Atomic structure and the periodic table

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THE ATOM AS A NUCLEUS WITH ORBITAL ELECTRONS

All atoms consist of a central nucleus surrounded by one or more orbital electrons. The nucleus always contains protons and all nuclei heavier than hydrogen contain neutrons too. The protons and neutrons together make up most of the mass of the atom. Both protons and neutrons are particles of unit mass, but a proton has one positive charge and a neutron is electrically neutral (i.e. carries no charge). Thus the nucleus is always positively charged. The number of positive charges on the nucleus is exactly balanced by an equal number of orbital electrons, each of which carries one negative charge. Electrons are relatively light – about 1/1836 the mass of a proton. The 103 or so elements at present known are all built up from these three fundamental particles in a simple way.

Hydrogen is the first and most simple element. It consists of a nucleus containing one proton and therefore has one positive charge, which is balanced by one negatively charged orbital electron. The second element is helium. The nucleus contains two protons, and so has a charge of +2. The nuclear charge of +2 is balanced by two negatively charged orbital electrons. The nucleus also contains two neutrons, which minimize the repulsion between the protons in the nucleus, and increase the mass of the atom. All nuclei heavier than hydrogen contain neutrons, but the number present cannot be predicted reliably.

This pattern is repeated for the rest of the elements. Element 3, lithium, has three protons in the nucleus (plus some neutrons). The nuclear charge is +3 and is balanced by three orbital electrons. Element 103, lawrencium, has 103 protons in the nucleus (plus some neutrons). The nuclear charge is +103 and is balanced by 103 orbital electrons. The number of positive charges on the nucleus of an atom always equals the number of orbital electrons, and is called the atomic number of the element.

In the simple planetary theory of the atom, we imagine that these electrons move round the nucleus in circular orbits, in much the same way as the planets orbit round the sun. Thus hydrogen and helium (Figure 1.1) have one and two electrons respectively in their first orbit. The first orbit is then full. The next eight atoms are lithium, beryllium, boron, carbon,

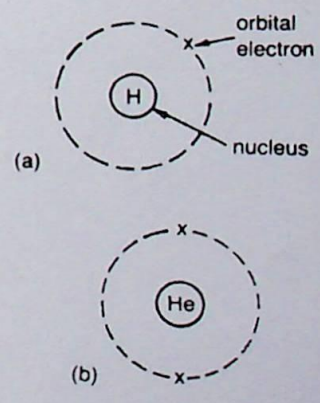

Figure 1.1 Structures of (a) hydrogen, symbol H, atomic number 1; and (b) helium, symbol He, atomic number 2.

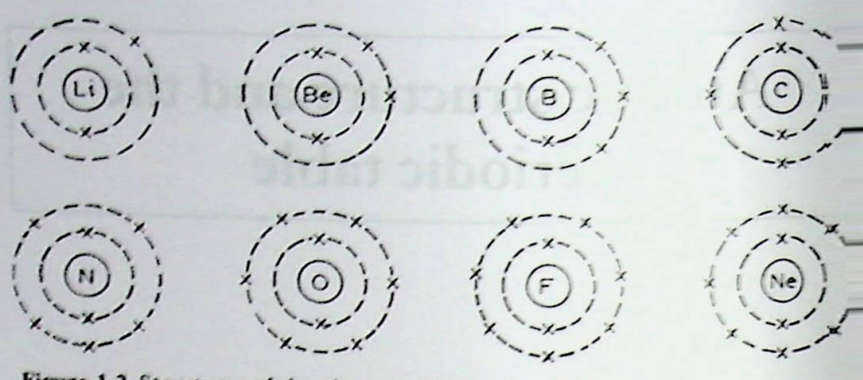

Figure 1.2 Structures of the elements lithium to neon.

nitrogen, oxygen, fluorine and neon. Each has one more proton in the nucleus than the preceding element, and the extra electrons go into the second orbit (Figure 1.2). This orbit is then full. In the next eight elements (with atomic numbers 11 to 18), the additional electrons enter a third shell.

The negatively charged electrons are attracted to the positive nucleus by electrostatic attraction. An electron near the nucleus is strongly attracted by the nucleus and has a low potential energy. An electron distant from the nucleus is less firmly held and has a high potential energy.

ATOMIC SPECTRA OF HYDROGEN AND THE BOHR THEORY

When atoms are heated or subjected to an electric discharge, they absorb energy, which is subsequently emitted as radiation. For example, if sodium chloride is heated in the flame of a Bunsen burner, sodium atoms are produced which give rise to the characteristic yellow flame coloration. (There are two lines in the emission spectrum of sodium corresponding to wavelengths of 589.0 nm and 589.6 nm.) Spectroscopy is a study of either the radiation absorbed or the radiation emitted. Atomic spectroscopy is an important technique for studying the energy and the arrangement of electrons in atoms.

If a discharge is passed through hydrogen gas (H_2) at a low pressure, atomic hydrogen atoms (H) are formed, which emit light in the visible region. This light can be studied with a spectrometer, and is found to comprise a series of lines of different wavelengths. Four lines can be seen by eye, but many more are observed photographically in the ultraviolet region. The lines become increasingly close together as the wavelength decreases, until the continuum is reached (Figure 1.3). Wavelengths, λ metres, are related to the frequency, ν, in Hertz (cycles/second) by the equation

$$\nu = \frac{c}{\lambda}$$

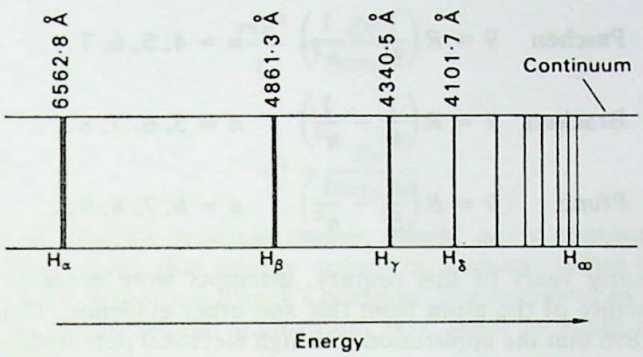

Figure 1.3 Spectrum of hydrogen in the visible region (Balmer series.)

where c is the velocity of light ($2.9979 \times 10^8 \,\mathrm{m\,s^{-1}}$). In spectroscopy, frequencies are generally expressed as wave numbers $\bar{\nu}$, where $\bar{\nu} = 1/\lambda \,\mathrm{m}^{-1}$.

In 1885 Balmer showed that the wave number $\bar{\nu}$ of any line in the visible spectrum of atomic hydrogen could be given by the simple empirical formula:

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

where R is the Rydberg constant and n has the values 3, 4, 5..., thus giving a series of lines.

The lines observed in the visible region are called the Balmer series, but several other series of lines may be observed in different regions of the spectrum (Table 1.1).

Similar equations were found to hold for the lines in the other series in the hydrogen spectrum.

Lyman $\quad \bar{\nu} = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right) \qquad n = 2, 3, 4, 5\ldots$

Balmer $\quad \bar{\nu} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \qquad n = 3, 4, 5, 6\ldots$

Table 1.1 Spectral series found in atomic hydrogen

	Region of spectrum
Lyman series	ultraviolet
Balmer series	visible/ultraviolet
Paschen series	infrared
Brackett series	infrared
Pfund series	infrared
Humphries series	infrared

Paschen $\bar{\nu} = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$ $n = 4, 5, 6, 7 \ldots$

Brackett $\bar{\nu} = R\left(\frac{1}{4^2} - \frac{1}{n^2}\right)$ $n = 5, 6, 7, 8 \ldots$

Pfund $\bar{\nu} = R\left(\frac{1}{5^2} - \frac{1}{n^2}\right)$ $n = 6, 7, 8, 9 \ldots$

In the early years of this century, attempts were made to obtain a physical picture of the atom from this and other evidence. Thomson had shown in 1896 that the application of a high electrical potential across a gas gave electrons, suggesting that these were present in atoms. Rutherford suggested from alpha particle scattering experiments that an atom consisted of a heavy positively charged nucleus with a sufficient number of electrons round it to make the atom electrically neutral. In 1913, Niels Bohr combined these ideas and suggested that the atomic nucleus was surrounded by electrons moving in orbits like planets round the sun. He was awarded the Nobel Prize for Physics in 1922 for his work on the structure of the atom. Several problems arise with this concept:

1. The electrons might be expected to slow down gradually.
2. Why should electrons move in an orbit round the nucleus?
3. Since the nucleus and electrons have opposite charges, they should attract each other. Thus one would expect the electrons to spiral inwards until eventually they collide with the nucleus.

To explain these problems Bohr postulated:

1. An electron did not radiate energy if it stayed in one orbit, and therefore did not slow down.
2. When an electron moved from one orbit to another it either radiated or absorbed energy. If it moved towards the nucleus energy was radiated and if it moved away from the nucleus energy was absorbed.
3. For an electron to remain in its orbit the electrostatic attraction between the electron and the nucleus which tends to pull the electron towards the nucleus must be equal to the centrifugal force which tends to throw the electron out of its orbit. For an electron of mass m, moving with a velocity v in an orbit of radius r

$$\text{centrifugal force} = \frac{mv^2}{r}$$

If the charge on the electron is e, the number of charges on the nucleus Z, and the permittivity of a vacuum ε_0

$$\text{Coulombic attractive force} = \frac{Ze^2}{4\pi\varepsilon_0 r^2}$$

so

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\varepsilon_0 r^2} \tag{1.1}$$

hence

$$v^2 = \frac{Ze^2}{4\pi\varepsilon_0 mr} \tag{1.2}$$

According to Planck's quantum theory, energy is not continuous but is discrete. This means that energy occurs in 'packets' called quanta, of magnitude $h/2\pi$, where h is Planck's constant. The energy of an electron in an orbit, that is its angular momentum mvr, must be equal to a whole number n of quanta.

$$mvr = \frac{nh}{2\pi}$$

$$v = \frac{nh}{2\pi mr}$$

$$v^2 = \frac{n^2h^2}{4\pi^2m^2r^2}$$

Combining this with equation (1.2)

$$\frac{Ze^2}{4\pi\varepsilon_0 mr} = \frac{n^2h^2}{4\pi^2m^2r^2}$$

hence

$$r = \frac{\varepsilon_0 n^2h^2}{\pi me^2 Z} \tag{1.3}$$

For hydrogen the charge on the nucleus $Z = 1$, and if

$n = 1$ this gives a value $r = 1^2 \times 0.0529\,\text{nm}$
$n = 2$ $r = 2^2 \times 0.0529\,\text{nm}$
$n = 3$ $r = 3^2 \times 0.0529\,\text{nm}$

This gives a picture of the hydrogen atom where an electron moves in circular orbits of radius proportional to 1^2, 2^2, 3^2... The atom will only radiate energy when the electron jumps from one orbit to another. The kinetic energy of an electron is $-\frac{1}{2}mv^2$. Rearranging equation (1.1)

$$E = -\tfrac{1}{2}mv^2 = -\frac{Ze^2}{8\pi\varepsilon_0 r}$$

Substituting for r using equation (1.3)

$$E = -\frac{Z^2e^4m}{8\varepsilon_0^2 n^2h^2}$$

If an electron jumps from an initial orbit i to a final orbit f, the change in energy ΔE is

$$\Delta E = \left(-\frac{Z^2e^4m}{8\varepsilon_0^2n_i^2h^2}\right) - \left(-\frac{Z^2e^4m}{8\varepsilon_0^2n_f^2h^2}\right)$$

$$= \frac{Z^2e^2m}{8\varepsilon_0^2h^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Energy is related to wavelength ($E = hc\bar{\nu}$ so this equation is of the same form as the Rydberg equation:

$$\bar{\nu} = \frac{Z^2e^4m}{8\varepsilon_0^2h^3c}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \qquad (1.4)$$

$$\bar{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \text{(Rydberg equation)}$$

Thus the Rydberg constant

$$R = \frac{Z^2e^4m}{8\varepsilon_0^2h^3c}$$

The experimental value of R is $1.097373 \times 10^7\,m^{-1}$, in good agreement with the theoretical value of $1.096776 \times 10^7\,m^{-1}$, The Bohr theory provides an explanation of the atomic spectra of hydrogen. The different series of spectral lines can be obtained by varying the values of n_i and n_f in equation (1.4). Thus with $n_f = 1$ and $n_i = 2, 3, 4\ldots$ we obtain the Lyman series of lines in the UV region. With $n_f = 2$ and $n_i = 3, 4, 5\ldots$ we get the Balmer series of lines in the visible spectrum. Similarly, $n_f = 3$ and $n_i = 4, 5, 6\ldots$ gives the Paschen series, $n_f = 4$ and $n_i = 5, 6, 7\ldots$ gives the Brackett series, and $n_f = 6$ and $n_i = 7, 8, 9\ldots$ gives the Pfund series. The various transitions which are possible between orbits are shown in Figure 1.4.

REFINEMENTS TO THE BOHR THEORY

It has been assumed that the nucleus remains stationary except for rotating on its own axis. This would be true if the mass of the nucleus were infinite, but the ratio of the mass of an electron to the mass of the hydrogen nucleus is 1/1836. The nucleus actually oscillates slightly about the centre of gravity, and to allow for this the mass of the electron m is replaced by the reduced mass μ in equation (1.4):

$$\mu = \frac{mM}{m + M}$$

where M is the mass of the nucleus. The inclusion of the mass of the nucleus explains why different isotopes of an element produce lines in the spectrum at slightly different wavenumbers.

The orbits are sometimes denoted by the letters K, L, M, N... counting outwards from the nucleus, and they are also numbered 1, 2, 3, 4... This number is called the principal quantum number, which is given the symbol

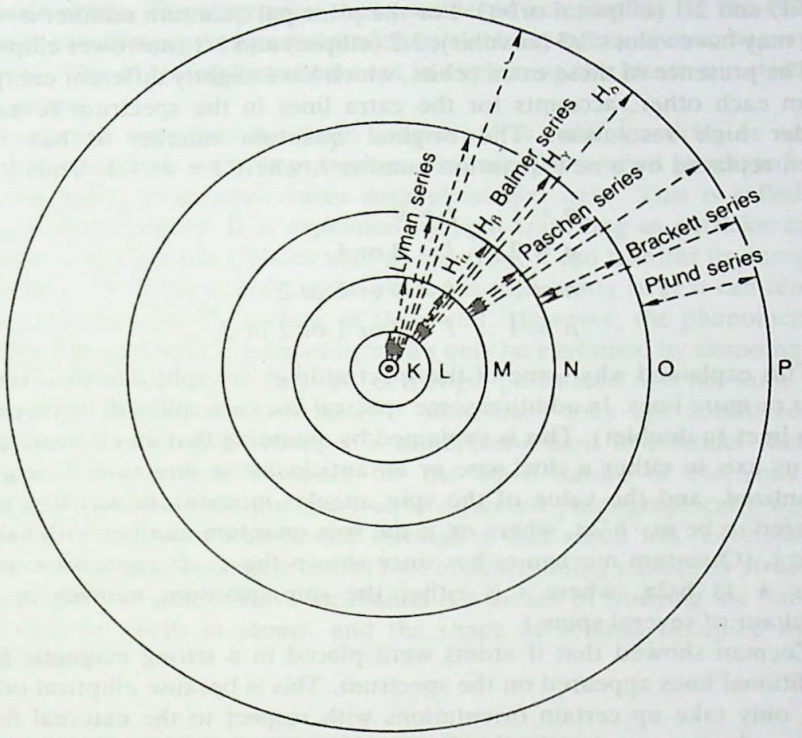

Figure 1.4 Bohr orbits of hydrogen and the various series of spectral lines.

n. It is therefore possible to define which circular orbit is under consideration by specifying the principal quantum number.

When an electron moves from one orbit to another it should give a single sharp line in the spectrum, corresponding precisely to the energy difference between the initial and final orbits. If the hydrogen spectrum is observed with a high resolution spectrometer it is found that some of the lines reveal 'fine structure'. This means that a line is really composed of several lines close together. Sommerfeld explained this splitting of lines by assuming that some of the orbits were elliptical, and that they precessed in space round the nucleus. For the orbit closest to the nucleus, the principal quantum number $n = 1$, and there is a circular orbit. For the next orbit, the principal quantum number $n = 2$, and both circular and elliptical orbits are possible. To define an elliptical orbit, a second quantum number k is needed. The shape of the ellipse is defined by the ratio of the lengths of the major and minor axes. Thus

$$\frac{\text{major axis}}{\text{minor axis}} = \frac{n}{k}$$

k is called the azimuthal or subsidiary quantum number, and may have values from $1, 2 \ldots n$. Thus for $n = 2$, n/k may have the values 2/2 (circular