

SESSION 4: Quantum Numbers

Overview: In this session we will:

- define quantum numbers
- see the origin and significance of quantum numbers
- determine the separation of the energy levels in hydrogen
- looking at shell and sub-shells in hydrogen
- looking at the emission spectra of hydrogen

Each atomic orbital (AO) is specified by a **principal quantum number n**, by an **orbital angular momentum (or azimuthal) quantum number ℓ** , and by a **magnetic quantum number m_ℓ** . All of these three quantum numbers come out of the solution of the SWE for the individual hydrogen atomic orbitals, and together they give the ‘address’ of the electron in the atom (i.e. the orbital in which the electron is located).

The principal quantum number, n is used to calculate the energy of the electron in the atom, and is equal to “the total number of nodes in an orbital plus one” and has values:

$$n = 1, 2, 3, \dots$$

The orbital angular momentum quantum number is equal to the number of angular nodes present in an orbital and has n possible values:

$$\ell = 0, 1, 2, 3, \dots (n - 1)$$

i.e. for a specific value of n, ℓ can have values from a minimum of zero up to a maximum of (n – 1).

For a given value of ℓ , there are $2\ell + 1$ values of the magnetic quantum number m_ℓ in the range:

$$m_\ell = 0, \pm 1, \pm 2 \dots \pm \ell. \quad (\text{or } +\ell, \ell - 1, \ell - 2, \dots -\ell)$$

Shells

In the **hydrogen atom**, the energy of an orbital depends only on the value of n. This means that all orbitals with the same value of n, regardless of the values of ℓ and m_ℓ , are degenerate (have the same energy). This is the reason that all orbitals in hydrogen with the same value of n are said to belong to the same shell. The values of n and the corresponding shell designations are:

$$\begin{array}{cccc}
 n = & 1 & 2 & 3 & 4 \dots \\
 & \text{K} & \text{L} & \text{M} & \text{N} \dots
 \end{array}$$

Sub-Shells

Orbitals with the same value of n , but different values of ℓ belong to different sub-shells which are denoted as follows:

$$\begin{array}{cccc}
 \ell = & 0 & 1 & 2 & 3 \\
 & s & p & d & f
 \end{array}$$

Each sub-shell contains $2\ell + 1$ individual orbitals corresponding to the $2\ell + 1$ values of m_ℓ (all with the same value of ℓ).

Table X. Shells, sub-shells and orbitals for a given value of n

shell	K	L		M		
n	1	← 2 →		← 3 →		
ℓ	0	0	1	0	1	2
m_ℓ	0	0	1, 0, -1	0	1, 0, -1	2, 1, 0, -1, -2
type	<i>s</i>	<i>s</i>	<i>p</i>	<i>s</i>	<i>p</i>	<i>d</i>
sub-orbitals	1	1	3	1	3	5
# of orbitals/shell	1	← 4 →		← 9 →		

It can be seen from the above table that for $n = 1$, there is only one value of ℓ (i.e. $\ell = 0$), and hence one value of m_ℓ and therefore only one orbital. Similarly for $n = 2$, there are 4 orbitals and for $n = 3$ there are 9. In fact, the number of orbitals for a shell of quantum number n is equal to n^2 . There is always one *s*-orbital in a shell and (whenever they are present), three *p*-orbitals and five *d*-orbitals.

Apart from splitting the n^{th} level into individual sub-levels, m_ℓ describes how each orbital is oriented relative to any arbitrary or preferred direction in space (such as that of a magnetic field). The magnetic quantum number, m_ℓ , is used to

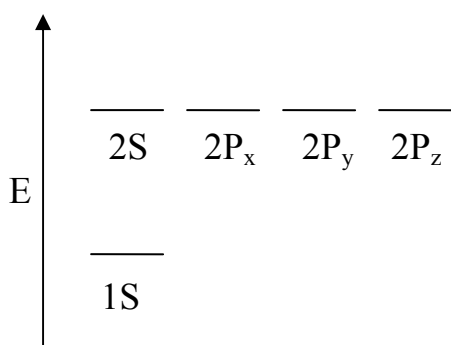
explain additional lines that appear in the emission line spectra when the atom is subjected to an external magnetic field.

Spin Quantum Number, m_s

There is, in fact, a fourth quantum number which gives the absolute configuration that the electron is allowed to have in an orbital. The spin quantum number m_s , is allowed the values of $+\frac{1}{2}$ and $-\frac{1}{2}$, signifying two possible spin configurations, α and β . At this time, these can be viewed simply as an *up* or *down* spin or a *clockwise* or *anticlockwise* spin. As you will see later on in the chapter, for two electrons to occupy the same orbital they must have opposite spins.

Energy Levels in Hydrogen

In the case of hydrogen, as stated previously, the energy depends only on n . Therefore **2s** and **2p** correspond to states of the same energy, as shown in the following diagram:



For hydrogen, when the electron is in the **2s** orbital the state is 2S, when the electron is in the **2p_x** orbital the state is 2P_x, and so on.

Separation of Energy Levels in Hydrogen Atom

When an electric discharge is passed through a sample of hydrogen gas, the atoms are able to absorb energy. In absorbing this energy, electrons are promoted to higher levels. When the electrons fall back to states with lower energy giving out energy in the form of radiation (photons), an emission spectrum is observed. This spectrum is seen to consist of discrete sharp lines which mean that the electrons are moving between specific energy levels and in

doing so are able to absorb or give out a discrete amount of energy. The energy levels in hydrogen are given quantitatively by:

$$E_n = -\frac{hcR_H}{n^2},$$

where n ($= 1, 2, 3 \dots$) is the principal quantum number and R_H ($= 109,678 \text{ cm}^{-1}$) is the Rydberg constant for hydrogen.

In this definition, the ionized atom ($\text{H}^+ + \text{e}^-$) is taken as the zero of energy and the energy levels lie at some negative value (more stable value) below this zero. Therefore, the first three energy levels in hydrogen would be:

$$E_1 = -\frac{hcR_H}{1^2} = -hcR_H, \quad E_2 = -\frac{hcR_H}{2^2} = -\frac{hcR_H}{4}, \quad \text{and} \quad E_3 = -\frac{hcR_H}{3^2} = -\frac{hcR_H}{9},$$

indicating how far below the zero each lies. As the value of n increases the separation between successive energy levels decreases:



The Separation of Energy Levels in the Hydrogen Atom

When the H-atom absorbs or emits energy, the electron has to move between these specific energy levels and therefore, absorbs or emits a specific amount of electromagnetic energy. As a consequence, a line spectrum is observed. The observed spectral emissions (lines) can be explained as follows:

Transition from $n = 3$ to $n = 2$ (in emission). The difference in energy, ΔE , is

$$\Delta E = E_3 - E_2 = \left(-\frac{hcR_H}{9}\right) - \left(-\frac{hcR_H}{4}\right) = hcR_H \left(\frac{1}{4} - \frac{1}{9}\right) = hcR_H \left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

Emission lines (4 to be exact) in the visible spectrum of hydrogen, occur when the electron falls from a higher level down to $n = 2$. The expression corresponding to these lines is

$$\Delta E = hcR_H \left(\frac{1}{2^2} - \frac{1}{n^2}\right), \text{ where } n = 3, 4, 5, 6.$$

This visible series of emission lines is known as the *Balmer Series*. Two other series: *Lyman* (ultra-violet) and *Paschen* (infra-red) occur when emissions terminate in the $n = 1$ and the $n = 3$ levels respectively.

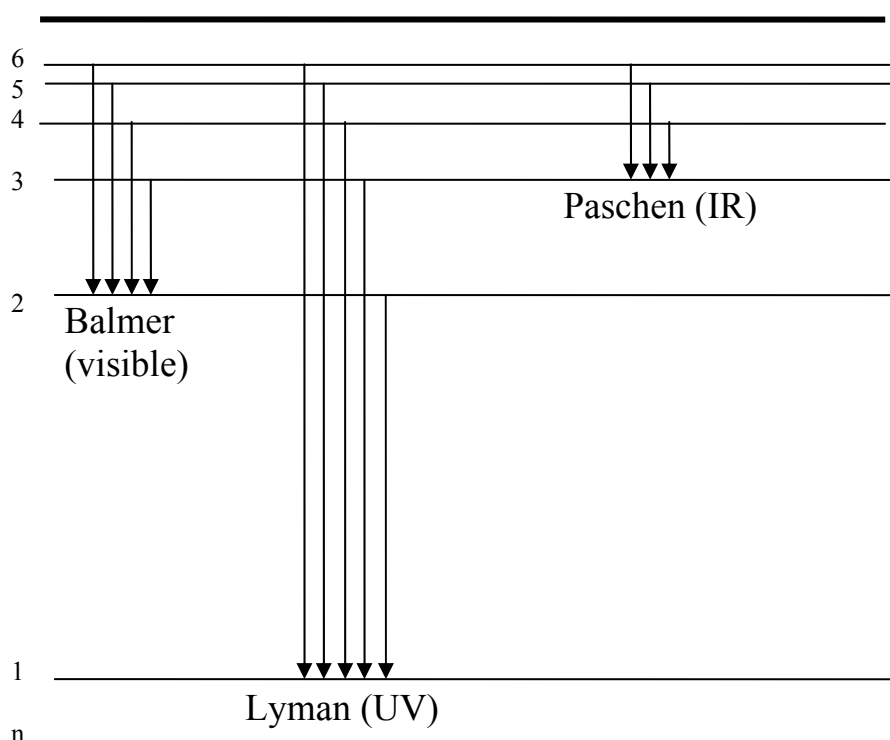


Figure showing the origin of the spectral series in hydrogen atom.

It can be seen from the above figure that if the series are placed in order of increasing energy the result is: Paschen (IR) < Balmer (vis) < Lyman (UV).

Exercise 6. Calculate the energy (in Joules) of the photon emitted when an electron falls from the $n = 4$ level to the $n = 2$ level in the hydrogen atom. Convert the energy of the photon from Joules to wavenumbers (cm^{-1}).

Solution

$$\begin{aligned} \text{Energy} &= hcR_H \left(\frac{1}{2^2} - \frac{1}{4^2} \right) \\ &= (6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^{10} \text{ cm s}^{-1})(109678 \text{ cm}^{-1})\left(\frac{1}{4} - \frac{1}{16}\right) \\ &= 4.085 \times 10^{-19} \text{ J} \end{aligned}$$

The wavenumber of the photon is determined from the expression

$$\begin{aligned} \bar{\nu} &= R_H \left(\frac{1}{n^2} - \frac{1}{m^2} \right), \text{ where } n \text{ and } m \text{ are the quantum numbers of the levels.} \\ &= (109678 \text{ cm}^{-1})\left(\frac{1}{4} - \frac{1}{16}\right) = 20565 \text{ cm}^{-1} \end{aligned}$$

The wavenumber of a radiation is the number of wavelengths that can fit in a length of 1 cm. In this example, 20565 wavelengths joined end-to-end would measure 1 cm.

Since we now have a fair understanding of what is happening in the hydrogen atom, we can now turn to the next higher atom, Helium. This should be more demanding since we now have to account for the repulsion experienced between the two electrons and the separate attractions between both electrons and the positive nucleus. In this section we will try to apply, what we have just learnt about hydrogen, to see if it can be used to explain the behaviour of the electrons in the Helium atom