}\right)^{1/2} \left\{ P_{0}^{0}(1) P_{l}^{m+1}(2) - P_{0}^{0}(2) P_{l}^{m+1}(1) \right\} S_{\beta}(1) S_{\beta}(2) . \end{split}$$

With no magnetic field, the secular equation is

$X-\epsilon$	au	-m	$-\tau'$	
au	$m-1-\epsilon$	au	0	
-m	au	— e	au'	=0
$-\tau'$	0	au'	$-m-1-\epsilon$	

Here

$$\tau = (\frac{1}{2})^{1/2} (l+m)^{1/2} (l-m+1)^{1/2}$$

and

$$\tau' = (\frac{1}{2})^{1/2}(l-m)^{1/2}(l+m+1)^{1/2}.$$

When the triplet and singlet can be handled separately, the energy values are:

$$\epsilon_{\mathrm{I}} = X, \qquad \epsilon_{\mathrm{II}} = l, \qquad \epsilon_{\mathrm{III}} = -1, \qquad \epsilon_{\mathrm{IV}} = -l-1.$$

The wave functions are:

$$\begin{split} \psi_{1} &= \phi_{1} \\ \psi_{II} &= \left\{ 1/(l+1)(2l+1) \right\}^{1/2} \left[\left(\frac{1}{2}\right)^{1/2} \left\{ (l+m)(l+m+1) \right\}^{1/2} \phi_{2} \\ &+ \left\{ (l-m+1)(l+m+1) \right\}^{1/2} \phi_{3} + \left(\frac{1}{2}\right)^{1/2} \left\{ (l-m)(l-m+1) \right\}^{1/2} \phi_{4} \right] \\ \psi_{3} &= \left\{ 1/l(l+1) \right\}^{1/2} \left[-\left(\frac{1}{2}\right)^{1/2} \left\{ (l+m)(l-m+1) \right\}^{1/2} \phi_{2} + m\phi_{3} \\ &+ \left(\frac{1}{2}\right)^{1/2} \left\{ (l-m)(l+m+1) \right\}^{1/2} \phi_{4} \right] \\ \psi_{IV} &= \left\{ 1/l(l+1) \right\}^{1/2} \left[\left(\frac{1}{2}\right)^{1/2} \left\{ (l-m)(l-m+1) \right\}^{1/2} \phi_{2} - (l^{2}-m^{2})^{1/2} \phi_{3} \\ &+ \left(\frac{1}{2}\right)^{1/2} \left\{ (l+m)(l+m+1) \right\}^{1/2} \phi_{4} \right]. \end{split}$$

Applying our previous method, we then solve the secular equation (j=l)

$$\begin{array}{c|ccc} & \psi_3 & \psi_1 \\ \psi_3 & -1 - \epsilon & -(l^2 + l)^{1/2} \\ \psi_1 & -(l^2 + l)^{1/2} & X - \epsilon \end{array} \Big| = 0$$

This results in

$$\psi_{\rm I} = (1/c_{\rm I}\Delta_l)^{1/2} \{ c_{\rm I}\psi_1 - (l^2 + l)^{1/2}\psi_3 \}$$

$$\psi_{\rm III} = (1/c_{\rm III}\Delta_l)^{1/2} \{ c_{\rm III}\psi_1 + (l^2 + l)^{1/2}\psi_3 \}$$

where

$$c_{\mathrm{I}} = |1 + \epsilon_{\mathrm{I}}|$$
 and $c_{\mathrm{III}} = |1 + \epsilon_{\mathrm{III}}| \cdot c_{\mathrm{I}}c_{\mathrm{III}} = l^2 + l$.

When X is large, $c_{\mathbf{I}} \cong \Delta_1$

For the 2p 3s configuration, the wave functions $\dot{\psi}_{I}$, ψ_{II} , ψ_{II} , ψ_{IV} are then used, with l=1, to find the matrix elements.

2. The Triplet Separations. For O III,

$${}^{1}S_{0} - {}^{3}P : \Delta \nu \cong 43130$$

 ${}^{1}D_{2} - {}^{3}P : \Delta \nu \cong 20120.$

It is at once seen that the ratio of separation 2:3 as derived from a first order perturbation calculation¹⁰ is not in agreement with experiment, perhaps due to second order effects. We shall use the experimental data for what follows.

$${}^{3}P_{2} - {}^{3}P_{1}:\Delta \nu = 193$$

 ${}^{3}P_{1} - {}^{3}P_{0}:\Delta \nu = 116.$

Then

$$\epsilon_{3} = \frac{1}{2} [Y_{1} + 1 - \{(Y_{1} - 1)^{2} + 8\}^{1/2}] = \frac{1}{2} \left[2 - \frac{4(Y_{1} + 1)}{(Y_{1} - 1)^{2}}\right]$$
$$\cong 1 - \frac{2}{Y_{1} - 3} \text{ so that } c_{3} \cong \frac{2}{Y_{1} - 3} \cdot \frac{8}{Y_{1} - 3} \cdot$$

Likewise,

$$c_1 \cong \frac{8}{Y_2 - 6}, \qquad \epsilon_1 \cong -2 - \frac{8}{Y_2 - 6}$$

If we assume

then

and

$$Y = 100$$
 ($\leq 309/3$)

$$Y_2 = 431, \quad Y_1 = 201$$

$$\epsilon_3 = 0.99, \quad \epsilon_1 = -2.02$$

The separation ratio is then 102:199, in much worse agreement with experiment than the results of Gaunt. It should be noted that the calculation here neglects the interaction between each electron and the orbit of the other, and also the magnetic interaction between the two electron spins.

For N II,

$${}^{1}S_{0} - {}^{3}P : \Delta \nu \cong 32670 ; {}^{3}P_{2} - {}^{3}P_{1} = 83$$

 ${}^{1}D_{2} - {}^{3}P : \Delta \nu \cong 15300 ; {}^{3}P_{1} - {}^{3}P_{0} = 50$

assuming14

 $\nu \cong 206160 \text{ for } {}^{1}S_{0}$.

If we take $\gamma = 45$ ($\cong 133/3$), then $Y_2 = 726$, $Y_1 = 340$ and $\epsilon_3 = .99$, $\epsilon_1 = -2.01$. Here the separation ratio is 101:199.

¹⁴ Reference 1, p. 65.

3. The Matrix Amplitudes. When one calculates integrals such as $\int \overline{\phi}_1 v \psi_{\epsilon}^2 d\tau$ the only ones that do not vanish are as in this case, where ϕ_1 and ψ_{ϵ}^2 have the same spin factor. We abbreviate as follows: $v(\psi_{\epsilon}^2) = \int \overline{\phi}_1 v \psi_{\epsilon}^2 d\tau$, etc., and $z(\psi_{\epsilon}^2) = \int \overline{\psi}_{\epsilon}^2 z \phi_1 d\tau$. Further let $a = \int \overline{P_0}^0 v P_1^{-1} d\tau$ and $b = \int \overline{P_1}^0 z P_0^0 d\tau$. A list of integrals needed in the further calculation is given below.

$$\begin{split} & v(\psi_{\epsilon}^{2}) = 0 \quad v(\psi_{\delta}^{1}) = 0 \qquad v(\psi_{\delta}^{0}) = a \quad v(\psi_{\epsilon}^{0}) = 0 \quad v(\psi_{\delta}^{-1}) = a \qquad v(\psi_{\epsilon}^{-2}) = a2^{1/2} \\ & v(\psi_{\alpha}^{2}) = 0 \quad v(\psi_{\alpha}^{1}) = a \quad v(\psi_{\alpha}^{0}) = 0 \qquad v(\psi_{\beta}^{0}) = -a \quad v(\psi_{\alpha}^{-1}) = a \qquad v(\psi_{\alpha}^{-2}) = -a \\ & v(\psi_{\gamma}^{1}) = 0 \quad v(\psi_{\gamma}^{0}) = a \quad v(\psi_{\gamma}^{-1}) = -a \quad v(\psi_{1V}^{0}) = a/3^{1/2} \quad v(\psi_{V}^{0}) = -a2^{1/2}/3^{1/2} \\ & z(\psi_{\epsilon}^{2}) = 0 \quad z(\psi_{\delta}^{1}) = b \quad z(\psi_{\delta}^{0}) = 0 \qquad z(\psi_{\epsilon}^{0}) = b2^{1/2} \qquad z(\psi_{\delta}^{-1}) = b \quad z(\psi_{\epsilon}^{-2}) = 0 \\ & z(\psi_{\alpha}^{2}) = b \quad z(\psi_{\alpha}^{1}) = 0 \quad z(\psi_{\alpha}^{0}) = b \qquad z(\psi_{\beta}^{0}) = b \qquad z(\psi_{\alpha}^{-1}) = 0 \quad z(\psi_{\alpha}^{-2}) = b \\ & z(\psi_{\gamma}^{1}) = b \quad z(\psi_{\gamma}^{0}) = 0 \quad z(\psi_{\gamma}^{-1}) = b \quad z(\psi_{1V}^{0}) = 2b/3^{1/2} \qquad z(\psi_{V}^{0}) = b2^{1/2}/3^{1/2}. \end{split}$$

One readily verifies the Laporte rule for dipole radiation for ${}^{1}D \rightarrow {}^{3}P$. The matrix components which we need follow.

$${}^{1}D_{2} \rightarrow {}^{1}P_{1}; \qquad z(m,m) = \frac{b(1+c_{4}c_{I})}{(c_{I}\Delta_{1}c_{4}\Delta_{2})^{1/2}} \cdot \left(\frac{4-m^{2}}{3}\right)^{1/2}$$

$${}^{1}D_{2} \rightarrow {}^{3}P_{2}'; \qquad z(m,m) = -\frac{b}{(c_{4}\Delta_{2})^{1/2}} \cdot \frac{m}{2^{1/2}}$$

$${}^{1}D_{2} \rightarrow {}^{3}P_{1}'; \qquad z(m,m) = \frac{b(-1+c_{4}c_{III})}{(c_{III}\Delta_{1}c_{4}\Delta_{2})^{1/2}} \cdot \left(\frac{4-m^{2}}{3}\right)^{1/2}$$

$${}^{1}P_{1} \rightarrow {}^{3}P_{2}; \quad v(m,m-1) = \frac{a(1+c_{1}c_{3})}{(c_{1}\Delta_{1}c_{3}\Delta_{2})^{1/2}} \cdot \left(\frac{1}{6}\right)^{1/2} [(3-m)(2-m)]^{1/2}$$

$${}^{1}P_{1} \rightarrow {}^{3}P_{1}; \quad v(m,m-1) = \frac{a}{2(c_{I}\Delta_{1})^{1/2}} [(1+m)(2-m)]^{1/2}$$

$${}^{1}P_{1} \rightarrow {}^{3}P_{0}; \quad v(m,m-1) = \frac{a}{(c_{I}\Delta_{1}c_{1}\Delta_{0})^{1/2}} [(2+m)(3-m)]^{1/2}$$

$${}^{3}P_{2}' \rightarrow {}^{3}P_{2}; \quad v(m,m-1) = \frac{a}{2(c_{3}\Delta_{2})^{1/2}} [(2+m)(1+m)]^{1/2}$$

$${}^{3}P_{1}' \rightarrow {}^{3}P_{2}; \quad v(m,m-1) = \frac{a(1-c_{3}c_{III})}{(c_{III}\Delta_{1}c_{3}\Delta_{2})^{1/2}} \left(\frac{1}{6}\right)^{1/2} [(3-m)(2-m)]^{1/2}$$

$${}^{3}P_{1}' \rightarrow {}^{3}P_{1}; \quad v(m,m-1) = \frac{a}{2(c_{III}\Delta_{1})^{1/2}} [(1+m)(2-m)]^{1/2}$$

$${}^{3}P_{1}' \rightarrow {}^{3}P_{1}; \quad v(m,m-1) = \frac{a}{2(c_{III}\Delta_{1})^{1/2}} [(1+m)(2-m)]^{1/2}$$

$${}^{3}P_{1}' \rightarrow {}^{3}P_{1}; \quad v(m,m-1) = \frac{a}{2(c_{III}\Delta_{1})^{1/2}} [(1+m)(2-m)]^{1/2}$$

$${}^{3}P_{1}' \rightarrow {}^{3}P_{0}; \qquad v(1,0) = \frac{a}{(c_{III}\Delta_{1}c_{1}\Delta_{0})^{1/2}} \left(\frac{2}{3}\right)^{1/2} (-4+c_{1}c_{III}).$$

It is seen, on going to the limit of non-intercombination, that these matrix elements are precisely equivalent to those ordinarily used, as for instance corresponding to the formulae given at the beginning of this paper. This is a useful check on the correctness of the calculation. Another check would be to go to the limit of (jj) coupling, but, to the writer's knowledge, the intensities have not been worked out for this case. Granted that this probem had been solved, however, it might be possible, without going through our perturbation calculation, to derive the necessary matrix components by a process of interpolation between the two limiting cases. This method should be particularly advantageous in treating the $2s2p^3$ configuration, where the wave functions appear in the form of determinants¹⁵ with four rows and columns, and where, by a straightforward method such as used here, one would need to solve two secular equations of the fourth degree, for j=2 and for j=1, respectively.

4. The Intensities (Amplitudes Squared) and the Summation Rule. In Table III, the squared amplitudes for the transitions of $2p3s - 2p^2$ are given,

	${}^{1}P_{1}$	³ P ₂	³ P ₁	³ P ₀	Sum	Limit of sum
¹ S ₀	$\frac{2}{c_5\Delta_0} \frac{\{c_{\mathrm{I}}c_5-4\}^2}{c_{\mathrm{I}}\Delta_1}$		$\frac{2}{c_5\Delta_0} \frac{\{c_{\mathrm{III}}c_5+4\}^2}{c_{\mathrm{III}}\Delta_1}$		2	2
¹ D ₂	$\frac{10}{c_4\Delta_2} \frac{\{1+c_4c_I\}^2}{c_I\Delta_1}$	$\frac{15}{c_4\Delta_2}$	$\frac{10}{c_4 \Delta_2} \frac{\{c_4 c_{\text{III}} - 1\}^2}{c_{\text{III}} \Delta_1}$		10	10
³ P ₂	$\frac{10}{c_{3}\Delta_{2}} \frac{\{c_{3}c_{1}-1\}^{2}}{c_{1}\Delta_{1}}$	$\frac{15}{c_3\Delta_2}$	$\frac{10}{c_{3}\Delta_{2}} \frac{\{1+c_{3}c_{111}\}^{2}}{c_{111}\Delta_{1}}$		10	10
³ P ₁	$\frac{3}{c_{\mathrm{I}}\Delta_{\mathrm{I}}}$	$\frac{5}{2}$	$\frac{3}{c_{III}\Delta_1}$	2	6	6
³ P ₀	$\frac{2}{c_1\Delta_0} \frac{\{c_{\mathrm{I}}c_1+4\}^2}{c_{\mathrm{I}}\Delta_1}$		$\frac{2}{c_{1}\Delta_{0}} \frac{\{4 - c_{1}c_{111}\}^{2}}{c_{111}\Delta_{1}}$		2	2
Sum	$\frac{12(c_{\mathrm{I}}^2+1)}{c_{\mathrm{I}}\Delta_1}$	10	$\frac{12(c_{\rm III}^2+1)}{c_{\rm III}\Delta_1}$	2	30	
Limit of sum	12	10	6	2		30

TABLE III. Intensities for $2p3s - 2p^2$.

together with sums from a given upper level or a given lower level. To calculate the sums, we use relations such as $c_1+c_5=\Delta_0$, $c_5^2+8=c_5\Delta_0$, etc. The limit of the sum, as the electrostatic interaction between the electrons is increased, is also given. In general, these limits are proportional to the statistical weights of the corresponding levels, excepting when ${}^{1}P_1$ is the upper level, where the limit is twice as much, probably due to the existence of two lower levels (${}^{1}S$ and ${}^{1}D$) of the same multiplicity. (The $2p3s {}^{3}P$ level may, in the limit, only combine with the one level $(2p)^{2} {}^{3}P$.

¹⁵ See J. C. Slater, Phys. Rev. (being published). The separations between multiplets of the $2s2p^3$ configuration, as well as of $2p^2$ are in fair agreement with theoretical expectations although there is probably a mutual disturbance, giving a second-order correction. I am indebted to Professor Slater for the privilege of seeing the manuscript before publication.

III. QUADRUPOLE RADIATION FOR INTERCOMBINATIONS BETWEEN STATES OF DIFFERENT MULTIPLICITIES

As before, we shall calculate for extreme cases, and suppose the actual relations of intensities to correspond to an intermediate case. Case 1. ^{1}P the intermediate state.

$$a. \quad {}^{1}D_{2} \rightarrow {}^{3}P_{2} \quad [zv](m,m-1) = \frac{ab(1+c_{4}c_{I})(1+c_{3}c_{I})(2-m)\left\{(2+m)(3-m)\right\}^{1/2}}{\Delta_{2}c_{I}\Delta_{1}(18c_{3}c_{4})^{1/2}}$$

$$\sum (zv)^{2} = \frac{11a^{2}b^{2}(1+c_{4}c_{I})^{2}(1+c_{3}c_{I})^{2}}{3c_{I}^{2}c_{3}c_{4}\Delta_{1}^{2}\Delta_{2}^{2}}$$

$$b. \quad {}^{1}D_{2} \rightarrow {}^{3}P_{1} \quad [zv](m,m-1) = \frac{ab(1+c_{4}c_{I})(2-m)\left\{(2+m)(1+m)\right\}^{1/2}}{c_{I}\Delta_{1}(12c_{4}\Delta_{2})^{1/2}}$$

$$\sum (zv)^{2} = \frac{7a^{2}b^{2}(1+c_{4}c_{I})^{2}}{6c_{I}^{2}\Delta_{1}^{2}c_{4}\Delta_{2}}$$

$$c. \quad {}^{1}D_{2} \rightarrow {}^{3}P_{0} \quad \left\{ [zv](1,0)\right\}^{2} = \frac{2a^{2}b^{2}(1+c_{4}c_{I})^{2}(4+c_{1}c_{I})^{2}}{3c_{I}^{2}c_{1}c_{4}\Delta_{0}\Delta_{1}^{2}\Delta_{2}}$$

For O III,

$$c_{\mathbf{I}} \cong \Delta_1 = 45.6$$
, $c_1 \cong \frac{8}{Y_2 - 6} = \frac{8}{425}$ and $c_3 \cong \frac{2}{Y_1 - 3} = \frac{2}{198}$.

The relative intensities are then a:b:c=3.9:1.2:1.9For N II,

$$c_{\rm I} \cong 4, \ c_{\rm 1} \cong \frac{8}{720}, \ \text{and} \ \ c_{\rm 3} \cong \frac{2}{337}.$$

Here the relative intensities are a:b:c=1.9:1.2:1.4Case 2. ${}^{3}P_{2}'$ the intermediate state.

$$a. \qquad {}^{1}D_{2} \rightarrow {}^{3}P_{2}{}^{i} \qquad [zv](m,m-1) = -\frac{abm\{(2+m)(3-m)\}^{1/2}}{\Delta_{2}(8c_{3}c_{4})^{1/2}}$$

$$\sum (zv)^{2} = \frac{13a^{2}b^{2}}{4\Delta_{2}{}^{2}c_{3}c_{4}}$$

$$b. \qquad {}^{1}D_{2} \rightarrow {}^{3}P_{1} \qquad [zv](m,m-1) = \frac{abm\{(2+m)(1+m)\}^{1/2}}{4 \cdot 3^{1/2}(c_{4}\Delta_{2})^{1/2}}$$

$$\sum (zv)^{2} = \frac{25a^{2}b^{2}}{24c_{4}\Delta_{2}} \cdot$$

The relative intensities are a:b=39:25. c=0

Case 3. ${}^{3}P'_{1}$ the intermediate state.

$$a. \ ^{1}D_{2} \rightarrow ^{3}P_{2} \quad [zv](m,m-1) = \frac{ab(-1+c_{4}c_{\mathrm{III}})(1-c_{3}c_{\mathrm{III}})(2-m)\left\{(2+m)(3-m)\right\}^{1/2}}{c_{\mathrm{III}\Delta_{1}\Delta_{2}}(18c_{3}c_{4})^{1/2}}$$

$$\sum(zv)^{2} \cong \frac{11a^{2}b^{2}(-1+c_{4}c_{\mathrm{III}})^{2}}{3c_{\mathrm{III}}^{2}c_{3}c_{4}\Delta_{1}^{2}\Delta_{2}^{2}}$$

$$b. \ ^{1}D_{2} \rightarrow ^{3}P_{1} \qquad \sum(zv)^{2} = \frac{7}{6} \frac{a^{2}b^{2}(-1+c_{4}c_{\mathrm{III}})^{2}}{c_{\mathrm{III}}^{2}\Delta_{1}^{2}c_{4}\Delta_{2}}$$

$$c. \ ^{1}D_{2} \rightarrow ^{3}P_{8} \qquad \left\{ [zv](10) \right\}^{2} = \frac{32}{3} \frac{a^{2}b^{2}(-1+c_{4}c_{\mathrm{III}})^{2}}{c_{\mathrm{III}}^{2}\Delta_{1}^{2}c_{1}\Delta_{0}c_{4}\Delta_{2}}$$

The relative intensities in this case are a:b:c=11:7:8. The experimental data indicates that the relative intensities should be approximately a:b:c=2:1:0.

DISCUSSION

The purpose of this paper has been to test the idea that quadrupole radiation is the important factor in causing the nebular lines (forbidden for dipole radiation) to be emitted. One result stands forth quite clearly, namely, that, with such an assumption, the line of a multiplet which should theoretically be strongest, is in fact such according to the experiments. We obtain a disagreement, however, when the relative intensities of the weaker line are considered. This may be because of the simplifications and approximations made during the course of the calculations.

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