

Emission Spectra

For centuries, it had been known that white light is comprised of the colours of the rainbow. Newton had demonstrated this by splitting white light with a prism and then recombining the coloured light to form a beam of white light.

In 1814, a lens maker, Josef von Fraunhofer (pictured right) extended Newton's work by spreading the dispersed light even more widely and demonstrated that sunlight did not comprise a continuum but that there were actually dark lines in the spectrum. Fraunhofer was able to accurately map and measure the wavelength of 574 of such lines. The origin of these lines was, however, a complete mystery



A very major step forward occurred when Gustav Kirchhoff (pictured left) invented his laboratory spectroscope (pictured right). Kirchhoff, working with Robert

Bunsen (below left), demonstrated that if he illuminated the flame with light from one of Bunsen's burners, the light turned into dark shadows. Kirchhoff managed to combine the light from the sun and from a flame together and the dark lines from both superimposed on each other exactly.



This was a colossal achievement not just in terms of the experimentation but the conclusion was ground breaking in many ways. It showed that emission and absorption of light were complementary and effectively the opposite of each other and that the sun was made of the same types of atom as found on Earth.



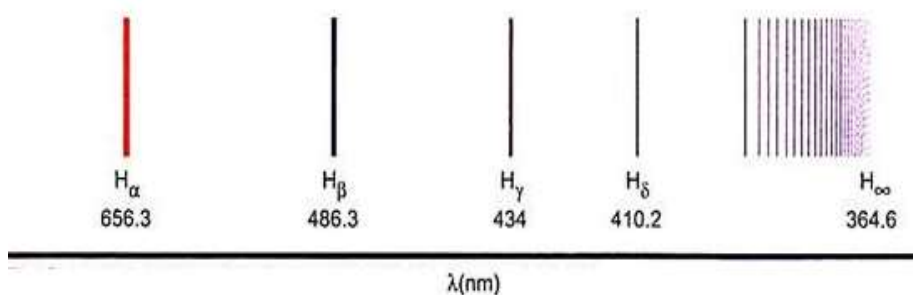
The consequences continued.

Kirchhoff and Bunsen tested many metals and solid compounds simply by holding them on a spatula in the flame and measured the emitted wavelengths of the bright light. The ability to measure precisely the wavelengths of star light permitted Edwin Hubble (1928) to demonstrate, from the *red shift* of hydrogen, that the stars are retreating from us and speeding up as they travel.

The ramifications for chemistry and geochemistry of the discoveries of Kirchhoff and Bunsen were immense. Microgram quantities of metals could be detected in a flame leading to huge advances in geology and geochemistry. Numerous chemists mapped the spectral lines of all known elements. Other lines which could not be assigned to known elements led directly to the discovery of the elements rubidium and caesium which were named after the most prominent red and blue lines in their spectra. Rubidium has a very similar spectrum to that of potassium and it was only through very precise measurements that rubidium could be distinguished and hence discovered.

There was still, however, no explanation for the appearance of the lines, their wavelength or the fact that the lines coalesced.

In 1885, Johann Balmer (pictured right) studied the measured wavelengths of hydrogen's visible spectrum which is shown below.



Balmer, derived a formula relating the lines to each other which was:
$$\lambda = B \left(\frac{n^2}{n^2 - 2^2} \right)$$

where λ is the wavelength, B is a constant and n is a integer of the form 1,3,4,5 . . etc but which is never equal to 2 since if n = 2 then the denominator becomes zero and the quantity in bracket equates to infinity.

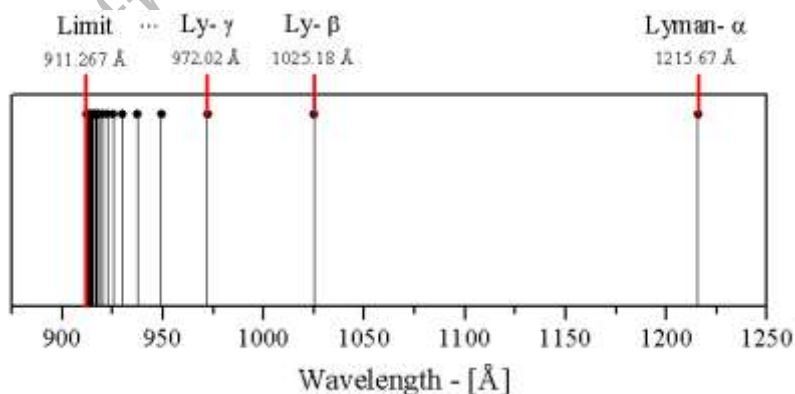
Another physicist, Johannes Rydberg, determined the relationship between the wavelengths of the lines and derived the following formula:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \text{ which simplifies to } \frac{1}{\lambda} = R_H \left(\frac{1}{4} - \frac{1}{n^2} \right)$$

where λ is the wavelength and n is an integer 1,3,4,5 . . . etc; and $R_H = 1.097 \times 10^7 \text{ m}^{-1}$.

This was a highly significant development but it could not be the final answer since it still did not explain the origin of the lines and it did not work for all elements.

In 1906, the Harvard physicist, Theodore Lyman, was studying the characteristic emissions of hydrogen in the ultraviolet region. He identified three series of lines which he designated α , β and γ .



Lyman noted three significant aspects of the spectrum which resonated with Balmer's discovery of the visible spectrum of the hydrogen atom:

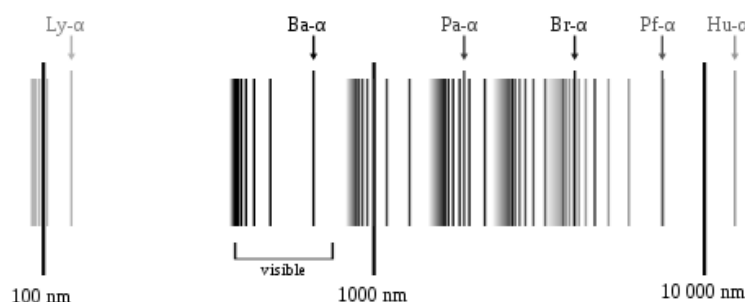
1. There were a series of discrete lines.
2. With decreasing wavelength, the lines came closer together.
3. At a particular wavelength the lines coalesced into a continuum.

After much work on different correlations, Lyman determined that the lines could be calculated according to the following formula:-

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where λ is the wavelength, n_1 and n_2 are integers 1,2,3,4... but $n_1 \neq n_2$ and $R_H = 1.097 \times 10^7 \text{ m}^{-1}$

This formula calculated all the lines in the Balmer and Lyman series and the other series which had also been discovered (Paschen, Brackett, Pfund and Humphreys).



The lines were clearly fundamental and arose from atomic structure since the absorption and emission structures complemented each other perfectly.

To reiterate, the Balmer series lies in the visible region, the Lyman series lies in the ultraviolet region, whilst the Paschen, Brackett, and Pfund series lie in the infrared region.

All lines can be calculated by a formula analogous to the Lyman formula:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where $n_1 = 1, 3, 4$ or 5 and $n_2 = 2, 4, 5$ or 6 respectively. The Lyman formula requires that $n_1 = 3$ and note again that $n_1 \neq n_2$.

This was further, definite, proof of the fundamental relationship of the spectral lines to atomic structure when further was collected from analysis of the spectra of other simple ions with one electron only, specifically the He^+ ion and the Li^{2+} ion. Each of these ions contain only one electron so are analogous, electronically, to the hydrogen atom and their spectral lines follow a similar formula. As an aside, all species with the same number of electrons e.g. ${}^1\text{H}$, ${}^2\text{He}^+$ and ${}^3\text{Li}^+$ are referred to as being *isoelectronic*.

Another hugely significant development was the proposal of Max Planck that energy is quantised i.e. exists as discrete bundles of energy known as *quanta*. Einstein used the concept to explain the photoelectric effect which is discussed in the next chapter.

The Bohr Model of the Structure of the Hydrogen Atom

In 1916, the Danish physicist, Niels Bohr (pictured below right) published a concept of a series of circular orbits indicating possible paths for an electron.

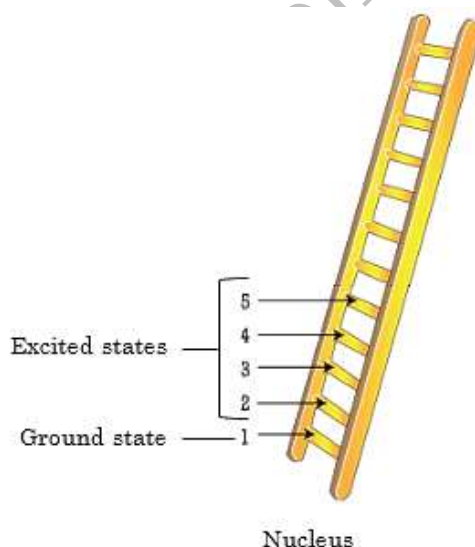


It is a fundamental principle in physics that everything exists in the lowest possible energy state, unless forced to behave otherwise, which explains why a ball dropped down a flight of steps does not stop until the ball is on the ground floor. The ball's gravitational potential energy (GPE) is converted to kinetic energy (KE) which is used to move the ball down the staircase until, on the ground floor, when its GPE is at a minimum. Likewise, a ball is given, acquires, GPE when it is carried upstairs.

Bohr extended this concept to a hydrogen atom.

The single electron exists in the lowest energy level (orbit) unless provided with sufficient energy to move to the next or an even higher energy level. The lowest energy level is the *ground state* whilst all other levels (orbits) which are of higher energy are known as excited states.

Bohr's stepladder analogy to the energy levels of the hydrogen atom accounts for the existence of specific lines in the absorption spectrum and in the emission spectrum.



When an atom absorbs radiation it only absorbs specific energies.

The rest of the light travels straight through and the measured spectrum has a number of dark lines, indicating the energies which have been absorbed and hence demonstrating the energies required for the electron to move from the ground state upwards.

When the irradiating energy is removed then the electron relaxes and moves from an excited state to the ground state releasing exactly the same quantity of energy required to move the electron from the ground state upwards. This explains why the absorption and emission spectra are exactly complementary and, superimposed, form a continuous spectrum.

Bohr went further:

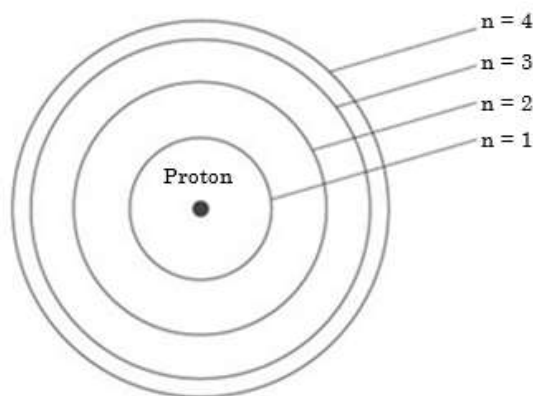
1. The stepladder analogy is a start but if the steps, i.e. orbits, are exactly the same distance apart then the wavelengths of the absorbed and emitted radiation would be simpler multiples of the lowest highest energy line (remember that frequency and wavelength multiplied together give us the speed of light – the higher the energy, the higher the frequency and the lower the wavelength).

They are not simple multiples of the lowest energy (lowest frequency, highest wavelength) line.

The lines get progressively closer together which implies that the orbits (the steps in the ladder) also get closer together the further one moves from the nucleus.

2. Eventually the lines are so close together that they can no longer be separated and then there are no further lines. This confirms the concept of the orbits getting closer together the further from the nucleus until the lines *coalesce* and can no longer be distinguished.

Showing only the first four energy levels, the hydrogen atom then, according to Bohr has the structure:



Bohr drew the conclusion that, from his model, the highest energy series of lines (the *Lyman series*) arose from transitions from the ground state ($n=1$, the orbit closest to the nucleus) and that the next highest energy, *Balmer*, series would be due to absorption of energy from second innermost orbit ($n=2$).

By assessing the exact wavelengths of the absorption spectrum he was able to calculate the exact distance (in energy terms) of the three next outer levels.

The transitions from $n=2$ outwards were determined to be as follows:

Transition	Energy (qualitatively)	Wavelength (nm)	Colour of line
$n_2 \rightarrow n_3$	Lowest	656	Red
$n_2 \rightarrow n_4$	↓	486	Aqua
$n_2 \rightarrow n_5$		434	Blue
$n_2 \rightarrow n_6$		Highest	410

3. Bohr was able to explain the existence of all of the remaining series: Paschen, Brackett, and Pfund as follows where n_1, n_2, n_3 etc; are the levels:

The energy differences between n_4 , n_5 and n_6 become successively smaller and are observed in the infrared region and are reconciled by Bohr's concept that the further from the nucleus the closer together the energy levels become, as demonstrated above.

Conventionally, it is more appropriate and convenient to discuss the energies of the different orbits as lines as shown below.

This is most easily understood when the two ways of describing the energy levels are considered together with the visible spectrum:

Paschen: $n_3 \longrightarrow n_4 \longrightarrow n_5 \longrightarrow n_6 \longrightarrow n_7 \dots \longrightarrow \infty$ (ionisation)

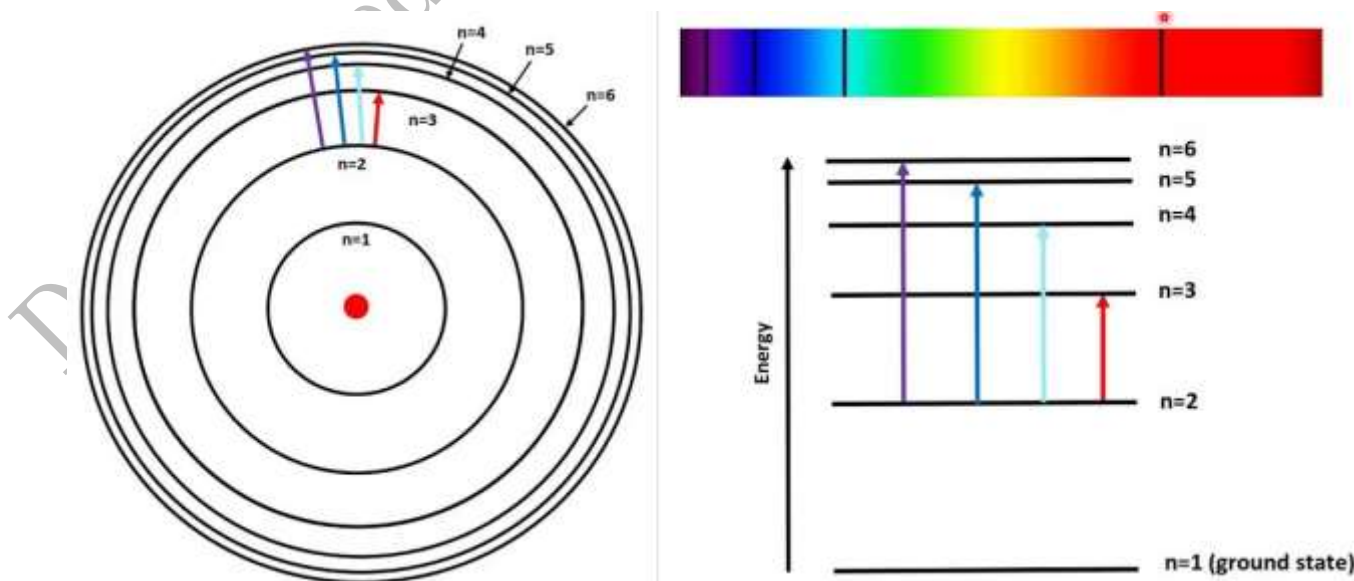
Brackett: $n_4 \longrightarrow n_5 \longrightarrow n_6 \longrightarrow n_7 \dots \longrightarrow \infty$ (ionisation)

Pfund: $n_5 \longrightarrow n_6 \longrightarrow n_7 \dots \longrightarrow \infty$ (ionisation)

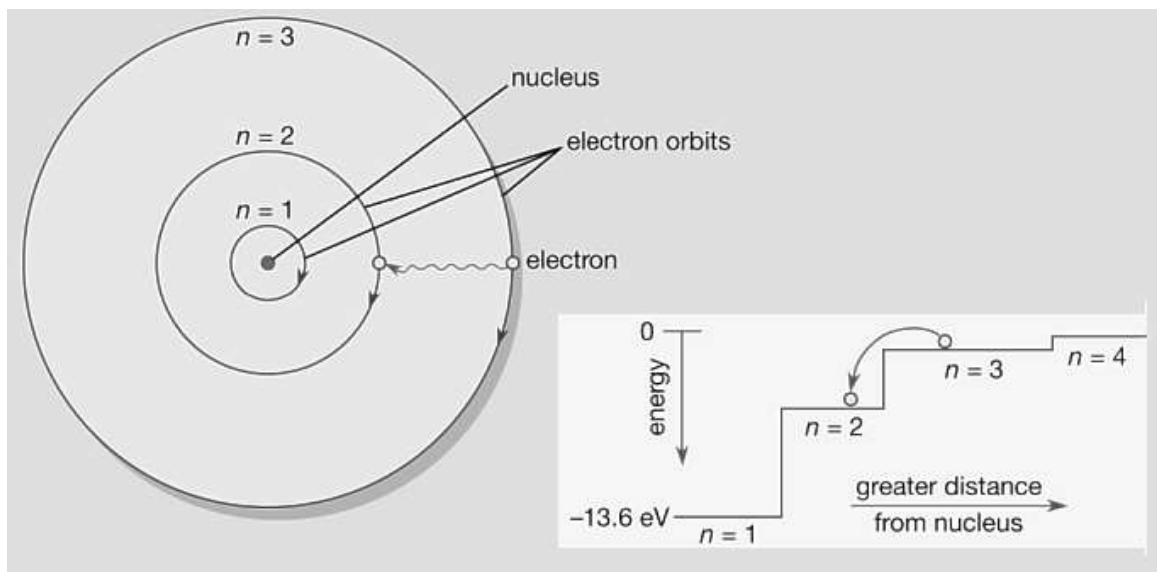
and can be summarised as follows:

Series	n_1	n_2	Spectral lines region
Lyman	1	2,3,4 etc;	Ultraviolet
Balmer	2	3,4,5 etc;	Visible
Paschen	3	4,5,6 etc;	Infrared
Brackett	4	5,6,7 etc;	Infrared
Pfund	5	6,7,8 etc;	Infrared

and visually described as below.



Bohr's model was an almost complete triumph as shown again below:-



It explained the:-

- Existence of a series of spectra in the uv (*Lyman series*), visible (*Balmer series*) and the three in the ir regions (*Paschen, Brackett and Pfund series*).
- Reasons for the individual lines within each series.
- Flame test colours.
- Superimposability of the absorption and emission spectra.
- Black lines in the absorption spectra and the coloured lines in the emission spectra which except for the coloured lines is completely black.
- Ionisation since once the electron had acquired sufficient energy to move beyond the highest energy level it was free of the atom which had been ionised.

Bohr's theory was also proven to be a good model since he was also able to explain the spectra of the He^+ ion and the Li^{2+} ions.

Each of the latter two ions involve a single electron orbiting a positively charged nucleus but it proved impossible to extend the model to atoms or ions containing more than one electron since it was impossible to know their velocity and their interactions with other electrons and the nucleus at the same time.

Bohr was able to calculate, using traditional classical electrodynamics of one charge passing by another, in these cases, the, negatively charged, electron orbiting a positively charged nucleus. Once two or more electrons were present, however, the calculations required knowledge of the velocities of both electrons and their interactions both with the nucleus and their mutual repulsions. Knowledge of the velocities of the two electrons was impossible to ascertain and it was at that point that Bohr's model was clearly, a huge step forward, it was not the final explanation.

Moreover, Bohr's theory still did not explain why electrons did not spiral into the nucleus as predicted by classical electrodynamics but the number of answers his theory provided demonstrated a huge step forward in understanding atomic structure.

Bohr's theory:-

- Created the concept of energy levels in the atom;
- Explained the emission spectra of different elements;
- Explained why the absorption spectra perfectly complemented emission spectra but;
- Did not explain why electrons do not spiral into the nucleus but did;
- Explained the ionisation of atoms since when the electron had sufficient energy to rise above the highest energy level it was free of the influence of the nucleus and the atom had become ionised;
- Laid the foundations of the most important chemical spectroscopic technique of all: *nuclear magnetic resonance* which depends on the theory of quantum mechanics which developed approximately ten years after Bohr's theory was published and is discussed next.

Downloaded from www.ellixiascience.co.uk