

Chapter 11

The Bohr Atom

Topics

The experiments of Thomson and Rutherford. The radiation problem and Bohr's postulates. De Broglie waves and Bohr's quantisation condition, experiments of Davisson and Germer and G.P. Thomson, particles as waves and the wave-particle duality. The Bohr model of the atom and the Balmer formula. Successes and failures.

11.1 The Experiments of Thomson and Rutherford

The next step is the application of the ideas of quanta to the understanding of atomic structure. This was the great achievement of Niels Bohr, but it relied heavily upon the discoveries of the electron by J.J. Thomson and of the nuclear structure of atoms by Ernest Rutherford.

11.1.1 J.J. Thomson and the Electron

The electron was discovered by J.J. Thomson in 1897 and the experiment by which he established that its mass-to-charge ratio is only about one two thousandth of that of hydrogen ions was carried out in the course *Fields, Oscillations and Waves*. The electron was the first sub-atomic particle to be discovered. As Thomson stated in his discovery paper,

‘... [the cathode rays constituted] a new state, in which the subdivision of matter is carried very much further than in the ordinary gaseous state.’

In summary, Thomson’s great achievements were:

- The demonstration that the cathode rays, which became known as *electrons*, were the particles which carried an electric current, were identical to the particles emitted in β decay and those emitted in the photoelectric effect.
- The demonstration, with Barkla, from X-ray scattering experiments that the number of electrons in an atom is about half its atomic weight, except for hydrogen. The number of electrons and, consequently, the amount of positive charge in the atom increases by units of the electronic charge.
- The invention of the ‘plum-pudding’ model of the atom, designed to minimise the loss of energy by electrons in orbit within the atom (see Section 11.2.1).

11.1.2 Rutherford and the Nuclear Atom

Rutherford had been very impressed by the fact that fast α -particles, which are emitted in radioactive decays and which are helium nuclei with mass almost four times that of the hydrogen atom, could pass through thin films rather easily, suggesting that much of the volume of the atoms is empty space. Furthermore, he found that some of the α -particles were deflected through very large angles indeed and a few of them were sent back more or less in the direction of incidence of the α -particles. Rutherford realised that it required a very considerable force to send the α -particle back along its track – the α -particles were travelling at 10,000 km s⁻¹. As he stated,

‘It was quite the most remarkable event that has ever happened to me in my life. It was almost as if you fire a fifteen-inch

shell at a piece of tissue paper and it came back and hit you.'

His guess was that all the positive charge was contained in a compact nucleus and that it was the electrostatic repulsion of the positively charged α -particle by the positively charged nucleus which was the origin of the repulsive force. The α -particle scattering experiments, which he carried out with Marsden and Geiger in 1910-11, showed that the predicted scattering law, that the probability of scattering through an angle ϕ per unit solid angle is

$$N(\phi) \propto \frac{1}{v_0^4} \operatorname{cosec}^4 \frac{\phi}{2} \quad (11.1)$$

was precisely followed even for very large deflections. This is the famous $\operatorname{cosec}^4(\phi/2)$ law which Rutherford derived theoretically – this form of scattering is known as *Rutherford scattering*.

They had, however, achieved much more. The fact that the scattering law was so precisely obeyed, even for large angles of scattering, meant that the inverse square law held good to very small distances indeed. An upper limit to the size of the nucleus could be found from the maximum angle for which the $\operatorname{cosec}^4(\phi/2)$ law holds good. They found that the nucleus had to have size less than about 10^{-14} m. This is very much less than the sizes of atoms, which are typically about 10^{-10} m.

11.2 The Radiation Problem and Bohr's Postulates

The first successful application of the concept of quantisation to atoms was made by the Danish physicist Niels Bohr in 1913. Once Rutherford had demonstrated that atoms consist of a compact nucleus with a positive charge surrounded by a cloud of electrons, each with negative charge e , it was natural to assume that the negatively charged electrons moved in bound orbits about the nucleus. There was, however, one very profound problem with this picture, according to classical physics.

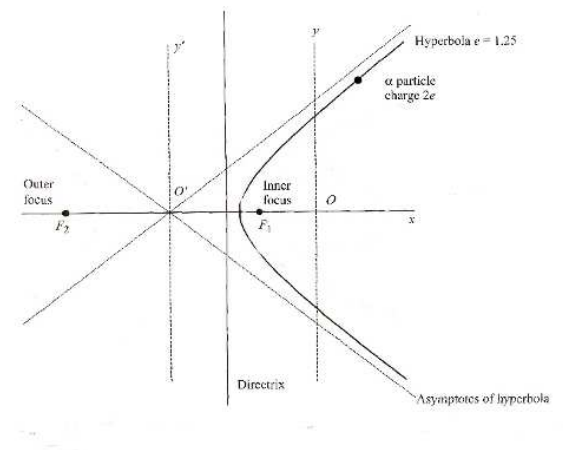


Figure 11.1. The geometry of Rutherford scattering of an α -particle by a positively charged nucleus. The α -particle follows a hyperbolic path with the nucleus in the outer focus.

An accelerated charged particle radiates electromagnetic waves. It is straightforward to show that, in the case of the hydrogen atom, as the electron loses energy, it moves into an orbit of smaller radius, loses energy more rapidly and spirals into the nucleus within about 10^{-10} seconds. This cannot be correct since atoms certainly exist.

This problem was solved by Bohr in an remarkable leap of the imagination. He realised that to solve the problem he had to adopt the concept of quantisation as expounded by Planck and Einstein. He noted the key point of their work, that only a finite number of energy states are allowed and not the infinite number allowed according to classical physics. He therefore introduced the concept of *stationary states* within the atom, which corresponded to the quantised energy states which were introduced by Planck and Einstein to account for the spectrum of black-body radiation. This postulate abolishes the problem of the radiation loss of the electrons because they are not allowed to assume a continuous set of energy states – they can only have the energies associated with the stationary states. He postulated that the electron could only lose energy by radiation by making transitions between the stationary states - the concept of *quantum jumps*. This was the process responsible for the origin of spectral lines.

The postulates which Bohr made in order to apply the concept of quanta to atoms were as follows:

1. Each electron in an atom can only exist in certain stable circular orbits of *definite energy* which are known as *stationary states*. These *energy levels* have energies E_1, E_2, E_3, \dots
2. The *angular momentum* J of an electron in a stationary state is *quantised* such that the only allowed values are those for which

$$J = m_e v_n r_n = n \frac{h}{2\pi} = n\hbar \quad (11.2)$$

where n can only take integral values, $n = 1, 2, 3, \dots$. We have introduced the quantity $\hbar = h/2\pi$, which is called ‘h-bar’. This quan-

The Radiation Problem

According to classical electrodynamics, an accelerated electron loses energy at a rate

$$-\left(\frac{dE}{dt}\right) = \frac{e^2 a^2}{6\pi\epsilon_0 c^3} = 5.7 \times 10^{-54} a^2 \text{ W},$$

where a is the acceleration of the electron. For an electron orbiting a hydrogen nucleus, for example, at a radius $r = 0.5 \times 10^{-10}$ m, you may wish to show that the centripetal acceleration is $a \approx 10^{23} \text{ m s}^{-2}$. The time it takes the electron to lose its energy is therefore roughly

$$T \approx \frac{E}{\left|\frac{dE}{dt}\right|} \approx 4 \times 10^{-11} \text{ second}.$$

The quantisation of angular momentum according to the old quantum theory

$$J = m_e v_n r_n = n \frac{h}{2\pi} = n\hbar$$

where n can only take integral values, $n = 1, 2, 3, \dots$.

tity turns up ubiquitously in quantum mechanics and you should feel equally at home with either h or \hbar .

3. Transitions are possible between different stationary states and, when the electron makes a transition between those with energies E_i and E_f , a photon is emitted with energy

$$E = h\nu = E_i - E_f \quad (11.3)$$

Notice that the key step is the introduction of the *quantisation of angular momentum*, postulate 2. This is not quite as arbitrary as it might seem since the dimensions of Planck's constant h are

$$\begin{aligned} [h] &= \text{J s} = [M][L]^2[T]^{-2} \times [T] \\ &= [M][L][T]^{-1}[L] = [mvr], \end{aligned}$$

that is, the dimensions of h are those of angular momentum.

The energy of a photon emitted in a transition between stationary states

$$E = h\nu = E_i - E_f$$

11.3 De Broglie Waves and Bohr's Quantisation Condition

Bohr's argument for quantising angular momentum originated from the need to quantise the energy levels in the atom. In fact, the rule for quantising angular momentum can be derived from the inspired guess made by Louis-Victor de Broglie in his doctoral dissertation of 1924. He suggested that, just as light waves have particle properties, so *particles have wave properties*. There was no experimental evidence for this hypothesis, but de Broglie showed how Bohr's quantisation rules could be derived from this hypothesis.

Einstein had shown that the light-quantum, or photon, has energy $E = h\nu$ and momentum $h\nu/c$. De Broglie made the hypothesis that, exactly as in the case of photons, the electron has wave properties such that its wavelength is

$$\lambda = \frac{h}{p} \quad (11.4)$$

where p is the momentum of the electron. Vectorially, $\mathbf{p} = (h/\lambda)\mathbf{i}$, where \mathbf{i} is the unit vector in the

direction of propagation of the electron. The wavelength λ is known as the *de Broglie wavelength* of the electron.

In the theory of black-body radiation, we required the wavelengths of permissible modes of oscillation within a box to be such that only a finite number of half wavelengths fit across any of its dimensions. De Broglie applied a similar condition to the waves associated with the electrons in their orbits about the nucleus. He argued that the *stationary states* of the electrons in the atom should be such that *there is an integral number of wavelengths around the orbit*. His reasoning was that, unless there is a finite number of complete wavelengths round the orbit, the waves would interfere destructively. His picture is illustrated schematically in Figure 11.2 which show the quantisation of the de Broglie waves for the $n = 3$ and $n = 6$ stationary states.

Adopting de Broglie's hypothesis,

$$n\lambda = 2\pi r_n \quad \frac{nh}{p} = 2\pi r_n \quad \frac{nh}{m_e v_n} = 2\pi r_n. \quad (11.5)$$

Therefore,

$$L_n = m_n v_n r_n = n \frac{h}{2\pi} = n\hbar. \quad (11.6)$$

This is precisely *Bohr's condition for the quantisation of angular momentum*.

A copy of de Broglie's dissertation reached Einstein, who immediately appreciated its deep significance. Through Einstein, the Austrian theoretical physicist *Erwin Schrödinger* learned of the idea of de Broglie waves and, from it, developed the theory of *wave mechanics*, one of the first successful realisations of quantum mechanics.

Evidence for the wave nature of the electron was only discovered in 1927 in two classic experiments.

The Davisson-Germer Experiment Clinton Davisson studied the elastic scattering of electrons by metal surfaces. The term *elastic* means that the electrons are reflected from the surface of the material *without loss of energy*. He found that the intensity of reflected electrons varied in a peculiar

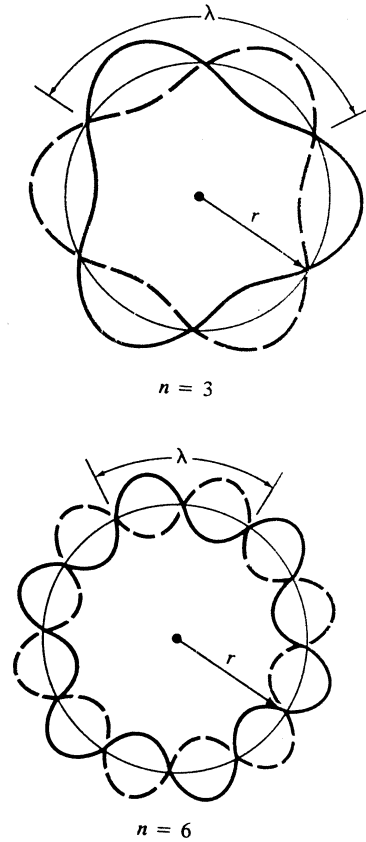


Figure 11.2. Illustrating De Broglie's construction for the quantisation of angular momentum states in hydrogen-like atoms.

The de Broglie wavelength of a particle of momentum p

$$\lambda = \frac{h}{p}$$

fashion with the angle of reflection. The key experiment was carried out using a carefully cleaned nickel crystal.

If the incident beam of electrons has wavelength λ , we can use the standard procedures of wave reflection by a crystal lattice to work out the intensity of scattered electrons in different directions. Figure 11.3 shows the construction for *Bragg reflection* from a crystal surface. We adopt the simplest picture of a regular cubic lattice and consider the interference of the reflected beam from the surface layer of the crystal. Constructive interference of the reflected waves is obtained when the path difference between the waves from neighbouring sites is a whole number of wavelengths

$$d \sin \theta = n\lambda \quad n = 1, 2, 3, \dots \quad (11.7)$$

In the experiment carried out by Davisson and Lester Germer, a pronounced maximum was observed at an angle of 50° for electrons of kinetic energy 54 eV. The momentum of a 54 eV electron is related to its kinetic energy by $E = p^2/2m_e$ and so

$$p = (2m_e E)^{1/2} = 3.97 \times 10^{-24} \text{ kg m s}^{-1}. \quad (11.8)$$

This can be compared with the momentum inferred from de Broglie's hypothesis. The separation between the atoms in the crystal structure was known to be 0.215 nm and so, taking $n = 1$, the de Broglie wavelength of the electron must be $\lambda = d \sin \theta = 0.165 \text{ nm}$. Therefore, its momentum was inferred to be

$$p = h/\lambda = 4.02 \times 10^{-24} \text{ kg m s}^{-1}, \quad (11.9)$$

in other words, essentially perfect agreement.

The G.P. Thomson Experiment George Thomson was the son of J.J. Thomson. At almost exactly the same time that Davisson and Germer completed their experiments, Thomson observed diffraction rings in the scattering of 15 keV electrons through a thin metal foil. The pattern of the rings was of exactly the same form as would have been expected

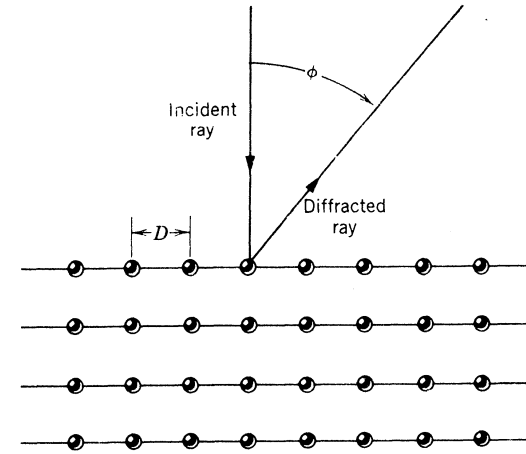


Figure 11.3. Illustrating Bragg reflection from the surface of a regular lattice.

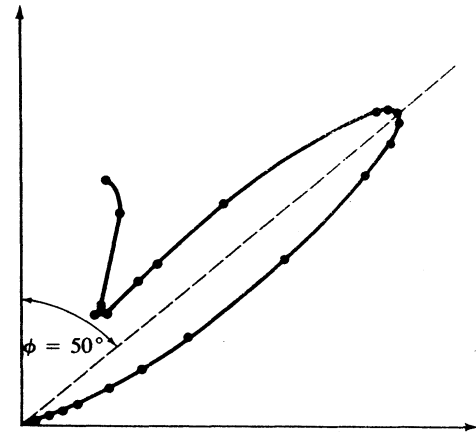


Figure 11.4. Illustrating the results of Davisson and Germer's electron scattering experiments from cleaned crystal surfaces.

if the electrons had wavelength $\lambda = h/p$. Examples of the diffraction patterns due to the scattering of X-rays and electrons of the same momenta by a target of powdered aluminium are shown in Figure 11.5.

It has been remarked that

Thomson, the father, was awarded the Nobel prize for having shown that the electron is a particle, and Thomson, the son, for having shown that the electron is a wave.

These experiments were conclusive evidence that electrons have wave properties. Similar experiments are now carried out routinely using α particles, neutrons and so on.

The fact that particles have wave properties is the second aspect of the *wave-particle duality*. A new formulation of the fundamental laws of physics was needed which could encompass both aspects of particles and waves and we will show how this can be done in the next chapter.

11.4 The Bohr Model of the Atom

Bohr adopted his three postulates in order to determine the stationary states of the hydrogen atom. The quantisation condition for angular momentum of the stationary state with quantum number n is

$$m_e v_n r_n = n\hbar \quad (11.10)$$

Equating the centripetal acceleration to the acceleration due to the electrostatic force between the nucleus and the electron for circular orbits,

$$\frac{m_e v_n^2}{r_n} = \frac{e^2}{4\pi\epsilon_0 r_n^2} \quad (11.11)$$

$$m_e v_n^2 = \frac{e^2}{4\pi\epsilon_0 r_n} \quad (11.12)$$

From the relations (11.10) and (11.12), we find expressions for the radii and speeds of the electrons

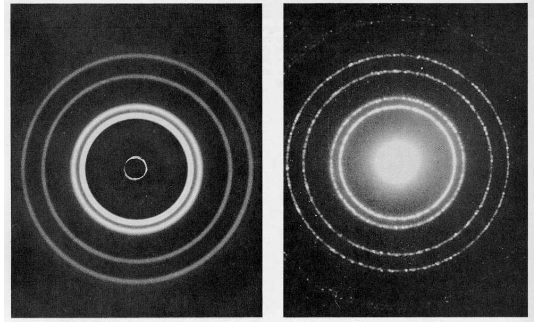


Figure 11.5. The diffraction patterns produced by X-rays (left) and electrons (right) of the same momenta on passing through a target of powdered aluminium.

in their stationary states

$$r_n = n^2 \left(\frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \right) = n^2 \left(\frac{\epsilon_0 \hbar^2}{\pi m_e e^2} \right) \quad (11.13)$$

$$v_n = \frac{1}{n} \left(\frac{e^2}{4\pi\epsilon_0\hbar} \right) = \frac{1}{n} \left(\frac{e^2}{2\epsilon_0 h} \right) \quad (11.14)$$

We can therefore find the radius a_0 of the orbit of the *ground state* of the hydrogen atom, $n = 1$. a_0 is called the *Bohr radius*.

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.529 \times 10^{-10} \text{ m} \quad (11.15)$$

This is a very convenient unit for atomic sizes. The speed of the electron in its ground state, $n = 1$, is

$$v_1 = \frac{e^2}{2\epsilon_0 h} = 2.2 \times 10^6 \text{ m s}^{-1}, \quad (11.16)$$

only about one hundredth of the speed of light. We do not need to bother about relativistic corrections in the first approximation.

We can now find the energies of the stationary states of the electrons in the hydrogen atom. We recall that, for circular orbits, the kinetic energy of the electron is $\frac{1}{2}m_e v^2$ and the electrostatic potential energy is $-e^2/4\pi\epsilon_0 r$. Therefore, remembering that the orbit is in centripetal balance,

$$\frac{m_e v^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2}, \quad (11.17)$$

the total energy of the orbit is

$$E = \frac{1}{2}m_e v^2 - \frac{e^2}{4\pi\epsilon_0 r} = -\frac{e^2}{8\pi\epsilon_0 r} \quad (11.18)$$

Thus, for the n th stationary state, since $r_n = n^2(\epsilon_0 \hbar^2 / \pi m_e e^2)$,

$$E_n = -\frac{e^2}{8\pi\epsilon_0 r_n} = -\frac{1}{n^2} \frac{m_e e^4}{8\epsilon_0^2 \hbar^2} \quad (11.19)$$

When the electron makes a transition from the stationary state m to n with $m > n$, the energy of the emitted photon is

$$E = h\nu = E_m - E_n = \frac{m_e e^4}{8\epsilon_0^2 \hbar^2} \left(\frac{1}{n^2} - \frac{1}{m^2} \right). \quad (11.20)$$

Note that the final state has the more negative energy. Therefore, the frequencies of the lines in the hydrogen spectrum are expected to be

$$\nu = \frac{m_e e^4}{8\epsilon_0^2 h^3} \left(\frac{1}{n^2} - \frac{1}{m^2} \right) \quad (11.21)$$

In the case of the Balmer series, the lines originate from transitions from energy levels with $m > 2$ into the $n = 2$ energy level and then

$$\nu = \frac{m_e e^4}{8\epsilon_0^2 h^3} \left(\frac{1}{2^2} - \frac{1}{m^2} \right). \quad (11.22)$$

Substituting for the values of the constants, we find

$$\nu = 3.29 \times 10^{15} \left(\frac{1}{2^2} - \frac{1}{m^2} \right). \quad (11.23)$$

Miraculously, this is precisely the expression for the *Balmer series* of hydrogen.

The expression for the Balmer series is often written in terms of wavelengths rather than frequencies and then it becomes

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{2^2} - \frac{1}{m^2} \right) \quad (11.24)$$

where R_∞ is known as the *Rydberg constant* and has value $R_\infty = 1.097 \times 10^7 \text{ m}^{-1}$. The subscript ∞ means that it is assumed that the mass of the nucleus is infinite, as has been assumed in our calculation.

If we had applied the rules of quantisation of angular momentum to the system consisting of both the electron and the proton, we would have written

$$\hbar n = m_e v_e r_e + m_N v_N r_N \quad (11.25)$$

with the electron and nucleus orbiting their common centre of mass. It is a useful exercise to show that for this case,

$$r_e = \frac{m_N R}{m_e + m_N} \text{ and } r_N = \frac{m_e R}{m_e + m_N} \quad (11.26)$$

where $R = r_e + r_N$ is the distance between the electron and the nucleus. If the angular velocity of the electron and the nucleus about their centre

The Balmer series of hydrogen

$$\nu = \frac{m_e e^4}{8\epsilon_0^2 h^3} \left(\frac{1}{2^2} - \frac{1}{m^2} \right)$$

Historical note. One pleasant discovery included in Bohr's paper of 1913 was the explanation of the *Pickering series* which had been discovered in astronomical spectra by the astronomer Edward Pickering. The Pickering series is a series of singly ionised helium observed in the spectra of hot stars. Since the nuclear charge is twice that of hydrogen, the spectrum is shifted to four times shorter wavelengths as compared with that of hydrogen. The Pickering series corresponds to transitions into the $n = 4$ energy level, similar to the Brackett series of hydrogen but at four times shorter wavelengths.

of mass is ω , the condition for the quantisation of angular momentum becomes

$$\hbar n = \mu \omega R^2 \quad (11.27)$$

where $\mu = m_e m_N / (m_e + m_N)$ is known as the *reduced mass* of the system. This is left as a revision exercise in mechanics. The stationary states are found from the corresponding energy equation with the kinetic energy being given by $\frac{1}{2} I \omega^2 = -E_n$ where $I = \mu R^2$.

The energy level diagram for the hydrogen atom is shown in Figure 11.6. The various energy levels are shown with their appropriate names. The transitions associated with the series are known as follows:

- The Lyman series: $n = 2, 3, 4, \dots$ to $m = 1$
- The Paschen series: $n = 4, 5, 6, \dots$ to $m = 3$
- The Brackett series: $n = 5, 6, 7, \dots$ to $m = 4$
- The Pfund series: $n = 6, 7, 8, \dots$ to $m = 5$

The energy levels can be written in the form

$$E_n = -\frac{1}{n^2} \frac{m_e e^4}{8 \epsilon_0^2 \hbar^2} = -\frac{13.6}{n^2} \text{ eV} \quad (11.28)$$

where $n = 1, 2, 3, \dots$ is known as the *principal quantum number*. This expression indicates how much energy is necessary to remove an electron from any stationary state of the atom. In particular, to ionise an atom, that is, to remove an electron from the ground state, $n = 1$ to $E = 0$, an energy $E_1 = 13.6$ eV is required, corresponding to the transition from $n = 1$ to $n = \infty$.

The Bohr theory of the hydrogen atom was a quite remarkable achievement and it indicated clearly that it is essential to incorporate quantum concepts into the theory of atomic structure. It was apparent, however, that it was an incomplete theory. This theory, often called the *old quantum theory*, was an uneasy mixture of classical and quantum concepts without any proper theoretical underpinning. There were also a number of basic problems which remained unsolved.

Historical note The necessity of using the reduced mass was important historically. Bohr argued that singly-ionised helium atoms would have exactly the same spectrum as hydrogen, but the wavelengths of the corresponding lines would be four times shorter, as observed in the Pickering series. Fowler objected, however, that the ratio of the Rydberg constants for singly-ionised helium and hydrogen was not 4, but 4.00163. Bohr realised that the problem arose from neglecting the contribution of the mass of the nucleus to the computation of the moments of inertia of the hydrogen atom and the helium ion. When the reduced masses of hydrogen and ionised helium are used, the ratio of the Rydberg constants is 4.00160.

In his biography of Bohr, Pais tells the story of Hevesy's encounter with Einstein in September 1913. When Einstein heard of Bohr's analysis of the Balmer series of hydrogen, Einstein remarked cautiously that Bohr's work was very interesting, and important if right. When Hevesy told him about the helium results, Einstein responded,

‘This is an enormous achievement. The theory of Bohr must then be right.’

1. It was not at all clear why the electrons in the atoms did not radiate. Bohr had to suppose that the classical laws of electromagnetic radiation did not apply on the atomic scale.
2. The theory does not allow us to calculate transition rates from one state to another, nor does it tell us whether or not all possible transitions between energy levels are allowed.
3. The theory worked extremely well for hydrogen and other one electron ions, such as ionised helium, but could not account for the spectra of other atoms.
4. The theory could give no account of the bonding between molecules.
5. Many of the spectral lines are actually doublets, that is, two very closely spaced lines, for example, the D-lines of sodium.

The period from 1913 to 1925 was one in which the fundamentals of classical physics had been thoroughly undermined by discoveries which necessitated the introduction of the concept of quanta and yet no satisfactory quantum theory was available. The Bohr model was patched up in various ways but these were ad hoc adjustments to a fundamentally flawed theory. It was the discovery of wave and quantum mechanics in 1925-6 by Schrödinger, Heisenberg and their colleagues which finally rewrote the fundamental laws of physics.

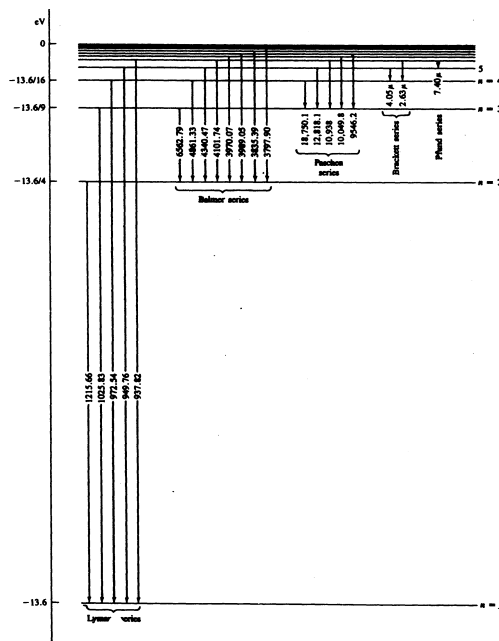


Figure 11.6. The term diagram for hydrogen showing the first four series.