

## CHAPTER I INTRODUCTION

### 1. The problem

When an atom is heated in a flame or excited by a spark discharge, it emits an immense number of lines, some perhaps visible but many more in the ultra-violet; to reduce these lines to order and to correlate them with the structure of the atom have been the two ideals towards which spectroscopists have always worked. The problem has been tackled both inductively and deductively; the observed spectrum has been arranged in systems and series, and the states of the atom have been deduced; and from the other end the states of the atom have been calculated with the aid of the simple vector model or the more elaborate wave mechanics, and the lines deduced have been compared with experiment. History shows that advance has been most rapid when the two methods have been used side by side; but in reviewing the work of the past, a better grip of the subject is probably obtained by presenting experiment first, and introducing theory only as a convenient method of correlating the facts; this order has at least the advantage that should the present theory ever be displaced by a better, the experimental facts would still be intelligible.

Half a century ago this work was scarcely begun, yet to-day one may simply, if also only roughly, predict the spectrum of any nuclear charge with any number of extra-nuclear electrons. Half the elements have been analysed in some detail, and there can be no doubt that in due course every line of every element will be labelled as arising from a particular transition within the atom. The scheme has already been developed; what remains will in all probability reveal no unsuspected difficulty, but will be a long piece of routine work.

### 2. Historical

The history of the investigation of spectra may be divided into four periods, an acoustic period, a series period, a quantum-theory period and a last period introduced by the quantum mechanics of

Schrödinger, Heisenberg and others. Like most other historical divisions, these are arbitrary; the periods really overlap and inter-weave, but it is necessary to be arbitrary in order to be clear.

The first period began with the earliest measurements of wave-length, and continued with the work of Boltzmann, Liveing and Dewar until 1881, when Schuster brought it to an abrupt conclusion. During this period any theories put forward were based on analogies with the harmonic ratios of sound. The one triumph was Johnstone Stoney's discovery that in the spectrum of hydrogen the frequencies of three of the four visible lines are in the ratio of 20:27:32.\* Schuster, however, suspected that this line of attack was unprofitable, and in a very interesting paper justified his suspicion by proving that the closeness of fit was only what chance would predict.†

Though he had stopped unprofitable speculation, Schuster put forward no new theory, and the second period did not open until four years later, when Balmer published his classic formula giving the wave-lengths of the visible lines of hydrogen. Written in a modern form, this states that the wave-length  $\lambda$  and the wave-number  $\nu$  are given by the equation

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

$R$  is here an absolute constant now commonly known as Rydberg's constant, while  $n$  assumes the values 3, 4, 5, 6 for the four visible lines.

This formula served as a first example of two important generalisations. Rydberg in the last decade of the century showed how the simple Balmer formula might be generalised to give an account of series in other elements. While later Ritz pointed out that written in the form

$$\nu = \frac{R}{n_1^2} - \frac{R}{n_2^2},$$

where  $n_1$  and  $n_2$  are both integers, the Balmer formula states that

\* Johnstone Stoney, *PM*, 1871, 41 291. A key to the letters used in referring to periodicals is given in Appendix I.

† Schuster, *PRS*, 1881, 31 337.

the wave-number of any spectral line may be written as the difference of two terms  $T'$  and  $T''$ ,

$$\nu = T'' - T'.$$

This is the important Rydberg-Ritz combination principle; though stated in 1908 before Bohr applied the quantum theory to solve atomic problems, it is so closely linked with his ideas that it is best considered as the first dawn of the third period.

In 1913 Bohr applied Planck's quantum theory to solve the problem of the radiating atom. He postulated that an electron, which revolves round the nucleus, must move in one of a number of orbits specified by quantum conditions; moving in one of these 'stationary states' the electron does not radiate as classical electrodynamics requires; instead radiation is emitted only when the electron jumps from one stationary state to another. In a second postulate Bohr added that the frequency of the line emitted depends on the difference in energy of the two states.

On this basis the whole complex structure of modern spectroscopy has been erected. Its great achievement is that it enables physicists to deduce from the spectrum of an element the energies of the stationary states of the atom. To correlate the energies of these states into some system was the next problem; a first step had been made in the work on series of an earlier day, and this has been continued in the so-called 'vector model' of the last decade. Conceived to describe the atom in terms of the classical mechanics and the theory of relativity, the model is to-day regarded simply as a convenient way of correlating experimental facts.

Like the geometrical theory of optics in another field, the vector model gives a satisfactory description of many spectroscopic laws. It is simple and easily visualised, and for these reasons it is valuable. But it covers only a part of the area covered by the wave mechanics, just as in optics the geometrical theory is less powerful than the wave theory.

The fundamental equations of the wave mechanics offer in principle a solution of any problem of atomic structure, and so also of spectral emission; but in practice the equations are so

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Excerpt

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difficult to solve that mathematicians have been able to apply the new theory only to some of the simpler problems.

The advent of the wave mechanics heralded the dawn of what must undoubtedly be considered a fourth period in the development of spectroscopy; but important as the new theory is, it has not, and almost certainly will not, displace the older vector model, for the physicist asks for something he can touch and see, or, as he often says, for something he can understand. This the vector model gives him, and with it the bulk of this book is concerned. Many of the results obtained by the wave mechanics will be noted, but the theory which underlies them will not be discussed.

## CHAPTER II

## THE HYDROGEN ATOM

**1. Series**

The hydrogen atom is the only neutral atom which does not contain more than the two bodies with which alone classical mechanics is able to deal, and if the band spectrum due to the molecule be ignored the spectrum is also simple. The lines produced by the atom are shown in Fig. 2·1, and may be divided into five groups, which are called technically 'series'.

Series occur not only in hydrogen, but in all simple spectra; starting with the line of longest wave-length in any series and moving towards the violet, one observes that the lines lie nearer and nearer together and at the same time decrease in intensity. When a large number of lines are visible, it is quite clear that the decreasing separation at the violet end of the series piles up the lines towards a sharply defined limit.

Experience shows that spectral laws take their simplest form when expressed as relations between frequencies rather than wave-lengths, and therefore in Fig. 2·1 as in all subsequent figures the scale is a uniform scale of frequency. But in that spectroscopists measure the wave-length and can calculate the absolute frequency only when they know the velocity of light, they commonly use the wave-number or reciprocal of the wave-length rather than the frequency. The visible spectrum extends roughly from 4000 to 8000 Å., when 1 Å. or angstrom is  $10^{-8}$  cm. or  $10^{-1}\mu\mu$ . In terms of wave-numbers this is 25000 to 12500  $\text{cm.}^{-1}$ . Again small separations are often important and it is sometimes convenient to remember that the separation of the yellow  $D_1 D_2$  doublet of sodium is 6 Å. or 17  $\text{cm.}^{-1}$ .

The five series of the hydrogen spectrum are named after their discoverers; of these Balmer\* was the first, for he showed, as early as 1885, that the four lines in the visible region may be

\* Balmer, *AP*, 1885, 25 80.

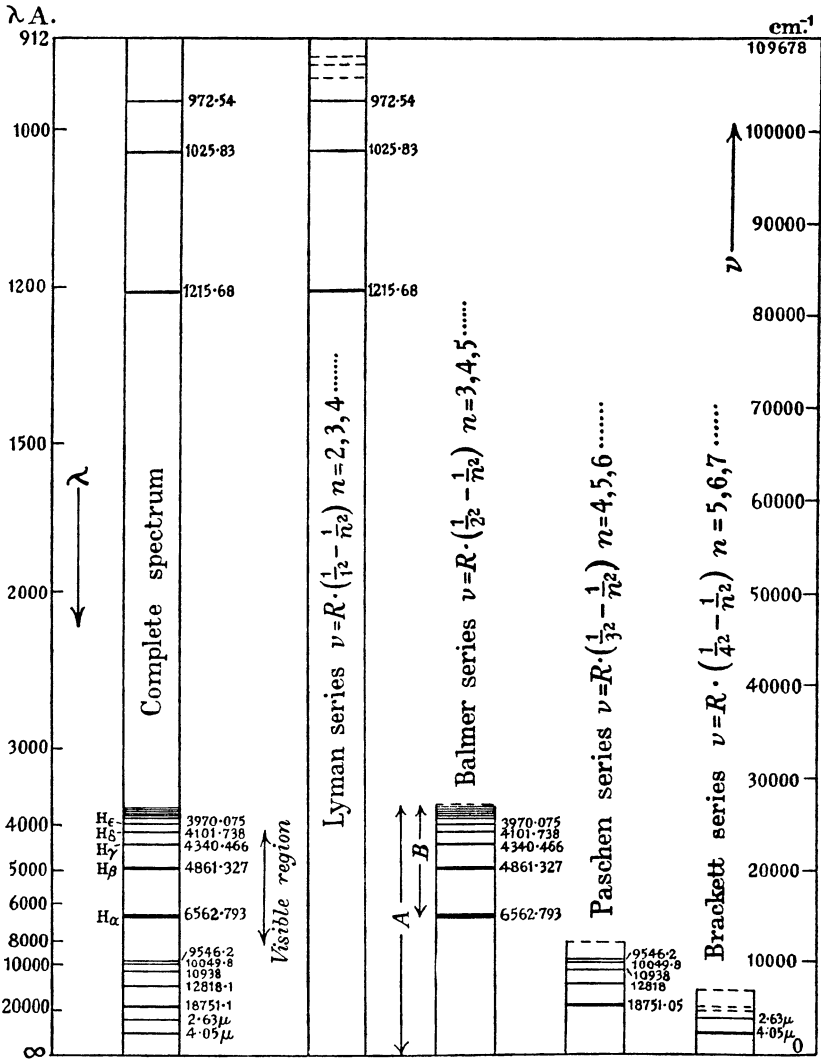


Fig. 2-1. Spectrum of hydrogen. After Grotrian, *Graphische Darstellung der Spektren*.

represented by a formula, which in modern notation takes the form

$$\nu = R \left\{ \frac{1}{2^2} - \frac{1}{n^2} \right\}, \quad \dots\dots(2.1)$$

where  $R$  is a constant of value  $109677.76 \text{ cm.}^{-1}$ , and  $n$  takes on the successive values 3, 4, 5, 6 for the four lines. Later workers measured many lines in the ultra-violet and found that these fit the formula with remarkable accuracy when  $n$  is given higher integral values. Fig. 2.2 gives a comparison of theory and experiment.

$n$	$\nu$ calculated <sup>a</sup>	$\lambda$ calculated	$\lambda$ observed <sup>b</sup>
3	15233.156	6564.628	6564.602
4	20564.760	4862.687	4862.680
5	23032.531	4341.685	4341.683
6	24373.049	4102.893	4102.891
7	25181.339	3971.195	3971.194
8	25705.950	3890.150	3890.149

Fig. 2.2. The first six lines of the Balmer series.

<sup>a</sup>  $R$  is taken as  $109678.72$ , this being the value which Curtis found to give the best fit.

<sup>b</sup> Curtis, *PRS*, 1919, **96** 147. The wave-lengths have been corrected to vacuo.

Later Lyman\* found another series of hydrogen lines in the far ultra-violet, while Paschen,† Brackett‡ and Pfund§ observed new series in the infra-red.

Generalised in the form

$$\nu = R \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\}, \quad \dots\dots(2.2)$$

the formula showed itself capable of accounting for all these new lines; indeed it was used to predict some of them.  $n_1$  is fixed in any given series and has the values 1, 3, 4, 5 for the Lyman, Paschen, Brackett and Pfund series respectively, while  $n_2$  takes on a series of integral values subject to the condition that  $n_2 > n_1$ . The limit of any series is obtained by making  $n_2$  tend to infinity, so that the limit of the Balmer series is simply  $R/4$  or  $27419.4 \text{ cm.}^{-1}$

\* Lyman, *AJ*, 1906, **23** 181.

† Paschen, *AP*, 1908, **27** 537.

‡ Brackett, *AJ*, 1922, **56** 154; Poetker, *PR*, 1927, **30** 418.

§ Pfund, *JOSA*, 1924, **9** 193.

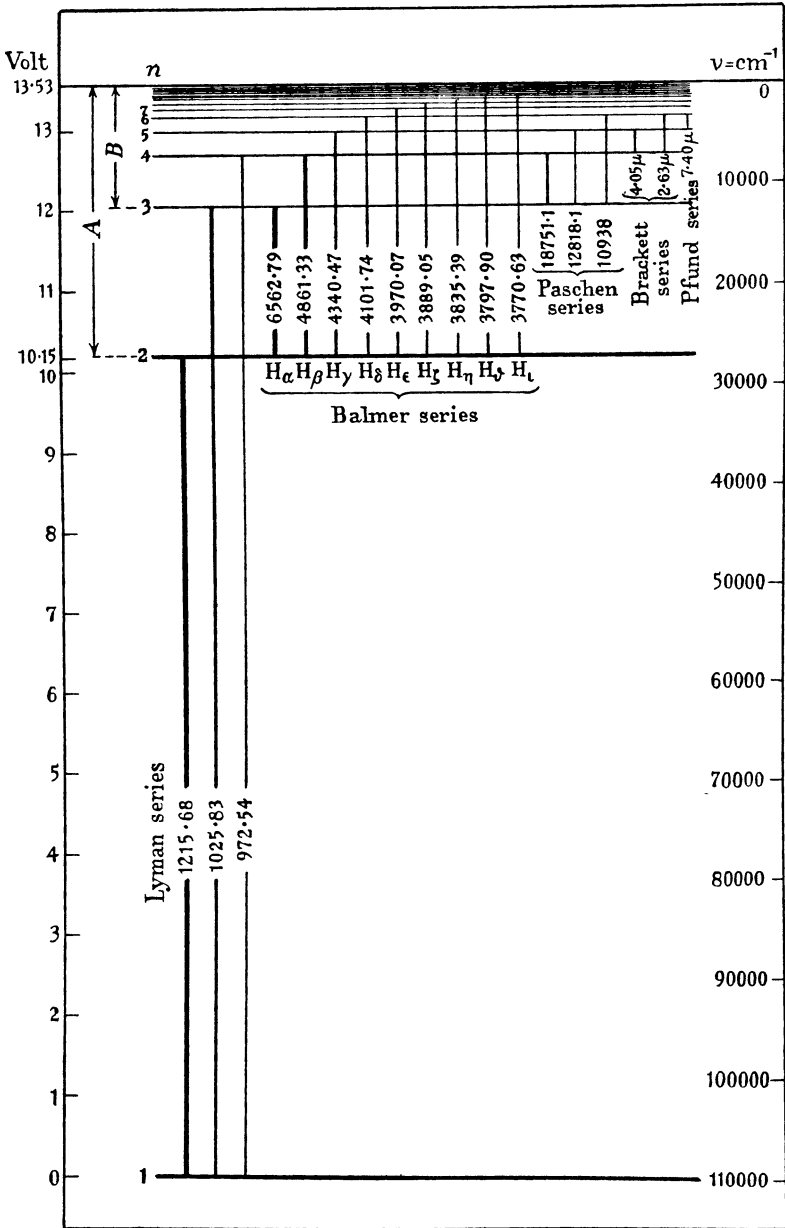


Fig. 2-3. Level diagram of hydrogen. Each vertical shows an electron jump; the numbers give the wave-length in angstroms, the thickness gives a rough indication of the intensity. After Grotrian, *Graphische Darstellung der Spektren*.



**2. Interpretation by diagram**

These facts are very simply illustrated by a diagram due to Grotrian (Fig. 2.3). Down a vertical line lengths  $R$ ,  $R/4$ , ...  $R/n^2$  are measured off, and horizontal lines are drawn through the

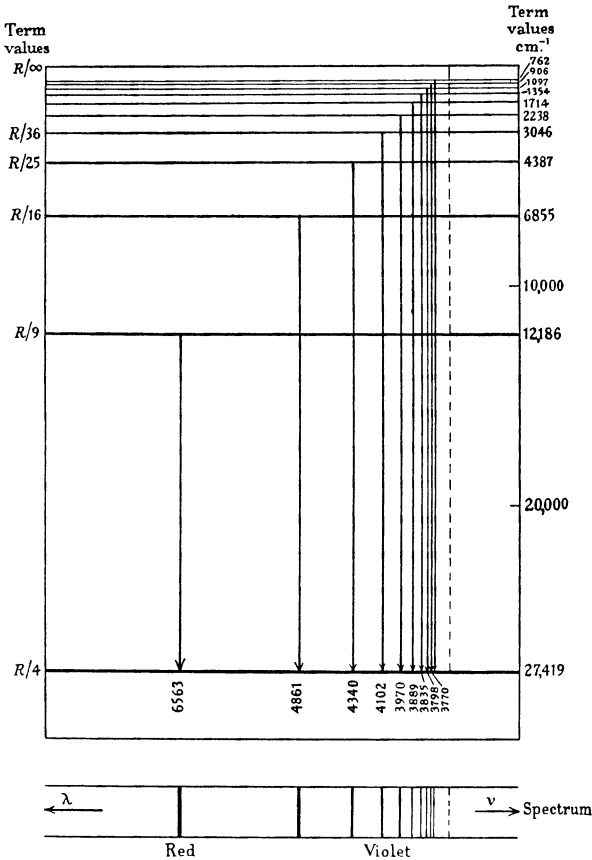


Fig. 2.4. Level diagram of the Balmer series. The spectrum shows the lines on a uniform scale of frequency.

points obtained to represent terms of the spectrum. Any transition between two terms may be represented by a vertical arrow, whose length will be a measure of the wave-number of the line emitted. The  $H_\alpha$  line represented by the equation

$$\nu = R \left\{ \frac{1}{2^2} - \frac{1}{3^2} \right\}$$

may be used to illustrate this; in both Figs. 2·1 and 2·3 it appears as the difference of two lengths marked  $A$  and  $B$ , which are in fact the quantities  $R/4$  and  $R/9$ ; but whereas in Fig. 2·1 they are measured from the limit of the Balmer series, in Fig. 2·3 they are measured down from a line which is the limit of the term sequence, being the value of  $R/n^2$  when  $n \rightarrow \infty$ . The limit will be seen later to represent an atom which has lost an electron.

Fig. 2·3 may be refined to give an even clearer picture of a series, by so spacing the arrows horizontally that if the spectral lines to which they correspond are shown at the bottom, these lines are correctly spaced along a frequency scale with the highest frequency on the right. This has been done for the Balmer series in Fig. 2·4.

### 3. Bohr's Theory

The hydrogen atom consists of a heavy nucleus and an electron revolving around it. In terms of a system so simple classical electrodynamics has always been unable to account for the line spectrum. If the revolving electron radiates as any accelerated charge must, then the system must lose energy and the electron will approach the nucleus and ultimately fall into it. Moreover, the system will give a continuous, not a line, spectrum.

Bohr first surmounted these difficulties in 1913, when he applied the quantum theory to the problem in two famous postulates. The first of these states that an electron can only revolve about the nucleus in certain orbits; these orbits Bohr called 'stationary states', because only in these orbits can the electron remain an appreciable time.\*

When the electron leaves one stationary state it must pass instantaneously to another; and if these two states have energies  $E'$  and  $E''$ , so that  $E' > E''$ , then Bohr's second postulate adds that a quantum of monochromatic light will be emitted, the frequency  $\nu'$  being determined by the equation

$$h\nu' = E' - E'', \quad \dots(2\cdot3)$$

where  $h$  is Planck's quantum of action  $6\cdot55 \cdot 10^{-27}$  erg sec. Sub-

\* Bohr, *PM*, 1913, 26 1, 476, 857.