

# The Spectroscope and the Atom\*

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IN his Thomas Hawksley Lecture of 1932, Lord Rutherford recounted the experiments with atomic projectiles which had given so much insight into the structure of atomic nuclei. My principal aim now will be to indicate how the spectroscope has contributed to our knowledge of the systems of electrons surrounding the nuclei of atoms, on which chemical and other properties are dependent.

## SPECTRUM OF HYDROGEN

The simplest spectrum of all is that of hydrogen, showing the well-known Balmer series of lines in the visible region, in which the wave-numbers,  $\nu$ , are represented by the formula,

$$\nu = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right)$$

where  $n=3, 4$ , and so on, and the *Rydberg constant*  $R=109,678$  as calculated from the lines themselves.

Other series of hydrogen lines similar in appearance to the Balmer series were afterwards discovered, and it was found that the entire spectrum could be represented by the general formula

$$\nu = R/n_1^2 - R/n_2^2 \text{ when } n_1 < n_2.$$

$n_1=1, n_2=2, 3, \dots$ , gives the Lyman series in the extreme ultra-violet;  $n_1=2, n_2=3, 4, \dots$ , the Balmer series;  $n_1=3, n_2=4, 5, \dots$ , the Paschen series in the infra-red, and so on. Theoretically, the number of series is infinite. The Rydberg constant  $R$  appears with slight modifications in the formulæ for series of lines in the spectra of elements other than hydrogen.

It is of special importance to note that the wave number of each spectrum line appears as the difference of two other numbers. These are the so-called *spectroscopic terms*, each of which, in accordance with Bohr's theory, is proportional to a particular energy state of the atom.

## SERIES IN OTHER SPECTRA

Similar regularities occur in the spectra of elements other than hydrogen. Many of these spectra are built up by a number of superposed

\* From the twenty-third Thomas Hawksley Lecture of the Institution of Mechanical Engineers, delivered on November 6, 1936.

separate series, illustrated for lithium and sodium in Fig. 1. Four of the series have received special names—*principal, sharp, diffuse* and *fundamental*, respectively.

As in the case of hydrogen, each of the above-mentioned series may be represented by the differences between a spectroscopic term representing the limit of the series and a *sequence of terms* given by a running number. In the simple form adopted in the classical work of Rydberg, a term  $R/n^2$  in the formula for hydrogen is replaced by  $R/(m+a)^2$ , where  $m$  stands for a sequence of integers and  $a$  is a fraction special to the particular series. It is found that the different series are closely related to each other, so that the limit of one series is a member of one of the other sequences of terms. The sequences, as distinct from the lines, are named *S, P, D, F*, after the series in which they occur. If the first terms of the *S, P, D* sequences are assigned the number 3, as would be the case for sodium, the relations between the series may be shown as follows:

Principal series	.	.	$3S - nP$	$n = 3, 4, 5, \dots$
Sharp series	.	.	$3P - nS$	$n = 3, 4, 5, \dots$
Diffuse series	.	.	$3P - nD$	$n = 3, 4, 5, \dots$
Fundamental series	.	.	$3D - nF$	$n = 4, 5, 6, \dots$

where  $n$  is known as the *principal quantum number*. The actual numbering of the terms in modern form is based upon theoretical considerations.

As first recognized by Ritz and expressed in his *combination principle*, other terms of a sequence besides the first may combine with terms from other sequences to produce subsidiary series, as, for example,  $4P - nD$ . The possible combinations in ordinary circumstances, however, are restricted by selection rules, one of which is that only terms from adjacent sequences in the order *S, P, D, F, G, \dots* combine to produce lines.

## MULTIPLE TERMS

When a family of series consists of doublets or triplets, the specification of the spectroscopic terms requires additions to the scheme for a singlet system. These are the so-called *inner quantum numbers, j*, which were empirical in the first instance but have since become of profound

theoretical importance. In modern form, the different types of terms are written as follows :

Singlet terms	$^1S_0$	$^1P_1$	$^1D_2$	$^1F_3$
Doublet terms	$^2S_{1/2}$	$^2P_{3/2}$	$^2D_{5/2}$	$^2F_{7/2}$
	$^2S_{1/2}$	$^2P_{1/2}$	$^2D_{3/2}$	$^2F_{5/2}$
Triplet terms	$^3S_1$	$^3P_2$	$^3D_3$	$^3F_4$
		$^3P_1$	$^3D_2$	$^3F_3$
		$^3P_0$	$^3D_1$	$^3F_2$

Here the index on the left of the symbol for each term indicates the multiplicity  $r$  of the system, while the suffix on the right is the inner quantum number  $j$ .

Terms of higher multiplicity than three occur in many spectra, giving quartets, quintets, sextets, septets, octets, or still greater complexities. Odd and even multiplicities, however, never appear

BOHR'S THEORY

The significance of series of lines in spectra had not begun to be understood until Bohr launched the epoch-making quantum theory of atomic spectra in 1913. The normal hydrogen atom was assumed to consist of a minute nucleus of mass  $M$  and positive charge  $E$ , with a single electron of mass  $m$  and negative charge  $e$  moving round it. When the atom was excited by the absorption of energy, the electron was supposed to traverse larger orbits, specified by the quantum condition that the angular momentum must be an integral multiple of  $h/2\pi$ , where  $h$  is Planck's constant. On the further assumption that a quantum of radiation  $h\bar{\nu}$  (where  $\bar{\nu}$  = oscillation frequency) was emitted when the electron returned from one orbit

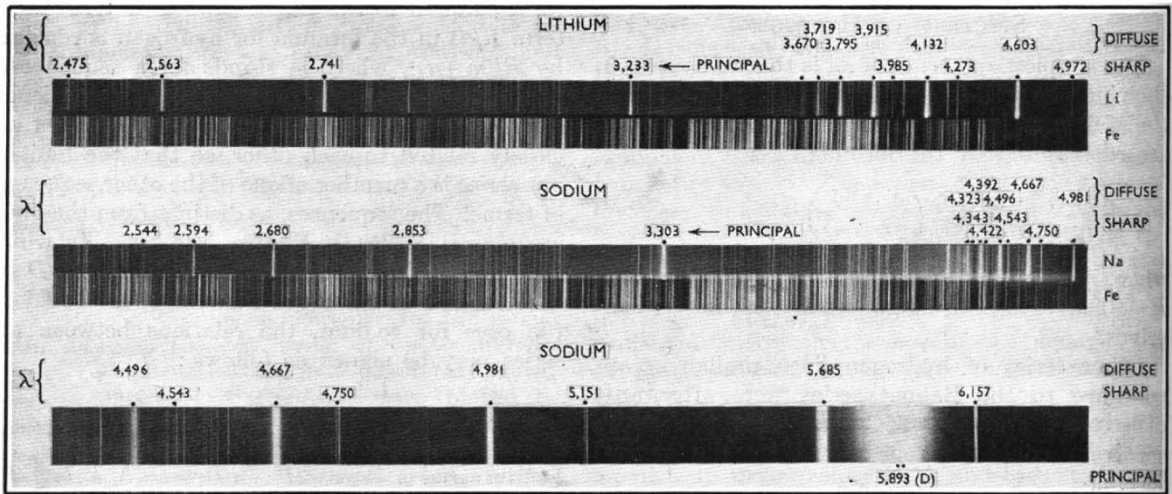


Fig. 1.

SERIES OF LINES IN THE SPECTRA OF LITHIUM AND SODIUM WITH IRON ARC COMPARISONS.

together, but occur alternately in passing through successive groups of elements in the Periodic Table. As many as three systems may occur in the same spectrum. The names given to these higher multiplicities indicate the *maximum* number of  $j$  values assigned to any of the terms.  $S$  terms are always single,  $P$  terms have never more than three components,  $D$  terms not more than five,  $F$  terms not more than seven, and so on.

Under ordinary conditions, combinations between different terms in the same spectrum are subject to two further selection rules, namely,  $\Delta r = \pm 2$  or 0, and  $\Delta j = \pm 1$  or 0, with  $j=0$  to  $j=0$  forbidden. This means that terms cannot combine to produce a line unless the  $r$  values differ by 2 or 0 and the  $j$  values by 1 or 0. The first selection rule already mentioned is expressed as  $\Delta l = \pm 1$ , where  $l=0, 1, 2, 3, \dots$  for  $S, P, D, F, \dots$  terms.

to another of lower energy, Bohr derived an expression for the hydrogen spectrum which is in agreement with that determined experimentally, and in which  $R$  took the form,  $\frac{2\pi^2 E^2 e^4}{ch^3} \cdot \frac{Mm}{M+m}$ , where  $E=e$  for hydrogen and  $c$  is the velocity of light.

A *term* represented an energy state of the atom, giving no radiation, and a *line* the emitted radiation when the atom passed from a state of higher to one of lower energy. This has been found to be applicable to all atoms, and the different states are regarded as *energy levels*, quite irrespective of any particular model of the atom.

IONIZED ATOMS

Strong support for the theory was given by its application to the spectrum of ionized helium, which is produced by intense electrical discharges through the gas. This spectrum is developed when

the atom has lost one of its electrons, the remainder then being similar to a hydrogen atom, except that the nucleus has a double positive charge, and a mass four times greater. The spectrum should accordingly be similar to that of hydrogen, but relatively displaced, and this agrees with observation, even in quantitative details. Following this, it was foreseen that an atom of any element might be deprived of its electrons one by one through increasing excitation, and that the series constant would change through values of approximately  $4R$ ,  $9R$ ,  $16R$ , and so on, until, when only one electron remained, the spectrum would become similar to that of hydrogen. All this has been verified by experiment, and, as was expected, it has been found in general that when an atom has become ionized its spectrum resembles that of the element

was found to require more elaboration. For an explanation of multiple terms, for example, it became necessary to suppose that the electron possessed a spin, the angular momentum of which, denoted by the quantum number  $s$ , was fixed at  $\pm\frac{1}{2}$ , according to the direction of rotation.

Despite such additions, however, it was ultimately realized that the orbital model was incapable of describing all the intricacies of spectra, and in more general considerations it was displaced in favour of a *vector model*, in which the various quantum numbers of the electron were no longer necessarily associated with orbits, but with angular momentum vectors the interpretation of which in the form of a picturable mechanism was not essential. In this model, five quantum numbers are used,  $n$ ,  $l$ ,  $s$ ,  $j$ , and  $m$ , but only four of these

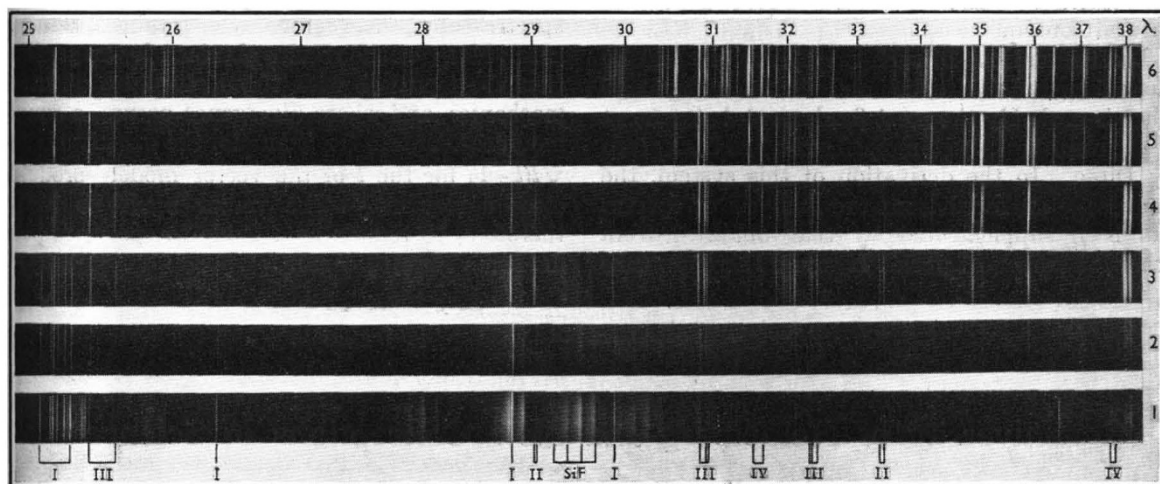


Fig. 2.

SUCCESSIVE SPECTRA OF SILICON PRODUCED BY GRADUALLY INCREASING INTENSITY OF DISCHARGE THROUGH A VACUUM TUBE CONTAINING SILICON TETRAFLUORIDE.

which precedes it in order of atomic number. If two electrons have been removed, the spectrum will resemble that of the element of atomic number  $Z-2$ , and so on indefinitely. It has been found convenient to represent the spectrum of a neutral atom by  $ZI$ , and the spectra at successive stages of ionization by  $ZII$ ,  $ZIII$ , etc., the corresponding states of the atom itself being indicated by  $Z$ ,  $Z^+$ ,  $Z^{++}$ , etc.

A good illustration of the changing spectrum of an element is given by the photographs of silicon spectra reproduced in Fig. 2. The experiments were made on the vapour of silicon tetrafluoride in a vacuum tube, the intensity of the electric discharge increasing gradually from 1 to 6.

#### THE VECTOR MODEL

As the finer details of spectra were taken into consideration, the Bohr conception of the atom

are independent, since  $j$  is the quantized resultant of  $l$  and  $s$ . In the simpler cases in which the orbital model is adequate, these vectors correspond respectively with the quantum numbers  $n$ ,  $l$ ,  $s$ , and  $j$  already described; while the number  $m$  corresponds with the quantized projection of  $j$  along the magnetic axis of the atom. In the general case, however, although the names suggested by the orbital conception are often used, they cannot be applied with their literal meanings, and the quantum numbers are used in calculations merely as symbols obeying certain rules.

It is not possible here to enter into intricate details of spectra. It must suffice to state that on the supposition that an atom is so constituted that the angular momenta of all the rotary motions can only change by unit steps, a complete scheme has been worked out by Hund by which the types of terms associated with a given distribution of electrons around the nucleus can be

calculated. The results of such calculations are in entire agreement with the types deduced from the numerous analyses of spectra which have now been made.

### QUANTUM MECHANICS

These developments of the theory of atomic structure took place in intimate relation with spectroscopic research. The result was a conception of the atom, definite so far as application to experimental results was concerned, but containing basic *ad hoc* assumptions which violated the principles of classical mechanics. Throughout the development of the theory it was evident that some fundamental system of mechanics was required from which the assumptions of the existing quantum theory would follow as natural consequences.

The foundations of such a system were laid by Heisenberg, de Broglie and Schrödinger, and what is probably the most fundamental statement of the resulting quantum mechanics has been given by Dirac. In the derivation of this system, the knowledge gathered from the analysis of spectra has been supplemented by that obtained from other experimental work. It would therefore take

us outside the scope of our subject to enter into these advances, and it only remains to indicate in general terms the reaction of quantum mechanics on the question of atomic structure. This may be summed up by the statement that, while the arbitrary postulates of the empirical theory have been expressed as necessary consequences of fundamental mechanical principles, the orbital picture and vector representation of the atom have been discarded, and no equally picturable substitute has been given. A partial picture is possible in terms of a rather indefinite distribution of electricity, one such distribution corresponding to each stationary state, or electron configuration, of the atom according to the earlier ideas. It is impossible, however, to locate the electron at a precise position in this distribution.

Nevertheless, for the practical purposes of spectroscopy, the vector model retains its usefulness. Many of the results obtained by its application are identical with those given by quantum mechanics, and where divergence occurs, a simple modification—as, for example, the substitution of  $\sqrt{l(l+1)}$  for the  $l$  of the vector model—produces close agreement. The vector model is likely, therefore, to remain as a guide to spectroscopists for some time to come.

## University of Heidelberg and New Conceptions of Science

### From a Correspondent

THE general character of the changes in the German universities was expounded by Herr Rust, Reichsminister for Education, at the recent celebration of the 'jubilee' of the University of Heidelberg. His address is translated in the November issue of the *Universities Review*. Herr Rust believes the New Germany to be the true heir of Sparta and suggests that these changes are as though Sparta had triumphed over Athens. Had that calamity befallen the world, all that we could have inherited from Greece would have been 'discipline', for Sparta had no other gifts to bestow. But the new "Weltanschauung", Herr Rust assures us, "is the life-blood of a new science . . . National Socialism has provided science with new principles from which she can derive the strength of self-confidence. . . . The old idea of science based on the belief in the supremacy of the intellect is finished."

The effect on a university of the arbitrary treatment of its staff is not numerically expressible. Injustice to one teacher may overawe the entire

faculty and deprive its work of all value. Staff changes at Heidelberg tell, therefore, of only a fraction of the injury to learning. We give, however, a summary of what has happened at Heidelberg; and it suggests what is going on throughout the universities of Germany.

The calendar of the University of Heidelberg for the academic year 1936-37 may be compared with that of 1932, the last year unaffected by the new regime. The historical account of the university, which opened previous calendars, is omitted this year. Any record of either benefactors or distinguished alumni would have to include names of many of Jewish or partly Jewish origin. The very title of the official head has been altered, and Rector Groh is now Führer Groh. The order and many of the titles of the staff are changed. After Führer Groh follows the *Leiter* of the body of dozenten, Herr Schlüter, who, oddly enough, is not himself a dozent. Next is the undergraduate Herr Ernst Kreuzer, who is both a member of the Senate and "Officially designated Undergraduate Leader at