41. ON THE EXPLANATION OF COMPLICATED SPECTRA OF ELEMENTS

During the whole of the last century the belief was almost universal that the atom was an indivisible particle of mass with certain combining powers. This belief is now completely shattered owing to the discovery of the proton and the electron, and recognition of the fact that all elements are made up of these primordial elements. But the first suspicion on the indivisibility of the atom was thrown from studies on spectroscopy, in which it was found that even the simplest element viz. hydrogen does not give a single line, but apparently a fairly large number of lines. An element like iron gives in the visible range not less than 6000 lines. This fact led Rowland to remark that the atom is more complicated than even a grand piano.

It is not so well-known that long before the discovery of the electron, Sir Norman Lockyer, guided by his experience on the spectrum of different classes of stars, put forward the hypothesis of protoelements and subatomic particles. Prof. A. Fowler (1) informs us that Lockyer performed thousands of experiments to break up the elements by purely electrical discharge. The elements were indeed being broken up, but Bohr's theory had not yet appeared, and he had no means of interpreting his results. Icarus-like were his attempts and their significance was quite unappreciated at his own times.

The spectrum is the most characteristic property of the atom, and it was perceived long ago that the proper interpretation of spectroscopic data is the key to the progress of atomic physics. But the task of interpretation is not so simple. Ever since the discovery of spectrum analysis by Kirchoff about seventy years ago, spectroscopic data are accumulating such quantity that even the seven thick volumes of Kayser and Runge, and Konen are barely sufficient for reporting all the results. The vastness of the data combined with their complexity repelled even the greatest physicists of the last century against such an attempt. A great physicist once declared that he did not wish to engulf himself in the bog of spectroscopy.

The various steps by which a better understanding of spectroscopic data has been arrived at are now well-known. The first great landmark was Balmer's discovery of regularity in the hydrogen spectrum. Close upon this, followed the researches of Rydberg and Ritz on the alkali-spectrum, the discovery of the principle of combination and of the universal Rydberg constant. While the work of systematisation of spectroscopic data was being continued by Fowler

and Paschen, there appeared in 1912, the epochmaking work of Bohr on the hydrogen spectrum, which gave the first Rutherford's atomic model; it also opened a general way for the interpretation of spectra. After Bohr's work, progress has been more rapid, and we can notice the following chief landmarks: Sommerfeld's generalisation of Bohr's theory (2), and the introduction of the various quantum number, n, k, j, r, m; Sommerfeld and Kossel's displacement law (3); Catalan's discovery of mutiplets (4); Landé's theory of Zeeman effect (5). The gradual clearing of our ideas on the electronic composition of atoms in the hands of Bohr, Stoner and Mainsmith; Pauli's principle of exclusion, and recognition of the fact that the doublet (or alkali type of) spectrum is the fundamental type (6). Pauli, Russel, Saunders (7) and Heisenberg's (8) principle of orbit or term synthesis. Utilising these principles, Hund (9) has achieved the apparently impossible task of explaining the whole data in complex spectra. Simultaneously a new quantum-mechanics has arisen in which, though much is still obscure, it is sure that a new way has been opened in the investigation of the atomic world. This is the wave-mechanics of De-Broglie-Schrödinger (10) with which the matrix-mechanics of Heisenberg, Born and Jordan (11) and the non-commutative mechanics of Dirac (12) are associated. We have also come to recognise that the electron is not merely a point-charge of electricity, but is also probably the fundamental magnetic unit—a fact which was first clearly stated by Goudsmit and Uhlenbeck (13). On the experimental side, we must mention the works of Millikan and Bowen who by applying the irregular doublet law, have very largely extended our knowledge of spectra of stripped atoms in the Schumann region.

The mechanical interpretation of spectra begun by Bohr and continued by Sommerfeld and others is however changing in a perplexing, rather kaleidoscopic way within the last few years. With Bohr, we believed in nonradiating orbits and quantum transitions. In Sommerfeld's generalisation not less than four quantum numbers had to be introduced to account for complex spectra, and were interpreted in terms of different mechanical quantities. Thus taking the symbol $n^r{}_{kj}$, to denote a spectral term, according to Sommerfeld,

n = total quantum number (i.e. energy of the orbit

approximately $= -R \dfrac{(z-s)^2}{n^2}$.

k = azimuthal quantum number 1, 2, 3, 4, for s, p, d, f orbits.

r = multiplicity quantum number, denoting the resultant magnetic moment of the atomic residue (rest of the atom minus the valence electron) 1, 2, 3, 4 for singlets, doublets, triplets, etc.

j = inner quantum number, defining the total magnetic moment of the atom which consists of magnetism due to the atomic residue plus magnetism due to the orbital motion of the valence electron. j is thus the vector sum of k and r.[1]

m = magnetic quantum, and is simply the quantumlike projection of j on a definite axis in space.

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[1] It is not yet clear how this magnetism arises. The idea of spinning introduced by Goudsmit and Uhlenbeck is merely symbolic. An attempt of Einstein to explain the existence of the electron from considerations of the theory of relativity has not yet borne fruit. (Einstein: Berl. Sitzungsberichte 1925). See also a discussion in "Nature", Vol. 116, p. 316.

It has been found that though all these quantum numbers (and probably more) e.g. five quantum numbers are required to describe an optical term completely, the mechanical interpretation put on these numbers is not always certain. In the original Bohr-Sommerfeld theory, all the quantum numbers were integral; gradually from study of Band spectra and Zeeman effect, half quantum numbers had to be introduced. Even before the rise of wave mechanics, it was found necessary to introduce associated quantum number. Thus instead of k, we now use i_k,

$$i_k = 0, 1, 2, 3 \text{ for } s, p, d \text{ and } f\text{-orbits}$$

which shows that an atom in the s-state (rather) has no magnetic moment, i.e. the first s-state say of hydrogen, does not correspond to an electron revolving in a circular orbit, but to a state inexpressible in ordinary mechanical terms; the magnetic moment being zero.

CHART I.

Similarly the mechanical interpretation put on the other quantum numbers has to be changed, and the meaning of some of them are still a bit mysterious.

Owing to the uncertainty in the meaning of the quantum numbers, I have attempted to present Hund's interpretation of spectra in terms of quantum numbers alone, dispensing with the mechanical analogy as much as possible (it is often impossible to do so). The main innovation consists in the introduction of a new atomic chart illustrating the electronic composition of atoms. It ought to be mentioned that the chart has been evolved out of the original conceptions of Bohr and Mainsmith-Stoner. It gives in one diagram a graphical representation of the origin of X-ray spectra, the periodic classification of elements, and origin of optical spectra. No new principles have been evolved, but principles already discovered have been represented in a new way.

On the Electronic Composition of Atoms.

Explanation of the Chart.—For an understanding of the chart, let us consider how the element with the atomic number N is built up. We have in the centre a nucleus with the positive charge N. We have to bring up N electrons about it one by one. These electrons take their position in different levels possessing definite quantummechanical characteristics. These levels are graphically shown in chart 1. They are first differentiated according to their total quantum number n. The innermost level K, has $n=1$, (mechanically, it roughly signifies that if an electron is in the K-orbit, it will have the energy $= - R \dfrac{(z-1)^2}{1^2}$). The K-level is single.

For the next level, $n=2$, and they are denoted by L. X-ray absorption experiments however show that the L-level is apparently triple i.e. consists of three sublevels. These were designated by L_{11}, L_{21}, L_{22} (here instead of L_{21} we write L_2; L_{21}, L_{22} are combined under L_2).

For the next level, $n=3$, and they are denoted by M. M is apparently quintuple, and the sublevels are denoted by M_{11}, M_{21}, M_{22}, M_{32}, M_{33} (denoted by M_1, M_2, M_3 in the chart).

We have now to explain the subscripts. They were introduced to explain the observed combinations and a perfect analogy which was discovered by Pauli between the X-ray levels, and the optical levels of the valency electron in alkali-spectrum say, in the spectrum of Na. As this analogy is of far-reaching importance, we shall dwell upon it more in detail. The optical terms of Na with their n, k, j-values are shown in diagram 1.
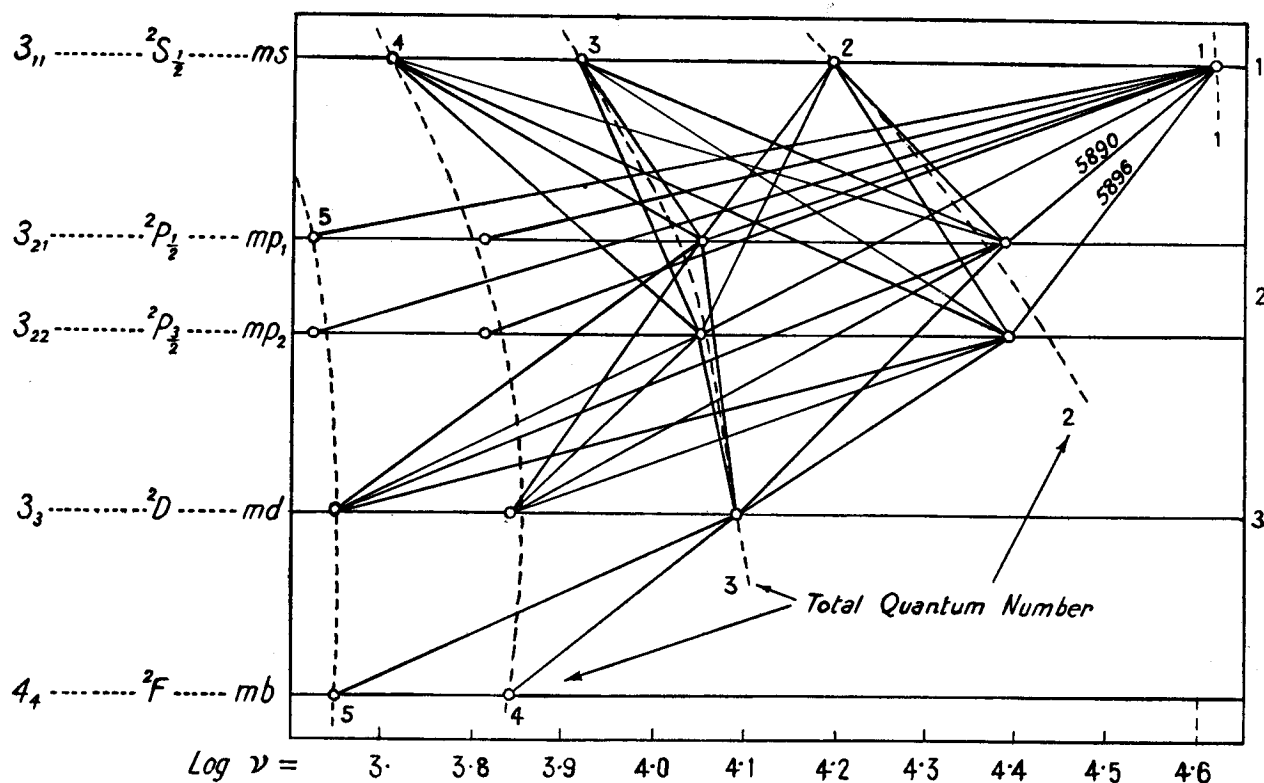
Diagram 1.

In the spectrum of Na, the fundamental level is a doublet S-term, for which $k=1$, $j=1$, $n=1$ according to the Sommerfeld-Landé notation. We can also designate the term according to the new notation introduced by Saunders and Russell. Then this would be written as $1\ ^2S_1$ (first term of the doublet S-series, with $j=1$). This term is followed by its Rydberg sequence for which n varies from $2, 3, \ldots$ They are shown in diagram 1), in the Saunders-Russell notation.

The next family is the doublet p-series, for which $k=2$, and each term is double. This fact is expressed by introducing a new quantum number j, and giving it the values 1 and 2 for the two terms respectively. The chief quantum number n begins with 2.

Then follows the doublet d-series, having $k=3$, $j=2$, 3 and n beginning with 3.

We therefore see that in the spectrum of Na, we can thus differentiate amongst the different groups of terms according to their chief quantum numbers.

(1) $n=1$; there is only one term $1^2S_1\ldots$ analogous to K_1 in the chart 1).

(2) $n=2$; there are three terms
$$2^2S_1\ ,\ \ \overbrace{3^2P_1\ \ {}^2P_2}$$

Corresponding to L_1, L_2 in chart (1).

(3) $n=3$; there are five terms
$$3^2S_1\ \ ,\ \ \overbrace{3^2P_1\ \ {}^2P_2}\ \ ,\ \ \overbrace{3\ ^2D_2\ \ 3\ ^2D_3}$$

corresponding to M_1, M_2, M_3 in chart (1).

The analogy is complete not only as regards n-values, but also as regards the k and j values; r is of course always$=2$. This perfect correspondence of the quantum-mechanical values for the two diagrams is derived from the observed combinations, and the particular k, j-values were assigned to the different levels to explain the combinations. We can say that the atomic chart(1) is simply the diagram(1) written in a slightly different form, and with slightly different meaning for each level.

The difference in the significance of the corresponding levels, say L_2, and ^2P is easily grasped. The optical levels of Na correspond to the position of the outermost electron when this is excited. The various K, L, M-levels in the chart indicate the quantum mechanical characteristics of any constituent electron, inner or outer, as they are brought up to build up the atom. The analogy suggests a periodicity, or reoccurrence of levels with the same quantum character-istics and this recurrence is at the basis of the quantum explanation of the periodic classification of elements, and periodicity in the structure of spectra. The periodicity is apparent from chart (1). Thus

(1) K_1, L_1, M_1 ... i.e. all levels lying along the first

diagonal with the same subscript, 1, impart to the electrons contained in them, the same quantum characte-ristics as are possessed by the $^2S_1$—term of alkalies. They differ only in the n-values. The electrons lying in such levels may for the sake of brevity be called s-electrons.

(2) L_2, M_2, N_2 ... i.e. all levels lying along the second diagonal with the subscript, 2, impart to the electrons contained in them the same quantum characteristics as are possessed by the P-terms of alkalies. The n-values begin from 2 (for L_2). The electrons lying in such levels may be called p-electrons.

Similarly electrons under M_3 or X_3 may be called d-electrons.

Let us now make the very important assumption—in fact an assumption which includes the whole significance of the present paper—that whatever the charge on the atomic nucleus may be, *the levels shown in chart 1) are always poten-tially present*. We have to make the further assumption that the levels can contain a maximum number of electrons, which is definite for each level. These numbers were first correctly given by Stoner, and explained by Pauli (13) on the basis of his famous principle of exclusion (Paulische Verbot). These numbers are 2 for an s-level (K, L ...), 6 for a p-level (L, M ...), 10 for a d-level (M, N ...) as indicated in the chart 1).

There are many points in the above sketch which will appear quite mysterious at the first reading. But without trying to lift up the mystery at this point, we shall follow the chart to its logical consequence. A glance at the chart shows that it affords a satisfactory explanation of the group-ing of elements with periodic repetitions of chemical and physical properties, if we suppose *that these properties depend entirely upon the constitution of the outermost shells*. The closed groups are chemically inert, e.g. He, Ne, or A .... In Li, Na, K, Rb and Cs ... there is only one s-electron outside of the closed groups, and hence they possess identical chemical properties. We shall return to this point later on. Let us now see how the spectra of elements can be explained from the atomic chart.

For this, we have to follow the assertion made pre-viously "*whatever the charge on the atomic nucleus may be, the levels shown in chart 1) are always potentially present*" to its logical consequence. This leads us to the following rules for.

The Deduction of the Nature of the Spectrum from the Atomic Chart.—Write out the K, L ... levels as in the atomic chart and below each write out the full number of electrons. Stop when the number of electrons is equal to the atomic number. Then take the last electron, and make it run through the higher unfilled levels. We get all the optical terms.

As the simplest case we take Na. We have the structure diagram shown below.

STRUCTURE DIAGRAM OF Na

K
2

L_1 L_2
2 6

M_1 M_2 M_3
(1) (1) (1)

N_1 N_2 N_3
(1) (1) (1)

O_1 O_1 O_1
(1) (1) (1)

| S-Series ^2S | P-Series ^2P | D-Series ^2D |
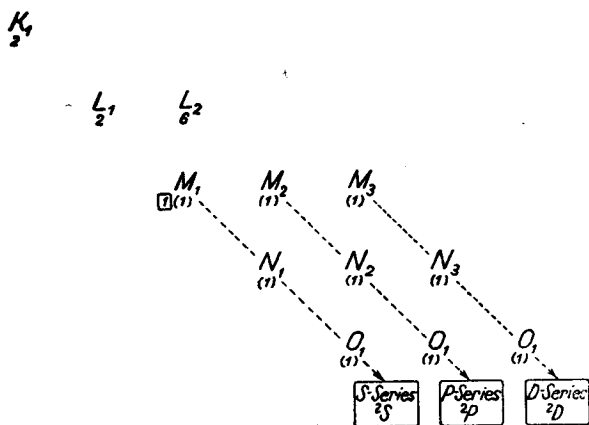
Sodium contain 11 electrons. Of these 2 fill up the K-level and 8 the L-levels completely. The remaining electron is normally at M_1 ... the normal level is $^2S_1$. The next transitions are shown by the symbol (1). We get successively the ^2P, ^3D-terms. All terms arising from a diagonal displacement from the successive numbers of a Rydberg sequence. This is indicated in the structure diagram. If we take any other alkali element, say Li, K, Rb or Cs, we find the same story repeated.

Rules of Transition.—We know that the s-terms can combine with p-terms only, and cannot generally combine with another s-term or a d-term. To come from a s-term to a p-term, we must displace the electron (horizontally or vertically both being regarded equal; but not diagonally) an odd number of times. To come from an s-term to another s-term or d-term, the number of displacements required is even. So we may formulate a general principle:—*Only such transitions of the electron are possible which involve an odd number of displacements. An even number of displacements is forbidden.*

We shall see that this rule is of universal application.

The Hydrogen Spectrum.—The hydrogen spectrum being the simplest, it would have been rather disconcerting if its spectrum did not correspond to the fundamental doublet type as it will be according to the rule given above. Landé was the first to show that the optical levels of hydrogen correspond in every respect to the levels of the alkali spectra and this fact was later elucidated by Goudsmit and Uhlenbeck, and Sommerfeld and Unsöld (15). There are therefore one set of s-terms, a double set of p-terms, a double set of d-terms. For practical purposes, the first two double set of p-terms need be considered because the other differences are rather too small. The fine structure of hydrogen lines is therefore not due to relativity-effect, but arises from the same cause as in the alkalies.

Spectra of Two Valence Elements.—Under the heading, we include the spectra of He, Be, Mg, Zn, Cd, Ca, Sr, Ba.

But for the sake of convenience, we shall begin with the spectrum of Mg. Let us write out the structure diagram.

We see that after the K and L-levels have been completed, there are two electrons at M_1. The normal orbit of Mg arises when both electrons are at M, the higher terms arise when one is kept permanently at M_1, the other is allowed to run through the higher levels.

STRUCTURE DIGRAM OF Mg

K
2

L_1 L_2
2 6

M_1 M_2 M_3
(1) (1) (1)

N_1 N_2 N_3
(1) (1) (1)

O_1 O_1 O_1
(1) (1) (1)

| S-Series ^1S ^3S | P-Series ^1p ^3p | D-Series ^1D ^3D |
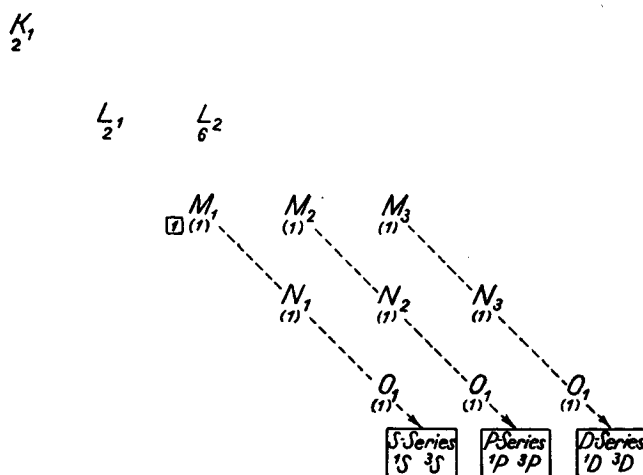
Let us now write out the term-levels of Mg. We are reproducing actually the term-scheme of Hg from ((Handbuch der Physik)), Band 23, (Quanten). The two term schemes are essentially the same, only in Hg, the P, and D-separations are much larger, and hence the scheme is shown to greater advantage (Diagram 2).

They consist of a set of singlet terms and triplet terms. The singlet terms consist of a sequence of s-terms, beginning with the chief quantum number 1; a set of P-terms beginning with $n=2$; a set of D-terms beginning with $n=3$.

The triplet terms consist of a sequence of s-terms beginning with $n=2$; a set of P-terms beginning with $n=2$, etc.

The first S-term of the singlet system is the normal term.

Looking at the structure diagram, we can assign the following origin for the different groups of terms:

M_1 M_1 (both electrons at M) gives $^1S_0$ (first term of s-sequence);

M N (one fixed electron at M, running electron at N) 2^1S_0, 2^3S_1;

M X_1 (two fixed electrons at M, running electron at X) x^1S_0, x^3S_1.

For the P-terms:

M_1 M_2 (one electron fixed at M_1, running electron at M_2) gives 2^1P, 2^3P-terms.

^3F $^3D_1$ $^3D_2$ $^3D_3$ $^3P_0$ $^3P_1$ $^3P_2$ $^3S_1$ $^1S_0$ $^1P_1$ $^1D_2$

Triplett-System *Singulett-System*
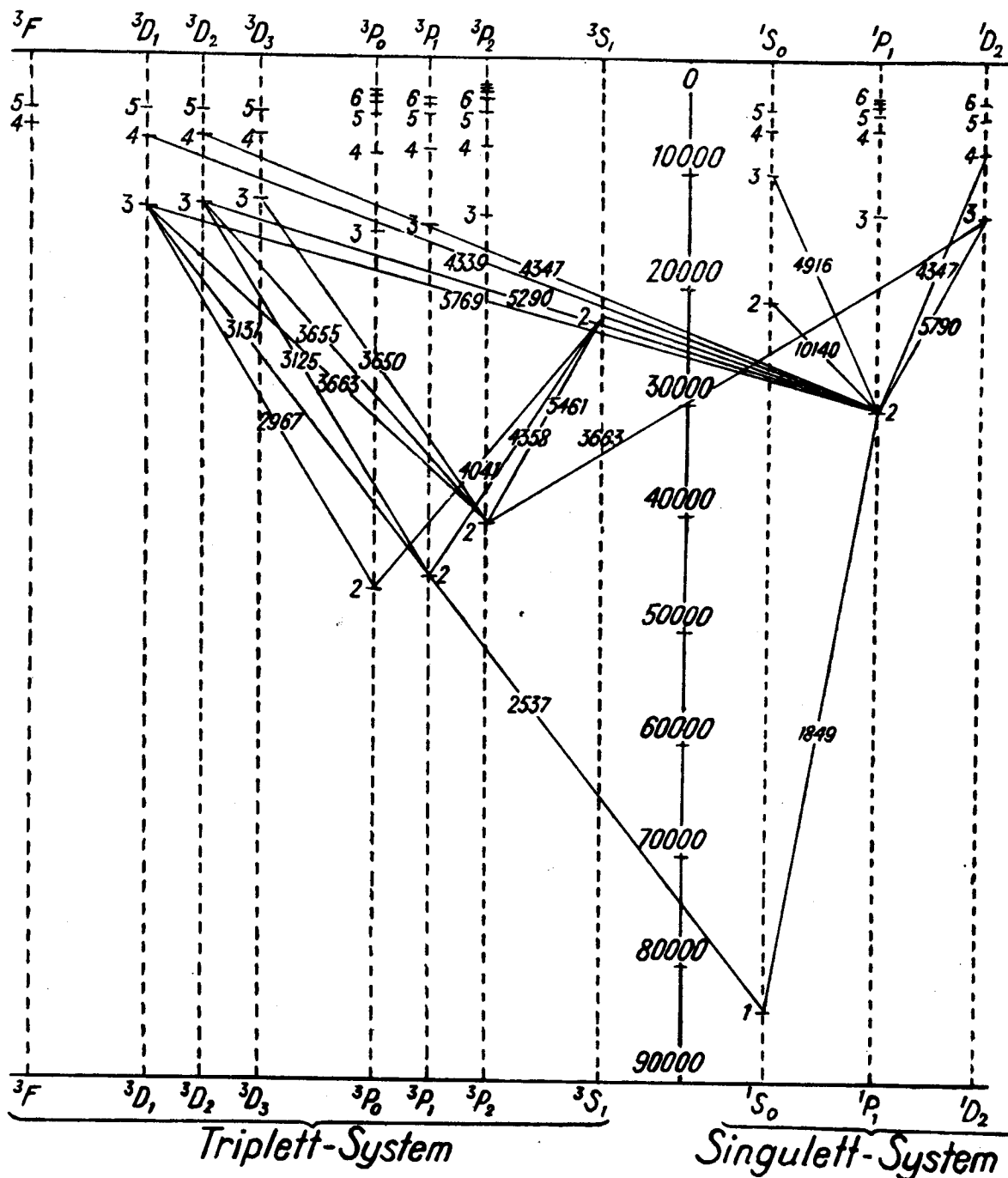
Diagram 2.

Similarly the D-set is obtained when the running electron is allowed to run through the X_3 levels. They are symbolically shown in the structure diagram.

The question now arises: how are we to explain the origin of terms? Why in the normal position, *we get only the singlet S-terms, and why is the triplet term missing?*

The answer was first given by Pauli and further elucidated and generalised by Russell and Saunders, and Heisenberg. Let us suppose that the electrons in the atom have the characteristics of a doublet term. Thus $M_1 M_1$ denotes

that both electrons have the characteristics of doublet S-terms, i.e. $^2S_1$. $M_1 M_3$ denotes that the first electron has the characteristics of a doublet S-term, the second of a doublet D-term (the subscription 1 stands for S-term, 2 stands for P-term, 3 for D-term, etc. . . . .). The resultant term is obtained when the quantum numbers of each constituent terms are added, vectorially.

Rules for Addition of Quantum Numbers.—These rules for the vectorial addition of quantum numbers are a bit

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perplexing. We have already remarked that according to Landé and Sommerfeld, each optical term can be represented by n^l_{kr}, where n=total quantum number, r=multiplicity quantum number, k=azimuthal quantum number, j=inner quantum number.

Now instead of using Landé's values of r, k, j for the different systems, we use Sommerfeld's values, which we denote by i_r, i_k, i_j.

$$\text{Now } i_r = 0, \quad \frac{1}{2}, \quad \frac{2}{2}, \quad \frac{3}{2} \cdots$$

for singlets, doublets, triplets, quartets etc., respectively.

r=usual Landé multiplicity quantum number

$$i_k = 0, \quad 1, \quad 2, \quad 3$$
$$\text{for} \qquad s, p, d, f\text{-term}, \ i_k = k-1$$

i_j=the vector sum of i_r and i_k, and the i_j-values for the different multiplet systems are shown in the Table 1.

TABLE 1.—Showing values of i_r, i_k, i_j

ODD MULTIPLETS							EVEN MULTIPLETS						
i_k \ i_j	0	1	2	3	4	5	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	$\frac{11}{2}$	i_j / i_k
$s=0$	0	Singlet $i_r=0$					$\frac{1}{2}$	Doublet $i_r=\frac{1}{2}$					$s=0$
$p=1$		1					$\frac{1}{2}$	$\frac{3}{2}$					$p=1$
$d=2$			2					$\frac{3}{2}$	$\frac{5}{2}$				$d=2$
$f=3$				3					$\frac{5}{2}$	$\frac{7}{2}$			$f=3$
$s=0$		1	Triplet $i_r=\frac{2}{2}$				$\frac{3}{2}$	Quartet $i_r=\frac{3}{2}$					$s=0$
$p=1$	0	1	2				$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$				$p=1$
$d=2$		1	2	3			$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$			$d=2$
$f=3$			2	3	4			$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$		$f=3$
$s=0$			2	Quintet $i_r=\frac{4}{2}$				$\frac{5}{2}$	Sextet $i_r=\frac{5}{2}$				$s=0$
$p=1$		1	2	3				$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$			$p=1$
$d=2$	0	1	2	3	4		$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$		$d=2$
$f=3$		1	2	3	4	5	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	$\frac{11}{2}$	$f=3$

Taking the case of two valence electrons, if electron (1) gives a term $(n^r_{kj})_1$, electron (2) gives a term $(n^r_{kj})_2 \ldots$ the resultant term is N^R_{Kj}

$$\text{where } i_R = \text{vector sum of } (i_r)_1 \ (i_r)_2$$
$$i_K = \quad ,, \qquad ,, \qquad ,, \quad (i_k)_1 \ (i_k)_2$$

The rule for addition of i_j is more complicated and will be taken later.

Thus taking $M_1 \ N_1$-state, we have

$$\text{for } M_1, \ i_r = \frac{1}{1}, \ i_k = 0$$
$$N_1, \ i_r = \frac{1}{2}, \ i_k = 0$$

$$t_R = \left| \frac{1}{2} + \frac{1}{2} \right| = 0 \text{ and } \frac{2}{2}$$
$$i_K = | \ 0 + 0 \ | = 0$$

The resultant terms are

(1) $i_R = 0, \quad i_K = 0$,   i.e. $^1S_0$

(2) $i_R = \frac{2}{2}, \quad i_K = 0$,   i.e. $^3S_1$

Taking, $M_1 \ N_2$ state, we have

$$\text{for} \quad M_1, \ i_r = \frac{1}{2}, \ i_K = 0 \left.\right\} \ i_R = 0, \text{ or } \frac{2}{2}$$
$$N_2, \ i_r = \frac{2}{1}, \ i_K = \frac{1}{2} \left.\right\} \ i_K = 1$$

The resultant terms are ^1P and ^3P.

Now we see that the origin of all the higher terms in Mg except in the normal state where instead of two terms $^1S_0$, $^3S_1$, only $^1S_0$ appears, $^3S_1$ is definitely absent. In $M_1 M_1$, both the electrons are in absolutely equivalent orbits. Hence there must be some law of exclusion forbidding the appearance of certain terms in equivalent orbits.

Rules for j-summation.—To understand this phenomena, i.e. non-appearance of the term when equivalent orbits are synthesised we take the rule for j-summation.

Now j denotes the total quantum number, and we know from Zeeman effect data that we have to introduce a magnetic quantum number m, which is the quantum-projection of j on an axis fixed in space

Hence
$$m = \pm(j, j-1, j-2 \ldots) \text{ up to } 0, \text{ or } \pm 1$$
$$i_m = \pm(i_j, i_{j-1} \ldots)$$

Thus for $^2S_1$-term, $i_j = \frac{1}{2}$, $i_m = \pm\frac{1}{2}$.

The two $^2S_{\frac{1}{2}}$-electrons (or their orbits) may be so oriented that their i_m-values $= \frac{1}{2}$ or $-\frac{1}{2}$. According to Pauli, if they are in the same level *the magnetic quantum number of no two electrons should be the same*. Thus

$$\text{if for electron (1) } i_m = +\frac{1}{2}$$
$$\text{for electron (2) } i_m = -\frac{1}{2}$$

and resultant $i_M = 0$.

Thus the shell will possess no resultant magnetic moment. This explains why in equivalent orbits there should be a normal $^1S_0$-term only and no $^3S_1$-term.

But when one electron is fixed in a $^2S_1$-orbit the second shifts to a higher $^2S_1$ $(n=2)$, we have

$$(i_m)_1 = \frac{1}{2} \cdots - \frac{1}{2}$$
$$(i_m)_2 = \frac{1}{2} \cdots - \frac{1}{2}$$
$$\overline{i_M . = 1 \quad 0 \quad - 1}$$

The last combination corresponds to a $^3S_1$-term. Pauli's Principle of Exclusion also explains why there should be no more than six electrons to fill up completely the L_2-shell (shells in which all electrons have doublet P-characteristics). For here the full number of magnetic quantum numbers is six, viz.

$$\left. \begin{array}{l} \text{for} \quad {}^2P_{\frac{1}{2}}, \quad i_m = \frac{1}{2} \quad -\frac{1}{2} \\[2mm] {}^2P_{\frac{3}{2}}. \quad i_m = \frac{3}{2}, \quad \frac{1}{2} - \frac{1}{2} - \frac{3}{2} \end{array} \right\}$$

If we take the L_2-level, the maximum number of electrons is the number corresponding to all the possible different values of i_m viz. 6. Hence 6-electrons are required to fill up any P_2-level completely. When this occurs, as in Ne, the resultant $i_r=0$, $i_k=0$, $i_m=0$, hence it gives an $^1S_0$-term, the atom is absolutely neutral.

A similar consideration applied to the d-level shows that the maximum number of electrons required to fill up this level is 10, for an f-level it is 14.

The Periodic Classification.–The periodic classification is now easily explained. Let us take the two groups of elements and consider the constitution of external levels lying beyond closed groups.

	Outer shell			Outer shell	
3. Li	$2K_1$ L_1	s^1	11. Na	$2K_1$ $8L$ M_1	s^1
4. Be	,, $2L_1$	s^2	12. Mg	......$2M_1$	s^2
5. B	,, $2L_1$ L_2	s^2p^1	13. Al	.......$2M_1$ M_2	s^2p^1
6. C	,, $2L_1$ $2L_2$	s^2p^2	14. Si	.......$2M_1$ $2M^2$	s^2p^2
7. N	,, ,, $3L_2$	s^2p^3	15. P	..........$3M^2$	s^2p^3
8. O	... ,, $4L_2$	s^2p^4	16. Se	..........$4M_2$	s^2p^4
9. Fl	.... ,, $5L_2$	s^2p^5	17. Cl	..........$5M_2$	s^2p^5
10. Ne	.... ,, $6L_2$	s^2p^6	18. A	..........$6M_2$	s^2p^6

The outer constitution is essential for chemical constitution. Both Li and Na contain only one s-electron, hence they are monovalent. Be and Mg each contain 2 s-electrons, they are divalent. B and Al each contain 3 electrons, two s-electrons and one p-electron. There is no great energy difference between s-and p-electrons and all three can contribute to chemical valency (more in detail later). Similar considerations apply to the other remaining elements.

The optical spectra of corresponding elements are essentially similar. The spectra of one valence and two valence elements have been already considered. From B to Ne or from Al to A, the outer shell consists of 2 s-electrons and 1, 2, ... up to 6 p-electrons. The normal optical levels are given by vectorial addition of the quantum characteristics of all these electrons. The 2 s-electrons, forming a closed shell contribute nothing. The terms arising out of the synethesis of the orbits of varying number of p-electrons are shown in Table 2. They are calculated (16) by applying Pauli's principle that in equivalent orbits, no two electrons will have the same i_m-value. The calculation of terms is extremely complicated and has not been reproduced.

TABLE 2

Number of p-Electrons			
1	$^2P_{1,2}$		
2	$^3P_{0,1,2}$	$^1\bar{D}_2$	$^1\bar{S}_0$
3	$^4S_2$	$^1\bar{D}_{2,3}$	$^2\bar{P}_{12}$
4	$^3P_{0,1,2}$	$^1\bar{D}_2$	$^1\bar{S}_0$
5	$^2P_{1,2}$		
6	$^1S_0$		

Dashed and Undashed Terms.—Some explanatory remarks may be made here regarding the dashing of terms. The rule is that if a number of terms arise from a particular combination of electron, they must have all the same combinatory properties, provided the selection rule for the inner quantum number j is verified. Supposing now that from a particular combination say p^2 above, S, P, and D terms arise, they must have all the same combinatory powers, and cannot combine amongst themselves. But if they are all denoted as merely S_1 P_1 D_1 then according to the usual convention, the P can combine with S or D-terms. To express that this is not possible, we provide S and $\bar{D}$ with a bar (dashing). Thus P and $\bar{D}$ have the same combinatory powers, and cannot combine amongst themselves, except under exceptional circumstances. We can express the same fact by dashing P, and keeping S and D undashed. It is purely a matter of convention in which we have to be guided by our previous knowledge of the spectrum of the element.

The next elements are	Outermost shell		
19. K $2K.8L.8M.$ $N_1:N_1$ ..	s^1	alkali-monovalent
20. Ca $2K.8L.8M.$ $2N_1:2N_1$ ..	s^2	alkaline-divalent earth

The constitution of the outermost level of K, and Ca are exactly similar to those of Na and Mg respectively. The chemical properties are therfore similar. But a new feature is now present. We have now an M_3-level next to the M_2-level horizontally and lying diagonally opposite N_1. Such a feature was not present in the elements treated

before, and this causes some difference in the chemical and spectroscopic properties of Na and K on the one hand, and of Mg and Ca on the other hand. Neither Na and K are perfectly analogous to each other, nor Mg and Ca are perfectly analogous to each other in their chemical or in their spectroscopic properties.

The Energy-values of Electron in different levels—The matter can be easily grasped from a consideration of the amount of energy which is required in order to take off an electron from a certain level to infinity. This is known from X-ray analysis. Let ν_x be the characteristic frequency in any level divided by R(Rydberg constant) we have generally

$$\nu_{K_1}$$
$$\nu_{L_1} > \nu_{L_2}$$
$$\vee$$
$$\nu_{M_1} > \nu_{M_2} > M_3$$
$$\vee$$
$$\nu_{N_1} > \nu_{N_2} > \nu_{N_3} > \nu_{N_4}$$
$$\vee$$
$$\nu_{O_1} > \nu_{O_2} > \nu_{O_3}$$
$$\vee$$
$$\nu_{P_1} > \nu_{P_2}$$
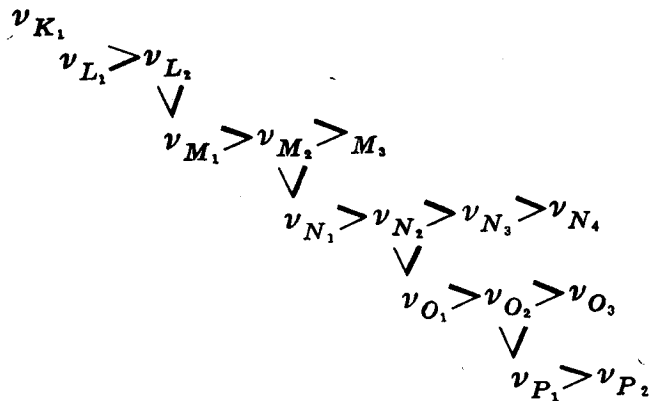
When we consider the energy-values of the term-pairs like M_3 and N_1, which lie diagonally opposite each other, in chart 1, we find a certain indeterminateness. In the curves given by Siegbahn, for the heavier elements ν_{N_1} is always $< \nu_{M_3}$, but for elements of lower atomic number, the curves for ν_{N_1} and ν_{M_3} cross each other. Hence for elements for which the M-level just begins to be filled up, the probability for the capture of the electron in M_3 and N_1 is of the same order of magnitude and is much larger than the probability for the capture of the electron in N_2.

This feature determines the whole spectroscopic and chemical properties of elements coming after Ca for Sc(21), the structure is

$$21.\ \text{Sc}\ 2K_1\ 8L\ 2M_1.\ 6M_2:\ \left.\begin{array}{l} M_3.\ 2N_1 \\ : 2M_3.\ N_1 \end{array}\right\}$$
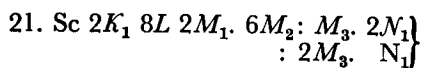
Thus Sc following Ca presents absolutely no similarity in structure to Al following Mg. The two alternative structures $M_3.\ 2N_1$, $2M_3.\ N_1$ are both obtained, and both are almost equally probable. Thus in Sc, we get an element with entirely new properties.

The same remark applied to elements following Sc. For the maximum electron capacity of M_3 is ten, and fresh electrons always pass to M_3. We thus get the following group of elements (Transitional group 1) with entirely new constitution and new properties.

ELECTRONIC COMPOSITION OF TRANSITIONAL GROUP I.

Atomic No.	Element	Composition	Optical terms	Remarks
21.	Sc	$\left.\begin{array}{l}M_3.2N_1 \\ 2M_3.\ N_1\end{array}\right\}$	$\ldots \quad {}^2D$ $\ldots {}^4\bar{F},\ {}^2\bar{F}$	
22.	Ti	$\left.\begin{array}{l}2M_3.2N_1 \\ 3M_3.\ N_1\end{array}\right\}$	${}^3F,\ {}^3P$ $\ldots {}^5F$ etc.	
23.	V	$\left.\begin{array}{l}3M_3.2N_1 \\ 4M_3.\ N_1\end{array}\right\}$	${}^4F,\ {}^4P$ $\ldots {}^6D,\ {}^4D$	
24.	Cr	$\left.\begin{array}{l}4M_3.2N_1 \\ 5M_3.\ N_1\end{array}\right\}$	$\ldots\ldots\ldots$	
25.	Mn	$\left.\begin{array}{l}5M_3.2N_1 \\ 6M_3.\ N_1\end{array}\right\}$	$\ldots {}^6S,\ {}^6D,\ {}^4D$ etc.	
26.	Fe	$\left.\begin{array}{l}6M_3.2N_1 \\ 7M_3.\ N_1\end{array}\right\}$	$\ldots {}^5D,\ {}^3F$	
27.	Co	$\left.\begin{array}{l}7M_3.2N_1 \\ 8M_3.\ N_1\end{array}\right\}$	$\ldots {}^4F,\ {}^4F$	
28.	Ni	$\left.\begin{array}{l}8M_3.2N_1 \\ 9M_3.\ N_1\end{array}\right\}$	$\ldots {}^3D,\ {}^1D,\ {}^3\bar{F},\ {}^3\bar{P}$	

The optical terms can be easily calculated with the aid of a table giving the optical synthesis of terms of varying number of electrons in d-orbits.

This is shown in the following table:

TABLE 3

Number d-of electrons	Terms
1.	${}^2D$
2.	${}^3F\ {}^3P\ {}^1\bar{G}\ {}^1\bar{D}\ {}^1\bar{S}_0$
3.	${}^4F,\ {}^4P,\ {}^2H,\ {}^2\bar{G},\ {}^2F,\ {}^2\bar{D},\ {}^2\bar{D},\ {}^2P$
4.	${}^5D\ {}^3\bar{H}\ {}^3G\ {}^3\bar{F}\ {}^3D\ {}^3\bar{P}$
5.	${}^6S,\ {}^4G,\ {}^4D,\ {}^4\bar{F},\ {}^4P$
6.	${}^5D,\ {}^3\bar{H},\ {}^3G,\ {}^3\bar{F},\ {}^3D,\ {}^3\bar{P}$
7.	${}^4F,\ {}^4P,\ {}^2H,\ {}^2\bar{G},\ {}^2F,\ {}^2\bar{D},\ {}^2\bar{D}$
8.	${}^3F,\ {}^3P,\ {}^1\bar{G},\ {}^1\bar{D},\ {}^1\bar{S}_0$
9.	${}^2D$
10.	${}^1S_0$

The next element Cu is very interesting, for chemically it behaves both as monovalent, and also as a divalent atom. This is fully confirmed by the behaviour of its spectrum. The normal terms are, as we shall see presently due to the two following configurations

$$29..\ \text{Cu} \ldots\ldots\ldots\ldots \quad \begin{array}{l} 10M_3\ N_1 \quad d^{10}\ s^1 \\ 9M_3\ 2N_1 \quad d^9\ s^2 \end{array}$$
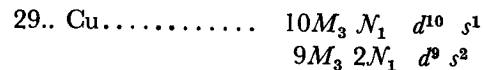
In the next elements, the N_2-level is being filled up. Thus we have

30. Zn $\ldots\ldots\ldots 10M_3.2N_1$	s^2	Similar to	Mg
31. Ga $\ldots\ldots\ldots\ldots 2N_1.N_2$	s^2p^1	$\ldots\ldots\ldots$	Al
32. Ge $\ldots\ldots\ldots\ldots 2N_1.2N_2$	s^2p^2	$\ldots\ldots\ldots$	Si
33. As $\ldots\ldots\ldots\ldots 3N_2$	s^2p^3	$\ldots\ldots\ldots$	P
34. Se $\ldots\ldots\ldots\ldots 4N_2$	s^2p^4	$\ldots\ldots\ldots$	S
35. Br $\ldots\ldots\ldots\ldots 5N_2$	s^2p^5	$\ldots\ldots\ldots$	Cl
36. Kr $\ldots\ldots\ldots\ldots 6N_2$	s^2p^6	$\ldots\ldots\ldots$	A

In 37 and 38 we have again the alkali and the alkaline earth:

$$37.\ \text{Rb} \ldots\ldots\ldots\ 6N_2\ O_1 \qquad s^1$$
$$38.\ \text{Sr} \ldots\ldots\ldots\ 6N_2.2O_1 \qquad s^2$$
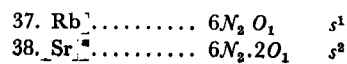
Now there is again an N_3-level with larger negative energy value than O_1, hence in element 39, the electron goes by preference to N_3. We thus get the formation of the next transitional group.

TRANSITIONAL GROUP II   (13)

39. Y	$2N_3 O_1$	$N_3.2O_1$	$d^2 s_1, ds^2$
40. Zr	$3N_3.O_1$	$2N_3.2O_1$	$d^3 s_1, d^2 s^2$
41. Nb	$4N_3 O_1$	$3N_3.2O_1$	$d^4 s^1, d^3 s^2$
42. Mo	$5N_3.O_1$	$4N_3.2O_1$	$d^5 s^1, d^4 s^2$
43. Ma.			
44. Ru	$8N_3, 7N_3 O_1, 6M_3.2O_1$		$d^8, d^7 s^1, d^6 s^2$
45. Rh	$8N_3 O_1$		$d^9, d^8 s^1, d^7 s^2$
46. Pd	$10N_3, 9N_3 O_1, 8N_3 3O_1$		$...d^{10}, d^9 s^1, d^8 s^2$

From 47 to 54, we have now another regular group formed. We have

47. Ag	$10N_3.O_1$	s^1
48. Cd	$10N_3.2O_1$	s^2
49. In	$10N_3.2O_1. O_2$	$s^2 p^1$
50. Sn	$2O_2$	$s_2 p^2$
51. Sb	$3O_2$	$s_2 p^3$
52. Te	$4O_2$	$s_2 p^4$
53. I	$5O_2$	$s_2 p^5$
54. Xe	$6O_2$	$s_2 p^6$

55 and 56 again give us an alkali and alkaline earth. Thus

55. Cs	$6O_2.P_1$	s^1
56. Ba	$6O_2.2P_1$	s^2

With the next element, a new feature reveals itself. We find from the table of energy values for different levels that N_4 has larger negative energy value than O_3. Hence in the next elements, the N_4-level will be filled up. This requires 14 electrons and we have accordingly a group of 14 elements from 57 La to 70 Yb with entirely new properties viz., the rare-earths. The composition of their outer shells is yet unknown, as their spectra have not yet been fully investigated.

In the formation of the next group of elements, the electrons fill the level O and thus form the transitional group III. The electronic structure of the outer levels will be similar to those of the other transitional groups or may differ from them in non-essential points.

The outer shell of Hf has the same electronic structure as Ti and Zr.

This was first pointed out by Bohr, whereas according to the older view element 72 was regarded as a rare earth and trivalent. As is well known Hevesy and Coster acting under the guidance of Bohr, discovered Hf in association with Zirconium minerals.

After the levels N_4 and O_3 are filled, the next electrons will continue to fill P_1, P_2; we thus get the following regular group ending in an inert gas.

79. Au	$14N_4.10O_3$	P_1	s^1
80. Hg		$2P_1$	s^2
81. Tl		$2P_1.P_2$	$s^2 p^1$
82. Pb		$2P_2$	$s^2 p^2$
83. Bi		$3P_2$	$s^2 p^3$
84.			
85.			
86. Rad Em.			

In the next elements, Q is being filled up. We get

87. Eka Cs	Q_1 Alkaline.
88. Ra	$2Q_1$ Alkaline Earth.

Elements 98 ... 102 will form Rare earth II.

102 ... 112 .... Transitional group IV.

112 ... 118 ....

118 being a rare earth.

But as is well-known, our knowledge at present ends with 92 (Ur).

The structure diagram thus probably affords the most satisfactory explanation of the origin of periodic properties of Atoms. It explains not only the general features, but also even the minute details.

Summary of the Periodic Classification.—Chart 1 thus graphically visualizes the formation of different groups in which the elements can be subdivided according to the structure of their outer shells, on which the chemical properties are assumed to depend. We have

a) H and He which quite stand apart. Spectroscopically they form the same group as the elements in which an s-level is being filled up, namely the short group of two consisting of an alkali and an alkaline earth. These are

1. 19 K and 20 Ca
2. 37 Rb ... 38 Sr
3. 55 Cs ... 56 Ba
4. 87   88 Ra

But owing to the very high ionisation potential, He is inert. Hydrogen quite stands apart. The spectra of corresponding elements are perfectly analogous.

In these short groups, the s-levels are being filled up.

b) Regular groups, 5 in all, consisting of

1. 3 Li to   10 Ne
2. 11 Na ..   18 A
3. 29 Cu ..   36 Kr
4. 47 Ag ..   54 Xe
5. 79 Au ..   86 Nt

Here the s and p-levels lying in the same horizontal line (with the same value of total quantum number) is being filled up. The valency varies from 1 to 7 and then falls to zero.

It might be thought that in B and Al, since the s-level is completely filled up, the p-electron would be the only one which can be easily detached off. But it is found that in these elements, and probably in the higher elements of these groups, the s-electron can easily pass to the p-stage i.e. we have lines corresponding to the transition (taking Al):
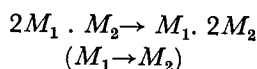
$$2M_1 . M_2 \to M_1. 2M_2$$
$$(M_1 \to M_2)$$
Again $M_1. 2M_2 \to 3M_2.$

Hence all the three electrons can contribute to valency. Similar inner transitions have been observed in C, and are probably true of all elements up to the combination $(2X_1 5X_2)$.

c) Transitional groups– three in number consisting of

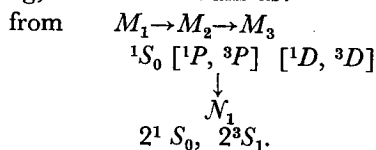1. 21 Sc to 28 Ni
2. 39 Y to 46 Pd
3. 71 Lu to 78 Pt

and a fractional group 89 Ac- 92 Ur and other undiscovered elements.

In these groups, the d-level is being filled up, the general composition of outer levels is $d^x s^2$, $d^{x+1} s^1$, x varying from 1 to 8.

d) The rare earths group consisting of 14 elements, 57 La to 70 Yb, in which the N_4, or the f-level is being filled up. The outer composition is still optically unknown. The composition may be $f^x d^y, s^{1\cdot2}$ where $x+y$ vary from 1 to 14, and f refers to N_4, d refers to O_3.

General Treatment of the Spectra of Elements. Two Valence Elements.

We have previously remarked that when we compare the structure diagrams of Mg and Ca, a difference is at once observed. We shall treat this phenomena more in detail. In Mg, the electron runs as:

from　$M_1 \to M_2 \to M_3$
$\quad {}^1S_0\ [{}^1P,\ {}^3P]\ [{}^1D,\ {}^3D]$
$\quad\quad\quad\quad \downarrow$
$\quad\quad\quad\quad N_1$
$\quad\quad 2^1 S_0,\ 2^3 S_1.$

2^1P_1 is approximately $\dfrac{R}{2^2}$, the first ${}^1D = \dfrac{R}{3^2}$. But let us take (vide page. 379).

In Ca, there is an empty M_3-level, lying diagonally opposite N, and hence equal in energy value to N. Actually the first D-term is found to be approximately $R/2^2$. These large D-levels form the characteristic feature of the spectra of Ca and also of Sr and Ba, while Cd and Hg are perfectly analogous to Mg. These levels are really metastable compared to the normal levels. According to Bohr's enumeration, the total quantum number corresponding to this D-term viz. 3, is less than even that of the first s-term viz. 4.

STRUCTURE DIAGRAM OF Ca
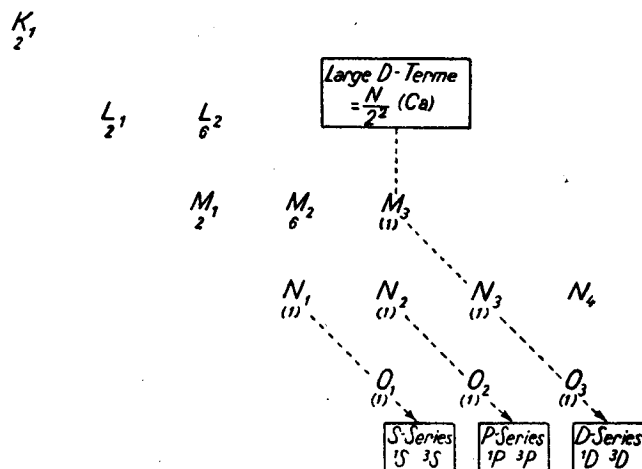
Anomalous Terms (19).—The influence of these metastable levels is clearly seen in the «anomalous terms» obtained in the spectra of Ca, Sr and Ba. They were first thoroughly investigated by Saunders and Russell. To obtain them, we have to keep the fixed electron at M_3 (for Ca), and allow the running electron to pass through the higher levels. The terms expected and observed are shown in Table 4.

There are anomalous terms in the spectra of Mg, Zn and Hg, but they are quite of a different nature. They are obtained when the fixed electron is kept at M_2, and the running electron runs through the higher levels.

Rydberg sequence in Anomalous Terms—Negative Terms— Even in anomalous terms, we get Rydberg sequence, when we collect terms obtained by displacing the electron diagonally. For example, take the $M_3 X_3$-combination in Ca, and compare the values of the successive p-terms arising from this combination with the values of the p-terms arising from the normal D-sequence of $N_1 X_3$ combination. They are shown graphically below:

M_3M_3	M_3N_3	M_3O_3	M_3P_3	M_3Q_3
${}^1\overline{P} {}^3\overline{P}$	$2^1\overline{P},\ 2^3\overline{P}$	$3^1\overline{P},\ 3^3\overline{P}$	$4^1\overline{P},\ 4^3\overline{P}$	$5^1\overline{P},\ 5^3\overline{P}$
N_1M_3	N_1N_3	N_1O_3	N_1P_3	N_1Q_3
${}^1D, {}^3D$	$2^1D, 2^3D$	$3^1D, 3^3D$	$4^1D, 4^3D$	$5^1D, 5^3D$

Of the set of terms from $M_3 X_3$, we have taken only the $\overline{P}$-set. Compare the values of each corresponding pair in each vertical column:

Now $M_3Q_3 \to N_1Q_3 = (M_3 \to N_1)Q_3$

$\quad = (M_3 \to V_1)$ of Ca$^+$, Q_3 being far off, is neglected
$\quad = {}^2D - {}^2S$ of Ca$^+$
$\quad = -13711$

TABLE 4

State	Present notation	Russell & Saunders' notation	Term values		
			Ca.	Sr.	Ba.
(a) M_3M_3	$^3\bar{F}_{4,3,2}$	..	..	..	19077·9 / 19510·1 / 19990·3 432·2 / 480·2
	$^3\bar{P}_{2,1,0}$	p'	10753·0 / 10839·8 / 10887·1 86·8 / 47·3	10250·7 / 10525·5 / 10731·8 247·8 / 206·3	18110·5 / 18549·3 / 18820·3 438·8 / 271·0
	$^1S_0$ $^1D_2$ $^1G_4$	X	8584·9	8964·9	9929·0
(b) M_5N_2	$^3F_{4,3,2}$	f''	13407·6 / 13485·9 / 13573·9 78·3 / 88·0	12006·0 / 12335·7 / 12658·5 329·7 / 322·8	18372·6 / 19082·1 / 19964·8 709·5 / 882·7
	$^3D_{3,2,1}$	d'	11045·3 / 11085·3 / 11112·0 40.0 / 26.7	9365·9 / 9543·4 / 9661·1 177·5 / 117·8	17049·8 / 17498·1 / 17837·6 448·3 / 339·5
	$^3P_{2,1,0}$	p''	9964·3 / 9969·1 / 9971·0 4·8 / 1·9	8588·5 / 8622·2 / 8633·0 33·7 / 10·8	16073·1 / 16325·5 / 16387·8 252·4 / 62·0
	$^1F_3$ $^1D_2$ $^1P_1$	Y	8767·0 ..	9836·1 ..	15213·4 13475·2
(c) M_5O_1	$^2D_{3,2,1}$ $^1D_2$		..	..	4526

i.e. the higher P-terms will be less than the corresponding P-terms by 13711. The actual values of the sequence are shown below:

	$1^3\bar{P}$.	$2^3\bar{P}$.	$3^3\bar{P}$.	$4^3\bar{P}$.	$5^3\bar{P}$.
	10840	767	−4983	−8313	−10063
$^3D−(^2S−^2D)$	15306	−2097	−7090	−9359	−10649
$^3D−(^1S−^2D)$	7106				

Thus the higher terms of a Rydberg sequence arising from a metastable fixed level become negative, as was first shown by Saunders and Russell.

Ionised Elements with two Valence Electrons.—The anomalous terms become more prominent as we pass on from Ca to Ba. This is because the unbalanced electrical field of the Barium nucleus is larger than that of the Ca-nucleus.

When we take the elements Sc⁺, Y⁺, and L⁺ which have got the same number of electrons as Ca, Sr and Ba respectively, we find actually that the d-level is much more stable than the s-level e.g. in Sc⁺, the M_3-level is much more stable than the N_1-level. So in the spectrum of Sc⁺, terms obtained with the fixed electron at M_3 are much larger than that the terms obtained with the fixed electron at N_1—in other words, though Sc⁺ has a structure similar to that of Ca, the spectrum is just reversed,—the anomalous terms become normal, and the normal terms become
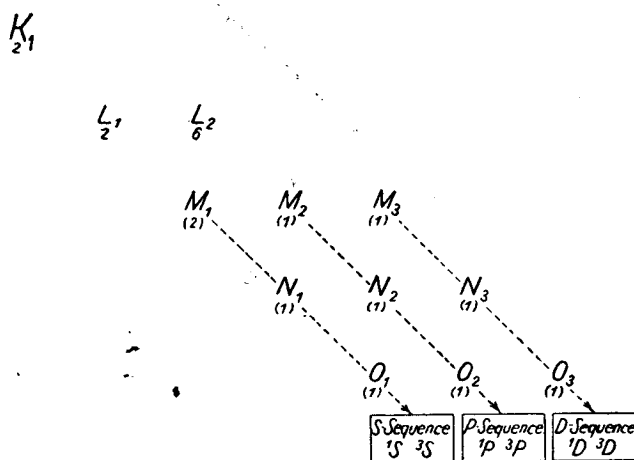
anomalous. Thus the displacement rule of Sommerfeld and Kossel is not strictly true or holds only in a qualified sense.

Spectra of Elements of Group III

B, Al, Ga, In and Tl.

Taking Al, we find that the structure diagram is:

STRUCTURE DIAGRAM OF AI

The term values and their origin *are. shown below.

Combination	Terms	Term-values	Remarks
b_0) M^2	$^2P_{1,2} =$ and sequence	$48168 \cdot 87$ $280 \cdot 88$ 15316 331 etc.	Normal terms
c_1) M_3	$^2D_{2,3} =$	$15845 \cdot 5$ $844 \cdot 2$ etc.	$b_0{}^2P\text{-}c_1{}^2D$ roughly follows the irregular doublet law, because the total quantum number is the same.
a_1) N_1	$^2S_1 =$	$22933 \cdot 3$ $10592 \cdot 6$	$b_0{}^2P\text{-}a_1{}^2S_1$ does not follow the irregular doublet law. Total quantum number different.
a_1) $M_1.2M_2$	$^4\bar{P}$ $^2\bar{P}_{1,2}$ $^2D_{2,3}$ $^2S_1$	? -8361 -8249 ? ?	Combination P$\bar{\text{P}}$ corresponding to the inner transition $2M_1M_2 \rightarrow M_1.2M_2$ has been discovered by Millikan and Bowen in case of Al, and by Kichlu in case of Si$^+$. So this transition is possible in all three valence spectra.

The spectra of three-valence elements including B, Al, Ga, In, Tl, are comparatively simple. If we compare the spectra of Al, Si$^+$, P^{++}, etc... which all ought to be similar, we find that the $^2P-^2D$ lines follow the irregular doublet law roughly, $^2P-^2S$ lines not at all (Table 5). The inner transition $2M_1.M_2 \rightarrow M_1.2M_2$ is very interesting. Here also the total quantum number remains unchanged, and the irregular doublet law is better followed than in the case of the $^2P-^2D$ lines, (Table 6), taken from a paper by Bowen and Millikan illustrates the point.

TABLE 5

	Al	Si$^+$	P^{++}	S^{+++}	Cl^{+4}
$^2P-^2D$	32325	79056	116321	151189	184390
	(46371)	(37265)	(34868)	(33200)	
$^2P_1-^2S$	25348	65495			
	(40147)				

TABLE 6

$2M_1\text{---}M_2$ $\downarrow$ $M_1\ 2M_2$	Al	Si$^+$	P^{++}	S^{+++}	Cl^{+4}
$^2P-^2\bar{P}$	56615 (27202)	83717 (25134)	108850 (24441)	133292 (24111)	157403
$^2P-^2D$		55305			
$^2P-^2S$		63613			
$^2P-^4\bar{P}$					

Literature—MILLIKAN & BOWEN, P. R., vol. 26, p. 160. P. K. KICHLU, I. O. S. A. vol. 14, p. 455.

Group IV - Four Valence Elements

STRUCTURE DIAGRAM OF SI.
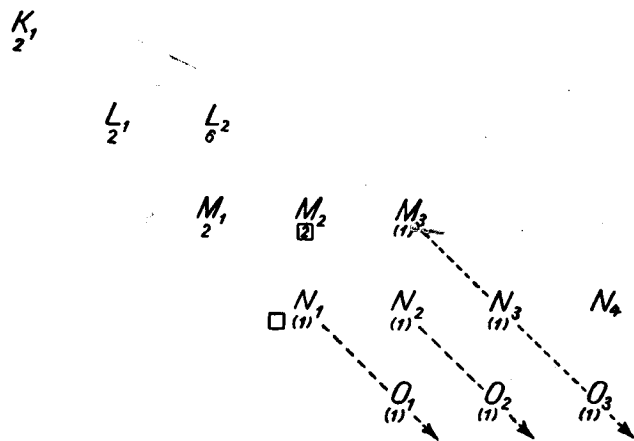
The expected terms and their values and combinations are shown below.

THE SPECTRUM OF SI

b_0) $^2M_2$ $a_1\ M_2N_1$		$^3P_0$ 64275	$^3P_1$ 64198	$^3P_2$ (6076) 64051	$^1D_2$ (9095) 57975	$^1S_0$ 48880
24592...	$^3\bar{P}_0$	—	(8) 39606	—	—	—
24515...	$^3\bar{P}_1$	(7) 39760	(7) 39683	(9) 39537	(5) 33461	(5) 24366
24320...	$^3\bar{P}_2$	—	(9) 39878	(10) 39732	—	—
23823...	$^1\bar{P}_1$	40991	40914	40768	(10) 34693	(9) 25598

c_1) M_2M_3

	$^3\bar{F}_2$		?	?	?	
	$\bar{F}_3$		?	?	?	
	$\bar{F}_4$					
18999...	$^3D_1$	45276	45199	45052	(35957)	(26862)
18982...	D_2		45216	45069	(35974)	
18954...	D_3			45098		
13672...	$^3\bar{P}_0$		50526			
13707...	$\bar{P}_1$	50568	50491	50344	(44268)	(35173)
13774...	$\bar{P}_2$		50424	50277		
	$^1\bar{F}_3$			?	?	
	$^1D_2$		?	?	?	
	$^1\bar{P}_1$	?	?	?	(41053)	

α_1) $M_1 3M_2$

$^4S_2$					
$^3S_1$					
$^3\bar{P}_0$					
$\bar{P}_1$			Still Unknown		
$\bar{P}_2$					
$^1\bar{P}_1$					
$^3D_1$					
D_2					
D_3					
$^1D_2$					

As regards the spectrum of C, it is not yet completely done. The spectra of Ge, Sn and Pb are exactly alike that of Si, only the intercombinations are stronger, in conformity with the general rule. The inner transition groups

$$2M_1\,2M_2 \rightarrow M_1\,3M_2$$
$$M_1 \rightarrow M_2$$

obey the irregular doublet law, as pointed out by Bowen and Millikan in the case of C, N⁺, O⁺⁺, Fl⁺⁺⁺ (Table 7).

In the case of Pb, owing to its large atomic weight, the $\Delta \nu^2$ P_1—$2P_2$ of Pb⁺ is abnormally large about 19010. Hence only terms proceeding from $^2P_1$ of Pb⁺ are developed completely. For details, see Sur, ⟨⟨Phil. Mag.⟩⟩, Vol. 2, p. 633.

TABLE 7

	$b_0{}^3P-\alpha_1{}^3S$	$b_0{}^3P-\alpha_1{}^3P$	$b_0{}^3P-\alpha_1{}^3D$
C		75211	64046
		33875	28060
N⁺	154996	109087	92106
	41785	32987	27612
O⁺⁺	196781	142075	119719
	40918	32551	27514
Fl⁺⁺⁺	237699	174627	147234

Elements of Group IV
C, Si, Ge, Sn, Pb.

In elements of this group, the normal electron configuration is $2X$ i.e. there are two electrons with p-characteristics. They will give us resultant terms

$$^3D \qquad ^3P \qquad ^3S$$
$$^1D \qquad ^1P \qquad ^1S$$

for $\quad (i_k)_1=1, \qquad (i_k)_2=1 \qquad I_k=2,\ 1,\ 0$

$\qquad\quad (i_r)_1=\tfrac{1}{2}, \qquad (i_r)_2=\tfrac{1}{2} \qquad I_r=0,\ \tfrac{2}{2}$

but of these terms, a few are forbidden by Pauli's exclusion principle, as long as electrons are both in M-positions. It is found that the admissible terms are $^3P_{0,1,2}$, $^1\bar{D}_2$, $^1\bar{S}_0$. The D and S-terms must be barred because they have the same combinatory properties as the P's.

Literature—MacLennan, P. R. S. (Canada), vol. 20 (1926), for Ge, C, Si, Sn, Pb; N. K. Sur, Zs. f. Physik, Bd. 41, p. 791, for Sn; for Si, Fowler, Phil. Trans., 225, p. 1. For Pb. Grotrian, Zs. f. Physik, Bd. 34, p. 374; Sur, Phil. Mag. vol. 2, p. 633. Bowen and Millikan, P. R. 29, p. 240.

Elements of Group V
N, P, As, Sb, Bi.

According to Hund's theory all these elements have $3P$-electrons in the normal state.

The typical structure diagram is given by that of Phosphorus:

STRUCTURE DIAGRAM OF P

K_1
2

$\quad L_1 \quad L_2$
$\quad 2 \quad\; 6$
$\qquad\quad M_1 \quad M_2 \quad \rightarrow \quad M_3$
$\qquad\quad 2 \qquad 3 \qquad\qquad (1)$
$\qquad\qquad\qquad \downarrow$
$\qquad\quad N_1 \quad \rightarrow \quad N_2 \quad N_3 \quad N_4$
$\qquad\quad (1) \qquad\qquad (1)$
$\qquad\qquad\qquad\qquad O_1 \quad O_2 \quad O_3$

Combination
(a) $3M_2$ $\qquad\qquad$ $^4S_2$ $^2D_{2,3}$ $^2\bar{P}_{1,2}$
(b) $2M_2\,N_1$ $\qquad\qquad$ ^4P, ^2P $^2\bar{S}$ ^2P
(c) $2M_2N_3$
(d) $2M_2N_2$
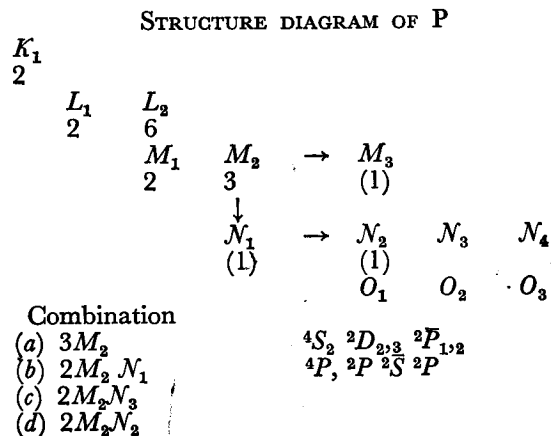
The spectra of none of elements have yet been completely cleared up, but the spectrum of O⁺ will have similar constitution, and this has been analysed partially by A. Fowler. R. H. Fowler and Hartree have shown that A. Fowler's analysis is completely in accord with Hund's theory. Recently Bowen and Millikan have identified the fundamental $^4S_2$-level of O⁺, and another two fundamental levels, but it is difficult to say if this is ^2P or ^2D.

Elements of Group VI

O, S, Se, Te, Po.

These elements have 4-P-electrons in the outer shell, and to get a picture of the spectrum, we can take the structure diagram of O.
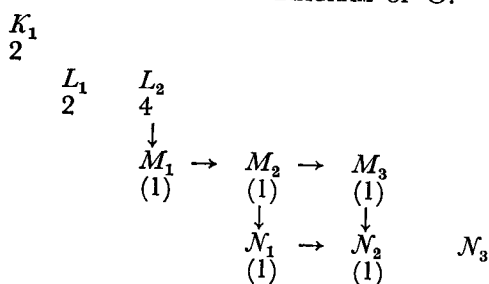
STRUCTURE DIAGRAM OF O.

K_1
2

L_1 L_2
2   4
        ↓
M_1 → M_2 → M_3
(1)   (1)   (1)
        ↓   ↓
N_1 → N_2 N_3
(1)   (1)

Combination	Terms expected	Terms observed
a) 4L	$^3P\,^1\overline{D}_2\,^1\overline{S}_3$	
b) $3L_2\,M_1$	$^5S,\,^3S;\,^3\overline{P}\,^1\overline{P},\,^3\overline{D}\,^1D$	
c) $3L_2\,M_2$	$^5P,\,^3P$	
d) $3L_2\,N_1$	$^5S,\,^3S;$	
e) $3L_2\,M_3$	$^5D,\,^3D$	

The normal terms ^3P have been obtained by Hopfield in the case of O and S. The lines of O and Se in the visible range have been partially analysed by Fowler, and they arise from the level b) Rydberg sequences corresponding to transitions $3M_2X_1$ ($X_1=N_1$, O_1, P_1, ...) have been obtained.

Elements of Group VII (Halogens)
Seven Electron Elements
STRUCTURE DIAGRAM

K_1
2

L_1 L_2
1   S, 1
        M_1 M_2 M_3
        (1)   (1)   (1)
                 N_1
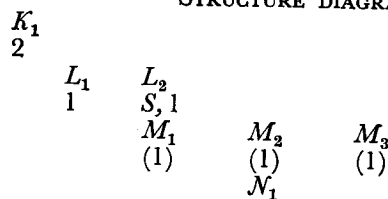
TABLE 8.

$4L_2M_1$	$4\overline{P}_1$ (160)	$4\overline{P}_2$ (274·5)	$4\overline{P}_3$	$_2\overline{P}_1$ (325)	$^2\overline{P}_2$	$^2D_2$	$^2D_3$	$^1S_1$	
5L² $^2P_1$ 409				104654	104331	123928	(?)		Fundamental terms
$^2P_2$				105063	104736		123518		
$4L_2M_2$									
$4\overline{D}_1$ 83	(20) 14468	(3) 14712							
$\overline{D}_2$ 177	(18) 14552	(18) 14628	(1) 14903						
$\overline{D}_3$ 144		(30) 14484	(20) 14758						
$\overline{D}_4$			(40) 14582						
$4P_1$ 102	(13302)	(12) 13462							
P_2 212	(5) 13201	(5) 13360	(18) 13634						
P_3		(5) 12238	(20) 13512						
$4\overline{S}_2$	(23) 15588	(28) 15748	(30) 16022						
$^2D_2$	14782	14942	15217						
D_3									
$^2P_1$ 145	15192	15032		(5) 14025	(4) 14351				
P_2				(15) 13881	(50) 14206				
$^2S_1$				(3) 15581	(1) 15727 (?)				

The spectra of Fl has been analysed by Dingle, de Bruin, and Bowen and of Ne⁺ which is similar to that of Fl) by P. K. Kichlu, and Bruin. The combinations in the case of Fl are shown in Table 8, intercombination have not yet been traced.

Elements of Group VIII (Inert Gases)

Eight Electron Elements (s^2p^6)

STRUCTURE DIAGRAM OF NEON

K_1
2

L_1 L_2
2   5,1

M_1 M_2 M_3
(1)   (1)   (1)

N_1 N_2 N_3 N_4
(1)   (1)   (1)   (1)

O_1 O_2 O_3 O_4
(1)   (1)   (1)   (1)

•
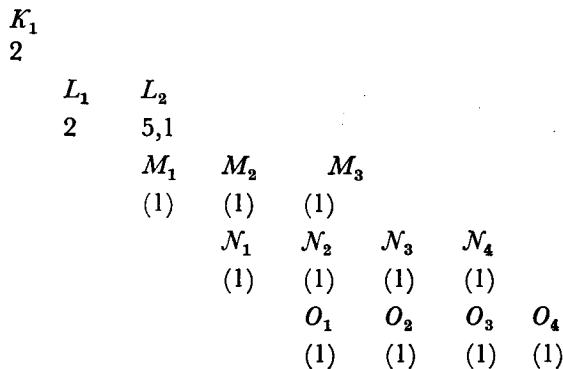
The spectrum of Neon was first analysed by Paschen and Meissner, and its interpretation in terms of the quantum mechanics has been successively given by Goudsmit, Hund, and Saha. The expected terms and combinations, with their values are shown below. The spectrum of Argon has recently been analysed by Meissner, and it is quite in agreement with Hund's theory.

The combination $5L_2\ M_2 - 5L_2\ M_3$ has also been disco-
$(M_2 \rightarrow M_3)$

vered, as well as the higher Rydberg sequence of all the previous sets. There is a certain amount of uncertainty in the designation of the terms, when the inner quantum number proves to be the same e.g. terms designated $^3\bar{P}_1$ and $^1\bar{P}_1$ may be interchanged. The spectrum of Neon also deviates from the general rule that in elements of small atomic weight, intercombinations are either absent, or very faint. The intercombinations in Ne are seen to be quite strong. Some of the sequences follow the Rydberg law only if 782 be added to them. They are the terms arising from the $^2P_2$ state of Ne⁺.

Spectra of Elements belonging to the Transitional Groups.

As has been remarked before, the outer shell of the transitional group of elements in the normal state has the constitution $d^x s^1$, $d^{x-1}\ s^2$. The normal terms can easily be calculated making use of Chart 1), and the other rules of term synthesis. The higher terms are obtained by allowing one

EXPECTED TERMS AND COMBINATIONS OF THE SPECTRUM OF NEON

5L₂M₁ P⁶S¹	³P₀ 39111	³P₁ 39470	³P₂ 39888	¹P₁ 38041	Remarks
b_0) 6L₂¹S₀ 173970	—	(743·5) 134500	—	(735·7) 135929	Normal state
b_1) 5L₂M₁	—	—	—	—	
³D₁ (23808)	(6) 15303	(12) 15662	(1?) 16080	(9) 14233	
³D₂ (23614)	—	(8) 15798	(12) 16220	(10) 14427	
³D₃ (24272)	—	—	(20) 15615	—	
³P₀ (23012)	—	(10) 16458	—	(7) 15029	
P₁ (22891)	(12) 16220	(10) 16579	(20) 16997	(15) 15150	
P₂ (23071)	—	(8) 16399	(8) 16817	(9) 14970	
³S₁ (25672)	(8) 13439	(10) 13798	(10) 14216	(8) 12369	
¹D₂ (24105)	—	(15) 15364	(10) 15782	(10) 13935	
¹P₁ (23157)	(15) 15954	(6) 16313	(12) 16730	(2) 14883	
¹S₀ (20959)	—	(50) 18511	—	(50) 17082	

outer electron, generally the s-electron, to run through the higher levels, as shown in the following diagram:

K_1
2

L_1 L_2
2   6

M_1 M_2 M_3
2   6 x

N_1 N_2 N_3 N_4
y (1)   (1)

O_1 O_2 O_3
(1)   (1)   (1)
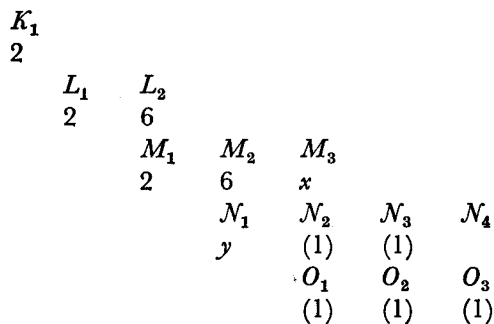
The term-systems are extremely complicated, but are in every case so far investigated, in complete agreement with Hund's theory. Usually only normal terms and the terms next to them have been obtained. Except in the case of Mn, Cr, and Co, Rydberg sequence has not yet been established in an unambiguous manner.

There are again slight differences in the composition of the outer shell in Group 1) and Group 2) of Transitional Elements. In group 1, the structure is generally

$$\left.\begin{array}{cc} x\,M_3\,\mathcal{N}_1 & \ldots\; d^x\,s^1 \\ (x-1)\;\;M_3\,2\mathcal{N}_1 & d^{x-1}s^2 \end{array}\right\}$$

In group 2, for a corresponding element, the structure is

$$\begin{array}{cc} (x+1)\;\;M_3 & d^{x+1} \\ x\,M_3\,\mathcal{N}_1 & d^x\,s^1 \end{array}$$

For example, let us compare the structure of Ni and Pd.

$$\left.\begin{array}{l} \mathcal{N}i\ldots8M_3.2\mathcal{N}_1\ldots d^8s^2 \\ \qquad 9M_3.\mathcal{N}_1\ldots d^9s^1 \end{array}\right\}\quad \begin{array}{l} Pd\ldots\;9\mathcal{N}_3\;\;O_1\ldots d^9s^1 \\ \qquad\qquad 10\mathcal{N}_3\;\;\ldots d^{10} \end{array}$$

Ionisation Potential of Elements.—Curve *A*) shows graphically the ionisation potential of elements from H to Ga. It will be seen that there are well-marked periods of 2, 6, and 10. Whenever a shell is completed the ionisation potential reaches a maximum value. For incomplete groups, the ionisation potential gradually increases with the number of electrons in the group, e.g. compare the part of the curve from Al to A, or from Sc to Ni.

Why the two apparently distinct sub-levels L_{21}, L_{22} *have been combined in one level.*

In the atomic diagram of Stoner and Mainsmith, the L_2 level was split up into two sublevels L_{21}, L_{22} containing 2 and 4 electrons respectively. Similarly the M_3-level was split up into M_{32}, M_{33}, containing 4 and 6 electrons respectively. This splitting is found unnecessary. No use has been made of it in the calculation of optical terms. If such a splitting existed, either the M_{32} or M_{33} level should first be filled up before the electron goes to the other sublevel.

In this case, the part of the ionisation potential curve, from Al to A, or Sc to Ni, would not be continuous but would show a maximum at Si, and Cr corresponding to the filling up of the L_{21} and M_{22} levels respectively. Since there is no evidence of such maxima, there is no statical splitting of these levels into two sublevels.

Characteristic X-Ray Spectra of Elements. (20)—It is sometimes thought that for the explanation of X-ray spectra of elements, the subdivision of the p or d-levels into two distinct sublevels is necessary. But as has been shown by Dr. B. B. Ray and the author, X-ray spectra can be explained on the same principles as optical spectra, e.g. let us take the K-series of any elements. We take the structure diagram, and suppose that either by electron bombardment or otherwise, one electron has been removed altogether from the K-level. Then the state is unstable, one electron will now fall from any p-level $(L_2, M_2, \mathcal{N}_2 \ldots)$ to the K-level. The process can be written as follows:

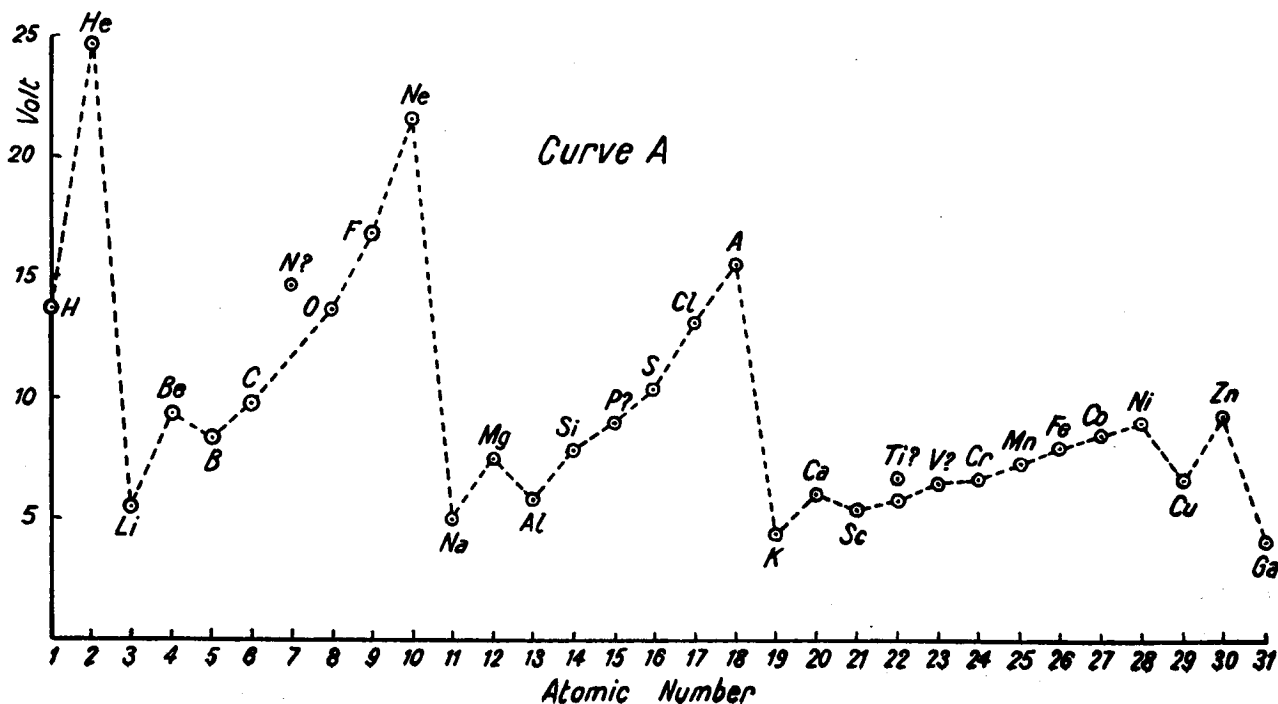$$K_1 . 6L_2 \rightarrow 2K_1 . 5L_2$$
$$(L_2 \rightarrow K_1) \ldots \text{gives us } K\alpha,\; K\alpha'$$
$$K_1\; 6M_2 \rightarrow 2K_1 . 5M_2$$
$$(M_2 \rightarrow K_1) \ldots\ldots\ldots\ldots K\beta,\; K\beta'$$

Now $K_1\; 6L_2$　　gives us a $^2S_1$　　-orbit.
　　　$2K_1 . 5L_2$　　gives us a $^2P_{1,2}$　　-orbit.

(K_1 gives $^2S_1$, $6L_2$ gives $^1S_0$; the resulting orbit is $^2S_1$. For the second state $^2K_1$ gives $^1S_0$, $^5L_2$ gives $^2P_{1,2}$ as in the halogens; the resulting orbit is $^2P_{12}$).

Curve A

So when the electron jumps from $L_2 \to K_1$, we get

	$^2P_1$	$^2P_2$
$^2S_1$	$K\alpha'$	$K\alpha$
	1	2

Similarly the origin of the L-spectra can also be explained. They arise when an electron is removed from any of the L-levels, and electron jumps from a higher level (M or N) to take its place.

If the above considerations be correct, it is perhaps wrong to say that the origin of X-ray spectra is similar to that of alkalies. The first term, arising from the presence of one electron in M is of course alkali-like. But the second pair of P-terms, arising from a defect of one electron from the completed L-level i.e. from the structure $2K_1\ 5L_2$, is halogenlike. Hence the difference $v_{k_{\alpha'}} - v_{k_\alpha}$ ought to be compared not to the value of $\varDelta\, v$ between the two p-terms of alkalies (as is usually done), but to the $\varDelta\, v$-value of the normal levels of Halogens.

CONCLUDING REMARKS

With the systematisation of the data on complicated spectra' a fresh crop of new problems suggest themselves to the theoretical physicist for solution (21). The future progress of theoretical physics must depend on the solution of these problems. We shall therefore examine the fundamental assumptions on which the interpretation of complex spectra has been built up. These are:

(1) The fundamental spectrum (i.e. the spectrum given out by an electron revolving round a single nucleus) must be of a doublet type (one s-term, two p-terms, two d-terms, etc.).

(2) Mechanical interpretation of different quantum numbers.

(3) Explanation of Pauli's rule of exclusion.

(4) Mechanical explanation of the principle of orbit synthesis.

It is rather remarkable that though the new developments in Quantum Mechanics viz.—Schrödingers' wave mechanics and Heisenberg's matrix mechanics, Dirac's non-commutative algebra—have made many points in the old quantum mechanics much clearer, they have scarcely been able to give a complete solution to any of the problems above mentioned. Let us take, for example, the first problem. The most satisfactory interpretation of the hydrogen spectrum is that of Schrödinger: following De-Broglie's ideas of the reconciliation between the wave theory, and the corpuscular theory of light, he has deduced an equation for the vibration of the hydrogen atom. It is shown that the hydrogen-atom can vibrate only when the negative energy takes up a number of discrete values made familiar by Bohr's theory. The theory has cleared

up the arbitrariness in Bohr's assumption of discrete quantum states, and has further given the quantum numbers correctly, for s, p, d, f-orbits, the value of $i_k = 0$, 1, 2, 3 respectively.

But Schrödinger's theory explained only the singlet spectrum; but we know that the spectrum of hydrogen is a doublet spectrum. The reason for the discrepancy is to be sought in the assumption of the electron as a point-charge only, whereas we know that the electron possesses also a definite amount of magnetic moment equal to

$\pm \dfrac{eh}{4\pi cm}$. Pauli (22) has made an attempt to perfect

Schrödinger's theory by taking the magnetic moment into account, but according to the author himself, the attempt has not yet been very successful. The usual equations of motion of the electron are now admitted to be imperfect, but the satisfactory equation is still to be found.

That the solution of the hydrogen spectrum offered by Schrödinger is still to be completed is also clear from the celebrated experiments of Stern and Gerlach on the deflection of atomic rays by a nonhomogeneous magnetic field. Recently these experiments have been extended to atomic rays of hydrogen (23) as well, and evidence has been obtained that the hydrogen atom in the fundamental

$^2S_0$-state possesses the magnetic moment of $\dfrac{eh}{4\pi cm}$. Now

according to Schrödinger, for the s-state, $i_k = 0$ and the hydrogen atom would be nonmagnetic if magnetism arose from orbital motion alone. The magnetism which is actually observed, therefore, arises not from the orbital-motion (as originally supposed) of the electron, for according to Schrödinger's theory, such orbital motion does not exist in the case of the s-state. It must therefore be traced to the electron itself, as has been assumed by Goudsmit and Uhlenbeck in their hypothesis of the rotating electron. But Schrödinger assumes the electron to be a point charge only ([1]).

---

[1] The assumption that the magnetic moment in atomic rays of H, Na or Cu, and Ag arise from the rotational motion of the valency electron, and not from their orbital motion clears up one very important objection raised against the theoretical understanding of Stern and Gerlach experiment by Einstein and Ehrenfest (Zs. für Physik, Bd II, page. 31). The atomic rays, as they enter the magnetic field, cannot have their magnetic axis in any definite direction. When they enter the field, the magnetic axis makes a precessional motion about the axis of the external field. This precessional motion gives rise to a radiation and a radiation damping. The time required by the damping factor to stop the precessional motion to rest, and align the magnetic axis of the atom parallel to the magnetic field was calculated by Einstein and Ehrenfest to be of the order of 10^{-15} sec., while the actual time of orientation must be $\ll 10^{-5}$ sec. But according to what has been said before, the electron, being a small magnet must execute not only a precessional motion, but also a nutational motion about the axis of the outer field. The moment of inertia of the electron being extremely small, the magnetic axis of the electron will soon set itself parallel to the outer field.

After hydrogen, the problem of the helium spectrum naturally suggests itself for solution. It is a time-honoured problem, and has baffled many attempts at solution. Recently solution on the basis of Schrödinger's theory have been published by Unsöld, Sugiura, and Kellner (24). Kellner has taken the calculations to the fourth place and finds an exact agreement between the theoretical and the experimental value. But this agreement does not exhaust all the points in the helium problem. One has to remember that the old Bohr theory gave the ionisation potential of hydorgen quite correctly, but it did not solve all the points in the hydrogen problem. In helium we have further to explain the origin of the parhelium and helium series, and the absence of inter combination amongst them. An explanation has been attempted by Heisenberg (25), and by Dirac, but both these authors have treated the electron merely as a point charge, while according to Hund's interpretation the difference in value between ^1S and ^3S is due only to the different orientation of the magnetic axis in the two cases. The $2\ ^1S_0$-terms arises with electron (1) at K_1, electron (2) at L_1, but with its magnetic axis directed in an antiparallel direction. For the $2\ ^3S_1$ term, electron (1) is at K_1, electron (2) at L_1, but their magnetic axes are now parallel. The difference in value seems to be of magnetic origin and not to electrical origin, as supposed by Heisenberg and Dirac.

Wigner (26) has attempted a general explanation of the origin of different groups of terms in complicated spectra on the basis of Heisenberg's theory, but it is yet too early to pronounce a critical opinion on these works.

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43(a). EXTENSION OF THE IRREGULAR DOUBLET LAW TO COMPLEX SPECTRA

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The Irregular Doublet Law was discovered by G. Hertz in 1921.[1] It states that if the square roots of the values of the L_1 and the L_{II}-absorption levels in X-ray Spectra are plotted against the atomic number, the two curves nearly run parallel to each other. Mathematically this means that

$$\sqrt{\nu_I} - \sqrt{\nu_{II}} = \text{constant.} \qquad \ldots (1)$$

The explanation on Bohr's theory is that the energy of the electron in the L-level is given by

$$\frac{\nu}{R} = \frac{(Z - \sigma_I)^2}{n^2}, \frac{(Z - \sigma_{II})^2}{n^2} \text{ respectively}$$

where Z = nuclear charge
n = Total quantum number for L_1 and L_{II}
σ_I = Screening constant while the electron is in the L_1-level
σ_{II} = Screening constant while the electron is in the L_{II}-level.
n has the same value in both cases, *viz.*, 2.

$$\sqrt{\nu_I} - \sqrt{\nu_{II}} = \frac{\sigma_I - \sigma_{II}}{n} \qquad \ldots (1')$$

The extension of the Irregular Doublet Law to optical region is due to Millikan and Bowen.[2] Starting from a

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[1] G. Hertz, Zs. f. Physik. Vol. 3. p. 19.

[2] Millikan and Bowen, Phy. Rev. Vol. 24, p. 209 (1924) and subsequent papers.