**5.5.5 Hydrogen Spectrum**

Hydrogen-spectrum is an important example of atomic spectrum. Hydrogen is illed in a discharge tube at a very low pressure a bluish light is emitted from the discharge tube. This light when viewed through a spectrometer shows several isolated sharp lines.

These are called spectral lines. The wavelengths of these lines lie in the visible, ultraviolet and infrared regions. These spectral lines can be classiied into ive groups called spectral series. These series are named after their discoverers as shown below.

(i) Lyman series (U.V region) (ii) Balmer series (visible region)

(iii) Paschen series (LR region) (iv) Brackett series (I.R region) (v) Pfund series (I.R region)

The irst four series were discovered before Bohr’s atomic model (1913). The wave numbers (m-1) of the series of lines in hydrogen spectrum are given in Table (5.2).

It is seen from the Table (5.2) that as we proceed from Lyman series to Pfund series, the wave numbers (m-1) of spectral lines decrease. The lines of Balmer series have been given speciic names as H α, H β ........, etc.

**Table (5.2)Wave numbers (m-1) of various series of hydrogen spectrum.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Lyman series (U.V. region)** | **Balmer series (Visible region)** | **Paschen series (I.R. region)** | **Brackett series (I.R. region)** | **Pfund series (I.R. region)** |
| 82.20 x 105 | 15.21 x 105 (H lá ine) | 5.30 x 105 | 2.46 x 105 | 1.34 x 105 |
| 97.20 x 105 | 20.60 x 105 (H lâ ine) | 7.80 x 105 | 3.80 x 105 | 2.14 x 105 |
| 102.20 x 105 | 23.5 x 105 (H lã ine) | 9.12 x 105 | 4.61 x 105 |  |
| 105.20 x 105 | 24.35 x 105 (H lä ine) | 9.95 x 105 |  |  |
| 106.20 x 105 | 25.18 x 105 |  |  |  |
| 107.20 x 105 |  |  |  |  |

**5.5.6 Origin of Hydrogen Spectrum on the Basis of Bohr’s Model**

According to Bohr, electron in hydrogen atom may revolve in any orbit depending upon its energy.

When hydrogen gas is heated or subjected to an electric discharge, its electron moves from one of the lower orbit to higher orbit, absorbing particular wavelength of energy. Subsequently, when it comes back, the same energy is released. This energy is observed as radiation of particular wavelengths in the form of bright lines seen in the certain region of the emission spectrum of hydrogen gas.

The spectral lines of Lyman series are produced when the electron jumps from n2= 2, 3,4,5, to, n, = 1 (Lyman did not know this reason). Similarly, spectral lines of Balmer series discovered in 1887 originated when an electron jumps from n2 = 3, 4, 5, 6,................. to n1= 2orbit.

In the same way, Paschen, Brackett and Pfund series of lines are produced as a result of electronic transitions from higher orbits to 3rd, 4th and 5th orbits, respectively Fig (5.17).

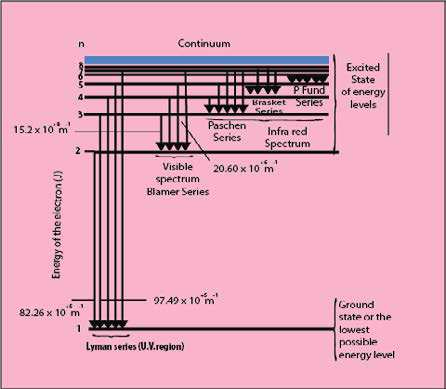
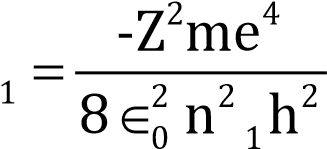


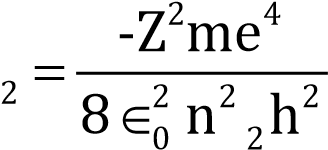
Fig (5.17) Electronic transitions in hydrogen atom and series of spectral lines, justiied by Bohr's model atom

**Calculations of Wave Numbers of Photons of Various Spectral Series by Bohr’s Theory**

The wavelength (l) or wave number (~~v~~) of a spectral line depends on the quantity of energy emitted by the electron. Suppose, an electron jumps from n2 to n, and emits a photon of light.

According to Bohr’s equation of energy

E

E

E1 and E2 are the energies of electrons in n1 and n2 respectively. The energy diference between the

two can be calculated as follows: ∆ =E E -E2 1 = Z me2∈20 h42 n112 -n122 Joules .......................... (22)

8

For H-atom; Z - 1

and 8me∈2 h4 2 = 2.18 x 10-18J(by putting the values of constants)

0

ÄE = 2.18x10-18 n112 -n122 Joules ...................................... (23) 

With the help of equation (23), the energy diference between any two orbits of Hatom can be calculated where nt is the lower level and n2 is higher level. It is not necessary that n1 and n2 are

|  |  |  |
| --- | --- | --- |
| adjacent orbits. |  |  |
| Since |  | ÄE = hv |
| Therefore |  | hv = me20 h4 2 n112 - n122   8∈ |
|  |  | = 2 3  12 - 12 Hz ............................... (24) me4  |

### 8∈0 h n1 n2 

Frequency (v) has the units of the cycles s-1 or Hz. (1 Hz = 1 cycle s-1)

Equation (24) gives us the frequency of a photon emitted, when electron jumps from higher orbit to lower orbit in H-atom. The frequency values go on decreasing between adjacent levels.

**Calculation of Wave Number**

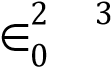
Since v=c~~v~~

Putting in equation (24)

Therefore c~~v~~ = 8Z me2∈20 h43 n112 - n122   ~~v~~ = Z me22 h c34 n11 - 1  -1 .............................. (25)

8∈0 2 n22 m

The value of the factor me4  in eq. (25) has been calculated to be 1.09678 x 107m-1

8 h c

This is called Rydberg constant. Putting Z = 1 for hydrogen atom, the equation (25)becomes. ~~v~~ =1.09678×107 n112 - n122 m-1 .......................... (26)

Equation (26) gives the values of wave number of photons emitted or absorbed when the electron jumps between n1 and n2 orbits.

Let us calculate, the wave numbers of lines of various series.

**Lyman Series:** Fig. (5.17)

Fitrst line n1 = 1(lower orbit), n2 = 2 (higher orbit)

|  |  |  |  |
| --- | --- | --- | --- |
|  | ~~v~~ =1.09678× | 107 112 -2~~=~~12   | 82.26x105m-1 |
| Second line | n1 = 1 | n2 = 3 |  |
|  | ~~v~~ =1.09678× | 107 112 -3~~=~~12   | 97.49x105m-1 |
| Limiting line | n1 = 1 | n2 = ∞ |  |
|  | ~~v~~ =1.09678× | 107  12 - ~~=~~12   | 109.678x105m-1 |

1 ∞ 

Limiting line is developed, when electron jumps from ininte orbit to, n = 1

The values of all these wave numbers lie in the U.Y region of the spectrum. It means that when electron of H-atom falls from all the possible higher levels to n = 1, then the photons of radiation emitted lie in the range of U.V region.

**Balmer Series:** Fig (5.17)

Fitrst line n1 = 2, n2 = 3

~~v~~ =1.09678× 107 212 -3~~=~~12  15.234x105m-1



Second line n1 = 2 n2 = 4 ~~v~~ =1.09678× 107 212 -4~~=~~12  20.566x105m-1  Third line n1 = 2 n2 = 5

~~v~~ =1.09678× 107 212 -5~~=~~12  23.00x105m-1  Limiting line n1 = 2 n2 = ∞

~~v~~ =1.09678× 107 212 - ∞~~=~~12  27.421x105m-1



The limiting line of Balmer series lies in U.V region, while other lines fall in visible region. Similarly, we can calculate the wave numbers for all the lines of Paschen, Brackett and Pfund series. These three series of lines lie in the infrared region.

**5.5.7 Defects of Bohr’s Atomic Model**

1. Bohr’s theory can successfully explain the origin of the spectrum of H-atom and ions like He+1, Li+2 and Be+3, etc. These are all one electron systems. But this theory is not able to explain the origin of the spectrum of multi-electrons or poly-electrons system like He, Li and Be, etc.
2. When the spectrum of hydrogen gas is observed by means of a high resolving power spectrometer, the individual spectral lines are replaced by several very ine lines, i.e. original lines are seen divided into other lines. The Hα- line in the Balmer series is found to consist of ive - component lines. This is called ine structure or multiple structure. Actually, the appearance of several lines in a single line suggests that only one quantum number is not suicient to explain the origin of various spectral lines.
3. Bohr suggested circular orbits of electrons around the nucleus of hydrogen atom, but researches have shown that the motion of electron is not in a single plane, but takes place in three dimensional space. Actually, the atomic model is not lat.
4. When the excited atoms of hydrogen (which give an emission line spectrum) are placed in a magnetic ield, its spectral lines are further split up into closely spaced lines. This type of splitting of spectral lines is called Zeeman efect. So, if the source which is producing the Na - spectrum is placed in a weak magnetic ield, it causes the splitting of two lines of Na into component lines. Similarly, when the excited hydrogen atoms are placed in an electrical ield, then similar splitting of spectral lines takes place which is called “Stark efect”. Bohr’s theory does not explain either Zeeman or Stark efect.

However, in 1915, Sommorfeld suggested the moving electrons might describe in addition to the circular orbits elliptic orbits as well wherein the nucleus lies at one of the focii of the ellipse.

#### 5.6 X-RAYS AND ATOMIC NUMBER

X-rays are produced when rapidly moving electrons collide with heavy metal anode in the discharge tube. Energy is released in the form of electromagnetic waves when the electrons are suddenly stopped. In the discharge tube, the electrons produced by a heated tungsten ilament are accelerated by high voltage Fig. (5.18). It gives them suicient energy to bring about the emission of X-rays on striking the metal target. X-rays are emitted from the target in all directions, but only a small portion of them is used for useful purposes through the windows. The wavelength of X-rays produced depends upon the nature of the target metal. Every metal has its own characteristic X-rays.

The X-rays are passed through a slit in platinum plate and then emerged through aluminum window. This is thrown on a crystal of K4[Fe(CN)6], which analyses the X-ray beam. The rays are difracted from the crystal and are obtained in the form of line spectrum of X-rays. This is allowed to fall on photographic plate. This line spectrum is the characteristic of target material used. This characteristic X-rays spectrum has discrete spectral lines. These are grouped into K-series, L-series and M-series, etc. Each series has various line as K α, K β, L α, L β, M α, M β etc.

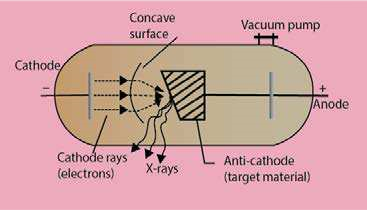


Fig (5.18) Production of X-rays

A systematic and comprehensive study of X-rays was undertaken by Moseley in 1913-1914. His researches covered a range of wavelengths 0.04 - 8 A. He employed thirty eight diferent elements from aluminium to gold, as target in X-rays tube. Moseley was able to draw the following important conclusions from a detailed analysis of the spectral lines which he obtained.

1. The spectral lines could be classiied into two distinct groups. One of shorter wavelengths are identiied by K-series and the other of comparatively longer wavelengths are identiied by L-series.
2. If the target element is of higher atomic number the wavelength of X-rays becomes shorter. (iii) A very simple relationship was found between the frequency (v) of a particular line of X-rays and the atomic number Z of the element emitting it.

v = a(Z-b) .................. (27)

Here ‘a’ and ‘b’ are the constants characteristic of the metal under consideration. This linear equation (27) is known as Moseley’s Law. ‘a” is proportionality constant and ‘b’ is called screening constant of the metals.

This law states that the frequency of a spectral line in X-ray spectrum varies as the square of atomic number of an element emitting it. This law convinces us that it is the atomic number and not the atomic mass of the element which determines its characteristic properties, both physical and chemical. If value of v for K-series are plotted against Z, then a straight line is obtained.

**Importance of Moseley Law**

1. Moseley arranged K and Ar, Ni and Co in a proper way in Mendeleev’s periodic table.
2. This law has led to the discovery of many new elements like Tc(43), Pr(59), Rh(45).
3. The atomic number of rare earths have been determined by this law.

#### 5.7 WAVE-PARTICLE NATURE OF MATTER (DUAL NATURE OF MATTER)

Planck’s quantum theory of radiation tells us that light shows a dual character. It behaves both as a material particle and as a wave. This idea was extended to matter particles in 1924 by Louis de- Broglie. According to de-Broglie, all matter particles in motion have a dual character. It means that electrons, protons, neutrons, atoms and molecules possess the characteristics of both the material particle and a wave.

This is called wave-particle duality in matter. de-Broglie derived a mathematical equation which relates the wavelength (l) of the electron to the momentum of electron.

l= h ........................ (28)

mv

Here l= de-Broglie’s wavelength, m = mass of the particle v = velocity of electron

According to this equation, the wavelength associated with an electron is inversely proportional to its momentum (mv).

This equation is derived as follows.

According to Planck’s equation

E = hv ........................ According to Einstein’s mass energy relationship

E = mc2 ........................ (29)

Where ’m’ is the mass of the material particle which has to convert itself into a photon; ‘and c’ is the velocity of photon. Equating two values of energy;

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Since |  |  |  | hv=mc2 |
|  |  |  |  | c  v=  l |
| So, |  | hc 2  = mc |  | or l= h ........................ (30) |

l mc

According to equation (30), the wavelength of photon is inversely proportional to the momentum of photon. Considering that nature is symmetrical, we apply this equation (30) to the moving electron of mass’m’ and velocity V. This idea gives us the de-Broglie’s equation (28)

l= h  ........................ (28)

#### mv

According to equation (28), the wavelength of electron is inversely proportional to momentum of electron. Now, consider an electron which is moving with a velocity of 2.188x106 ms-1 in the irst orbit of Bohr’s model of hydrogen atom. Then, wavelength associating with it, can be calculated with the help of equation(28)

h = 6.626x10-34 Js me = 9.108x10-31 kg

##### 6.626×10−34Js 2 -2

l=9.108×10−31kg ×2.188×106ms-1 Since (J = kg m s )

l=0.33x10-9m (10-9m=1mm)

l=0.33 nm

This value of wavelength (l)of electron while moving in the irst orbit of H-atom is comparable to the wavelength of X-rays and can be measured.

If we imagine a proton moving in a straight line with the same velocity as mentioned for electron, it’s wavelength will be 1836 times smaller than that of electron. Similarly, an α-particle moving with the same velocity should have a wavelength 7344 times smaller as compared to that of ejectron. Now, consider a stone of mass one gram moving with a velocity of 10 ms-1, then its wavelength will be:

6.626×10−34Js

l=10−3kg ×10ms-1

= 6.626x10-30 m

This wavelength is so small, that it cannot be measured by any conceivable method. It means that heavy material particles have waves associated with them, but they cannot be captured and we say that the macroscopic bodies don’t have the waves.

##### 5.7.1 Experimental Veriication of Dual Nature of Matter

In 1927, two American scientists, Davisson and Germer did an experiment to verify the wave nature of moving electron. Electrons were produced from heated tungsten ilament and accelerated by applying the potential diference through charged plates. Davisson and Germer proved that the accelerated electrons undergo difraction, like waves, when they fall on a nickel crystal. In this way, the wave nature of electron got veriied. Davisson ahd Germer got the nobel prize for inventing an apparatus to prove the matter waves and de Broglie got the separate nobel prize for giving the equation of matter wave.

##### 5.8 HEISENBERG'S UNCERTAINTY PRINCIPLE

According to Bohr’s theory, an electron is a material particle and its position as well as momentum can be determined with great accuracy. But with the advent of the concept of wave nature of electron, it has not been possible for us to measure simultaneously the exact position and velocity of electron. This was suggested by Heisenberg, in 1927.

Suppose, that Δx is the uncertainty in the measurement of the position and Δp is the uncertainty in the measurement of momentum of an electron, then

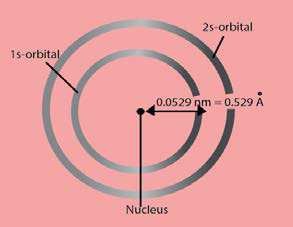
∆ ∆ ≥x p 4hp

This relationship is called uncertainty principle. This equation shows that if Δx is small then Δp will be large and vice versa. So, if one quantity is measured accurately then the other becomes less accurate. Hence, certainty in the determination of one quantity introduces uncertainty in the determination of the other quantity.

The uncertainty principle is applicable only for microscopic particles like electrons, protons and neutrons, etc. and has no signiicance for large particles, i.e. macroscopic particles.

Compton’s efect can help us understand the uncertainty principle, Suppose, we wish to determine the position of electron. Visible light cannot help us, because the wavelength of visible light is millions time large as compared to the diameter of electron. For this purpose, we have to use X-rays which have very short wavelength as compared to that of visible light. When this photon of X-rays strikes an electron, the momentum of electron will change. In other words, uncertainty of momentum will appear due to change of velocity of electron. Smaller the wavelength of X-rays, greater will be the energy of the photon. Hence, the collision of X-rays with electron will bring about the greater uncertainty in momentum. So, an efort to determine the exact position of electron has rendered its momentum uncertain. When we use the photons of longer wavelength to avoid the change of momentum, the determination of the position of electron becomes impossible.

**Concept of Orbital**

 Following this principle, the Bohr’s picture of an atom does not appear to be satisfactory. In Bohr’s atom, the electrons are moving with speciic velocities in orbits of speciied radii, and according to uncertainty principle, both these quantities cannot be measured experimentally. A theory involving quantities, which cannot be measured does not follow the tradition of scientiic work.

In order to solve this diiculty, Schrodinger, Heisenberg and Dirac worked out wave theories of the atom. The best known treatment is that of Schrodinger. He set up a wave equation for hydrogen atom. According to Schrodinger, although the position of an electron cannot be found exactly, the probability of inding an electron at a certain position at any time can be found. Fig (5.19) Probable electron density diagram for hydrogen atom.

The solution of the wave equation gives probability of inding an electron present in a given small region of space. When the probability of inding the electron at a distance r from the nucleus is calculated for the hydrogen atom in the ground state, Fig (5.19) is obtained.

The maximum probability of inding the electron is at a distance of 0.053 nm. It is the same radius as calculated for the Bohr’s irst orbit. There is a possibility that the electron is either closer to the nucleus or outside the radius of 0.053 nm, where probability of inding electron decreases sharply.

The volume of space in which there is 95% chance of inding an electron is called atomic orbital. The term orbital should not be confused with the term orbit as used in the Bohr’s theory. The orbital can be regarded as a spread of charge surrounding the nucleus. This is often called the “electron cloud”.

###### **5.8.1 Quantum Numbers**

Schrodinger wave equation, has been solved for hydrogen atom. It may have different solutions. Quantum numbers are the sets of numerical values which give the acceptable solutions to Schrodinger wave equation for hydrogen atom. An electron in an atom is completely described by its four quantum numbers. You know that a complete address of a person comprises his name, city in which he lives, the block, street and the house number. On the similar grounds, quantum numbers serve as identiicatio numbers or labels, which completely describe an electron. These quantum numbers specify position of electron in an atom.

There are four quantum numbers which can describe the electron completely.

1. Principal quantum number (n)
2. Azimuthal quantum number ()
3. Magnetic quantum number (m)
4. Spin quantum number (s) Let us discuss these quantum numbers one by one.

**Principal Quantum Number (n)**

The diferent energy levels in Bohr’s atom are represented by ‘n’. This is called principal quantum number by Schrodinger. Its values are non-zero, positive integers upto ininity.

n = 1, 2, 3, 4, 5,.........................,

The value of n represents the shell or energy level in which the electron revolves around the nucleus. Letter notations K, L, M, N, etc are also used to denote the various shells. For example, when n =1, it is called K shell, for n = 2, it is L shell and so on. The values of n also determine the location of electron in an atom, i.e the distance of electron from the nucleus, greater the value of ‘n’ greater will be the distance of electron from the nucleus. It is a quantitative measure of the size of an electronic shell, ‘n’ also provides us the energy of electron in a shell. Bohr’s results help us to know the relationships of distance and energy of electron.

**Azimuthal Quantum Number (**  **)**

It has already been mentioned in the defects of Bohr’s model that a spectrometer of high resolving power shows that an individual line in the spectrum is further divided into several very ine lines. This thing can be explained by saying that each shell is divided into subshells. So, only principal quantum number (n) is not suicient to explain the line spectrum. There is another subsidiary quantum number called azimuthal quantum number and is used to represent the subshells. The values of azimuthal quantum number () are

=0, 1, 2, 3, .....................................................(n-1)

Its value depends upon n. These values represent diferent subshells, which are designated by small letters, s, p, d, f. They stand for sharp, principal, difused and fundamental, respectively. These are the spectral terms used to describe the series of lines observed in the atomic spectrum. The values of azimuthal quantum number always start from zero.

A subshell may have diferent shapes depending upon the value of (‘’). It may be spherical, dumb-bell, or some other complicated shapes. The value of ‘’ is related to the shape of the subshell as follows:

 = 0 s-subshell spherical

 = 1 p-subshell dumb-bell

 = 2 d-subshell (complicated shape)

The relationship between principal and azimuthal quantum numbers is as follows. n = 1 K-shell { = 0 {s-subshell should be called as 1s

n = 2 L-shell ==10 s-subshellp-subshell 22sp

= 0 s-subshell 3s

n = 3 M-shell =1 p-subshell 3p

= 2 d-subshell 3d

= 0 s-subshell 4s

n = 4 N-shell ==12 d-subshellp-subshell 44pd



= 3 f-subshell 4f

In 1s, 2s, ........, etc, the digit represents the value of principal quantum number.’ ’ values also enable us to calculate the total number of electrons in a given subshell. The formula for calculating electrons is 2 (2 + 1).

when  = 0 s-subshell total electrons = 2  = 1 p-subshell total electrons = 6

 = 2 d-subshell total electrons = 10

 = 3 f-subshell total electrons = 14

**Magnetic Quantum Number (m)**

In the defects of Bohr’s model, it has been mentioned that strong magnetic ield splits the spectral lines further. In order to explain this splitting, a third quantum number called the magnetic quantum number (m) has been proposed. Its values are m = 0, ± 1, ± 2, ± 3,..........................

The value of’m’ depends upon values of ‘’

when  = 0 s-subshell m=0

 = 1 p-subshell m=0, ±1(p-subshell has three degenerate orbitals)

 = 2 d-subshell m=0,±1, ±2(d-subshell has ive degenerate orbitals)

 = 3 f-subshell m=0,±1, ±2, ±3(f-subshell has seven degenerate orbitals) This above description shows that for a given value of ‘’ the total values of’m’ are (2 +1).

Actually, the value of m gives us the information of degeneracy of orbitals in space. It tells us the number of diferent ways in which a given s, p, d or f-subshell can be arranged along x, y and z-axes in the presence of a magnetic ield. Thus, diferent values of’m’ for a given value of ‘‘, represent the total number of diferent space orientations for a subshell.

In case of s-subshell  = 0, so, m = 0. It implies that s-subshell of any energy level has only one space orientation and can be arranged in space only in one way along x, y and z-axes. So s-subshell is not sub-divided into any other orbital. The shape of’s’ orbital is such that the probability of inding the electron in all the directions from the nucleus is the same. It is a spherical and symmetrical orbital. Fig (5.20).

For p-subshell,  = 1 and m = 0, ±1. These values of’m’ imply that p-subshell of any energy level has three space orientations and can be arranged in space along x, y, and z axes Fig. (5.21). These three orbitals are perpendicular to each other and named as px, py, and pz. They have egg shaped lobes which touch each other at the origin. They are disposed symmetrically along one of the three axes called orbital axis. In the absence of the magnetic ield, all the three p-orbitals have the same energy and are called degenerate orbitals. Since, they are three in number, so these orbitals are said to be 3-fold degenerate or triply degenerate.

For d-subshell  = 2 m = 0, ±1, ±2. It implies that it has ive space orientations and are designated as dxy (m = -2), dyz (m = -1), dzx(m = +1), dx2-y2(m = +2) and dz2(m - 0) Fig. (5.22).

All these ive d-orbitals are not identical in shape. In the absence of a magnetic ield, all ive d-orbitals have the same energy and they are said to be ive fold degenerate orbitals.

For f-subshell, = 3 and m = 0, ±1, ±2, ±3. They have complicated shapes.

The whole discussion shows that magnetic quantum number determines the orientation of orbitals, so it is also called orbital orientation quantum number.

**Spin Quantum Number (s)**

Alkali metals have one electron in their outermost shell. We can record their emission spectra, when the outermost electron jumps from an excited state to a ground state. When the spectra are observed by means of high resolving power spectrometer, each line in the spectrum is found to consist of pair of lines, this is called doublet line structure. We should keep it in mind, that doublet line structure is diferent from the ine spectrum of hydrogen (as we have discussed in azimuthal quantum number).

It should be made clear that lines of doublet line structure are widely separated from each other, while those of ine structure are closely spaced together.

In 1925, Goudsmit and Uhlenbech suggested that an electron while moving in an orbital around the nucleus also rotates or spins about its own axis either in a clockwise or anti-clockwise direction. This is also called self-rotation. This spinning electron is associated with a magnetic ield and hence a magnetic moment. Hence, opposite magnetic ields are generated by the clockwise and anti-clockwise spins of electrons. This spin motion is responsible for doublet line structure in the spectrum.

The four quantum numbers of all the electrons in the irst four shells are summarized in Table (5.3). Notice, that each electron has its own set of quantum numbers and this set is diferent for each electron.

Table (5.3) Quantum Numbers of Elections

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Principal  Quantum  Number ‘n’ | Azimuthal  Quantum  number ‘  ’ | Magnetic  Quantum  number ‘m’ | Spin  Quantum  number ‘s’ | Number of electrons  accommodated |
| 1 K | 0 s | 0 | **+½,-½** | 2 |
| 2 L | 0 s  1  p | 0  +1, 0, −1 | **+½,-½**  **+½,-½** | **2**  **6 8** |
| 3 M | 0 s  1  p  2  d | 0  +1, 0, −1  +2, +1, 0, −1, −2 | **+½,-½**  **+½,-½**  **+½,-½** | **2**  **6 18 10** |
| 4 N | 0 s  1  p  2  d  3 f | 0  +1, 0, −1  +2, +1, 0, −1, −2  +3, +2, +1, 0, −1, −2, −3 | **+½,-½**  **+½,-½**  **+½,-½**  **+½,-½** | **2**  **6 32**  **10 14** |

**5.8.2 Shapes of Orbitals**

In section 5.8.1, we were introduced to the four types of orbitals depending upon the values of azimuthal quantum number. These orbitals are s, p, d and f having azimuthal quantum number values as  = 0,1, 2,3, respectively. Let us, discuss the shapes of these, orbitals. **Shapes of s-Orbitals**

s-orbital has a spherical shape and is usually represented by a circle, which in turn, represents a cut of sphere, Fig. (5.20). With the increase of value of principal quantum number (n), the size of s-orbital increases. 2s-orbital is larger in size than ls-orbital. 2s-orbital is also further away form the nucleus Fig. (5.20). The probability for inding the electron is zero between two orbitals. This place is called nodal plane or nodal surface.

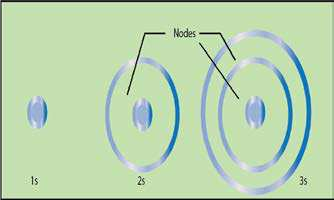


Fig (5.20) Shapes of s-orbitals with increasing principal quantum number

**Shapes of p-Orbitals**

There are three values of magnetic quantum numbef for p-subshell. So, p-subshell has three orientations in space i.e. along x, y and z-axes. All the three p-orbitals namely, px, py and pz have dumb-bell shapes, Fig. (5.21). So, p-orbitals have directional character which determines the geometry of molecules. All the p-orbitals of all the energy levels have similar shapes, but with the increase of principal quantum number of the shell their sizes are increased.

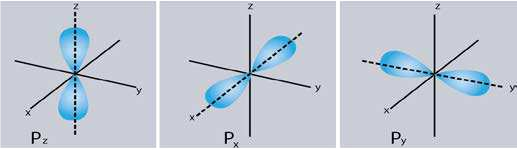


Fig (5.20) Shapes of p-orbitals

**Shapes of d-Orbitals**

For d subshell there are ive values of magnetic quantum number. So, there are ive space orientations along x, yand z-axes. Fig (5.22). They are designated as dxy, dyz, dxz, dx -y2 2 , dz2 .The lobes of irst three d-orbitals lie between the axis. The other lie on the axis.

They are not identical in shape. Four d-orbitals out of these ive contain four lobes each, while the ifth orbital dz2 consists of only two lobes, Fig (5.22). In the absence of magnetic ield, all the ive d-orbitals are degenerate. The shape of f-orbital is very complicated.

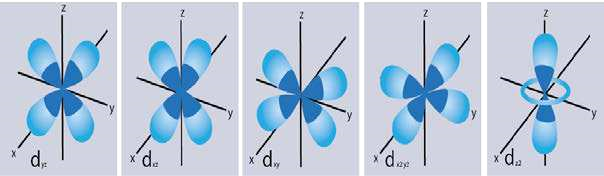


Fig (5.22) Shapes of d-orbitals

##### 5.9 ELECTRONIC DISTRIBUTION

In order to understand the distribution of electrons in an atom, we should know the following facts. 1. An orbital like s, px, py, pz and dxy, etc. can have at the most two electrons.

2. The maximum number of electrons that can be accommodated in a shell is given by 2n2 formula where n is principal quantum number and it cannot have zero value. Moreover, following rules have been adopted to distribute the electrons in subshells or orbitals.

1. Aufbau principle
2. Pauii’s exclusion principle
3. Hand’s rule

But, before we use these rules, the subshells should be arranged according to (n + ) rule, Table(5.4). This rule says that subshells are arranged in the increasing order of (n + ) values and if any two subshells have the same (n + ) values, then that subshell is placed irst whose n value is smaller.

The arrangement of subshells in ascending order of their energy may be as follows: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s and so no.

**Aufbau Principle Table (5.4) Arrangement of orbitals**

**according to (n+1) rule**

|  |  |  |  |
| --- | --- | --- | --- |
|  | n |  | n +  |
| 1s | 1 | 0 | 1 + 0 = 1 |
| 2s | 2 | 0 | 2 + 0 = 2 |
| 2p | 2 | 1 | 2 + 1 = 3 |
| 3s | 3 | 0 | 3 + 0 = 3 |
| 3p | 3 | 1 | 3 + 1 = 4 |
| 3d | 3 | 2 | 3 + 2 = 5 |
| 4s | 4 | 0 | 4 + 0 = 4 |
| 4p | 4 | 1 | 4 + 1 = 5 |
| 4d | 4 | 2 | 4 + 2 = 6 |
| 4f | 4 | 3 | 4 + 3 = 7 |
| 5s | 5 | 0 | 5 + 0 = 5 |
| 5p | 5 | 1 | 5 + 1 = 6 |
| 5d | 5 | 2 | 5 + 2 = 7 |
| 5f | 5 | 3 | 5 + 3 = 8 |
| 6s | 6 | 0 | 6 + 0 = 6 |
| 6p | 6 | 1 | 6 + 1 = 7 |
| 6d | 6 | 2 | 6 + 2 = 8 |
| 6f | 6 | 3 | 6 + 3 = 9 |
| 7s | 7 | 0 | 7 + 0 = 7 |

The electrons should be illed in energy subshells in order of increasing energy values. The electrons are irst placed in Is, 2s, 2p and soon.

**Pauli’s Exclusion Principle**

This principle can be stated as follows: It is impossible for two electrons residing in the same orbital of a poly-electron atom to have the same values of four quantum numbers, or Two electrons in the same orbital should have opposite spins (↓↑).

**Hund’s Rules**

If, degenerate orbitals are available and more than one electrons are to be placed in them, they should be placed in separate orbitals with the same spin rather than putting them in the same orbital with opposite spins.

According to the rule, the two electrons in 2p subshell of carbon will be distributed as follows.

6C = 1 2 2p 2↓↑ ↓↑ ↑*s s* x p 2p↓ y o z

The three orbitals of 2p subshell are degenerate.

###### **5.9.1 Electronic Coniguration of Elements**

Keeping in view the rules mentioned above, the electronic conigurations of irst thirty six elements are given in Table (5.5).

###### **Table (5.5) Electron conigurations of elements**

|  |  |  |
| --- | --- | --- |
| Element | Atomic number | Electron Coniguration Notation |
| Hydrogen | 1 | ↑  1s |
| Helium | 2 | 1s2 |
| Lithium | 3 | ↑  1s 2s2 |
| Beryllium | 4 | 1s22s2 |

**Table (5.5) continued**

|  |  |  |
| --- | --- | --- |
| Element | Atomic number | Electron Coniguration Notation |
| Boron | 5 | ↑ 0 0  1s 2s 2p 2p 2p2 2 x y z |
| Carbon | 6 | ↑ ↑ 0  1s 2s 2p 2p 2p2 2 x y z |
| Nitrogen | 7 | ↑ ↑ ↑  1s 2s 2p 2p 2p2 2 x y z |
| Oxygen | 8 | ↑ ↑  1s 2s 2p2 2 2x 2p 2py z |
| Fluorine | 9 | ↑ 1s 2s 2p2 2 2x 2p2y 2pz |
| Neon | 10 | 1s 2s 2p2 2 2x 2p2y 2p2z |
| Sodium | 11 | ↑  [Ne]3s |
| Magnesium | 12 | ↑↓  [Ne]3 s |
| Aluminum | 13 | ↑ 0 0  [Ne]3s 3p 3p 3p2 x y z |
| Silicon | 14 | ↑ ↑ 0  [Ne]3s 3p 3p 3p2 x y z |
| Phosphorus | 15 | ↑ ↑ ↑  [Ne]3s 3p 3p 3p2 x y z |
| Sulphur | 16 | ↑ ↑  [Ne]3s 3p2 2x 3p 3py z |
| Chlorine | 17 | ↑  [Ne]3s 3p2 2x 3p2y 3pz |
| Argon | 18 | [Ne]3s 3p2 2x 3p2y 3p2z |
| Potassium | 19 | ↑  [Ar] 4s |
| Calcium | 20 | [Ar] 4s2 |

(continued on next page)

|  |  |  |
| --- | --- | --- |
| Element | Atomic number | Electron Coniguration Notation |
| Scandium | 21 | ↑ 0 0 0 0  [Ar] 4s 3d2 xy 3dyz 3dxz 3dx -y2 2 3dz2 |
| Titanium | 22 | ↑ ↑ 0 0 0  [Ar] 4s 3d2 xy 3dyz 3dxz 3dx -y2 2 3dz2 |
| Vanadium | 23 | ↑ ↑ ↑ 0 0  [Ar] 4s 3d2 xy 3dyz 3dxz 3dx -y2 2 3dz2 |
| Chromium | 24 | ↑ ↑ ↑ ↑ ↑ ↑  [Ar] 4 3d*s* xy 3dyz 3dxz 3dx -y2 2 3dz2 |
| Manganese | 25 | ↑ ↑ ↑ ↑  [Ar] 4s 3d2 2xy 3dyz 3dxz 3dx -y2 2 3dz2 |
| Iron | 26 | ↑ ↑ ↑  [Ar] 4s 3d2 2xy 3d2yz 3dxz 3dx -y2 2 3dz2 |
| Cobalt | 27 | ↑ ↑  [Ar] 4s 3d 3d 3d 3d2 xy yz xz x -y2 2 3dz2 |
| Nickel | 28 | ↑ [Ar] 4s 3d 3d 3d 3d2 xy yz xz x -y2 2 3dz2 |
| Copper | 29 | ↑  [Ar] 4s3d2xy 3d2yz 3d2xz 3d2x -y2 2 3d2z2 |
| Zinc | 30 | [Ar] 4s 3d2 2xy 3d2yz 3d2xz 3d2x -y2 2 3d2z2 |
| Gallium | 31 | ↑ 0 0  [Ne] 4s 3d 4p 4p 4p2 10 *x y* z |
| Germanium | 32 | ↑ ↑ 0  [Ne] 4s 3d 4p 4p 4p2 10 *x y* z |
| Arsenic | 33 | ↑ ↑ ↑  [Ne] 4s 3d 4p 4p 4p2 10 *x y* z |
| Selenium | 34 | ↑ ↑  [Ne] 4s 3d 4p2 10 2*x*4p 4p*y* z |
| Bromine | 35 | ↑  [Ne] 4s 3d 4p2 10 2*x*4p2 *y*4pz |
| Krypton | 36 | [Ne] 4s 3d 4p2 10 2*x*4p2 *y*4p2z |

##### KEY POINTS

1. Matter is made up of extremely small particles called atoms.
2. Cathode rays and positive rays were discovered during discharge tube experiments. The properties of cathode rays showed them to be negatively charged particles called electrons, whereas, the positive rays were found to contain positively charged particles called protons.
3. Neutron was discovered through artiicial radioactivity.
4. Electrons, protons and neutrons are regarded as the fundamental particles of an atom.
5. Rutherford discovered the nucleus and successfully explained the presence of moving electrons around the nucleus.
6. In 1905, Planck put forward his famous Planck’s quantum theory.
7. Neil Bohr explained the structure of hydrogen atom by using Planck’s quantum theory. He also calculated the radius and energy of electron in the nth shell of hydrogen atom.
8. Bohr’s atomic model successfully explained the origin of line spectrum and the lines present in the spectrum of hydrogen atom in the visible and invisible regions.
9. X-rays are produced when rapidly moving electrons collide with heavy metal anode in the discharge tube.
10. Moseley discovered a simple relationship between the frequency of X-rays and the atomic number of the target element.
11. de-Broglie discovered wave particle duality of material particles. According to him, all material particles in motion have a dual character. Davisson and Germer experimentally veriied the wave concept of an electron.
12. Heisenberg pointed out that it is not possible for us, to measure the exact position and the exact momentum of electron simultaneously.
13. After the failure of Bohr’s atomic model, Schrodinger developed the wave mechanical model of hydrogen atom. According to him, although the position of an electron cannot be found exactly, the probability of inding an electron at a certain position at any time can be calculated.
14. An electron in an atom is completely described by its four quantum numbers. Three out of these four quantum numbers, have been derived from Schrodinger wave equation, when it is solved for hydrogen atom.

##### EXERCISE

Q1. Select the most suitable answer for the given one.

1. The nature of the positive rays depend on
   1. the nature of the electrode (b) the nature of the discharge tube

(c) the nature of the residual gas (d) all of the above

1. The velocity of photon is
   1. independent of its wavelength (b) depends on its wavelength

(c) equal to square of its amplitude (d) depends on its source

1. The wave number of the light emitted by a certain source is 2 x 106 m-1. The wavelength of this light will be
   1. 500 nm (b) 500 m (c) 200nm (d) 5xl07m
2. Rutherford’s model of atom failed because
   1. the atom did not have a nucleus and electrons
   2. it did not account for the attraction between protons and neutrons
   3. it did not account for the stability of the atom
   4. there is actually no space between the nucleus and the electrons
3. Bohr model of atom is contradicted by
   1. Planck’s quantum theory (b) dual nature of matter

(c) Heisenberg’s uncertainty principle (d) all of the above

1. Splitting of spectral lines when atoms are subjected to strong electric ield is called,
   1. Zeeman efect (b) Stark efect

(c) Photoelectric efect (d) Compton efect

1. In the ground state of an atom, the electron is present
   1. in the nucleus (b) in the second shell

(c) nearest to the nucleus (d) farthest from the nucleus

1. Quantum number values for 2p orbitals are
   1. n = 2,  = 1 (b) n = 1,  = 2

(c) n = 1,  = 0 (d) n = 2,  = 0

1. Orbitals having same energy are called
   1. hybrid orbitals (b) valence orbitals

(c) degenerate orbitals (d) d-orbitals

1. When 6d orbital is complete, the entering electron goes into (a) 7f (b) 7s (c) 7p (d) 7d

Q2. Fill in the blanks with suitable words.

* 1. b-particles are nothing but \_\_\_\_\_\_\_\_\_\_\_ moving with a very high speed.
  2. The charge on one mole of electrons is\_\_\_\_\_\_\_\_\_\_\_coulombs.
  3. The mass of hydrogen atom is\_\_\_\_\_\_\_\_\_\_\_\_\_ grams.
  4. The mass of one mole of electrons is\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ .
  5. Energy is \_\_\_\_\_\_\_\_\_\_\_ when electron jumps from higher to a lower orbit.
  6. The ionization energy of hydrogen atom can be calculated from\_\_\_\_\_\_model of atom.
  7. For d-subshell, the azimuthal quantum number has value of \_\_\_\_\_\_\_\_\_\_\_.
  8. The number of electrons in a given subshell is given by formula\_\_\_\_\_\_\_\_\_\_ .(ix) The electronic coniguration of H+ is\_\_\_\_\_\_\_\_\_\_\_ .

Q3. Indicate true or false as the case may be.

* 1. A neutron is slightly lighter particle than a proton.
  2. A photon is the massless bundle of energy but has momentum.
  3. The unit of Rydberg constant is the reciprocal of unit of length.
  4. The actual isotopic mass is a whole number.
  5. Heisenberg’s uncertainty principle is applicable to macroscopic bodies.
  6. The nodal plane in an orbital is the plane of zero electron density.
  7. The number of orbitals present in a sublevel is given by the formula (2 + 1).
  8. The magnetic quantum number was introduced to explain Zeeman and Stark efect.
  9. Spin quantum number tells us the direction of spin of electron around the nucleus.

Q 4: Keeping in mind the discharge tube experiment, answer the following questions.

1. Why is it necessary to decrease the pressure in the discharge tube to get the cathode rays?
2. Whichever gas is used in the discharge tube, the nature of the cathode rays remains the same. Why?
3. Why e/m value of the cathode rays is just equal to that of electron?
4. How the bending of the cathode rays in the electric and magnetic ields shows that they are negatively charged?
5. Why the positive rays are also called canal rays?
6. The e/m value of positive rays for diferent gases are diferent but those for cathode rays the e/m values are the same. Justify it.
7. The e/m value for positive rays obtained from hydrogen gas is 1836 times less than that of cathode rays. Justify it.

Q5 (a) Explain Millikan’s oil drop experiment to determine the charge of an electron.

1. What is J.J Thomson’s experiment for determining e/m value of electron?
2. Evaluate mass of electron from the above two experiments.

Q6 (a) Discuss Chadwick’s experiment for the discovery of neutron. Compare the properties of electron, proton and neutron.

(b) Rutherford’s atomic model is based on the scattering of a-particles from a thin gold foil. Discuss it and explain the conclusions.

Q7. (a) Give the postulates of Bohr’s atomic model. Which postulate tells us that orbits are stationary and energy is quantized?

1. Derive the equation for the radius of nth orbit of hydrogen atom using Bohr’s model.
2. How does the above equation tell you that
   1. radius is directly proportional to the square of the number of orbit.
   2. radius is inversely proportional to the number of protons in the nucleus.
3. How do you come to know that the velocities of electrons in higher orbits, are less than those in lower orbits of hydrogen atom?
4. Justify that the distance gaps between diferent orbits go on increasing from the lower to the higher orbits.

Q8 Derive the formula for calculating the energy of an electron in nth orbit using Bohr’s model. Keeping in view this formula explain the following:

1. The potential energy of the bounded electron is negative.
2. Total energy of the bounded electron is also negative.
3. Energy of an electron is inversely proportional to n2, but energy of higher orbits are always greater than those of the lower orbits.
4. The energy diference between adjacent levels goes on decreasing sharply. Q9. (a) Derive the following equations for hydrogen atom, which are related to the (i) energy diference between two levels, n1 and n2.
5. frequency of photon emitted when an electron jumps from n2to n1.
6. wave number of the photon when the electron jumps from n2 to n1.

(b) Justify that Bohr’s equation for the wave number can explain the spectral lines of Lyman, Balmer and Paschen series.

Q10. (a) What is spectrum. Diferentiate between continuous spectrum and line spectrum.

1. Compare line emission and line absorption spectra.
2. What is the origin of line spectrum?

Q11. (a) Hydrogen atom and He+ are mono-electronic system, but the size of He+ is much smaller than H+, why?

(b) Do you think that the size of Li+2 is even smaller than He+? Justify with calculations.

Q12. (a) What are X-rays? What is their origin? How was the idea of atomic number derived from the discovery of X-rays?

(b) How does the Bohr’s model justify the Moseley’s equation?

Q13. Point out the defects of Bohr’s model. How these defects are partially covered by dual nature of electron and Heisenberg’s uncertainty principle?

Q14. (a) Briely discuss the wave mechanical model of atom. How has it given the idea of orbital.

Compare orbit and orbital.

1. What are quantum numbers? Discuss their signiicance.
2. When azimuthal quantum number has a value 3, then there are seven values of magnetic quantum number. Give reasons.

Q15. (a) Discuss rules for the distribution of electrons in energy subshells and in orbitals. (b) What is (n + ) rule. Arrange the orbitals according to this rule. Do you think that this rule is applicable to degenerate orbitals?

(c) Distribute electrons in orbitals of 57La, 29Cu, 79Au, 24Cr, 531, 86Rn.

Q16 Draw the shapes of s, p and d-orbitals. Justify these by keeping in view the azimuthal and magnetic quantum numbers.

Q17 A photon of light with energy 10-19 J is emitted by a source of light.

(a) Convert this energy into the wavelength, frequency and wave number of the photon in terms of meters, hertz and m-1, respectively.

(Ans:1.51xl014s-1; 1.98x10-6m; 5xl05m-1) (b) Convert this energy of the photon into ergs and calculate the wavelength in cm, frequency in Hz and wave number in cm-1.

[h = 6.626x 10-34 Js or 6.625x 10-27 ergs, c = 3x108 ms-1 or 3x 10+10 cms-1]

(Ans:1.51xl014s-1; 1.98xl0-4cm; 5xl03cm-1) Q18 The formula for calculating the energy of an electron in hydrogen atom given by Bohr’s model

###### -m e2 4

En = 8e02h n2 2

Calculate the energy of the electron in irst orbit of hydrogen atom. The values of various parameters are same as provided in Q19.

(Ans:-2.18xlO-18J) Q 19 Bohr’s equation for the radius of nth orbit of electron in hydrogen atom is

###### rn =∈p0 e mh n22 2

(a) When the electron moves from n = 1 to n = 2, how much does the radius of the orbit increases.

(Ans: 1.587 Ao ) (b) What is the distance travelled by the electron when it goes from n=2 to n=3 and n=9 ton=10?

[e0 = 8.85x 10-12 c2J-1 m-1 , h = 6.624 x.10-34 js, p = 3.14, m = 9.108x 10-31 kg, e = 1.602 x 10-19c] while doing calculations take care of units of energy parameter.

[J = kgm2 s-2, c = kg1/2 m3/2 s-1]

(Ans: 2.65 Ao ; 10.05 Ao ) Q 20 Answer the following questions, by performing the calculations.

1. Calculate the energy of irst ive orbits of hydrogen atom and determine the energy diferences between them.
2. Justify that energy diference between second and third orbits is approximately ive times smaller than that between irst and second orbits.
3. Calculate the energy of electron in He+ in irst ive orbits and justify that the energy diferences are diferent from those of hydrogen atom.
4. Do you think that groups of the spectral lines of He+ are at diferent places than those for hydrogen atom? Give reasons.

Q 21 Calculate the value of principal quantum number if an electron in hydrogen atom revolves in an orbit of energy- 0.242 xlO-18 J.

(Ans:n=3) Q 22 Bohr’s formula for the energy levels of hydrogen atom for any system say H, He+,Li2+ ,etc. is

En = -Z e m22 4

###### 8e0 h n2 2

or

En = -K nZ22 

For hydrogen:Z = 1 and for He+, Z = 2.

1. Draw an energy level diagram for hydrogen atom and He+ .
2. Thinking that K = 2.18 x 10-18J, calculate the energy needed to remove the electron from hydrogen atom and from He+.

(Ans: 2.18 x 10-18J; 8.72x10-18J)

1. How do you justify that the energies calculated in (b) are the ionization energies of H and He+? (d) Use Avogadro’s number to convert ionization energy values in kJmol-1 for H and He+.

(Ans: 1313.3kJmol-1; 5249.4kJmol-1) (e) The experimental values of ionization energy of H and He+ are 1331 kJ mol-1 and 5250 kJ mol-1, respectively. How do you compare your values with experimental values?

(Ans: 5249kJ mol-1) Q 23 Calculate the wave number of the photon when the electron jumps from

(i) n = 5 to n = 2. (Ans: 2.3 x 106 m-1) (ii) n = 5 to n = 1 (Ans: 1.05 x 107 m-1 )

In which series of spectral lines and spectral regions these photons will appear.

(Ans: (i) Balmer Series (ii) Lyman Series) Q 24 A photon of a wave number 102.70 x 10 m is emitted when electron jumps from higher to n = 1.

(a) Determine the number of that orbit from where the electron falls.

(Ans: n=4) (b) Indicate the name of the series to which this photon belongs.

(Ans: Lyman series) (c) If the electron will fall from higher orbit to n = 2, then calculate the wave number of the photon emitted. Why this energy diference is so small as compared to that in part (a)?

(Ans: 20.5 x 105m-1) Q 25. (a) What is de-Broglie’s wavelength of an electron in meters travelling at half a speed of light? [m = 9.109 x 10-31 kg , c = 3 x 108 ms-1]

(Ans: l=0.048 Ao ) (b) Convert the mass of electron into grams and velocity of light into cms-1 and then calculate the wavelength of an electron in cm. (Ans:0.048x10-8 cm)

(c) Convert the wavelength of electron from meters to

(i) nm (ii) Ao (iii) pm. o

(Ans: 0.0048nm; 0.048; 4.85A pm)