UNIT 1 SPECTRA OF ATOMS

Structure

1.1 INTRODUCTION

This is the first unit of the 'Spectroscopy' course. As suggested to you, we assume that by now you must have studied "Atoms and Molecules" (CHE-01) course. Since there must have been some time gap in-between, it will be useful to begin with by refreshing some of the concepts dealt with in the 'Atoms and Molecules' course.

This unit is devoted to the spectra of Atoms. You are aware from Unit 1 of "Atoms and Molecules" course that atomic spectra results due to the interaction of electromagnetic radiation with atoms. Hence, we will start our discussion by defining what is electromagnetic radiation and how it propagates in space. We will also enlist some characteristics of electromagnetic radiation followed by the explanation of its interaction with atoms. We will discuss the atomic spectra of hydrogen and hydrogen like atoms in detail followed by that of helium and sodium. We will also explain the spectroscopic states by taking the example of carbon. Then Zeeman effect will be discussed. Finally, two techniques such as X-ray fluorescence and photoelectron spectroscopy used in the determination of atomic spectra will be explained.

Objectives

After studying this unit, you should be able to:

- describe electromagnetic radiation,
- define and relate various parameters such as wavelength, frequency, wavenumber etc. associated with the electromagnetic radiation,
- discuss the origin of various series of spectral lines in the atomic spectrum of hydrogen,

- explain the fine structure of hydrogen atom spectrum,
- predict the spectra of hydrogen like atoms,
- discuss the possible transitions in the atomic spectrum of helium,
- write spectroscopic terms of an atom from its electron configuration,
- explain Zeeman effect and
- give importance of the x-ray flourescence and photoelectron spectroscopy.

1.2 THE ELECTROMAGNETIC RADIATION

Since atoms and molecules cannot be seen, we derive information about their structure by their interaction with electromagnetic radiation. You may recall from Units 1 and 6 of 'Atoms and Molecules' course that electromagnetic radiation consists of oscillating electric and magnetic fields directed perpendicularly to each other and also to the direction of propagation of radiation, as is shown in Fig. 1.1.

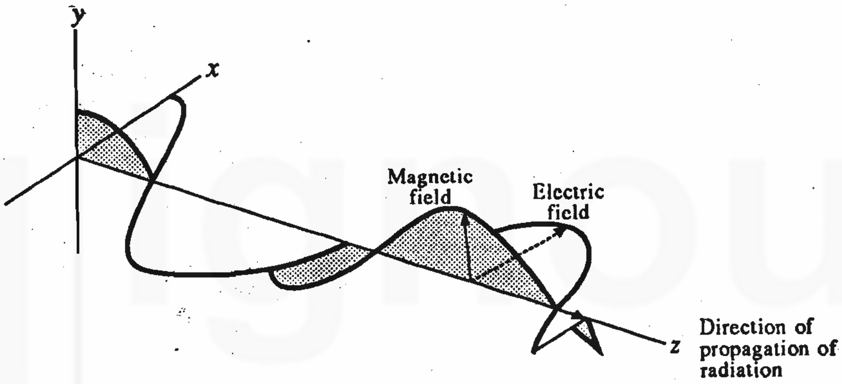

Fig. 1.1: The electric and magnetic fields of the electromagnetic radiation.

Similar to the other transverse wave motions such as that of stretched string or water wave, the electromagnetic radiation carries energy from one place to another. But unlike the other wave motions it does not require any medium for its propagation.

The electromagnetic radiation can be described in terms of certain parameters such as **wavelength, frequency, wave number and energy**. Although these parameters have been explained in Block 1, Unit 1, Sec. 1.4 of 'Atoms and Molecules' course, let us revise them and refresh our memory as you will be using them very often throughout this course.

Wavelength (λ) can be defined as the distance between two successive crests or troughs (see Fig. 1.2). The wavelength depends on the system through which the radiation is passing.

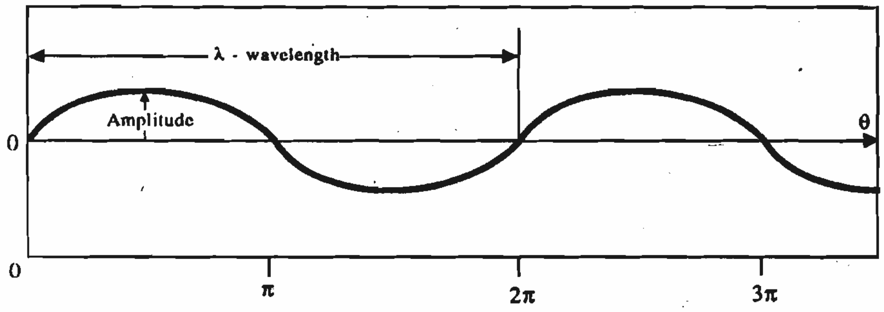

Fig. 1.2: Wavelength associated with the electromagnetic radiation.

Frequency (ν) is the number of waves per second.

Wave number ($\bar{\nu}$) is the reciprocal of wavelength and it is the number of waves per unit length.

The symbols and SI units of wavelength, frequency and wave number are listed in Table 1.1.

Table 1.1 : Some characteristics associated with electromagnetic radiation.

Parameter	Symbol	SI Unit
Wavelength	λ (lambda)	metre (m)
Frequency	ν (nu)	hertz (Hz)
Wave Number	$\bar{\nu}$ (nu bar)	metre^{-1} (m^{-1})

These parameters are related to each other by the following relations:

The longer the wavelength, the lower is the frequency; and the shorter the wavelength, the higher is the frequency.

$$\lambda = \frac{c}{\nu} \qquad \text{...(1.1)}$$

where c is the velocity of the radiation in the medium. However, in vacuum $c = 2.998 \times 10^8 \text{ m s}^{-1}$.

$$\text{and} \qquad \bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \qquad \text{...(1.2)}$$

You may also recall from Unit 1 of 'Atoms and Molecules' course that certain phenomena like black body radiation, heat capacity variation, photoelectric effect and atomic spectra could not be explained with the help of classical mechanics. The classical mechanics puts no restrictions on the value of a dynamic variable (e.g., energy, momentum etc.). The quantum theory proposed by Max Planck in 1900, suggested that the energy can be emitted or absorbed **only by a specified amount**, called the **quanta and not continuously**. Also when we consider the interaction of radiation with matter, its wave like description fails to explain the interaction. Therefore, the particle nature of the radiation has to be considered. These particles are known as **photons**. The **energy** (E) of the photon can be related to the **frequency** (ν) of the radiation by the following expression:

You are advised to go through Unit 1, Secs. 1.5 and 1.6 for details of these phenomena.

$$E = h\nu \qquad \text{...(1.3)}$$

where h is the Planck's constant and has the value 6.626×10^{-34} J s.

From Eq. 1.1, we can say that

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

Substituting the above value of υ in Eq. 1.3, we get

$$E = \frac{hc}{\lambda} \qquad \text{...(1.4)}$$

From Eq.1.2, $\bar{\nu} = \frac{1}{\lambda}$. Substituting this in Eq.1.4, we can write

$$E = hc\bar{\nu} \qquad \text{...(1.5)}$$

Learn the above relationships by heart and do not confuse one with the other. If you do not feel confident, go through them once again.

Fig.1.3 shows the range of electromagnetic radiation in terms of the above parameters. Carefully go through the values given for various regions. Try to apply the above relationships (Eq.1.1 to Eq.1.5) to these values.

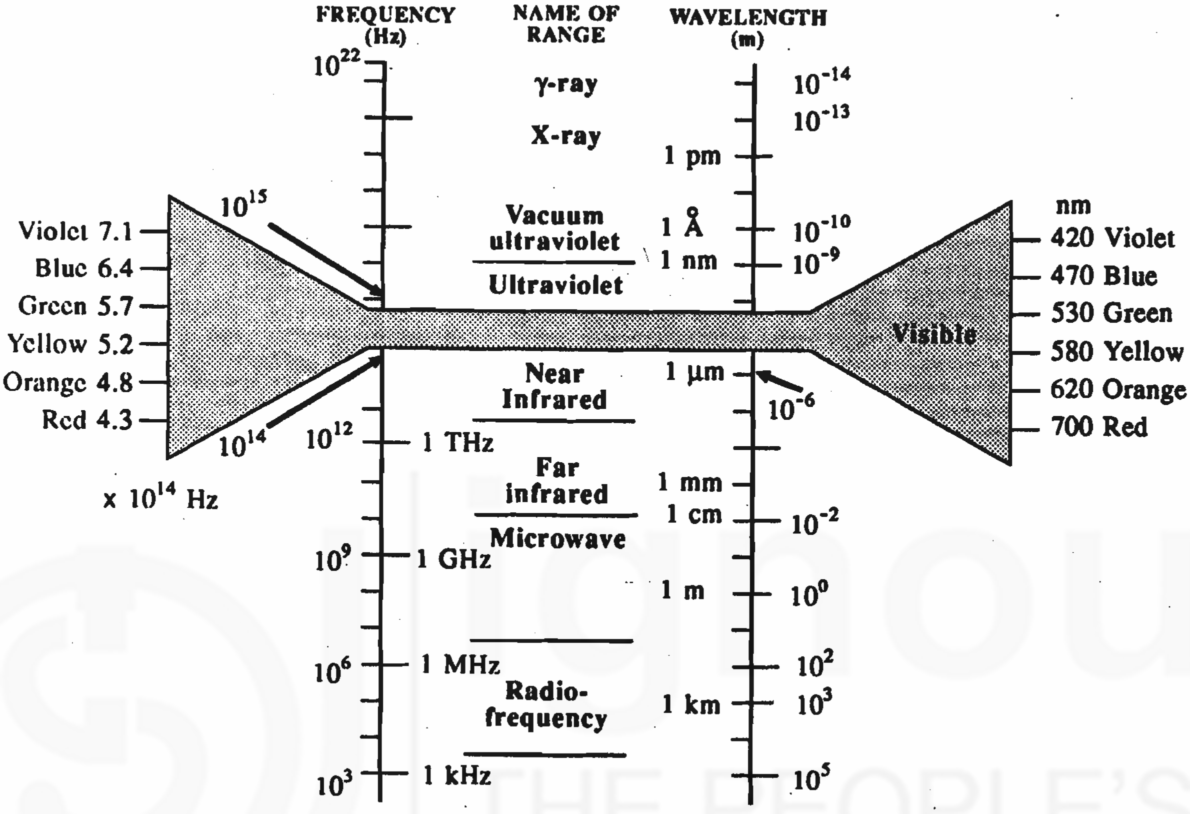

Fig. 1.3: The Range of Electromagnetic radiation.

After understanding the above section, answer the following SAQs.

Although you know the following conversions from Unit 1 of 'Atoms & Molecules' course (CHE-01), you are advised to go through them again and refresh your memory.

1 millimetre = 1 mm = 10^{-3} m
1 micrometre = 1 μm = 10^{-6} m
1 nanometre = 1 nm = 10^{-9} m
1 picometre = 1 pm = 10^{-12} m
1 Angstrom = 1 Å = 10^{-10} m

SAQ 1

Calculate the energy associated with a radiation having wavelength (λ) = 400 nm.

SAQ 2

Generally, the energy is reported per mole. How will you convert the energy value obtained above in terms of energy per mole ?

Avagadro Number = 6.022×10^{23} mol^{-1}

....

....

1.3 INTERACTION OF RADIATION WITH MATTER

From the above discussion you have an idea about what a radiation is? You are also familiar with the fact that matter consists of atoms or molecules. When electromagnetic radiation comes in contact with matter, there may be an exchange of energy between the photons and matter. As mentioned in the last section, according to Planck, energy can change only in terms of **quanta**. Thus, a system may absorb energy and go from the lower energy state E_1 to the higher energy state E_2. Alternatively, a system initially in the higher energy state E_2 can lose energy and go to the lower energy state E_1. The energy difference, ΔE, between these two states is given by the following equation.

$$\Delta E = E_2 - E_1 = h\nu \qquad \text{... (1.6)}$$

where $h\nu$ is the energy abosrbed or emitted. This is also shown in Fig. 1.4.

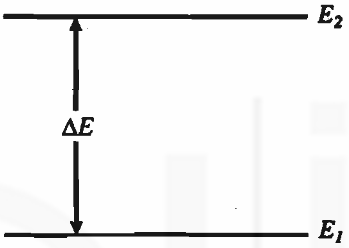

Fig.1.4: Energy levels of a system.

The lower energy state is called the **ground state** whereas the higher energy state obtained by absorption of energy is called the **excited state** for that particular system.

At this moment, can you think of the importance of the absorption or emission of energy by a system as discussed above? Obviously, by determining the energy absorbed or emitted, you can know about the energy levels present in an atom or a molecule. In other words, these energy changes can be related to the structure of the atom or the molecule.

The next question which will come to your mind is how to determine what amount of energy is absorbed or emitted? Depending upon which one of the two modes (absorption or emission) we choose for determining the energy change, we use the instrument called **absorption** or **emission spectrophotometer**. These instruments are designed to measure which frequencies of radiation are absorbed or emitted by a particular sample on irradiation. The **absorption spectrophotometer** (Fig.1.5 a) consists of a source which gives radiation of known frequency range. The radiation, thus obtained, is passed through the sample. The sample absorbs some of the frequencies and transmits the others. The transmitted radiation is then analysed, detected and the frequencies absorbed are recorded. The **emission spectrophotometer** (Fig. 1.5 b) consists of a source of excitation which energises the sample. The sample then emits a characteristic radiation which can then be resolved into its components and finally detected.

Do not worry about the details of instrumentation at this stage. You will study them in Unit 9 of Block 3 and at other appropriate places in this course.

At this stage, you may be curious to know how the absorption and emission spectra look? In absorption spectra, certain frequencies are absorbed by the sample under observation. When the transmitted radiation is analysed, these particular frequencies will be missing and if a photographic plate is used as a detector, one

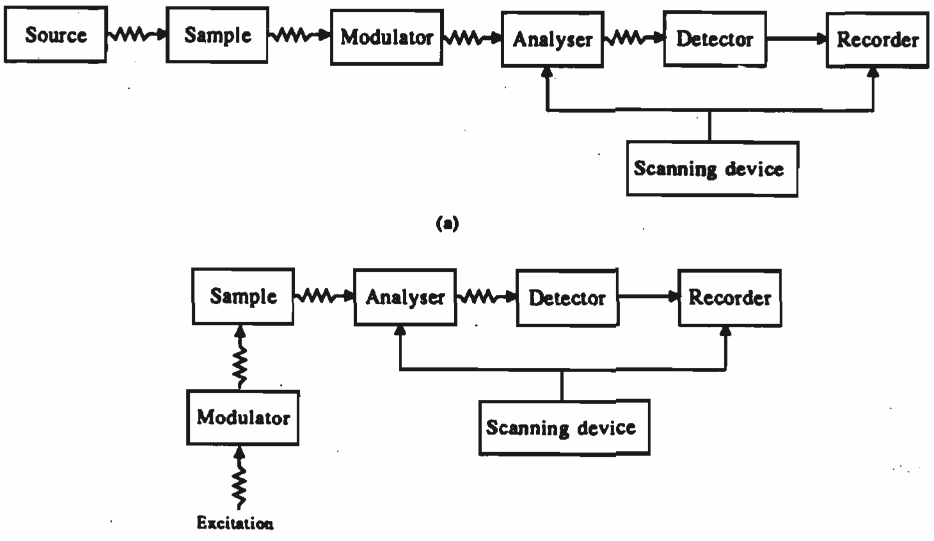

Fig.1.5: Schematic representation of (a) an absorption spectrophotometer and (b) an emission spectrophotometer.

can expect dark lines for each of these absorptions. This is shown in Fig. 1.6 (a). Fig 1.6 (b) shows an emission spectrum which shows discrete set of lines, each corresponding to the emission of radiation (energy) when the system changes from the higher energy state to the lower energy state. In this transition, the electronic configuration of the atom changes and it gives a signal in the spectrum of the sample.

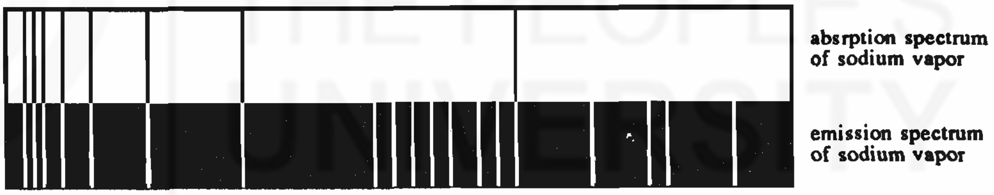

Fig.1.6: (a) A typical absorption spectrum; (b) An emission spectrum.

Since in this unit, we will be restricting our discussion to the spectra of atoms, we will be mainly concerned with the transition of electrons from one atomic energy level to the other. Let us start our study of atoms with the simplest atom, i.e., hydrogen.

Keep in mind that the value of E_n given by Eq. 1.7 is correct when the mass of the nuclei is infinite. Strictly speaking, when the motion of the nuclei is also taken into account, the value of E_n is given as follows:

$$E_n = \frac{-Z^2 e^4 \mu}{8\,\varepsilon_0^2 h^2 n^2}$$

where μ is the reduced mass of hydrogen atom.

1.4 THE ATOMIC SPECTRUM OF HYDROGEN

The hydrogen atom has a single electron. You can recall from Sec. 1.10, Unit 1, Block 1 of 'Atoms and Molecules' course (CHE-01) that the energy of an electron in *n*th orbit of the hydrogen atom, E_n, can be given by the following expression.

$$E_n = \frac{-Z^2 e^4 m}{8\,\varepsilon_0^2 h^2 n^2} \qquad \text{... (1.7)}$$

where Z is the atomic number,

e is the charge of the electron,

m is the mass of the electron,

ε_0 is the permittivity in vacuum and has the value $8.854 \times 10^{-12}\ \mathrm{C^2\,N^{-1}\,m^{-2}}$,

h is Planck's constant,

and n is the number of the orbit.

Let us consider the energy difference between the first and the second energy state. This can be given as

$$\Delta E = E_2 - E_1 = \frac{-Z^2 e^4 m}{8\varepsilon_0^2 h^2 n_2^2} - \frac{-Z^2 e^4 m}{8\varepsilon_0^2 h^2 n_1^2}$$

$$= \frac{Z^2 e^4 m}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \text{... (1.8)}$$

Using Eq.1.5, we can say that the wave number of the radiation associated with the above energy difference can be expressed as given in Eq.1.9.

$$\bar{\nu} = \frac{\Delta E}{hc} = \frac{Z^2 e^4 m}{8\varepsilon_0^2 h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \text{... (1.9)}$$

The term $\dfrac{Z^2 e^4 m}{8\varepsilon_0^2 h^3 c}$ is called the **Rydberg constant** and is denoted by symbol R_{H} for hydrogen. Thus, we can rewrite Eq.1.9 as given below:

$$\bar{\nu} = R_{\mathrm{H}}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \text{... (1.10)}$$

The experimental value of Rydberg constant as obtained from spectral data is $1.09677 \times 10^7\ \mathrm{m^{-1}}$.

The theoretical value of Rydberg constant can be calculated by substituting the values of various terms as given below:

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

$$= \frac{(1)^2 \times (1.602 \times 10^{-19}\ \mathrm{C})^4 \times 9.109 \times 10^{-31}\ \mathrm{kg}}{8 \times (8.854 \times 10^{-12}\ \mathrm{C^2\,N^{-1}\,m^{-2}})^2 \times (6.626 \times 10^{-34}\ \mathrm{J\,s})^3 \times 2.998 \times 10^8\ \mathrm{m\,s^{-1}}}$$

$$= 1.09737 \times 10^7\ \mathrm{m^{-1}}$$

The theoretical value of Rydberg constant is denoted by R_∞.

This difference between the experimental value of Rydberg constant (R_{H}) and theoretical value of Rydberg constant (R_∞) is about 60 $\mathrm{cm^{-1}}$ This is because the calculation was made on the basis of an infinitely massive nucleus. If we take into account the finite mass of the nucleus then we have to consider the hydrogen atom as a two particle system having masses m_1 and m_2.

Such a motion is described in detail in Unit 3.

The motion of a two particle system having masses m_1 and m_2 takes place around the centre of gravity. If the centre of gravity is at rest, the motion of this two particle system can be described in terms of the motion of a single (fictitious) particle around their centre of gravity having the mass μ. This mass μ is referred to as the **reduced mass** and is given by the following equation.

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

where m_1 and m_2 are the masses of the two particles. The reduced mass of the hydrogen atom can be calculated as

$$\begin{aligned}\mu &= \frac{m_n m_e}{m_n + m_e}\\ &= m_e \frac{m_n}{m_n + m_e}\\ &= m_e \left(\frac{1}{1 + \frac{m_e}{m_n}}\right)\end{aligned}$$

where m_n is the mass of the nucleus and m_e is the mass of the electron.

Thus, a correction of $\left(\frac{1}{1 + \frac{m_e}{m_n}}\right)$ is to be applied to the theoretically calculated value of the Rydberg constant, R_∞. Thus the value of the Rydberg constant for hydrogen should be

$$R_H = R_\infty \left(\frac{1}{1 + \frac{m_e}{m_n}}\right) \qquad \text{... (1.11)}$$

$$= 1.09737 \times 10^7\ \text{m}^{-1} \times \left(\frac{1}{1 + \frac{9.109 \times 10^{-31}\ \text{kg}}{1.6726 \times 10^{-27}\ \text{kg}}}\right)$$

$$= 1.09677 \times 10^7\ \text{m}^{-1}$$

Using spectroscopic determination, ratio of the mass of proton to the mass of electron was found to be 1836.15, i.e.

$$\frac{m_p}{m_e} = 1836.15$$

Thus, Eq.1.10 for hydrogen atom rewritten as,

$$\bar{\nu}_H = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \text{... (1.12)}$$

where R_H is given by Eq.1.11.

Therefore, we can expect that when the hydrogen atom goes from its ground state H($1s^1$) to the excited state H($1s^0 2s^1$ or $1s^0 2p^1$) i.e., when the electron in hydrogen atom goes from the first orbit ($n = 1$) to second orbit ($n = 2$), a radiation corresponding to wave number given by Eq. 1.12 should be absorbed. In the reverse process, when the atom changes from its excited state to the ground state, the radiation with $\bar{\nu}$ given by Eq.1.12 should be emitted.

But what about the higher energy levels? Let us see Fig.1.7 which shows energy levels for $n = 1$ to $n = 5$.

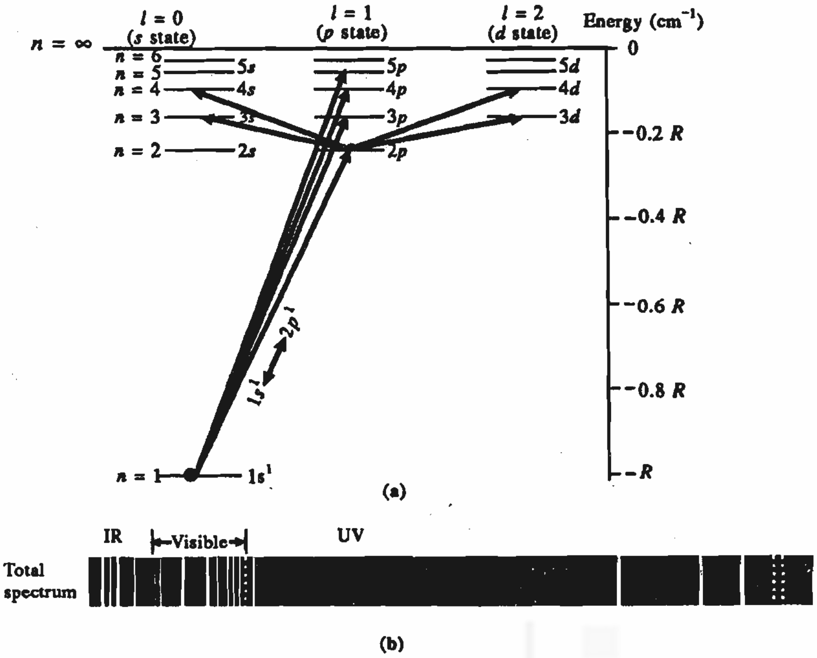

Fig. 1.7: (a) Possible transitions from ground state to excited states in hydrogen atom.
(b) Hydrogen atom spectrum.

One thing which you can immediately observe in the figure is that for a particular n value, s, p and d levels are placed at the same level, i.e., they have **same** energy. This is also evident from Eq.1.7. If you see Eq.1.7 carefully, you can note that all other terms except n are constant. Thus, for a particular atom, energy is governed by n. You may also recall from Units 1 and 2 of 'Atoms and Molecules' course (CHE-01) that n was called the **principal quantum number.**

You can also see in Fig.1.7 (a) that there are various possible energy levels. But if you analyse Fig. 1.7 (b), you will find that the spectral lines appear only at discrete wavelengths (or wave numbers). Thus, we can say that all the transitions from all the levels are not allowed; or in other words, we say that only some transitions **are allowed** and others are not allowed. Now, to decide which transitions are allowed we can derive certain selection rules with the help of (time dependent) **Schrödinger equation.**

In this course, we will not discuss the details of how these selection rules are derived from Schrödinger equation. But we will discuss what these rules are and how they are applied in case of various atoms to understand their spectra.

The selection rules for the hydrogen atom are:

(i) Δn = any value

and (ii) $\Delta l = \pm 1$.

Using these rules, let us begin from the lowest possible level, i.e., $1s$ level. For this level, $n = 1$ and $l = 0$. Thus, electron from this level ($n = 1$) can go to any higher level with $n = 2, 3, 4$... etc. but with the restriction that Δl should be equal to ± 1. Here Δl can only be $+1$. Therefore, $l = 1$ for the excited state which means that the s electron can go only to p states of higher levels. These transitions are shown in Fig. 1.7 (a). Let us also write value of $\bar{\nu}$ from Eq. 1.12 for these transitions.
Here $n_1 = 1$ and $n_2 = 2, 3, 4$...... So we can say that

Remember that the energy levels having same energy are called **degenerate.**

Remember that the four quantum numbers about which you studied in Unit 2 of Block 1 of 'Atoms and Molecules' are principal (n), azimuthal (l), magnetic (m_l) and spin (m_s) quantum numbers. The principal quantum number (n) represents the major energy level. The azimuthal or angular momentum quantum number (l) represents the angular momentum and shape of the orbital. The magnetic quantum number (m_l) determines the possible quantised orientations of the angular momentum and the orbital in space. The spin angular quantum number (m_s) denotes the spin of an electron.

Note that according to the selection rules the transition for $1s^1 \longrightarrow 2s^1$ is forbidden but the transition from $1s^1 \longrightarrow 2s^0\,2p^1$ state is allowed.

You may recall that Schrödinger equation has been discussed in Unit 2 of Block 1 of 'Atoms and Molecules' course.

The Schrödinger equation can be written as

$$H\psi = E\psi \text{ where } H = \frac{-h^2}{8\pi^2 m}\nabla^2 + V$$

$$\text{in which } \nabla^2 \text{ is } \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

This form of Schrödinger equation was time independent Schrödinger equation and was used to calculate the energy of the energy levels. But, for the derivation of selection rules for spectral transitions, we have to use time-dependent Schrödinger equation. The time-dependent Schrödinger equation can be written as follows:

$$\frac{-h^2}{8\pi^2 m}\frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x)\,\Psi(x,t) = \frac{h^2}{4\pi^2 i}\frac{\partial \Psi}{\partial t}$$

Note that according to the selection rules, $1s^1$ to $2s^1$ transition is forbidden.

Remember l represents the azimuthal quantum number and can take values from 0 to $n-1$.

$$\bar{\nu} = R_H \left(\frac{1}{(1)^2} - \frac{1}{n_2^2} \right) \qquad \text{... (1.13)}$$

When we substitute the above values of n_2 in Eq.1.13, we can get the values for $\bar{\nu}$. For example,

when $$n_2 = 2, \bar{\nu} = R_H \left(\frac{1}{1} - \frac{1}{(2)^2} \right) = R_H (1 - \frac{1}{4}) = R_H \times \frac{3}{4} = \frac{3}{4} R_H$$

Thus, we can get

$$\bar{\nu} = \frac{3}{4} R_H, \frac{8}{9} R_H, \frac{15}{16} R_H, \frac{24}{25} R_H \,\ldots\ldots\, \text{cm}^{-1}$$

for $n_2 = 2, 3, 4, 5,$ ... respectively.

Such a series of lines with above wave numbers was observed in the atomic spectrum of hydrogen by Lyman and is called **Lyman series** after him. Experimentally, this series was observed in the **ultraviolet region** of the electromagnetic spectrum. You can see the lines corresponding to this series in Fig. 1.9 and also in detail in Fig. 1.8.

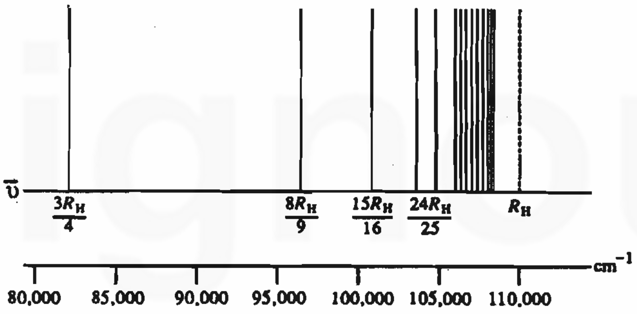

Fig.1.8: Lyman series showing convergence at $\bar{\nu} = R_H$.

The value of $\bar{\nu}_H$ as determined from the observed spectrum of hydrogen also led to the calculation of precise value of R_H which is equal to 109677.581 cm^{-1}.

Wave number is related to energy as

$$1\,\text{cm}^{-1} = 1.987 \times 10^{-23}\,\text{J}.$$

Ionisation energy can be obtained with the help of **photoelectron spectrosocpy** which you will study in detail in Sec. 1.12 of this unit.

Decreasing spacing between spectral lines for Balmer series of hydrogen spectrum.

n_2	Observed $\bar{\nu}$(cm^{-1})	Calculated $\bar{\nu}$(cm^{-1})	Spacing $\bar{\nu}$(cm^{-1})
3	15230	15233	5340
4	20570	20565	2460
5	23030	23032	1340
6	24370	24373	810
7	25180	25181	530
8	25710	25706	

You can see in Fig. 1.8 that when $\bar{\nu} = R_H$, there is a **continuum** after this point in the spectrum. From Eq. 1.13, you can see that $\bar{\nu} = R_H$ only when $n_2 = \infty$. In other words, this represents the removal of the electron from the atom which means ionisation of the atom. **Thus, we can measure the ionisation energy of the electron by knowing R_H or $\bar{\nu}$.**

Similar series of spectral lines called **Balmer, Paschen, Brackett** and **Pfund** series were also observed for $n_1 = 2, 3, 4, 5$ respectively and $n_2 = (n_1 + 1), (n_1 + 2), (n_1 + 3)$.... etc. The energy levels, electronic transitions and spectral lines corresponding to these series are shown in Fig.1.9.

Fig. 1.9 also shows that in each series as the value of n_2 **increases**, the separation between the energy levels **decreases**. In other words, separation between the spectral lines **decreases** with **increasing** value of n_2 till it reaches a convergence limit at $n_2 = \infty$. As you know this convergence limit represents the ionisation of the electron, any energy greater than this limit, if supplied to the system, will only increase the kinetic energy of the ejected electron and will result in the **Increase** in the velocity of the ejected electron. Since the kinetic energy is not quantised, it can be increased **any amount** by supplying energy to the electron and that is why the spectrum in this region shows a **continuum.**

Till this point, we have been successful in explaining the origin of different lines in the atomic spectrum of hydrogen. However, when closely observed, hydrogen spectrum reveals a fine structure. For example, in the Lyman series, every line was observed to be consisting of two lines (doublet) very close to each other. Thus, unless these lines were properly resolved, these two lines appeared as a single line. The spectrum becomes more complicated for other series where every line shows a multiplet structure.

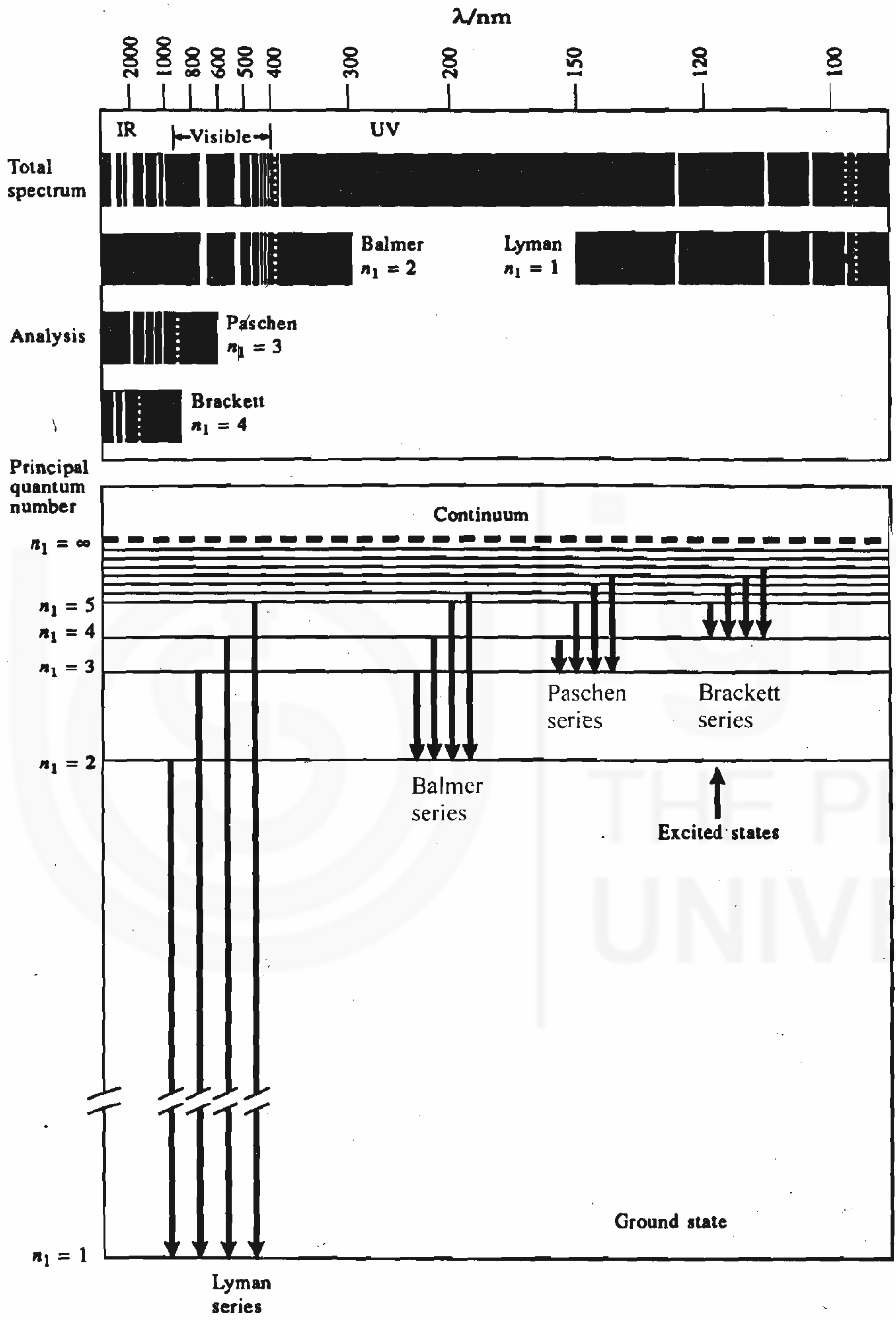

Fig. 1.9: A sketch of energy levels for various series of spectral lines observed in the atomic spectrum of hydrogen.

Let us study the next section to find out the reason for the fine structure of hydrogen atom spectrum.

But before that you can check your understanding of the above section by answering the following SAQ.

SAQ 3

If the ratio of mass of electron to the mass of nucleus for deuterium is 0.00027148, calculate the value of Rydberg constant for deuterium. (use the same value of R_∞ for deuterium as used for hydrogen). Also calculate the wave number for the first Balmer line for deuterium.

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1.5 FINE STRUCTURE OF HYDROGEN ATOM SPECTRUM

So far we have based our discussion on the Eq. 1.7, which relates the energy (E) of an energy level with the principal quantum number, n. But to understand the fine structure, we have to consider the effect of *other quantum numbers* as well on the energy levels.

An electron possesses an **orbital angular momentum** ($\mathbf{l}$) and **spin angular momentum** ($\mathbf{s}$). The magnitude of these momenta $|\mathbf{l}|$ and $|\mathbf{s}|$ is given by the following equations:

Note that we are using $\hbar$ to represent $\frac{h}{2\pi}$.

Note that we have used modulus sign (| |) to represent the magnitude of a vector in Eqs. 1.14 (a) and 1.14(b). Thus, magnitude of **l** is represented as $|\mathbf{l}|$. The same convention will be followed for other equations also.

Note that we are now using s to denote the *spin quantum number*.

Orbital angular momentum, $|\mathbf{l}| = \sqrt{l\,(l+1)}\,.\,\frac{h}{2\pi}$ .... (1.14 a)

Spin angular momentum, $|\mathbf{s}| = \sqrt{s\,(s+1)}\,.\,\frac{h}{2\pi}$ ... (1.14 b)

In the above two equations l represents the *angular momentum quantum number* and can take values from 0 to $(n-1)$ and s represents the *spin quantum number.* Since these momenta are always expressed as multiples of $\frac{h}{2\pi}$ ($= 1.055 \times 10^{-34}$ J s), we can take $\frac{h}{2\pi}$ as one unit and represent it as $\hbar$. Thus, we can rewrite Eqs. 1.14a and 1.14b as given below:

$$|\mathbf{l}| = \sqrt{l\,(l+1)} \text{ in units of } \hbar = \sqrt{l\,(l+1)}\,\hbar \quad \text{... (1.15)}$$

and

$$|\mathbf{s}| = \sqrt{s\,(s+1)} \text{ in units of } \hbar = \sqrt{s\,(s+1)}\,\hbar \quad \text{... (1.16)}$$

The **total angular momentum** of the electron, **j** has contribution from both **orbital** and **spin angular momenta** and can be expressed as,

$$\mathbf{j} = \vec{\mathbf{l}} + \vec{\mathbf{s}} \quad \text{...(1.17)}$$

Conventionally, vector quantities may be represented by using an arrow on it, for example, vector **l** can be represented $\vec{\mathbf{l}}$. But we are using bold letters to denote vector quantities.

But here l and s both are vectors and their sum as given by Eq. 1.17 is a **vector addition.**

Let us now study about the vector nature of orbital angular momentum and spin angular momentum.

For a *vector* quantity, e.g., orbital angular momentum of an electron, to be completely described, it is required that **both** its **direction** and **magnitude** should be specified. The magnitude of **l** is specified as given in Eq. 1.14a (or 1.15) and is quantised. Now what about its direction? The quantum theory says that a **reference direction** can be specified by applying the magnetic or electric field; and the angular momentum vector can have **only** those directions whose components along the reference direction are integral multiples of $\hbar$. Such a reference direction is shown in Fig. 1.10 as pointing in **vertical direction** and is conventionally used to represent z – axis, see Fig. 1.10a.

Note that for a free atom there is no preference direction. Hence, the Schrodinger equation tells us that the total angular momentum is quantised and only one component of the angular momentum out of the three components has a definite value. You may call it l_x, l_y or l_z but by convention we call it l_z. However, when the aom is placed in a magnetic field, there is a reference direction of the magnetic field (which is called z direction) and the component of the angular momentum in the direction of the field becomes quantised.

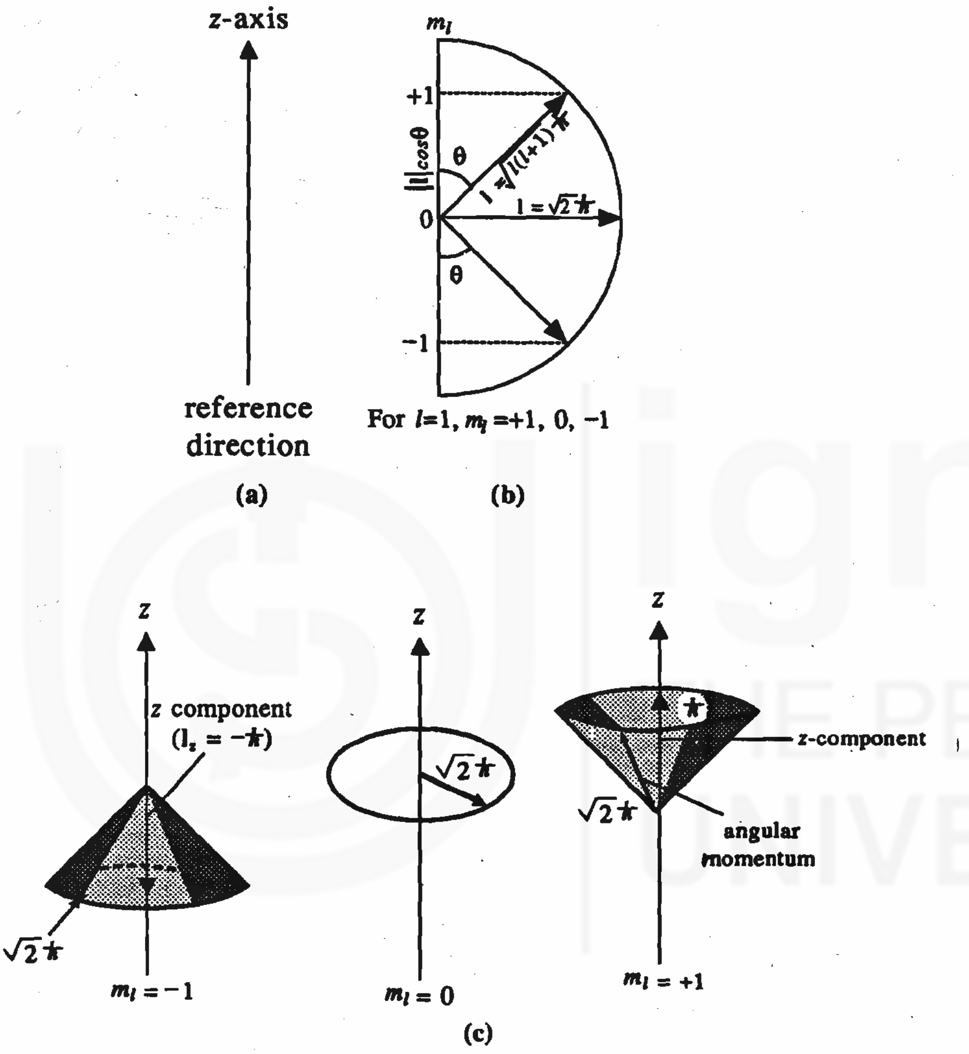


Fig.1.10: a) The reference direction.
b) Allowed directions for the angular momentum vector and
c) The components of angular momentum in the reference direction.

Note that the magnitude of the orbital angular momentum,

$|l| = \sqrt{l(l+1)}\,\hbar$ and the maximum value of its components in a particular direction is $l\hbar$. Since $|l| > l_z$, the angular momentum vector cannot point in the direction of the applied field. The angle between angular momentum vector and the direction of the field is given by θ.

Now, the angular momentum can point in such a way that its components in the z direction are integral multiples of $\hbar$, Fig. 1.10b. If l_z is the component of angular momentum (l) in z direction, then

$$|l_z| = m_l \hbar \qquad \text{... (1.18)}$$

Here m_l is an integral number called **magnetic quantum number** and can have values as given below:

$$m_l = l, (l-1), \ldots 0, \ldots -(l-1), -l \qquad \text{...(1.19)}$$

In Fig. 1.10(b)

$$\cos\theta = \frac{l_z}{|l|} = \frac{\hbar}{\sqrt{l(l+1)}\,\hbar}$$

$$= \frac{1}{\sqrt{l(l+1)}}$$

$$\text{For } m_l = 1, \cos\theta = \frac{1}{\sqrt{l(l+1)}} = \frac{1}{\sqrt{2}}$$

$$\therefore \quad \theta = 45^\circ$$

$$m_l = 0, \ \cos\theta = 0$$

$$\therefore \quad \theta = 90^\circ$$

$$m_l = -1, \cos\theta = \frac{-1}{\sqrt{l(l+1)}} = \frac{-1}{\sqrt{2}}$$

$$\theta = 135^\circ$$

Now what will be the value of m_l for $l = 0$? It will be zero as per Eq.1.19 and the angular momentum will also be zero according to Eq 1.15.

Similarly, for $l = 1, m_l = +1, 0, -1$ from Eq.1.19. When we substitute these integral values of m_l in Eq.1.18, we get z components of angular momentum (m_l) as given below:

When $m_l = +1,\ \mathbf{l}_z = 1.\ \hbar\ = \hbar$ ...(1.20a)

$m_l = 0,\ \ \mathbf{l}_z = 0\,\hbar$ ...(1.20b)

$m_l = -1,\ \mathbf{l}_z = -1.\ \hbar\ = -\hbar$ ...(1.20c)

The angular momentum $\mathbf{l}$ and its $\mathbf{l}_z$ components for $l = 1 (m_l = +1, 0, -1)$ are shown in Fig.1.10(c).

Also note in Fig. 1.10(c) that the values of $\mathbf{l}_z$ for $l = 1$ are $-\hbar$, 0 and $+\hbar$.

Remember that the magnitude of angular momentum ($\mathbf{l}$) whose z components are given by the above Eqs.1.20a, 1.20b, 1.20c, is given by Eq.1.15 as

$$
\begin{aligned}
|\mathbf{l}| &= \sqrt{l(l+1)}\,\hbar \\
&= \sqrt{1(1+1)}\,\hbar \\
&= \sqrt{2}\,\hbar \qquad \text{...(1.21)}
\end{aligned}
$$

Thus, **the magnitude of angular momentum vector for $l = 1$ is $\sqrt{2}\ \hbar$.** This is shown in Fig.1.10(b).

Going back to Eq. 1.20, we can say that the z component of the angular momentum has precise values. If we apply **Heisenberg uncertainty principle** it says that the angle of orientation of the angular mementum vector around the z-axis **is completely indefinite.** Thus, there is an equal probability of locating the angular momentum vector in all the directions around z axis. Thus, this vector takes the conical shape as shown in Fig.1.10(c). Note that vector $m_l = 0$, has no z component ($\mathbf{l}_z = 0$) lies in the xy–plane.

You will study in Sec 1.10 that this degeneracy can be lifted in the presence of the magnetic field.

It is also worth mentioning here that the energy of electron depends on the **magnitude of the angular momentum and not on its direction.** This leads us to conclude that all the values of m_l (corresponding to a particular l) have same value of **l** and have equal energy and are, therefore, **degenerate.**

Note that in case of hydrogen atom, the energy depends upon the principal quantum number (n) only but for multi-electron systems it depends both on n and l.

Vector Nature of Spin Angular Momentum

You are aware that the spin quantum number s is equal to 1/2. The quantum laws again specify that spin angular momentum, **s**, can take only those directions for which its components in the reference direction ($\mathbf{s}_z$) are **half integral** multiples of $\hbar$. Thus,

$$\mathbf{s}_z = m_s\,\hbar$$

where m_s is equal to +1/2 or –1/2 and is known as *spin magnetic quantum number.*

You should not confuse between s and m_s. The spin quantum number s of an electron (which is generally referred as spin) has the value $\frac{1}{2}$. But m_s, which is the magnetic spin quantum number for the z component of spin angular momentum can take the values $+\frac{1}{2}$ and $-\frac{1}{2}$.

The allowed directions for the spin angular momentum vectors are shown in Fig. 1.11.

$$\cos\theta = \frac{\mathbf{s}_z}{|\mathbf{s}|} = \frac{m_s\hbar}{\sqrt{s(s+1)}\,\hbar}$$

When $m_s = +\frac{1}{2}$

At this juncture, you have enough knowledge of orbital and spin angular momenta. Therefore, we can now proceed to the concept *of total angular momentum* as given by Eq. 1.17.

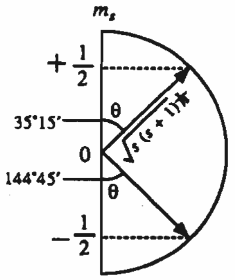


Fig. 1.11: The allowed directions of spin angular momentum for an electron.

Similar to Eqs. 1.15 and 1.16, we can represent **j** in terms of **total angular momentum quantum number,** j such that the magnitude of **j** can take the following values:

$$|\mathbf{j}| = \sqrt{j(j+1)}\,\hbar = \sqrt{j(j+1)} \text{ in units of } \hbar \qquad \text{...(1.22)}$$

where j can take values $|(l+s|,\ |(l+s-1|,\ ...,\ |(l-s)|$

Let us find out j for an s electron.

Here $l = 0$ and $s = ½$.

Thus $\quad j = |(l+s)|,\ |(l+s-1|,\ ...,\ |(l-s)|$

$$= |(0+\tfrac{1}{2})|,\ |(0+\tfrac{1}{2}-1)|,\ ....\ |(0-\tfrac{1}{2})|$$

$$= |\tfrac{1}{2}|,\ |(-\tfrac{1}{2})|$$

$$= \frac{1}{2}$$

Hence, $\quad \mathbf{j} = \sqrt{j(j+1)j}\,\hbar$

$$= \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\,\hbar$$

$$= \sqrt{\frac{1}{2}\cdot\frac{3}{2}}\,\hbar = \frac{\sqrt{3}}{2}\hbar$$

Next we will do similar steps for a p electron. For a p electron, $l = 1$ and $s = \frac{1}{2}$.

Substituting these values of l and s in the following expression,

$$|j| - |(l+s)|,\ |(l+s-1)|,......,|(l-s)|$$

we get, $\quad j = \left(1+\frac{1}{2}\right),\ \left(1-\frac{1}{2}\right)$

$$= \frac{3}{2},\ \frac{1}{2}$$

These two values of j yield $\mathbf{j} = \sqrt{\frac{15}{2}}\,\hbar$ and $\sqrt{\frac{3}{2}}\,\hbar$ using Eq. 1.22.

The two values of **j** represent two values of energy; thus, indicating the existence of two energy levels of a p electron corresponding to $l = 1$. It may also be emphasised here that all p-levels will be split into two energy levels corresponding to $j = 1/2$ and $j = 3/2$, irrespective of whether they are $2p$, $3p$, $4p$ ..... states.

Similarly, for a d level when $l = 2$ and $s = \frac{1}{2}$ we can say that

$$\cos\theta = \frac{\frac{1}{2}\hbar}{\sqrt{s(s+1)}\,\hbar}$$

$$= \frac{\frac{1}{2}}{\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}}$$

$$= \frac{\frac{1}{2}}{\sqrt{\frac{3}{4}}} = \frac{1}{\sqrt{3}}$$

$\therefore\ \theta = 35°\,15'$

When $m_s = -\frac{1}{2}$

$$\cos\theta = \frac{-\frac{1}{2}\hbar}{\sqrt{\frac{1}{2}(\frac{1}{2}+1)}\hbar} = -\frac{1}{\sqrt{3}}.$$

Therefore, $\theta = 144°\ 45'$

For s electron

$l = 0, s = \frac{1}{2}$

$j = |(l+s)|,\ |(l+s-1)|,\ ...\ |(l-s)|$

$j = \left|\left(0+\frac{1}{2}\right)\right|, \left|\left(0+\frac{1}{2}-1\right)\right|,\ ...\ |(0-\frac{1}{2})|$

$= \frac{1}{2}$

For p electron

$l = 1, s = \frac{1}{2}$

$j = |(1+\frac{1}{2})|,\ |(0+\frac{1}{2}-1)|, ...\ |(1-\frac{1}{2})|$

$= \frac{3}{2}, \frac{1}{2}$

For d electron

$l = 2, s = \frac{1}{2}$

$j = |(2+\frac{1}{2})|,$

$|(2+\frac{1}{2}-1)|,\ ...(2-\frac{1}{2})$

$= 5/2, 3/2$

Note that $l + s$ gives the maximum value of j and $l - s$ (or $s - l$ if $s > l$) gives the minimum value of j. The j can take all positive values from maximum to minimum, the succesive values deffering by one unit only.

For an s electron only the spin angular momentum is responsible for the total angular momentum.

$$j = \left(2+\frac{1}{2}\right) \quad \text{and} \quad = \left(2-\frac{1}{2}\right)$$

$$= \frac{5}{2} \qquad\qquad = \frac{3}{2}$$

You will now learn about the nomenclature of these states using Term Symbols.

Term Symbols

The energy levels of an atom are called **terms (or spectral terms)**. A term can be designated by a **term symbol.** A term symbol can be denoted as

J can be replaced by j in case of a single electron system.

$$^{2S+1}L_J$$

Here,

L is the orbital or angular momentum quantum number and can take the values 0, 1, 2, 3, 4 ... etc. and corresponding to these values L can be represented by a letter as S, P, D, F, G... etc.

Note that capital letters are used to denote various L values corresponding to the state of an atom. Similar small letters s, p, d... have been used for the states of electrons.

The superscript $^{2S+1}$ gives the **multiplicity** of the energy state and the subscript, J, *is the total angular momentum quantum number* (as expressed by Eq. 1.22).

Let us first take the example of hydrogen atom for determining the term symbol.

For the ground state of hydrogen atom, the electronic configuration is $1s^1$.

Here, $s = \frac{1}{2}$ and $l = 0$. Thus,

Note that we are representing $L = 0$ by S in the term symbol.

$$j = l + s = 0 + \frac{1}{2} = \frac{1}{2}$$

and the term symbol will be

$$^{2S+1}L_j \quad = {}^{2\times\frac{1}{2}+1}S_{1/2} \quad = {}^2S_{1/2}$$

Similarly, for a p electron, in hydrogen atom, we have

$$s = \frac{1}{2} \text{ and } l = 1$$

$$j = (l+s), (l+s-1), \dots, (l-s)$$
$$= \left(1+\frac{1}{2}\right), \left(1+\frac{1}{2}-1\right), \dots, \left(1-\frac{1}{2}\right)$$

$$= \frac{3}{2}, \frac{1}{2}$$

So, the term symbols for the two energy levels of a p state for hydrogen atom about which you studied above are

$$^{2S+1}L_j = {}^{(2\times\frac{1}{2}+1)}L_{\frac{1}{2}} \text{ and } {}^{2\times\frac{1}{2}+1}L_{\frac{3}{2}}$$
$$= {}^2P_{\frac{1}{2}} \text{ and } {}^2P_{\frac{3}{2}}$$

In the light of the above discussion, let us now see Fig.1.12. It shows the fine structure of energy levels of hydrogen atom.

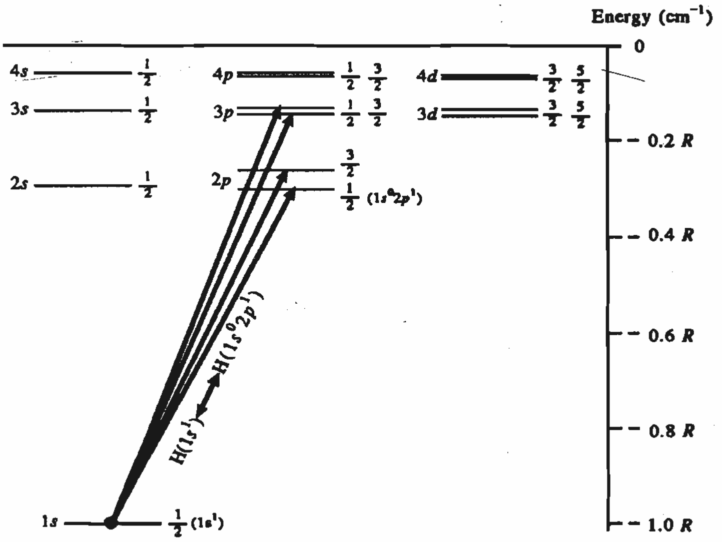


Fig. 1.12 : Splitting of *p* states into two energy levels corresponding to two values of *j*. The configuration of some lower atomic states is given in bracketts. Similarly, we can write the configuration of atomic states corresponding to higher energy levels.

The electronic configuration $1s^0 2p^1$ implies that the electron is present in p orbital and s orbital is vacant.

Note that the electron configuration $1s^0 2p^1$ of hydrogen atom gives rise to two levels with term symbols $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$ Each level is $(2j+1)$ fold degenerate. Thus, $^2P_{\frac{1}{2}}$ level with $j = \frac{1}{2}$ is two $(2j + 1 = 2 \times \frac{1}{2} + 1 = 2)$ fold degenerate and $^2P_{\frac{3}{2}}$ level with $j = \frac{3}{2}$ is four $(2j + 1 = 2 \times \frac{3}{2} + 1 = 4)$ fold degenerate. You will study in Sec. 1.10, Fig. 1.16 that these degeneracies can be removed by the application of the magnetic field.

The j values for the various p energy states are also shown in the figure. Now, if an electron in 1s energy level absorbs energy and gets excited to the 2p state; it has **two options** corresponding to **two** j levels. Here the selection rules say that in addition to the earlier restrictions of Δn = anything and $\Delta l = \pm 1$;

$$\Delta j = 0 \text{ or } \pm 1$$

By applying these selection rules to the above transitions from 1s to 2p level, we can get the following results:

$$1s\left(j = \frac{1}{2}\right) \longrightarrow 2p\left(j = \frac{1}{2}\right) \text{ and } \Delta j = 0$$

and

$$1s\left(j = \frac{1}{2}\right) \longrightarrow 2p\left(j = \frac{3}{2}\right), \text{ and } \Delta j = +1$$

So both these transitions are allowed and the spectrum of hydrogen shows one line for each of these transitions.

Thus, we can expect a doublet for the transition of an electron from an s to a p level. This is called the **fine structure of hydrogen atom spectrum.** This pattern of lines is similar to Lyman series but the difference is that each line obtained is a *doublet*. In the case of hydrogen spectrum, the spacing between the lines is very–very less and they are difficult to resolve. The spacing as shown in Fig.1.12 is many times greater than the actual splitting observed.

Actually the spacing between the lines is 0.365 cm^{-1} and requires the use of high resolution instruments for resolving these lines.

Further transitions from doublet P (2p) state to ^2D or ^2S states are possible but we will not go into details of these transitions.

In the next section, you will be studying the spectra of hydrogen like atoms.

1.6 SPECTRA OF HYDROGEN–LIKE ATOMS

The atoms of all the elements of the Ist group in the Periodic Table have a single electron in their outermost shell. The inner closed shells have zero total angular momentum. Thus, these elements can be considered similar to hydrogen atom as far as their spectrum is concerned. The energy level diagram of sodium is shown in Fig. 1.13.

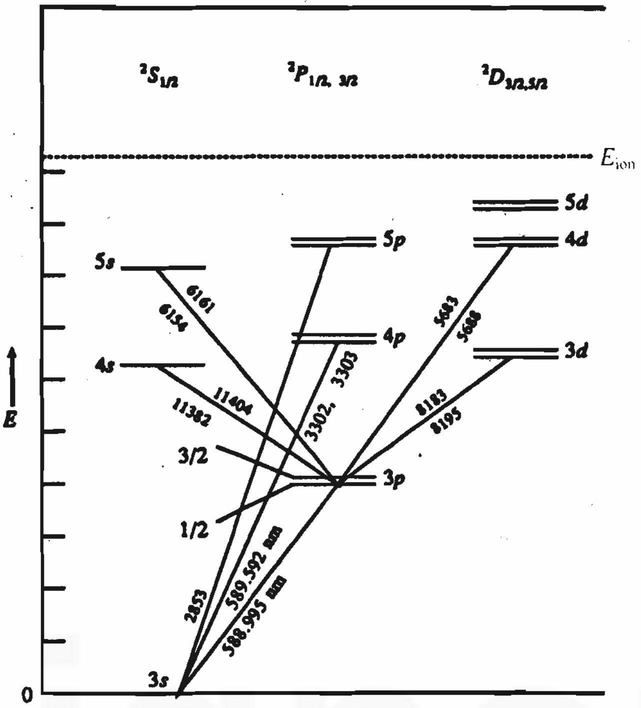
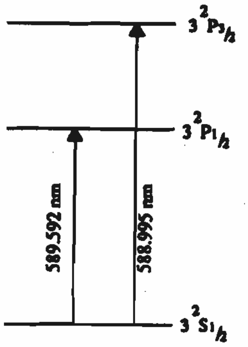


Fig. 1.13: The energy level diagram of sodium atom.



Energy level diagram for transitions corresponding to D-lines of sodium.

Here, the 3*s* electron will require least energy to get excited as compared to the inner electron of first and second shell. Similar to the hydrogen atom, there are two energy levels available (corresponding to $j = \frac{3}{2}$ and $j = \frac{1}{2}$) at the 3*p*, 4*p*, ... etc. levels. The 3*s* electron can be excited to any of these two 3*p* levels and the energy required for these excitations corresponds to 588.995 nm and 589.592 nm. These two lines of atomic spectrum of sodium are commonly known as *D*-lines (Fig. 1.13). Also note that on further absorption of energy this electron from 3*p* levels can be promoted to higher *s* and *d* states ($\Delta l = +1$). But we will not go into details of these transitions and stop our discussion of spectrum of sodium here. Other species such as He^+, Be^+ and B^{2+} which have one electron in their outermost shelll show a spectrum similar to hydrogen.

For 3*s* to 3*p* (or 4*p*, 5*p*,... transitions, $\Delta l = +1$.

SAQ 4

Calculate the difference in the energy of the energy levels in J units corresponding to two *D* lines in the atomic spectrum of sodium if $\Delta \bar{\nu} = 17.19\ \text{cm}^{-1}$.

....

....

....

....

1.7 MULTI-ELECTRON SYSTEMS

So far, you have studied about the spectra of atoms containing a single electron in their outermost orbit. In this section, we will discuss the spectrum of multi-electron atoms which have more than one electron in their outermost orbit.

In these kinds of atoms, interelectronic interactions also affect the energy states. There are two ways in which the orbital and spin angular momenta of many electron systems can combine. The first method is called the L–S coupling (or the Russel–Saunders coupling) and the second method is called the $j-j$ coupling. Let us now study about these two schemes. We will discuss L–S coupling in detail because it is more relevant to our discussion regarding lighter elements.

L–S Coupling

This scheme of coupling explains the atomic spectra of elements having atomic number upto 30. In this method, we assume that the orbital angular momenta of all the electrons combine to give the **total orbital angular momentum**, L. Similarly, the spin angular momenta of various electrons can be combined to give **total spin angular momontum**, S. Finally, the total orbital angular momentum and total spin angular momentum could be added to get the **total angular momentum, J.**

Eq. 1.24 is also known as Clebsch– Gordan series.

Note that

$$\vec{L} = \sum \vec{l_i}$$

where l_i is the angular momentum of individual electron.

Total orbital angular momentum $|\mathbf{L}| = \sqrt{L(L+1)}$ in units of $\hbar$ ...(1.23)

Also, $M_L = \sum m_{l_i}$

where m_{l_i} is the z-component of angular momentum of individual electron and M_L gives the component of total angular momentum in the z-direction

where L is the **total orbital angular momentum quantum number** and can be obtained according to the following equation for the electrons 1 and 2.

$$L = |(l_1 + l_2)|, |(l_1 + l_2 - 1)|, \ldots, |(l_1 - l_2)| \quad \ldots (1.24)$$

Similarly we can write **total spin angular momentum**, S of individual electrons 1, 2, ... etc. as

$$|\mathbf{S}| = \sqrt{S(S+1)} \text{ in units of } \hbar \quad \ldots (1.25)$$

Similarly

$$\vec{S} = \sum s_i$$

where s_i is the spin angular momentum of the individual electron.

where S is the **total spin quantum number** of individual electrons. It can be obtained by summation of the individual quantum numbers $s_1, s_2, \ldots$ etc. of electrons 1, 2, ... etc. and can take the values as

$$S = |(s_1 + s_2)|, |(s_1 + s_2 - 1)|, \ldots, |(s_1 - s_2)| \quad \ldots (1.26)$$

Also,

$$M_S = \sum m_{s_i}$$

where m_{s_i} is the z – component of spin angular momentum of individual electron and M_S is the component of total spin angular momentum in the z – direction.

Now, we have L and S as given by Eqs.1.23 and 1.25 and can calculate **J**. For this the L and S can be obtained from Eqs. 1.24 and 1.26 and combined to give J such that

$$J = |(L + S)|, |(L + S - 1)|, \ldots, |(L - S)| \quad \ldots (1.27)$$

This total angular momentum quantum number, J is related to total angular momentum, **J**, as

$$|\mathbf{J}| = \sqrt{J(J+1)} \text{ in units of } \hbar \quad \ldots (1.28)$$

Thus, from the above equation, we can calculate J values corresponding to various values of J, which correspond to various energy levels for a given atom.

With this we finish our discussion of L–S coupling. Before going to the next section which deals with the Atomic Spectrum of Helium, let us briefly go through what is known as j–j coupling. For larger atoms, the orbital angular momentum and the spin angular momentum of each individual electron is combined to yield total angular momentum j as given below:

$$l_1 + s_1 = j_1$$

Then, $j_1, j_2, \ldots$ for all electrons are combined to finally yield **J** as

$$\mathbf{J} = j_1 + j_2 + \ldots$$

Let us now study about the atomic spectrum of helium.

1.8 ATOMIC SPECTRUM OF HELIUM

Remember that according to Pauli's Exclusion Principle no two electrons can have the same four quantum numbers.

Helium represents the simplest multi–electron system. Let us first derive the term symbols for the ground state of helium atom. The electron configuration of helium is $1s^2$. Here l_1 and l_2, the quantum numbers of electrons 1 and 2, respectively have the value 0. Hence $L = l_1 + l_2 = 0$. Now, in the lowest energy state (i.e., ground state) both these electrons occupy $1s$ orbital. If the values of three quantum numbers n, l, m_l are same for the two electrons, the value of m_s should be different according to the Pauli's exclusion principle. Thus, if $m_{s_1} = +\frac{1}{2}$ then $m_{s_2} = -\frac{1}{2}$. We can calculate S by (i) the summation of m_{s_1} and m_{s_2}. to first give M_s or (ii) Eq. 1.26.

We can write the quantum numbers of two electrons of He as given below:

	n	l	m_l	s	m_s
Ist electron	1	0	0	$\frac{1}{2}$	$+\frac{1}{2}$
IInd electron	1	0	0	$\frac{1}{2}$	$-\frac{1}{2}$

The state of an electron can further be described as α or β depending upon its s and m_s values.

For α state $(s, m_s) = \left(\frac{1}{2}, \frac{1}{2}\right)$

and for β state $(s, m_s) = \left(\frac{1}{2}, -\frac{1}{2}\right)$

(i) By summation of m_{s_1} and m_{s_2}

$$M_s = m_{s_1} + m_{s_2} = +\frac{1}{2} - \frac{1}{2} = 0$$

Since $M_s = 0$, hence $S = 0$.

Knowing L and S, we can calculate J as $J = L + S$. Thus, $J = 0 + 0 = 0$. Thus, the term symbol for the ground state of helium ${}^{2S+1}L_J$ will be ${}^{2\times 0+1}L_0 = {}^1S_0$

(Remember that $L = 0$ is denoted as S).

So we can say that for the ground state of helium ($1s^2$), the atomic state can be represented by the term symbol ${}^1S_0$.

${}^1S_0$ is pronounced as "singlet ess zero".

Note that capital italicised J is used in the term symbol ${}^{2S+1}L_J$ of an atom having more than one electron.

Let us consider the excited state of helium. If one of the electron is excited to a higher state, the electron configuration will change. The excited electron can now occupy ns^1, np^1, nd^1, ... etc. orbitals where $n \geq 2$. The corresponding electronic configurations for helium atom in excited states could be written as follows,

$$1s^1\,ns^1,\ 1s^1\,np^1,\ 1s^1\,nd^1,\ \ldots.\text{etc.}$$

We are considering the excitation of only one electron, since a very large amount of energy would be required to excite both the electrons simultaneously.

Corresponding to each of the above configurations, we have two possibilities:

i) the two electrons can have *opposite* spins, i.e., $m_{s_1} = +\frac{1}{2}$ and $m_{s_2} = -\frac{1}{2}$.

This will lead to $M_s = m_{s_1} + m_{s_2} = +\frac{1}{2} - \frac{1}{2} = 0$.

ii) the two electrons can have *parallel* spins; i.e., $m_{s_1} = +\frac{1}{2}$ and $m_{s_2} = +\frac{1}{2}$

leading to $M_s = m_{s_1} + m_{s_2} = \left(+\frac{1}{2}\right) + \left(+\frac{1}{2}\right) = 1$.

The component $M_s = 1$ can arise only when $S = 1$.

When the principal quantum number, n for the two electrons is different, then m_{s_1} and m_{s_2} can take values $+\frac{1}{2}$ and $+\frac{1}{2}$ leading to M_s (and S) = 1 as well as $+\frac{1}{2}$ and $-\frac{1}{2}$ yielding M_s (and S) = 0. This gives rise to states with triplet and singlet levels.

(ii) S can also be calculated using Eq. 1.26

$$S = |(s_1 + s_2)|,\ |(s_1 + s_2 - 1), \ldots\ldots,\ |(s_1 - s_2)|$$

$$\left(\frac{1}{2} + \frac{1}{2}\right), \left(\frac{1}{2} + \frac{1}{2} - 1\right), \ldots\ldots\ldots, \left(\frac{1}{2} - \frac{1}{2}\right) = 1, 0$$

From the above S values (0 and 1) we can get *multiplicity* of a state which is given as $2S + 1$, as stated earlier.

Hence, when $S = 0, 2S + 1 = 2 \times 0 + 1 = 1$

and when $S = 1, 2S + 1 = 2 \times 1 + 1 = 2 + 1 = 3$

Thus, we have two spin states for each of the above configuration depending upon the value of S. For $S = 0$, when multiplicity is 1, the state is termed as a singlet state.

Similarly, when $S = 1$ and multiplicity is 3, the state is called a **triplet state.** These states are illustrated in Fig. 1.14.

To decide transitions to which of these states are allowed, we have the selection rules for multi-electron systems as

$$\Delta S = 0, \ \Delta L = \pm 1, \ \Delta J = 0, \ \pm 1$$

Here, $\Delta S = 0$ implies that S should not change for an allowed transition. Thus, the transition will be allowed from

$$S = 1 \longrightarrow S = 1$$

or

$$S = 3 \longrightarrow S = 3$$

Thus, all electronic configurations $1s^1 ns^1$, $1s^1 np^1$, $1s^1 nd^1$ where $n \geq 2$ give rise to both singlet and triplet levels.

Remember that singlet to triplet or triplet to singlet transitions are not allowed.

Thus, transitions from **singlet to singlet** and **triplet to triplet** states will be allowed. Since the ground state of helium has $S = 1$ and is a **singlet** state, the allowed transitions are only to higher **singlet states.**

Let us next consider what $\Delta L = \pm 1$ implies? $\Delta L = \pm 1$ means that when L was 0 (zero) in the ground state, the excited state can have $L = 1$. This indicates that the excited state should be a P state.

Now what about its J value? J can be calculated as $L + S$. For this state $L = 1$ and $S = 0$, so $J = L + S = 1 + 0 = 1$.

The term symbol for the excited state will be

$${}^{2S+1}L_J = {}^{2\times0+1}L_J = {}^1P_1 \qquad \text{(Remember that } L = 1 \text{ state is denoted by } P \text{ letter)}$$

Note that for the singlet excited state of He having the atomic configuration $1s^1 2p^1$, the term symbol is ${}^1P_1$.

Thus, the allowed transition will be from

$${}^1S_0 \longrightarrow {}^1P_1 \text{ state.} \qquad \text{(Remember that one electron still occupies } 1s \text{ orbital and the configuration is } 1s^1 2p^1\text{.}$$

Note that this ${}^1P_1$ state could belong to any of the levels having $n \geq 2$. These transitions are depicted in Fig.1.14 (a).

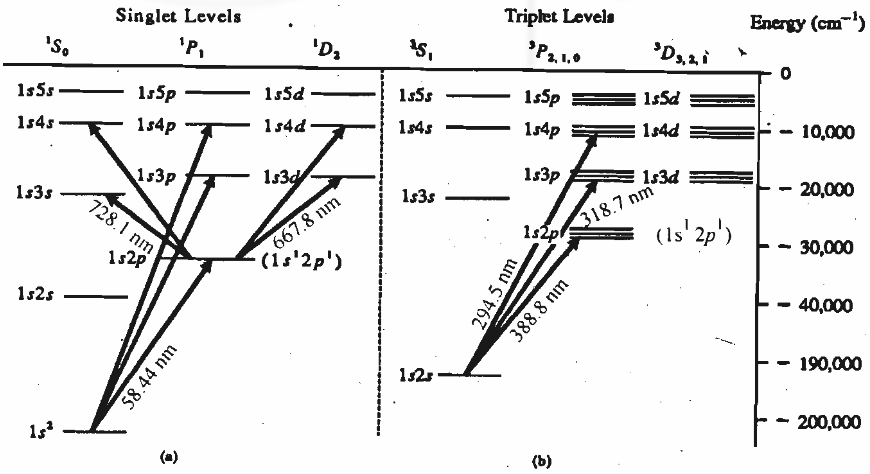


Fig. 1.14: Energy levels (for electrons) of Helium atom showing (a) singlet to singlet transitions and (b) triplet to triplet transitions.

The three $2P$ states where 2 is the value of n in the excited triplet state of helium (as shown in Fig. 1.14b) can be designated as follows:

$$2^3P_{2,1,0} \begin{cases} 2^3P_0 \\ 2^3P_1 \\ 2^3P_2 \end{cases}$$

You should also note that these triplet levels correspond to atomic configuration $1s^1 2p^1$.

These levels arise as a result of spin-orbit coupling.

From this excited state, further transitions are possible in accordance to the selection rule $\Delta L = \pm 1$. When $\Delta L = +1$, transitions will occur to higher S or D states and when $\Delta L = -1$, the system will return to the ground state (with $L = 0$).

But if the helium atom is already present in the excited triplet state, its configuration in the lowest level will be $1s^1 2s^1$. From this level one electron can be excited to higher **triplet** levels. ($\Delta S = 0$). These transitions are shown in Fig. 1.14 (b). Let us study the transition from $1s2s$ to $1s2p$ level.

For the $1s2s$ triplet level.

$$\begin{aligned} M_s &= m_{s_1} + m_{s_2} \\ &= \frac{1}{2} + \frac{1}{2} \\ &= 1 \text{ ; hence } S = 1 \end{aligned}$$

$$L = l_1 + l_2 = 0 + 0 = 0$$

$$J = L + S = 0 + 1 = 1$$

Term symbol of this atomic state $^{2S+1}L_J$ will be $^3S_1$.

Thus, the configuration $1s^1 2p^1$ gives size to $^1P_1$ (singlet) as well as $^3P_{2,1,0}$ (triplet) states.

For a $1s2p$ level (which is an excited state).

$$M_s = m_{s_1} + m_{s_2} = \frac{1}{2} + \frac{1}{2} = 1. \text{ Thus } S = 1.$$

So, $$2S + 1 = 2 \times 1 + 2 = 3$$

$$\begin{aligned} L &= |(l_1 + l_2)|, |(l_1 + l_2 - 1)|, \ldots, |(l_1 + l_2)| \\ &= (0+1), (0+1-1)), \ldots, |(0-1)| = 1, 0 \\ J &= |(L+S)|, |(L+S-1)|, \ldots, |(L-S)| \\ &= |(L+S)|, |(L+S-1)|, \ldots, |(L-S)| \\ &= (1+1), (1+1-1), (1-1) \\ &= 2, 1, 0 \end{aligned}$$

Thus, the term symbols for this level will be

$$^{2S+1}L_J = {}^{2\times1+1}P_{2,1,0} = {}^3P_{2,1,0}$$

Thus, this level has three states corresponding to $^3P_2$, $^3P_1$ $^3P_0$. Its triplet nature is indicated by the $2S + 1 (= 3)$ value as a superscript in the atomic term symbol. You should also keep in mind that the subscript gives the value of J, the total angular momentum quantum number associated with a particular state.

Let us now come to the transitions from $^3S_1$ to $^3P_2$ $^3P_1$ and $^3P_0$ states.

To check whether these are allowed or not, let us calculate J for them.

$$\text{For } {}^3S_1 \longrightarrow {}^3P_2 \text{ ; } \Delta J = 2 - 1 = 1$$

$$\text{For } {}^3S_1 \longrightarrow {}^3P_1 \text{ ; } \Delta J = 1 - 1 = 0$$

and $$\text{For } {}^3S_1 \longrightarrow {}^3P_0 \text{ ; } \Delta J = 0 - 1 = -1$$

Thus, $\Delta J = +1, 0$ and -1.

This is in accordance with the selection rule $\Delta J = \pm 1, 0$. So these transitions are allowed. Thus, these transitions will appear as triplets in the atomic spectrum.

Further transitions from ^3P states to ^3D or ^3S states are possible and give complex patterns. But we will not go into details of these transitions and that is the reason why these transitions are not shown in Fig. 1.14 (b).

At this stage, it is enough for you to know that the spectrum of helium shows two types of transitions, viz., from **singlet to singlet** and from **triplet to triplet states**. Since $\Delta S = 0$, transitions from **singlet to triplet** or **triplet to singlet** states are not allowed and are called spin forbidden transitions.

The alkaline earth metals such as beryllium, magnesium, calcium etc. and other species having two electrons in their valence shell show spectrum similar to that of helium.

Helium atoms in singlet states constitute *parahelium* and those in **triplet states constitute *orthohelium*. Ordinary helium is a mixture of parahelium and orthohelium. Parahelium and orthohelium are inter convertible by exchange of energy.**

SAQ 5

Why for the ground state of He atom having configuration $1s^2$, triplet state ($S = 1$) is not possible?

....

....

1.9 SPECTROSCOPIC STATES OF CARBON

The electronic configuration of carbon is $1s^2\ 2s^2\ 2p^2$. We can term the two electrons in $2p^2$ orbital as equivalent as they have same values of n and l. The $1s$ and $2s$ orbitals being completely filled, do not contribute to the angular momentum. Therefore, only $2p^2$ electrons will be responsible for the angular momentum. For these two electrons, $l_1 = 1$ and $l_2 = 1$;

so
$$L = |(l_1 + l_2)|, |(l_1 + l_2 - 1)|, |(l_1 + l_2 - 1)| \ldots |(l_1 - l_2)|$$
$$= |(1+1)|, |(1+1-1)|, |(1+1-2)|$$
$$= 2, 1, 0$$

Hence, the corresponding states will be denoted by D, P and S. Similarly, S can also take values 0 and 1, depending upon whether the spins are paired or not. So, we have singlet and triplet levels for each of D, P and S states. Thus, the possible states are ^3D, ^3P, ^3S, ^1D, ^1P and ^1S.

By applying Pauli's exclusion principle, we can derive the allowed energy states which are ^1D, ^1S and ^3P states. To determine which one of the three states is a ground state, Hund's rule is used. According to this rule,

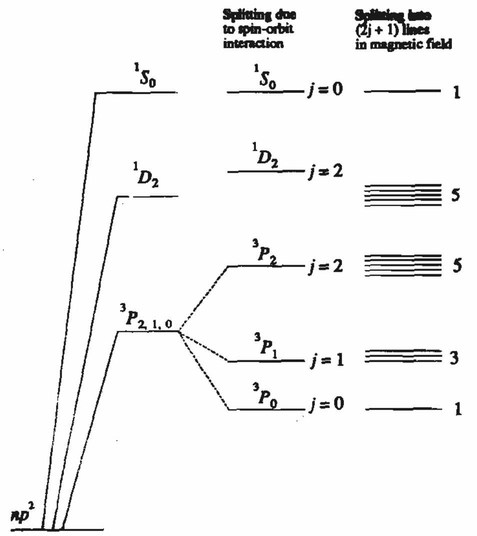


Fig. 1.15: Energy level diagram for carbon.

(i) The state of **greatest multiplicity** is the lowest energy state and

Do not worry about the details of how these allowed energy states are derived.

(ii) In case the **multiplicity is same** the state with *greatest* L value is the lowest energy state. Thus, ^3P state is of lowest energy and is the ground state. Can you predict the next higher state? It is ^1D (because it has greater L value). Then comes ^1S state. The ^3P state being a triplet has three energy levels $^3P_2$, $^3P_1$ and $^3P_0$.

(iii) For half less than filled atomic orbitals, out of the states with same L value, the state with lowest J value will be the most stable state. For more than half filled orbitals, states having higher J values have lower energy. Thus, out of $^3P_2$, $^3P_1$ and $^3P_0$ states, $^3P_0$ will be having the lowest energy. Such an energy level diagram is shown in Fig. 1.15.

Similarly, we can arrive at the possible energy states of other atoms from their electronic configuration.

Note that $\frac{e\hbar}{2m}$ can be represented as Bohr magneton (β_e). You will read more about Bohr magneton in Unit 11 of Block 4.

In the next section, you will be studying about the effect of magnetic field on the splitting of energy levels.

1.10 THE ZEEMAN EFFECT

When an atom is subjected to a magnetic field, each line in its spectrum splits into a number of components. The splitting of the lines is proportional to the strength of the applied magnetic field. This effect was first observed by Zeeman in 1896 and is known as **Zeeman effect**.

Let us now understand why this effect is observed? You know that electrons have charge. The motion of charge (electrons around nucleus) produces a circulating electric current and this in turn generates a magnetic field. The magnetic dipole of the atom (μ) is related to the total angular momentum quantum number (J) by the following expression:

$$\mu = -\frac{g_e e}{2m}\sqrt{J(J+1)}\,\hbar\, J\,T^{-1} = -g_e\beta_e\sqrt{J(J+1)} \quad \text{... (1.29)}$$

Here,

m is the mass of the electron

and e is the charge of the electron

g_e is called the Lande's splitting factor which can be calculated as

$$g_e = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad \text{... (1.30)}$$

The component of this magnetic dipole in the z direction (μ_z) can be written as

$$\mu_z = -g_e\beta_e m_J \quad \text{... (1.31)}$$

where m_J represents the components of **J** (the total angular momentum) in the z direction and m_J can have the following values:

$$m_J = J, J-1, \ldots, \frac{1}{2} \text{ or } 0, \ldots, -J \quad \text{... (1.32)}$$

In other words, we can say that for a particular value of J we have $(2J + 1)$ components in the z direction. Also, note that m_J will be integral or half integral depending upon whether J is integral or half integral.

Note that a charged particle having angular momentum (e.g. an electron or nucleus) acts like a tiny magnet and has a magnetic moment (μ) which is proportional to the angular momentum (J).

Thus, $\vec{\mu} \propto \vec{J}$

or $\vec{\mu} = \gamma\vec{J}$

where γ, the proportionality constant called gyromagnetic ratio, is given by $\frac{g_e e}{2m}$ or $\frac{g_e \beta_e}{\hbar}$.

Hence $|\vec{\mu}| = \frac{g_e\beta_e}{\hbar}\cdot\sqrt{J(J+1)}\,\hbar$

$= g_e\beta_e\sqrt{J(J+1)}$

In a magnetic field because of the interaction between the magnetic moment of the charged particle and the applied field, the charged particle experiences a torque which makes the angular momentum precess around the direction of the applied field. This is shown in Fig 10.3. The precessional frequency (called **Larmor frequency** is directly proportional to the applied field, i.e.

$\omega = \gamma B$

Since the component of the angular momentum in the direction of the field is also quantised and can take only discrete values of m_J therefore, only certain allowed orientations of angular momentum are possible. These allowed orientations have slightly different energies as is also shown in Fig. 1.16.

When we substitute different values of m_J in Eq. 1.31, we get different μ_z components.

The extent of interaction of different μ_z components with external magnetic field (B_z) will be different leading to different energy values and can be given as follows:

$$\text{interaction} = \Delta E = \mu_z B_z = -g_e \beta_e m_J . B_z \qquad \text{... (1.33)}$$

Thus we will have $(2J + 1)$ different values for ΔE in the above expression. In other words, this indicates the **lifting of degeneracy** by the application of external magnetic field. This means that in the presence of external magnetic field, the energy levels which were earlier degenerate, split into $2J + 1$ levels.

Let us reconsider the hydrogen (or sodium) spectrum.

Here, the lowest term is $^2S_{\frac{1}{2}}$. It has $L = 0, S = \frac{1}{2}$ and hence $J = L + S = \frac{1}{2}$.

So, $\quad m_J = +J \ldots -J = +\frac{1}{2}, -\frac{1}{2}$.

Therefore, this level will be split into two $(2J + 1 = 2 \times \frac{1}{2} + 1 = 2)$ levels in the presence of magnetic field.

You may also remember that the two doublet P states were characterised as $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$.

The first state, $^2P_{\frac{1}{2}}$ has $J = \frac{1}{2}$. Thus, it will lead to

$$m_J = \frac{1}{2} \text{ and } -\frac{1}{2} \text{ (using Eq. 1.32)}$$

Hence, when $\quad m_J = \frac{1}{2}, \; \mu_z = -g_e \beta_e \times \frac{1}{2} = -\frac{1}{2} g_e \beta_e \qquad$ (by Eq. 1.31)

And from Eq. 1.33

$$\Delta E = -\frac{1}{2} g_e \beta_e B_z \qquad \text{... (1.34)}$$

Similarly for $\quad m_J = -\frac{1}{2}, \mu_z = -g_e \beta_e \times -\frac{1}{2} = \frac{1}{2} g_e \beta_e \qquad$ ... (by Eq. 1.31)

and

$$\Delta E = \frac{1}{2} g_e \beta_e . B_z \qquad \text{... (1.35)}$$

Thus, according to the above equations, i.e., Eqs. 1.34 and 1.35 $^2P_{\frac{1}{2}}$ level is further split into two energy levels in the presence of magnetic field. These levels are separated by an energy difference of $g_e \beta_e B_z$. What about $^2P_{\frac{3}{2}}$ state? For this $J = \frac{3}{2}$ and it will be split into $2J + 1 = 2 \times \frac{3}{2} + 1 = 3 + 1 = 4$ levels.

The m_J values for these four levels will be as given below:

$$m_J = J, J-1, \ldots, 0 \text{ or } \frac{1}{2}, \ldots, -J$$
$$= \frac{3}{2}, \frac{3}{2} - 1, \ldots, -\frac{3}{2}$$
$$= \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$$

Eq. 1.31 can also be expressed in terms of γ as follows:

$$\mu_z = \gamma m_J \hbar$$

Gyromagnetic ratio (γ) is the ratio of magnetic moment to the angular momentum.

$\gamma = \frac{\mu}{J}$ Using μ from Eq. 1.29 and J **from Eq. 1.28,**

we get $\gamma = \frac{-g_e \beta_e \sqrt{J(J+1)}}{\sqrt{J(J+1)}\,\hbar}$

$= \frac{-g_e \beta_e}{\hbar}$

Hence, Eq. 1.33 can be rewritten as $\Delta E = \gamma \hbar \; m_J B_z$.

We can also write $h\nu$ in place of ΔE in the above equation.

Thus,

$$h\nu = \gamma \hbar m_J B_Z$$

$$= \frac{\gamma h m_J B_Z}{2\pi}$$

or

$$\nu = \frac{\gamma m_J B_Z}{2\pi}$$

or $2\pi\nu = \gamma m_J B_Z$

When the two energy levels differ by $m_J = 1$, we get $2\pi\nu = \gamma B_Z$

The term $2\pi\nu$ is the angular frequency. It can be denoted by ω and is expressed in radians sec^{-1}.

As you will study later in Block 4 Unit 10, Sec 10.3, it is also known as Larmor frequency.

This is diagramatically represented in Fig. 1.16 below.

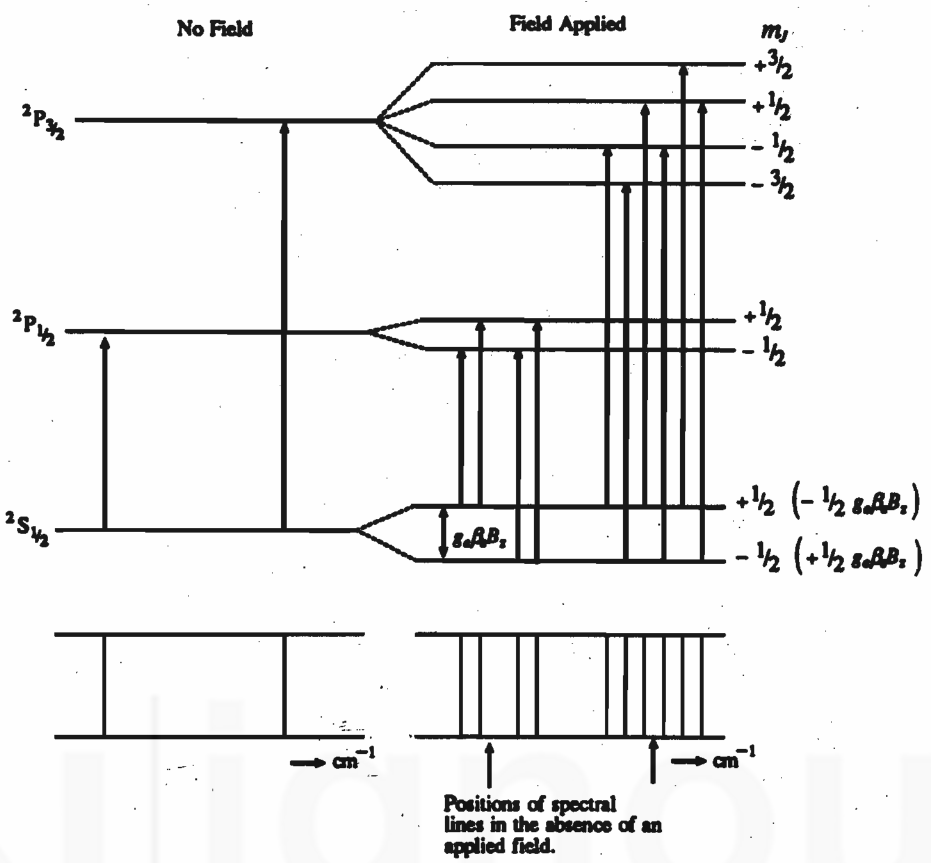


Fig.1.16: Splitting of various energy levels in the presence of magnetic field.

Thus, a transition from the lower $^2S_{\frac{1}{2}}$ level to $^2P_{\frac{1}{2}}$ level (which was a single line in the absence of magnetic field) will show **four lines** according to the four transitions possible in the presence of magetic field. In other words, we can say that the original single line in the absence of magnnetic field is split into four lines in the presence of magnetic field. Here, the additional selection rule is $\Delta m_J = 0, \pm 1$. Similarly, a transition from $^2S_{\frac{1}{2}}$ to $^2P_{\frac{3}{2}}$ yields **6 lines** in the presence of magnetic field.

Let us now understand the magnitude of splitting of these lines. If we calculate g_e for $^2S_{\frac{1}{2}}$, $^2P_{\frac{1}{2}}$, $^2P_{\frac{3}{2}}$ levels using Eq.1.30, we get, $g_e = 1, \frac{1}{3}$ and $\frac{2}{3}$, respectively for these levels. These values are in the ratio 3:1:2. Since splitting is proportional to g, these levels are split in the above ratio. In other words, we can say that **splitting is not uniform or equal for all the levels. This is known as anomalous Zeeman effect.** Now, you may be curious to know what is **normal Zeeman effect?** When the splitting of levels is **identical** in the presence of magnetic field, then the effect is known as **normal Zeeman effect**. For example, in helium atom consider the singlet states. For these states $2S + 1 = 1$. It yields, $S = 0$. Then, $L = J$. Therefore, from Eq. 1.30.

$$g_e = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

$$= 1 + \frac{J(J+1) + 0 - L(L+1)}{2J(J+1)}$$

$$= 1 + \frac{J(J+1) - J(J+1)}{2J(J+1)} = 1 + 0 = 1$$

[since $L = J$
$L(L+1) = J(J+1)$]

Therefore, from Eq.1.33, when $g_e = 1$ splitting will be identical and proportional to the applied magnetic field only and will have a constant value for a particular value of the applied magnetic field, B_z.

Thus, the Zeeman effect gives very useful information which can be used to deduce the term symbols in the following way:

i) Number of lines obtained in presence of magnetic field is related to the J value of the initial and final states involved in that particular transition.

ii) g_e values obtained from the splitting tell about the L and S values of the electron undergoing the transition.

In the next two sections, you will study about two techniques which help us in the experimental determination of energy levels of atoms.

1.8 X-RAY FLUORESCENCE SPECTROSCOPY

When an X–ray or a fast moving electron collides with an atom, its energy may be absorbed by the atom. In case the energy is sufficient to knock one of the electrons from the inner shell (K, L, M, etc.) of the atom, it removes the electron creating there a vacant position. Then, the outer electron falls into this vacant position and the X–ray photons are emitted in this process. The X–rays so emitted are characteristic of the element bombarded.

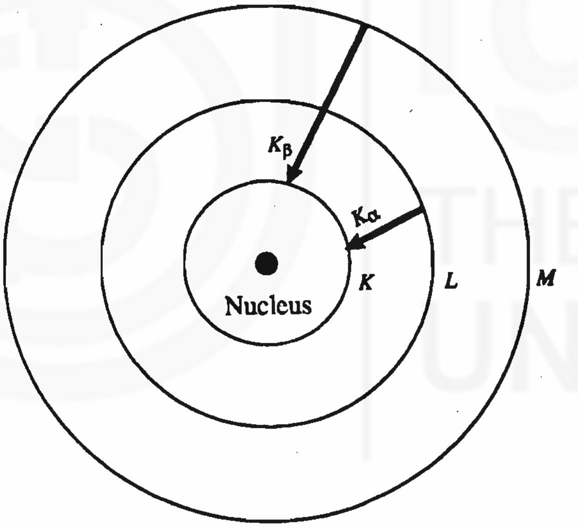


Fig. 1.17: Various shells of an atom.

Here, you should note that within a shell, there are many energy levels. The electron can be knocked off from any one of these levels (transitions between these may also take place) giving rise to a range of radiation. This is shown in Fig. 1.17.

In case the initial excitation is brought about by X–rays, the phenomenon is known as **flourescence.** In this case, the spectrum so obtained is termed as **X–ray fluorescence spectrum.** In such a spectrum, the emitted radiation is always lower in energy than the exciting X–rays.

The innermost shell is K shell and the maximum amount of energy is required to remove an electron from this shell.

When the transition of the electron (to fill the gap) takes place from the L to the K shell, the lines appearing in the spectrum are called K_α X–rays. These can be further subdivided as K_{α_1}, K_{α_2} ... etc. corresponding to the electrons originating from the various sublevels of the L shell. This is shown in Fig. 1.18.

Similarly, when the lines originate due to the transition of the electron from the *M* to *K* level, they are termed as K_β lines. Similar to K_α lines, they can also be subdivided as K_{β_1}, K_{β_2}, etc.

If an electron is ejected from the *L* shell and an electron from *M* shell takes its vacant place, then the lines corresponding to this emitted X–ray radiation in the spectrum will be called as *L* lines.

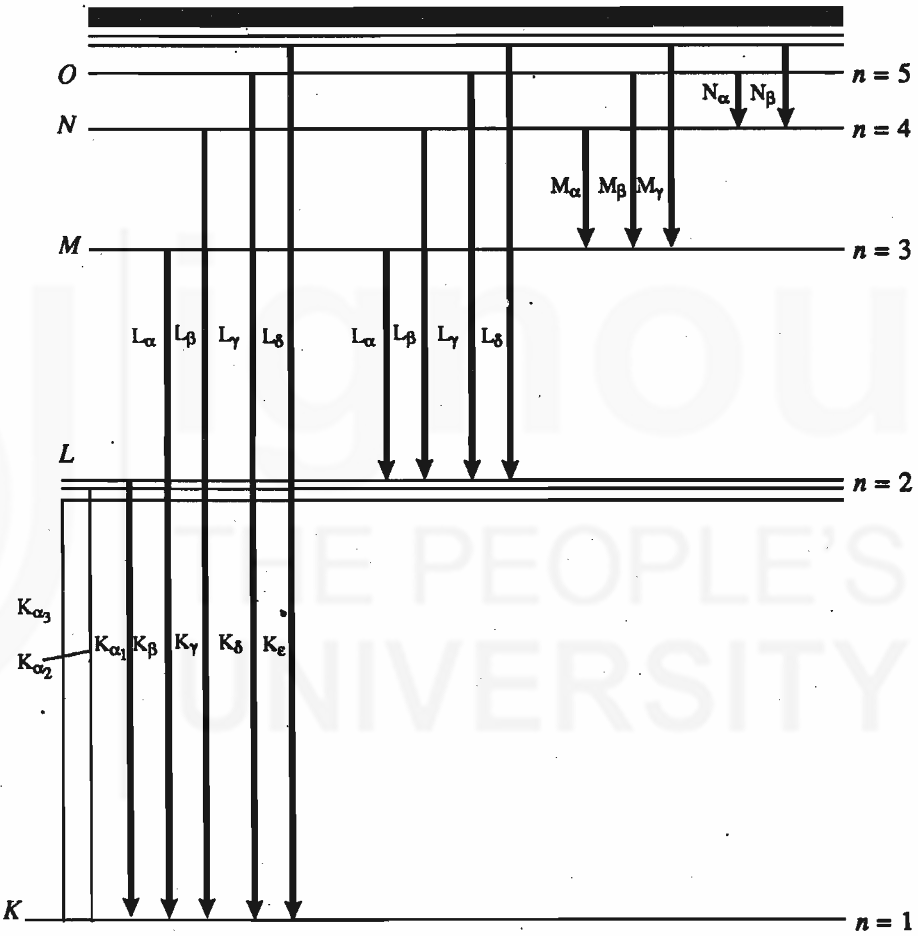


Fig. 1.18: Various transitions responsible for origin of lines in X–ray spectrum.

The X–ray emission spectrum so obtained is similar for all elements. But they differ from each other in the fact that the wavelengths at which various lines appear are different and depend upon the atomic number of the element. Such a relationship between wavelength and atomic number was discovered by Moseley and is known as Moseley's Law. This can be mathematically stated as

$$\lambda = \frac{c}{\nu} = a\,(Z - \sigma)^2 \qquad \text{... (1.36)}$$

Here, *Z* is the atomic number and σ is a constant which depends upon series of lines under consideration and *a* is another constant.

Since the X–ray fluorescence spectrum is characteristic of a particular atom, it can be used in its identification both qualitatively and quantitatively. The quantitative measurements involve the measurement of intensity of the lines.

Elements having atomic numbers between 12 and 92 can be analysed in air; but for elements having atomic numbers between 5 and 11, the experiment is to be carried out in vacuum because the fluorescence is absorbed by the air.

This method of detection of elements is non–destructive and does not require much sample preparation. Its applications are numerous and range from determination of trace elements in plants, analysis of ores, vulcanisation of rubber (detection of sulphur ensuring high quality of rubber) to the analysis of objects of art and antiques.

1.12 PHOTOELECTRON SPECTROSCOPY

You now know that various energy levels exist in an atom. In this section, you will study about a technique with the help of which electronic energy levels (of atoms and molecules) can be determined.

In this method, the sample is irradiated with monochromatic X–rays of known energy. This results in the ejection of an electron from the sample. The remaining excess energy of the X–rays is imparted to the electron as its kinetic energy. Thus, we can say that

$$\text{Energy of the incident X–ray radiation} = \text{Binding Energy} + \text{Kinetic energy} \qquad \ldots (1.37)$$

The kinetic energy of the electron is measured. The binding energy of the electron can then be obtained from the above relationship by knowing the energy of the incident X–rays and kinetic energy of the ejected electron. Experimentally, the number of electrons ejected as a function of their kinetic energy are detected. This leads to the measurement of binding energies of all the electrons present in the system. This information is also characteristic of a particular element and hence can be used to identify it.

An X–ray of wavelength 1 nm has an energy of 2×10^{-16} J. This amount of energy can cause ejection of electrons from the inner shells of many atoms.

Binding energy of an electron is the energy required to remove it from the atom. It is also called ionisation energy, which was referred earlier.

Similar to X–ray photoelectron spectroscopy is the technique of ultraviolet photoelectron spectroscopy. In UV photoelectron spectroscopy, UV radiation is used as incident radiation. The energy of this radiation is sufficient to eject a valence electron whose kinetic energy is determined as done in case of X–ray photoelectron spectroscopy.

1.13 INTENSITY OF SPECTRAL LINES

We have based most of our discussion on the spectra of individual atoms. But what happens when there is a bulk of particles and a number of possible energy levels are available to them? Do all the particles occupy the lowest energy level? The answer to

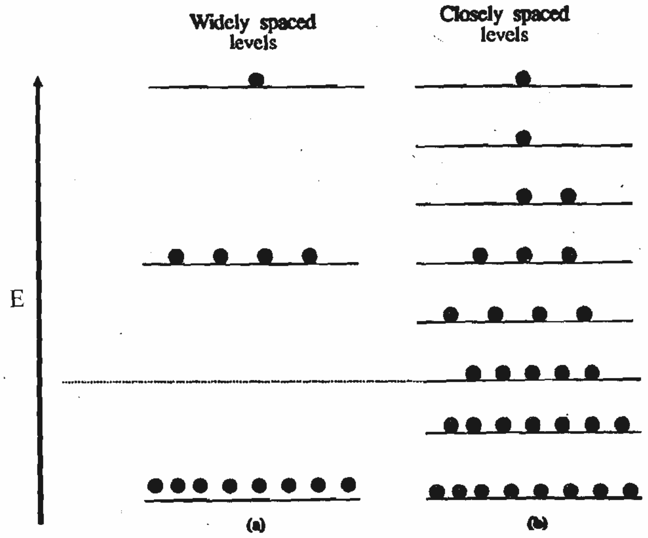


Fig. 1.19: The distribution of atoms or molecules in various energy levels.

this question is NO. Fig.1.19 shows the distribution of atoms or molecules in widely spaced and closely spaced energy levels.

The number of atoms or molecules N_j in a state with energy E_j relative to the number N_i with the lower energy E_i is given by Boltzmann distribution as follows:

$$\frac{N_j}{N_i} = e^{-\Delta E/kT} \qquad \text{... (1.38)}$$

where N_j is the population (no. of particles) in the upper energy level (E_j),

N_i is the population of lower energy level (E_i),

ΔE is the energy difference between two levels,

T is the temperature in Kelvin.

and k is the Boltzmann constant having value 1.38×10^{-23} J K^{-1}.

Certainly, as the energy difference between the levels (ΔE) increases, the relative population of the upper level decreases.

Since the intensity of the spectral lines depends upon the initial population of the level. Other factors being equal, the transition arising from the **most populated** level will give rise to the most intense spectral line.

1.14 SUMMARY

In this unit, you learnt about the nature and characteristics of electromagnetic radiation. Various parameters such as frequency, wavelength etc. associated with electromagnetic radiation were defined and their interrelationship was discussed. Then, we discussed about the particle nature of electromagnetic radiation. The interaction of electromagnetic radiation with atoms was explained by taking the example of hydrogen atom spectrum. A detailed discussion of hydrogen atom spectrum was done including its fine structure. These concepts were extended to the spectra of hydrogen-like atoms. Then, spectra of multi-electron systems were taken and coupling schemes ($L-S$ and $J-J$) of angular momentum of these system were explained. In these systems, nomenclature of various energy states by using term symbols was also discussed. The spectra of helium and carbon were dealt as examples of multi–electron systems. Finally, the effect of magnetic field on atomic spectra was discussed under the title Zeeman effect. This was followed by sections on experimental techniques followed in detection of elements using atomic spectra which include techniques such as X–ray fluorescence spectroscopy and photoelectron spectroscopy. Lastly, the intensity of spectral lines was dealt.

1.15 TERMINAL QUESTIONS

1. Calculate the $\bar{\nu}$ for the first spectral line of Balmer series for hydrogen atom.

2. Which of the following elements would have singlet and triplet states in their atomic energy levels?

   Na, Mg, Cl, Ca, Cu, Ag, Ba

3. Derive the term symbol for the D state of a hydrogen atom.

1.16 ANSWERS

Self Assessment Questions

1. $E = \frac{hc}{\lambda}$

$$= \frac{6.626 \times 10^{-34}\ \text{J s} \times 2.998 \times 10^{8}\ \text{m s}^{-1}}{400\ \text{nm}}$$

$$= \frac{6.626 \times 10^{-34}\ \text{J s} \times 2.998 \times 10^{8}\ \text{m s}^{-1}}{400 \times 19^{-9}\ \text{m}}$$

$$= 4.966187 \times 10^{-19}\ \text{J} = 4.97 \times 10^{-19}\ \text{J}$$

2. **To obtain energy per mole, the above value of energy is to be multiplied by the Avogadro's Number. Thus**

$$E_{\text{per mole}} = 4.966187 \times 10^{-19}\ \text{J} \times 6.022 \times 10^{23}\ \text{mol}^{-1}$$

$$= 299063\ 78114\ \text{J mol}^{-1} = 299.06378114\ \text{kJ mol}^{-1}$$

$$= 2.99 \times 10^{5}\ \text{J mol}^{-1}$$

3. $\dfrac{m_e}{m_n} = 0.00027148$

$$R_D = R_\infty \frac{1}{1 + 0.00027148}$$

$$= 1.09737 \times 10^{7}\ \text{m}^{-1} \times \frac{1}{1.00027148} = 1.09707419 \times 10^{7} \text{m}^{-1}$$

$= 1.09707 \times 10^{7}\ \text{m}^{-1}$ (approximated using significant figures)

$$\bar{\nu}\ \text{Balmer} = R_D\left(\frac{1}{4} - \frac{1}{9}\right) = \frac{5}{36}R_D = 15237\ \text{cm}^{-1}$$

4. $\Delta\bar{\nu} = 17.19\ \text{cm}^{-1}$

$$\Delta E = hc\bar{\nu}$$

$$= 6.626 \times 10^{-34}\ \text{J s} \times 2.998 \times 10^{8}\ \text{m s}^{-1} \times 17.19\ \text{cm}^{-1}$$

$$= 4.4 \times 10^{-24}\ \text{J}$$

5. **Because Pauli's Exclusion principle is violated, as $S = 1$ means m_{s_1} and m_{s_2} should be $+\frac{1}{2}$.**

Terminal Questions

1. $\bar{\nu}_{\text{Balmer}} = R_H\left(\dfrac{1}{4} - \dfrac{1}{9}\right) = R_H\left(\dfrac{9-4}{36}\right) = \dfrac{5}{36}R_H\ \text{cm}^{-1}$

$$= \frac{5}{36} \times 1.09677 \times 10^{7}\ \text{m}^{-1} = 15233\ \text{cm}^{-1}$$

2. **Mg, Ca, Ba.**

3. **For a D state, $l = 2$ and $s = \frac{1}{2}$.**

Now, $j = l + s = 2 + \dfrac{1}{2} = \dfrac{5}{2}$

and $j = l - s = 2 - \dfrac{1}{2} = \dfrac{3}{2}$

Thus, $2S + 1 = 2 \times \frac{1}{2} + 1 = 2$; leading to term symbols $^2D_{\frac{5}{2}}$ and $^2D_{\frac{3}{2}}$.