Spectra and Atoms.

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ONE of the chief purposes of present-day spectroscopy is the correlation of the structure of spectra with the structure of atoms. The possibility of such a correlation was clearly in the minds of some of the earlier workers in spectroscopy, but nothing very definite emerged until the advent of the Rutherford–Bohr theory nearly fifteen years ago. Meanwhile, however, substantial progress had been made in disentangling the structure of the spectra themselves.

The spectra of most of the elements are very complicated—some containing thousands of lines—and it was only by reducing them to simpler terms that there could be any hope of finding a theoretical interpretation. Fortunately, the spectra of a few of the elements are relatively simple, and it was the study of these that paved the way to the quantum theory of spectra and afterwards to the elucidation of the more complex spectra.

The earlier investigations were primarily directed to the identification of regular *series* of lines which could be represented by simple formulæ. Such a series, as exemplified by the well-known Balmer series of hydrogen and the arc spectra of the alkali metals, consists of a number of lines of gradually diminishing intensity, and diminishing distance apart in passing to shorter wave-lengths, and each series approaches a definite limit. Near the limit the lines become very closely crowded together, but no series has actually been observed to its limit. Rydberg's original formula represents lines of a series with sufficient accuracy for our present purposes, namely,

$$\nu = A - R/(m + \mu)^2.$$

Here ν represents the wave-numbers of the series lines corresponding to successive integral values of m; A is the wave-number of the limit ($m = \infty$); R is the " Rydberg constant " (= 109678 as calculated from the hydrogen series); and μ is a constant (usually a fraction) special to each series and determined, together with A, from the observed lines. Each line of a series is thus represented by the difference of two terms.

Different types of series were early recognised. In the alkali spectra, that which includes the strongest lines was called the Principal series; the next brightest, consisting of somewhat diffuse lines, was called the Diffuse series; and another was called the Sharp series in consequence of the frequent occurrence of sharply-defined lines in series of this type. Other types of series were afterwards recognised, only one of which, however —the badly-named Fundamental series—has received a special designation.

The work of Rydberg showed that the various series in the same spectrum were closely related to one another, and this naturally brought about a considerable simplification in the mode of representing them. For example, the limiting term A in the formula for a given series is also a term of one of the associated series. The word " term " has thus come to have a special meaning in spectroscopy, representing something quite different from the spectrum lines themselves. The wave-number of a spectrum *line* always appears as the difference of two *terms*, and in attempting to analyse the structure of a spectrum we are really trying to find out the spectroscopic terms from which it is built up.

The consideration of these matters is greatly facilitated by the use of an abbreviated notation. The initial letters of the names previously assigned to the actual series are now universally adopted for the respective sequences of terms. If the first member of each term sequence be denoted by 1, we have

Principal series $= 1S - mP$
Sharp ,, $= 1P - mS$
Diffuse ,, $= 1P - mD$
Fundamental ,, $= 1D - mF$
FG ,, $= 1F - mG$, etc.

It is to be understood that $1S$, for example, means the first term of the S sequence, whereas mS represents a regular sequence of terms ($1S$, $2S$ . . .), and that a *sequence* of terms in combination with the first term of another sequence gives rise to one of the main series of lines.

Ritz was the first to recognise clearly, as expressed in the " Combination Principle," that other terms besides the first of a sequence might combine with terms from other sequences to produce spectrum lines; as, for example, $2S - mP$. The possible combinations, however, are not so numerous as Ritz appears to have thought; they are restricted by certain selection rules, which will be stated more fully a little later. Meanwhile, it will suffice to remark that if the term sequences are written in the order *S*, *P*, *D*, *F* . . ., the combinations which ordinarily occur in the simpler spectra are only those between terms indicated by adjacent letters.

It should be further observed that in some spectra all terms other than those of *S* type have two values (in most cases not very different), giving series consisting of doublets, as in the well-known spectrum of sodium. In other spectra, all terms except *S* have three values, giving rise to triplets. A combination of two doublet terms, however, does not give four lines, as might have been expected, but only three; and, similarly, a combination of two triplet terms yields only six of the nine lines which are arithmetically possible. Clearly, another selection principle comes into operation, and for its application it is necessary to distinguish the components of each multiple term by what are now called "inner quantum" numbers.

These early investigations showed, among other things, that the spectra of the alkali metals were all of similar character, but differed in the fact that corresponding lines were mostly displaced to longer wave-lengths with increase of atomic weight, and that the doublet separations increased roughly as the squares of the atomic weights. All elements of the second group were similarly found to exhibit singlet and triplet series, and here also the triplet separations were found to vary approximately as the squares of the atomic weights. In the third group the elements of the aluminium sub-group were found to be characterised by doublets.

The spectra of rather more than 20 elements had been wholly or partly resolved into series before the year 1913, when Bohr's theory came to illuminate the subject of spectral structure by its interpretation of spectroscopic terms as energy levels of the atom. On this theory, an excited atom can exist temporarily in certain "stationary" or non-radiating states, each of a definite energy value, and not in any intermediate state, the possible states being governed by quantum considerations. A spectrum line is to be regarded as representing the energy lost by an atom when it passes from one state of a certain energy to another of lesser energy. In its normal unexcited state, the atom is in the state of lowest energy, but it may pass to states of greater energy by the absorption of radiation or by collisions of certain types.

In terms of electron orbits, the spectrum of a neutral atom is supposed to be generated, one line at a time, by the migrations of the most loosely bound electron between the different orbits permitted by quantum conditions, and the whole spectrum is the integration of the multitude of transitions going on in different atoms at the same time. This theory, I need scarcely remind you, accounted quantitatively for the spectrum of hydrogen and that of ionised helium, and in a general way for the series spectra of other elements.*

The energy representative of an orbit is, in the first place, dependent upon its size, and, in the simplest consideration, is the same whether the orbit be a circle or an ellipse having a major axis equal to the diameter of the circle. It was shown by Sommerfeld, however, that in consequence of the varying velocity of an electron in an elliptic orbit, and the consequent relativistic variation of its mass, the energies of orbits of different eccentricities, though having the same major axes, must be slightly different. It was in this way that he predicted the " fine structure " of the lines of the Balmer series of hydrogen. In more complex atoms, the migrating electron is subjected to a perturbing action arising from the presence of additional electrons, but here the effect is much greater than that due to relativity considerations, and gives rise to the separate series.

It thus became necessary to use two quantum numbers to define an electron orbit. They are written in the form n_k, where n is called the *principal quantum number* and k the *azimuthal quantum number*. In a rough approximation, n determines the major axis and k the minor axis of the ellipse, both being restricted to definite integral values.

In the earlier days of the theory it was supposed that only a single electron was involved in the production of the spectrum, and that the type of a spectroscopic term corresponded to the k value of the electron orbit in accordance with the scheme:

Term	S	P	D	F
k	1	2	3	4

For example, if the largest spectroscopic term, or " ground term," in a spectrum was found to be of P type, it was supposed that the electron last added in the formation of the atom occupied an orbit for which $k = 2$. Or if the atom was excited, and the series electron occupied a 3_2 orbit, the corresponding term would be $3P$. It will be noted that the selection rule previously mentioned is equivalent

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* The orbital picture of atomic structure is adopted for convenience of description, but it should be understood that this may not represent the final interpretation.

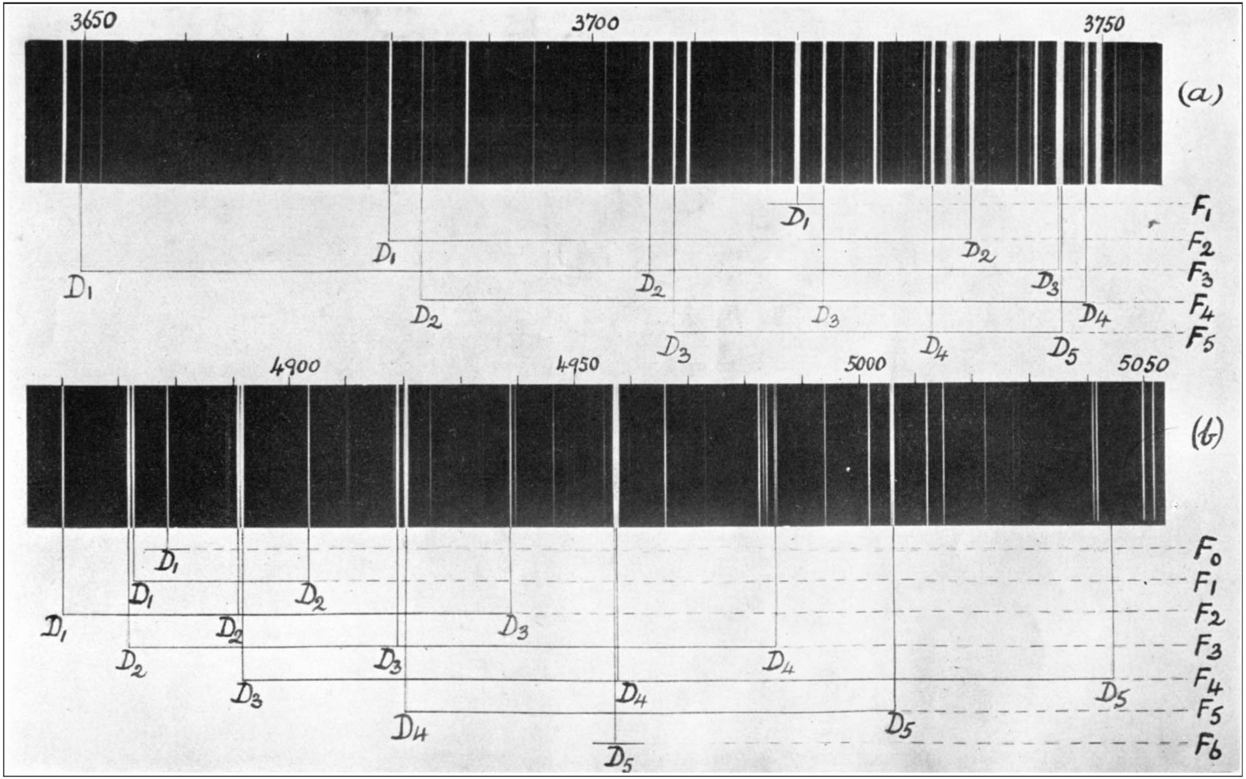
to stating that an electron can only change from one orbit to another for which k differs by ± 1. All this was in entire agreement with the spectroscopic data then available.

From the spectroscopic data, considering also the general chemical and physical properties of the elements, Bohr built up his well-known table (1922) showing the probable distribution of the electrons in n_k groups in the atoms of a considerable number of elements. These ideas of Bohr have been modified in certain details, and remarkably extended in recent years, so that it has become possible to specify with certainty the electron arrangements for the great majority of the elements and the most probable arrangement for the remainder. These developments have been made possible by advances in the analysis of complex spectra and in the general theory.

The key to the structure of the more complex spectra was furnished, in 1922, by Catalán, who was then working in my laboratory at the Imperial College. Up to that time the search for regularities in spectra had been mainly guided by the idea of extended regular series of lines, and definite results had only been obtained for about one-quarter of the chemical elements. Singlet, doublet, and triplet terms were all that were then known, but in his work on manganese and a few other elements, Catalán discovered complex groups of related lines which involved terms of higher multiplicities. Sommerfeld soon afterwards showed how the scheme of inner quantum numbers which he had devised for the simpler terms could be extended to the new multiplicities, and the identification of what Catalán had called " multiplets " in numerous spectra rapidly followed. Strictly speaking, of course, the name *multiplet* is applicable to all combinations of spectroscopic terms other than those of a singlet system.

Many spectra which had previously defied analysis have thus been found to be built up chiefly of complicated multiplets, each of which can be represented by taking differences between two multiple terms, subject to appropriate selection rules. The same multiple term may be involved in several multiplets, but Rydberg sequences extending to more than two or three consecutive terms are infrequent.

The discovery of higher multiplicities has necessitated considerable extension of the notation for spectroscopic terms. The term types being represented by their original symbols, the multiplicity (r) of the system to which a term belongs is indicated by a numerical superscript on the left of the symbol, and the inner quantum number by a subscript on the right; as $^3P_2$, $^5F_4$, and so on. A term itself



Multiplets in the arc spectrum of iron. $(a) = {}^5D\,{}^5F$. $(b) = {}^7D\,{}^7F$.

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is distinguished from others of the same type in various ways, and there is, as yet, no general agreement on this point. Examples will appear in due course.

The inner quantum numbers (j), which play so large a part in determining the permissible combinations, are indicated in the following table :

Inner Quantum Numbers (j).

Odd Multiplicities.

Terms	L.	Singlet $r = 1$.	Triplet $r = 3$.	Quintet $r = 5$.	Septet $r = 7$.
S	0	0	1	2	3
P	1	1	0 1 2	1 2 3	2 3 4
D	2	2	1 2 3	0 1 2 3 4	1 2 3 4 5
F	3	3	2 3 4	1 2 3 4 5	0 1 2 3 4 5 6
G	4	4	3 4 5	2 3 4 5 6	1 2 3 4 5 6 7

Even Multiplicities.

Terms	L.	Doublet $r = 2$.	Quartet $r = 4$.	Sextet $r = 6$.	Octet $r = 8$.
S	0	1	2	3	4
P	1	1 2	1 2 3	2 3 4	3 4 5
D	2	2 3	1 2 3 4	1 2 3 4 5	2 3 4 5 6
F	3	3 4	2 3 4 5	1 2 3 4 5 6	1 2 3 4 5 6 7
G	4	4 5	3 4 5 6	2 3 4 5 6 7	1 2 3 4 5 6 7 8

The values here assigned to the inner quantum numbers are not only in empirical accordance with the actual spectroscopic observations, but now have a theoretical basis. When two multiple terms enter into combination to form a multiplet, lines appear only when the j values differ by unity or zero; *i.e.*, $\Delta j = \pm 1$ or 0; also, a transition 0 to 0 is never found. It will readily be seen, for example, that a combination of a ^3D with a ^3P term will give six, and not nine, lines.

Terms of different multiplicities occur in most spectra, but in a given spectrum all the terms are either all odd or all even. Intersystem combinations, still subject to the j condition, only occur for systems in which $\Delta r = \pm 2$.

The two multiplets from the arc spectrum of iron which are shown in Plate I will illustrate the application of the inner quantum selection rule. The first shows a quintet D in combination with a quintet F term, and the second a corresponding combination of septet terms. The lines selected from the far greater number among which they appear are justified by the following schemes of wave-number differences :

	$^5D_0$.		$^5D_1$.		$^5D_2$.		$^5D_3$.		$^5D_4$.
$^5F_1$	26688·31	*89·91*	26778·22	*184·11*	26962·43				
			106·77		*106·76*				
$^5F_2$			26671·45	*184·12*	26855·57	*288·09*	27143·66		
					164·88		*164·90*		
$^5F_3$					26690·69	*288·07*	26978·76	*415·91*	27394·67
							227·88		*227·85*
$^5F_4$							26750·88	*415·94*	27166·82
									292·29
$^5F_5$									26874·53

	$^7D_1$.		$^7D_2$.		$^7D_3$.		$^7D_4$.		$^7D_5$.
$^7F_0$	20493·53								
	25·55								
$^7F_1$	20519·08	*130·43*	20388·65						
	52·41		*52·34*						
$^7F_2$	20571·49	*130·50*	20440·99	*198·91*	20242·08				
			81·55		*81·56*				
$^7F_3$			20522·54	*198·90*	20323·64	*271·30*	20052·34		
					114·26		*114·26*		
$^7F_4$					20437·90	*271·30*	20166·60	*347·51*	19819·09
							150·80		*150·85*
$^7F_5$							20317·40	*347·46*	19969·94
									195·44
$^7F_6$									20165·38

Other types of terms, H, J, K . . ., are found in some spectra, but the number of components of a term never exceeds the maximum indicated by the name of the system to which it belongs.

One result of great significance arising out of the analysis of these complex spectra was that the largest spectroscopic term—representing the normal state of the atom in question—was sometimes of a type which could not possibly be regarded as showing the k value of the last-bound electron. For example, the "ground term" of titanium (22) is of the type ^3F, and on the simple theory this would require the last electron to be bound in a 4_4 orbit. This would place it far beyond all the other electrons, in an orbit which it would be very unlikely to occupy unless in an excited state.

The original theory, in fact, left other details unexplained, even in connexion with atoms which had been considered comparatively simple. For instance, in copper there are many lines of the arc spectrum which are not included in the system of doublets. Again, in the alkaline earths there are groups of lines (known to spectroscopists as PP', DD', etc., multiplets) which are not included in the regular triplet series, although involving some of the ordinary triplet terms.

The next great advance in the theory of spectra arose out of an investigation by Russell and Saunders of such groups of lines in the arc spectrum of calcium. Some of the new triplet terms involved in these groups, which apparently violated the familiar selection rule for k, were found to represent greater amounts of energy than that necessary to drive a single electron completely out of the atomic system. Russell and Saunders were thus forced to the conclusion that in some of the atoms of calcium a second electron was displaced while the first still remained within the system and that the emission represented the combined energies due to simultaneous jumps of both electrons to smaller orbits. The quantum numbers which defined the spectroscopic terms could therefore no longer be identified with those which specified the orbit of a single electron. Consequently, the spectroscopic terms have now to be defined by " group quantum " numbers, representing a kind of resultant of the k orbital numbers. These new numbers are mostly represented by L, which equals 0, 1, 2 . . . for S, P, D . . .

Arising out of this brilliant new idea in the theory of spectra, to which important contributions were also made by Pauli and Heisenberg, a complete scheme has been developed by Hund whereby the types of spectroscopic terms corresponding to any specified arrangement of the electrons in n_k orbits can be calculated. Or, conversely, the orbital numbers can be indicated when the terms have been identified. There is no time to explain how this is done, but I may say that the results given by the theory have been abundantly confirmed by the recent analyses of many complex spectra. The whole theory is based upon the assumption that an atom is so constituted that the angular momenta of all its rotary motions can only change by unit steps, the unit being $h/2\pi$. It gives a physical meaning to the inner quantum numbers by identifying them with the resultant angular momenta of the entire atom in its various possible quantised states.

The new theory has also an important bearing on the theory of the Periodic System in virtue of Pauli's principle, which forbids more than one electron to occupy an orbit having the same four quantum numbers now necessary to define the motions completely. One of the new quantum numbers involves the orientation of the orbit, and the other the orientation of spin of the electron; they are called magnetic quantum numbers.

Pauli's principle of exclusion at once leads to a modification of Bohr's original distribution of electrons in n_k sub-groups, identical with that to which Main Smith and Stoner had been led independently, chiefly by the consideration of chemical and physical properties respectively. In the new scheme, the inner sub-levels have fewer electrons and there is a greater concentration in the outer sub-levels of each n_k group. The spectroscopic theory, however, does not give the distribution of electrons in all the X-ray sub-levels, but only the arrangement in n_k sub-groups. It results from the theory that the maximum number in any of these sub-groups is given by $4k - 2$, in agreement with Main Smith and Stoner. There are accordingly strong theoretical foundations for the new table of electron arrangements. It has not yet been confirmed for every element by spectroscopic methods, but this seems to be merely a question of time.

Table of Atomic Structures.

Element	Atomic Number	Extra-nuclear Electronic Configurations.																							
		K	L		M			N				O					P						Q		
		1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2	6_3	6_4	6_5	6_6	7_1	7_2	7_3
H	1	1																							
He	2	2																							
Li	3	2	1																						
Be	4	2	2																						
B	5	2	2	1																					
C	6	2	2	2																					
N	7	2	2	3																					
O	8	2	2	4																					
F	9	2	2	5																					
Ne	10	2	2	6																					
Na	11	2	2	6	1																				
Mg	12	2	2	6	2																				
Al	13	2	2	6	2	1																			
Si	14	2	2	6	2	2																			
P	15	2	2	6	2	3																			
S	16	2	2	6	2	4																			
Cl	17	2	2	6	2	5																			
A	18	2	2	6	2	6																			
K	19	2	2	6	2	6		1																	
Ca	20	2	2	6	2	6		2																	
Sc	21	2	2	6	2	6	1	2																	
Ti	22	2	2	6	2	6	2	2																	
V	23	2	2	6	2	6	3	2																	
Cr	24	2	2	6	2	6	5	1																	
Mn	25	2	2	6	2	6	5	2																	
Fe	26	2	2	6	2	6	6	2																	
Co	27	2	2	6	2	6	7	2																	
Ni	28	2	2	6	2	6	8	2																	
Cu	29	2	2	6	2	6	10	1																	
Zn	30	2	2	6	2	6	10	2																	
Ga	31	2	2	6	2	6	10	2	1																
Ge	32	2	2	6	2	6	10	2	2																
As	33	2	2	6	2	6	10	2	3																
Se	34	2	2	6	2	6	10	2	4																
Br	35	2	2	6	2	6	10	2	5																
Kr	36	2	2	6	2	6	10	2	6																
Rb	37	2	2	6	2	6	10	2	6			1													
Sr	38	2	2	6	2	6	10	2	6			2													
Y	39	2	2	6	2	6	10	2	6	1		2													
Zr	40	2	2	6	2	6	10	2	6	2		2													
Nb	41	2	2	6	2	6	10	2	6	4		1													
Mo	42	2	2	6	2	6	10	2	6	5		1													
Ma	43	2	2	6	2	6	10	2	6	6		1													
Ru	44	2	2	6	2	6	10	2	6	7		1													
Rh	45	2	2	6	2	6	10	2	6	8		1													
Pd	46	2	2	6	2	6	10	2	6	10															
Ag	47	2	2	6	2	6	10	2	6	10		1													
Cd	48	2	2	6	2	6	10	2	6	10		2													
In	49	2	2	6	2	6	10	2	6	10		2	1												
Sn	50	2	2	6	2	6	10	2	6	10		2	2												
Sb	51	2	2	6	2	6	10	2	6	10		2	3												
Te	52	2	2	6	2	6	10	2	6	10		2	4												
I	53	2	2	6	2	6	10	2	6	10		2	5												
Xe	54	2	2	6	2	6	10	2	6	10		2	6												
Cs	55	2	2	6	2	6	10	2	6	10		2	6				1								
Ba	56	2	2	6	2	6	10	2	6	10		2	6				2								

Extra-nuclear Electronic Configurations.

Element	Atomic Number	K	L		M			N				O					P						Q		
		1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2	6_3	6_4	6_5	6_6	7_1	7_2	7_3
La ...	57	2	2	6	2	6	10	2	6	10		2	6	1			2								
Ce ...	58	2	2	6	2	6	10	2	6	10	1	2	6	1			2								
Pr ...	59	2	2	6	2	6	10	2	6	10	2	2	6	1			2								
Nd ...	60	2	2	6	2	6	10	2	6	10	3	2	6	1			2								
Il ...	61	2	2	6	2	6	10	2	6	10	4	2	6	1			2								
Sa ...	62	2	2	6	2	6	10	2	6	10	5	2	6	1			2								
Eu ...	63	2	2	6	2	6	10	2	6	10	6	2	6	1			2								
Gd ...	64	2	2	6	2	6	10	2	6	10	7	2	6	1			2								
Tb ...	65	2	2	6	2	6	10	2	6	10	8	2	6	1			2								
Ds ...	66	2	2	6	2	6	10	2	6	10	9	2	6	1			2								
Ho ...	67	2	2	6	2	6	10	2	6	10	10	2	6	1			2								
Er ...	68	2	2	6	2	6	10	2	6	10	11	2	6	1			2								
Tu ...	69	2	2	6	2	6	10	2	6	10	12	2	6	1			2								
Yb ...	70	2	2	6	2	6	10	2	6	10	13	2	6	1			2								
Lu ...	71	2	2	6	2	6	10	2	6	10	14	2	6	1			2								
Hf ...	72	2	2	6	2	6	10	2	6	10	14	2	6	2			2								
Ta ...	73	2	2	6	2	6	10	2	6	10	14	2	6	3			2								
W ...	74	2	2	6	2	6	10	2	6	10	14	2	6	4			2								
Re ...	75	2	2	6	2	6	10	2	6	10	14	2	6	5			2								
Os ...	76	2	2	6	2	6	10	2	6	10	14	2	6	6			2								
Ir ...	77	2	2	6	2	6	10	2	6	10	14	2	6	7			2								
Pt ...	78	2	2	6	2	6	10	2	6	10	14	2	6	9			1								
Au ...	79	2	2	6	2	6	10	2	6	10	14	2	6	10			1								
Hg ...	80	2	2	6	2	6	10	2	6	10	14	2	6	10			2								
Tl ...	81	2	2	6	2	6	10	2	6	10	14	2	6	10			2	1							
Pb ...	82	2	2	6	2	6	10	2	6	10	14	2	6	10			2	2							
Bi ...	83	2	2	6	2	6	10	2	6	10	14	2	6	10			2	3							
Po ...	84	2	2	6	2	6	10	2	6	10	14	2	6	10			2	4							
EkaI	85	2	2	6	2	6	10	2	6	10	14	2	6	10			2	5							
Rn ...	86	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6							
EkaCs	87	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6					1		
Ra ...	88	2	2	8	2	6	10	2	6	10	14	2	6	10			2	6					2		
Ac ...	89	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6	1				2		
Th ...	90	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6	3				1		
U-*X*	91	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6	4				1		
U ...	92	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6	5				1		

The way in which the spectroscopic terms are now correlated with the electron configurations may be gathered from the relatively simple case of magnesium, as shown below.

Magnesium.

K	*L*		*M*			*N*					
1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4		Terms.
2	2	6	2							$3s$	^1S
2	2	6	1	1						$3p$	^1P ^3P
2	2	6	1		1					$3d$	^1D ^3D
2	2	6	1			1				$4s$	^1S ^3S
2	2	6	1				1			$4p$	^1P ^3P
2	2	6	1					1		$4d$	^1D ^3D
2	2	6		2						$3p'$	^1S ^1D ^3P
2	2	6		1	1					$3d'$	^1P ^1D ^1F ^3P ^3D ^3F

The table shows the arrangement of electrons in the neutral atom and in a number of excited states. The normal state, with two electrons in 3_1 orbits, is represented by the singlet term ^1S. When one of the 3_1 electrons is excited to a 3_2 orbit, the corresponding terms are ^1P and ^3P; and so on. It should be remarked here that in deducing the terms, all n_k sub-groups which have their full quotas may be disregarded, as their angular momenta cancel out. Further, it should be explained that an n_k configuration may be represented by more than one spectroscopic term in consequence of the dependence of the energy, in part, on the orientation of the orbit and on that of spin of the electron.

In this case, when only one of the outermost electrons is displaced, the term types correspond with the k's of the electrons, as in the earlier theory. When two electrons are displaced in the way shown in the lower part of the diagram, new terms arise for which the types are no longer directly indicated by the k of an electron. The type is now related to the quantised vectorial sum of the k values of the individual electrons. The selection rules have accordingly to be transferred from the terms to the electrons. Combinations between terms arising from different configurations can occur only when k changes by ± 1 for one electron and by ± 2 or 0 for the other, it being supposed that not more than two electrons make simultaneous jumps.

Thus, in magnesium, the terms $3p'\,^1S$, etc., may combine with $3p\,^1P$, $3p\,^3P$, but not with $3d\,^1D$, $3d\,^3D$; $3d'\,^1P$, etc., may combine with $3p'\,^1S$, etc., or with $3d\,^1D$, but not with $3p\,^1P$. Combinations between terms in the upper part of the table, always subject to inner quantum restrictions, give the series which were long ago recognised by Rydberg and by Kayser and Runge; and combinations between the rows of terms in the lower part, or of these with selected rows of terms in the upper part, give multiplets of the kind discussed by Russell and Saunders.

It will be interesting to survey the spectra of some of the elements in relation to the new table of atomic structures. In general, elements in which the incompletely filled n_k sub-groups have the same number of electrons—the completely occupied sub-groups "cancelling out"—give spectra of similar character. Thus, the similarity of the spectra of the alkali metals, all of which consist of doublets, arises from the fact that there is only a single electron lying outside completed sub-groups. The spectra of Cu, Ag, and Au of Group I also include doublet series, but some interesting points in connexion with these may be more conveniently considered later.

As will be seen on reference to the table, all elements of Group II have two electrons in n_1 orbits, and all the underlying sub-groups of orbits, if occupied at all, are completed. We have already seen that the spectra of all these elements are of similar character, consisting of singlets and triplets.

In boron and the aluminium sub-group of elements there is only a single n_2 electron outside closed n_k sub-groups, and the spectra are again characterised by doublets. Odd and even multiplicities, in fact, alternate without exception right across the columns of the periodic table.

The spectra of the scandium sub-group of Group III are of exceptional interest, inasmuch as, though showing even multiplicity, they are very different from those of the aluminium sub-group in other respects. Here, in the normal atom, we observe that all the occupied n_k sub-groups are completely filled with the exception of the n_3 orbits. In scandium, the 3_3 sub-group contains only one electron and accordingly gives ^2D for the ground term, as compared with ^2P in aluminium. The continuity of the electron configurations for successive atoms is first interrupted at potassium, where the 19th electron occupies a 4_1 in preference to a 3_3 orbit. That this must be so is certainly indicated by the potassium spectrum, and it follows that at this stage the last added electron is more firmly bound in 4_1 than in 3_3. The same is true when the 20th electron also goes into a 4_1 orbit in the formation of the calcium atom. But when the 21st electron is added to form the scandium atom, it is most firmly bound in a 3_3 orbit.

In compiling his original table, showing this arrangement for scandium, Bohr argued from a comparison of the spectrum of potassium (K I) with the similar spectrum of ionised calcium (Ca^+ or Ca II), for both of which the spectroscopic terms were known. As shown in the appended diagram,* it was clear that as the nuclear charge increased, the $3D$ term was tending to approach the $4S$ term in magnitude, and Bohr inferred that in doubly-ionised scandium (Sc^{++} or Sc III) the $3D$ term would be the largest. This has lately been verified experimentally by Russell, whose results for Ti IV also provide further confirmation.

This change in the electron structure at Sc is naturally accompanied by a change in the character of the spectrum and in the chemical properties of the element, as compared with Al, which also has three outer electrons, but arranged differently.

The filling up of the 3_3 orbits continues from Sc to Ni in the way shown in the table, forming the first transition group of elements. All their spectra are very complicated, but the main features of their structures have been determined and completely verify the normal electron arrangements specified for them.

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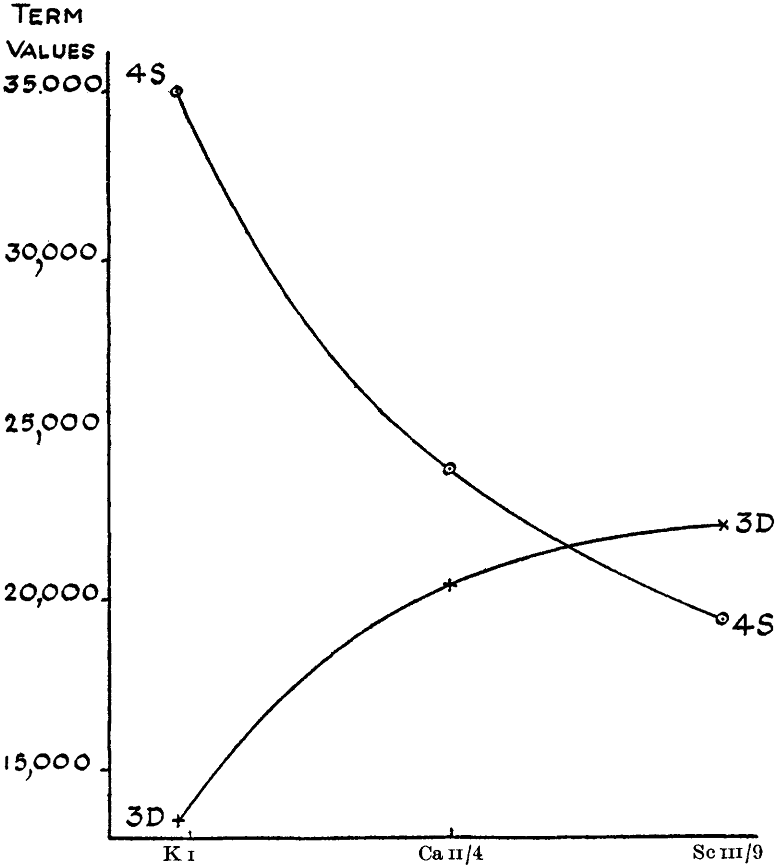
* As usual in such comparisons, the terms of Ca II have been divided by 4 and those of Sc III by 9.

The second set of transition elements, Y to Pd, is similarly marked by the filling up of the 4_3 sub-group, but the order of filling up, which has also been confirmed by the analyses of the spectra, is not exactly the same. Thus, whereas Ni (28), marking the end of the first set, has eight 3_3 and two 4_1 electrons, the end of the second set is marked by Pd (46) with ten 4_3 electrons. The Pd atom thus has all its occupied sub-groups completely filled, more or less resembling a rare gas, and is consequently very stable. The ground term of Pd is accordingly a ^1S term, whereas that of Ni is a ^3F term.



The effect of this difference is seen when the next consecutive elements are respectively formed by the addition of another electron. In the case of Ag (47), which follows Pd, the added electron falls into a 5_1 orbit, and its spectrum is of the simple alkali type, consisting of doublet series; and the simplicity of the spectrum, it will be observed, is matched by the simple univalence of silver.

On the other hand, the arc spectrum of Cu (29), which follows Ni, gives many lines in addition to those of the alkali type which depend on a single electron outside completed n_k groups. In consequence of the tendency of Cu to approach the Ni configuration, a system of nine 3_3 and two 4_1 electrons is nearly as stable as one having ten 3_3 and one 4_1. Two electrons are thus liable to displacement, and it is in this way that the added complexity of the Cu spectrum, as compared with Ag, is accounted for. Presumably, this also accounts for the two valencies of copper.

The general outcome of such investigations, which I cannot pursue further for want of time, is to show, not only the beautifully systematic character of atom-building, but also that all the main features of the spectrum of an atom, however complex, can now be theoretically predicted if the electron configurations are known. Or, conversely, from a knowledge of the spectroscopic terms the corresponding configurations of electrons can be correctly deduced.

So far, I have dealt chiefly with the spectra of neutral atoms, but the spectra of ionised atoms are also of great importance as supporting the general theory. Bohr's theory, in the first instance, was greatly strengthened by its extension from hydrogen to ionised helium, the spectrum of which was already known from my own observations, though its origin had previously been misunderstood. When one electron has been entirely removed by the exciting agency, the helium atom resembles that of hydrogen, except that the mass of the nucleus is four times as great and its positive charge twice as great. It follows that the lines of ionised helium should be given, in a first approximation, by the same formula as that for hydrogen, except that the Rydberg constant, R, must be replaced by $4R$. Actually, a slight difference between R_{H} and R_{He} (= 109678 and 109722, respectively) was fully explained by taking account of the difference in mass of the respective nuclei, which does not otherwise affect the spectrum. Subsequent investigations showed that the value $4R$ was characteristic of the series lines of singly-ionised atoms generally, so that a spectrum arising from such atoms could be certainly identified as such if $4R$ appeared in the formula representing its series lines.

Bohr further foresaw that if an atom has lost two electrons, the remainder, or "core," of the atom must have a double positive charge with respect to the migrating electron, and that the series lines would be characterised by $9R$. If three electrons had been removed so that the atom was trebly-ionised, the series constant would become $16R$; and so on. These expectations were, in the first instance, most completely verified by Paschen's work on Al III and my own work on Si IV, the spectra being produced by the action of strong discharges. Here the observational data were ample for the calculation of the series constants, and Bohr's predictions were fully established.

When atoms resemble each other in everything but nuclear charge and mass, they are said to be "iso-electronic," and the relations between their spectra are beautifully simple. They are, of course, all of similar type, but corresponding lines are systematically displaced to shorter wave-lengths as the nuclear charge increases. The displacements in wave-numbers are, in fact, almost linear, in accordance with the "irregular doublet" law deduced by Sommerfeld for *X*-ray spectra. The separations in the doublets also increase systematically with higher atomic number in agreement with the "regular doublet" law of Sommerfeld. Comparing the iso-electronic atoms Na I, Mg II, Al III, Si IV, the following table will illustrate the simple relations in question.

	Na I.	Mg II.	Al III.	Si IV.
Wave-lengths	5,896	2,803	1,863	1,402
	5,890	2,796	1,855	1,394
Wave-numbers.........	16,956	35,669	53,680	71,280
	16,973	35,761	53,918	71,740
Separations	17	92	238	460

Many spectra have since been investigated, with similar results, even among more complex spectra, as shown, for example, by the work of Gibbs and White on the displacements and separations of corresponding multiplets in the spectra of Sc I, Ti II, and V III.

Special attention has been given by Millikan and Bowen, and by myself, to elements in the first row of the periodic table. All the possible states of these atoms are included in the following scheme:

	Atomic no.								
Series constant.	1.	2.	3.	4.	5.	6.	7.	8.	9.
R	H	He I	Li I	Be I	B I	C I	N I	O I	F I
4*R*	He II	Li II	Be II	B II	C II	N II	O II	F II	
9*R*	Li III	Be III	B III	C III	N III	O III	F III		
16*R*	Be IV	B IV	C IV	N IV	O IV	F IV			
25*R*	B V	C V	N V	O V	F V				
36*R*	C VI	N VI	O VI	F VI					
49*R*	N VII	O VII	F VII						
64*R*	O VIII	F VIII							
81*R*	F IX								

Many of these spectra have actually been produced and identified, at least in part, even as far as O VI. On account of the extremely short wave-lengths of the chief lines of highly-ionised atoms, however, the identification of the stage of ionisation which they represent cannot often be verified by calculation of the constants of the series to which they belong. Their identity has then been deduced by Millikan and Bowen from the expected positions and separations of the doublets or triplets as predicted by the irregular and regular doublet laws, and there can be no doubt that the identifications are correct.

Investigations of ionised atoms are not only of interest as supporting the general theory of atomic structures. They are of great importance in the interpretation of the spectra of the sun and stars, which give a great range of surface temperatures. In the cooler stars, the lines which appear are chiefly those of neutral atoms or compounds, but at successively higher temperatures these are gradually replaced by lines of ionised or multiply-ionised atoms. For instance, in what are believed to be the hottest stars, lines of O III, C III, and C IV have been identified. The knowledge of these spectra which has been gained from laboratory experiments has led to important deductions with regard to the temperatures and densities in stellar atmospheres, through investigations by Saha and by Fowler (R. H.) and Milne.

Another application to an astrophysical problem of great interest has recently been made by Bowen. Apart from a few lines of hydrogen and helium, the spectra of gaseous nebulæ consist of a small number of more or less conspicuous lines, which for a long time were rather vaguely attributed to an unknown element called "nebulium." The advance of atomic physics, however, made the existence of such an element extremely improbable, and we were driven to the conclusion that the nebular lines must be due to a known element, or elements, under conditions not yet imitated in laboratory experiments. The most likely source seemed to be a highly excited, light element, existing in nebulæ under conditions of extremely low density; so low that in the small quantity of gas available in a laboratory experiment no luminosity could be produced. By combining his results with my own, Bowen has proved that several of the brighter lines are due to singly-ionised oxygen and nitrogen, and doubly-ionised oxygen. The structures of these spectra have been very fully investigated, and although the counterparts of the nebular lines do not appear in the laboratory spectra, their positions can be calculated with great accuracy. It is only necessary to suppose that in the nebulæ combinations of terms take place which have been regarded as "forbidden" by the ordinary selection rules. Taking one example, the normal state of the O III atom is represented by two 1_1, two 2_1, and two 2_2 electrons. This configuration gives rise to ${}^3P_{012}$, ${}^1D_2$, and ${}^1S_0$ terms, of which ${}^3P_0$ is the largest and represents the most stable state of the atom. The last two terms are regarded as metastable states, so that the electron, having come to occupy a corresponding orbit, after excitation, cannot directly pass from one to the other, or to the ^3P state. The relatively small differences in energy of these terms, it should be recalled, is to be attributed to different arrangements of orientation of orbits and spin within the atom, the size and shape of the orbits being the same for all. On account of the extremely low density in nebulæ, it may be supposed that the atoms have a long enough time to change from $^1S_0$ to $^1D_2$ or from $^1D_2$ to $^3P_{12}$ before they are raised to higher states by collision or by the absorption of radiation from stars. The corresponding differences of wave-number agree precisely with the wave-numbers of three important lines in the spectra of the nebulæ. Similar data and reasoning prove that other nebular lines are due to O II and N II, and the long-standing mystery of the nebular spectrum is at last solved. Nebulium no longer menaces our conceptions as to the structure of the periodic table of the elements.

I am well aware that in this rapid survey I have omitted to mention many matters of importance, but I hope I have been able to convey some idea of the contributions of spectroscopy to atomic theory.