TRANSITION PROBABILITIES OF FORBIDDEN LINES

Thesis by

Simon Pasternack

In Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy

California Institute of Technology
Pasadena, California

1939

TABLE OF CONTENTS

Abstract

Acknowledgements

I. Introduction

II. Outline of the Radiation Theory

III. Calculation of Eigenfunctions

IV. Calculation of Magnetic Dipole Line Strengths

V. Calculation of Electric Quadrupole Line Strengths

VI. Numerical Calculations

VII. Discussion of the Result

Bibliography

ABSTRACT

Recent work on forbidden lines has made it desirable to re-examine and extend the calculations made by Condon on the theoretical transition probabilities of these lines for a few atoms in the np^2, np^3 and np^4 configurations.

The method developed by Condon for the computation of these transition probabilities is described and discussed. A few modifications are introduced, such as the use of recently developed formulae for magnetic dipole line strengths in LS coupling and the use of second-order approximations to the wave functions in special cases. The evaluation of the parameters involved in the breakdown of LS coupling is also carried out in a somewhat different manner.

Formulae are derived for the magnetic dipole and electric quadrupole contributions to the transition probabilities for the p^2, p^3, p^4 and d^2 configurations. A few errors are found in Condon's calculations for the p^k configurations; in particular, a non-zero value is found for the probability of the $^3P_0 - {}^1D_2$ transition in the p^2 configuration. This line was recently observed in O III.

Numerical computations are made of the transition probabilities of fifty-one atoms in the p^k configurations. The formulae for the d^2 configuration are applied to the single case of Fe VII. The difficulties which arise in these calculations are discussed with regard to their implications about the general validity of the method.

A short discussion is given of an application of the calculations to a question concerning the permitted lines of O III present in nebular spectra.

ACKNOWLEDGMENTS

I should like to express my appreciation to Professor W. V. Houston for his continued assistance and advice during the performance of this research. I wish also to thank Professor I. S. Bowen for suggesting the problem, and for many helpful discussions.

I. INTRODUCTION

A. Purpose

In view of recent work on the identification of forbidden lines in nebular spectra, and on their application to problems concerning physical conditions in the nebulae and novae, it has become desirable to have theoretical values for the transition probabilities of these lines for a number of atoms. It is our purpose here to present a discussion of the method of evaluation of these transition probabilities, together with the application of the method to atoms in the configurations np^2, np^3, np^4 and nd^2. Numerical calculations of the transition probabilities are carried out for fifty-two atoms and ions in the first few rows of the periodic table.

B. Historical Survey

In 1927 Professor I. S. Bowen2) showed that some of the most prominent unclassified lines in nebular and novae spectra could be identified with forbidden transitions between the metastable levels of the ground configurations of N I, O II and O III. Later work by a number of investigators established the existence of forbidden lines in auroral spectra3) and in the spectra of certain peculiar stars.4) The list of identified forbidden lines was greatly extended, until it included those of many of the atoms in the first few rows of the periodic table. A complete list of the forbidden lines observed in astrophycical spectra up to the present time is given in a forthcoming article by

Bowen and Wyse[5)].

The study of the intensities of the forbidden lines has yielded a great deal of valuable information about physical conditions in the nebulae and novae - such as the density of matter and radiation, the mechanisms of excitation of the atoms, and the relative abundance of the elements present in these astrophysical objects. A survey of the developments of this type up to 1936 was made by Professor Bowen in an article in the Reviews of Modern Physics[6)].

In making quantitative interpretations of this sort it is necessary to have theoretical values for the absolute transition probabilities of the various forbidden lines. Very rough calculations of the transition probabilities for some atoms were made by Bartlett[7)] in 1929. Formulae were developed by Rubinowicz[8)] for the relative quadrupole line strengths in multiplets in pure Russell-Saunders coupling. In 1932, Stevenson[9)] worked out the absolute transition probabilities for the forbidden lines of the $2p^2$ configuration of O III, N II and C I. Later Condon[10)] developed a method for the computation of the transition probabilities which was considerably different from that of Stevenson. He calculated separately the contributions to the transition probabilities of the magnetic dipole radiation and the electric quadrupole radiation. He treated the p^2, p^3 and p^4 configurations, and made numerical calculations for the cases of O I, O II, O III, N I, N II and C I.

Condon's results for O III did not agree with those of

Stevenson, except in the order of magnitude of the various transition probabilities, and in the three to one ratio of the components of the "chief nebular doublet", ($^3P_{2,1}$ - $^1D_2$). Also he found a zero probability for the transition ($^3P_0$ - $^1D_2$), whereas Stevenson calculated the probability of this transition to be 6.7×10^{-6} sec^{-1}. The recent observation of this line by Bowen and Wyse[11)] consequently cast doubt upon Condon's calculations, and it was decided to check his work, since his method of procedure appeared to be more straightforward then that of Stevenson. The recalculation not only yielded a non-zero probability for the transition ($^3P_0$ - $^1D_2$) of O III, but also brought to light several other errors in Condon's calculations, both in the formulae he used and in his numerical work.

The recent work[5)] on forbidden lines has made it desirable to extend the transition probability calculations to a number of other ions in the p^k configurations, and also to extend the treatment to the d^k configurations. The latter extension has only been partially carried out here, as only the d^2 configuration has been investigated.

C. Plan of Procedure

In view of the complicated nature of the calculation of transition probabilities it was deemed advisable to preface the calculations themselves with a fairly detailed account of the method of procedure. This method is essentially that of Condon, with but a few modifications, such as the use of recently developed formulae for magnetic dipole line strengths in pure Russell-Saunders coupling, and the use of second-order approximations to the wave functions in special cases (section III, equation 23'). The evaluation of the parameters involved in the breakdown of pure Russell-Saunders coupling is also carried out in a somewhat different manner.

The various steps involved in the calculations are treated in some detail in different places in Condon and Shortley, 'The Theory of Atomic Spectra', (1935). These parts of the calculation are here organized in such a way as to show where and how they fit into the problem of the calculation of the transition probabilities of forbidden lines. We use the notation and nomenclature set up in Condon and Shortley's book. Since we shall make numerous references to this book, we shall adopt for it the abbreviation CS. Thus 'CS, § $7^4(3)$' refers to Condon and Shortley, Chapter 4, article 7, equation (3).

In the following section we recall some of the concepts and results of radiation theory, which lead to the formulae for line intensities in terms of transition probabilities, and for transition probabilities in terms of line strengths. The latter are essentially the sums of squares of the absolute values of matrix elements of the magnetic dipole and electric quadrupole moments of the atom.

In section III the methods of calculation of the wave functions in the perturbed Russell-Saunders scheme are discussed, insofar as they bear on the problem of computing the necessary matrix elements. The methods outlined are applied to the cases of the p^2, p^3, p^4 and d^2

configurations. Sections IV and V outline the methods of computing the magnetic dipole and electric quadrupole line strengths, respectively, and give the results for the four configurations under consideration. The special problems arising in the numerical calculations are treated in section VI, and the results of these calculations for a large number of atoms and ions in these configurations are tabulated. In section VII the results are discussed and interpreted.

II. OUTLINE OF THE RADIATION THEORY

A. Line Intensities

Given a source consisting of a large number of identical atoms subject to some steady means of excitation, the total intensity or energy of the radiation emitted in the spontaneous transitions of atoms from a state "a" to a state "b" of lower energy is given, under steady conditions, by the formula

$$I(a,b) = N(a)\,h\nu\,A(a,b), \tag{1}$$

where N(a) is the average number of atoms in the upper state 'a', ν is the frequency of the radiation emitted, and the factor of proportionality A(a,b) is the so-called transition probability for the transition from state 'a' to state 'b'. A(a,b)dt represents the probability that one atom in state 'a' will make the transition to state 'b' in time dt.

A modification of this formula is necessitated by the degeneracy of the states with respect to the quantum number M, which represents the z component of the total angular momentum. The intensity of a line A - B, that is, of the totality of all transitions from states in a level A to states in a level B of lower energy, is given by summation of the above formula over 'a' and 'b'. Under conditions of 'natural excitation', (CS, § 7^4), it can be written in the form

$$I(A,B) = N(A)\,h\nu\,A(A,B), \tag{2}$$

where N(A), the average number of atoms in the upper level A, is given by

$$N(A) = (2J_A + 1)\ N(a) \tag{3}$$

and A(A,B), the transition probability of the line (A,B), is given by the equation

$$A(A,B) = \frac{1}{2J_A + 1} \sum_{a,b} A(a,b) \tag{4}$$

Under steady conditions the number of atoms leaving the level A per second by any process is equal to the number of atoms arriving in the level A per second. If we denote the latter number by n, we have

$$n = N(A) \left\{ \sum_{B} A(A,B) + C + R \right\}, \tag{5}$$

where the summation is taken over all levels B of lower energy than A, and where the terms C and R are added to allow for the possibilities of removal of atoms from the level A by collisions with other particles, or by absorption of radiation, respectively. Making use of this relation, equation (2) becomes

$$I(A,B) = \frac{n}{\sum_{B'} A(A,B') + C + R}\ A(A,B)\ h\nu \tag{6}$$

This final equation indicates that the intensity of the line A - B depends upon the mechanism and conditions of excitation, which determine n; upon the relation between A(A,B) and the probabilities of transition to other lower levels; and upon the relation between the probability, $\sum_{B'} A(A,B')$, of removal of an atom from state A by spontaneous transition, and the probabilities C and R of removal by collisions or by absorption of radiation. As a consequence of this relation, the experimentally observed line intensities, together with the theoretically evaluated transition probabilities, can provide information about the mechanism of excitation and about other physical conditions in the source under observation$^{6)}$.

B. The Radiation Field

A quantum mechanical treatment of the emission and absorption of radiation was developed by Dirac$^{12)}$. It leads to expressions for the spontaneous transition probabilities in terms of matrix elements of the electric and magnetic multipole moments of an atomic system.

A clear exposition is presented in CS, Chapter 4, of the derivation of the formulae for the transition probabilities by means of the application of the Bohr correspondence principle to the classical theory of radiation. Since we shall need these formulae, it may be well to sketch very briefly the main features of this derivation.

In classical electromagnetic theory, the electric and magnetic field strengths are expressible in terms of a scalar potential function ϕ and a vector potential **A**, which can be written in the retarded potential forms

$$\phi = \int \frac{\rho(x,y,z,t-\frac{R}{c})}{R}\,d\tau, \qquad \mathbf{A} = \int \frac{\mathbf{I}(x,y,z,t-\frac{R}{c})}{R}\,d\tau. \qquad (7)$$

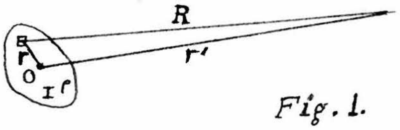


Fig. 1.

If ρ and $\mathbf{I}$ vary harmonically with the time, with frequency ν, and if further

$$\frac{\nu r'}{c} \gg 1, \quad \frac{\nu r}{c} \ll 1,$$

then the expressions for ϕ and $\mathbf{A}$ may be expanded in a series of powers of $\frac{\nu r}{c}$, and in powers of $\frac{c}{\nu r'}$. Retaining only the first few terms, we obtain

$$\begin{aligned} \phi &= \mathrm{Rl}\left[\frac{e^{2\pi i\nu(t-\frac{r'}{c})}}{r'}\left\{Q + \frac{2\pi\nu i}{c}(\mathbf{r}_1 \cdot \mathbf{P}) - \frac{2\pi^2\nu^2}{c^2}(\mathbf{r}_1 \cdot \mathcal{Q} \cdot \mathbf{r}_1)\right\}\right], \\ \mathbf{A} &= \mathrm{Rl}\left[\frac{e^{2\pi i\nu(t-\frac{r'}{c})}}{r'}\left\{\frac{2\pi i\nu}{c}\mathbf{P} - \frac{2\pi i\nu}{c}[\mathbf{r}_1 \times \mathbf{M}] - \frac{2\pi^2\nu^2}{c^2}(\mathbf{r}_1 \cdot \mathcal{Q})\right\}\right], \end{aligned} \tag{8}$$

where $\mathbf{r}_1$ is the unit vector in the direction of $\mathbf{r}'$, and

$$\begin{aligned} Q &= \int \rho \, d\tau = 0, \text{ by hypothesis.} \\ \mathbf{P} &= \int \rho \mathbf{r} \, d\tau. \\ \mathbf{M} &= \tfrac{1}{2}\int [\mathbf{r} \times \mathbf{I}] \, d\tau. \\ \mathcal{Q} &= \int \rho \mathbf{r}\mathbf{r} \, d\tau. \end{aligned} \tag{9}$$

The various terms in this expansion may be treated separately. Thus, the terms involving $\mathbf{P}$ have just the form of the potentials at large distances from an oscillating electric dipole whose electric moment is $\mathbf{P}$. The terms involving $\mathbf{M}$ and $\mathcal{Q}$ give, respectively, the potentials at large distances of an oscillating magnetic dipole of moment $\mathbf{M}$, and an oscillating electric quadrupole of moment $\mathcal{Q}$. Each of these oscillating multipoles contributes to the total radiation from the charge distribution. The contributions of higher multipoles need not be treated here.

A radiating atom may be considered as a harmonically varying charge distribution, whose moments about the nucleus are

$$\begin{aligned} \mathbf{P} &= -e \sum_i \mathbf{r}_i \\ \mathcal{N} &= -e \sum_i \mathbf{r}_i \mathbf{r}_i \\ \mathbf{M} &= -\frac{e}{2mc} \sum_i (\mathbf{L}_i + 2\mathbf{S}_i) , \end{aligned} \tag{10}$$

where the summations are taken over the electrons of the atom. In the third of these expressions the contribution of the spin to the total magnetic dipole moment is included. A reasonable justification for this inclusion is provided by the results of Brinkman$^{13)}$, who showed that, in the Dirac relativistic theory of the hydrogen atom, the spin could be interpreted as giving an additional contribution to the current $\mathbf{I}$ in terms of which the vector potential is evaluated.

The separate contributions to the total radiation of each of the oscillating multipoles may be readily evaluated. Thus, retaining only terms involving $\mathbf{P}$ in the potentials, we can obtain at once the field strengths $\mathbf{E}$ and $\mathbf{H}$, together with the rate of radiation or energy flow

$$\mathbf{S} = \frac{c}{4\pi} (\mathbf{E} \times \mathbf{H}) . \tag{11}$$

The time average rate of radiation at large distances turns out to be

$$\mathbf{S}_{av.} = \frac{2\pi^3 \nu^4}{c^3 r^2} \left(|\mathbf{P}|^2 - |\mathbf{r}_1 \cdot \mathbf{P}|^2 \right) \mathbf{r}_1 \tag{12}$$

The total rate of radiation through a large sphere surrounding the charge distribution is obtained by integration over angle. It is

$$\left(\frac{dE}{dt}\right)_{\text{el.dip.}} = \frac{16\pi^4\sigma^4 c}{3} P^2. \tag{13}$$

where $\sigma = \nu/c$ is the wave number of the radiation, and P^2 is the square of the absolute value of **P**.

The magnetic dipole calculation is quite similar to the electric dipole calculation. Indeed, it may be obtained by replacing **E** by **H** and **H** by **-E** in the electric dipole case. Hence we get

$$\left(\frac{dE}{dt}\right)_{\text{mag.dip.}} = \frac{16\pi^4\sigma^4 c}{3} M^2. \tag{14}$$

For the electric quadrupole radiation field, a similar calculation leads to the result

$$\mathbf{S}_{\text{av.}} = \frac{2\pi^5\nu^6}{c^5 r^2}\left|(\mathcal{Q}\cdot\mathbf{r}_1) - (\mathbf{r}_1\cdot\mathcal{Q}\cdot\mathbf{r}_1)\right|^2 \mathbf{r}_1 . \tag{15}$$

Now, from equations (10), $\mathcal{Q}$ is a symmetric dyad, and can therefore be written as a linear combination of six independent dyads

$$\mathbf{ii},\ \mathbf{jj},\ \mathbf{kk},\ \mathbf{ij}+\mathbf{ji},\ \mathbf{ik}+\mathbf{ki},\ \mathbf{jk}+\mathbf{kj}.$$

More conveniently, we take the six dyads

$$\begin{aligned}
\mathcal{J} &= \mathbf{ii} + \mathbf{jj} + \mathbf{kk}\,,\\
\mathcal{Q}(0) &= \sqrt{\tfrac{2}{3}}\,(\mathbf{kk} - \tfrac{1}{2}\,\mathbf{ii} - \tfrac{1}{2}\,\mathbf{jj}),\\
\mathcal{Q}(\pm 1) &= \tfrac{1}{2}\left\{(\mathbf{ki} + \mathbf{ik}) \pm i(\mathbf{kj} + \mathbf{jk})\right\},\\
\mathcal{Q}(\pm 2) &= \tfrac{1}{2}\left\{\mathbf{ii} - \mathbf{jj} \pm i(\mathbf{ij} + \mathbf{ji})\right\}.
\end{aligned} \tag{16}$$

These dyads occur in the matrix elements of $\mathcal{N}$, which we shall discuss later (section V, equations 5). For any linear combination of these dyads, the term involving $\mathcal{J}$ vanishes in the expression

$$(\mathcal{N} \cdot \mathbf{r}_1 - \mathbf{r}_1 \cdot \mathcal{N} \cdot \mathbf{r}_1).$$

Hence the spherically symmetric part of $\mathcal{N}$ makes no contribution to the radiation. On evaluating the total rate of radiation through a large sphere, we get

$$\frac{dE}{dt} = \frac{8\pi^6}{5} \sigma^6 c \widetilde{\mathcal{N}}^2, \tag{17}$$

where $\widetilde{\mathcal{N}}^2$ is the double dot product $\mathcal{N} : \mathcal{N}$, with the spherically symmetric part left out.

C. Transition Probabilities and Line Strengths

We now apply the Bohr correspondence principle, which postulates that the radiation field accompanying a spontaneous transition from a state 'a' to a state 'b' of lower energy is the same as that given by the classical theory for a charge distribution whose time average moment is

$$2 \, |(a| \quad |b)|^2 ,$$

where $(a| \quad |b)$ is the matrix component of the kind of electric or magnetic moment under consideration. Moreover the spontaneous transition probability is taken as $\frac{1}{h\nu}$ times the classical rate of radiation of this charge distribution.

In the electric dipole case, this principle leads to the transition probability

$$A_{\text{el. dip.}}(a,b) = \frac{64\,\pi^4\sigma^3}{3\,h}\,|(a\,|\mathbf{P}|\,b)|^2. \tag{18}$$

From equation (4) we then get the formula for the electric dipole transition probability of a line

$$A_{\text{el. dip.}}(A,B) = \frac{64\,\pi^4\sigma^3}{3\,h}\;\frac{1}{(2J_A+1)}\;\sum_{a,b}\;|(a\,|\mathbf{P}|\,b)|^2. \tag{19}$$

The sum occurring in this equation is called the line strength, and is denoted by

$$S_{\text{el. dip.}}(A,B) = \sum_{a,b}\;|(a\,|\mathbf{P}|\,b)|^2. \tag{20}$$

Similarly, for magnetic dipole radiation, we get the formulae

$$A_{\text{mag. dip.}}(A,B) = \frac{64\,\pi^4\sigma^3}{3\,h}\;\frac{1}{(2J_A+1)}\;S_{\text{mag. dip.}}(A,B), \tag{21}$$

where

$$S_{\text{mag. dip.}}(A,B) = \sum_{a,b}\;|(a\,|\mathbf{M}|\,b)|^2. \tag{22}$$

In the electric quadrupole case, the results are

$$A_{\text{el. quad.}}(A,B) = \frac{32\,\pi^6\sigma^5}{5\,h}\;\frac{1}{(2J_A+1)}\;S_{\text{el. quad.}}(A,B), \tag{23}$$

where

$$S_{\text{el. quad.}}(A,B) = \sum_{a,b}\;|(a\,|\widetilde{\mathcal{N}}|\,b)\,^2. \tag{24}$$

In this last formula, $\widetilde{\mathcal{N}}$ represents the dyadic $\mathcal{N}$ minus its spherically symmetric part.

As we shall see, the electric dipole moment cannot contribute to the radiation in a transition to which the magnetic dipole and electric quadrupole moments contribute, and conversely. However the latter two moments may both contribute to the radiation emitted in a single transition. In this case the treatment of the radiation field in which both types of radiation occur leads to the result that the total transition probability is merely the sum of the separate probabilities which are given in equations (21) and (23).

D. Permitted and Forbidden Lines

Investigation of the commutation properties of the operators **P**, **M** and $\mathcal{N}$ which occur in the above equations, leads to the well-known sets of selection rules for the different types of radiation.

(a) Electric dipole selection rules:

$$\Delta(\sum_i \ell_i) = \pm 1. \quad \text{(Parity must change)}$$
$$\Delta J = 0, \pm 1. \quad 0 \nrightarrow 0. \qquad (25)$$
$$\left.\begin{array}{l}\Delta L = 0, \pm 1\\ \Delta S = 0\end{array}\right\} \text{for LS coupling.}$$

(b) Magnetic dipole selection rules:

$$\Delta(\sum_i \ell_i) = 0. \quad \text{(Parity remains unchanged)}$$
$$\Delta J = 0, \pm 1. \quad 0 \nrightarrow 0. \qquad (26)$$
$$\left.\begin{array}{l}\Delta S = 0\\ \Delta L = 0\end{array}\right\} \text{for LS coupling.}$$

(c) Electric quadrupole selection rules:

$$\Delta\left(\sum_i l_i\right) = 0. \quad \text{(Parity remains unchanged)}$$

$$\Delta J = 0, \pm 1, \pm 2. \quad 0 \nrightarrow 0, \tfrac{1}{2} \nrightarrow \tfrac{1}{2}, 0 \not\rightleftarrows 1.$$

$$\left.\begin{aligned} \Delta S &= 0 \\ \Delta L &= 0, \pm 1, \pm 2 \end{aligned}\right\} \text{for LS coupling.} \tag{27}$$

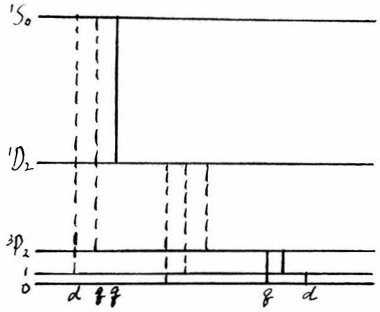
Lines which satisfy the electric dipole selection rules are called permitted lines. All other lines are called forbidden lines.

Numerical evaluation of the transition probabilities shows that the electric dipole probabilities are of the order of 10^3 to 10^8 sec^{-1}, whereas the magnetic dipole and electric quadrupole probabilities are of the order of 10^{-5} to 10^2 sec . For this reason the latter types of radiation are of importance only under exceptional circumstances, such as prevail in the nebulae and novae.

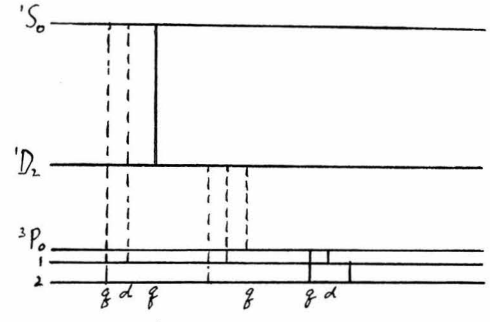
For convenience the transitions which satisfy the magnetic dipole or electric quadrupole selection rules are depicted in the figures below for the four configurations which will be discussed in detail in the following sections. The solid vertical lines denote transitions which are possible in LS coupling. The dotted vertical lines indicate transitions which are possible when there is a departure from LS coupling due to the spin-orbit interaction. Transitions which are purely magnetic dipole in character, or purely electric quadrupole, are indicated by the letters d or q, respectively, placed below the corresponding lines in the diagrams.

Fig. 1

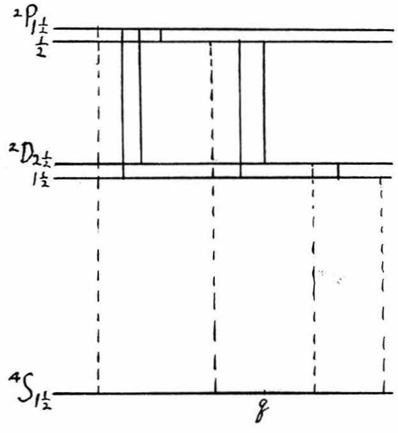
p^2 Configuration



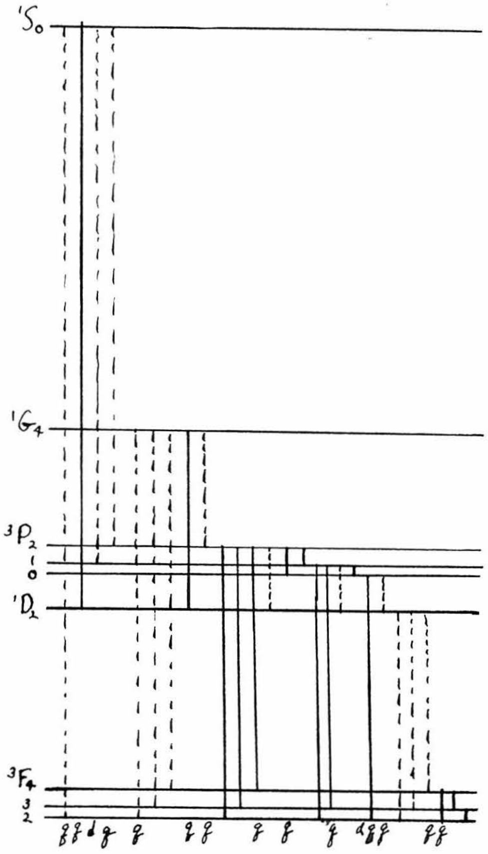
p^4 Configuration



p^3 Configuration



d^2 Configuration



III. CALCULATION OF EIGENFUNCTIONS

A. Method of Calculation

As a preliminary to the evaluation of the matrix elements involved in the formulas for transition probabilities, it is necessary to determine expressions for the wave functions characteristic of the atomic states, in terms of individual electron wave functions. This must be done in the following steps:

(a) We first set up all possible zero-order wave functions composed of antisymmetrized products of one-electron wave functions,

$$\underline{X}\,(n^1\ell^1m_s^1m_\ell^1,\ n^2\ell^2m_s^2m_\ell^2,\ldots)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_1(n^1\ell^1m_s^1m_\ell^1) & \cdot & \cdot & \cdot & \phi_N(n^1\ell^1m_s^1m_\ell^1)\\ \phi_1(n^2\ell^2m_s^2m_\ell^2) & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \phi_1(n^N\ell^Nm_s^Nm_\ell^N) & \cdot & \cdot & \cdot & \phi_N(n^N\ell^Nm_s^Nm_\ell^N)\end{vmatrix}, \tag{1}$$

where N is the total number of electrons in the atomic system, and $\phi(n,\ell,m_s,m_\ell)$ is the one-electron wave-function

$$\phi(n,\ell,m_s,m_\ell) = \frac{1}{r}R(n,\ell)\,\Theta(\ell,m_\ell)\,\Phi(m_\ell)\,\sigma(m_s) \tag{2}$$

The superscripts 1,2,... refer to the set of quantum numbers. The subscripts refer to the coordinates of the individual electrons. As we shall be dealing exclusively here with equivalent electron configurations, we shall henceforth suppress for brevity the quantum numbers n and ℓ of the individual electrons.

(b) We next set up the wave functions

$$\Phi\,(n^1l^1, n^2l^2, \ldots S, L, M_S, M_L) \equiv \Phi\,(S, L, M_S, M_L)$$

as linear combinations of the zero-order wave functions. Three methods for carrying out this computation are described in CS, Chapter 8. These are direct diagonalization, use of angular momentum operators and use of vector coupling formulae.

In the case of two-electron configurations, the most convenient method is the last-mentioned, which was developed by Bartlett$^{15)}$. In it, use is made of the transformation from the m_1m_2 scheme of wave functions to the jm scheme.

$$\psi\,(j_1, j_2, j, m) = \sum_{m_1, m_2} \phi\,(j_1\, j_2\, m_1\, m_2)\,(j_1\, j_2\, m_1\, m_2 \mid j_1\, j_2\, j\, m), \tag{3}$$

where

$$\mathbf{J}_1 + \mathbf{J}_2 = \mathbf{J}\,. \tag{4}$$

A general formula for the coefficients in this transformation was developed by Wigner$^{16)}$. The formula may be written in the following useful forms:

$$\begin{aligned}(j_1\, j_2\, m_1\, m_2 \mid j_1 j_2 j m) &= (-1)^{j_2+m_2}\,\delta(m, m_1+m_2)\sqrt{\frac{(j+j_1-j_2)!\,(j_1+j_2-j)!\,(j-m)!\,(j_1-m_1)!\,\{(j+j_2+m_1)!\}^2}{(j+j_1+j_2+1)!\,(j-j_1+j_2)!\,\{(j_1-j_2-m)!\}^2\,(j+m)!\,(j_1+m_1)!}}\\ &\quad\times\sqrt{\frac{(2j+1)}{(j_2-m_2)!\,(j_2+m_2)!}}\;F\begin{bmatrix} j_1-m_1+1, & -j-m, & -j+j_1-j_2 \\ j_1-j_2-m+1, & -j-j_2-m_1 & \end{bmatrix},\\ &= (-1)^{j_1+j_2-j}\,\delta(m, m_1+m_2)\sqrt{\frac{(j+j_1-j_2)!\,(j_1-m_1)!\,(j-m)!\,(j+m)!\,\{(2j_2)!\}^2}{(j+j_1+j_2+1)!\,\{(j-j_2-m_1)!\}^2\,(j_1+m_1)!\,(j_2-m_2)!}}\\ &\quad\times\sqrt{\frac{(2j+1)}{(j_2+m_2)!\,(j-j_1+j_2)!\,(j-j_1-j_2)!}}\;F\begin{bmatrix} j+j_1-j_2+1, & -j_2+m_2, & j-j_1-j_2 \\ j-j_2-m_1+1, & -2j_2 & \end{bmatrix},\end{aligned} \tag{5}$$

where $F\begin{bmatrix} a,b,c \\ e,f \end{bmatrix}$ is the generalized hypergeometric series with unit argument,

$$F\begin{bmatrix} a,b,c \\ e,f \end{bmatrix} = \sum_{r=0}^{\infty} \frac{a(a+1)\ldots(a+r-1)\,b(b+1)\ldots(b+r-1)\,c(c+1)\ldots(c+r-1)}{e(e+1)\ldots(e+r-1)\,f(f+1)\cdots(f+r-1)\quad r!} . \tag{6}$$

The second formula may be obtained from the first by means of one of the relations given by Bailey[16)]. The hypergeometric series terminates if one of the upper indices is negative, and, indeed, consists of only one or two terms in practically all of the cases under consideration, if the more convenient of the two formulae is chosen.

In these formulae it is assumed that $j_1 \geqq j_2$. If this condition is not fulfilled, use can be made of the relation

$$\psi(j_2\, j_1\, j\, m) = (-1)^{j_1+j_2-j}\, \psi(j_1\, j_2\, j\, m). \tag{7}$$

Tables of the coefficients for small values of j_2 ($j_2 = \frac{1}{2}, 1, 1\frac{1}{2}, 2$) are given in CS, § 14^3.

Bartlett's method consists of the application of this transformation to the two cases corresponding to the correlations

$$j_1 = s^1,\ j_2 = s^2,\ j = S,\ m = M_S\ , \tag{8}$$

and

$$j_1 = \ell^1,\ j_2 = \ell^2,\ j = L,\ m = M\ . \tag{9}$$

Thus, for example, we find from table 1^3 of CS that

$$\psi(s^1 = \tfrac{1}{2},\ s^2 = \tfrac{1}{2}, S = 1, M_S = 0) = \tfrac{1}{\sqrt{2}}\left\{\sigma_1(\tfrac{1}{2})\sigma_2(-\tfrac{1}{2}) + \sigma_1(-\tfrac{1}{2})\sigma_2(\tfrac{1}{2})\right\},$$

where $\sigma(m_s)$ is the Pauli spin function. Similarly, from table 2^3,

$$\psi(\ell^1 = 1, \ell^2 = 1, L = 1, M_L = 1) = \tfrac{1}{\sqrt{2}}\left\{\phi_1'(1,1)\,\phi_2'(1,0) - \phi_1'(1,0)\,\phi_2'(1,1)\right\},$$

where $\phi'(l,m_l)$ is the one-electron wave function (2), without the spin factor. The multiplication of these functions then gives us the desired wave function

$$\Phi\,(l^1=1,\ l^2=1,\ S=1,\ L=1,\ M_S=0,\ M_L=1)=\frac{1}{\sqrt{2}}\,\overline{\underline{X}}\,(l^1=1,m_s^1=\tfrac{1}{2},m_l^1=1;\ l^2=1,m_s^2=-\tfrac{1}{2},m_l^2=0)$$
$$-\frac{1}{\sqrt{2}}\,\overline{\underline{X}}\,(l^1=1,\ m_s^1=-\tfrac{1}{2},\ m_l^1=0;\ \ l^2=1,\ m_s^2=-\tfrac{1}{2},\ m_l^2=1).$$

All the wave functions thus obtained for a given two-electron configuration possess a definite phase relationship with one another, CS § 5^3, § 10^3 , viz., that wave functions for states of the same term satisfy the relations (12) and (13), and that the non-diagonal elements of the matrices of the operators $\mathbf{S}_z$ and $-\mathbf{L}_z$ are all positive.

In the case of configurations containing more than two equivalent electrons, the most convenient method is that of Gray and Wills17). In this method use is made of the angular momentum operators

$$\mathcal{L} = \mathbf{L}_x - i\,\mathbf{L}_y = (\mathbf{L}_x^1 - i\,\mathbf{L}_y^1) + (\mathbf{L}_x^2 - i\,\mathbf{L}_y^2) = \mathcal{L}^1 + \mathcal{L}^2, \qquad (10)$$

and

$$\mathcal{S} = \mathbf{S}_x - i\,\mathbf{S}_y = \mathcal{S}^1 + \mathcal{S}^2. \qquad (11)$$

These operators have the properties:

$$\mathcal{L}\,\Phi(S,L,M_S,M_L) = \hbar\sqrt{(L+M_L)(L-M_L+1)}\ \ \Phi(S,L,M_S,M_L-1). \qquad (12)$$
$$\mathcal{S}\,\Phi(S,L,M_S,M_L) = \hbar\sqrt{(S+M_S)(S-M_S+1)}\ \ \Phi(S,L,M_S-1,M_L). \qquad (13)$$
$$\mathcal{L}^i\,\phi_i(n,s,l,m_s,m_l) = \hbar\sqrt{(l+m_l)(l-m_l+1)}\ \ \phi_i(n,s,l,m_s,m_l-1). \qquad (14)$$
$$\mathcal{S}^i\,\phi_i(n,s,l,m_s,m_l) = \hbar\sqrt{(s+m_s)(s-m_s+1)}\ \ \phi_i(n,s,l,m_s-1,m_l). \qquad (15)$$

Thus, if we have an expression for Φ $(S, L, M_S = S, M_L = L)$ in terms of the zero-order wave functions $\bar{\chi}$ $(m_s^1, m_\ell^1, m_s^2, m_\ell^2, \cdots)$, then successive applications of the operators $\mathcal{L}$ and $\mathcal{S}$ enable us to obtain expressions for Φ (S, L, M_S', M_L'), for all possible M_S' and M_L'. For the states of any given term, these expressions have the correct relative phases according to the convention mentioned above (CS $\S\ 8^3$).

The expressions for many of the wave functions of the type Φ $(S, L, M_S = S, M_L = L)$ in terms of zero-order wave functions are evident on inspection. Thus, for example, in the case of the p^3 configuration (see Table 1(b)),

$$\Phi(\ell^1=1, \ell^2=1, \ell^3=1, S=1\tfrac{1}{2}, L=0, M_S=1\tfrac{1}{2}, M_L=0) = \underline{\bar{\chi}}\,(m_s^1=\tfrac{1}{2}, m_\ell^1=1, m_s^2=\tfrac{1}{2}, m_\ell^2=0, m_s^3=\tfrac{1}{2}, m_\ell^3=-1),$$

since the latter function is the only zero-order wave function with $M_S = 1\frac{1}{2}$, $M_L = 0$.

In cases where the expressions for Φ $(S, L, M_S = S, M_L = L)$ are not obvious, they may be obtained by use of the orthogonality of the wave functions. Thus, in the p^3 case (Table 2) the wave function Φ $(S = \frac{1}{2}, L = 1, M_S = \frac{1}{2}, M_L = 1)$ is that linear combination of the two zero-order functions with $M_S = \frac{1}{2}$, $M_L = 2$, which is orthogonal to the wave function Φ $(S = \frac{1}{2}, L = 2, M_S = \frac{1}{2}, M_L = 1)$.

The wave functions obtained in the manner described above have no definite phase relationship for states of different terms.

(c) We next set up the wave functions Ψ (S L J M) as linear combinations of the functions Φ (S L M M).

$$\Psi\,(S\ L\ J\ M) = \sum_{M_S, M_L} \Phi(S\ L\ M_S\ M_L)(S\ L\ M_S\ M_L |\ S\ L\ J\ M) \qquad (16)$$

The coefficients in this expansion are given by the formula of Wigner (equations (5)), or the tables in CS, $\S\ 13^3$, with the correlation

$$j_1 = S,\ j_2 = L,\ j = J,\ m = M, \qquad (17)$$

together with the relation (7). The wave functions for the states within any term have definite relative phases. For the states comprising a level characterized by quantum numbers S, L, J, the wave functions satisfy the relation

$$\mathcal{J}\,\Psi\,(S,L,J,M) = \hbar\sqrt{(J + M)(J - M + 1)}\ \Psi\,(S,L,J,M-1), \qquad (18)$$

where

$$\mathcal{J} = \mathcal{S} + \mathcal{L}. \qquad (19)$$

For levels within the same term, the wave functions possess the phase relationship given in CS, $\S\ 10^3$, namely that the non-diagonal elements of the matrix of $\boldsymbol{S}_z$ are all positive.

The above relation (18) may be used to simplify the computations somewhat, in that it is then necessary to use the tables of CS, $\S\ 1^3$, for only one wave function in each level (the one for which $M = J$); for the other wave functions can be obtained by the successive application of the operator $\mathcal{J}$ to $\Psi\,(S,L,J,M)$ and the operator $\mathcal{L} + \mathcal{S}$ to the expression for $\Psi\,(S,L,J,M)$ in terms of the functions $\Phi\ (S,L,M_S,M_L)$.

It is to be noted that in the Gray-Wills method the functions representing the states of different terms have no definite phase relation, whereas in the Bartlett method, which applies to two-electron configurations only, these functions have a definite phase relation. In the case of the p^3 configuration, which is the only more-than-two electron configuration treated in detail in this thesis, the relative term phases were chosen to agree with those given by CS, § 4^8.

(d) The fourth and final stage in the computation of the eigenfunctions is the introduction of the breakdown of the pure Russell-Saunders or LS coupling due to the small spin-orbit perturbation

$$H' = \sum_{i=1}^{n} \xi(r_i)\, \mathbf{L}_i \cdot \mathbf{S}_i, \tag{20}$$

where

$$\xi(r_i) = \frac{1}{2\mu^2 c^2} \frac{1}{r_i} \frac{\partial U(r_i)}{\partial r_i}. \tag{21}$$

$U(r_i)$ is a potential function representing the "effective" central field in which the i^{th} electron exists, and μ is the reduced mass of the electron. Since this spin-orbit interaction does not commute with the operators $\mathbf{S}$ and $\mathbf{L}$, the quantum numbers S and L are no longer rigorously characteristic of the states. On the other hand the interaction term commutes with $\mathbf{J}$, so that J and M still characterize the states rigorously. As a first approximation we use the usual procedure of taking linear combinations of the pure Russell-Saunders wave functions for states with the same J and M. If we have r such states, represented by wave functions $\Psi_1, \Psi_2, \ldots \Psi_r$, we write

$$\overline{\Psi_i(S_iL_iJM)} = \sum_{k=1}^{r} a_{ik}\ \Psi_k(S_kL_kJ\,M), \tag{22}$$

where, in the cases which we consider, the diagonal coefficients a are approximately unity, since the deviation from LS coupling is small. If we put this function into the Hamiltonian equation

$$(H^\circ + H')\overline{\Psi_i} = (E_i^\circ + E_i')\overline{\Psi_i} ,$$

then the standard first-order perturbation procedure for non-degenerate levels leads to the result

$$a_{ik} = \frac{H'_{ki}}{E_i^\circ - E_k^\circ} , \qquad k \neq i, \tag{23}$$

where

$$\begin{aligned} H'_{kj} &= \int \Psi_k^* H' \Psi_j \, d\tau \\ &= (S_kL_kJM \,|\, \sum_i \xi(r_i)\ \mathbf{L}_i\cdot\mathbf{S}_i \,|\, S_jL_jJM). \end{aligned} \tag{24}$$

The value of a_{ii} is given by the normalization condition on $\overline{\Psi_i}$, viz.

$$\alpha_{ii} \equiv a_{ii} = 1 - \tfrac{1}{2}\sum_{k\neq i} |a_{ik}|^2 . \tag{25}$$

In a few special cases it is necessary to use the second-order approximation to the wave functions. (Such cases are the $^2D_{1\frac{1}{2}}$ and $^4S_{1\frac{1}{2}}$ wave functions in the p^3 configuration, and the $^3F_2$ and $^3P_2$ wave functions in the d^2 configuration.) In these cases the standard second-order approximation method for non-degenerate levels$^{18)}$ leads to the replacement of equation (23) by the equation

$$a_{ik} = \frac{H'_{ki}}{(E_i^0 - E_k^0)} + \frac{1}{(E_i^0 - E_k^0)} \sum_{m \neq k} \frac{H'_{im} H'_{mk}}{(E_k^0 - E_m^0)} - \frac{H'_{ik} H'_{kk}}{(E_i^0 - E_k^0)^2}, \quad k \neq i. \qquad (23')$$

For small deviations from LS coupling, the second-order correction to a_{ik} is clearly negligible with respect to the first-order value, except when the latter vanishes. Only two such cases occur in the configurations treated here. Where they occur the wave functions will be denoted by $\overline{\Psi_i}$, to distinguish them from the first-order wave functions Ψ_i.

The term energy separations, $(E_i^0 - E_k^0)$, are obtained by applying to the pure Russell-Saunders states (before the spin-orbit interaction is introduced) a first-order perturbation treatment involving the mutual electrostatic interaction of the electrons

$$V' = \sum_{i<j} \frac{e^2}{r_{ij}}. \qquad (27)$$

The theoretical evaluation of the term energies will not be discussed here, as it is treated fully in CS, Chapters 6 and 7. In particular, in § 2^7 of CS the evaluation is carried out in detail for the p^2 configuration; and in § 5^7 the term energies are listed and compared with experiment for a number of configurations, including all the cases treated in this thesis, namely the p^2, p^3, p^4 and d^2 configurations. The term energies for these latter configurations are reproduced in the tables below. They involve two parameters, $F_2(nl,nl)$ and $F_4(nl,nl)$, the latter occurring only in the d^2 case. These parameters are defined by the equation

$$F^k(nl,n'l') = e^2 \int_0^\infty \int_0^\infty \frac{r_<^k}{r_>^{k+1}} R_1^2(nl)\, R_2^2(n'l')\, dr_1\, dr_2 , \qquad (28)$$

together with the auxiliary definitions (CS, § 8[6]):

$$F_2(np,np) = \frac{1}{25} F^2(np,np).$$
$$F_2(nd,nd) = \frac{1}{49} F^2(nd,nd). \qquad (29)$$
$$F_4(nd,nd) = \frac{1}{441} F^4(nd,nd).$$

Here R(nl) is the radial part of the one-electron wave function defined in (2), and the subscripts 1, 2 refer to the coordinates of the individual electrons. The parameters F_2 and F_4 are chosen so as to fit as well as possible the experimentally observed term energies[19].

In the theoretical treatment of these term energies, the following assumptions are made:

1) The spin-orbit interaction is much smaller than the electrostatic interaction.

2) The electrostatic and spin-orbit interactions between configurations may be neglected.

3) Each electron in a given configuration is assumed to move in the same effective central potential field, so that the radial part of the one-electron functions is independent of the m_l values of the individual electrons.

It may be necessary to modify the second and third of these assumptions in order to obtain better agreement with the experimental energies.

Likewise the evaluation of the spin-orbit interaction matrix elements $(S\ L\ J\ M|\sum_i \xi(r_i)\ L_i.S_i\ |S'L'J\ M)$ will not be discussed here, as the method is fully described in CS, Chapters 8 and 11 (in particular, § 3^8, § 1^{11} and § 2^{11}). These matrix elements are listed in CS, tables 1^{11}, for a number of configurations, including all the cases considered here, and are reproduced in the tables below for the latter cases. They all involve a parameter $\zeta_{n\ell}$, which is related to the separations of the energy levels within multiplets, since the displacements of the energy levels due to the spin-orbit interaction are given by the solutions of the secular equations involving this interaction. Indeed, for small spin-orbit interactions, these displacements are in general given by the diagonal elements in the spin-orbit matrix. For the p^3 configuration, however, the diagonal elements all vanish, and it is necessary to solve the secular equation up to terms of the order of $(\zeta_{np})^2$.

The parameter $\zeta_{n\ell}$ is defined by the equation

$$\zeta_{n\ell} = \hbar^2 \int_0^\infty R^2(n,\ell)\ \xi(r)\ d\mathbf{r}, \qquad (30)$$

where $\xi(r)$ is defined in equation (21). It is chosen so as to agree as well as possible with the experimentally observed level separations within multiplets. This is not possible, however, for the $2p^3$ configuration, in which other perturbations invert the doublets which occur. In this case satisfactory estimates of the values of ζ_{np} are obtained by interpolation between the $2p^2$ and $2p^4$ configurations[19).

The second and third of the assumptions listed above in the term energy discussion are also made in the treatment of the spin-orbit interaction. Here, too, they may need modification in order to get better agreement with the experimental results.

B. Eigenfunctions for the Configurations p^2, p^3, p^4 and d^2.

The above procedure has been applied to the p^2, p^3, p^4 and d^2 configurations, with results as given below.

For the p^4 configuration use was made of Shortley's result[20)] that the formulae for an almost closed shell with, say, η electrons missing, can be taken over almost unchanged from the formulae for the same shell when it contains only η electrons. Thus, for the p con-figuration, the possible S, L, J, M values are the same as for the p^2 configuration, and corresponding states in pure Russell-Saunders coupling are the same linear combinations of corresponding zero-order states. The application of the spin-orbit interaction also leads to similar results, the only difference being that the sign of the parameter ζ_{np} is changed.

Tables 1(b), 1(c), 2(b), 2(c), 3(d) and 3(e) are taken directly out of Condon and Shortley, § 5^7 and table 1^{11}.

For convenience, abbreviations of the form used by CS, § 5^8, have been introduced. Thus, we write

$$\chi \; (m_s^1 = +\tfrac{1}{2}, \; m_\ell^1 = 1; \; m_s^2 = -\tfrac{1}{2}, \; m_\ell^2 = 0) \equiv (1^+, 0^-).$$

$$\Phi \; (S = 0, \; L = 2, \; M = 0, \; M = 1) \equiv ({}^1D, 0, 1).$$

$$\Psi \; (S = 0, \; L = 2, \; J = 2, \; M = 1) \equiv ({}^1D_2^1).$$

$$\Psi' \; (S = 0, \; L = 2, \; J = 2, \; M = 1) \equiv ({}^1\overline{D}_2^1).$$

The zero-order wave functions have also been given labels A,B,C,... Wave functions whose phases were arbitrarily chosen are marked with an asterisk.

Case 1. p^2 Configuration

Table 1(a). Wave Functions in Pure Russell-Saunders Scheme

$(m_s^1, m_\ell^1, m_s^2, m_\ell^2)$		(S,L,M_s,M_2)	(S,L,J,M)
$(1^+,1^-)$	A	$({}^1D,0,2)^* = A$	$({}^1D_2^2)^* = A$
$(1^+,0^-)$	B	$({}^1D,0,1) = \frac{1}{\sqrt{2}}(B - C)$	$({}^1D_2^1) = \frac{1}{\sqrt{2}}(B - C)$
$(1^-,0^+)$	C	$({}^1D,0,0) = \frac{1}{\sqrt{2}}(2F + D - E)$	$({}^1D_2^0) = \frac{1}{\sqrt{6}}(2F + D - E)$
$(1^+,-1^-)$	D	$({}^1D,0,-1) = \frac{1}{\sqrt{2}}(Q - R)$	$({}^1D_2{}^1) = \frac{1}{\sqrt{2}}(Q - R)$
$(1^-,-1^+)$	E	$({}^1D,0,-2) = S$	$({}^1D_2{}^2) = S$
$(0^+,0^-)$	F	$({}^3P,1,1) = G$	$({}^3P_2^2) = G$
$(1^+,0^+)$	G	$({}^3P,1,0) = H$	$({}^3P_2^1) = H$
$(1^+,-1^+)$	H	$({}^3P,1,-1) = L$	$({}^3P_2^0) = I$
$(0^+,-1^+)$	I	$({}^3P,0,1) = \frac{1}{\sqrt{2}}(B + C)$	$({}^3P_2{}^1) = \frac{1}{\sqrt{2}}(B + C)$
$(1^-,0^-)$	M	$({}^3P,0,0) = \frac{1}{\sqrt{2}}(D + E)$	$({}^3P_2{}^2) = \frac{1}{\sqrt{2}}(D + E)$
$(1^-,-1^-)$	N	$({}^3P,0,-1) = \frac{1}{\sqrt{2}}(Q + R)$	$({}^3P^1) = \frac{1}{\sqrt{2}}(Q + R)$
$(0^-,-1^-)$	P	$({}^3P,-1,1) = M$	$({}^3P^0) = M$
$(0^+,-1^-)$	Q	$({}^3P,-1,0) = N$	$({}^3P^{\,1}) = N$
$(0^-,-1^+)$	R	$({}^3P,-1,-1) = P$	$({}^3P_0^0) = P$
$(-1^+,-1^-)$	S	$({}^1S,0,0) = \frac{1}{\sqrt{3}}(D - E - F)$	$({}^1S_0^0) = \frac{1}{\sqrt{3}}(D - E - F)$

Table 1(b). Term Energies

$$E({}^1S) = F_0 + 10\,F_2$$

$$E({}^1D) = F_0 + F_2$$

$$E({}^3P) = F_0 - 5\,F_2$$

p^2 Configuration

Table 1(c). Matrix of Spin-Orbit Interaction ($\zeta = \zeta_{np}$)

	$^1D_2$	$^3P_2$	$^3P_1$	$^3P_0$	$^1S_0$
$^1D_2$	0	$\frac{1}{\sqrt{2}}\zeta$			
$^3P_2$	$\frac{1}{\sqrt{2}}\zeta$	ζ			
$^3P_1$			$-\frac{1}{2}\zeta$		
$^3P_0$				$-\zeta$	$-\sqrt{2}\,\zeta$
$^1S_0$				$-\sqrt{2}\,\zeta$	0

Table 1(d). Wave Functions for the Perturbed System $\Psi'(SLJM)$

$$\left.\begin{aligned} (^1\bar{D}_2^M) &= \alpha(^1D_2^M) + b(^3P_2^M) \\ (^3\bar{P}_2^M) &= -b(^1D_2^M) + \alpha(^3P_2^M) \end{aligned}\right\} \quad M = 0, \pm1, \pm2. \quad b = \frac{\sqrt{2}\,\zeta_{np}}{12\,F_2}. \quad \alpha = \sqrt{1-b^2}.$$

$$\left.\begin{aligned} (^1\bar{S}_0^0) &= \gamma(^1S_0^0) + d(^3P_0^0) \\ (^3\bar{P}_0^0) &= -d(^1S_0^0) + \gamma(^3P_0^0) \end{aligned}\right\} \quad d = -\frac{\sqrt{2}\,\zeta_{np}}{15\,F_2} = -\frac{4}{5}b. \quad \gamma = \sqrt{1-d^2}.$$

$$(^3\bar{P}_1^M) = (^3P_1^M) \quad \Big\} \quad M = 0, \pm1.$$

Case 2. p^3 Configuration

Table 2(a). Wave Functions in LS Coupling

$(1^+,0^+,-1^+)$	A	$({}^4S,1\frac{1}{2},0)^* = A$	$({}^4S^{1\frac{1}{2}}_{1\frac{1}{2}})^* = A$
$(1^+,1^-;0^+)$	B	$({}^4S,\frac{1}{2},0) = \frac{1}{\sqrt{3}}(E+F+G)$	$({}^4S^{\frac{1}{2}}_{1\frac{1}{2}}) = \frac{1}{\sqrt{3}}(E+F+G)$
$(1^+,1^-,-1^+)$	C	$({}^4S,-\frac{1}{2},0) = \frac{1}{\sqrt{3}}(N+P+Q)$	$({}^4S^{-\frac{1}{2}}_{1\frac{1}{2}}) = \frac{1}{\sqrt{3}}(N+P+Q)$
$(1^+,0^+,0^-)$	D	$({}^4S,-1\frac{1}{2},0) = U$	$({}^4S^{-1\frac{1}{2}}_{1\frac{1}{2}}) = U$
$(1^+,0^+,-1^-)$	E	$({}^2D,\frac{1}{2},2)^* = -B$	$({}^2D^{2\frac{1}{2}}_{2\frac{1}{2}})^* = -B$
$(1^+,0^-,-1^+)$	F	$({}^2D,\frac{1}{2},1) = \frac{1}{\sqrt{2}}(D-C)$	$({}^2D^{1\frac{1}{2}}_{2\frac{1}{2}}) = \frac{1}{\sqrt{5}}\{-K+\sqrt{2}(D-C)\}$
$(1^-,0^+,-1^+)$	G	$({}^2D,\frac{1}{2},0) = \frac{1}{\sqrt{6}}(E+G-2F)$	$({}^2D^{\frac{1}{2}}_{2\frac{1}{2}}) = \frac{1}{\sqrt{10}}\{\sqrt{2}(M-L)-2F+G+E\}$
$(1^+,-1^+,-1^-)$	H	$({}^2D,\frac{1}{2},-1) = \frac{1}{\sqrt{2}}(H-I)$	$({}^2D^{-\frac{1}{2}}_{2\frac{1}{2}}) = \frac{1}{\sqrt{10}}\{\sqrt{2}(H-I)+2P-N-Q\}$
$(0^+,0^-,-1^+)$	I	$({}^2D,\frac{1}{2},-2) = J$	$({}^2D^{-1\frac{1}{2}}_{2\frac{1}{2}}) = \frac{1}{\sqrt{5}}\{\sqrt{2}(R-S)+J\}$
$(0^+,-1^+,-1^-)$	J	$({}^2D,-\frac{1}{2},2) = -K$	$({}^2D^{-2\frac{1}{2}}_{2\frac{1}{2}}) = T$
$(1^+,+1^-,0^-)$	K	$({}^2D,-\frac{1}{2},1) = \frac{1}{\sqrt{2}}(M-L)$	$({}^2D^{1\frac{1}{2}}_{1\frac{1}{2}}) = \frac{1}{\sqrt{10}}(2\sqrt{2}K+D-C)$
$(1^+,1^-,-1^-)$	L	$({}^2D,-\frac{1}{2},0) = \frac{1}{\sqrt{6}}(2P-Q-N)$	$({}^2D^{\frac{1}{2}}_{1\frac{1}{2}}) = \frac{1}{\sqrt{30}}\{3(L-M)+\sqrt{2}(E+G-2F)\}$
$(1^-,0^+,0^-)$	M	$({}^2D,-\frac{1}{2},-1) = \frac{1}{\sqrt{2}}(R-S)$	$({}^2D^{-\frac{1}{2}}_{1\frac{1}{2}}) = \frac{1}{\sqrt{30}}\{3(H-I)+\sqrt{2}(N+Q-2P)\}$
$(1^+,0^-,-1^-)$	N	$({}^2D,-\frac{1}{2},-2) = T$	$({}^2D^{-1\frac{1}{2}}_{1\frac{1}{2}}) = \frac{1}{\sqrt{10}}\{S-R+2\sqrt{2}\,J\}$
$(1^-,0^+,-1^-)$	P	$({}^2P,\ ,1)^* = \frac{1}{\sqrt{2}}(C+D)$	$({}^2P^{1\frac{1}{2}}_{1\frac{1}{2}})^* = \frac{1}{\sqrt{2}}(C+D)$
$(1^-,0^-,-1^+)$	Q	$({}^2P,\ ,0) = \frac{1}{\sqrt{2}}(E-G)$	$({}^2P^{+\frac{1}{2}}_{1\frac{1}{2}}) = \frac{1}{\sqrt{6}}\{L+M+\sqrt{2}\,(E-G)\}$
$(1^-,-1^+,-1^-)$	R	$({}^2P,\ ,-1) = \frac{1}{\sqrt{2}}(H+I)$	$({}^2P^{-\frac{1}{2}}_{1\frac{1}{2}}) = \frac{1}{\sqrt{6}}\{H+I+\sqrt{2}\,(N-Q)\}$
$(0^+,0^-,-1^-)$	S	$({}^2P,-\ ,1) = \frac{1}{\sqrt{2}}(L+M)$	$({}^2P^{-1\frac{1}{2}}_{1\frac{1}{2}}) = \frac{1}{\sqrt{2}}(R+S)$
$(0^-,-1^+,-1^-)$	T	$({}^2P,-\ ,1) = \frac{1}{\sqrt{2}}(N-Q)$	$({}^2P^{\frac{1}{2}}_{\frac{1}{2}}) = \frac{1}{\sqrt{6}}\{E-G-\sqrt{2}\,(L+M)\}$
$(1^-,0^-,-1^-)$	U	$({}^2P,-\ ,-1) = \frac{1}{\sqrt{2}}(R+S)$	$({}^2P^{-\frac{1}{2}}_{\frac{1}{2}}) = \frac{1}{\sqrt{6}}\{Q-N+\sqrt{2}\,(H+I)\}$

p^3 Configuration

Table 2(b). Term Energies

$$E(^2P) = 3\,F_0$$

$$E(^2D) = 3\,F_0 - 6\,F_2$$

$$E(^4S) = 3\,F_0 - 15\,F_2$$

Table 2(c). Matrix of Spin-Orbit Interaction ($\zeta = \zeta_{np}$)

	$^2D_{2\frac{1}{2}}$	$^2D_{1\frac{1}{2}}$	$^4S_{1\frac{1}{2}}$	$^2P_{1\frac{1}{2}}$	$^2P_{\frac{1}{2}}$
$^2D_{2\frac{1}{2}}$	0				
$^2D_{1\frac{1}{2}}$		0	0	$\frac{\sqrt{5}}{2}\zeta$	
$^4S_{1\frac{1}{2}}$		0	0	ζ	
$^2P_{1\frac{1}{2}}$		$\frac{\sqrt{5}}{2}\zeta$	ζ	0	
$^2P_{\frac{1}{2}}$					0

Table 2(d). Wave Functions in the Perturbed System $\psi'(S,L,J,M) \equiv \overline{(S,L,J,M)}$

$$(^2D^M_{2\frac{1}{2}}) = (^2D^M_{2\frac{1}{2}}) \quad \Big\} \quad M = \pm\tfrac{1}{2},\ \pm 1\tfrac{1}{2},\ \pm 2\tfrac{1}{2}.$$

$$\left.\begin{array}{l} (^2D^M_{1\frac{1}{2}})^* = \alpha(^2D^M_{1\frac{1}{2}}) + u(^4S^M_{1\frac{1}{2}}) - a(^2P^M_{1\frac{1}{2}}) \\ (^4S^M_{1\frac{1}{2}})^* = v(^2D^M_{1\frac{1}{2}}) + \beta(^4S^M_{1\frac{1}{2}}) - b(^2P^M_{1\frac{1}{2}}) \\ (^2P^M_{1\frac{1}{2}}) = a(^2D^M_{1\frac{1}{2}}) + b(^4S^M_{1\frac{1}{2}}) + \gamma(^2P^M_{1\frac{1}{2}}) \end{array}\right\} \begin{array}{l} M = \pm\tfrac{1}{2},\ \pm 1\tfrac{1}{2}. \\ a = \dfrac{\sqrt{5}\,\zeta}{12\,F_2}. \qquad b = \dfrac{\zeta}{15\,F_2}. \\ u = -\dfrac{\sqrt{5}\,\zeta^2}{108\,F_2^2} = -\tfrac{5}{3}ab,\ v = \dfrac{\sqrt{5}\,\zeta^2}{270\,F_2^2} = \tfrac{2}{3}ab \\ \alpha = \sqrt{1-a^2}\ ;\ \beta = \sqrt{1-b^2}\ ;\ \gamma = \sqrt{1-a^2-b^2}. \end{array}$$

$$(^2P^M_{\frac{1}{2}}) = (^2P^M_{\frac{1}{2}}) \quad \Big\} \quad M = \pm\tfrac{1}{2}.$$

* Second-order approximations, using equation (23').

Case 3. p^4 Configuration

All of the formulae for the p^4 configuration are the same as for the p^2 configuration, except that in the expressions for b and d, ζ_{np} is replaced by $-\zeta_{np}$; and that in the term energy expressions of Table 1(b), F_0 is replaced by 6 F_0.

Case 4. d^2 Configuration

Table 3(a). Wave Functions in the Zero-Order Scheme $\underline{\bar{\chi}}(m_s^1, m_\ell^1, m_s^2, m_\ell^2)$

$\underline{\bar{\chi}}(m_s^1, m_\ell^1, m_s^2, m_\ell^2)$		$(m_s^1, m_\ell^1, m_s^2, m_\ell^2)$		$\underline{\bar{\chi}}(m_s^1, m_\ell^1, m_s^2, m_\ell^2)$	
$(2^+,2^-)$	A	$(-1^+,2^-)$	Q	$(1^+,-1^+)$	f
$(2^+,1^-)$	B	$(-1^+,1^-)$	R	$(1^+,-2^+)$	g
$(2^+,0^-)$	C	$(-1^+,0^-)$	S	$(0^+,-1^+)$	h
$(2^+,-1^-)$	D	$(-1^+,-1^-)$	T	$(0^+,-2^+)$	i
$(2^+,-2^-)$	E	$(-1^+,-2^-)$	U	$(-1^+,-2^+)$	j
$(1^+,2^-)$	F	$(-2^+,2^-)$	V	$(2^-,1^-)$	k
$(1^+,1^-)$	G	$(-2^+,1^-)$	W	$(2^-,0^-)$	l
$(1^+,0^-)$	H	$(-2^+,0^-)$	X	$(2^-,-1^-)$	m
$(1^+,-1^-)$	I	$(-2^+,-1^-)$	Y	$(2^-,-2^-)$	n
$(1^+,-2^-)$	J	$(-2^+,-2^-)$	Z	$(1^-,0^-)$	p
$(0^+,2^-)$	K	$(2^+,1^+)$	a	$(1^-,-1^-)$	q
$(0^+,1^-)$	L	$(2^+,0^+)$	b	$(1^-,-2^-)$	r
$(0^+,0^-)$	M	$(2^+,-1^+)$	c	$(0^-,-1^-)$	s
$(0^+,-1^-)$	N	$(2^+,-2^+)$	d	$(0^-,-2^-)$	t
$(0^+,-2^-)$	P	$(1^+,0^+)$	e	$(-1^-,-2^-)$	u

d^2 Configuration

Table 3(b). Wave Functions in LS Coupling $\Phi\,(S,L,M_s,M_L)$

$(^1S,0,0) = \frac{1}{\sqrt{5}}(E + V + M - I - R)$

$(^1D,0,2) = \frac{1}{\sqrt{7}}\{\sqrt{2}\,(C + K) - \sqrt{3}\,G\}$

$(^1D,0,1) = \frac{1}{\sqrt{14}}\{\sqrt{6}\,(D + Q) - (H + L)\}$

$(^1D,0,0) = \frac{1}{\sqrt{14}}\{2(E + V) - 2M + I + R\}$

$(^1D,0,-1) = \frac{1}{\sqrt{14}}\{\sqrt{6}\,(J + W) - (N + S)\}$

$(^1D,0,-2) = \frac{1}{\sqrt{7}}\{\sqrt{2}\,(P + X) - \sqrt{3}\,T\}$

$(^1G,0,4) = A$

$(^1G,0,3) = \frac{1}{\sqrt{2}}(B + F)$

$(^1G,0,2) = \frac{1}{\sqrt{14}}\{\sqrt{3}\,(C + K) + 2\sqrt{2}\,G\}$

$(^1G,0,1) = \frac{1}{\sqrt{14}}\{D + Q + \sqrt{6}\,(H + L)\}$

$(^1G,0,0) = \frac{1}{\sqrt{70}}\{(E + V) + 4(I + R) + 6M\}$

$(^1G,0,-1) = \frac{1}{\sqrt{14}}\{J + W + \sqrt{6}\,(N + S)\}$

$(^1G,0,-2) = \frac{1}{\sqrt{14}}\{\sqrt{3}\,(X + P) + 2\sqrt{2}\,T\}$

$(^1G,0,-3) = \frac{1}{\sqrt{2}}(U + Y)$

$(^1G,0,-4) = Z$

$(^3P,0,1) = \frac{1}{\sqrt{10}}\{\sqrt{2}\,(D - Q) + \sqrt{3}\,(L - H)\}$

$(^3P,0,0) = \frac{1}{\sqrt{10}}\{2(E -, V) - (I - R)\}$

$(^3P,0,-1) = \frac{1}{\sqrt{10}}\{\sqrt{2}\,(J - W) - \sqrt{3}\,(N - S)\}$

$(^3P,1,1) = \frac{1}{\sqrt{5}}(\sqrt{2}\,c - \sqrt{3}\,e)$

$(^3P,1,0) = \frac{1}{\sqrt{5}}(2d - f)$

$(^3P,1,-1) = \frac{1}{\sqrt{5}}(\sqrt{2}\,g - \sqrt{3}\,h)$

$(^3P,-1,1) = \frac{1}{\sqrt{5}}(\sqrt{2}\,m - \sqrt{3}\,p)$

$(^3P,-1,0) = \frac{1}{\sqrt{5}}(2n - q)$

$(^3P,-1,-1) = \frac{1}{\sqrt{5}}(\sqrt{2}\,r - \sqrt{3}\,s)$

$(^3F,1,3) = a$

$(^3F,1,2) = b$

$(^3F,1,1) = \frac{1}{\sqrt{5}}(\sqrt{3}\,c + \sqrt{2}\,e)$

$(^3F,1,0) = \frac{1}{\sqrt{5}}(d + 2f)$

$(^3F,1,-1) = \frac{1}{\sqrt{5}}(\sqrt{3}\,g + \sqrt{2}\,h)$

$(^3F,1,-2) = i$

$(^3F,1,-3) = j$

$(^3F,0,3) = \frac{1}{\sqrt{2}}(B - F)$

$(^3F,0,2) = \frac{1}{\sqrt{2}}(C - K)$

$(^3F,0,1) = \frac{1}{\sqrt{10}}\{\sqrt{3}\,(D - Q) + \sqrt{2}\,(H - L)\}$

$(^3F,0,0) = \frac{1}{\sqrt{10}}\{(E - V) + 2(I - R)\}$

$(^3F,0,-1) = \frac{1}{\sqrt{10}}\{\sqrt{3}\,(J - W) + \sqrt{2}\,(N - S)\}$

$(^3F,0,-2) = \frac{1}{\sqrt{2}}(P - X)$

$(^3F,0,-3) = \frac{1}{\sqrt{2}}(U - Y)$

$(^3F,-1,3) = k$

$(^3F,-1,2) = \ell$

$(^3F,-1,1) = \frac{1}{\sqrt{5}}(\sqrt{3}\,m + \sqrt{2}\,p)$

$(^3F,-1,0) = \frac{1}{\sqrt{5}}(n + 2q)$

$(^3F,-1,-1) = \frac{1}{\sqrt{5}}(\sqrt{3}\,r + \sqrt{2}\,s)$

$(^3F,-1,-2) = t$

$(^3F,-1,-3) = u$

d^2 Configuration

Table 3(c). Wave Functions in LS Coupling Ψ (S,L,J,M)

$${}^1S_0^0 = \frac{1}{\sqrt{5}}(E+V+M-I-R)$$

$${}^1D_2^2 = \frac{1}{\sqrt{7}}\{\sqrt{2}\ (C+K)-\sqrt{3}\ G\}$$

$${}^1D_2^1 = \frac{1}{\sqrt{14}}\{\sqrt{6}\ (D+Q)-(H+L)\}$$

$${}^1D_2^0 = \frac{1}{\sqrt{14}}\{2(E+V)-2M+I+R\}$$

$${}^1D_2^{-1} = \frac{1}{\sqrt{14}}\{\sqrt{6}\ (J+W)-(N+S)\}$$

$${}^1D_2^{-2} = \frac{1}{\sqrt{7}}\{\sqrt{2}\ (P+X)-\sqrt{3}\ T\}$$

$${}^1G_4^4 = A$$

$${}^1G_4^3 = \frac{1}{\sqrt{2}}(B+F)$$

$${}^1G_4^2 = \frac{1}{\sqrt{14}}\{\sqrt{3}\ (C+K)+2\sqrt{2}\ G\}$$

$${}^1G_4^1 = \frac{1}{\sqrt{14}}\{D+Q+\sqrt{6}\ (H+L)\}$$

$${}^1G_4^0 = \frac{1}{\sqrt{70}}\{E+V+4(I+R)+6M\}$$

$${}^1G_4^{-1} = \frac{1}{\sqrt{14}}\{J+W+\sqrt{6}\ (N+S)\}$$

$${}^1G_4^{-2} = \frac{1}{\sqrt{14}}\{\sqrt{3}\ (X+P)+2\sqrt{2}\ T\}$$

$${}^1G_4^{-3} = \frac{1}{\sqrt{2}}(U+Y)$$

$${}^1G_4^{-4} = Z$$

$${}^3P_2^2 = \frac{1}{\sqrt{5}}(\sqrt{2}\ c-\sqrt{3}\ e)$$

$${}^3P_2^1 = \frac{1}{2\sqrt{5}}\{\sqrt{2}\ (D-Q)+\sqrt{5}\ (L-H)+\sqrt{2}\ (2d-f)\}$$

$${}^3P_2^0 = \frac{1}{\sqrt{30}}\{2\sqrt{2}\ (E-V)-\sqrt{2}\ (I-R)-\sqrt{3}\ (p+h)+\sqrt{2}(g+m)\}$$

$${}^3P_2^{-1} = \frac{1}{2\sqrt{5}}\{\sqrt{2}(J-W)-\sqrt{3}\ (N-S)\ +\sqrt{2}\ (2n-q)\}$$

$${}^3P_2^{-2} = \frac{1}{\sqrt{5}}(\sqrt{2}\ r-\sqrt{3}\ s)$$

$${}^3P_1^1 = \frac{1}{2\sqrt{5}}\{\sqrt{2}\ (2d-f)-\sqrt{2}\ (D-Q)-\sqrt{3}\ (L-H)\}$$

$${}^3P_1^0 = \frac{1}{\sqrt{10}}\{\sqrt{2}\ (g-m)+\sqrt{3}\ (p-h\}$$

$${}^3P_1^{-1} = \frac{1}{2\sqrt{5}}\{\sqrt{2}\ (q-2n)+\sqrt{2}\ (J-W)-\sqrt{3}\ (N-S)\}$$

$${}^3P_0^0 = \frac{1}{\sqrt{30}}\{2(m+g)-\sqrt{6}\ (p+h)-2(E-V)+(I-R)\}$$

$${}^3F_4^4 = a$$

$${}^3F_4^3 = \frac{1}{2\sqrt{2}}(B-F+\sqrt{6}\ b)$$

$${}^3F_4^2 = \frac{1}{2\sqrt{7}}\{\sqrt{6}\ (C-K)+\sqrt{5}\ (\sqrt{3}\ c+\sqrt{2}\ e)+k\}$$

$${}^3F_4^1 = \frac{1}{2\sqrt{14}}\{3(D-Q)+\sqrt{6}(H-L)+\sqrt{6}\,\ell+2d+4f\}$$

$${}^3F_4^0 = \frac{1}{10\sqrt{2}}\{4(I-R)+2(E-V)+\sqrt{6}(p+h)+3(m+g)\}$$

$${}^3F_4^{-1} = \frac{1}{2\sqrt{14}}\{3(J-W)+\sqrt{6}(N-S)+\sqrt{6}\ i+2n+4q\}$$

$${}^3F_4^{-2} = \frac{1}{2\sqrt{7}}\{\sqrt{6}(P-X)+\sqrt{5}(\sqrt{3}\ r+\sqrt{2}\ s)+j\}$$

$${}^3F_4^{-3} = \frac{1}{2\sqrt{2}}(U-Y+\sqrt{6}\ t)$$

$${}^3F_4^{-4} = u$$

$${}^3F_3^3 = \frac{1}{2\sqrt{2}}\{\sqrt{2}\ b-\sqrt{3}\ (B-F)\}$$

$${}^3F_3^2 = \frac{1}{2\sqrt{3}}\{\sqrt{2}\ e+\sqrt{3}\ c-\sqrt{3}\ k-\sqrt{2}\ (6-K)\}$$

$${}^3F_3^1 = \frac{1}{2\sqrt{30}}\{2\sqrt{3}(d+2f)-5\sqrt{2}\,\ell-\sqrt{2}(H-L)-\sqrt{3}(D-Q)\}$$

$${}^3F_3^0 = \frac{1}{\sqrt{10}}\{\sqrt{3}(g-m)+\sqrt{2}\ (h-p)\}$$

$${}^3F_3^{-1} = \frac{1}{2\sqrt{30}}\{-2\sqrt{3}(n+2q)+5\sqrt{2}\,i+\sqrt{2}(N-S)+\sqrt{3}(J-W)\}$$

$${}^3F_3^{-2} = \frac{1}{2\sqrt{3}}\{\sqrt{2}(P-X)+\sqrt{3}\ j-\sqrt{2}\ s-\sqrt{3}\ r\}$$

$${}^3F_3^{-3} = \frac{1}{2\sqrt{2}}\{\sqrt{3}\ (U-Y)-\sqrt{2}\ t\}$$

$${}^3F_2^2 = \frac{1}{\sqrt{210}}\{\sqrt{6}\ c+2e-5(C-K)+5\sqrt{6}\ k\}$$

$${}^3F_2^1 = \frac{1}{\sqrt{105}}\{\sqrt{3}(d+2f)+5\sqrt{2}\,\ell-2\sqrt{2}(H-L)-2\sqrt{3}(D-Q)\}$$

$${}^3F_2^0 = \frac{1}{\sqrt{210}}\{2\sqrt{6}(p+h)+6(g+m)-3(E-V)-6(I-R)\}$$

$${}^3F_2^{-1} = \frac{1}{\sqrt{105}}\{\sqrt{3}(n+2q)+5\sqrt{2}\,i-2\sqrt{2}(N-S)-2\sqrt{3}(J-W)\}$$

$${}^3F_2^{-2} = \frac{1}{\sqrt{210}}\{\sqrt{6}\ r+2s+5\sqrt{6}\ j-5(P-X)\}$$

d^2 Configuration

Table 3(d). Term Energies

$$E(^1S) = F_0 + 14\,F_2 + 126\,F_4$$

$$E(^3P) = F_0 - 7\,F_2 - 84\,F_4$$

$$E(^1D) = F_0 - 3\,F_2 + 36\,F_4$$

$$E(^3F) = F_0 - 8\,F_2 - 9\,F_4$$

$$E(^1G) = F_0 + 4\,F_2 + F_4$$

Table 3(e). Matrix of Spin-Orbit Interaction ($\zeta = \zeta_{nd}$)

$$\begin{array}{c|ccccccccc}
 & {}^1G_4 & {}^3F_4 & {}^3F_3 & {}^3F_2 & {}^1D_2 & {}^3P_2 & {}^3P_1 & {}^3P_0 & {}^1S_0 \\
\hline
{}^1G_4 & 0 & \zeta & & & & & & & \\
{}^3F_4 & \zeta & \frac{3}{2}\zeta & & & & & & & \\
{}^3F_3 & & & -\frac{1}{2}\zeta & & & & & & \\
{}^3F_2 & & & & -2\zeta & -2\sqrt{\frac{3}{5}}\,\zeta & 0 & & & \\
{}^1D_2 & & & & -2\sqrt{\frac{3}{5}}\,\zeta & 0 & \sqrt{\frac{21}{10}}\,\zeta & & & \\
{}^3P_2 & & & & 0 & \sqrt{\frac{21}{10}}\,\zeta & \frac{1}{2}\zeta & & & \\
{}^3P_1 & & & & & & & -\frac{1}{2}\zeta & & \\
{}^3P_0 & & & & & & & & -\zeta & -\sqrt{6}\,\zeta \\
{}^1S_0 & & & & & & & & -\sqrt{6}\,\zeta & 0
\end{array}$$

d^2 Configuration

Table 3(f). Wave Functions in the Perturbed System $\underline{\Psi}'(S,L,J,M) \equiv (\overline{S,L,J,M})$

$$\left.\begin{aligned}({}^1\overline{G}{}^M_4) &= \alpha({}^1G^M_4) + b({}^3F^M_4)\\ ({}^3\overline{F}{}^M_4) &= -b({}^1G^M_4) + \alpha({}^3F^M_4)\end{aligned}\right\} \quad M = 0,\pm1,\pm2,\pm3,\pm4$$

$$\left.({}^3\overline{F}{}^M_3) = ({}^3F^M_3)\right\} \quad M = 0,\pm1,\pm2,\pm3$$

$$\left.\begin{aligned}({}^3\overline{\overline{F}}{}^M_2)^* &= \beta({}^3F^M_2) + f({}^1D^M_2) + u({}^3P^M_2)\\ ({}^1\overline{D}{}^M_2) &= -f({}^3F^M_2) + \gamma({}^1D^M_2) + k({}^3P^M_2)\\ ({}^3\overline{\overline{P}}{}^M_2)^* &= v({}^3F^M_2) - k({}^1D^M_2) + \delta({}^3P^M_2)\end{aligned}\right\} \quad M = 0,\pm1,\pm2$$

$$\left.({}^3\overline{P}{}^M_1) = ({}^3P^M_1)\right\} \quad M = 0,\pm1$$

$$({}^3\overline{P}{}^0_0) = \varepsilon({}^3P^0_0) + d({}^1S^0_0)$$

$$({}^1\overline{S}{}^0_0) = -d({}^3P^0_0) + \varepsilon({}^1S^0_0)$$

$$b = \frac{\zeta}{12F_2 + 10F_4} \qquad \alpha = \sqrt{1 - b^2}$$

$$f = \frac{2\sqrt{15}\,\zeta}{25(F_2 + 9F_4)} \qquad \beta = \sqrt{1 - f^2}$$

$$k = \frac{-\sqrt{210}\,\zeta}{100(F_2 - 12F_4)} \qquad \gamma = \sqrt{1 - f^2 - k^2}$$

$$u = \frac{-\sqrt{14}\,\zeta^2}{125(F_2 - 5F_4)(F_2 + 9F_4)} \qquad \delta = \sqrt{1 - k^2}$$

$$v = \frac{-\sqrt{14}\,\zeta^2}{250(F_2 - 5F_4)(F_2 - 12F_4)}$$

$$d = \frac{\sqrt{6}\,\zeta}{7(F_2 + 30F_4)} \qquad \varepsilon = \sqrt{1 - d^2}$$

* Second-order approximations, using equation (23'0.

IV. CALCULATION OF MAGNETIC DIPOLE LINE STRENGTHS

A. Method of Calculation

The magnetic dipole line strengths are given by the formula

$$S\,(\overline{S\ L\ J},\overline{S'L'J'}) = \sum_{M,M'} \left|(S\ L\ J\ M|\mathbf{M}|S'L'J'M')\right|^{2} \qquad (1)$$

where, as before, $(\overline{S\ L\ J\ M})$ denotes the perturbed Russell-Saunders wave functions, and

$$\mathbf{M} = 2\,\mathbf{S} + \mathbf{L} = (2\,\mathbf{S}' + \mathbf{L}') + (2\,\mathbf{S}^{2} + \mathbf{L}^{2}) + \cdots \qquad (2)$$

Since we now possess expressions for the wave functions $\Psi'(S\ L\ J\ M)$ in terms of products of one-electron wave functions (section III), we could carry out the evaluation of the line strengths in the following five steps:

(a) Calculation of the one-electron matrix elements, $(n\ s\ l\ m_s\ m_\ell\,|\ 2\,\mathbf{S}' + \mathbf{L}'|\ n\ s\ l\ m_s'\ m_\ell')$.

(b) Calculation in terms of these matrix elements of the matrix elements of the type $(A\ |2\,\mathbf{S} + \mathbf{L}|\ B)$.

(c) Calculation in terms of these of the matrix elements $(S\ L\ J\ M\ |\ 2\,\mathbf{S} + \mathbf{L}|\ S'L'J'M')$.

(d) Calculation in terms of these of the matrix elements $(\overline{S\ L\ J\ M}\ |2\,\mathbf{S} + \mathbf{L}|\overline{S'L'J'M'})$.

(e) Squaring the absolute values of the latter set of matrix elements and summing over M and M' to get the line strengths.

Essentially this procedure will have to be used in the computation of the electric quadrupole line strengths. However in the magnetic dipole case it is fortunately possible to derive formulae for the matrix elements and line strengths in pure Russell-Saunders coupling. Thus we find

$$S(SLJ, SLJ) = \frac{(2J+1)\{S(S+1) - L(L+1) + 3J(J+1)}{4J(J+1)} . \qquad (3)$$

$$S(SLJ, SLJ-1) = S(SLJ-1, SLJ) = \frac{\{J^2-(L-S)^2\}\{(S+L+1)^2 - J^2\}}{4J} . \qquad (4)$$

$$S(SLJ, SLJ+1) = S(SLJ+1, SLJ) = \frac{\{(J+1)^2-(L-S)^2\}\{(S+L+1)^2-(J+1)^2\}}{4(J+1)} . \qquad (5)$$

All other line strengths vanish. A sum rule useful for checking purposes may be obtained by summation, viz.

$$\sum_{J'} S(SLJ, SLJ') = (2J+1)\{2J(J+1) + 2S(S+1) - L(L+1)\} . \qquad (6)$$

Equations (4) and (5) were first derived by Brinkman$^{21)}$. All of these equations can be quite easily deduced from some formulae in CS, Chapter 3, as follows:

In § 8^3 and § 9^3 of CS there is given Born and Jordan's$^{22)}$ derivation of the dependence on m of the matrix elements of a vector operator $\mathbf{T}$ in the jm scheme; that is, for a system of wave functions characterized by the quantum numbers j,m, and by other quantum numbers which are grouped together as "α". The operator $\mathbf{T}$ has the commutation properties

$$\begin{aligned} [\mathbf{J}_x, \mathbf{T}_x] &= \mathbf{J}_x \mathbf{T}_x - \mathbf{T}_x \mathbf{J}_x = 0 \\ [\mathbf{J}_x, \mathbf{T}_y] &= i \hbar \mathbf{T}_z \\ [\mathbf{J}_x, \mathbf{T}_z] &= -i \hbar \mathbf{T}_y \end{aligned} \tag{7}$$

together with other relations obtainable by cyclic permutation of the x, y and z. The matrix elements of $\mathbf{T}$ are expressed in terms of scalar quantities $(\alpha j \vdots T \vdots \alpha' j')$, independent of m and m', multiplied by factors dependent on j and m only. Thus, for example

$$(\alpha j m|\mathbf{T}|\alpha' j+1\ m\pm 1) = \mp (\alpha j \vdots T \vdots \alpha' j+1) \tfrac{1}{2} \sqrt{(j \pm m+1)(j\pm m+2)}\ (\mathbf{i} + i\mathbf{j}), \tag{8}$$

where $\mathbf{i}$, $\mathbf{j}$ and $\mathbf{k}$ are unit vectors in the x, y and z directions, respectively. Only those matrix elements do not vanish for which

$$(j' - j) = 0, \pm 1; (m' - m) = 0, \pm 1. \tag{9}$$

In § 13^3 is given the result of squaring the absolute values of these matrix elements and summing over m and m':

$$\begin{aligned} \sum_{m,m'} |(\alpha j m|\mathbf{T}|\alpha' j' m')|^2 &= |(\alpha j \vdots T \vdots \alpha' j\pm 1)|^2 \tfrac{1}{2}(2j+1)(2j+1\pm 1)(2j+1\pm 2), \quad \text{if } j' = j\pm 1; \\ &= |(\alpha j \vdots T \vdots \alpha' j)|^2 (2j+1)\, j(j+1), \quad \text{if } j' = j. \end{aligned} \tag{10}$$

In § 10^3 of CS it is then shown that, if

$$\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2, \tag{11}$$

then $\mathbf{J}_1$ and $\mathbf{J}_2$ are operators of type $\mathbf{T}$; and, further, that for these operators it is possible to evaluate the quantities occurring in the formulae of type (8), in the $\gamma\, j_1\, j_2\, j\, m$ representation[23]. They are

$$(\gamma\, j_1\, j_2\, j \vdots J_1 \vdots \gamma\, j_1\, j_2\, j) = \frac{j_1(j_1+1) - j_2(j_2+1) + 3j(j+1)}{2j(j+1)}\,\hbar,$$

$$(\gamma\, j_1\, j_2\, j \vdots J_2 \vdots \gamma\, j_1\, j_2\, j) = \frac{j_2(j_2+1) - j_1(j_1+1) + 3j(j+1)}{2j(j+1)}\,\hbar,$$

$$(\gamma\, j_1\, j_2\, j \vdots J_1 \vdots \gamma\, j_1\, j_2\, j-1) = (\gamma\, j_1\, j_2\, j-1 \vdots J_1 \vdots \gamma\, j_1\, j_2\, j)$$

$$= -(\gamma\, j_1\, j_2\, j \vdots J_2 \vdots \gamma\, j_1\, j_2\, j-1) = -(\gamma\, j_1\, j_2\, j-1 \vdots J_2 \vdots \gamma\, j_1\, j_2\, j)$$

$$= \frac{\hbar}{2J}\sqrt{\frac{\{j^2-(j_1-j_2)^2\}\{(j_1+j_2+1)^2-j^2\}}{(4j^2-1)}}\,. \tag{12}$$

All other such quantities vanish.

If we then make the correlation

$$\begin{gathered}\mathbf{J}_1 = \mathbf{S},\quad \mathbf{J}_2 = \mathbf{L},\quad \mathbf{J} = \mathbf{J}\\ j_1 = S,\quad j_2 = L,\quad j = J,\quad m = M,\end{gathered} \tag{13}$$

then the above formulae give us the matrix elements in the S L J M scheme of $\mathbf{S}$ and $\mathbf{L}$ and hence of $\mathbf{M} = 2\,\mathbf{S} + \mathbf{L}$. Thus, by addition, we get

$$(S\,L\,J \vdots 2S+L \vdots S\,L\,J) = \frac{S(S+1) - L(L+1) + 3J(J+1)}{2J(J+1)}\,\hbar.$$

$$(S\,L\,J \vdots 2S+L \vdots S\,L\,J-1) = (S\,L\,J-1 \vdots 2S+L \vdots S\,L\,J) \tag{14}$$

$$= \frac{\hbar}{2J}\sqrt{\frac{\{J^2-(S-L)^2\}\{(S+L+1)^2-J^2\}}{(4J^2-1)}}\,.$$

Substitution of these expressions into the equations of type (8) give the matrix elements of $\mathbf{M}$, and substitution into the equations (10) yields the desired line strengths given in equations (3), (4) and (5).

It is to be noted that in the above formulae the relative phases of the wave functions have been chosen in accordance with the convention discussed in section III, step (b).

From equations (3), (4) and (5), or from equations (14), it is seen that the selection rules for magnetic dipole radiation in LS coupling are those given in equation (26) of section II.

The evaluation of the magnetic dipole line strengths is thus reduced to the following two steps:

(a) Calculation of the line strengths in pure Russell-Saunders coupling.

(b) Introduction of the breakdown of pure Russell-Saunders coupling.

For the second step we have, from equation (22) of section III, together with the selection rules for magnetic dipole radiation,

$$\begin{aligned}(\overline{S_iL_iJM}\,|\,2\mathbf{S}+\mathbf{L}\,|\,\overline{S_jL_jJM}) &= \Big(\sum_k a_{ik}^{*}\Psi_k^{*}(S_kL_kJM)\,\Big|\,2\mathbf{S}+\mathbf{L}\,\Big|\sum_{\ell} a_{j\ell}\Psi_{\ell}(S_{\ell}L_{\ell}J'M')\Big) \\ &= \sum_k a_{ik}^{*}a_{jk}\,(S_kL_kJM\,|\,2\mathbf{S}+\mathbf{L}\,|\,S_kL_kJ'M') \qquad (15) \\ &= \sum_k a_{ik}^{*}a_{jk}\,(S_kL_kJ\,\vdots\,2S+L\,\vdots\,S_kL_kJ')\,\mathbf{F}(J,J',M,M').\end{aligned}$$

The last form is due to the fact that the factor depending on M and M' in the matrix elements is independent of S_k and L_k. Squaring the absolute values of these matrix elements, summing over M and M', and making use of the fact that

$$S(\overline{S_k L_k J}, \overline{S_k L_k J'}) = |(S_k L_k J \vdots 2S+L \vdots S_k L_k J')|^2 \sum_{M,M'} |\mathbf{f}(J,J',M,M')|^2,$$

we see that

$$S(\overline{S_i L_i J}, \overline{S_j L_j J'}) = |\sum_k a^*_{ik} a_{jk} |(S_k L_k J \vdots 2S+L \vdots S_k L_k J')|^2 \sum_{M,M'} |\mathbf{f}(J,J',M,M')|^2,$$

and hence

$$S(S_i L_i J, S_j L_j J') = |\sum_k a^*_{ik} a_{jk} \sqrt{S(S_k L_k J, S_k L_k J')}|^2. \qquad (17)$$

That the positive square root is to be taken in all cases is seen from equations (14), in which the quantities $(S\ L\ J \vdots 2S + L \vdots S\ L\ J')$ are always positive. (This is not strictly true, since $(S\ L\ J \vdots 2S + L \vdots S\ L\ J)$ may be negative in some special cases, such as when $J = L - S$ and $S < L < 2S - 1$. However, such special cases do not arise for the equivalent configurations p^2, p^3, p^4 and d^2, which are treated here, nor indeed for any equivalent configurations up to f^5).

In general the non-zero matric elements of type (16) possess non-vanishing terms of the first order of approximation in the coefficients of breakdown of pure Russell-Saunders coupling. That is, either $(S_i L_i J \vdots 2S + L \vdots S_i L_i J')$ and a_{ji} do not vanish, or $(S_j L_j J \vdots 2S + L \vdots S_j L_j J')$ and a^*_{ij} do not vanish. (The diagonal coefficients a^*_{ii} and a_{jj} are of the order of magnitude of unity.) In a few cases, however, this is not the situation, and the only non-vanishing terms are of the second order of approximation. In these special cases, in order to include all terms of the second order of approximation, it is necessary to use the second-order approximation to the wave functions within the configuration instead of the first-order approximations. This amounts to replacing the coefficients a_{ik} defined in equation (23) of section III by the coefficients given in equation (23') of that section. The formula for the line strengths still has the form (17), except that the bars over the quantum numbers on the left-hand side of the equation are replaced by double bars.

It should be noted here that no attempt was made to include all of the second-order terms in the line strengths. In order to do this, all of the wave functions would have to be calculated to the second-order approximation. However, the normalization coefficients $\alpha_{ii} \equiv a_{ii}$, which by equation (26) of section III differ from unity by terms of the second order in the coefficients a_{ik}, have been retained, since their inclusion in the formulae is a relatively simple matter.

B. Magnetic Dipole Line Strengths for the Configurations p^2, p^3, p^4 and d^2.

The above procedure has been applied to the p^2, p^3, p^4 and d^2 configurations, with results as given in the following tables. In the tables for line strengths in LS coupling, blank spaces indicate that the corresponding line strengths vanish. In the tables for the perturbed systems, the diagonal elements are not filled in, since they have no significance in the problem of transition probabilities.

Case 1. p^2 Configuration

Table 4(a). Line Strengths in LS Coupling S(SLJ, SLJ')

	${}^1D_2$	${}^3P_2$	${}^3P_1$	${}^3P_0$	${}^1S_0$
${}^1D_2$	30				
${}^3P_2$		$\frac{135}{2}$	$\frac{5}{2}$	0	
${}^3P_1$		$\frac{5}{2}$	$\frac{27}{2}$	2	
${}^3P_0$		0	2	0	
${}^1S_0$					0

Table 4(b). Line Strengths in the Perturbed System $S(\overline{SLJ}, \overline{S'L'J'})$

	${}^1\overline{D}_2$	${}^3\overline{P}_2$	${}^3\overline{P}_1$	${}^3\overline{P}_0$	${}^1\overline{S}_0$
${}^1\overline{D}_2$		$\frac{15}{2}\alpha^2 b^2$	$\frac{5}{2} b^2$	0	0
${}^3\overline{P}_2$	$\frac{15}{2}\alpha^2 b^2$		$\frac{5}{2}\alpha^2$	0	0
${}^3\overline{P}_1$	$\frac{5}{2} b^2$	$\frac{5}{2}\alpha^2$		$2\gamma^2$	$2d^2$
${}^3\overline{P}_0$	0	0	$2\gamma^2$		0
${}^1\overline{S}_0$	0	0	$2d^2$	0	

Case 2. p^3 Configuration

Table 5(a). Line Strengths in LS Coupling S(SLJ, SLJ')

	$^2D_{2\frac{1}{2}}$	$^2D_{1\frac{1}{2}}$	$^4S_{1\frac{1}{2}}$	$^2P_{1\frac{1}{2}}$	$^2P_{\frac{1}{2}}$
$^2D_{2\frac{1}{2}}$	$\frac{378}{5}$	$\frac{12}{5}$			
$^2D_{1\frac{1}{2}}$	$\frac{12}{5}$	$\frac{48}{5}$			
$^4S_{1\frac{1}{2}}$			60		
$^2P_{1\frac{1}{2}}$				$\frac{80}{3}$	$\frac{4}{3}$
$^2P_{\frac{1}{2}}$				$\frac{4}{3}$	$\frac{2}{3}$

Table 5(b). Line Strengths in the Perturbed System $S(\overline{SLJ}, \overline{S'L'J'})$

	$^2\overline{D}_{2\frac{1}{2}}$	$^2\overline{D}_{1\frac{1}{2}}$	$^4\overline{S}_{1\frac{1}{2}}$	$^2\overline{P}_{1\frac{1}{2}}$	$^2\overline{P}_{\frac{1}{2}}$
$^2\overline{D}_{2\frac{1}{2}}$		$\frac{12}{5}\alpha^2$	$\frac{12}{5}\nu^2$ *	$\frac{12}{5}a^2$	0
$^2\overline{D}_{1\frac{1}{2}}$	$\frac{12}{5}\alpha^2$		$\frac{484}{15}a^2b^2$ *	$\frac{16}{15}a^2(5\gamma-3\alpha)^2$	$\frac{4}{3}a^2$
$^4\overline{S}_{1\frac{1}{2}}$	$\frac{12}{5}\nu^2$ *	$\frac{484}{15}a^2b^2$ *		$\frac{20}{3}b^2(3\beta-2\gamma)^2$	$\frac{4}{3}b^2$
$^2\overline{P}_{1\frac{1}{2}}$	$\frac{12}{5}a^2$	$\frac{16}{15}a^2(5\gamma-3\alpha)^2$	$\frac{20}{3}b^2(3\beta-2\gamma)^2$		$\frac{4}{3}\gamma^2$
$^2\overline{P}_{\frac{1}{2}}$	0	$\frac{4}{3}a^2$	$\frac{4}{3}b^2$	$\frac{4}{3}\gamma^2$	

* These are second-order line strengths, $S(^4\overline{S}_{1\frac{1}{2}}, {}^2\overline{D}_{1\frac{1}{2}})$, etc.

Case 3. p^4 Configuration

The line strengths for the p^4 configuration have the same form as those for the p^2 configuration.

Case 4. d^2 Configuration

Table 6(a). Line Strengths in LS Coupling $S(SLJ, SLJ')$

	$^1G_4$	$^3F_4$	$^3F_3$	$^3F_2$	$^1D_2$	$^3P_2$	$^3P_1$	$^3P_0$	$^1S_0$
$^1G_4$	180								
$^3F_4$		$\frac{1125}{4}$	$\frac{27}{4}$	0					
$^3F_3$		$\frac{27}{4}$	$\frac{1183}{12}$	$\frac{20}{3}$					
$^3F_2$		0	$\frac{20}{3}$	$\frac{40}{3}$					
$^1D_2$					30				
$^3P_2$						$\frac{135}{2}$	$\frac{5}{2}$	0	
$^3P_1$						$\frac{5}{2}$	$\frac{27}{2}$	2	
$^3P_0$						0	2	0	
$^1S_0$									0

Table 6(b). Line Strengths in the Perturbed System $S(\overline{SLJ}, \overline{S'L'J'})$

	$^1\overline{G}_4$	$^3\overline{F}_4$	$^3\overline{F}_3$	$^3\overline{F}_2$	$^1\overline{D}_2$	$^3\overline{P}_2$	$^3\overline{P}_1$	$^3\overline{P}_0$	$^1\overline{S}_0$
$^1\overline{G}_4$		$\frac{45}{4}\alpha^2 b^2$	$\frac{27}{4}b^2$	0	0	0	0	0	0
$^3\overline{F}$	$\frac{45}{4}\alpha^2 b^2$		$\frac{27}{4}\alpha^2$	0	0	0	0	0	0
$^3\overline{F}_3$	$\frac{27}{4}b^2$	$\frac{27}{4}\alpha^2$		$\frac{20}{3}\beta^2$	$\frac{20}{3}f^2$	$\frac{20}{3}v^2$ *	0	0	0
$^3\overline{F}_2$	0	0	$\frac{20}{3}\beta^2$		$\frac{10}{3}f^2(3\gamma-2\beta)^2$	$30(fk-\frac{3}{2}u-\frac{2}{3}v)^2$ *	$\frac{5}{2}u^2$ *	0	0
$^1\overline{D}_2$	0	0	$\frac{20}{3}f^2$	$\frac{10}{3}f^2(3\gamma-2\beta)^2$		$\frac{15}{2}k^2(3\delta-2\gamma)^2$	$\frac{5}{2}k^2$	0	0
$^3\overline{P}_2$	0	0	$\frac{20}{3}v^2$ *	$30(fk-\frac{3}{2}u-\frac{2}{3}v)^2$ *	$\frac{15}{2}k^2(3\delta-2\gamma)^2$		$\frac{5}{2}\delta^2$	0	0
$^3\overline{P}_1$	0	0	0	$\frac{5}{2}u^2$ *	$\frac{5}{2}k^2$	$\frac{5}{2}\delta^2$			
$^3\overline{Po}$	0	0	0	0	0	0			0
$^1\overline{So}$	0	0	0	0	0	0		0	

* These are second-order approximation line strengths $S(^3\overline{\overline{F}}_2, ^3\overline{\overline{P}}_2)$,etc.

V. CALCULATION OF ELECTRIC QUADRUPOLE LINE STRENGTHS

A. Method of Calculation

The electric quadrupole line strengths are given by the formula

$$S_q(\overline{S\,L\,J}, \overline{S\,L\,J}) = \sum_{M,M'} |(S\,L\,J\,M|\tilde{\mathcal{Q}}|S'L'J'M')|^2 \tag{1}$$

where

$$\mathcal{Q} = -e \sum_i \mathbf{r}_i\mathbf{r}_i , \tag{2}$$

and

$$\bar{\mathcal{Q}} = \mathcal{Q} - (\text{the spherically symmetric part of } \mathcal{Q}) \tag{3}$$

In this case simple expressions for the line strengths in LS coupling are not available. Formulae have been developed by Rubinowicz$^{24)}$ for the dependence on M and M' of the matrix elements in LS coupling (see CS, § 6^4). He made use of the fact that $\mathbf{r}_i$ is a vector of the type $\mathbf{T}$ defined in equation (7) of section IV. From the quantum mechanics,

$$(\alpha JM|\mathbf{T}_1\mathbf{T}_2|\alpha'J'M') = \sum_{\alpha''J''M''} (\alpha JM|\mathbf{T}_1|\alpha''J''M'')(\alpha''J''M''|\mathbf{T}_2|\alpha'J'M') \tag{4}$$

where α represents all the quantum numbers, other than J and M, which characterize the atomic states. Since the dependence on M and M' of the matrix of $\mathbf{T}$ is known (section IV, equation (18)), the dependence on M and M' of the matrix of $\mathbf{r}_i\mathbf{r}_i$, and hence of $\mathcal{Q}$ may readily be found. The results are given in CS, § 6^4(6). For convenience they are reproduced here.

$$
\begin{aligned}
(\alpha J M|\mathcal{H}|\alpha' J\ M\pm 2) &= D\sqrt{(J\mp M)(J\mp M-1)(J\pm M+1)(J\pm M+2)}\ \mathcal{Q}(\pm 2)\\
(\alpha J M|\mathcal{H}|\alpha' J\ M\pm 1) &= D\,(2M\pm 1)\sqrt{(J\mp M)(J\pm M+1)}\ \mathcal{Q}(\pm 1)\\
(\alpha J M|\mathcal{H}|\alpha' J\ M) &= D\sqrt{\tfrac{2}{3}}\,(3M^2-J^2-J)\ \mathcal{Q}(0)+f(\alpha,\alpha',J)\,\mathcal{J}\\
(\alpha J M|\mathcal{H}|\alpha' J\text{-}1\ M\pm 2) &= \pm\tfrac{1}{2}E\sqrt{(J\mp M)(J\mp M-1)(J\mp M-2)(J\pm M+1)}\ \mathcal{Q}(\pm 2)\\
(\alpha J M|\mathcal{H}|\alpha' J\text{-}1\ M\pm 1) &= \tfrac{1}{2}E\,(J\pm 2M+1)\sqrt{(J\mp M)(J\mp M-1)}\ \mathcal{Q}(\pm 1)\\
(\alpha J M|\mathcal{H}|\alpha' J\text{-}1\ M) &= \sqrt{\tfrac{3}{2}}\,E\,M\sqrt{(J^2-M^2)}\ \mathcal{Q}(0)\\
(\alpha J M|\mathcal{H}|\alpha' J\text{-}2\ M\pm 2) &= \tfrac{1}{2}F\sqrt{(J\mp M)(J\mp M-1)(J\mp M-2)(J\mp M-3)}\ \mathcal{Q}(\pm 2)\\
(\alpha J M|\mathcal{H}|\alpha' J\text{-}2\ M\pm 1) &= \pm F\sqrt{(J^2-M^2)\{(J-1)^2-M^2\}}\ \mathcal{Q}(\pm 1)\\
(\alpha J M|\mathcal{H}|\alpha' J\text{-}2\ M) &= \sqrt{\tfrac{3}{2}}\,F\sqrt{(J^2-M^2)\{(J-1)^2-M^2\}}\ \mathcal{Q}(0).
\end{aligned}
\tag{5}
$$

The dyadics $\mathcal{Q}$ and $\mathcal{J}$ are defined in equations (16) of section II. The matrix elements for $J'-J=+1$ or $+2$ are obtained from these equations by replacing J with $J+1$ or $J+2$, and using the Hermitian character of the matrix $(\alpha J M|\mathcal{H}|\alpha' J' M')$. All other matrix elements vanish. The quantities D, E and F involved in the equations are functions of α, α' and J. Thus, for a given configuration, there are as many quantities D as there are levels.

The line strengths in pure Russell-Saunders coupling may then be found, in terms of the quantities D, E and F, by squaring the absolute values of these matrix elements (first dropping the spherically symmetric term $f(\alpha,\alpha',J)\,\mathcal{J}$), and summing over M and M. We have

$$
\begin{aligned}
S(\alpha J,\alpha' J) &= \tfrac{2}{3}J(J+1)(2J+1)(2J-1)(2J+3)\,D^2\\
S(\alpha J,\alpha' J\text{-}1) &= S(\alpha' J\text{-}1,\alpha J)=\tfrac{1}{2}J(J+1)(J-1)(2J+1)(2J-1)\,E^2\\
S(\alpha J,\alpha' J\text{-}2) &= S(\alpha' J\text{-}2,\alpha J)=J(J-1)(2J+1)(2J-1)(2J-3)\,F^2.
\end{aligned}
\tag{6}
$$

$S(\alpha J, \alpha' J + 1)$ and $S(\alpha J, \alpha' J + 2)$ can be obtained by replacing J by $J + 1$ or $J + 2$ in the appropriate formulae. All other line strengths vanish, in agreement with the selection rules (27) of section II.

As a consequence of equations (5) it is necessary to find the matrix elements for only one pair of values of M and M', for a given α, α', J, J'. The problem of evaluating the electric quadrupole line strengths may then be treated in the following steps:

(a) We first evaluate all the matrix elements $(nslm_sm_l|-e\mathbf{rr}|nslm_s'm_l')$ in the one-electron scheme of wave functions. Since $(-e\mathbf{rr})$ is independent of spin, the matrix is diagonal in the spin quantum number, and we have

$$(nslm_s m_l|-e\mathbf{rr}|nslm_s'm_l') = \delta(m_s,m_s')(nlm_l|-e\mathbf{rr}|nlm_l') \tag{7}$$

where, from equation (2) of section III,

$$(nlm|-e\mathbf{rr}|nlm') = -e\int_0^\infty\int_0^\pi\int_0^{2\pi} R^2(nl)\,\Theta(lm)\,\Theta(lm')\,\Phi^*(m)\,\Phi(m')\,\mathbf{rr}\sin^2\theta\, dr\, d\theta\, d\phi \tag{8}$$

and $\mathbf{r} = r\sin\theta\cos\phi\,\mathbf{i} + r\sin\theta\sin\phi\,\mathbf{j} + r\cos\phi\,\mathbf{k}$

The integration over ϕ and θ may be easily carried out, the latter with the aid of some recurrence relations in CS, § 4^4(21). Hence, if we define

$$S_2 = -e\int_0^\infty R^2(nl)\, r^2\, dr, \tag{9}$$

we obtain the formulae

$$\begin{aligned}(nlm|-e\mathbf{rr}|nlm) &= \frac{s_2}{(2l-1)(2l+3)}\left\{(l^2+l-1+m^2)(\mathbf{ii}+\mathbf{jj}) + (2l^2+2l-1-2m^2)\mathbf{kk}\right\} \\ &= \sqrt{\tfrac{2}{3}}\,\frac{l^2+l-3m^2}{(2l-1)(2l+3)}\,s_2\,\mathcal{Q}(0) + \tfrac{1}{3}s_2\,\mathcal{J}.\end{aligned} \tag{10}$$

$$(n\ell m|-e\mathbf{rr}|n\ell m\pm 1) = -\frac{(2m\pm 1)\sqrt{(\ell\mp m)(\ell\pm m+1)}}{(2\ell-1)(2\ell+3)}\, s_2\, \tilde{\mathcal{Q}}(\pm 1). \qquad (11)$$

$$(n\ell m|-e\mathbf{rr}|n\ell m\pm 2) = -\frac{\sqrt{(\ell\mp m)(\ell\mp m-1)(\ell\pm m+1)(\ell\pm m+2)}}{(2\ell-1)(2\ell+3)}\, s_2\, \tilde{\mathcal{Q}}(\pm 2). \qquad (12)$$

The matrix elements for $m' = m - 1$ and $m - 2$ follow, as before, from the elements for $m' = m + 1$ and $m + 2$, respectively, by use of the Hermitian character of the matrix. All other matrix elements vanish.

In what follows, we shall drop the spherically symmetric term $\frac{1}{3} s_2 \mathcal{Y}$, in accordance with our previous considerations.

(b) We next evaluate the matrix elements of $\mathcal{H}$ in the $\bar{\underline{\chi}}$ scheme of wave functions. This evaluation is greatly simplified by the following theorem, proved in CS, § 6[6]:

Theorem: If we denote the set of individual electron quantum numbers $n^k, \ell^k, m_s^k, m_\ell^k$ by a^k, then the matrix component $(A|F|B)$ in the $\bar{\underline{\chi}}$ scheme of the quantity

$$F = \sum_{i=1}^{n} f(i) \qquad (13)$$

(1) vanishes if B differs from A by more than one individual set;

(2) has the value

$$(A|F|B) = \pm(a^k|f|b^k) \qquad (14)$$

if all the individual sets in A agree with all those in B except that $a^k \neq b^k$. The sign is positive or negative according to the parity of the permutation which changes the conventional order of B into one in which sets in B which match those in A all stand at the same places in the lists;

(3) and, if B = A, the diagonal element is

$$(A|F|A) = \sum_{i=1}^{n} (a^i|\, f|a^i\,). \tag{15}$$

(c) The next step is the evaluation of the matrix elements $(S\ L\ J\ M|\tilde{\mathfrak{R}}|\,S'L'\,J'M')$ for all possible quantum numbers S, L, J, S′, L′, J′, and for any convenient pair of values of M and M′. In doing this we use the expressions for $\Psi\,(S\ L\ J\ M)$ in terms of $\underline{X}\,(n^1, l^1, m_s^1, m_\ell^1;\ n^2, l^2, m_s^2, m_\ell^2;\ \cdots)$ as developed in section III of this thesis.

(d) We then apply equations (5) to determine the quantities D, E and F from the matrix elements obtained in step (c). These values may then be substituted into equations (6) to obtain the line strengths for LS coupling.

(e) The final step is the introduction of the breakdown of pure Russell-Saunders coupling. This may be treated in the same manner as in the magnetic dipole case, section IV, step (b), with $(S_k L_k J \,\vdots\, 2S + L \,\vdots\, S_\ell L_\ell J')$ replaced by D, E or F, and $\mathbf{f}\,(J,J',M,M')$ replaced by a dyadic $\mathcal{F}$ dependent on the same quantum numbers. The result is evidently

$$S_q\,(\overline{S_i L_i J}, \overline{S_j L_j J'}) = \Big|\sum_{k\ell} a_{ik}^{*}\, a_{j\ell} \pm\sqrt{S_q\,(S_k L_k J, S_\ell L_\ell J')}\,\Big|^2. \tag{16}$$

Here we must be careful as to which signs we take for the square roots.

We shall clearly be consistent if we give to $\sqrt{S(S_k L_k J, S_\ell L_\ell J')}$ the same sign as is possessed by the quantity D, E or F which is present in the matrix element $(S_k L_k J M | \tilde{\pi} | S_\ell L_\ell J' M')$.

A further reduction of the problem of evaluating the electric quadrupole line strengths was made by Rubinowicz$^{8)}$. He developed some rather complicated formulae for the line strengths in LS coupling in terms of quantities G, H and I, which depend only on S, L, S′, L′, and not on J and J′. These formulae are given in CS, table 4^9. Use of them would effect a simplification of the calculations described above. For in step (c) it would then be necessary to evaluate only one matrix element $(S\ L\ J\ M | \tilde{\pi} | S' L' J' M')$ between each pair of terms S, L, and S′, L′, (or between the levels of one term), instead of one matrix element for each pair of levels S, L, J and S′, L′, J′. Step (d) would then yield only one line strength for each multiplet (a multiplet being the totality of lines joining the levels of one term to those of another, or the totality of lines connecting levels of the same term). Use of Rubinowicz's formulae would enable us to find the corresponding quantities G, H and I, from which all the other line strengths could be calculated by means of other formulae of the set.

However, it was decided not to use these formulae of Rubinowicz directly in the calculations, but to use them instead for checking the results of the calculations as obtained by use of steps (a) to (d) above. In view of the complications involved in the calculations, it was thought desirable to have as many checks as possible. Also, there is an ambiguity in the procedure described in CS, § 5^9, for obtaining the matrix quantities D, E and F from the quantities G, H and I. The statement that one should attach the sign given in the table to the positive square root of a certain quotient should be understood to imply the taking of a "formally positive" square root. That is, the signs in the formulae for D, E and F in terms of G, H and I are to be chosen independently of the signs which may later be introduced in the values of G, H and I, as well as in some of the bracketed expressions in the table.

As in the magnetic dipole case, it is necessary in a few cases to use wave functions of the second order of approximation. These cases are marked wherever they occur. There was no attempt to retain all terms of the second order, except, as before, in the normalization constants a_{iL}.

B. Electric Quadrupole Line Strengths for the Configurations p^2, p^3, p^4 and d^2.

The procedure described above has been applied to the p^2, p^3, p^4 and d^2 configurations, with results as given in the tables below. In the tables of matrix elements only those matrix elements which occur on the principal diagonal, or to the right of the principal diagonal, were listed, since the other elements may be obtained by use of the Hermitian character of the matrices. Except for this feature, blank spaces in the tables indicate that the corresponding matrix elements (or line strengths) vanish. In cases where it is necessary to break up the matrix into sections in order to accomodate them on the pages, the matrix elements between states occurring in different sections vanish, unless otherwise stated.

In the p^2 and p^3 configurations all of the matrix elements of $\tilde{\pi}$ in the S L J M scheme were computed, although, as was indicated in step (c), only a fraction of these were necessary. In the case of the d^2 configuration, the matrix elements $(S\ L\ J\ M|\tilde{\pi}|S'L'J'M')$ were computed for at least two sets of values of M and M′, for each pair of levels S L J and S′L′J′. This was done in order to provide further check in the calculations.

In order to save space, the matrix elements $(A|\tilde{\pi}|B)$, in the zero-order scheme of wave functions, were tabulated for the p^2 configuration only. In the tables of line strengths in LS coupling, the sign of the D, E or F corresponding to each line strength is indicated by the addition of (+) or (−) after the value of the line strength.

Case 1. p^2 Configuration

Let $(n1m|-e\mathbf{r}|n1m') \equiv \alpha_{mm'} = \alpha^*_{m'm}$.

Then

$$\alpha_{11} = \alpha_{-1-1} = -\frac{s_2}{5}\sqrt{\tfrac{2}{3}}\,\tilde{\mathcal{R}}(0) + \tfrac{1}{3}s_2\,\mathcal{Y}$$

$$\alpha_{00} = \frac{2s_2}{5}\sqrt{\tfrac{2}{3}}\,\tilde{\mathcal{R}}(0) + \tfrac{1}{3}s_2\,\mathcal{Y}$$

$$\alpha_{10} = -\alpha_{0-1} = -\sqrt{2}\,\frac{s_2}{5}\,\tilde{\mathcal{R}}(-1)$$

$$\alpha_{01} = -\alpha_{-10} = -\sqrt{2}\,\frac{s_2}{5}\,\tilde{\mathcal{R}}(+1)$$

$$\alpha_{1-1} = -\frac{2s_2}{5}\,\tilde{\mathcal{R}}(-2)$$

$$\alpha_{-11} = -\frac{2s_2}{5}\,\tilde{\mathcal{R}}(+2)$$

p^2 Configuration

Table 7(a). Matrix Elements in the $\bar{\lambda}$ Scheme $(A|\mathcal{H}|B)$

	A	B	C	D	E	F	Q	R	S	G	H	I	M	N	P
A	$2\alpha_{11}$	α_{10}	$-\alpha_{10}$	α_{1-1}	$-\alpha_{1-1}$	0	0	0	0						
B		$\alpha_{11}+\alpha_{00}$	0	α_{0-1}	0	α_{10}	0	$-\alpha_{1-1}$	0						
C			$\alpha_{11}+\alpha_{00}$	0	α_{0-1}	$-\alpha_{10}$	$-\alpha_{1-1}$	0	0						
D				$\alpha_{11}+\alpha_{-1-1}$	0	0	α_{10}	0	α_{1-1}						
E					$\alpha_{11}+\alpha_{-1-1}$	0	0	α_{10}	$-\alpha_{1-1}$						
F						$2\alpha_{00}$	α_{0-1}	$-\alpha_{0-1}$	0						
Q			Complex Conjugates				$\alpha_{00}+\alpha_{-1-1}$	0	α_{0-1}						
R								$\alpha_{00}+\alpha_{-1-1}$	$-\alpha_{0-1}$						
S									$2\alpha_{-1-1}$						
G										$\alpha_{11}+\alpha_{00}$	α_{0-1}	$-\alpha_{1-1}$			
H											$\alpha_{11}+\alpha_{-1-1}$	α_{10}			
I												$\alpha_{00}+\alpha_{-1-1}$			
M													$\alpha_{11}+\alpha_{00}$	α_{0-1}	$-\alpha_{1-1}$
N														$\alpha_{11}+\alpha_{-1-1}$	α_{10}
P															$\alpha_{00}+\alpha_{-1-1}$

p^2 Configuration

Table 7(b). Matrix Elements in LS Coupling $(SLJM|\tilde{\pi}|S'L'J'M')$

	${}^1D_2^2$	${}^1D_2^1$	${}^1D_2^0$	${}^1D_2^{-1}$	${}^1D_2^{-2}$	${}^1S_0^0$
${}^1D_2^2$	$-\frac{2}{3}\sqrt{\frac{2}{3}}s_2\,\hat{\mathcal{A}}(0)$	$-\frac{2}{5}s_2\,\hat{\mathcal{A}}(-1)$	$-\frac{2}{5}\sqrt{\frac{2}{3}}s_2\,\hat{\mathcal{A}}(-2)$			$-\frac{4s_2}{5\sqrt{3}}\hat{\mathcal{A}}(-2)$
${}^1D_2^1$		$\frac{1}{5}\sqrt{\frac{2}{3}}s_2\,\hat{\mathcal{A}}(0)$	$-\frac{1}{5}\sqrt{\frac{2}{3}}s_2\,\hat{\mathcal{A}}(-1)$	$-\frac{1}{5}\sqrt{\frac{2}{3}}s_2\,\hat{\mathcal{A}}(-2)$		$\frac{4s_2}{5\sqrt{3}}\hat{\mathcal{A}}(-1)$
${}^1D_2^0$			$\frac{2}{5}\sqrt{\frac{2}{3}}s_2\,\hat{\mathcal{A}}(0)$	$\frac{1}{5}\sqrt{\frac{2}{3}}s_2\,\hat{\mathcal{A}}(-1)$	$-\frac{2}{5}\sqrt{\frac{2}{3}}s_2\,\hat{\mathcal{A}}(-2)$	$\frac{-4s_2}{5\sqrt{3}}\hat{\mathcal{A}}(0)$
${}^1D_2^{-1}$	Complex Conjugates			$\frac{1}{5}\sqrt{\frac{2}{3}}s_2\,\hat{\mathcal{A}}(0)$	$\frac{2}{5}s_2\,\hat{\mathcal{A}}(-1)$	$\frac{-4s_2}{5\sqrt{3}}\hat{\mathcal{A}}(1)$
${}^1D_2^{-2}$					$-\frac{2}{5}\sqrt{\frac{2}{3}}s_2\,\hat{\mathcal{A}}(0)$	$\frac{-4s_2}{5\sqrt{3}}\hat{\mathcal{A}}(2)$
${}^1S_0^0$						0

	${}^3P_2^2$	${}^3P_2^1$	${}^3P_2^0$	${}^3P_2^{-1}$	${}^3P_2^{-2}$	${}^3P_1^1$	${}^3P_1^0$	${}^3P_1^{-1}$	${}^3P_0^0$
${}^3P_2^2$	$\frac{2s_2}{5\sqrt{6}}\hat{\mathcal{A}}(0)$	$\frac{s_2}{5}\hat{\mathcal{A}}(-1)$	$\frac{2s_2}{5\sqrt{6}}\hat{\mathcal{A}}(-2)$	0	0	$\frac{s_2}{5}\hat{\mathcal{A}}(-1)$	$\frac{2s_2}{5\sqrt{2}}\hat{\mathcal{A}}(-2)$	0	$\frac{2s_2}{5\sqrt{3}}\hat{\mathcal{A}}(-2)$
${}^3P_2^1$		$\frac{-s_2}{5\sqrt{6}}\hat{\mathcal{A}}(0)$	$\frac{s_2}{5\sqrt{6}}\hat{\mathcal{A}}(-1)$	$\frac{s_2}{5}\hat{\mathcal{A}}(-2)$	0	$\frac{-3s_2}{5\sqrt{6}}\hat{\mathcal{A}}(0)$	$\frac{-s_2}{5\sqrt{2}}\hat{\mathcal{A}}(-1)$	$\frac{s_2}{5}\hat{\mathcal{A}}(-2)$	$\frac{-2s_2}{5\sqrt{3}}\hat{\mathcal{A}}(-1)$
${}^3P_2^0$			$\frac{-2s_2}{5\sqrt{6}}\hat{\mathcal{A}}(0)$	$\frac{-s_2}{5\sqrt{6}}\hat{\mathcal{A}}(-1)$	$\frac{2s_2}{5\sqrt{6}}\hat{\mathcal{A}}(-2)$	$\frac{-3s_2}{5\sqrt{6}}\hat{\mathcal{A}}(1)$	0	$\frac{-3s_2}{5\sqrt{6}}\hat{\mathcal{A}}(-1)$	$\frac{2s_2}{5\sqrt{3}}\hat{\mathcal{A}}(0)$
${}^3P_2^{-1}$				$-\frac{s_2}{5\sqrt{6}}\hat{\mathcal{A}}(0)$	$-\frac{s_2}{5}\hat{\mathcal{A}}(-1)$	$-\frac{s_2}{5}\hat{\mathcal{A}}(2)$	$\frac{-s_2}{5\sqrt{2}}\hat{\mathcal{A}}(1)$	$\frac{3s_2}{5\sqrt{6}}\hat{\mathcal{A}}(0)$	$\frac{2s_2}{5\sqrt{3}}\hat{\mathcal{A}}(1)$
${}^3P_2^{-2}$					$\frac{2s_2}{5\sqrt{6}}\hat{\mathcal{A}}(0)$	0	$\frac{-2s_2}{5\sqrt{2}}\hat{\mathcal{A}}(2)$	$\frac{s_2}{5}\hat{\mathcal{A}}(1)$	$\frac{2s_2}{5\sqrt{3}}\hat{\mathcal{A}}(2)$
${}^3P_1^1$	Complex Conjugates					$\frac{-s_2}{5\sqrt{6}}\hat{\mathcal{A}}(0)$	$\frac{-s_2}{5\sqrt{2}}\hat{\mathcal{A}}(-1)$	$\frac{-s_2}{5}\hat{\mathcal{A}}(-2)$	0
${}^3P_1^0$							$\frac{2s_2}{5\sqrt{6}}\hat{\mathcal{A}}(0)$	$\frac{s_2}{5\sqrt{2}}\hat{\mathcal{A}}(-1)$	0
${}^3P_1^{-1}$								$-\frac{s_2}{5\sqrt{6}}\hat{\mathcal{A}}(0)$	0
${}^3P_0^0$									0

p^2 Configuration

Table 7(c). The Quantities D,E,F and G,H,I

$$D(D_2, D_2) = -\frac{1}{15}\, s_2 \qquad G(D, D) = -\frac{1}{30}\, s_2$$

$$D(S_0, S_0) = 0 \qquad G(S, S) = 0$$

$$F(D_2, S_0) = -\frac{2\sqrt{2}}{15}\, s_2 \qquad I(D, S) = -\frac{1}{15\sqrt{2}}\, s_2$$

$$\left.\begin{array}{l} D({}^3P_2, {}^3P_2) = \frac{1}{30}\, s_2 \\ D({}^3P_1, {}^3P_1) = -\frac{1}{10}\, s_2 \\ E({}^3P_2, {}^3P_1) = -\frac{1}{5\sqrt{3}}\, s_2 \\ F({}^3P_2, {}^3P_0) = \frac{\sqrt{2}}{15}\, s_2 \end{array}\right\} \quad G({}^3P, {}^3P) = \frac{1}{10}\, s_2$$

Table 7(d). Line Strengths in LS Coupling S(SLJ, SL'J')

	${}^1D_2$	${}^3P_2$	${}^3P_1$	${}^3P_0$	${}^1S_0$
${}^1D_2$	$\frac{28}{15} s_2^2 (-)$				$\frac{16}{15} s_2^2 (-)$
${}^3P_2$		$\frac{7}{15} s_2^2 (+)$	$\frac{3}{5} s_2^2 (-)$	$\frac{4}{15} s_2^2 (-)$	
${}^3P_1$		$\frac{3}{5} s_2^2 (-)$	$\frac{1}{5} s_2^2 (-)$	0	
${}^3P_0$		$\frac{4}{15} s_2^2 (-)$	0	0	
${}^1S_0$	$\frac{16}{15} s_2^2 (-)$				0

p^2 Configuration

Table 7(e). Line Strengths for the Perturbed System $S(\overline{SLJ}, \overline{S'L'J'})$

	${}^1\overline{D}_2$	${}^3\overline{P}_2$	${}^3\overline{P}_1$	${}^3\overline{P}_0$	${}^1\overline{S}_0$
${}^1\overline{D}_2$		$\frac{21}{5}\alpha^2 b^2 s_2^2$	$\frac{3}{5}b^2 s_2^2$	$\frac{4}{15}(2\alpha d+\gamma b)^2 s_2^2$	$\frac{4}{15}(2\alpha\gamma-bd)^2 s_2^2$
${}^3\overline{P}_2$	$\frac{21}{5}\alpha^2 b^2 s_2^2$		$\frac{3}{5}\alpha^2 s_2^2$	$\frac{4}{15}(\alpha\gamma-2bd)^2 s_2^2$	$\frac{4}{15}(2\gamma b+\alpha d)^2 s_2^2$
${}^3\overline{P}_1$	$\frac{3}{5}b^2 s_2^2$	$\frac{3}{5}\alpha^2 s_2^2$		0	0
${}^3\overline{P}_0$	$\frac{4}{15}(2\alpha d+\gamma b)^2 s_2^2$	$\frac{4}{15}(\alpha\gamma-2bd)^2 s_2^2$	0		0
${}^1\overline{S}_0$	$\frac{4}{15}(2\alpha\gamma-bd)^2 s_2^2$	$\frac{4}{15}(2\gamma b+\alpha d)^2 s_2^2$	0	0	

Case 2. p^3 Configuration

The expressions α_{mn} which were evaluated in case (1) occur here also.

Table 8(a)

Matrix Elements in the Pure Russell-Saunders Scheme $(SLJM|\tilde{\mathcal{R}}|S'L'J'M')$

	$^2P_{1\frac{1}{2}}^{1\frac{1}{2}}$	$^2P_{1\frac{1}{2}}^{\frac{1}{2}}$	$^2P_{1\frac{1}{2}}^{-\frac{1}{2}}$	$^2P_{1\frac{1}{2}}^{-1\frac{1}{2}}$	$^2P_{\frac{1}{2}}^{\frac{1}{2}}$	$^2P_{\frac{1}{2}}^{-\frac{1}{2}}$
$^2D_{2\frac{1}{2}}^{2\frac{1}{2}}$	$-\frac{2}{5}s_2\tilde{\mathcal{R}}(-1)$	$\frac{-4s_2}{5\sqrt{3}}\tilde{\mathcal{R}}(-2)$	0	0	$\frac{-2\sqrt{2}}{5\sqrt{3}}s_2\tilde{\mathcal{R}}(-2)$	0
$^2D_{2\frac{1}{2}}^{1\frac{1}{2}}$	$\frac{2\sqrt{6}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(0)$	$\frac{2s_2}{5\sqrt{15}}\tilde{\mathcal{R}}(-1)$	$\frac{-8s_2}{5\sqrt{15}}\tilde{\mathcal{R}}(-2)$	0	$\frac{4\sqrt{2}}{5\sqrt{15}}s_2\tilde{\mathcal{R}}(-1)$	$\frac{-2\sqrt{2}}{5\sqrt{15}}s_2\tilde{\mathcal{R}}(-2)$
$^2D_{2\frac{1}{2}}^{\frac{1}{2}}$	$\frac{3\sqrt{2}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(1)$	$\frac{2s_2}{5\sqrt{5}}\tilde{\mathcal{R}}(0)$	$\frac{\sqrt{2}s_2}{\sqrt{15}}\tilde{\mathcal{R}}(-1)$	$-\frac{2\sqrt{2}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(-2)$	$-\frac{2\sqrt{2}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(0)$	$\frac{4s_2}{5\sqrt{15}}\tilde{\mathcal{R}}(-1)$
$^2D_{2\frac{1}{2}}^{-\frac{1}{2}}$	$\frac{2\sqrt{2}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(2)$	$\frac{\sqrt{2}s_2}{\sqrt{15}}\tilde{\mathcal{R}}(1)$	$\frac{-2s_2}{5\sqrt{5}}\tilde{\mathcal{R}}(0)$	$\frac{3\sqrt{2}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(-1)$	$-\frac{4s_2}{5\sqrt{15}}\tilde{\mathcal{R}}(1)$	$-\frac{2\sqrt{2}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(0)$
$^2D_{2\frac{1}{2}}^{-1\frac{1}{2}}$	0	$\frac{8s_2}{5\sqrt{15}}\tilde{\mathcal{R}}(2)$	$\frac{2s_2}{5\sqrt{15}}\tilde{\mathcal{R}}(1)$	$-\frac{2\sqrt{6}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(0)$	$-\frac{2\sqrt{2}}{5\sqrt{15}}s_2\tilde{\mathcal{R}}(2)$	$-\frac{4\sqrt{2}}{5\sqrt{15}}s_2\tilde{\mathcal{R}}(1)$
$^2D_{2\frac{1}{2}}^{-2\frac{1}{2}}$	0	0	$\frac{4s_2}{5\sqrt{3}}\tilde{\mathcal{R}}(2)$	$-\frac{2}{5}s_2\tilde{\mathcal{R}}(1)$	0	$-\frac{2\sqrt{2}}{5\sqrt{3}}s_2\tilde{\mathcal{R}}(2)$
$^2D_{1\frac{1}{2}}^{1\frac{1}{2}}$	$\frac{\sqrt{6}s_2}{5\sqrt{5}}\tilde{\mathcal{R}}(0)$	$\frac{2\sqrt{3}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(-1)$	$\frac{2\sqrt{3}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(-2)$	0	$\frac{-\sqrt{6}s_2}{5\sqrt{5}}\tilde{\mathcal{R}}(-1)$	$\frac{-2\sqrt{6}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(-2)$
$^2D_{1\frac{1}{2}}^{\frac{1}{2}}$	$\frac{2\sqrt{3}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(1)$	$\frac{-\sqrt{6}s_2}{5\sqrt{5}}\tilde{\mathcal{R}}(0)$	0	$\frac{2\sqrt{3}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(-2)$	$\frac{2\sqrt{3}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(0)$	$\frac{3\sqrt{2}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(-1)$
$^2D_{1\frac{1}{2}}^{-\frac{1}{2}}$	$\frac{2\sqrt{3}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(2)$	0	$\frac{-\sqrt{6}s_2}{5\sqrt{5}}\tilde{\mathcal{R}}(0)$	$\frac{-2\sqrt{3}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(-1)$	$\frac{3\sqrt{2}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(1)$	$\frac{-2\sqrt{3}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(0)$
$^2D_{1\frac{1}{2}}^{-1\frac{1}{2}}$	0	$\frac{2\sqrt{3}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(2)$	$\frac{-2\sqrt{3}}{5\sqrt{5}}\tilde{\mathcal{R}}(1)$	$\frac{\sqrt{6}s_2}{5\sqrt{5}}\tilde{\mathcal{R}}(0)$	$\frac{2\sqrt{6}}{5\sqrt{5}}s_2\tilde{\mathcal{R}}(2)$	$\frac{-\sqrt{6}s_2}{5\sqrt{5}}\tilde{\mathcal{R}}(1)$

All the other matrix elements vanish, except for the elements $(^2P_J^M|\tilde{\mathcal{R}}|^2D_{J'}^{M'})$, which are the complex conjugates of $(^2D_{J'}^{M'}|\tilde{\mathcal{R}}|^2P_J^M)$.

p^3 Configuration

Table 8(b). The Quantities D,E,F, and G,H,I.

$$\left.\begin{aligned} E({}^2D_{2\frac{1}{2}},\ {}^2P_{1\frac{1}{2}}) &= \frac{4s_2}{15\sqrt{5}} \\ F({}^2D_{2\frac{1}{2}},\ {}^2P_{\frac{1}{2}}) &= -\frac{2s_2}{15\sqrt{5}} \\ D({}^2D_{1\frac{1}{2}},\ {}^2P_{1\frac{1}{2}}) &= \frac{s_2}{5\sqrt{5}} \\ E({}^2D_{1\frac{1}{2}},\ {}^2P_{\frac{1}{2}}) &= \frac{4s_2}{5\sqrt{5}} \end{aligned}\right\} \qquad I({}^2D,\ {}^2P) = \frac{s_2}{10\sqrt{3}}$$

Table 8(c). Line Strengths in Pure Russell-Saunders Coupling S(SLJ,SL'J')

	${}^2D_{2\frac{1}{2}}$	${}^2D_{1\frac{1}{2}}$	${}^4S_{1\frac{1}{2}}$	${}^2P_{1\frac{1}{2}}$	${}^2P_{\frac{1}{2}}$
${}^2D_{2\frac{1}{2}}$				$\frac{56}{25}s_2^2(+)$	$\frac{16}{25}s_2^2(-)$
${}^2D_{1\frac{1}{2}}$				$\frac{24}{25}s_2^2(+)$	$\frac{24}{25}s_2^2(+)$
${}^4S_{1\frac{1}{2}}$					
${}^2P_{1\frac{1}{2}}$	$\frac{56}{25}s_2^2(+)$	$\frac{24}{25}s_2^2(+)$			
${}^2P_{\frac{1}{2}}$	$\frac{16}{25}s_2^2(-)$	$\frac{24}{25}s_2^2(+)$			

p^3 Configuration

Table 8(d). Perturbed System Line Strengths $S(\overline{SLJ}, \overline{S'L'J'})$

	${}^2\overline{D}_{2\frac{1}{2}}$	${}^2\overline{D}_{1\frac{1}{2}}$	${}^4\overline{S}_{1\frac{1}{2}}$	${}^2\overline{P}_{1\frac{1}{2}}$	${}^2\overline{P}_{\frac{1}{2}}$
${}^2\overline{D}_{2\frac{1}{2}}$		$\frac{56}{25}a^2s_2^2$	$\frac{56}{25}b^2s_2^2$	$\frac{56}{25}\gamma^2s_2^2$	$\frac{16}{25}s_2^2$
${}^2\overline{D}_{1\frac{1}{2}}$	$\frac{56}{25}a^2s_2^2$		$\frac{24}{25}\alpha^2b^2s_2^2$	$\frac{24}{25}\alpha^2\gamma^2s_2^2$	$\frac{24}{25}\alpha^2s_2^2$
${}^4\overline{S}_{1\frac{1}{2}}$	$\frac{56}{25}b^2s_2^2$	$\frac{24}{25}\alpha^2b^2s_2^2$		$\frac{24}{25}(\gamma v-ab)^2s_2^2$	$\frac{24}{25}v^2s_2^2$
${}^2\overline{P}_{1\frac{1}{2}}$	$\frac{56}{25}\gamma^2s_2^2$	$\frac{24}{25}\alpha^2\gamma^2s_2^2$	$\frac{24}{25}(\gamma v-ab)^2s_2^2$ *		$\frac{24}{25}a^2s_2^2$
${}^2\overline{P}_{\frac{1}{2}}$	$\frac{16}{25}s_2^2$	$\frac{24}{25}\alpha^2s_2^2$	$\frac{24}{25}v^2s_2^2$ *	$\frac{24}{25}a^2s_2^2$	

* These are second order line strengths $S({}^4\overline{\overline{S}}_{1\frac{1}{2}}, {}^2\overline{\overline{P}}_{1\frac{1}{2}})$, etc.

Case (3). p^4 Configuration

The line strengths for the p^4 configuration have the same form as those for the p^2 configuration.

Case (4). d^2 Configuration

Let

$$(n\,2\,m|-e\mathbf{rr}|\,n\,2\,m') \equiv \beta_{mm'} = \beta^*_{m'm}$$

Then

$$\beta_{22} = \beta_{-2-2} = -\frac{2}{7}\sqrt{\frac{2}{3}}\,s_2\,\mathcal{Q}(0)$$

$$\beta_{11} = \beta_{-1-1} = \frac{1}{7}\sqrt{\frac{2}{3}}\,s_2\,\mathcal{Q}(0)$$

$$\beta_{00} = \frac{2}{7}\sqrt{\frac{2}{3}}\,s_2\,\mathcal{Q}(0)$$

$$\beta_{12} = -\beta_{-2-1} = -\frac{2}{7}\,s_2\,\mathcal{Q}(1) \qquad \beta_{21} = -\beta_{-1-2} = -\frac{2}{7}\,s_2\,\mathcal{Q}(-1)$$

$$\beta_{01} = -\beta_{-10} = -\frac{1}{7}\sqrt{\frac{2}{3}}\,s_2\,\mathcal{Q}(1) \qquad \beta_{10} = -\beta_{0-1} = -\frac{1}{7}\sqrt{\frac{2}{3}}\,s_2\,\mathcal{Q}(-1)$$

$$\beta_{02} = \beta_{-20} = -\frac{2}{7}\sqrt{\frac{2}{3}}\,s_2\,\mathcal{Q}(2) \qquad \beta_{20} = \beta_{0-2} = -\frac{2}{7}\sqrt{\frac{2}{3}}\,s_2\,\mathcal{Q}(-2)$$

$$\beta_{-11} = -\frac{2}{7}\,s_2\,\mathcal{Q}(2) \qquad \beta_{1-1} = -\frac{2}{7}\,s_2\,\mathcal{Q}(-2)$$

d^2 Configuration

Table 9(a).

Matrix Elements in the Pure Russell-Saunders Scheme $(SLJM|\tilde{\mathcal{H}}|S'L'J'M')$

$({}^1S_0^0\ |\tilde{\mathcal{H}}|\ {}^1S_0^0) = 0$

$({}^3P_0^0\ |\tilde{\mathcal{H}}|\ {}^3P_0^0) = 0$

$({}^1D_2^2\ |\tilde{\mathcal{H}}|\ {}^1D_2^2) = \frac{6}{49}\sqrt{\frac{2}{3}}\, s_2\, \hat{\mathcal{Q}}(0)$

$({}^1G_4^4\ |\tilde{\mathcal{H}}|\ {}^1G_4^4) = -\frac{4}{7}\sqrt{\frac{2}{3}}\, s_2\, \hat{\mathcal{Q}}(0)$

$({}^1D_2^2\ |\tilde{\mathcal{H}}|\ {}^1S_0^0) = -\frac{4}{105}\, s_2\, \hat{\mathcal{Q}}(-2)$

$({}^1G_4^4\ |\tilde{\mathcal{H}}|\ {}^1D_2^2) = -\frac{8}{7\sqrt{21}}\, \hat{\mathcal{Q}}(-2)$

$({}^3P_2^2\ |\tilde{\mathcal{H}}|\ {}^3P_2^2) = \frac{1}{5}\sqrt{\frac{2}{3}}\, \hat{\mathcal{Q}}(0)$

$({}^3P_1^1\ |\tilde{\mathcal{H}}|\ {}^3P_1^1) = -\frac{1}{10}\sqrt{\frac{2}{3}}\, \hat{\mathcal{Q}}(0)$

$({}^3F_4^4\ |\tilde{\mathcal{H}}|\ {}^3F_4^4) = -\frac{1}{7}\sqrt{\frac{2}{3}}\, \hat{\mathcal{Q}}(0)$

$({}^3F_3^3\ |\tilde{\mathcal{H}}|\ {}^3F_3^3) = -\frac{3}{28}\sqrt{\frac{2}{3}}\, \hat{\mathcal{Q}}(0)$

$({}^3F_2^2\ |\tilde{\mathcal{H}}|\ {}^3F_2^2) = -\frac{24}{245}\sqrt{\frac{2}{3}}\, \hat{\mathcal{Q}}(0)$

$({}^3P_2^2\ |\tilde{\mathcal{H}}|\ {}^3P_1^1) = \frac{1}{5}\, s_2\, \hat{\mathcal{Q}}(-1)$

$({}^3P_2^2\ |\tilde{\mathcal{H}}|\ {}^3P_0^0) = \frac{2}{5\sqrt{3}}\, s_2\, \hat{\mathcal{Q}}(-2)$

$({}^3F_4^4\ |\tilde{\mathcal{H}}|\ {}^3F_3^3) = -\frac{1}{14}\sqrt{\frac{2}{3}}\, s_2\, \hat{\mathcal{Q}}(-1)$

$({}^3F_4^4\ |\tilde{\mathcal{H}}|\ {}^3F_2^2) = \frac{2}{21\sqrt{35}}\, s_2\, \hat{\mathcal{Q}}(-2)$

$({}^3F_3^3\ |\tilde{\mathcal{H}}|\ {}^3F_2^2) = \frac{-3\sqrt{2}}{7\sqrt{105}}\, s_2\, \hat{\mathcal{Q}}(-1)$

$({}^3F_4^4\ |\tilde{\mathcal{H}}|\ {}^3P_2^2) = -\frac{4\sqrt{2}}{7\sqrt{5}}\, s_2\, \hat{\mathcal{Q}}(-2)$

$({}^3F_3^3\ |\tilde{\mathcal{H}}|\ {}^3P_2^2) = \frac{4}{7\sqrt{15}}\, s_2\, \hat{\mathcal{Q}}(-1)$

$({}^3F_3^3\ |\tilde{\mathcal{H}}|\ {}^3P_1^1) = \frac{-8}{7\sqrt{15}}\, s_2\, \hat{\mathcal{Q}}(-2)$

$({}^3F_2^2\ |\tilde{\mathcal{H}}|\ {}^3P_2^2) = \frac{-8}{35\sqrt{21}}\, s_2\, \hat{\mathcal{Q}}(0)$

$({}^3F_2^2\ |\tilde{\mathcal{H}}|\ {}^3P_1^1) = \frac{4\sqrt{2}}{15\sqrt{7}}\, s_2\, \hat{\mathcal{Q}}(-1)$

$({}^3F_2^2\ |\tilde{\mathcal{H}}|\ {}^3P_0^0) = -\frac{4\sqrt{2}}{5\sqrt{21}}\, s_2\, \hat{\mathcal{Q}}(-2)$

Table 9(b). The Quantities D,E,F, and G,H,I.

$D({}^1S_0, {}^1S_0) = 0$

$D({}^1D_2, {}^1D_2) = \frac{1}{49} s_2 \qquad G({}^1D, {}^1D) = \frac{1}{98} s_2$

$D({}^1G_4, {}^1G_4) = -\frac{1}{49} s_2 \qquad G({}^1G, {}^1G) = -\frac{1}{98} s_2$

$$\left.\begin{array}{l} D({}^3P_2, {}^3P_2) = \frac{1}{30} s_2 \\ D({}^3P_1, {}^3P_1) = -\frac{1}{10} s_2 \\ D({}^3P_0, {}^3P_0) = 0 \\ E({}^3P_2, {}^3P_1) = -\frac{1}{5\sqrt{3}} s_2 \\ F({}^3P_2, {}^3P_0) = \frac{\sqrt{2}}{15} s_2 \\ E({}^3P_1, {}^3P_0) = 0 \end{array}\right\} \qquad G({}^3P, {}^3P) = \frac{1}{10} s_2$$

d^2 Configuration

Table 9(b). The Quantities D,E,F, and G,H,I. (continued)

$D(^3F_4, ^3F_4) = -\frac{1}{196} s_2$

$D(^3F_3, ^3F_3) = -\frac{1}{140} s_2$

$D(^3F_2, ^3F_2) = -\frac{4}{245} s_2$

$E(^3F_4, ^3F_3) = \frac{1}{42\sqrt{21}} s_2$

$F(^3F_4, ^3F_2) = -\frac{1}{735\sqrt{3}} s_2$

$E(^3F_3, ^3F_2) = \frac{1}{35\sqrt{7}} s_2$

$G(^3F, ^3F) = -\frac{1}{210} s_2$

$F(^1D_2, ^1S_0) = -\frac{2\sqrt{2}}{3\sqrt{35}} s_2$ $\qquad I(^1D, ^1S) = -\frac{1}{3\sqrt{70}} s_2$

$F(^1G_4, ^1D_2) = \frac{-4}{147\sqrt{5}} s_2$ $\qquad I(^1G, ^1D) = -\frac{1}{147\sqrt{5}} s_2$

$F(^3F_4, ^3P_2) = \frac{-2\sqrt{2}}{35\sqrt{21}} s_2$

$E(^3F_3, ^3P_2) = \frac{-2\sqrt{2}}{105} s_2$

$F(^3F_3, ^3P_1) = \frac{-4\sqrt{2}}{105\sqrt{3}} s_2$

$D(^3F_2, ^3P_2) = \frac{-2\sqrt{2}}{105\sqrt{7}} s_2$

$E(^3F_2, ^3P_1) = \frac{-4\sqrt{2}}{15\sqrt{21}} s_2$

$F(^3F_2, ^3P_0) = -\frac{4}{15\sqrt{7}} s_2$

$I(^3F, ^3P) = -\frac{1}{105} s_2$

Table 9(c). Line Strengths in LS Coupling $S(SLJ, SL'J')$

	$^1G_4$	$^3F_4$	$^3F_3$	$^3F_2$	$^1D_2$	$^3P_2$	$^3P_1$	$^3P_0$	$^1S_0$
$^1G_4$	$\frac{1320}{343} s_2^2 (-)$				$\frac{192}{343} s_2^2 (-)$				
$^3F_4$		$\frac{165}{686} s_2^2 (-)$	$\frac{5}{98} s_2^2 (+)$	$\frac{4}{1715} s_2^2 (-)$		$\frac{288}{245} s_2^2 (-)$	0	0	
$^3F_3$		$\frac{5}{98} s_2^2 (+)$	$\frac{9}{10} s_2^2 (-)$	$\frac{12}{245} s_2^2 (+)$		$\frac{32}{105} s_2^2 (-)$	$\frac{64}{105} s_2^2 (-)$	0	
$^3F_2$		$\frac{4}{1715} s_2^2 (-)$	$\frac{12}{245} s_2^2 (+)$	$\frac{192}{1715} s_2^2 (-)$		$\frac{32}{735} s_2^2 (-)$	$\frac{32}{105} s_2^2 (-)$	$\frac{32}{105} s_2^2 (-)$	
$^1D_2$	$\frac{192}{343} s_2^2 (-)$				$\frac{60}{343} s_2^2 (+)$				$\frac{16}{21} s_2^2 (-)$
$^3P_2$		$\frac{288}{245} s_2^2 (-)$	$\frac{32}{105} s_2^2 (-)$	$\frac{32}{735} s_2^2 (-)$		$\frac{7}{15} s_2^2 (+)$	$\frac{3}{5} s_2^2 (-)$	$\frac{4}{15} s_2^2 (+)$	
$^3P_1$		0	$\frac{64}{105} s_2^2 (-)$	$\frac{32}{105} s_2^2 (-)$		$\frac{3}{5} s_2^2 (-)$	$\frac{1}{5} s_2^2 (-)$	0	
$^3P_0$		0	0	$\frac{32}{105} s_2^2 (-)$		$\frac{4}{15} s_2^2 (+)$	0	0	
$^1S_0$					$\frac{16}{21} s_2^2 (-)$				0

d^2 Configuration

Table 9(d). Perturbed System Line Strengths $S(\overline{SLJ}, \overline{S'L'J'})$

	$^1\overline{G}_4$	$^3\overline{F}_4$	$^3\overline{F}_3$	$^3\overline{F}_2$	$^1\overline{D}_2$
$^1\overline{G}_4$		$\frac{1485}{686}\alpha^2 b^2 s_2^2$	$\frac{5}{98} b^2 s_2^2$	$\frac{4}{1715}(\gamma b - 4\sqrt{15}\alpha f)^2 s_2^2$	$\frac{192}{343}\left(\alpha\delta - \sqrt{\frac{21}{10}} bk - \frac{bf}{\sqrt{240}}\right)^2 s_2^2$
$^3\overline{F}_4$	$\frac{1485}{686}\alpha^2 b^2 s_2^2$		$\frac{5}{98}\alpha^2 s_2^2$	$\frac{4}{1715}(\alpha\gamma - 4\sqrt{15} bf)^2 s_2^2$	$\frac{192}{343}\left(b\delta - \sqrt{\frac{21}{10}}\alpha k - \frac{\alpha f}{\sqrt{240}}\right)^2 s_2^2$
$^3\overline{F}_3$	$\frac{5}{98} b^2 s_2^2$	$\frac{5}{98}\alpha^2 s_2^2$		$\frac{12}{245}\gamma^2 s_2^2$	$\frac{32}{105}\left(k + \frac{3f}{2\sqrt{14}}\right)^2 s_2^2$
$^3\overline{F}_2$	$\frac{4}{1715}(\gamma b - 4\sqrt{15}\alpha f)^2 s_2^2$	$\frac{4}{1715}(\alpha\gamma - 4\sqrt{15} bf)^2 s_2^2$	$\frac{12}{245}\gamma^2 s_2^2$		$\frac{60}{343}\left(\delta f + \frac{4\gamma f}{5} - \frac{2\sqrt{14}}{15}\gamma k\right)^2 s_2^2$
$^1\overline{D}_2$	$\frac{192}{343}\left(\alpha\delta - \sqrt{\frac{21}{10}} bk - \frac{1}{\sqrt{240}} bf\right)^2 s_2^2$	$\frac{192}{343}\left(b\delta - \sqrt{\frac{21}{10}}\alpha k - \frac{\alpha f}{\sqrt{240}}\right)^2 s_2^2$	$\frac{32}{105}\left(k + \frac{3f}{2\sqrt{14}}\right)^2 s_2^2$	$\frac{60}{343}\left(\delta f + \frac{4}{5}\gamma f - \frac{2\sqrt{14}}{15}\gamma k\right)^2 s_2^2$	
$^3\overline{P}_2$	$\frac{192}{343}\left(\alpha k - \sqrt{\frac{21}{10}} b\varepsilon\right)^2 s_2^2$	$\frac{288}{245}\left(\alpha\varepsilon + kb\sqrt{\frac{10}{21}}\right)^2 s_2^2$	$\frac{32}{105}\varepsilon^2 s_2^2$	$\frac{32}{735}\left(\gamma\varepsilon + \frac{15fk}{2\sqrt{14}}\right)^2 s_2^2$	$\frac{60}{343}\left(k\delta - \frac{49}{30}k\varepsilon + \frac{2\sqrt{14}}{15}f\varepsilon\right)^2 s_2^2$
$^3\overline{P}_1$	0	0	$\frac{64}{105} s_2^2$	$\frac{32}{105}\gamma^2 s_2^2$	$\frac{3}{5}\left(k - \frac{4\sqrt{2}}{3\sqrt{7}} f\right)^2 s_2^2$
$^3\overline{P}_0$	0	0	0	$\frac{32}{105}\left(\beta\gamma + df\sqrt{\frac{5}{2}}\right)^2 s_2^2$	$\frac{32}{105}\left(f\beta - \delta d\sqrt{\frac{5}{2}} + k\beta\sqrt{\frac{7}{8}}\right)^2 s_2^2$
$^1\overline{S}_0$	0	0	0	$\frac{32}{105}\left(\gamma d - \beta f\sqrt{\frac{5}{2}}\right)^2 s_2^2$	$\frac{16}{21}\left(\beta\delta + \frac{1}{2}dk + fd\sqrt{\frac{2}{5}}\right)^2 s_2^2$

	$^3\overline{P}_2$	$^3\overline{P}_1$	$^3\overline{P}_0$	$^1\overline{S}_0$
$^1\overline{G}_4$	$\frac{192}{343}\left(\alpha k - \sqrt{\frac{21}{10}} b\varepsilon\right)^2 s_2^2$	0	0	0
$^3\overline{F}_4$	$\frac{288}{245}\left(\alpha\varepsilon + kb\sqrt{\frac{10}{21}}\right)^2 s_2^2$	0	0	0
$^3\overline{F}_3$	$\frac{32}{105}\varepsilon^2 s_2^2$	$\frac{64}{105} s_2^2$	0	0
$^3\overline{F}_2$	$\frac{32}{735}\left(\gamma\varepsilon + \frac{15}{2\sqrt{14}} fk\right)^2 s_2^2$	$\frac{32}{105}\gamma^2 s_2^2$	$\frac{32}{105}\left(\beta\delta + df\sqrt{\frac{5}{2}}\right)^2 s_2^2$	$\frac{32}{105}\left(\gamma d - \beta f\sqrt{\frac{5}{2}}\right)^2 s_2^2$
$^1\overline{D}_2$	$\frac{60}{343}\left(k\delta - \frac{49}{30}k\varepsilon + \frac{2\sqrt{14}}{15}f\varepsilon\right)^2 s_2^2$	$\frac{3}{5}\left(k - \frac{4\sqrt{2}}{3\sqrt{7}} f\right)^2 s_2^2$	$\frac{32}{105}\left(f\beta - \delta d\sqrt{\frac{5}{2}} + k\beta\sqrt{\frac{7}{8}}\right)^2 s_2^2$	$\frac{16}{21}\left(\beta\delta + \frac{1}{2}dk + fd\sqrt{\frac{2}{5}}\right)^2 s_2^2$
$^3\overline{P}_2$		$\frac{3}{5}\varepsilon^2 s_2^2$	$\frac{4}{15}\left(\beta\varepsilon + dk\sqrt{\frac{20}{7}}\right)^2 s_2^2$	$\frac{4}{15}\left(d\varepsilon - \beta k\sqrt{\frac{20}{7}}\right)^2 s_2^2$
$^3\overline{P}_1$	$\frac{3}{5}\varepsilon^2 s_2^2$		0	0
$^3\overline{P}_1$	$\frac{4}{15}\left(\beta\varepsilon + dk\sqrt{\frac{20}{7}}\right)^2 s_2^2$	0		0
$^1\overline{S}_0$	$\frac{4}{15}\left(d\varepsilon - \beta k\sqrt{\frac{20}{7}}\right)^2 s_2^2$	0	0	

VI. NUMERICAL CALCULATIONS

A. Discussion of Method

Numerical calculations were made of the magnetic dipole and electric quadrupole transition probabilities for the np^2, np^3, np^4 and $3d^2$ configurations, n having the values 2, 3 and 4. About fifteen atoms were treated in each of the p^k configurations, these being atoms in different stages of ionization. The formulae for the d^2 configuration were applied to only one case, that of Fe VII. All calculations were carried out to three figures; and two figures were taken as significant in the final results. The calculations were repeated in a slightly different manner for checking purposes, and were checked in other ways wherever possible.

Data concerning the extent of the breakdown of pure Russell-Saunders coupling for the p^k configurations were taken from a paper by Robinson and Shortley$^{19)}$. They made a detailed analysis of the p^2, p^3 and p^4 configurations from the point of view of intermediate coupling theory (CS, Chapter 11). By considering the deviations of the term and multiplet interval ratios from the values predicted by the pure Russell-Saunders coupling scheme, they obtained values of the parameters $F_2(np,np)$ and ζ_{np} for a large number of atoms in various stages of ionization. These parameters enter into the expressions for the coefficients, defined in equation (23) of section III, which give the perturbed wave functions in terms of the pure Russell-Saunders wave functions (cf. Tables 2(e) and 3(e)).

Robinson and Shortley found that the parameters F_2 and ζ agreed fairly well with the values which were obtained by using hydrogenlike radial wave functions in the equations defining F_2 and ζ, together with appropriate screening constants which were taken to be constant along each iso-electronic sequence. The screening constants for F_2 and ζ are different. Thus, if we substitute into equations (28) and (30) of section III the expressions

$$R(n\ell) = \sqrt{\frac{Z(n-\ell-1)!}{n^2 a_0 \{(n+\ell)!\}^3}}\; e^{-\frac{Zr}{na_0}} \left(\frac{2Zr}{na_0}\right)^{\ell+1} L^{2\ell+1}_{n+\ell}\left(\frac{2Zr}{na_0}\right),$$

and

$$\xi(r) = \frac{-Ze^2}{r},$$

and then introduce screening constants, we get

$$\begin{aligned} F_2(2p,2p) &= 771.6\,(Z - \sigma_{2p}) \\ F_2(3p,3p) &= 315.9\,(Z - \sigma_{3p}) \qquad (1) \\ F_2(4p,4p) &= 174.9\,(Z - \sigma_{4p}) \end{aligned}$$

$$\zeta_{n\ell} = \frac{5.822\,(Z - S_{n\ell})}{n^3 \ell(\ell + \frac{1}{2})(\ell + 1)} \qquad (2)$$

The wave numbers of the forbidden lines for the atoms of the p^k configurations were computed from the term levels taken from a number of sources. These sources, which are among those listed in the bibliography to the paper of Robinson and Shortley, are also listed in the bibliography to this thesis[24). The atoms whose term values are recorded in each of these articles is placed in brackets following each reference.

The expressions for the transition probabilities in the electric quadrupole case also involve the square of the integral

$$s_2(n\ell) = -e\int_0^\infty \{R(n\ell)\}^2 r^2\,dr. \tag{3}$$

These integrals were evaluated numerically by Condon[10)] for O I, O II and O III, using Hartree self-consistent field wave functions calculated by Hartree and Black[25)]. However, such wave functions were not available for all the atoms treated here, so that a cruder approximation was necessary. It was decided to compute s_2 by using hydrogenlike wave functions, together with appropriate screening constants. The integral, which is essentially the mean value of r^2, is then given by the formula, in atomic units

$$s_2(n,\ell) = \frac{n^2(5\,n^2 + 1 - 3\ell^2 - 3\ell)}{2(Z - \sigma_{n\ell})^2}. \tag{4}$$

That this screening constant method is a reasonable procedure is indicated by the results of Robinson and Shortley for the parameters F_2 and ζ. In the absence of a set of screening constants characteristic of s_2, the screening constants corresponding to the parameter F_2 were used. These are the intercepts on the Z axis, in the diagram of F_2 as a function of Z, of the straight lines (with hydrogenlike slopes given by equations (1)) which best fit the values of F_2 determined by Robinson and Shortley. The screening constants for F_2 were used rather than those for ζ, because $\zeta_{n\ell}$ is essentially an average value of r^{-3}, whereas F_2 is essentially an average value of r^{-1} and $-s_2/e$ is the mean value of r^2. Hence the screening constant for F_2 should be closer to the true screening constant for s_2 than that of $\zeta_{n\ell}$.

There is an alternative method of securing a screening constant for use in the computation of s_2. This consists of the use of the following approximate formulae for the absolute term energies,

$$\nu(n,l) = \frac{R}{n^2}(Z - \sigma_{n\ell})^2 ,$$

$$= \frac{R Z_1^2}{(n+1)^2} + \nu_0 , \qquad (5)$$

where $\nu(n,l)$ is the wave number difference between the $(nl)^k$ configuration and the $(nl)^{k-1}$ configuration; $\nu_0(n,l)$ is the wave number difference between the $(nl)^k$ configuration and the $(nl)^{k-1}(n+1\,\ell)$ configuration; Z_1 is the net charge on the core consisting of the atom under consideration minus one electron, and $(Z - \sigma_{n\ell})$ is the effective atomic number of the $(nl)^k$ configuration. The second expression for ν must be used in the case of Fe VII, where the absolute term values are not known. This method was not used, however, for the computation of the transition probabilities, as it is not likely to give satisfactory values of the screening constant for atoms in low stages of ionization.

For the $3d^2$ configuration of Fe VII, all of the term values except that for ${}^1S_0$ were taken from data of Bowen and Edlén$^{26)}$. The ${}^1S_0$ value (65707 cm^{-1}) was taken from some unpublished work of Edlén.

(Term values for the $3d^2$ configuration for the iso-electronic sequence from Mn VI to Ni IX had been obtained by Cady[27], but they were later shown to be in error, and were therefore not used here.) In this case the theoretical expressions for the term separations involve the two parameters F_2 and F_4. These constants were computed from the experimental values of the $^1D - ^3F$ and $^3P - ^3F$ separations. The reason for using these two separations rather than all of the term levels is that the $^1D - ^3P$ interval is of critical importance in the evaluation of one of the coefficients (k) in the breakdown of LS coupling, and it was considered advisable to take the value of this interval equal to the experimental one. The values of F_2 and F_4 thus obtained fit the $^1S - ^3F$ separation fairly well, but the $^1G - ^3F$ theoretical separation is then 2340 cm^{-1} too low. The lack of good agreement is indicated in Fig. 3, which is a plot of the separations

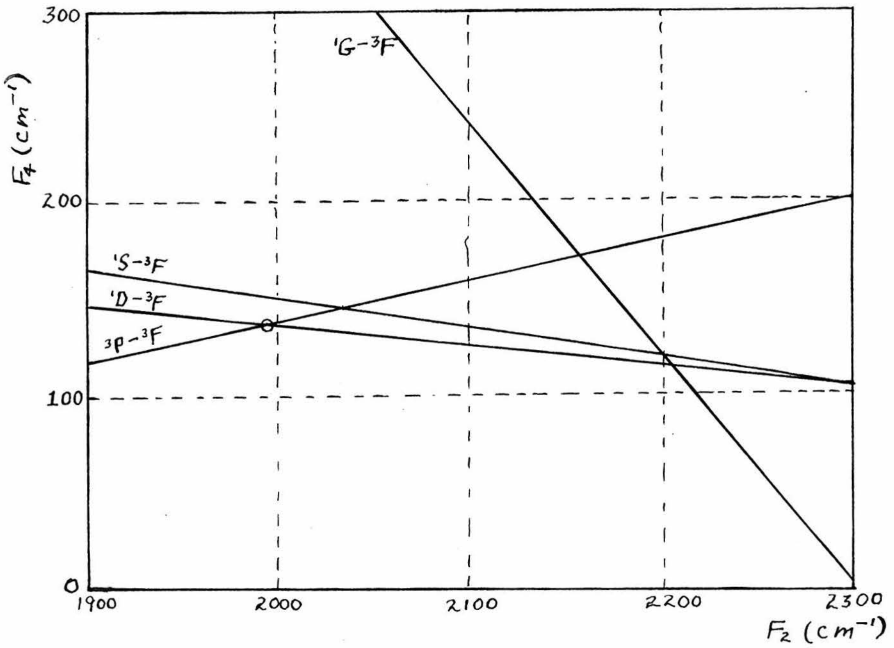
$$\begin{aligned} E(^1D_2) - E(^3F_m) &= 5\,F_2 + 45\,F_4 = 16129 \\ E(^3P_m) - E(^3F_m) &= 15\,F_2 - 75\,F_4 = 19509 \\ E(^1G_4) - E(^3F_m) &= 12\,F_2 + 10\,F_4 = 27570 \\ E(^1S_0) - E(^3F_m) &= 22\,F_2 + 135\,F_4 = 64361\,. \end{aligned} \tag{6}$$

The numbers on the right hand sides of these equations are the experimental values, where the statistical means of the levels in the ^3P (and ^3F) terms have been taken, according to the formula

$$E(^3L_m) = \frac{\sum_J (2J+1)\,E(^3L_J)}{\sum_J (2J+1)}\,. \tag{7}$$

Theoretically the four straight lines should intersect in a common point. The figure indicates that at least one level disagrees with the Slater formula.

Fig. 3. Term Separations for Fe VII



The parameter ζ_{3d} for Fe VII was taken as the average of the values obtained from the ^3P and ^3F multiplets, using the fact that the displacements of the levels within the multiplets by the spin-orbit interaction are approximately given by the diagonal elements of the matrix of table 3(d).

The integral s_2 was obtained by use of hydrogenlike wave functions, together with a screening constant. The latter was taken to be the mean of the two screening constants deduced from the values chosen for F_2 and F_4, with the aid of the hydrogenlike formulae

$$\begin{aligned} F_2(3d,3d) &= 203.4\ (Z - \sigma_{3d}), \\ F_4(3d,3d) &= 14.7\ (Z - \sigma_{3d}). \end{aligned} \tag{8}$$

B. Numerical Results

In order to give some idea of the uncertainties involved in the calculation of the integral s_2, table 10 lists the values of s_2 obtained for several atoms, using the two approximate methods described above. For O I, O II and O III, the values of s_2 obtained by numerical integration, using the Hartree-Black[25) approximate wave functions, are also tabulated; and for C I, N I and N II the values obtained by Condon[10) from the Brown, Bartlett and Dunn approximate wave functions[28) are listed.

As was pointed out before, several errors occur in the calculations which Condon[10) made of the transition probabilities for a few of the most important atoms of the p^k configurations. In order to facilitate comparison of his results with the ones obtained here, both sets of results are listed in Tables 11 for the cases O III, O II and O I. Stevenson's results[9) for O III are also given in Table 11(a). Since Condon used a more accurate method of computing s_2 (numerical integration, using Hartree approximate wave functions), another column has been added to the table, giving the results obtained by application of the more accurate values of s_2 to the formulae developed in the preceding sections. It is interesting also to compare this column with the results obtained when the less accurate values of s_2 were used. Some of the smaller differences between Condon's results and the results obtained here by use of the more accurate values of s_2 are due to slight differences in the procedure of calculation.

In Tables 12 are listed the magnetic dipole and electric quadrupole transition probabilities for fifty-one atoms in the configurations np^2, np^3 and np^4 (where n = 2, 3 or 4). The values of the parameters F_2, ζ_{np} and s_2 used in the calculations are also listed, together with the coefficients b, d and a, b, which are a measure of the extent of breakdown of LS coupling. These tables indicate the relative contributions of the two types of radiation to the total transition probabilities.

The total transition probabilities for these atoms in the np^k configurations are listed in Tables 13. In these tables there are also given for convenience the wave lengths of those astronomically observable lines which would be expected to be strong under nebular conditions. The lines which have been observed up to the present time are indicated by underlining the corresponding wave lengths. These wave lengths, and the information as to which lines have been observed, are taken from a forthcoming article by Bowen and Wyse5).

Table 14 contains the magnetic dipole, electric quadrupole, and total transition probabilities for the $3d^2$ configuration of Fe VII. The parameters F_2, F_4, ζ_{3d} and s_2 are also listed, together with the coefficients b, d, f, k, u, v which occur in the wave functions for the perturbed system. As in the case of the p^k configurations, the wave lengths of the astronomically observable lines are given in the same table, the observed lines being underlined.

In order to illustrate the extent of agreement of the theoretically determined transition probabilities with the experimental relative intensities, the relative intensities observed for the forbidden lines of O III, O II, O I and Fe VII are listed in Tables 11(a), 11(b), 11(c) and 14, respectively. These values are taken from the article by Bowen and Wyse$^{5)}$.

For convenience we shall use a slightly different notation in the tables than was used in the discussion of transition probabilities in section II. The probability of transition from a state A to a state B of lower energy will be denoted by the expression

$$A(B - A)$$

instead of the former expression

$$A(A,B).$$

Table 10. Comparative Values of the Integrals $s_2(n,l) = -e\int_0^\infty R^2(n,l)\, r^2 dr$, in atomic units.

Configuration	Atom	s_2, from Approx. Wave Functions	s_2, from Screening Constants of F_2, F	s_2, from Screening Constants of Absolute Term Values
$2p^2$	C I	5.35	5.21	9.06
	N II	2.5	2.59	3.45
	O III	1.32	1.55	1.86
	Al VIII		.339	.357
$3p^2$	Si I		12.5	35.4
	Cl IV		2.33	5.09
$2p^3$	N I	3.45	4.80	7.01
	O II	1.75	2.45	2.90
	Si VIII		.332	.335
$2p^4$	O I	2.44	2.94	7.49
	Si VII		.355	.415
$3d^2$	Ti III		7.62	6.46
	Fe VII		1.38	1.52

Table 11(a). Comparison of Results with Those of Condon and Stevenson, for O III.

Transition	Type of Rad'n.	Trans. Probs. Using Screening Const. value of s_2, in sec^{-1}	Trans. Probs. using Hartree Wave Function value of s_2 in sec^{-1}	Condon's Results in sec^{-1}	Stevenson's Results in sec^{-1}	Observed Relative Intensities NGC 7027
s_2		1.55	1.32	1.24		
$A(^3P_1 - {}^1S_0)$	d	.14	.14	.102	.38	
$A(^3P_2 - {}^1S_0)$	q	.0011	.00081	.00015	1.9×10^{-5}	
$A(^1D_2 - {}^1S_0)$	q	2.7	2.0	1.8	9.6	23
$A(^3P_0 - {}^1D_2)$	q	1.3×10^{-6}	9.6×10^{-7}	0	6.7×10^{-6}	4
$A(^3P_1 - {}^1D_2)$	d	.0055	.0055	.006		
	q	8.0×10^{-6}	5.8×10^{-6}	6×10^{-6}		
	Total	.0055	.0055	.006	.0096	430
$A(^3P_2 - {}^1D_2)$	d	.016	.016	.018		
	q	5.3×10^{-5}	3.9×10^{-5}	1.8×10^{-5}		
	Total	.016	.016	.018	.029	1200
$A(^3P_0 - {}^3P_2)$	q	5.8×10^{-11}	4.2×10^{-11}			
$A(^3P_1 - {}^3P_2)$	d	9.7×10^{-5}	9.7×10^{-5}			
	q	1.3×10^{-12}	9.4×10^{-12}			
	Total	9.7×10^{-5}	9.7×10^{-5}			
$A(^3P_0 - {}^3P_1)$	d	2.6×10^{-5}	2.6×10^{-5}			

Table 11(b). Comparison of Results with those of Condon, for O II

Transition	Type of Rad'n.	Trans. Probs. using Screening Const. value of s_2 in sec^{-1}	Trans. Probs. using Hartree Wave Function value of s_2 in sec^{-1}	Condon's Results in sec^{-1}	Observed Relative Intensities (NGC 7027)
s_2		2.45	1.70	1.75	
$A(^2D_{2\frac{1}{2}} - {}^2P_{1\frac{1}{2}})$	d	.0084	.0084	.50	
	q	.265	.128	1.8	
	Total	.27	.14	2.3	
$A(^2D_{2\frac{1}{2}} - {}^2P_{\frac{1}{2}})$	q	.15	.073	1.0	
$A(^2D_{1\frac{1}{2}} - {}^2P_{1\frac{1}{2}})$	d	.0149	.0149	.90	
	q	.113	.0544	.78	
	Total	.13	.069	1.7	
$A(^2D_{1\frac{1}{2}} - {}^2P_{\frac{1}{2}})$	d	.0093	.0093	1.7	
	q	.226	.109	1.6	
	Total	.24	.12	3.3	
$A(^4S_{1\frac{1}{2}} - {}^2P_{1\frac{1}{2}})$	d	.078	.077	.041	
	q	1.6×10^{-8}	7.5×10^{-9}	0	
	Total	.078	.078	.041	
$A(^4S_{1\frac{1}{2}} - {}^2P_{\frac{1}{2}})$	d	.031	.031	.049	
	q	1.3×10^{-7}	6.0×10^{-8}	0	
	Total	.031	.031	.049	
$A(^4S_{1\frac{1}{2}} - {}^2D_{2\frac{1}{2}})$	q	1.4×10^{-4}	6.5×10^{-5}	3.7×10^{-5}	11
$A(^4S_{1\frac{1}{2}} - {}^2D_{1\frac{1}{2}})$	d	2.26×10^{-5}	1.86×10^{-5}	4.0×10^{-7}	
	q	8.76×10^{-5}	4.22×10^{-5}	2.38×10^{-5}	
	Total	1.1×10^{-4}	7.1×10^{-5}	2.42×10^{-5}	20
$A(^2P_{1\frac{1}{2}} - {}^2P_{\frac{1}{2}})$	d	6.01×10^{-11}	6.01×10^{-11}		
	q	7.68×10^{-25}	3.70×10^{-25}		
	Total	6.0×10^{-11}	6.0×10^{-11}		
$A(^2D_{2\frac{1}{2}} - {}^2D_{1\frac{1}{2}})$	d	1.5×10^{-7}	1.5×10^{-7}		
	q	4.7×10^{-19}	2.3×10^{-19}		
	Total	1.5×10^{-7}	1.5×10^{-7}		

Table 11(c). Comparison of Results with those of Condon, for O I

Transition	Type of Rad'n.	Trans. Probs. using Screening Const. value of s_2 in sec^{-1}.	Trans. Probs. using Hartree Wave Function value of s_2 in sec^{-1}.	Condon's Results in sec^{-1}	Observed Relative Intensities (NGC 7027)
s_2		2.94	2.44	2.44	
$A(^3P_2-{}^1S_0)$	q	.0019	.0013	.00016	
$A(^3P_1-{}^1S_0)$	d	.10	.10	.18	
$A(^1D_2-{}^1S_0)$	q	2.8	1.9	2.0	8
$A(^3P_2-{}^1D_2)$	d	.013	.013		
	q	9.4×10^{-5}	6.5×10^{-5}		
	Total	.013	.013	.0075	50
$A(^3P_1-{}^1D_2)$	d	.0040	.0040		
	q	1.3×10^{-5}	8.8×10^{-6}		
	Total	.0040	.0040	.0025	25
$A(^3P_0-{}^1D_2)$	q	2.0×10^{-6}	1.4×10^{-6}	0	
$A(^3P_2-{}^3P_0)$	q	2.3×10^{-10}	1.6×10^{-10}		
$A(^3P_1-{}^3P_0)$	d	1.7×10^{-5}	1.7×10^{-5}		
$A(^3P_2-{}^3P_1)$	d	8.8×10^{-5}	8.8×10^{-5}		
	q	2.8×10^{-11}	2.0×10^{-11}		
	Total	8.8×10^{-5}	8.8×10^{-5}		

Table 12(a). Mag. Dipole and Elec. Quadrupole Transition Probabilities for $2p^2$ Configurations, in sec^{-1}.

	Type of Rad'n.	C I	N II	O III	F IV	Na VI	Mg VII	Al VIII
F_2 (cm^{-1})		1694	2537	3354	3970	5826	6554	7282
ζ_{2p} (cm^{-1})		27.1	85.0	201	405	1250	1940	2650
b		.00189	.00395	.00707	.0120	.0249	.0349	.0429
d		-.00151	-.00316	-.00566	-.00962	-.0199	-.0280	-.0343
s_2 (at. units)		5.21	2.59	1.55	1.03	.548	.425	.339
A($^3P_1$ - $^1S_0$)	d	.00123	.0165	.137	.749	8.74		
A($^3P_2$ - $^1S_0$)	q	.0000292	.000246	.00111	.00405	.0252		
A($^1D_2$ - $^1S_0$)	q	.950	1.89	2.69	3.41	4.75		
A($^3P_0$ - $^1D_2$)	q	$3.38x10^{-8}$	$2.82x10^{-7}$	$1.32x10^{-6}$	$5.04x10^{-6}$	$3.71x10^{-5}$	$8.69x10^{-5}$	$1.51x10^{-4}$
A($^3P_1$ - $^1D_2$)	d	.0000500	.000740	.00547	.0302	.371	1.05	2.26
	q	$2.15x10^{-7}$	$1.74x10^{-6}$	$7.98x10^{-6}$	$2.99x10^{-5}$	$2.10x10^{-4}$	$4.67x10^{-4}$	$7.98x10^{-4}$
A($^3P_2$ - $^1D_2$)	d	.000149	.00218	.0159	.0864	1.01	2.78	5.64
	q	$1.39x10^{-6}$	$1.18x10^{-5}$	$5.32x10^{-5}$	.000193	.00125	.00259	.00410
A($^3P_0$ - $^3P_2$)	q	$3.26x10^{-14}$	$2.35x10^{-12}$	$5.79x10^{-11}$	$8.16x10^{-10}$	$5.88x10^{-8}$	$3.51x10^{-7}$	$1.06x10^{-6}$
A($^3P_1$ - $^3P_2$)	d	$2.78x10^{-7}$	$7.42x10^{-6}$	$9.67x10^{-5}$	$7.81x10^{-4}$	.0208	.0794	.247
	q	$8.48x10^{-19}$	$5.03x10^{-13}$	$1.29x10^{-11}$	$1.87x10^{-10}$	$1.27x10^{-8}$	$7.04x10^{-8}$	$2.98x10^{-7}$
A($^3P_0$ - $^3P_1$)	d	$5.78x10^{-8}$	$2.11x10^{-6}$	$2.60x10^{-5}$	$2.03x10^{-4}$	.00606	.0255	.0457

Table 12(b). Mag. Dipole and Elec. Quadrupole Trans. Probabilities for $3p^2$ and $4p^2$ Configurations, in sec^{-1}.

	Type of	$(3p^2)$							$(4p^2)$	
	Rad'n.	Si I	P II	S III	Cl IV	A V	K VI	Ca VII	Ge I	As II
F_2 (cm^{-1})		1020	1430	1790	2130	2470	2800	3120	1000	1340
ζ_{np} (cm^{-1})		148	314	555	885	1330	1920	2650	924	1660
b		.0171	.0259	.0365	.0489	.0636	.0807	.100	.108	.146
d		-.0137	-.0207	-.0292	-.0392	-.0509	-.0646	-.0801	-.0867	-.117
s_2 (at. units)		12.5	7.83	5.36	3.90	2.96	2.33	1.88	12.2	9.38
$A(^3P_1 - {}^1S_0)$	d	.0359	.226	.885	2.70	7.11			1.59	
$A(^3P_2 - {}^1S_0)$	q	.00233	.0110	.0309	.0686	.135			.0842	
$A(^1D_2 - {}^1S_0)$	q	1.72	3.58	5.07	6.28	7.30			1.76	
$A(^3P_0 - {}^1D_2)$	q	$1.45x10^{-6}$	$7.20x10^{-6}$	$2.27x10^{-5}$	$5.71x10^{-5}$	.000130	.000277	.000558	.000103	.000619
$A(^3P_1 - {}^1D_2)$	d	.000939	.00592	.0239	.0747	.203	.493	1.11	.0445	.210
	q	$8.44x10^{-6}$	$4.10x10^{-5}$	.000124	.000299	.000640	.00127	.00239	.000430	.00225
$A(^3P_2 - {}^1D_2)$	d	.00262	.0160	.0616	.183	.470	1.07	2.24	.0868	.361
	q	.0000525	.000240	.000676	.00150	.00292	.00520	.00871	.00146	.00632
$A(^3P_0 - {}^3P_2)$	q	$7.63x10^{-10}$	$1.25x10^{-8}$	$1.02x10^{-7}$	$5.81x10^{-7}$	$2.65x10^{-6}$	$1.01x10^{-5}$	$3.43x10^{-5}$	$7.27x10^{-6}$	$7.96x10^{-5}$
$A(^3P_1 - {}^3P_2)$	d	.0000416	.000374	.00205	.00819	.0269	.0765	.192	.00818	.0421
	q	$2.07x10^{-10}$	$3.16x10^{-10}$	$2.51x10^{-9}$	$1.35x10^{-8}$	$5.62x10^{-7}$	$1.99x10^{-6}$	$6.04x10^{-6}$	$1.35x10^{-6}$	$1.21x10^{-5}$
$A(^3P_0 - {}^3P_1)$	d	$8.15x10^{-6}$	$8.24x10^{-5}$	.000467	.00210	.00792	.0257	.0765	.00506	.0211

Table 12(c). Mag. Dipole and Elec. Quadrupole Transition Probabilities for $2p^3$ Configuration, in sec^{-1}.

	Type of Rad'n.	N I	O II	F III	Ne IV	Na V	Mg VI	Al VII	Si VIII
$F_2(cm^{-1})$		1600	2280	2910	3520	4140	4740	5360	6020
$\zeta_{2p}(cm^{-1})$		69.7	175	421	703	1140	1890	2640	3840
a		.00811	.0143	.0270	.0373	.0512	.0745	.0922	.119
b		.00290	.00513	.00967	.0133	.0183	.0267	.0330	.0427
s_2 (at. units)		4.80	2.45	1.48	.992	.710	.533	.415	.332
$A(^4S_{1\frac{1}{2}}-{}^2P_{1\frac{1}{2}})$	d	.00896	.0777	.571		5.64	18.3	41.0	101
	q	1.13×10^{-9}	1.56×10^{-8}	2.42×10^{-7}		3.87×10^{-6}	1.98×10^{-5}	5.51×10^{-5}	.000177
$A(^4S_{1\frac{1}{2}}-{}^2P_{\frac{1}{2}})$	d	.00559	.0311	.228		2.24	7.19	16.0	38.5
	q	9.01×10^{-9}	1.25×10^{-7}	1.94×10^{-6}		3.07×10^{-5}	.000156	.000411	.00136
$A(^2D_{1\frac{1}{2}}-{}^2P_{1\frac{1}{2}})$	d	.00166	.0149	.110	.375	1.15	3.70	8.28	20.2
	q	.0754	.113	.141	.167	.192	.217	.248	.298
$A(^2D_{1\frac{1}{2}}-{}^2P_{\frac{1}{2}})$	d	.00104	.00930	.0689	.235	.719	2.30	5.11	12.6
	q	.151	.226	.282	.334	.382	.427	.482	.582
$A(^2D_{2\frac{1}{2}}-{}^2P_{1\frac{1}{2}})$	d	.000936	.00840	.0624	.212	.651	2.10	4.69	11.3
	q	.177	.265	.332	.392	.450	.511	.579	.679
$A(^2D_{2\frac{1}{2}}-{}^2P_{\frac{1}{2}})$	q	.101	.152	.190	.224	.256	.287	.321	.379
$A(^2P_{\frac{1}{2}}-{}^2P_{1\frac{1}{2}})$	d		6.01×10^{-11}		8.89×10^{-9}	5.27×10^{-7}	1.61×10^{-5}	1.53×10^{-4}	2.16×10^{-4}
	q		7.68×10^{-25}		5.40×10^{-21}	4.72×10^{-18}	1.72×10^{-15}	6.78×10^{-14}	1.30×10^{-13}
$A(^4S_{1\frac{1}{2}}-{}^2D_{2\frac{1}{2}})$	d	1.88×10^{-8}	4.99×10^{-7}	.0000129		.000444	.00302	.0130	.0416
	q	.0000316	.000156	.000586		.00246	.00591	.0103	.0203
$A(^4S_{1\frac{1}{2}}-{}^2D_{1\frac{1}{2}})$	d	8.46×10^{-7}	.0000226	.000584		.0200	.136	.463	1.85
	q	.0000203	.0000876	.000379		.00159	.00379	.00653	.0126
$A(^2D_{1\frac{1}{2}}-{}^2D_{2\frac{1}{2}})$	d	8.21×10^{-9}	1.48×10^{-7}	7.47×10^{-7}	2.50×10^{-7}	2.50×10^{-7}	1.48×10^{-7}	1.86×10^{-6}	2.07×10^{-4}
	q	4.60×10^{-21}	4.67×10^{-19}	8.98×10^{-18}	1.22×10^{-18}	1.19×10^{-18}	6.08×10^{-19}	5.01×10^{-17}	1.39×10^{-13}

Table 12(d). Mag. Dipole and Elec. Quadrupole Trans. Probabilities for $3p^3$ and $4p^3$ Configurations, in sec^{-1}.

	Type of Rad'n.	($3p^3$) P I	S II	Cl III	A IV	K V	Ca VI	Sc VII	($4p^3$) Se II
F_2 (cm^{-1})		1220	1610	1940	2270	2580	2890	3190	1540
ζ_{np} (cm^{-1})		343	538	825	1230	1760	2440	3340	2310
a		.0522	.0624	.0792	.101	.127	.157	.196	.280
b		.0187	.0223	.0283	.0360	.0453	.0563	.0700	.100
s_2 (at. units)		10.2	6.67	4.69	3.47	2.68	2.13	1.73	9.38
A($^4S_{1\frac{1}{2}}-{}^2P_{1\frac{1}{2}}$)	d	.103	.332	.967	2.53	6.06	13.7		6.96
	q	1.02×10^{-6}	3.45×10^{-6}	1.19×10^{-5}	3.79×10^{-5}	.000112	.000319		.00280
A($^4S_{1\frac{1}{2}}-{}^2P_{\frac{1}{2}}$)	d	.0406	.131	.378	.977	2.30	5.06		2.18
	q	8.03×10^{-6}	2.71×10^{-5}	9.22×10^{-5}	.000289	.000833	.00227		.0158
A($^2D_{1\frac{1}{2}}-{}^2P_{1\frac{1}{2}}$)	d	.0311	.101	.295	.772	1.86	4.19	9.22	2.46
	q	.0910	.152	.204	.248	.296	.352	.420	.415
A($^2D_{1\frac{1}{2}}-{}^2P_{\frac{1}{2}}$)	d	.0193	.0628	.182	.470	1.12	2.47	5.31	1.34
	q	.179	.298	.392	.471	.545	.621	.705	.606
A($^2D_{2\frac{1}{2}}-{}^2P_{1\frac{1}{2}}$)	d	.0175	.0566	.165	.428	1.02	2.28	4.94	1.29
	q	.211	.351	.462	.560	.651	.751	.865	.789
A($^2D_{2\frac{1}{2}}-{}^2P_{\frac{1}{2}}$)	q	.119	.196	.255	.302	.342	.377	.409	.318
A($^2P_{\frac{1}{2}}-{}^2P_{1\frac{1}{2}}$)	d	1.51×10^{-7}	1.02×10^{-6}	7.58×10^{-6}	5.22×10^{-5}	2.84×10^{-4}	1.49×10^{-4}	6.42×10^{-3}	5.11×10^{-3}
	q	1.26×10^{-16}	1.85×10^{-15}	4.25×10^{-14}	9.53×10^{-13}	1.53×10^{-11}	2.30×10^{-10}	2.86×10^{-9}	1.27×10^{-7}
A($^4S_{1\frac{1}{2}}-{}^2D_{2\frac{1}{2}}$)	d	6.67×10^{-6}	3.07×10^{-5}	.000145	.000599	.00224	.00776		.00978
	q	.000429	.00100	.00214	.00417	.00764	.0138		.0272
A($^4S_{1\frac{1}{2}}-{}^2D_{1\frac{1}{2}}$)	d	.000299	.00137	.00658	.0265	.0982	.344		.384
	q	.000273	.000635	.00134	.00257	.00461	.00802		.0128
A($^2D_{1\frac{1}{2}}-{}^2D_{2\frac{1}{2}}$)	d	3.45×10^{-8}	3.33×10^{-7}	3.20×10^{-6}	2.27×10^{-5}	.000140	.000755	.00320	.00230
	q	1.24×10^{-17}	3.29×10^{-16}	1.15×10^{-14}	2.71×10^{-13}	5.38×10^{-12}	8.76×10^{-11}	1.02×10^{-9}	3.81×10^{-8}

Table 12(e). Mag. Dipole and Elec. Quadrupole Transition Probabilities for $2p^4$ Configuration, in sec^{-1}.

	Type of Rad'n	O I	F II	Ne III	Na IV	Mg V	Al VI	Si VII
F_2 (cm^{-1})		1990	2670	3320	3960	4590	5230	5870
ζ_{2p} (cm^{-1})		150	330	600	1050	1720	2620	3840
b		-.00884	-.0147	-.0212	-.0312	-.0442	-.0589	-.0760
d		.00707	.0118	.0170	.0250	.0354	.0471	.0608
s_2 (at. units)		2.94	1.70	1.11	.781	.579	.446	.355
$A(^3P_2 - {}^1S_0)$	q	.00189	.00727	.0190	.0466	.104	.207	
$A(^3P_1 - {}^1S_0)$	d	.102	.657	2.57	9.02	27.0	68.6	
$A(^1D_2 - {}^1S_0)$	q	2.82	4.13	5.23	6.22	7.18	8.12	
$A(^3P_2 - {}^1D_2)$	d	.0125	.0790	.311	1.07	3.18	8.20	21.0
	q	.0000944	.000347	.000891	.00206	.00439	.00865	.0186
$A(^3P_1 - {}^1D_2)$	d	.00404	.0251	.0961	.318	.905	2.21	5.31
	q	.0000128	.0000457	.000112	.000243	.000482	.000862	.00167
$A(^3P_0 - {}^1D_2)$	q	2.00×10^{-6}	7.15×10^{-6}	1.72×10^{-5}	3.62×10^{-5}	6.95×10^{-5}	1.19×10^{-4}	2.19×10^{-4}
$A(^3P_2 - {}^3P_0)$	q	2.29×10^{-10}	3.65×10^{-9}	3.64×10^{-8}	2.62×10^{-7}	1.50×10^{-6}	7.25×10^{-6}	2.95×10^{-5}
$A(^3P_1 - {}^3P_0)$	d	.0000173	.000176	.00116	.00554	.0220	.0700	.192
$A(^3P_2 - {}^3P_1)$	d	.0000881	.000889	.00592	.0301	.125	.454	1.45
	q	2.84×10^{-11}	4.46×10^{-10}	4.49×10^{-9}	3.36×10^{-8}	1.99×10^{-7}	1.01×10^{-6}	4.44×10^{-6}

Table 12(f). Mag. Dipole and Elec. Quadrupole Trans. Probabilities for $3p^4$ and $4p^4$ Configurations, in sec^{-1}.

	Type of Rad'n	$(3p^4)$ S I	Cl II	A III	K IV	Ca V	Sc VI
F_2 (cm)		1090	1540	1980	2370	2770	3070
(cm)		386	670	1070	1590	2270	3100
b		-.0418	-.0513	-.0636	-.0789	-.0966	-.119
d		.0535	.0410	.0509	.0632	.0773	.0952
s_2 (at. units)		8.89	5.95	4.26	3.20	2.49	1.99
A(P - S)	q					.601	1.03
A(P - S)	d					22.7	46.8
A(D - S)	q					10.6	11.5
A(P - D)	d	.0552		.445	1.09	2.48	5.48
	q	.00130		.00552	.0105	.0189	.0349
A(P - D)	d	.0162		.116	.265	.552	1.11
	q	.000149		.000524	.000878	.00138	.00215
A(P - D)	q	.0000218		.0000697	.000111	.000167	.000244
A(P - P)	q	$2.19x10^{-7}$	$1.22x10^{-6}$	$7.63x10^{-6}$	$3.05x10^{-5}$	.000102	.000310
A(P - P)	d	.000299	.000939	.00511	.0147	.0352	.0756
A(P - P)	d	.00139	.00735	.0305	.104	.306	.825
	q	$2.59x10^{-8}$	$1.86x10^{-7}$	$1.03x10^{-6}$	$4.42x10^{-6}$	$1.64x10^{-5}$	$5.50x10^{-5}$

Table 12(g). Mag. Dipole and Elec. Quadrupole Trans. Probabilities for $3p^4$ and $4p^4$ Configurations, in $\sec^{-1}$.

	Type of Rad'n	($3p^4$) Ti VII	V VIII	Cr IX	Mn X	Fe XI	($4p^4$) Se I
F_2 (cm^{-1})		3570	3670	3980	4240	4510	1410
ζ_{np} (cm^{-1})		4160	5320	6950	8760	10910	1821
b		-.146	-.171	-.206	-.243	-.285	-.152
d		.116	.137	.165	.195	.228	.122
s_2 (at. units)		1.63	1.36	1.15	.988	.857	9.38
$A(^3P_2 - {}^1S_0)$	q	1.79	2.85	4.81	7.83	12.7	.728
$A(^3P_1 - {}^1S_0)$	d	91.8	164	304	527	891	6.76
$A(^1D_2 - {}^1S_0)$	q	12.4	13.4	14.6	15.3	15.9	5.29
$A(^3P_2 - {}^1D_2)$	d	11.7	22.7	46.5	89.7	171	.794
	q	.0631	.108	.201	.358	.649	.0225
$A(^3P_1 - {}^1D_2)$	d	2.12	3.67	6.62	11.5	18.7	.135
	q	.00324	.00454	.00676	.00967	.0136	.00102
$A(^3P_0 - {}^1D_2)$	q	.000343	.000478	.000694	.000990	.00156	.000112
$A(^3P_2 - {}^3P_0)$	q	.000817	.00196	.00448	.00860	.0178	.000592
$A(^3P_1 - {}^3P_0)$	d	.132	.207	.274	.252	.276	.00853
$A(^3P_2 - {}^3P_1)$	d	2.04	4.67	10.4	20.9	41.7	.171
	q	.000167	.00464	.00127	.00305	.00734	.0000889

Table 13(a). Total Transition Probabilities for 2p^2 Configuration, in sec^{-1}.

Transition	Type of Rad'n	C I	N II	O III	F IV	Ne VI	Na VI	Mg VII	Al VIII
A($^3P_1$ − $^1S_0$) λ	d	.0012 4621.4	.019 3063.0	.14	.75		8.7		
A($^3P_2$ − $^1S_0$)	q	.000029	.00025	.0011	.0040		.025		
A($^1D_2$ − $^1S_0$) λ	q	.95	1.9 5755.0	2.7 4363.2	3.4 3532.2		4.8		
A($^3P_0$ − $^1D_2$) λ	q	3.4x10^{-8}	2.8x10^{-7}	1.3x10^{-6} 4931.8	5.0x10^{-6}		3.7x10^{-5}	8.7x10^{-5}	1.5x10^{-4}
A($^3P_1$ − $^1D_2$) λ	d	.000050	.00074 6548.4	.0055 4959.5	.030 3996.3	3345.8	.37	1.1	2.3
A($^3P_2$ − $^1D_2$) λ	d	.00015	.0022 6583.9	.016 5007.6	.087 4059.3	3425.8	1.0	2.8	5.6
A($^3P_0$ − $^3P_2$)	q	3.3x10^{-14}	2.3x10^{-12}	5.8x10^{-11}	8.2x10^{-10}		5.9x10^{-8}	3.5x10^{-7}	1.1x10^{-6}
A($^3P_1$ − $^3P_2$)	d	2.8x10^{-7}	7.4x10^{-6}	9.7x10^{-5}	7.8x10^{-4}		.021	.079	.25
A($^3P_0$ − $^3P_1$)	d	5.8x10^{-8}	2.1x10^{-6}	2.6x10^{-5}	2.0x10^{-4}		.0061	.026	.046

Table 13(b). Total Transition Probabilities for $3p^2$ and $4p^2$ Configurations, in $\sec^{-1}$.

Transition	Type of Rad'n	$(3p^2)$ Si I	P II	S III	Cl IV	A V	K VI	Ca VII	$(4p^2)$ Ge I	As II
$A({}^3P_1 - {}^1S_0)$ λ	d	.036 6526.9	.23 4669.4	.89 3721.1	2.7 3116.3	7.1			1.6	
$A({}^3P_2 - {}^1S_0)$	q	.0023	.011	.031	.069	.135			.084	
$A({}^1D_2 - {}^1S_0)$ λ	q	1.7	3.6	5.1 6310.2	6.3 5322.2	7.3			1.8	
$A({}^3P_0 - {}^1D_2)$	q	1.5×10^{-6}	7.2×10^{-6}	2.3×10^{-5}	5.7×10^{-5}	.00013	.00028	.00056	.00010	.00062
$A({}^3P_1 - {}^1D_2)$ λ	d	.00095	.0060	.024	.075 7530.9	.20 6432	.49 5603	1.1 4939	.045	.21
$A({}^3P_2 - {}^1D_2)$ λ	d	.0027	.016	.062	.18 8046.1	.47 7003	1.1 6229	2.2 5616	.068	.37
$A({}^3P_0 - {}^3P_2)$	q	7.6×10^{-10}	1.3×10^{-8}	1.0×10^{-7}	5.8×10^{-7}	2.7×10^{-6}	1.0×10^{-5}	3.4×10^{-5}	7.3×10^{-6}	8.0×10^{-5}
$A({}^3P_1 - {}^3P_2)$	d	.000042	.00037	.0020	.0082	.027	.076	.19	.0082	.042
$A({}^3P_0 - {}^3P_1)$	d	.0000082	.000082	.00047	.0021	.0079	.026	.077	.0051	.021

Table 13(c). Total Transition Probabilities for $2p^3$ Configuration, in $\sec^{-1}$.

Transition	Type of Rad'n	N I	O II	F III	NeIV	Na V	Mg VI	Al VII	Si VIII
$A(^4S_{1\frac{1}{2}} - {}^2P_{1\frac{1}{2}})$ λ	d	.0090 3466.4	.078	.57		5.6	18	41	100
$A(^4S_{1\frac{1}{2}} - {}^2P_{\frac{1}{2}})$ λ	d	.0036 3466.4	.031	.23		2.2	7.2	16	39
$A(^2D_{1\frac{1}{2}} - {}^2P_{1\frac{1}{2}})$ λ	d,q	.077	.13 7330.3	.25 5733.0	.54 4719.7	1.3 4021.6	3.9 3503.0	8.5 3098.7	20
$A(^2D_{1\frac{1}{2}} - {}^2P_{\frac{1}{2}})$ λ	d,q	.15	.24 7330.3	.35 5733.0	.57 4719.7	1.1 4017.5	2.7 3500.4	5.6 3093.4	13
$A(^2D_{2\frac{1}{2}} - {}^2P_{1\frac{1}{2}})$ λ	d,q	.18	.27 7319.0	.39 5721.2	.60 4714.1	1.1 4015.3	2.6 3488.1	5.3 3074.0	12
$A(^2D_{2\frac{1}{2}} - {}^2P_{\frac{1}{2}})$ λ	q	.10	.15 7319.0	.19 5721.2	.22 4714.1	.26 4011.2	.29 3485.5	.32 3068.8	.38
$A(^2P_{\frac{1}{2}} - {}^2P_{1\frac{1}{2}})$	d		6.0×10^{-11}		8.9×10^{-9}	5.5×10^{-7}	1.6×10^{-5}	1.5×10^{-4}	2.2×10^{-4}
$A(^4S_{1\frac{1}{2}} - {}^2D_{2\frac{1}{2}})$ λ	d,q	.000032 5200.7	.00014 3729.1	.00060		.0029	.0089	.023	.062
$A(^4S_{1\frac{1}{2}} - {}^2D_{1\frac{1}{2}})$ λ	d,q	.000021 5198.5	.00011 3726.2	.00096		.022	.140	.470	1.86
$A(^2D_{1\frac{1}{2}} - {}^2D_{2\frac{1}{2}})$	d	8.2×10^{-9}	1.5×10^{-7}	7.5×10^{-7}	2.5×10^{-7}	2.5×10^{-7}	1.5×10^{-7}	1.9×10^{-6}	2.1×10^{-4}

Table 13(d). Total Transition Probabilities for $3p^3$ and $4p^3$ Configurations, in sec^{-1}.

Transition	Type of Rad'n	($3p^3$) P I	S II	Cl III	A IV	K V	Ca VI	Sc VII	($4p^3$) Se II
$A(^4S_{1\frac{1}{2}}-{}^2P_{1\frac{1}{2}})$	d	.10	.33	.97	2.5	6.1	14		7.0
λ		5332.4	<u>4068.5</u>	3342.7					
$A(^4S_{1\frac{1}{2}}-{}^2P_{\frac{1}{2}})$	d	.041	.13	.38	.98	2.3	5.1		2.2
λ		5339.7	<u>4076.5</u>	3353.4					
$A(^2D_{1\frac{1}{2}}-{}^2P_{1\frac{1}{2}})$	d,q	.12	.25	.50	1.0	2.2	4.5	9.6	2.9
λ					7169.1	6223.4	5460.0		
$A(^2D_{1\frac{1}{2}}-{}^2P_{\frac{1}{2}})$	d,q	.20	.36	.57	.94	1.7	3.1	6.0	1.9
λ					7263.3	6349.5	5631.6		
$A(^2D_{2\frac{1}{2}}-{}^2P_{1\frac{1}{2}})$	d,q	.25	.41	.63	.99	1.7	3.0	5.8	2.1
λ					7236.0	6316.6	5587.2		
$A(^2D_{2\frac{1}{2}}-{}^2P_{\frac{1}{2}})$	q	.12	.20	.26	.30	.34	.38	.41	.32
λ					7332.0	6446.5	5766.4		
$A(^2P_{\frac{1}{2}}-{}^2P_{1\frac{1}{2}})$	d	$1.5x10^{-7}$	$1.0x10^{-6}$	$7.6x10^{-6}$	$5.2x10^{-5}$	.00028	.0015	.0064	.0051
$A(^4S_{1\frac{1}{2}}-{}^2D_{2\frac{1}{2}})$	q	.00044	.0010	.0023	.0048	.0099	.022		.037
λ			<u>6717.3</u>	<u>5517.2</u>	<u>4711.4</u>	<u>4120</u>			
$A(^4S_{1\frac{1}{2}}-{}^2D_{1\frac{1}{2}})$	d,q	.00057	.0020	.0077	.029	.10	.34		.40
λ			<u>6731.5</u>	<u>5537.7</u>	<u>4740.3</u>	<u>4160</u>			
$A(D_{1\frac{1}{2}}-D_{2\frac{1}{2}})$	d	$3.5x10^{-8}$	$3.3x10^{-7}$	$3.2x10^{-6}$	$2.3x10^{-5}$	.00014	.00076	.0032	.0023

Table 13(e). Total Transition Probabilities for $2p^4$ Configuration, in sec^{-1}.

Transition	Type of Rad'n	O I	F II	Ne III	Na IV	Mg V	Al VI	Si VII
$A(^3P_2 - {}^1S_0)$	q	.0019	.0073	.019	.047	.10	.21	
$A(^3P_1 - {}^1S_0)$	d	.10	.66	2.6	9.0	27	69	
$A(^1D_2 - {}^1S_0)$	q	2.8	4.1	5.2	6.2	7.2	8.1	
λ		5577.3	4157.5	3342.8				
$A(^3P_2 - {}^1D_2)$	d	.013	.079	.31	1.1	3.2	6.2	21
λ		6300.2	4789.5	3868.7	3245			
$A(^3P_1 - {}^1D_2)$	d	.0040	.025	.096	.32	.90	2.2	5.3
λ		6363.9	4869.2	3967.5	3366			
$A(^3P_0 - {}^1D_2)$	q	2.0×10^{-6}	7.1×10^{-6}	1.7×10^{-5}	3.6×10^{-5}	6.9×10^{-5}	1.2×10	2.2×10
$A(^3P_2 - {}^3P_0)$	q	2.3×10^{-10}	3.6×10^{-9}	3.6×10^{-8}	2.6×10^{-7}	1.5×10^{-6}	7.2×10^{-6}	3.0×10^{-5}
$A(^3P_1 - {}^3P_0)$	d	.000017	.00018	.0012	.0055	.022	.070	.19
$A(^3P_2 - {}^3P_1)$	d	.000088	.00089	.0059	.030	.13	.45	1.5

Table 13(f). Total Transition Probabilities for $3p^4$ and $4p^4$ Configurations, in sec^{-1}.

Transition	Type of Rad'n	$(3p^4)$ S I	Cl II	A III	K IV	Ca V	Sc VI
$A(^3P_2 - {}^1S_0)$	q					.60	1.0
$A(^3P_1 - {}^1S_0)$	d					23	47
$A(^1D_2 - {}^1S_0)$	q					11	12
λ						3996.3	3590.8
$A(^3P_2 - {}^1D_2)$	d	.056		.45	1.1	2.5	5.5
λ				7135.7	6101.1	5308.9	4672.2
$A(^3P_1 - {}^1D_2)$	d	.016		.12	.27	.55	1.1
λ				7751.0	6794.8	6085.9	5539.6
$A(^3P_0 - {}^1D_2)$	q	2.2×10^{-5}		7.0×10^{-5}	.00011	.00017	.00024
$A(^3P_2 - {}^3P_0)$	q	2.2×10^{-7}	1.2×10^{-6}	7.6×10^{-6}	3.0×10^{-5}	.00010	.00031
$A(^3P_1 - {}^3P_0)$	d	.00030	.00094	.0051	.015	.035	.076
$A(^3P_2 - {}^3P_1)$	d	.0014	.0073	.031	.10	.31	.83

Table 13(g). Total Transition of Probabilities for $3p^4$ and $4p^4$ Configurations (cont.)

Transition	Type of Rad'n	($3p^4$) Ti VII	V VIII	Cr IX	Mn X	Fe XI	($4p^4$) Se I
A($^3P_2 - {}^1S_0$)	q	1.8	2.9	4.8	7.8	13	.73
A($^3P_1 - {}^1S_0$)	d	92	160	300	580	890	6.8
A($^1D_2 - {}^1S_0$)	q	12 3261.7	13	15	15	16	5.3
A($^3P_2 - {}^1D_2$)	d	12 4144.8	23 3686.3	47 3273.5	90	170	.82
A($^3P_1 - {}^1D_2$)	d	2.1 5105.6	3.7 4733.5	6.6 4407.9	11 4407.9	19 3871.9	.14
A($^3P_0 - {}^1D_2$)	q	.00034	.00048	.00069	.00099	.0014	.00011
A($^3P_2 - {}^3P_0$)	q	.00082	.0020	.0045	.0086	.018	.00039
A($^3P_1 - {}^3P_0$)	d	.13	.21	.27	.25	.28	.0085
A($^3P_2 - {}^3P_1$)	d	2.0	4.7	10	21	42	.17

Table 14.

Transition Probabilities for $3d^2$ Configuration of Fe VII, in sec^{-1}.

F_2 = 1986 cm^{-1} b = .0294 u = 0.00393
F_4 = 137.5 cm^{-1} d = .0425 v = -.0188
ζ_{3d} = 742 cm^{-1} f = .713
s_2 = 1.87 at. units k = 0.318

Transition	Mag. Dipole Trans. Prob.	Elec. Quad. Trans. Prob.	Total Trans. Prob.	Wave Lengths	Observed Rel. Intensities NGC 7027
$A(^3P_2 - {}^1S_0)$		4.86	4.9		
$A(^3P_1 - {}^1S_0)$	8.95		9.0		
$A(^1D_2 - {}^1S_0)$		55.3	55		
$A(^3F_2 - {}^1S_0)$		.585	.59		
$A(^3P_2 - {}^1G_4)$		.000268	.00027		
$A(^1D_2 - {}^1G_4)$		.00354	.0035		
$A(^3F_4 - {}^1G_4)$	.542	.00872	.55	3759.9	< 5
$A(^3F_3 - {}^1G_4)$	.374	.000885	.37	3587.2	
$A(^3F_2 - {}^1G_4)$		.00192	.0019	3457.3	
$A(^3P_1 - {}^3P_2)$	.00732	1.49×10^{-8}	.0073		
$A(^3P_0 - {}^3P_2)$		4.20×10^{-8}	4.2×10^{-8}		
$A(^1D_2 - {}^3P_2)$	.203	2.19×10^{-7}	.20		
$A(^3F_4 - {}^3P_2)$		.162	.16	5276.1	3 ±
$A(^3F_3 - {}^3P_2)$	.104	.00619	.11	4942.5	3 ?
$A(^3F_2 - {}^3P_2)$	.0283	.00977	.038	4699.0	
$A(^3P_0 - {}^3P_1)$	.00107	0	.0011		
$A(^1D_2 - {}^3P_1)$	.0580	1.94×10^{-6}	.058		
$A(^3F_3 - {}^3P_1)$		.224	.22	5158.3	5
$A(^3F_2 - {}^3P_1)$	.00291	.114	.12	4893.9	3 ?
$A(^1D_2 - {}^3P_0)$		8.95×10^{-7}	9.0×10^{-7}		
$A(^3F_2 - {}^3P_0)$		.312	.31	4989.4	4 ?
$A(^3F_4 - {}^1D_2)$		.00686	.0069	6599.7	
$A(^3F_3 - {}^1D_2)$	.801	.00194	.80	6085.5	<4
$A(^3F_2 - {}^1D_2)$	.345	.00143	.35	5720.9	4
$A(^3F_3 - {}^3F_4)$	.0419	6.16×10^{-9}	.042		
$A(^3F_2 - {}^3F_4)$		5.21×10^{-9}	5.2×10^{-9}		
$A(^3F_2 - {}^3F_3)$	.0294	2.79×10^{-9}	.029		

VII. DISCUSSION OF THE RESULTS, AND CONCLUSIONS

A. Validity of the Method

The theoretical derivation of the formulae used in the calculations involves the following assumptions:

1. The electrons may to a first approximation be regarded as moving in a central field, without mutual interaction. That is, the difference between the mutual electrostatic interaction of the electrons and some appropriately chosen central potential field is small enough to be treated by first-order perturbation theory.
2. Each electron in a given configuration is assumed to move in the same effective central potential field, so that the radial parts of the one-electron wave functions is independent of the m_ℓ values of the individual electrons.
3. The electrostatic interactions between configurations may be neglected.
4. The spin-orbit interaction between configurations may be neglected.
5. The spin-orbit interaction is very small in comparison with the electrostatic interaction.

The first two of these assumptions are necessary for the Slater method of handling many-electron problems (CS, Chapter 6). The second is involved also in the theory of the Hartree self-consistent field. The neglect of configuration interaction and of the spin-orbit perturbation then leads to the Russell-Saunders scheme of characterizing energy levels (CS, Chapter 7), in which the theoretical expressions for the term levels are derived which are listed in Tables 1(c), 2(c) and 3(d) for the configurations of interest here. The fifth assumption is also necessary in the discussion given in section III of the breakdown of pure Russell-Saunders coupling.

Some doubts are cast on the validity of the Slater treatment by the partial lack of agreement of the theoretically predicted term separations with the experimentally observed separations. Thus for the $2p^2$ configuration the Slater treatment predicts the interval ratio

$$\frac{E(^1S) - E(^1D)}{E(^1D) - E(^3P)} = 1.50$$

For CI, N II and O III this ratio turns out to be about 1.14 (CS, § 5^7). It may be possible to account for the discrepancy on the basis of interaction of the $2p^2$ configuration with the 2p np configurations or with the $2p^4$ configuration. Similar discrepancies occur for the p^3 and p^4 configurations. For the $3d^2$ configuration of Fe VII it is seen from Figure 3 that the Slater formulae do not fit very well. Here also configuration interaction may be the cause of the discrepancy.

Difficulties also arise in the comparison of the theoretical expressions for the multiplet intervals with the observed values. These differences could perhaps also be resolved if a treatment of the configuration interaction were available.

The size of the spin-orbit interaction relative to the electrostatic interaction determines the extent of breakdown of LS coupling. A measure of this breakdown of coupling is obtained from the coefficients a,b,c, ... , which give the wave functions for the perturbed system in terms of the unperturbed Russell-Saunders wave functions. It is seen from the numerical data in Tables 12 and 14 that these coefficients are for the most part small, being less than 0.1. This furnishes a justification for the use of the first-order approximation method, since the second-order corrections are of the order of (0.1) times the first-order terms.

However, the coefficients of breakdown of coupling increase with increasing degree of ionization. The first-order treatment is therefore less dependable for the more highly ionized atoms. In the case of Fe VII, one of the coefficients is numerically about 0.3. Hence the first-order treatment there is probably inadequate.

The treatment of the s_2 integral is also rather inadequate, as may be seen from an inspection of Table 10. A more complete set of Hartree self-consistent field wave functions would clear up this difficulty to a great extent.

In spite of all the difficulties discussed above, the method is substantially a sound one. This is borne out by the reasonably good agreement which is obtained with the observed intensities in nebular and novae spectra.

B. Accuracy of the Results

All of the calculations were carried out to three figures, and two figures were retained as significant in the final results. It is hoped that the numerous checking devices which were used succeeded in eliminating numerical errors in calculation.

The determination of the parameters F_2, F_4, ζ, and the coefficients in the breakdown of pure Russel-Saunders coupling is complicated by the difficulties discussed in the preceding section. A detailed analysis of the p^2, p^3 and p^4 configurations was made by Robinson and Shortley[19], and the values which they determine for the parameters are probably as good as one could get without a complete investigation of the effect of configuration interaction. These values should be good to within 5%.

In the case of Fe VII, the parameters chosen may be as much as 10% off, due to the difficulties illustrated in Figure 3. The choice of the parameters F_2 and F_4 is unfortunately quite critical for the evaluation of the coefficient k (defined in Table 3(f)), due to the factor (F_2 - 12 F_4) in the denominator. A change of k in either direction by a factor of two is quite feasible. It is suspected, however, that the value of k actually chosen is somewhat too large numerically. The large value of k also renders the first order approximation treatment for Fe VII probably inadequate. A complete second-order perturbation treatment would probably change some of the transition probabilities by as much as 15%.

The evaluation of the integral s_2 introduces an additional uncertainty into the absolute values of the electric quadrupole transition probabilities. From Table 10 it is seen that the value of s_2^2 (which occurs in all the electric quadrupole transition probabilities) is uncertain by about a factor of two.

Summarizing the above discussion, it would seem that the magnetic dipole transition probabilities are accurate in absolute value to within about 25% for the p^k configurations; and the electric quadrupole transition probabilities should be good in absolute value to within a factor of two. The relative values for purely dipole transitions, or for purely quadrupole transitions, are of course considerably more accurate. Until the difficulties in the $3d^2$ configuration of Fe VII are cleared up, so that the value of k can be reliably determined, the results obtained for Fe VII are valid only as an indication of the type of results to be expected for this atom.

C. Agreement with Observation

From the results listed in Tables 11(a), (b) and (c) it is seen that the agreement of the observed relative intensities of lines possessing the same upper level with the theoretically predicted relative values is quite good for the observed forbidden lines of O III, O II and O I. The agreement for other atoms of the p^k configurations is also quite satisfactory. Of course it is to be remembered that the observable lines possessing the same upper level usually are members of a multiplet, for which approximate values of the relative intensities are predictable without the extended analysis presented here.

The agreement with observation for the relative intensities in the case of Fe VII is surprisingly good, in view of the difficulties discussed above. The theoretical results present all the features of the observed relative intensities. This suggests that the deficiencies of the theory may have been overestimated.

D. General Features of the Results

As Condon pointed out from his calculations[10)], it is of interest to note that in many cases the magnetic dipole transition probabilities in a multiplet are much larger than the electric quadrupole probabilities for the same multiplet. In particular, this is true for all the atoms in the p^2 and p^4 configurations, and for most of the multiplets of Fe VII.

It is also of considerable interest to note that in all of the cases which were calculated, the probabilities of transitions between levels of the same term are negligibly small in comparison with the probabilities of other transitions from the same upper level. This is of importance in the discussion of the intensities of the lines. For the probabilities of the unobservable intra-term transitions enter into the denominator of the formula (6) of section II, which gives the intensities of other lines having the same upper level. Hence the latter lines would be weakened tremendously if the intra-term transition probabilities were relatively large.

E. Some Special Results for O III

1. The Line $^3P_0 - {}^1D_2$. According to the calculations recorded in Table 11(a), the line $^3P_0 - {}^1D_2$ for O III possesses a non-vanishing

transition probability, about 1/10,000 that of the strongest line of the multiplet $^3P - {}^1D_2$. This result clears up the problem which developed when Bowen and Wyse11) observed this line, although it had been predicted by Condon10) to have a zero probability. The observed intensity of the line relative to the other lines of the multiplet is somewhat greater than the calculated value, and therefore agrees better with Stevenson's result (cf. Table 11(a)).

The Permitted Lines of O III. Professor I. S. Bowen has pointed out one further result of considerable interest that can be deduced from the transition probability calculations. It was found some time ago that a few of the permitted lines of O III were observed in nebular spectra. These lines were either transitions from the level 2p3d^3P to lower levels, or transitions from these lower levels down to still lower levels. In 1935 Professor Bowen29) interpreted this phenomenon on the basis of the almost exact coincidence between the wave length of the resonance line of He II and the wave length of the O III line 2p^2 $^3P_2$ - 2p3d$^3P_2$. He assumed that some of the radiation available in the nebulae in the form of this resonance line of He II is absorbed by atoms of O III in the level 2p^2 $^3P_2$, thus raising these atoms to the energy level 2p3d$^3P_2$, from which they descend with the emission of permitted lines.

Since the 2p^2 $^3P_2$ level is not the ground level of O III, the above mechanism of excitation could apply only if a large proportion of the atoms of O III existed in the $^3P_2$ level instead of in the ground level $^3P_0$. This state of affairs would be impossible if the transition probabilities between the levels of the ^3P term were much larger than the probability C of removal from the $^3P_2$ level by collision (see section II). For if the transition probabilities were much larger than C, then atoms could not remain in the upper levels long enough for thermodynamic equilibrium to be established between the atoms in the $^3P_0$, $^3P_1$ and $^3P_2$ levels under the influence of collisions. Hence the population of the $^3P_2$ level would be depleted.

From table 11(a) we see that

$$A(^3P_1 - {}^3P_2) = 9.7 \times 10^{-5} \text{ sec}^{-1}$$
$$A(^3P_0 - {}^3P_2) = 5.8 \times 10^{-11} \text{ sec}^{-1}$$
$$A(^3P_0 - {}^3P_1) = 2.6 \times 10^{-5} \text{ sec}^{-1}$$

That these values are smaller than the collision probability C can be established by the following consideration. In comparing the intensities of the forbidden lines of O I, O II and O III in the nebulae, the transition $^2D - {}^4S$ of O II is found to be only 1/5 to 1/10 as strong as it should be if C were neglected in the intensity formulae. This means that C is about five to ten times as large as the probability of this transition. But, from Table 11(b), the value of $A(^2D - {}^4S)$ is about 1×10^{-4} sec^{-1}. Hence C is about 5 or 10 x 10^{-4} sec , which is considerably larger than $A(^3P_{1,0} - {}^3P_2)$. Thus the condition for existence of the above absorption mechanism of excitation of O III is fulfilled.

F. Concluding Remarks

A fundamental difficulty present in the method of calculation of transition probabilities which has been described here is the lack of precise information about the effect of configuration interaction. A thorough investigation of this effect might resolve many of the bothersome points which arose in the calculations.

The method of calculation appears to be capable of extension to the d^3 configuration, although the complexity of the calculations would be increased by the large number of energy levels in this configuration. This extension would have important applications6), especially in connection with the lines of Fe VI and Fe II (the latter because of Shortley's treatment of nearly closed shells20)).

In conclusion, it is hoped that the numerical results obtained here will be of value in the investigations of forbidden lines, and in the interpretations of astrophysical nature to which these investigations lead.

BIBLIOGRAPHY

1) Condon and Shortley, 'The Theory of Atomic Spectra", (1935). This book is referred to in the thesis as 'CS'.

2) I. S. Bowen, Publ. Astron. Soc. Pacific 39, 295 (1927); Astro-Phys. Journ. 67, 1 (1928).

3) J. C. McLennan, Proc. Roy. Soc. A, 120, 327 (1928).

4) J. W. Merrill, Contr. Mt. Wilson Obs., 354 (1928); 460 (1933).

5) Bowen and Wyse, Lick Observatory Bulletin (1939).

6) I. S. Bowen, Rev. Mod. Phys. 8, 55 (1936).

7) J. H. Bartlett, Phys. Rev. 34, 1247 (1929).

8) A. Rubinowicz, Zeits. fur Phys. 65, 662 (1930); Ergeb. der exakten Naturwiss., 11, 170 (1932).

9) A. F. Stevenson, Proc. Royal Soc. A. 137, 298 (1932).

10) E. U. Condon, Astrophys. Journ. 79, 217 (1934).

11) Bowen and Wyse, Publ. Astron. Soc. Pacific 50, 348 (1938)

12) P. A. M. Dirac, 'Quantum Mechanics', Chapt. 11.

13) H. C. Brinkman, Physica 1, 97 (1933).

14) J. H. Bartlett, Phys. Rev. 38, 1623 (1931).

15) E. Wigner, Gruppentheorie, p. 206.

16) G. N. Bailey, Generalized Hypergeometric Functions, (Camb. Tract No. 32), page 23.

17) Gray and Wills, Phys. Rev. 38, 248 (1931).

18) E. C. Kemble, Fundamental Principles of Quantum Mechanics, page 384.

19) Robinson and Shortley, Phys. Rev. 52, 713 (1937).

BIBLIOGRAPHY (continued)

20) G. H. Shortley, Phys. Rev. 40, 185 (1932).

21) H. L. Brinkman, Zur Quantenmechanik der Multipolstrahlung, p. 53.

22) Born and Jordan, Elementare Quantenmechenik.

23) Güttinger and Pauli, Zeits. fur Phys. 67, 743 (1931).

24) Bacher and Goudsmit, Atomic Energy States [N I, O I, Cl II, Si I, Ge I].

Badermi and Rao, Proc. Royal Soc. A 140, 597 (1933) [Ge I, As II, Se III].

Bowen, Phys. Rev. 45, 401 (1934); 46, 377 (1934) [Cl III, Cl IV].

Bowen, unpublished [A V].

Bowen, Phys. Rev. 46, 791 (1934) [K IV, K V, Ca V, Ca VI].

Bowen and Edlén, Nature 143, 374 (1939) [Fe VII].

Boyce, Phys. Rev. 46, 378 (1934) [Ne III, Ne IV].

Boyce, Phys. Rev. 48, 396 (1936); 49, 351 (1936) [A III, A IV, A V].

Edlén, Nova Acta Req. Soc. Sci. Ups., 1934. [C I, N II, O II, O III].

Edlén, Zeits. fur Phys. 92, 19 (1934) [F IV].

Edlén, Zeits. fur Phys. 93, 433 (1935) [F II, F III].

Edlén, Zeits. fur Phys. 104, 188 (1937) [Ti VII, V VIII, Cr IX, Mn X, Fe XI].

Ekefors, Zeits. fur Phys. 63, 437 (1930) [N I].

Hunter, Trans. Royal Soc. A 233, 303 (1934) [S II].

Martin, Phys. Rev. 48, 938 (1935) [Se II].

BIBLIOGRAPHY (continued)

Murakawa, Zeits. fur Phys. 96, 117 (1935) [Cl II].

Pattin and Kruger, Phys. Rev. 51, 1019 (1937); 52, 621 (1937) [Sc VI, Sc VII].

Robinson, Phys. Rev. 49, 297 (1936) [P I, P II].

Robinson, Phys. Rev. 52, 724 (1938); Nature 137, 992 (1936) [S III, K VI, Ca VII].

Ruedy, Phys. Rev. 44, 758 (1933) [S I].

Ruedy and Gibbs, Phys. Rev. 46, 880 (1934) [Se I].

Soderqvist, Nova Acta Reg. Soc. Sci. Ups., 1934 [Na IV, Na V, Na VI, Mg V, Mg VI, Mg VII, Al VI, Al VII, Al VIII, Si VII, Si VIII].

25) Hartree and Black, Proc. Royal Soc. A, 139, 311 (1933).

26) Bowen and Edlén, Nature 143, 374 (1939).

27) W. M. Cady, Phys. Rev. 43, 322 (1933).

28) Brown, Bartlett and Dunn, Phys. Rev. 44, 296 (1933).

29) I. S. Bowen, Astrophys. Journ. 81, 1 (1935).