2. ATOMIC STRUCTURE

1. INTRODUCTION

The word atom in Greek means indivisible, i.e. an ultimate particle which cannot be further subdivided. This idea of all matter ultimately consisting of extremely small particles was conceived by ancient Indian and Greek philosophers. The old concept was put on firm footing by John Dalton with his atomic theory that was developed by him during the years 1803–1808.

1.1 Dalton's Atomic Theory

Dalton's atomic theory (1808) is based on the following two laws: law of conservation of mass and law of definite proportions. He also proposed law of multiple proportions, as a logical consequence of his theory.

(a) Every element is composed of extremely small indestructible particles called atoms ('atom' in Greek means indivisible).

(b) Atoms of any one element are all similar but they differ from atoms of another element.

(c) Atoms of each element are fundamental particles, have a characteristic mass but do not have any structure.

(d) Atoms of various elements take part in a chemical reaction to form compound (which is called molecule).

(e) In any compound, the relative number and kinds of atoms are constant.

2. DISCOVERY OF FUNDAMENTAL PARTICLES

2.1 Cathode Rays – Discovery of Electron

(a) In mid-1800s, scientists (William Crookes 1879, Julius Plucker 1889) started to study the discharge of electricity through partially evacuated tubes. Gases are normally poor conductor of electricity and they do not conduct electricity under normal pressure even with an applied potential of 1000 volt. However when the pressure was reduced to 10^{-2} mm at a potential of 1000 volt, Crookes and Plucker noticed that:

(i) From the cathode surface a glow surrounding the cathode began and the space left between the glow and cathode was named Crookes dark space. Under this condition electric current starts to flow from one electrode to other.

(ii) When the pressure is sufficiently low, the glow fills whole of the tube.

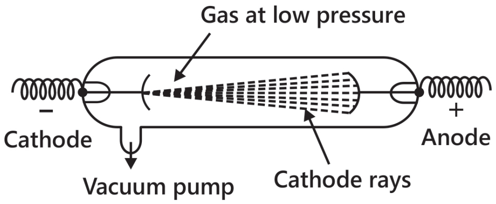


Figure 2.1: Cathode ray tube

Subsequently Thomson (1897) carried out the discharge through a vacuum tube which was filled with a gas at very low pressure (10^{-2} to 10^{-3} mm); he noticed the emission of invisible rays which produced fluorescence on the glass and influenced photographic plate. These rays were called cathode rays.

Important characteristics of cathode rays are as follows:

(a) Cathode rays travel in straight lines with high speed of the order of 10^7 ms^{-1}, producing shadows of the objects placed in their path.

(b) Cathode rays can pass through thin layers of matter.

(c) Cathode rays are emitted from the surface of the cathode; their direction is not affected by the position of the anode.

(d) Cathode rays have high kinetic energy and therefore:

- **(i)** They can exert mechanical pressure on the object on which they fall.
- **(ii)** They can produce heat when stopped by matter.
- **(iii)** They can ionize a gas.

(e) Cathode rays are deflected, both, by electric and magnetic fields.

(f) Cathode rays produce fluorescence when they fall on certain substances like ZnS. The color of fluorescence varies with the chemical nature of substance.

(g) Cathode rays can produce chemical changes and thus they affect photographic plates.

(h) Cathode rays produce X-rays, when they strike a metal target of high atomic number such as tungsten, which are highly penetrating. In 1897 J. J. Thomson determined the e/m value (charge/mass) of the electron by studying the deflection of cathode rays in electric and magnetic fields. The value of e/m has been found to be − 1.7588 × 10^8 coulomb/g.

2.1.1 Millikan's Oil-Drop Experiment

In 1909, the first precise measurement of the charge on an electron was made by Robert A. Millikan using his oil drop experiment. The charge on the electron was calculated to be − 1.6022 × 10^{-19} coulomb. An electron has the smallest charge known; so it was, designated as unit negative charge.

Mass of the electron: The mass of the electron is calculated from the values of e/m.

$$\text{e. m} = e = \frac{e}{e/m} = \frac{-1.6022\times10^{-19}}{-1.7588\times10^{8}} = 9.1096 \times 10^{-28}\text{ g or } 9.1096 \times 10^{-31}\text{ kg}$$

This is known as the rest mass of the electron; that is, the mass of the electron when it is moving with low speed. For calculating the mass of a moving electron, the following formula is used.

Mass of moving electron = $\dfrac{\text{rest mass of electron}}{\sqrt{1-\left(\frac{\upsilon}{c}\right)^2}}$, where υ is the velocity of the electron and c is the velocity of light. When υ is equal to c, mass of the moving electron is infinity and when the velocity of the electron becomes greater than c, the mass of the electron becomes imaginary.

Note: An electron can, thus be defined as a subatomic particle which carries charge − 1.60 ×10^{-19} coulomb, that is, one unit negative charge and has mass 9.1 × 10^{-19} g, that is, $\frac{1}{1837}$ the mass of the hydrogen atom (0.000549 amu).

2.2 Discovery of Protons – Positive Rays

(a) Goldstein (1886) repeated the discharge tube experiment but he used perforated cathode and noticed the emission of positive rays or canal rays.

Note: These rays do not originate from anode, and so it is wrong to call them anode rays.

(b) The specific charge (e/m) of canal rays particles varied with nature of gas and was found to be maximum if H_2 was used.

(c) The positive rays particles were thus, called positively charged gaseous atoms left after the removal of electron or ionized gaseous atoms. However, if H_2 gas is used in discharges, the positive rays particles are named as protons (usually represented as P).

(d) Thus, a subatomic particle, that is a fundamental constituent of all matter, is called a proton; it has a mass 1.673×10^{-27} kg and charge $+ 1.603 \times 10^{-19}$ C.

PLANCESS CONCEPTS

- The specific charge (e/m) of proton is 9.58×10^{7} C/kg.
- Mass of 1 mole proton= $N \times m_p = 6.023 \times 10^{23} \times 1.673 \times 10^{-27}$ kg $= 1.0076 \times 10^{-3}$ kg = 1.0076 g.
- The radius of proton = 1.53×10^{-13} cm.
- The volume of proton = $\frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (1.53 \times 10^{-13})^3 = 1.50 \times 10^{-38}$ cm^3.
- The charge on positive rays is usually +1 but it may have +2, +3 values.

Saurabh Gupta (JEE 2010, AIR 443)

The TV QUESTION

Q. What is the basic principle of a television picture tube or fluorescent light tubes?

Ans. The television picture tube is a cathode ray tube; the picture is produced due to fluorescence on the television screen coated with suitable material. Likewise florescent light tubes are also cathode ray tubes. These are coated inside with suitable materials which produce visible light when hit with cathode rays.

3. EARLIER MODELS OF ATOMS

3.1 Thomson's Model

After the discovery of protons and electrons, Thomson in 1898 proposed a watermelon model; the atom is considered as a sphere of positive charge with the electrons distributed within the sphere of radius of 10^{-10} m so as to give the most stable electrostatic agreement. In this model, the atom is visualized as a pudding or cake of positive charge with raisins (electrons) embedded in it. A major point of this model is that the mass of atom is considered to be spread uniformly over the atom.

3.2 Rutherford's Experiment

Rutherford conducted a series of experiments using α-particles. A beam of α-particles was directed against a thin foil of gold, platinum, silver, or copper. The foil was surrounded by a circular fluorescent zinc screen. Whenever an α-particle struck the screen, it produced a flash of light.

The following observations were made:

(a) Most of the α-particles went straight without suffering any deflection.

(b) Some of them were deflected through small angles.

(c) A very small number (about 1 in 20,000) did not pass through the foil at all but suffered large deflections or even rebound.

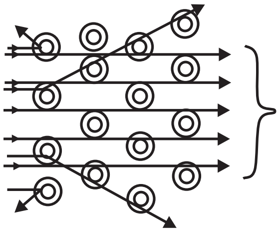


Figure 2.2: Gold leaf experiment

Following conclusions were drawn from these observations:

(a) Many of the particles went straight through the metal foil undeflected, indicating that there must be very large empty space within the atom.

(b) Some of the α-particles were deflected from their original paths through moderate angles, indicating that whole of the positive charge is concentrated in a space called nucleus. It is proposed to be present at the center of the atom.

(c) A very small number of the α-particles suffered strong deflections or even rebound on their path indicating that the nucleus is rigid and α-particles recoil due to direct collision with the positively charged heavy mass.

<u>Note:</u> Information of Rutherford's scattering equation can be memorized by the following relations:

(i) Kinetic energy of α-particles: $N = K_1/[(1/2)m\upsilon^2]^2$

(ii) Scattering angle 'θ': $N = K_2 / [(\sin^4(\theta / 2)]$

(iii) Nuclear charge: $N = K_3(Ze)^2$

Here, N = Number of α-particle striking the screen and K_1, K_2 and K_3 are the constants.

3.3 Moseley's Experiment

Moseley studied the X-ray spectra of 38 different elements, starting from aluminium to gold by measuring the frequency of principal lines of a particular series (the a-lines in the k-series) of the spectra. He observed that the frequency of the particular spectral line was related to the serial number of the element in the periodic table which he termed atomic number (Z). He presented the following relationship

$$\sqrt{\mathbf{v}}=a(Z-b)$$

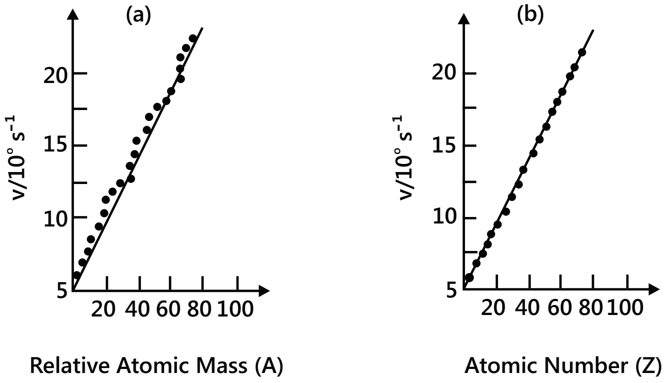


Figure 2.3: Moseley's plots

where ν = frequency of X-rays, Z = atomic number, a and b are constants. When the values of square roots of the frequency were plotted against atomic number of the element producing X-rays, a straight line was obtained. It was pointed out that the atomic number of an element is equal to the total positive charge of the nucleus.

PLANCESS CONCEPTS

Atomic number of the element
= Serial number of the element in periodic table
= Charge on the nucleus of the atom of the element
= Number of protons present in the nucleus of the atom of the element
= Number of extra nuclear electrons present in the atom of the element

Neeraj Toshniwal (JEE 2009, AIR 21)

3.4 Discovery of Neutron and Rutherford's Model

Chadwick bombarded beryllium with a stream of α-particles. He observed that the produced penetrations were not affected by electric and magnetic fields. These radiations consisted of neutral particles, which were called neutrons.

$$\underset{\text{Beryllium}}{{}^{9}_{4}\text{Be}} + \underset{\alpha\text{–particle}}{{}^{4}_{2}\text{He}} \rightarrow \underset{\text{Carbon}}{{}^{12}_{6}\text{C}} + \underset{\text{Neutron}}{{}^{1}_{0}\text{n}}$$

The mass of the neutron was determined to be 1.675×10^{-24} g, that is, nearly equal to the mass of proton.

Thus a neutron is a subatomic particle having a mass of 1.675×10^{-24} g, approximately 1 amu or nearly equal to the mass of proton or hydrogen atom and carrying no electrical charge. The e/m of neutron is zero.

Rutherford's Model of Atom: Rutherford proposed a model of the atom known as nuclear atomic model. As per this model,

(a) An atom consists of a positively charged heavy nucleus where all the protons and neutrons are present. The number of the positive charge on the nucleus is different for different atoms.

(b) The volume of the nucleus is very small and is only a very small fraction of the total volume of the atoms.

$$\frac{\text{Diameter of atom}}{\text{Diameter of the nucleus}} = \frac{10^{-8}\text{ cm}}{10^{-13}\text{ cm}} = 10^{5}$$

Thus, the diameter of an atom is 100,000 times the diameter of the nucleus.

The radius of a nucleus is proportional to the cube root of the mass number.

Radius of the nucleus = $1.33 \times 10^{-13} \times A^{1/3}$ cm where A is the mass number.

(c) There is an empty space around nucleus called extra nuclear part, where electrons are present. The number of electrons in an atom is always equal to the number of protons present in the nucleus. The volume of the atom is about 10^{15} times the volume of the nucleus.

$$\frac{\text{Volume of the atom}}{\text{Volume of the nucleus}} = \frac{(10^{-8})^{3}}{(10^{-13})^{3}} = \frac{10^{-24}}{10^{-39}} = 10^{15}$$

(d) The electrons revolve around the nucleus in closed orbits with high speeds. Centrifugal force is acting on the revolving electrons and is being counterbalanced by the force of attraction between electrons and the nucleus.

This model is similar to solar system; the nucleus representing the Sun and the electrons the Planets. The electrons are, therefore, generally referred to as planetary electrons.

Drawbacks of Rutherford's Model

(a) According to wave theory, when a charged particle moves under the influence of an attractive force, it loses energy continuously in the form of electromagnetic radiations. Thus, the electron which moves in an attractive field (created by protons present in the nucleus) will emit radiations.

As result the electron will lose energy at every turn and move closer and closer to the nucleus following a spiral path and finally fall into the nucleus, thereby making the atom unstable. But the atom is quite stable meaning the electrons do not fall into nucleus, thus this model does not explain the stability of the atom.

(b) If the electrons lose energy continuously, the observed spectra should be continuous. But the observed spectra consists of well-defined lines of definite frequency. Hence, in an atom, the loss of energy by the electrons is not continuous.

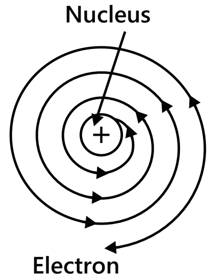


Figure 2.4: Spiral path of electron

3.5 Atomic Number and Mass Number

Atomic number of an element = Total number of protons present in the nucleus

= Total number of electrons present in the neutral atom

Mass number of an element = No. of protons + No. of neutrons

3.6 Isotopes, Isobars, Isotones and Isoelectronic

Such atoms of the same element having the same atomic number but different mass numbers are known as isotopes. Such atoms of different elements having different atomic numbers, but same mass number, e.g. $^{40}_{18}Ar$, $^{40}_{19}K$, $^{40}_{20}Ca$, are known as isobars. Such atoms of different elements containing the same number of neutrons, e.g. $^{14}_{6}C$, $^{15}_{7}N$, $^{16}_{8}O$, are called isotones. Each of these atoms contains eight neutrons. They differ in atomic number as well mass number. Such species (atoms or ions) containing the same number of electrons, e.g. O^{2-}, F^{-}, Na^{+}, Mg^{2+} Al^{3+}, Ne are called isoelectronic. Each of these contains 10 electrons each and so they are isoelectronic.

PLANCESS CONCEPTS

- **Retain in Memory:** Isotopes have same number of protons but different number of neutrons. Isobars have different number of protons as well as different number of neutrons. Isotones have different number of protons but same number of neutrons.
- **Retain in Memory:** In a neutral atom ($^{A}_{Z}X$), No. of protons = No. of electrons = Atomic no.

  In a negative ion (X^{n-}), No. of electrons > No. of protons.

  No. of electrons = Z +n

  In a positive ion (M^{n+}), No. of electrons < No. of protons.

  No. of electrons = Z − n

  However, No. of protons is always = Z and No. of neutrons is always = A − Z.

Nikhil Khandelwal (JEE 2009, AIR 94)

Illustration 1: Find out the atomic number, mass number, number of protons, electrons and neutrons present in the element with the notation $^{238}_{92}U$. **(JEE MAIN)**

Sol: Number of protons = Number of electrons = Atomic number (Z)

Number of neutrons = Mass number − Atomic number

Atomic number (Z) = 92

Mass number (A) = 238

$\therefore$ Number of protons = 92 and Number of electrons = 92

Further, A − Z = 238 − 92 = 146

Illustration 2: The nuclear radius is of the order of 10^{-13} cm while atomic radius is of the order 10^{-8} cm. If the nucleus and the atoms are assumed to be spherical, what is the fraction of the atomic volume occupied by the nucleus? **(JEE MAIN)**

Sol: Considering the spherical conditions, the volume of a sphere = $4\pi r^3/3$ where r is the radius of the sphere.

$\therefore$ Volume of the nucleus = $4\pi r^3/3 = 4\pi\ (10^{-13})^3/3\ \text{cm}^3$

Similarly, volume of the atom = $4\pi r^3/3 = 4\pi\ (10^{-8})^3/3\ \text{cm}^3$

$\therefore$ Fraction of the volume of atom occupied by the nucleus = $\dfrac{4\pi(10^{-13})^3\ /\ 3\quad \text{cm}^3}{4\pi(10^{-8})^3\ /\ 3\quad \text{cm}^3} = 10^{-15}$

4. ELECTROMAGNETIC RADIATIONS

Electromagnetic Radiations (EMR) are energy radiations which do not need any medium for propagation, e.g. visible, ultraviolet, X-rays, etc. Following are the important characteristics of EMR:

(a) All electromagnetic radiations or waves travel with the velocity of light.

(b) These consist of electric and magnetic fields that oscillate in directions perpendicular to each other and perpendicular to the direction in which the wave is travelling.

4.1 Characteristics of Waves

A wave is always characterized by the following six characteristics:

(a) **Wavelength:** The distance between two nearest crests or nearest troughs is called the wavelength. It is denoted by λ (lambda) and is measured in units of centimetre (cm), angstrom (Å), micrometre, (μm) or nanometre (nm).

1 Å = 10^{-8} cm = 10^{-10} m

1 μm = 10^{-4} cm = 10^{-6} m

1 nm = 10^{-7}cm = 10^{-9} m

1 cm = 10^{8} Å = 104 μm = 10^{7} nm

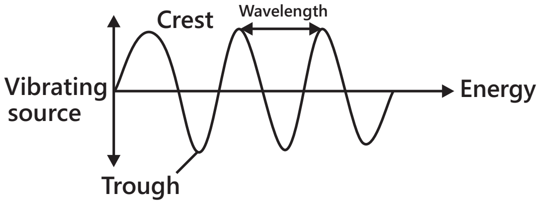


Figure 2.5: Representation of a wave and wavelength

(b) **Frequency:** It is defined as the number of waves passing through a point in one second. It is denoted by the symbol (nu) and is measured in terms of cycles (or waves) per second (cps) or hertz (Hz). $\lambda\nu$ = Distance travelled in one second = Velocity = c or $\nu = \dfrac{c}{\lambda}$

(c) **Velocity:** It is defined as the distance covered in one second by the wave. It is denoted by the letter 'c'. All electromagnetic waves travel with the same velocity, that is, 3 × 10^{10} cm/sec. $\lambda\nu = 3 \times 10^{10}$. Thus, a wave of higher frequency has shorter wavelength while a wave of lower frequency has a longer wavelength.

(d) **Wave number:** This is the reciprocal of wavelength, i.e. the number of wavelength per centimeter. It is denoted by the symbol $\bar{\nu}$ (nu bar). $\bar{\nu} = \dfrac{1}{\lambda}$. It is expressed in cm^{-1} or m^{-1}.

(e) **Amplitude:** It is defined as the height of the crest or depth of the trough of a wave. It is denoted by the letter 'A'. It determines the intensity of the radiation.

(f) **Time period:** Time taken by one wave to complete a cycle or vibration is called time period. It is denoted by T. $T = \frac{1}{\nu}$

Unit: Second per cycle.

4.2 Electromagnetic Spectrum

The arrangement of various types of electromagnetic radiations in the order of their increasing or decreasing wavelengths or frequencies is known as electromagnetic spectrum.

$$\nu \equiv 3 \times 10^{7} \text{ (cycle/sec)} \xrightarrow{\text{Frequency}} 3 \times 10^{21}$$

$$\lambda\text{(cm)} = 10^{3} \xrightarrow{\text{Wavelength}} 10^{-11}$$

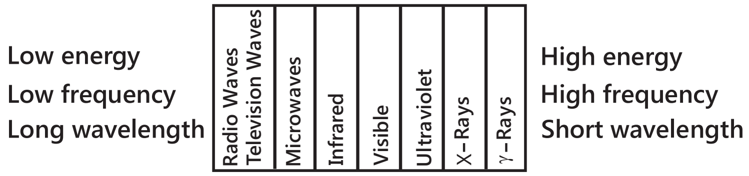


Figure 2.6: Electromagnetic spectrum

5. ATOMIC SPECTRA OF HYDROGEN

The impression produced on a screen when radiations of particular wavelengths are passed through a prism or diffraction grating is known as spectrum. It is broadly of two types: Emission spectra and Absorption spectra

Differences between emission spectrum and absorption spectrum

Emission spectrum	Absorptions spectrum
1. It gives bright lines (colored on the dark background.	1. It gives dark lines on the bright background.
2. Radiations from emitting source are analyzed by the spectroscope.	2. It is observed when the white light is passed through the substance and the transmitted radiations are analyzed by the spectroscope.
3. It may be continuous (if source emits white light) and may be discontinuous (if the source emits colored light).	3. These are always discontinuous.

5.1 Emission Spectra

It is obtained from the substances which emit light on excitation, that is, either by heating the substances on a film or by passing electric discharge through a thin filament of high melting point metal. Emission spectra are of two types:

(a) **Continuous spectra:** When white light is allowed to pass through a prism, the light gets resolved into several colours. This spectrum is a rainbow of colours, meaning violet merges into blue, blue into green and so on. This is a continuous spectrum.

(b) **Discontinuous spectra:** When gases or vapours of a chemical substance are heated in an electric arc or in a Bunsen flame, light is emitted. When a ray of this light is passed through a prism, a line spectrum is produced.

This spectrum consists of limited number of lines, each of which corresponds to a different wavelength of light. Each element has a unique line spectrum. Spectrum of hydrogen is an example of line emission spectrum or atomic emission spectrum. If an electric discharge is passed through hydrogen gas at low pressure, a bluish light is emitted. If a ray of this light is passed through a prism, a discontinuous line spectrum of many isolated sharp lines is obtained. The wavelengths of the different lines show that these lines are in the visible, ultraviolet and infrared regions. The lines observed in the hydrogen spectrum can be classified into six series.

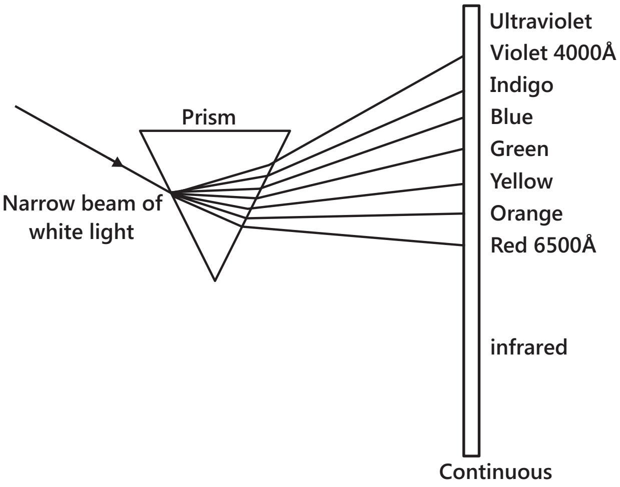


Figure 2.7: Continuous spectrum

Spectral series	Discovered by	Appearing in
Lyman series	Lyman	Ultraviolet region
Balmer series	Balmer	Visible region
Paschen series	Paschen	Infrared region
Brackett series	Brackett	Infrared region
Pfund series	Pfund	Infrared region
Humphrey series	Humphrey	Far-infrared region

5.2 Ritz Mathematical Formula

Ritz presented a mathematical formula to find the wavelengths of various hydrogen lines.

$\bar{v} = \frac{1}{\lambda} = \frac{v}{c} = \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ where, R is universal constant, known as Rydberg constant. Its value is 0.9678 cm^{-1}, n_1 and n_2 are integers (such that $n_2 > n_1$). For a given spectral series, n_1 remains constant while n_2 varies from line to line in the same series. The value of n_1 is 1, 2, 3, 4 and 5 for the Lyman, Balmer, Paschen, Brackett and Pfund series respectively. n_2 is greater than n_1 by at least 1.

Following are the values of n_1 and n_2 for various series:

Spectral series	Value of n_1	Value of n_2
Lyman series	1	2, 3, 4, 5,.....
Balmer series	2	3, 4, 5, 6,.....
Paschen series	3	4, 5, 6, 7,.....
Brackett series	4	5, 6, 7, 8,.....
Pfund series	5	6, 7, 8, 9,.....

Note: (i) Atoms give line spectra while molecules give band spectra.

(ii) Balmer, Paschen, Brackett, Pfund series are found in emission spectrum.

5.3 Absorption Spectra

When the radiations from a continuous source like a hot body (sunlight) containing the quanta of all wavelengths pass through a sample of hydrogen gas, then the wavelength missing in the emergent light gives dark lines on the bright background. This type of spectrum that contains lesser number of wavelengths in the emergent light than in incident light is called absorption spectrum.

Illustration 3: Which has a higher energy, a photon of violet light with wavelength 400 Å or a photon of red light with wavelength 7000Å? [h = 6.62×10^{-34} Js] **(JEE MAIN)**

Sol: Using photoelectric effect, $E = h\nu = h\dfrac{c}{\lambda}$

Given h = 6.62×10^{-34} Js, c = s, c = 3×10^{8} ms^{-1}

For a photon of violet light λ = 4000 Å = 4000×10^{-10} m; $E = 6.62 \times 10^{-34} \times \dfrac{3\times10^{8}}{4\times10^{-7}} = 4.96 \times 10^{-19}$

For a photon of red light, L = 7000 Å = 7000×10^{-10} m

$$E = 6.62 \times 10^{-34} \times \frac{3\times10^{8}}{7000\times10^{-10}} = 2.83\times10^{-19}\,\text{J}$$

Hence, a photon of violet light has higher energy than a photon of red light.

Illustration 4: Calculate the wavelength of the spectral line, when the electron in the hydrogen atom undergoes a transition from the energy level 4 to energy level 2. **(JEE MAIN)**

Sol: According to Rydberg equation $\dfrac{1}{\lambda} = R\left(\dfrac{1}{x^2} - \dfrac{1}{y^2}\right)$

R = 109678 cm^{-1}; x = 2; y = 4; $\dfrac{1}{\lambda} = 109{,}678\left[\dfrac{1}{4} - \dfrac{1}{16}\right] = 109{,}678\times\dfrac{3}{16}$

On solving, λ = 486 nm.

6. QUANTUM THEORY OF RADIATION

In 1905, Einstein pointed out that light can be considered to consist of a stream of particles, called photons. The energy of each photon of light depends on the frequency of the light, that is, E = hv. According to Einstein, energy is also related as $E = mc^2$ where m is the mass of photon. Thus, he pointed out that light has wave as well as particle characteristics (dual nature).

Though the wave theory successfully explains many properties of electromagnetic radiations such as reflection, refraction, diffraction, interference, polarization etc. it fails to explain some phenomena like blackbody radiation, photoelectric effect etc. A new theory which is known as quantum theory of radiation was presented by Max Planck in 1901, to explain the blackbody radiation and photoelectric effect. According to this theory, a hot body emits radiant energy not continuously but discontinuously in the form of small packets of energy called quantum (quanta in plural). The energy associated with each quantum of a given radiation is proportional to the frequency of the emitted radiation. $E \propto \nu$ or $E = h\nu$ where h is a constant known as Plank's constant. Its numerical value is 6.624×10^{-27} erg/sec. The energy emitted or absorbed by a body can be either one quantum or any whole number multiple of $h\nu$, that is, $2h\nu$, $3h\nu$, $4h\nu$,..., $nh\nu$ quanta of energy.

6.1 Photoelectric Effect

The emission of electrons from a metal surface when exposed to light radiations of appropriate wavelength is called photoelectric effect. The emitted electrons are called photoelectrons. Work function or threshold energy may be defined as the minimum amount of energy required to eject electrons from a metal surface. According to Einstein, maximum kinetic energy of the ejected electron = Absorbed energy − Work function $\frac{1}{2}mv_{max}^2 = h\nu - h\nu_0 = hc\left[\frac{1}{\lambda} - \frac{1}{\lambda_0}\right]$, where ν_0 and λ_0 are threshold frequency and threshold wavelength respectively.

Stopping potential: Stopping potential is the minimum potential at which the photoelectric current becomes zero. If ν_0 is the stopping potential, then $\nu_0 = h(\nu - \nu_0)$.

Laws of Photoelectric Effect

(a) Rate of emission of photoelectrons from a metal surface is directly proportional to the intensity of incident light.

(b) The maximum kinetic energy of photoelectrons is directly proportional to the frequency of incident radiation; also, it is independent of the intensity of light used.

(c) There is no time lag between incidence of light and emission of photoelectrons.

(d) For emission of photoelectrons, the frequency of incident light must be equal or greater than the threshold frequency.

PLANCESS CONCEPTS

If kinetic energy of the emitted photoelectrons is plotted against the frequency of the absorbed photons, a straight line of slope h is obtained as shown in Fig. 2.8 A. If kinetic energy of the photoelectrons is plotted against intensity of the incident radiation (keeping frequency constant), a horizontal line is obtained as shown in Fig. 2.8 B.

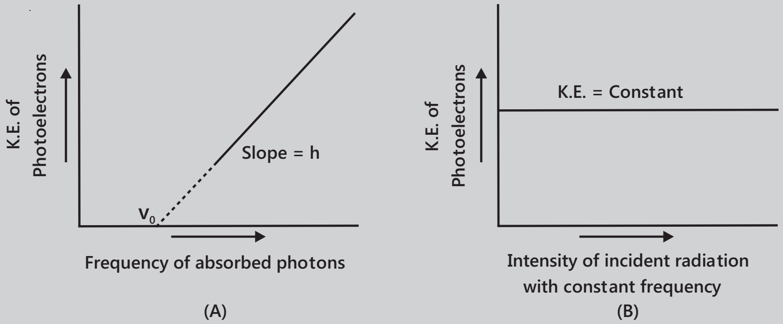


Figure 2.8: Plot of kinetic energy of photoelectrons emitted versus (A) frequency of absorbed photons and (B) intensity of the incident radiation with constant frequency

Aman Gour (JEE 2012, AIR 230)

The Heated Iron!!!

Q. When an iron bar is heated, it first becomes red, then yellow and finally begins to glow with white light and then blue light. Why?

Ans. The change in colour is because of increase in the frequency of radiation emitted on heating as red colour lies in the lower frequency region while blue colour lies in the high frequency region.

Illustration 5: When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium metal, electrons are emitted with a kinetic energy of 1.68×10^5 J mol^{-1}. What is the minimum energy needed to remove an electron from sodium? What is the maximum wavelength that will cause a photoelectron to be emitted?

(JEE MAIN)

Sol: The minimum energy needed to remove an electron is the threshold energy and the maximum wavelength would be obtained from the same equation. Thus, we use the following equations $E = h\nu = h\frac{c}{\lambda}$

For one electron, we multiply by the Avogadro's number, which gives us for one mole of photons, which is then subtracted from the kinetic energy and then divided by Avogadro's number again.

$E = E_0 + KE$

The maximum wavelength is found by the equation stated at the beginning.

Energy of a photon of radiation of wavelength 300 nm will be

$$E = h\nu = h\frac{c}{\lambda} = \frac{(6.626\times10^{-34}\,\text{Js})(3.0\times10^{8}\,\text{ms}^{-1})}{(300\times10^{-9})\text{m}} = 6.626\times10^{-19}\,\text{J}$$

$\therefore$ Energy of 1 mole of photons = $(6.626 \times 10^{-19}\ \text{J}) \times (6.022 \times 10^{23}\ \text{mol}^{-1}) = 3.99 \times 10^{5}\ \text{J mol}^{-1}$

As $E = E_0 + KE$ of photoelectrons emitted.

$\therefore$ Minimum energy (E_0) required to remove 1 mole of electrons from sodium = E-KE

$$= (3.99 - 1.68)\,10^{5}\ \text{J mol}^{-1} = 2.31\text{x}10^{5}\ \text{J mol}^{-1}$$

$\therefore$ Minimum energy required to remove one electron = $\dfrac{2.31\text{x}10^{5}\ \text{J mol}^{-1}}{6.022\text{x}10^{23}\ \text{mol}^{-1}} = 3.84\text{x}10^{-19}\ \text{J}$

The wavelength corresponding to this energy can be calculated using the formula, $E = h\nu = h\dfrac{c}{\lambda}$

$\therefore \lambda = \dfrac{hc}{E} = \dfrac{(6.626\text{x}10^{-34}\,\text{Js})(3.0\text{x}10^{8}\,\text{ms}^{-1})}{3.84\text{x}10^{-19}} = 5.17\text{x}10^{-7}\text{m} = 517\text{x}10^{-9}\ \text{m} = 517\text{nm}$ which corresponds to green light.

Illustration 6: O_2 undergoes photochemical dissociation into one normal oxygen atom and one excited oxygen atom. 1.976 eV more energetic than normal. The dissociation of O_2 into two normal atoms of oxygen requires 498 kJ mol^{-1}. What is the maximum wavelength effective for photochemical dissociation of O_2? **(JEE MAIN)**

Sol: Frame the dissociation reaction of oxygen and arrange the data. Calculate the energy required for the simple dissociation and then add it to the extra energy quoted in the question. Using this energy, solve for maximum wavelength.

Given $O_2 \longrightarrow O_{\text{Normal}} + O_{\text{Excited}}$; H = ?

$O_2 \longrightarrow ON + ON$; $\Delta H = 498$ kJ/mol

Energy required for simple dissociation of O_2 into two normal atoms = $\dfrac{498\times10^{3}}{6.023\times10^{23}} = 8.268\times10^{-19}\,\text{J}\ \ \text{mol}^{-1}$ Since, one atom has more energy (1.967 eV) in excited state when photochemical dissociation takes place, then energy required for photochemical dissociation of $O_2 = 8.268 \times 10^{-19} + 1.967 \times 1.602 \times 10^{-19} = 114.19 \times 10^{-20}$ J

Now using $E = \dfrac{hc}{\lambda}$; $114.19 \times 10^{-20} = \dfrac{6.626\times10^{-34}\times3.0\times10^{8}}{\lambda}$; $\lambda = 1740.52 \times 10^{-10}$ m = 1740.52 Å

7. BOHR'S ATOMIC MODEL

Bohr proposed a quantum mechanical model of the atom, to overcome the objections of Rutherford's model and to explain the hydrogen spectrum. This model was based on the quantum theory of radiation and the classical laws of physics. The important postulates on which Bohr's model is based are the follows:

(a) The atom has a nucleus where all the protons and neutrons are present. The size of the nucleus is very small. It is present at the center of the atom.

(b) Negatively charged electrons are revolving around the nucleus in a similar way as the Planets are revolving around the Sun. The path of the electron is circular. The force of attraction between the nucleus and the electron is equal to centrifugal force of the moving electron.

Force of attraction toward nucleus = Centrifugal force

(c) Out of infinite number of possible circular orbits around the nucleus, the electron can revolve only on those orbits whose angular momentum is an integral multiple of $\frac{h}{2\pi}$, that is, $mvr = n\frac{h}{2\pi}$ where

m = Mass of the electron, v = Velocity of electron, r = Radius of the orbit and n = 1, 2, 3,…. number of the orbit. The angular momentum can have values such as, $\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}$, etc., but it cannot have fractional value. Thus, the angular momentum is quantized. The specified or circular orbits (quantized) are called stationary orbits.

(d) When the electron remains in any one of the stationary orbits, it does not lose energy. Such a state is called ground of normals.

In the ground state potential energy of electron will be minimum, hence it will be the most stable state.

(e) Each stationary orbit is associated with a definite amount of energy. The greater is the distance of the orbit from the nucleus, more shall be the energy associated with it. These orbits are also called energy levels and are numbered as 1, 2, 3, 4, ….or K, L, M, N,… from nucleus outward, i.e. $E_1 < E_2 < E_3 < E_4$ …. $(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3)$.

(f) The emission or absorption of energy in the form of radiation can occur only when an electron jumps from one stationary orbit to another. $\Delta E = E_{high} - E_{low} = h\nu$; energy is absorbed when the electron jumps from an inner to an outer orbit and it is emitted when the electron moves from an outer to an inner orbit.

When the electron moves from an inner to an outer orbit by absorbing definite amount of energy, the new state of the electron is said to be excited state.

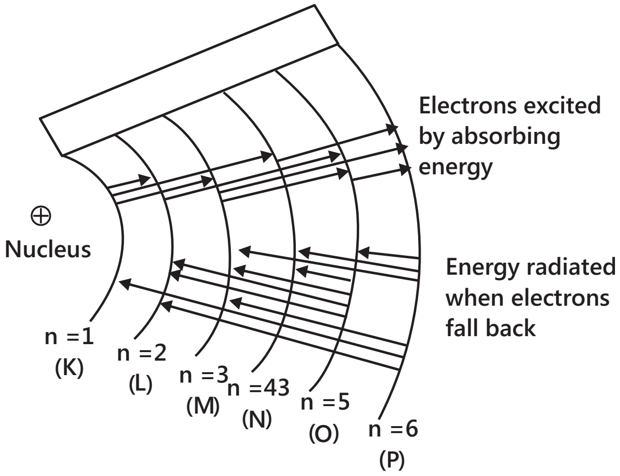


Figure 2.9: Excitation and De- excitation

7.1 Some Important Results of Bohr's Equation

Consider a H-atom in which an electron of mass 'm', charge 'e' revolving round a nucleus of charge Ip (unit + ve) with a tangential velocity 'v' at a distance 'r' from the nucleus. The necessary centripetal force required to keep the electron moving is provided by the electrostatic attraction between the electron and the nucleus,

i.e. $$\frac{e^2}{r^2} = \frac{mv^2}{r} \quad \text{... (i)}$$

Since $$mvr = \frac{nh}{2\pi} \quad \text{... (ii)}$$

(a) **The radius:** Therefore, by Eqs. (1) and (2),

$$\frac{e^2}{r^2} = m\frac{n^2h^2}{m^2.r^2 4\pi^2.r} \quad \text{or} \quad r_n = \frac{n^2h^2}{4\pi^2me^2} = n^2\frac{h^2}{4\pi^2me^2} \quad \text{... (iii)}$$

or $r_n = n^2 \times r_1$ ... (iv)

Also, $r_1 = \dfrac{h^2}{4\pi^2 me^2}$

For H-atom; $r_{1H} = \dfrac{(6.626\times10^{-27})^2}{4\times(3.14)^2\times(9.108\times10^{-28})\times(4.803\times10^{-10})^2}$; $r_{1H} = 0.529 \times 10^{-8}$ cm = 0.529 Å

For H like atoms; (He^+, Li^{2+}, Be^{3+},..., etc.). The charge on nucleus is +Z and therefore, $\dfrac{Ze^2}{r^2} = \dfrac{mv^2}{r}$
Similarly, we get

$$r_n = \frac{n^2h^2}{4\pi^2 mZe^2} \quad \text{... (v)}$$

$$\text{Or } r_{nH-\text{like atom}} = r_{nH} / Z \quad \text{... (vi)}$$

where Z is atomic number of atom

(b) Velocity: The velocity of an electron in nth orbit of H-atom can be derived by Eqs. (1) and (2), as

$$v_n = \frac{2\pi e^2}{nh} \quad \text{... (vii)}$$

$$= \frac{2\times3.14\times(4.803\times10^{-10})^2}{n\times6.626\times10^{-27}} = \frac{2.18\times10^8}{n}\text{cm sec}^{-1};\ \therefore \quad v_{1H} = 2.18 \times 10^8 \text{ cm sec}^{-1} \quad \text{... (viii)}$$

$$\text{Also, } v_n = \frac{v_1}{n} \text{ For H like atom; } \quad v_n = \frac{2\pi Ze^2}{nh} \quad \text{... (ix)}$$

$$\text{Or } v_{n_{\text{H like atom}}} = v_{n_{z-\text{atom}}} \times Z \quad \text{... (x)}$$

(c) Time required to complete one revolution by an electron round nucleus in an orbit: Let $2\pi r_n$ be the circumference of orbit and vn is velocity of electron in that orbit T for one revolution in an orbit = $\dfrac{2\pi r_n}{v_n}$ ... (xi)

(d) Number of revolutions per second made by an electron round the nucleus in an orbit:

$$\text{Number of revolutions} = \frac{v_n}{2\pi r_n} \quad \text{... (xii)}$$

(e) Energy: Total energy ET of an electron for H-atom in a shell can be given by,

$$E_T = \text{Potential energy + Kinetic energy; } E_T = \left(-\frac{e^2}{r_n}\right) + \left(\frac{1}{2}.\frac{e^2}{r_n}\right) = -\frac{e^2}{2r_n} \quad \text{... (xiii)}$$

$$\text{By Eqs. (3) and (13), } E_T = \frac{2\pi^2 me^4}{n^2h^2} \quad \text{... (xiv)}$$

$$= -\frac{2\times(3.14)^2\times9.108\times10^{-28}\times(4.803\times10^{-10})^4}{n^2\times(6.625\times10^{-27})^2}\text{er} = -\frac{21.77\times10^{-12}}{n^2}\text{erg} = -\frac{21.77\times10^{-19}}{n^2}\text{J (107 erg = 1 J)}$$

$$E_T = -\frac{13.6}{n^2}\text{eV } (1.602 \times 10^{-19} \text{ J = 1 eV}); \ E_1H = -13.6 \text{ eV} \quad \text{... (xv)}$$

For H like atom; ET = $-\frac{2\pi^2 mZ^2e^4}{n^2h^2}$

$$E_T = \frac{-21.77\times10^{-12}}{n^2}\times Z^2 \quad \text{erg} \qquad \text{... (xvi)}$$

Also, for H-atom: $E_n \propto -\frac{1}{n^2}$ and $E_n = \frac{E_1}{n_2}$; E_1 for H-atom $= -\frac{13.6}{1^2} = -13.6$ eV

E_2 for H-atom $= -\frac{13.6}{2^2} = 3.4$ eV ; E_3 for H-atom $= -\frac{13.6}{3^2} = -1.51$ eV

E_∞ for H-atom $= -\frac{13.6}{\infty^2} = 0$ eV ; E_1 for H like atom = E_1 for H × Z_2 = −13.6 × Z_2 eV ... (xvii)

(f) Frequency (ν), wavelength (λ) and wave number $(\overline{\nu})$ during electron transition:

Furthermore, $\Delta E = h\nu = E_{n_2} - E_{n_1}$ ... (xviii)

$$\Delta E = h\nu = \frac{hc}{\lambda} = \frac{2\pi^2 me^4}{h^2}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right] \qquad \text{... (xix)}$$

$$\text{Or } \overline{\nu} = \frac{1}{\lambda} = \frac{2\pi^2 me^4}{ch^3}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]\text{cm}^{-1} \qquad \text{... (xx)}$$

where $\overline{\nu}$ is wave number, λ is wavelength of light involved during electronic transition.

$$\frac{1}{\lambda} = 1.096\times10^5\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]\text{cm}^{-1} \qquad \text{... (xxi)}$$

7.2 Interpretation of Hydrogen Spectrum

Maximum number of lines produced when an electron jumps from n^{th} level to ground level is equal to $\frac{n(n-1)}{2}$.

For example, in the case of n = 4, the number of lines produced is six (4 → 3, 4 → 2, 4 → 1, 3 → 2, 3 → 1, 2 → 1). When an electron returns from n_2 to n_1 state, the number of lines in the spectrum will be equal to $\frac{(n_2-n_1)(n_2-n_1+1)}{2}$.

If the electron returns from energy level having energy E_2 to energy level having energy E_1, then the difference may be expressed in terms of energy of photon as: $E_2 - E_1 = \Delta E = h\nu$.

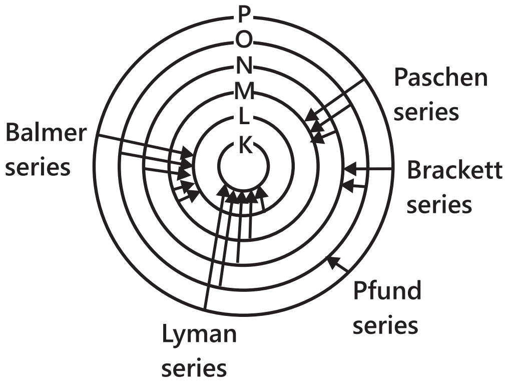


Figure 2.10: Interpretation of Hydrogen Spectrum

Or the frequency of the emitted radiation in given by $\nu = \frac{\Delta E}{h}$.

Since, ΔE can be only definite values depending on the definite energies of E_2 and E_1, ν will have only fixed values in an atom, or $\nu = \frac{c}{\lambda} = \frac{\Delta E}{h}$ or $\lambda = \frac{hc}{\Delta E}$.

Since, h and c are constants, ΔE corresponds to definite energy; thus, each transition from one energy level to another will produce a light of definite wavelength. This is actually observed as a line in the spectrum of hydrogen atom. Thus, the different spectral lines in the spectra of atoms correspond to different transitions of electrons from higher energy levels to lower energy levels.

7.3 Derivation of Rydberg Equation

Let an excited electron from n_2 shell come to the n_1 shell with the release of radiant energy. The wave number $\bar{\nu}$ of the corresponding spectral line may be calculated in the following manner:

$$\Delta E = E_2 - E_1 = (-)\frac{2\pi^2 mZ^2e^4}{n_2^2h^2} - (-)\frac{2\pi^2 mZ^2e^4}{n_1^2h^2}; \quad \frac{hc}{\lambda} = \frac{2\pi^2 mZ^2e^4}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Where $\Delta E = h\nu = \frac{hc}{\lambda}; \therefore \bar{\nu} = \frac{1}{\lambda} = 2\pi^2 mZ^2e^4\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ Or $\bar{\nu} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

where $R = \frac{2\pi^2 me^4}{ch^3}$ = Rydberg constant = 109,743 cm^{-1}

This value of R is in agreement with experimentally determined value 109,677.76 cm^{-1}. Rydberg equation for hydrogen may be given as, $\bar{\nu} = \frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

7.4 Modification of Rydberg's Equation

According to the Rydberg's equation: $\bar{\nu}_{\text{wave number}} = \frac{2\pi^2 mZ^2e^4}{ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

It can be considered that the electron and the nucleus revolve around their common center of mass. Therefore, instead of the mass of the electron, the reduced mass of the system was introduced and the equation becomes

$$\bar{\nu} = \frac{2\pi^2 \mu Z^2e^4}{2h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Reduced mass 'μ' can be calculated as, $\frac{1}{\mu} = \frac{1}{m} + \frac{1}{M}$

Where m = Mass of electron and M = Mass of nucleus. $\therefore \mu = \frac{mM}{m+M}$

Some Important Points to be Remembered

First Line of a Series

(a) First line of a series: It is the line of longest wavelength' or 'line of shortest energy'

$n_2 = (n_1 + 1)$; $\bar{\nu} = \frac{1}{\lambda_{\text{first}}} = R\left[\frac{1}{n_1^2} - \frac{1}{(n_1+1)^2}\right]$

Similarly for second, third and fourth lines, $n_2 = n_1 + 2$; $n_2 = n_1 + 3$ and $n_2 = n_1 + 4$ respectively

$\therefore$ Rydberg's equation may be written as, $\bar{\nu} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{(n_1+x)^2}\right]$ where x = Number of line in the spectrum.

e.g. x = 1, 2, 3, 4,... for first, second, third and fourth lines in the spectrum respectively.

Series Limit or Last Line of a Series

(b) Series limit or last line of a series: It is the line of shortest wavelength or line of highest energy.

For last line, $n_2 = \infty$; $\bar{\nu}_{last} = \frac{1}{\lambda_{Last}} = \frac{R}{n_1^2}$

Lyman limit = $\frac{R}{1^2}$; Balmer limit = $\frac{R}{2^2}$

Paschen limit = $\frac{R}{3^2}$; Brackett limit = $\frac{R}{4^2}$

Pfund limit = $\frac{R}{5^2}$; Humphrey limit = $\frac{R}{6^2}$

Intensity of Spectral Lines

(c) The intensities of spectral line in a particular series decrease with increase in the value of n_2, i.e. higher state e.g. **Lyman series** $(2 \rightarrow 1) > (3 \rightarrow 1) > (4 \rightarrow 1) > (5 \rightarrow 1)$,

$(n_2 \rightarrow n_1)$

Balmer series $(3 \rightarrow 2) > (4 \rightarrow 2) > (5 \rightarrow 2) > (6 \rightarrow 2)$

$(n_2 \rightarrow n_1)$ $\xrightarrow{\hspace{4cm}}$

Decreasing intensity of the spectral lines

7.5 Ionization Energy, Excitation Energy and Separation Energy

Excitation potential for $n_1 \rightarrow n_2 = \frac{E_{n_2} - E_{n_1}}{\text{Electronic charge}}$

Ionization potential for $n_1 \rightarrow \infty = \frac{E_{n_1}}{\text{Electronic charge}}$

The energy required to remove an electron from the ground state to form cation, i.e. to take the electron to infinity, is called ionization energy.

$IE = E_\infty - E_{ground}$; $IE = 0 - E_1(H) = 13.6 \text{ eV atom}^{-1} = 2.17 \times 10^{-18} \text{ J atom}^{-1}$

$$IE = \frac{Z^2}{n^2} \times 13.6 \quad eV ; \frac{I_1}{I_2} = \frac{Z_1^2}{n_1^2} \times \frac{n_2^2}{Z_2^2} ; (IE)Z = \frac{(IE)_H \times Z^2}{n^2}$$

If an electron is already present in the excited state, then the energy required to remove that electron is called separation energy. $E_{separation} = E_\infty - E_{excited}$

7.6 Limitations of Bohr's Model

(a) It does not explain the spectra of multi-electron atoms.

(b) By using a high resolving power spectroscope it is observed that a spectral line in the hydrogen spectrum is not a simple line but a collection of several lines which are very close to one another. This is known as fine spectrum. Bohr's theory does not explain the fine spectra of even the hydrogen atom.

(c) Spectral lines split into a group of inner lines under the influence of magnetic field (Zeeman effect) and electric field (Stark effect); but, Bohr's theory does not explain this.

(d) Bohr's theory is not in agreement with Heisenberg's uncertainty principle.

Illustration 7: Find out the number of waves made by a Bohr-electron in one complete revolution in its third Bohr orbit of H-atom. **(JEE MAIN)**

Sol: These 3 formulas need to be considered.

$$r_n = \frac{n^2h^2}{4\pi^2me^2}; v_n = \frac{2\pi e^2}{nh}; \text{ number of waves in one round } = \frac{2\pi r_3}{\lambda} = \frac{2\pi r_3}{h/mv_3}\left(\because \lambda = \frac{h}{mv}\right)$$

Number of waves made by an electron in Bohr's orbit is equal to number of orbits.

$$\therefore \text{ No. of waves in one round } = \frac{2\pi r_3 \times v_3 \times m}{h} = \frac{2\pi \times n^2h^2}{4\pi^2me^2} \times \frac{2\pi e^2}{nh} \times \frac{m}{h}; \;\; n = 3$$

Illustration 8: Calculate the shortest and longest wavelengths in hydrogen spectrum of Lyman series.

Or

calculate the wavelengths of the first line and the series limit for the Lyman series for hydrogen. (R_H = 109678 cm^{-1})

Sol: (a) For Lyman series, $n_1 = 1$

For shortest wavelength in Lyman series (i.e. series limit), the energy difference in two states showing transition should be maximum, i.e. n = ∞.

$$\text{So, } \frac{1}{\lambda} = R_H\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) = R_H; \lambda = \frac{1}{109678} = 9.117 \times 10^{-6} \text{ cm } = 911.7 \text{ Å}$$

(b) For longest wavelength in Lyman series (i.e. first line), the energy difference in two states showing transition should be minimum, i.e. $n_2 = 2$

$$\text{So, } \frac{1}{\lambda} = R_H\left[\frac{1}{1^2} - \frac{1}{2^2}\right] = \frac{3}{4}R_H \text{ or } \lambda = \frac{4}{3} \times \frac{1}{R_H} = \frac{4}{3 \times 109678} = 1215.7 \times 10^{-8} \text{cm } = 1215.\,7 \text{ Å}$$

Illustration 9: Calculate the ratio of the time required for an electron taking one round of second orbit of H^- atom and He^+ ion. **(JEE MAIN)**

Sol: Use the time formula $\frac{2\pi r_n}{v_n}$. This is the time required to complete one round in nth orbit where v is the velocity of electron.

For H-like atom, $T_{He^+} = \frac{2\pi r_1 \times n^2}{Z} \times \frac{n}{v_1 \times Z}$ needs to be used.

For second orbit of H-atom: When r_n and r_1 are radii of H-atom: v_n and v_1 are velocities of electron in nth and first orbit of H-atom. Time required to complete one round in nth orbit is $\frac{2\pi r_n}{v_n}$ where vn is velocity of electron in nth orbit of H-atom

Time required to complete one round in nth orbit is $\frac{2\pi r_n}{v_n}$ where v_n is velocity of electron in nth orbit and r_n is radius of nth orbit. $T_H = \frac{2\pi r_n}{v_n}$ $\left(\because \; r_n = r_1 \times n_2 \;\text{ and }\; v_n = \frac{v_1}{n}\right)$

$$= \frac{2\pi r_1 \times n^2 \times n}{v_1} \quad \left(\because v_1 = \frac{2\pi e^2}{h}\right) \quad = \frac{2\pi r_1 \times n^3 \cdot h}{2\pi e^2} \quad T_H = \frac{r_1 n^3 h}{e^2} \qquad \text{...(i)}$$

For second orbit of He⁺: $T_{He^+} = \frac{2\pi r_{nHe^+}}{v_{n\ He^+}}$; $[r_{nHe^+} = \frac{r_{1H} \times n^2}{Z}; v_{n\ He^+} = v_{nH} \times Z$ and $v_{nH} = \frac{v_1}{n}]$

$$T_{He^+} = \frac{2\pi r_1 \times n^2}{Z} \times \frac{n}{v_1 \times Z};\ T_{He^+} = \frac{2\pi r_1 n^3 \times h}{Z^2 \times 2\pi e^2} = \frac{r_1 n^3 h}{e^2.Z^2};\ \therefore\ \frac{T_{H^+}}{T_{He^+}} = Z^2 = 4 \qquad (Z = 2 \text{ for } He^+)$$

Illustration 10: Find out the quantum number 'n' corresponding the excited state of He^- ion if on de-excitation to the ground state that ion emits only two photons in succession with wavelength 1023.7 and 304 Å ($R_H = 1.097 \times 10^7\ m^{-1}$) **(JEE MAIN)**

Sol: For two successive transitions say from n to n_1 and n_1 to 1.

$$\Delta E = (E_n - E_{n_1})(E_{n_1} - E_1) = E_n - E_1 = \frac{hc.R_H Z^2}{n^2} + \frac{hcR_H Z^2}{1^2} = hcR_H Z^2\left[\frac{n^2 - 1}{n^2}\right] \qquad \text{... (i)}$$

$$\text{Also given, } \Delta E_1 = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2} = hc\left[\frac{\lambda_1 + \lambda_2}{\lambda_1.\lambda_2}\right] \qquad \text{...(ii)}$$

$$\therefore \text{ By Eqs. (i) and (ii) } \frac{n^2 - 1}{n^2} = \left[\frac{\lambda_2 + \lambda_2}{\lambda_1 \lambda_2}\right] \times \frac{1}{R_H.Z^2} = \frac{1}{1.097 \times 10^7 \times 4}\left[\frac{(1026.7 + 304) \times 10^{-10}}{1026.7 \times 304 \times 10^{-20}}\right] = 0.9716;\ \therefore n = 6$$

8. SOMMERFIELD'S EXTENSION OF BOHR'S THEORY

To explain the fine spectrum of hydrogen atom, Sommerfield in 1915 proposed that the moving electron might describe elliptical orbits in addition to circular orbits and the nucleus is situated at one of the foci. In a circular motion only the angle of revolution changes while the distance from the nucleus remains the same but in an elliptical motion both the angle of revolution and the distance of the electron from the nucleus change. The distance from the nucleus is termed as radius vector and the angle revolution is known as azimuthal angle. The tangential velocity of the electron at a particular instant can be resolved into two components: one along the radius vector called radial velocity and the other perpendicular to the radius vector called transverse or angular velocity. These two velocities give rise to radial momentum and angular or azimuthal momentum. Sommerfeld proposed that both the moments must be integral multiples of $\frac{h}{2\pi}$

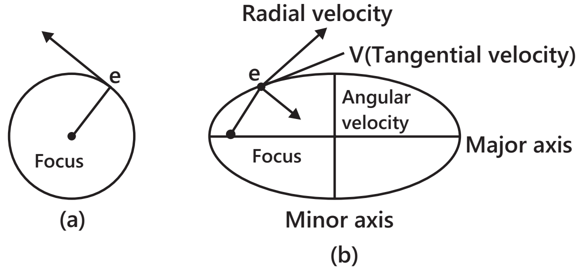


Figure 2.11: Sommerfield's extension

Radial momentum = $n_r \frac{h}{2\pi}$;

azimuthal momentum = $n_\phi \frac{h}{2\pi}$

n_r and n_ϕ are related to the main orbit 'n' as:

$n = n_r + n_\phi$ or

$$\frac{n}{n_\phi} = \frac{n_r + n_\phi}{n_\phi} = \frac{\text{Length of major axis}}{\text{Length of minor axis}}$$

(i) 'n_ϕ' cannot be zero because under this condition, ellipse shall take the shape of a straight line.

(ii) 'n_ϕ' cannot be more than 'n' because the minor axis is always smaller than major axis; when the major axis becomes equal to minor axis the ellipse takes the shape of a circle. Thus, n_2 can have all integral values up to 'n' but not zero. When the values are less than 'n', orbits are elliptical and when it becomes equal to 'n'. The orbit becomes circular in nature.

For n = 1, n_ϕ can have only one value, i.e. 1. Therefore, the first orbit is circular in nature.

For n = 2, n_ϕ can have two values 1 and 2, i.e. the second orbit has two sub orbits; one is elliptical and the other is circular in nature.

For n = 3, n_ϕ can have three values 1, 2 and 3, i.e. the third orbit has three sub orbits, two are elliptical and one is circular in nature. For n = 4, n_ϕ can have four values 1, 2, 3 and 4, i.e. fourth orbit has four suborbitssub orbits, theree are elliptical and fourth one is circular in nature (Fig.2.12). Sommerfield thus introduced the concept of sub-energy shells. In a main energy shell, the energies of sub-shells differ slightly from one another. Hence, the jumping of an electron from one energy shell to another energy shell will involve slightly different amount of energy as it will depend on sub-shell also. This explains to some extent the final spectrum of hydrogen atom. However, Sommerfield extension fails to explain the spectra of multi-electron atoms.

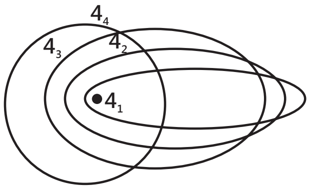


Figure 2.12: Elliptical path

9. PARTICLE AND WAVE NATURE OF ELECTRON

In 1924, **Louis de Broglie** proposed that an **electron**, like light behaves both as a material particle and as wave. This proposal gave birth to a new theory as **wave mechanical theory of matter**. According to this theory, the electrons, protons and even atoms, when in motion, possess wave properties.

De Broglie derived an expression for calculating the wavelengths of the wave associated with the electron. Using

Planck's equation, $E = h\nu = h.\frac{c}{\lambda}$ ...(i)

On the basis of Einstein's mass−energy relationship the energy of a photon is $E = mc^2$ ...(ii)

where c is the velocity of the electron

Equating both the equations, we get $h\frac{c}{\lambda} = mc^2$; $\lambda = \frac{h}{mc} = \frac{h}{p}$

Momentum of the moving electron is inversely proportional to its wavelengths.

Let kinetic energy of the particle of mass 'm' is E. $E = \frac{1}{2}mv^2$; $2Em = m^2v^2$

$\sqrt{2Em} = mv = p(\text{momentum})$; $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2Em}}$

9.1 Davisson and Germer Modification

Davisson and German made the following modification to de Broglie equation:

When a charged particle say an electron is accelerated with a potential of V; then the kinetic energy is given as:

$\frac{1}{2}mv^2 = eV$; $m^2v^2 = 2eVm$; $mv^2 = \sqrt{2eVm} = p$; $\lambda = \frac{h}{\sqrt{2eVm}}$

$\lambda = \frac{h}{\sqrt{2qVm}}$ for charged particles of charge q

De Broglie waves are not radiated into space, i.e. they are always associated with electron. Since the wavelength decreases if the value of mass (m) increases, in the case of heavier particles the wavelength is too small to be measured. De Broglie equation is applicable in the case of smaller particles like electron and has no significance for larger particles.

(a) de Broglie wavelengths associated with charged particles

(i) For electron: $\lambda = \frac{12.27}{\sqrt{V}}$Å (ii)For proton: $\lambda = \frac{0.286}{\sqrt{V}}$Å

(iii) For α- particles: $\lambda = \frac{0.101}{\sqrt{V}}$Å where V = acceleration potential of these particles

(b) de Broglie wavelength associated with uncharged particles

(i) For neutrons: $\lambda = \frac{h}{\sqrt{2Em}} = \frac{6.62\times10^{-34}}{\sqrt{2\times1.67\times10^{-27}\times E}} = \frac{0.286}{\sqrt{E(eV)}}$Å

(ii) For gas molecules: $\lambda = \frac{h}{m\times v_{rms}} = \frac{h}{\sqrt{3mkT}}$ where, k = Boltzmann constant

9.2 Bohr's Theory vs. de Broglie Equation

Bohr's Theory versus de Broglie equation: Bohr's theory postulates that angular momentum of an electron is an integral multiple of h/2π. This postulate can be derived with the help of de Broglie concept of wave nature of electron.

Consider an electron moving in a circular orbit around nucleus. The wave train would be associated with the circular orbit as shown in the figure. If the two ends of an electron wave meet to give a regular series of crests and troughs, the electron wave is said to be in phase, i.e. the circumference of Bohr orbit is equal to whole number multiple of the wavelength of the electron wave.

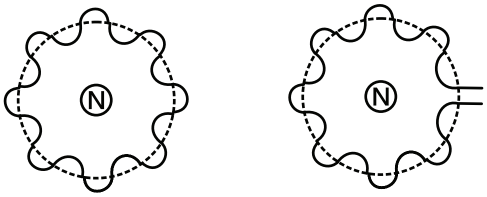


Figure 2.13: Wave in phase and out of phase

So, $2\pi r = m\lambda$ Or $\lambda = \frac{2\pi r}{n}$ ...(i)

From de Broglie equation, $\lambda = \frac{h}{mv}$ ...(ii)

Thus, $\frac{h}{mv} = \frac{2\pi r}{n}$ or $mvr = n.\frac{h}{2\pi}$ (v = velocity of electron and r = radii of the orbit)

i.e. Angular momentum = $n.\frac{h}{2\pi}$ ...(iii)

This proves that the concepts of de Broglie and Bohr are in perfect agreement with each other.

Illustration 11: With what velocity must an electron travel so that its momentum is equal to that of a photon of wavelength of λ = 5200 Å **(JEE MAIN)**

Sol: Momentum=mv and λ = h/mv. They are the momentum of an electron and photon respectively. Thus, by equating them would give the velocity.

$\because \lambda = h/mv \therefore$ Momentum of photon = mv = h/λ = $\frac{6.626\times10^{-34}}{5200\times10^{-10}}$ kg m sec^{-1}

Also, momentum of electron = mv = $9.108 \times 10^{-31} \times v$ kg m sec^{-1}

Since, both are same and thus equating the two $9.108 \times 10^{-31} \times v = \dfrac{6.626\times10^{-34}}{5200\times10^{-10}}$

$\therefore$ v = 1400 m sec^{-1}

Illustration 12: The wavelength of an electron moving in second orbit of H-atom is an integral multiple of its circumference. **(JEE MAIN)**

Calculate:

(a) Number of wave in the second orbit,

(b) Speed of electron in the second orbit.

(c) How much potential must be applied to an electron so that the electron becomes stationary at a point?

Sol: Circumference is 2πr and it is said that the wavelength is an integral multiple of the circumference. Thus, $n\lambda = 2\pi r$. Moreover, number of waves made by an electron in Bohr's orbit is equal to number of orbits.

(a) No. of waves (n) in the second orbit = 2

(b) Also $2\pi r_2 = 2 \times 3.14 \times 0.529 \times 10^{-8} \times 4 = 13.28 \times 10^{-8}$ cm

Since, $n\lambda = 2\pi r \;\therefore\; \lambda = \dfrac{13.28\times10^{-8}}{2} = 6.64 \times 10^{-8}$ cm= 6.64×10^{-10} m

$$\therefore v = \frac{h}{\lambda m} = \frac{6.626\times10^{-34}}{6.64\times10^{-10}\times9.108\times10^{-31}} = 1.09 \times 10^{6} \text{ m/s}$$

(c) Also $eV_0 = \dfrac{1}{2}mv^2 \;\therefore\; V_0 = \dfrac{9.108\times10^{-31}\times(1.09\times10^{6})^2}{2\times1.602\times10^{-19}} = 3.38V$

10. HEISENBERG'S UNCERTAINTY PRINCIPLE

We see around us all moving particles, e.g. a car, a ball thrown in the air etc. move along definite paths. Hence their position and velocity can be measured accurately at any instant of time. Likewise is it possible to measure the position and velocity for the subatomic particle also?

Heisenberg, in 1927 gave a principle about the uncertainties in simultaneous measurement of position and momentum (mass × velocity) of small particles. This principle is due to the consequence of dual nature of matter.

This Principle States: 'It is impossible to measure simultaneously the position and momentum of a small microscopic moving particle with absolute accuracy or certainty', i.e. if an attempt is made to measure any one of these two quantities with higher accuracy, the other becomes less accurate. The product of the uncertainty in position (Δx) and the uncertainty in the momentum ($\Delta p = m.\Delta v$ where m is the mass of the particle and Δv is the uncertainty in velocity) is equal to or greater than $h/4\pi$ where h is the Planck's constant. Thus, the mathematical expression for the Heisenberg's uncertainty principle is readily written as $\Delta x.\Delta p \geq h/4\pi$

Explanation of Heisenberg's uncertainty principle: Let us attempt to measure both the position and momentum of an electron; to pinpoint the position of the electron we have to use light so that the photon of light strikes the electron and the reflected photon is seen in the microscope. As a result of the hitting, both the position and the velocity of the electron are disturbed. The accuracy with which the position of the particle can be measured depends upon the wavelength of the light used.

The uncertainty in position is $\pm \lambda$. The shorter the wavelength, the greater is the accuracy. But shorter wavelength means higher frequency and hence higher energy. This high energy photon on striking the electron changes its speed as well as direction. But this is not true for a moving macroscopic particle. Hence Heisenberg's uncertainty principle does not apply to macroscopic particles.

Illustration 13: Why cannot the electron exist inside the nucleus according to Heisenberg's uncertainty principle? **(JEE MAIN)**

Sol: Following the Heisenberg's Uncertainty principle, the location of the electron is justified. Use $\Delta x.\Delta p \geq h/4\pi$ or $\Delta x.\Delta p - h/4\pi$.

Diameter of the atomic nucleus is of the order of 10^{-15} m

The maximum uncertainty in the position of electron is 10^{-15}

Mass of electron = 9.1×10^{-31} kg.;

$\Delta x\,.\Delta p - h/4\pi$;

$\Delta x \times (m.\Delta v) - h/4\pi$;

$\Delta v = h/4\pi \times 1/\Delta x.\ M = 6.53 \times 10^{-34}/4x\ (22/7)x\ 1/10^{-15} \times 9.1 \times 10^{-31}$; $\Delta v = 5.80 \times 10^{10}\ ms^{-1}$

The value is much higher than the velocity of light and hence not possible.

Illustration 14: What is the uncertainty in the position of electron, if uncertainty in its velocity is 0.0058 m/s? **(JEE MAIN)**

Sol: $\Delta x \times \Delta v = h/4\pi m$; $\Delta x = 6.62 \times 10^{-34} / 4x\ 3.14 \times 9.1 \times 10^{-31} \times 0.0058$; $\Delta x = 0.01$ m

11. WAVE MECHANICAL MODEL OF ATOMS

Erwin Schrodinger in 1920 put forward this model by taking into account the de Broglie concept of dual nature of matter and Heisenberg's uncertainty principle. In this model, the discrete energy levels or orbits proposed by Bohr's model are replaced by mathematical function ψ (psi) which is related with probability of finding electrons around the nucleus. The wave equation for an electron wave propagating in 3-D space is: $\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$

where y is the amplitude of the electron wave at point with coordinates x, y, z, E = total energy and V = potential energy of the electron; ψ is also called wave function and ψ^2 gives the probability of finding the electron at (x, y, z). The acceptable solutions of the above equation for the energy E are called Eigen values and the corresponding wave functions are called **Eigen functions**.

Every function is not an Eigen function. An acceptable solution for Schrodinger wave equation must satisfy the following conditions:

1. The function should be finite.
2. It should always bear a single value at a particular point in space.
3. It should be a continuous function. Schrodinger wave equation can be written as

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi+\frac{8\pi^2 m}{h^2}(E-V)\psi=0;\ \text{or}\ \nabla^2\psi+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$$

where $\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$ is called Laplacian operator This equation can be rewritten as $\nabla^2\psi=-\frac{8\pi^2 m}{h}(E-V)\psi$;

or $\left(-\frac{h^2}{8\pi^2 m}\nabla^2+V\right)\psi=E\psi$; or $H\psi = E\psi$, where $H = -\frac{h^2}{8\pi^2 m}\nabla^2+V$, is called Hamiltonian operator

In this operator, the first term represents kinetic energy operator (T) and the second term represents potential energy operator (V).

Significance of ψ: It represents the amplitude of an electron wave. It can be positive or negative. It has no physical value.

Significance of ψ^2: It is a probability function. It determines the probability of finding an electron within a smaller region of space around nucleus. The space in which there is maximum probability of finding an electron is termed as orbital.

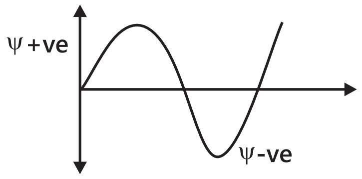


Figure 2.14: Significance of ψ

12. QUANTUM NUMBERS

An atom contains large number of shells and sub-shells. These are distinguished from one another on the basis of their size, shape and orientation (direction) in space. The parameters are given in terms of different numbers called **quantum numbers**.

Quantum numbers may be defined as a set of four numbers with the help of which we can get complete information about all the electrons in an atom. It tells us the address of the electron i.e. location, energy, the type of orbital occupied and orientation of that orbital.

12.1 Principal Quantum Number

(a) This is denoted by n, an integer.

(b) The values of n are from 1 to n. n = 1 K shell; n = 2 L shell

n = 3 M shell; n = 4 N shell

(c) ‘n’ represents the major energy shell to which an electron belongs.

(d) The values of ‘n’ signify the size and energy level of major energy shells.

(e) As the value of ‘n’ increases, the energy of the electron increases and thus, the electron is less tightly held with nucleus.

(f) Angular momentum can be calculated using principal quantum number: $mvr = nh/2\pi$

12.2 Azimuthal Quantum Number

This is denoted by *l*.

(a) The values of *l* are from 0 to (n − 1)

(b) *l* = 0, s-sub-shell, spherical (The representation is independent of the value of n)

l = 1, p-sub-shell, dumbbell

l = 2, d-sub-shell, double dumbbell or like leaf

(c) The letters s, p, d, f designate old spectral terms.

Sharp (s), principal (p), diffuse (d), fundamental (f)

(d) For a given value of n, total values of ‘*l*’ are n.

(e) The values of *l* signify the shape and energy level of sub-shells in a major energy shell.

(f) The angular momentum of an electron in an orbital is given by $nh/2\pi$.

(g) The energy level for sub-shells of a shell shows the order: $s < p < d < f$

12.3 Magnetic Quantum Number

(a) Denoted by m_l, an integer.

(b) Zeeman effect: Zeeman studied the fine spectrum of H using a spectroscope of high resolving power as well as putting the source under the influence of magnetic field. He noticed that the spectral line splits up to more than one component

(c) Each frequency of radiation emitted by the atom in the presence of magnetic field splits up into components if the angular momentum of the electron along the magnetic field are restricted to the value, $m_l = \frac{h}{2\pi}$

(d) The values of m_l lie from ± l through zero.

(e) The positive values of magnetic quantum number m_l represent the angular momentum component of the orbital in the direction of the applied magnetic field whereas the negative values of m_l account for the angular momentum component of orbital in the opposite direction of applied magnetic field.

(f) Total values of m_l for a given value of $n = n^2$.

(g) Total values of m_l for a given value of $l = (2l + 1)$

(h) The values of m_l signify the possible numbers of orientations of a sub-shell.

(i) In the absence of magnetic field, the three p-orbitals are equivalent in energy and are said to be threefold degenerate, i.e. sub sub-shell (orbitals) having same energy level are known as **degenerate orbitals**.

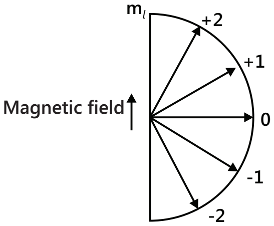


Figure 2.15: Magnetic quantum number

12.4 Spin Quantum Number

(a) Wave mechanical treatment required no more than three quantum number n, l and m. The existence of multiple, i.e. doublet structure led to the introduction of a spin quantum number m_s.

(b) The values of ms are $+\frac{1}{2}$ and $-\frac{1}{2}$. This is due to the fact of the doublet structures of spectral lines which can be explained by proposing only two directions of spin of electron along its own axis.

(c) The values of ms signify the direction of rotation or spin of an electron in its axis during its motion.

(d) Spin angular momentum is given by $\frac{h}{2\pi}\sqrt{m_s(m_s+1)} = \frac{h}{2\pi}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)} = \frac{\sqrt{3}}{4}\frac{h}{\pi} = \frac{\sqrt{3}}{2}h$.

(e) The spin may be clockwise $\left(+\frac{1}{2}\text{or}-\frac{1}{2}\right)$ or anticlockwise $\left(-\frac{1}{2}\text{or}+\frac{1}{2}\right)$

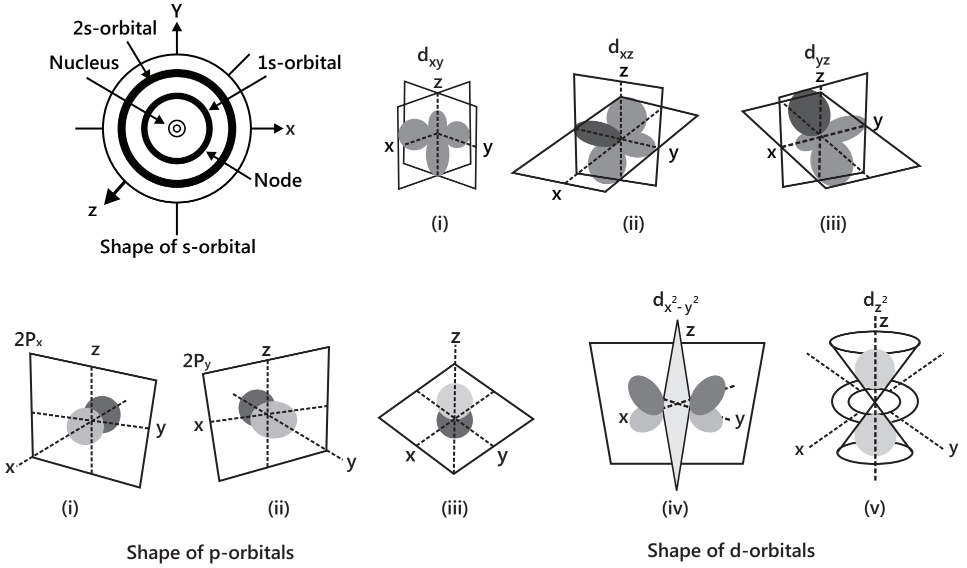
(f) Spin multiplicity of an atom = $\sqrt{s(s+1)}$.

12.5 Shapes of Orbitals

The electron cloud represents the shape of the orbital. It is not uniform but it is dense where the probability for finding the electron is maximum.

(a) s-orbitals do not vary with angles, i.e. they do not have directional dependence. Thus, all s-orbitals are called spherically symmetrical. Their size increases with increases in the value of n. 1s-orbital has no nodal plane (the plane at which zero electron density is noticed). 2s-orbital has one nodal plane; 3s-orbital has two nodal planes. Thus it is evident that the number of nodal planes increases with increasing value of principal quantum number.

(b) All orbitals with $l \neq 0$ have angular dependence. Therefore, p and d and other higher angular momentum orbitals are not spherically symmetrical. p-orbitals consist of two lobes to form dumbbell shaped structure. The three p-orbitals along *x*, *y*, *z*-axes named as p_x , p_y , p_z orbitals are perpendicular to each other. All the three p-orbitals of a sub-shell have the same size and shape but differ from each other in orientation. The subscripts *x*, *y* and *z* indicate the axis along which the orbitals are oriented and possess maximum electron density. Also, the orbitals of a sub-shell having same energy are referred as **degenerate orbitals**.



Shape of s-orbital

Shape of p-orbitals

Shape of d-orbitals

Figure 2.16: Shapes of orbitals

Illustration 15: Given below are the sets of quantum numbers for given orbitals. Name these orbitals.

(JEE MAIN)

(a)	(b)	(c)	(d)
$n = 2$	$n = 4$	$n = 3$	$n = 4$
$l = 1$	$l = 2$	$l = 1$	$l = 2$
$m_l = 2$	$m_l = 0$	$m_l = \pm 1$	$m_l = \pm 2$

Sol: (a) $\because$ $n = 2$ and $l = 1$ $\therefore$ 2p Since, $m_l = -1$ $\therefore$ $2p_y$ or $2p_x$ similarly for others

(b) $4d_{z^2}$ (c) $3p_x$ or $3p_y$ (d) $4d_{x^2-y^2}$ or $4d_{xy}$

Illustration 16: For n = 6 suggest **(JEE MAIN)**

(a) Total number of electrons that it can have

(b) Total number of sub-shells which can exist

(c) Total number of sub sub-shells (orbitals) which can exist.

Sol: Having the knowledge of quantum numbers and the existing combinations, the following can be predicted.

(a) 72 (b) 6 (c) 36

13. SCHRODINGER WAVE EQUATION FOR H-ATOM

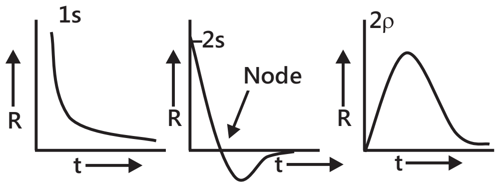
Since the electron in the hydrogen atom seems to be a spherically symmetric potential spherical polar coordinates are used to solve the equation. The potential energy is simply that of a point charge, $U(r) = -e^2/4\pi\varepsilon_0 r$. When the value of potential energy is substituted in the equation and is solved in polar coordinate form, the total energy is found to be $E = -me^4/8\varepsilon^2 n^2 h^2$, which is the same as given by the Bohr's model. The solutions of Schrodinger wave equation is obtained by separating the variables so that the wave function is represented by the product – $\psi(r,\theta,\phi) = \underbrace{R(r)}_{\text{Radial part}}\ \underbrace{\Theta(\theta)\Phi(\phi)}_{\text{Angular part}}$. Since the function R depends only on r_1, it describes the distribution of the electron as function of r from the nucleus. These two functions, Θ and Φ depend upon two quantum numbers, n and l and taken together give the angular distribution of the electron. The radial part of the wave function for some orbitals may be given as,

n	*l*	Rn	
1s	1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Z/a_0}$;
2s	2	0	$\frac{1}{\sqrt{3}}\left(\frac{Zr}{2a_0}\right)^{3/2} e^{-Zr/a_0}$

where Z = atomic number, a_0 = radius of first Bohr orbit of hydrogen

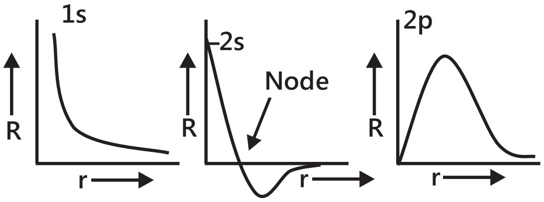
14. PLOTS OF GRAPHS

14.1 Plots of Graphs of R (Radial Wave Function) vs. r (Radius of Atom)



Note: The point where the wave function changes its sign is called node. The number of radial nodes can be determined by the formula: (n − *l* - 1).

14.2 Plots of Graphs of R^2 (Radial Probability Density) vs. r (Radius of Atom)



(a) For 1s and 2s orbitals, the function is not defined at r = 0 (asymptotic behaviour) as the probability of finding electron inside nucleus is not known but there can be a probability of finding electron just outside the nucleus as s orbital lies very closer to nucleus.

(b) For 2p orbital, at r = 0, probability is zero.

14.3 Plots of Graphs of R^2r (Radial Probability Distribution) vs. r (Radius of Atom)

In order to visualize the electron cloud, consider the space around nucleus divided into a large number of small concentric spherical shells of radius dr. The volume of such a shell can be −

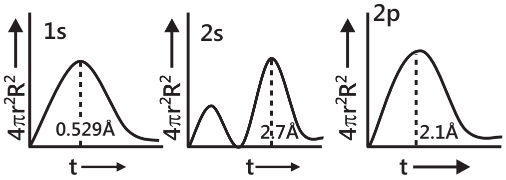
$dv = 4\pi/3(r+dr)^3 \;\; 4\pi/3r^3$ So, $dv = 4\pi r^2 dr$

This volume is called radial volume and the probability of finding an electron within this shell is called radial probability distribution function.

R.P.F. = (Volume of spherical shell) × probability density

$= (4\pi r^2 \, dr) \times R$

Radial probability distribution = $4\pi r^2 dr \, R^2$



PLANCESS CONCEPTS

- For 1s orbital, radial probability increases with increase in distance from the nucleus, reaches a maximum and then decreases. The maxima are the maximum probability of finding an electron which is also called 'radius of maximum probability' and is also same as Bohr's radius.
- For 2s, the graph has two maxima. In between these two maxima, the curve passes through a zero value indicating that there is zero probability of finding the electron at that distance. This point is a nodal point which can be a radial/spherical node.

Neeraj Toshniwal (JEE 2009, AIR 21)

14.4 Angular Node/Nodal Plane

The probability of finding an electron in nucleus is zero; so it is called a nodal point. Any plane passing through that point where the probability of finding an electron is zero is called a nodal plane.

PLANCESS CONCEPTS

- s orbital doesn't have any nodal plane.
- p orbital has one nodal plane. Nodal plane for p_x is YZ plane, for p_y is XZ plane and for p_z is XY plane.
- d orbital has two nodal planes. Nodal planes for d_{xy} are XZ and YZ, for d_{xz} are YZ and XY, for d_{yz} are XY and XZ, for $d_{x^2-y^2}$ are the lines inclined at 45° with X and Y axes.
- So, number of angular nodes = l

Saurabh Gupta (JEE 2010, AIR 443)

Important Points: Key Take-Away

Type of information	Principal Quantum No. (n)	Azimuthal Quantum No. (l)	Magnetic Quantum m_l	Spin Quantum No. m_s
1. Whys is it required?	To explain the main lines of a spectrum	To explain the line structure of the line spectrum	To explain the splitting of lines in a magnetic field	To explain the magnetic properties of substances
2. What does it tell?	(i) Main shell in which the electron resides	(i) No. of sub-shells present in any main shell	No. of orbitals present in any sub-shell or the number of orientiation of each sub-shell	Direction of electron spin, i.e. clockwise or anti clockwise
	(ii) Approx distance of the electron from the nucleus	(ii) Relative energies of the sub-shell		
	(iii) Energy of the shell	Shapes of orbitals		
	(iv) Max. no. of electrons present in the sheell ($2n_1^2$)			
3. What are the symbols?	n	l	m or m_l	s or m_s
4. What are the values?	1, 2, 3, 4 etc. i.e. any integer	For a particular value of n, l = 0 to n - 1	For a particular value of i.e.= -1 to +1 including zero	For a particular value of m,
5. Othe designations?	K, L, M, N, etc.	l = 0, s-sub-shell; l = 1, p--sub-shell; l = 2, d-sub-shell; l = 3, f-sub-shell	For p-sub-shell m_l = -1, 0, +1, designated as p_x, p_y and p_z	Two arrows pointing in opposite directions, i.e. ↑ and ↓

PLANCESS CONCEPTS

- Number of radial nodes = $(n - l - 1)$
- Number of angular nodes = l
- Total number of nodes = $(n - l)$
- Number of nodal planes = l

Aman Gour (JEE 2012, AIR 230)

15. PAULI'S EXCLUSION PRINCIPLE

The principle states that no two electrons in an atom can have the same set of all the numbers. In other words, no orbital can have more than two electrons.

Conclusion:

(a) The maximum capacity of a main energy shell is equal to $2n^2$ electrons.

(b) The maximum capacity of a sub-shell is equal to $2(2l + 1)$ electrons.

(c) Number of sub-shells in a main energy shell is equal to the value of n.

(d) Number of orbitals in a main energy shell is equal to n^2.

(e) One orbital cannot have more than two electrons. If two electrons are present, their spins should be in opposite directions.

16. AUFBAU PRINCIPLE

The word 'aufbau' originates from the German word 'Aufbauen' which means 'to build'. This gives us a sequence in which various sub-shells are filled up depending on the relative order of the energy of the sub-shells. The sub-shell of the lowest energy is filled up first, then the next sub-shell of higher energy starts filling. The sequence in which various sub-shells are filled is the following:

1s, 2s, 2p, 3s, 4s, 3d, 5s, 4d, 5s, 4d, 5p, 6s, 4d, 5d, 6p, 7s, 5f, 6d, 7p

Using (n + l) Value:

The sequence in which various sub-shells are filled up can also be determined with the help of (n + l) value. When two or more sub-shells have same (n + l) value, the sub-shell with the lowest value of 'n' is filled up first.

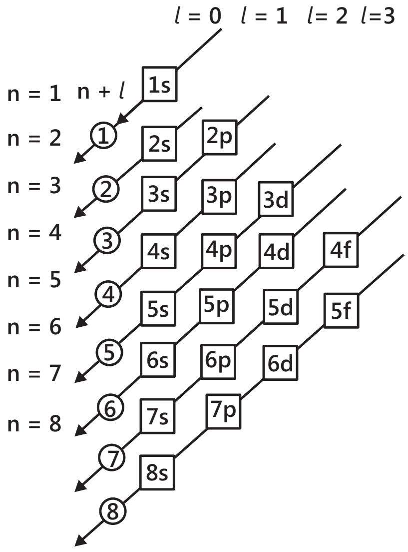


Figure 2.17: Aufbau rule

Sub - shell	**n**	***l***	**$(n+l)$**	
1s	1	0	0	
2s	2	0	2	
2p	3	0	3	Lowest value of n
3s	3	0	3	
3p	3	1	4	Lowest value of n
4s	4	0	4	
3d	3	2	5	Lowest value of n
4p	4	1	5	
5s	5	0	5	
4d	4	2	6	Lowest value of n
5p	5	1	6	
6s	6	0	6	
4f	4	3	7	Lowest value of n
5d	5	2	7	
6p	6	1	7	
7s	7	0	7	
5f	5	3	8	Lowest value of n
6d	6	2	8	
7p	7	1	8	

The principal quantum number solely determines the energy of the electron in a hydrogen atom and other single electron species like He^+, Li^{2+} and Be^{3+}. The energy of orbitals in hydrogen and hydrogen like species increases as follows: $1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f <$ .....

Exceptions to Aufbau Principle: In some instances it is noted that actual electronic arrangement is slightly different from the arrangement expected by Aufbau principle. A simple reason behind this is that half-filled and full-filled sub-shells have got extra stability.

Cr_{24} → $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^4, 4s^2$ (wrong)

→ $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^5, 4s^1$ (right)

Cr_{29} → $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^9, 4s^2$ (wrong)

→ $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^1$ (right)

Similarly the following elements have slightly different configurations than expected:

$Nb_{41} \longrightarrow [Kr]4d^4\ 5s^1$

$Mo_{42} \longrightarrow [Kr]4d^5\ 5s^1$

$Ru_{44} \longrightarrow [Kr]4d^7\ 5s^1$

$Rh_{45} \longrightarrow [Kr]4d^8\ 5s^1$

$Pd_{46} \longrightarrow [Kr]4d^{10}\ 5s^0$

$Ag_{47} \longrightarrow [Kr]4d^{10}\ 5s^1$

$Pt_{78} \longrightarrow [Xe]4f^{14}\ 5d^9\ 6s^1$

$Au_{79} \longrightarrow [Xe]4f^{14}\ 5d^{10}\ 6s^1$

$La_{57} \longrightarrow [Kr]4d^{10}\ 5s^2\ 5p^6\ 5d^1\ 6s^2$

$Ce_{58} \longrightarrow [Kr]\ 4d^{10}\ 5s^2\ 5p^6\ 5d^0\ 6s^2$

$Gd_{64} \longrightarrow [Kr]\ 4d^{10}\ 4f^7\ 5s^2\ 5p^6\ 5d^1\ 6s^2$

17. HUND’S RULE OF MAXIMUM MULTIPLICITY (ORBITAL DIAGRAMS)

It states that electrons are distributed among the orbitals of sub-shell in such a way as to give the maximum number of unpaired electrons with parallel spins. This means that the orbitals available in a sub-shell are first filled singly before they begin to pair i.e. the pairing of electrons occurs with the introduction of the second electron in the s-orbital, the fourth electron in the p-orbitals, the sixth electron in the d-orbitals and the eighth electron in the f-orbitals. The rule is based on the fact that electrons have the same charge and repel each other and hence try to keep further apart from each other as much as possible. The electrons thus occupy different orbitals of the sub-shell as to minimize the inter-electronic repulsion and increase the stability of the atom. Orbitals tend to become half-filled or completely filled since such an arrangement will be more stable on account of symmetry.

The orbital diagram for nitrogen, oxygen, fluorine and neon are as follows:

Nitrogen (7) [He] $\underline{\uparrow\downarrow}\ \underbrace{\underline{\uparrow}\ \underline{\downarrow}\ \underline{\uparrow}}_{2p}$

Oxygen (8) [He] $\underline{\uparrow\downarrow}\ \underbrace{\underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}}_{2p}$

Fluorine (9) [He] $\underline{\uparrow\downarrow}\ \underbrace{\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}}_{2p}$

Neon (10) [He] $\underline{\uparrow\downarrow}\ \underbrace{\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}}_{2p}$

The orbital diagrams of elements from atomic number 21 to 30 can be represented on similar lines as below:

Sc[Ar]$3d^1$ $4d^2$	↑	–	–	–	–	↑↓
Ti [Ar]$3d^2$ $4s^2$	↑	↑	–	–	–	↑↓
V[Ar]$3d^3$ $4s^2$	↑	↑	↑	–	–	↑↓
Cr[Ar]$3d^5$ $4s^1$	↑	↑	↑	↑	↑	↑
Mn[Ar]$3d^5$ $4s^2$	↑	↑	↑	↑	↑	↑↓
	3d					4s

Fe[Ar]$3d^6$ $4s^2$	↑↓	↑	↑	↑	↑	↑↓
Co[Ar]$3d^7$ $4s^2$	↑↓	↑↓	↑	↑	↑	↑↓
Ni[Ar]$3d^8$ $4s^2$	↑↓	↑↓	↑↓	↑	↑	↑↓
Cu[Ar]$3d^{10}$ $4s^1$	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Zn[Ar]$3d^{10}$ $4s^2$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
	3d					4s

All those atoms which consist of at least one of the orbitals singly occupied behave as paramagnetic materials because these are weakly attracted to a magnetic field, while all those atoms in which all the orbitals are doubly occupied behave as diamagnetic materials because they have no attraction for magnetic field. However, these are slightly repelled by magnetic field due to induction.

Magnetic moment may be calculated as, 1 BM (Bohr magneton) = where n = No. of unpaired electrons

Illustration 17: Predict total spin for each configuration. **(JEE MAIN)**

(a) $1s^2, 2s^2, 2p^5$ (b) $1s^2, 2s^2, 2p^3$ (c) $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^5, s^2$ (d) $1s^2, 2s^2$

Sol: Use Total spin of an electron = $\left(\pm\frac{1}{2}\right)$ × no. of unpaired electrons

$\therefore$ (a) Total spin $= 1\times\left(\pm\frac{1}{2}\right) = \pm\frac{1}{2}$ (b) Total spin $= 3\times\left(\pm\frac{1}{2}\right) = \pm(3/2)$

(c) Total spin $= 5\times\left(\pm\frac{1}{2}\right) = \pm(5/2)$ (d) Total spin $= 0\times\left(\pm\frac{1}{2}\right) = 0$

Illustration 18: Write the electronic configurations of the elements with the following atomic numbers: 3, 8, 14, 17, 21, 38, 57. Also mention the groups of the periodic table to which they belong. **(JEE MAIN)**

Sol:

Atomic No.	Electronic configuration	Group of periodic Table
3	$1s^2\ 2s^1$	1
8	$1s^2, 2s^2, 2p_{x^2}, 2p_{y^1}, 2p_{z^1}$	16
14	$1s^2, 2s^2, 2p^6, 3s^2, 3p_{x^1}, 3p_{y^1}$	14
17	$1s^2, 2s^2, 2p^6, 3s^2, 3p_{x^2}, 3p_{y^2}, 3p_{z^2}$	17
21	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^1, 4s^2$	3

Atomic No.	Electronic configuration	Group of periodic Table
22	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 5s^2$	2
57	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^2, 5p^6, 5d^1, 6s^2$	2

Note: Here one electron enters the 5d orbital before filling up of the 4f begins.

Rules for finding the group number

(i) If the last shell contains one , two electrons, then the group number is 1, 2 respectively.

(ii) If the last shell contains more than two electrons, then the group number is the total number of electrons in the last shell plus 10.

(iii) If electrons are present in (n – 1)d orbital in addition to those in the ns orbital, then the group number is equal to the total number of electrons present in the (n – 1)d orbital and ns orbital.

Illustration 19: Give the electronic configuration of the following ions:

(i) Cu^{2+} (ii) Cr^{3+} (iii) Fe^{2+} and Fe^{3+} (iv) H^- (v) S^{2-} **(JEE MAIN)**

Sol: During the formation of cations, electrons are lost while in the formation of anions, electrons are added to the valence shell. The number of electrons added or lost is equal to the numerical value of the charge present on the ion.

Following this general concept, we can write the electronic configurations of all the ions given in the equation.

(i) $Cu^{2+} = {}_{29}Cu - 2e^- = 1s^2\ 2s^2\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1 - 2e^- = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$

(ii) $Cr^{3+} = {}_{24}Cr - 3e^- = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1 - 3e^- = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

$Fe^{3+} = {}_{26}Fe - 3e^- = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5 = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_{x^2}\ 3p_{y^2}\ 3p_{z^2}\ 3d^5$

(iii) $H^- = {}_1H + 1e^- = 1s^1 + 1e^1 = 1s^2$

(iv) $S^{2-} = {}_{16}S + 2e^- = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_{x^2}\ 3p_{y^1}\ 3p_{z^1} + 2e^- = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_{x^2}\ 3p_{y^2}\ 3p_{z^2}$

POINTS TO REMEMBER

Representation of a chemical symbol	$X_Z^{A......A=Z+n}$	X = Element, A = Mass number = No. of protons (p) + No. of neutrons(n) Z = Atomic number = No. of protons
Millikan's oil drop experiment	$m = \dfrac{m_0}{[1-(v/c)^2]^{1/2}}$	m = Moving mass of an electron m_0 = Rest mass of an electron
Reduced mass (μ) $\dfrac{1}{\mu} = \dfrac{1}{M} + \dfrac{1}{m} = \dfrac{mM}{m+M}$	Radius of the nucleus (R_n) $R_n = R_1(A)^{1/3}$, $R_1 = 1.33 \times 10^{-13}$ cm A = Mass number	
Moseley's experiment $\sqrt{v} = a(Z - b)$ where ν = Frequency of X-rays, Z = atomic number, a and b are constants,	Ritz mathematical formula $\dfrac{1}{\lambda_{vac}} = \bar{v} = R\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$ Where $\bar{v}$ = Wave number, R = Rydberg's constant, n_1 and n_2 are integers (such that $n_2 > n_1$) integers or energy levels.	Maximum kinetic energy of the ejected electron Max. KE = Absorbed energy − Work function $\dfrac{1}{2}mv_{max}^2 = h\nu - h\nu_0 = hc\left[\dfrac{1}{\lambda} - \dfrac{1}{\lambda_0}\right]$

Bohr's model inputs Radius of an atom = $r_a = \frac{n^2}{Z} \times \frac{h^2}{a\pi^2 e^2 m}$ Velocity of an electron = $v = \frac{z}{n} \times \frac{2\pi e^2}{h}$ Energy of an electron= $E_n = \frac{E_1}{n^2} z^2 - \frac{2\pi}{n} = -z^2$	De Broglie's hypothesis $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2Em}}$ where λ = wavelength, p = Momentum, h = Planck's constant, E = Kinetic energy	Heisenberg's uncertainty principle $\Delta x \, \Delta p \geq \frac{h}{4\pi}$ Δx = Change in position, Δp = Change in momentum
Orbital angular momentum $L = \frac{h}{2\pi}\sqrt{l(l+1)}$	Spin angular momentum $S = \frac{h}{2\pi}\sqrt{S(S+1)}$	Magnetic moment (μ) $= \mu\sqrt{n(n+2)}$ B.M. n = Number of unpaired e^-
Some important points to be remembered	Total no. of e^- in an energy level = $2n^2$ Total no. of e^- in a sublevel = $2(2l + 1)$ Maximum no. of e^- in an orbital =2 Total no. of orbitals in a sublevel = $(2l + 1)$ No. of sub-shells in main energy shell = n No. of orbitals in a main energy shell = n^2 l = 0 1 2 3 4 s p d f g	

Solved Examples

JEE Main/Boards

Example 1: When a certain metal was irradiated with light of frequency 3.2×10^{16} Hz, the photoelectrons emitted had twice the energy as did photoelectrons emitted when the same metal was irradiated with light of frequency 2.0×10^{16} Hz. Calculate v_0 for the metal.

Sol: Threshold frequency needs to be calculated. The incident frequency has been given and a condition of photons emission has been given.

Applying photoelectric equation,

$KE = hv - hv_0$

It can be also written as $(v - v_0) = \frac{KE}{h}$; Given

$KE_2 = 2KE_1$

$$v_2 - v_0 = \frac{KE_2}{h} \quad \text{... (i)}$$

$$\text{and } v_1 - v_0 = \frac{KE_1}{h} \quad \text{...(ii)}$$

Dividing equation (i) by equation (ii)

$$\frac{v_2 - v_0}{v_1 - v_0} = \frac{KE_2}{KE_1} = \frac{2KE_1}{KE_1} = 2; \text{ or } v_2 - v_0 = 2v_1 - 2v_0$$

or $v_0 = 2v_1 - v_2 = 2(2.0 \times 10^{16}) - (3.2 \times 10^{16})$

$= 8.0 \times 10^{15}$ Hz

Example 2: An electron moves in an electron field with a kinetic energy of 2.5 eV. What is the associated de Broglie wavelength?

Sol: The de-Broglie equation is $\lambda = \frac{h}{p} = \frac{h}{mv}$. Modifying the equation according to the given data and taking the help of kinetic energy, we solve it.

Kinetic energy = $\frac{1}{2}mv^2 \left(v = \frac{h}{m\lambda}\right)$

$$= \frac{1}{2}m\left(\frac{h}{m\lambda}\right)^2 = \frac{1}{2}\frac{h^2}{m\lambda^2} \quad \text{or} \quad \lambda^2 = \frac{1}{2}\frac{h^2}{m \times KE}$$

$$\lambda = \frac{h}{\sqrt{2m \times KE}} \begin{pmatrix} m = 9.108 \times 10^{-28} \ \text{g} \\ h = 6.626 \times 10^{-27} \text{erg.sec} \\ 1\text{ev} = 1.602 \times 10^{-12} \ \text{erg} \end{pmatrix}$$

$$= \frac{6.626 \times 10^{-27}}{\sqrt{2 \times 9.108 \times 10^{-28} \times 2.5 \times 1.602 \times 10^{-12}}}$$

= 7.7 × 10^{-8} cm

Example 3: The minimum energy required to overcome the attractive force between an electron and the surface of Ag metal is 5.52 × 10^{-19} J. What will be the maximum kinetic energy of electron ejected out from Ag which is being exposed to UV light λ = 362 Å?

Sol: The photoelectric equation gives the minimum energy and the maximum kinetic energy.

Energy of the photon absorbed

$$= \frac{h.c}{\lambda} = \frac{6.625 \times 10^{-27} \times 3 \times 10^{10}}{360 \times 10^{-8}} = 5.52 \times 10^{-11} \text{ erg}$$

= 5.52 × 10^{-18} J

E(photon) = work function + KE

KE = 5.52 × 10^{-8} −7.52 × 10^{-19} = 47.68 × 10^{-19} J

Example 4: How many orbits, orbitals and electrons are there in an atom having atomic mass 24 and atomic number 12?

Sol: The atomic number gives the no. of electrons which when arranged according to the Aufbau's principle gives the orbits and the orbitals of the given atom.

Atomic Number = No. of protons =

No. of electrons = 12

Electronic configuration =2, 8, 2

No. of orbits = (K, L and M)

No. of orbitals on which electrons are present

= (one 1s + one 2s + three 2p + one 3s)

Example 5: Consider the hydrogen atom to be a proton embedded in a cavity of radius ae (Bohr's radius) whose charge is neutralized by the addition of an electron to the cavity in vacuum, infinitely slowly?

(a) Estimate the average of total energy of an electron in its ground state in a hydrogen atom as the work done in the above neutralization process. Also, if the magnitude of the average kinetic energy is half the magnitude of the average potential energy, find the average potential energy.

(b) Also derive the wavelength of the electron when it is a0 from the proton. How do we compare with the wavelength of an electron in the ground state Bohr's orbit?

Sol: As explained below in the respective steps.

Work obtained in the neutralization process is given by:

$$W = -\int_{e}^{da} F.da = -\int_{e}^{da} \frac{1}{4\pi\varepsilon_0} \frac{(-)e^2}{o_n^2} - da_0$$

$$W = -\frac{e^2}{4\pi\varepsilon_0 . a_0}$$

(a) This work is to be called potential energy. However in doing so, one should note that this energy is simply lost during the process of attraction between proton and electron. As reported in the problem at this condition, the electron simply possesses potential energy.

Thus, TE = PE + KE − PE = $-\dfrac{e^2}{4\pi\varepsilon_0 . a_0}$ ...(i)

Now in order, the electron to be captured by the proton to form a ground state hydrogen atom, it should also attain kinetic energy $e^2/(8\pi r_2 a_2)$ (as it is half of the potential energy given in question). Thus, the energy of the electron if it attains the ground state in H-atom.

$$TE = PE + KE = -\frac{e^2}{4\pi\varepsilon_0 a_0} + \frac{e^2}{8\pi\varepsilon_0 a_0}$$

$$TE = -\frac{e^2}{8\pi\varepsilon_0 a_0}$$

(b) The wavelength of electron when it is simply at a distance a0 from the proton can be given as:

$$\lambda = \frac{h}{mv} = \frac{h}{p} \text{ Also, } KE = \frac{1}{2}mv^2 = \frac{p^2}{m}; (\because p = mv)$$

Thus, $\lambda = \dfrac{h}{\sqrt{2m(KE)}}$

Since, KE = 0 at this situation, thus l = ∞

Also, when electron is at a distance a_0 in

Bohr's orbit of H-atom. $\lambda = \dfrac{h}{\sqrt{2m(KE)}} = \dfrac{h}{\sqrt{\dfrac{2me^2}{2a_0 . 4\pi\varepsilon_0}}}$

Example 6: The velocity of an electron in a certain Bohr orbit of H-atom bears the ratio 1:275 to the velocity of light.

(a) What is the quantum no. of orbit?

(b) Calculate the wave numbers of radiation when electron jumps from (n + 1) state to ground state.

Sol: Use the Rydberg's equation to get the wave number and the application of the given statement to get the velocity of the electron. This in turn can be used to find the quantum no. by $u_n = \frac{2\pi e^2}{nh}$.

Given velocity of electron in a certain Bohr orbit of H-atom = (1/275) × velocity of light

= (1/275) × 3 × 10^8 = 1.09 × 10^8 cm sec^{-1}.

(a) Since, $u_n = \frac{2\pi e^2}{nh}$;

$$\therefore 1.09 \times 10^8 = \frac{2.\times 3.14 \times (4.803 \times 10^{-10})^2}{6.626 \times 10^{-27} \times n}$$

∴ n = 2.006 = 2 (an integer value)

(b) Thus, during the jump of electron from (n + 1), i.e. 3rd shell to ground state

$$\bar{v} = \frac{1}{\lambda} = R_H\left[\frac{1}{1^2} - \frac{1}{3^2}\right] = 109678\left[\frac{1}{1} = \frac{1}{9}\right]$$

= 9.75 × 10^4 cm^{-1}

Example 7: The series limit of Balmer series of H spectrum occurs at 3664 Å.

(a) ionization energy of H-atom

(b) wavelength of the photon that would remove the electron in the ground state of the H-atom

Sol: Since it is the Balmer series, n_1 = 2. Using the given λ and $n_2 = \infty$, calculate ionization energy and wavelength by $\Delta E = E_\infty - E_2$

$= -E_2 - \frac{hc}{\lambda}$ and the usual energy formula respectively.

Given series is Balmer series, i.e.

λ = 3664 Å and thus, $n_1 = 2$; $n_2 = \infty$

(a) ∵ E/photon of series limit = $\Delta E = E_\infty - E_2$

$$= -E_2 - \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{3664 \times 10^{-10}}$$

Or $E_2 = -5.42 \times 10^{-19}$ J

∵ $E_1 = E_2 \times n_2 = -4 \times 5.42 \times 10^{-19}$ J

$= -21.68 \times 10^{-19}$ J

(b) Now for removal of electron from the first orbit

$\frac{hc}{\lambda} = 21.68 \times 10^{-19}$; 21.68×10^{-19}

$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{\lambda}$; λ = 916 Å

Example 8: How many elements would be there in the second period of the periodic table if the spin quantum number m could have the values $-\frac{1}{2}$, 0, $\frac{1}{2}$?

Sol: For second period n = 2, hence

l	m_l	m_s
0	0	$+\frac{1}{2}$, 0, $-\frac{1}{2}$
1	−1	$+\frac{1}{2}$, 0, $-\frac{1}{2}$
	0	$+\frac{1}{2}$, 0, $-\frac{1}{2}$
	+1	$+\frac{1}{2}$, 0, $-\frac{1}{2}$

Hence, total number of electrons = 12

(= total values of spin quantum number)

Example 9: The uncertainty in momentum of a particle is 3.31 × 10^{-2} kg m sec^{-1}. Calculate uncertainty in its position.

Sol: Use Heisenberg's uncertainty principle to determine the above.

$$\Delta x = \frac{h}{4\pi} - \Delta p$$

$\Delta p = 3.31 \times 10^{-2}$ kg m sec^{-1}

Since, $\Delta p . \Delta x = \frac{h}{4\pi}$ ∴ ΔX

$$= \frac{h}{4\pi . \Delta p} = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 3.31 \times 10^{-2}}$$

= 1.6 × 10^{-33} m

JEE Advanced/Boards

Example 1: The wave function (ψ) of 2s-orbital is given by:

$$\psi_{2s} = \frac{1}{\sqrt{32\pi}}\left[\frac{1}{a_0}\right]^{3/2}\left[2 - \frac{r}{a_0}\right]e^{t/2a_0}$$

At r = r_0, radial node is formed. Calculate r_0 in terms of a_0.

Sol: $\psi_{2s} = \frac{1}{\sqrt{32\pi}}\left[\frac{1}{a_0}\right]^{3/2}\left[2-\frac{r}{a_0}\right]e^{t/2a_0}$

For radial node at r = r_0, $\psi_{2s}^2 = 0$. This is possible only when $\left[2-\frac{r_0}{a_0}\right] = 0$; ∴ $r_0 = 2a_0$

Example 2: 2.4 mole of H_2 sample was taken. In one experiment, 60% of the sample exposed to continuous radiation of frequency 4.47 × 10^{15} Hz, of which all the electrons are removed from the atom. In another experiment, remaining sample was irradiated with light of wavelength 600 Å, when all the electrons are removed from the atom. In another experiment, remaining sample was irradiated with light of wavelength 600Å , when all the electrons are removed from the surface. Calculate the ratio of maximum velocity of the ejected electron in each case. Assume that ejected electrons do not interact with any photon (Ionization potential of H = 13.6 eV).

Sol: Calculate 60% of the sample exposure from the given data and apply the photoelectric equation.

Moles of H_2 exposed to radiation of 4.47 × 10^{15} Hz

$-\frac{60}{100}\times 2.4 = 1.44$

Moles of atoms obtained by 60% sample

= 1.44 × 2 = 2.88

No. of atoms obtained = 2.88 × 6.023 × 10^{23} = 1.73 × 10^{14}

∴ No. of electron ejected = 1.73 × 10^{24}

(Each H-atom has one electron)

Applying photoelectric effect,

$h\nu = KE + IE$; $h\nu = KE + 13.6 \times 1.6 \times 10^{-19}$

KE = $[6.626 \times 10^{-14} \times 4.47 \times 10^{15}] - [13.6 \times 1.6 \times 10^{-19}]$ = 7.86×10^{-19} (∵ = 4.47 × 10^{15} Hz);

∵ KE = $mv_1^2/2$

$$v_1 = \sqrt{\frac{1\times 7.86\times 10^{-39}}{9.1\times 10^{-31}}} = 1.3\times 10^6 \text{ m/s}$$

Applying photoelectric effect

$h\nu = KE + 13.6 \times 1.6 \times 10^{-19}$

$$KE = \left[\frac{6.626\times 10^{-34}\times 3\times 10^8}{600\times 10^{-10}}\right] - [13.6\times 1.6\times 10^{-19}]$$

$$= 1.137 \times 10^{-18}\text{ J}\left[\because \nu = \frac{c}{\lambda} = \frac{3\times 10^8}{600\times 10^{-10}}\right]$$

$$v_2 = \sqrt{\frac{2\times 1.137\times 10^{-18}}{9.1\times 10^{-31}}};\ v_2 = 1.58 \times 10^9 \text{ m/s}$$

$$\frac{v_1}{v_2} = \frac{1.3\times 10^6}{1.56\times 10^6} = 0.83;\ \frac{v_2}{v_1} = 1.22$$

Example 3: Calculate the following:

(i) Velocity of electron in first Bohr orbit of H-atom (r = a_0)

(ii) De Broglie wavelength of electron in first Bohr orbit of H-atom

(iii) Orbit angular momentum of 2p-orbitals in term of $\frac{h}{2\pi}$ unit. $-\sqrt{l(l+1)}\times\frac{h}{2\pi}$

$= \sqrt{2}\times\frac{h}{2\pi} = \sqrt{2}h$

Sol: Using one of the Bohr's postulates, apply the centripetal force equation. Secondly, solve the De-Broglie equation for the wavelength.

(i) $mvr = \frac{nh}{2\pi}$; ∴ $v = \frac{nh}{2\pi mr}$

$$= \frac{1\times 6.626\times 10^{-34}}{2\times 3.14\times 9.108\times 10^{-31}\times 0.529\times 10^{-10}}$$

(ii) $\lambda = \frac{h}{mv} = \frac{6.626\times 10^{-34}}{9.108\times 10^{-31}\times 2.19\times 10^6} = 3.32\times 10^{-10}\text{m}$

Example 4: A gas of identical H-like atom has some atoms in the lowest (ground) energy level A and some atoms in a particular upper (excited) energy level B and there are not atoms in any other energy level. The atoms of the gas make transition to a higher energy level by absorbing monochromatic light of photon energy 2.7 eV. Subsequently, the atoms emit radiation of only six different photon energies. Some of the emitted photons have energy 2.7 eV. Some have more and some have less than 2.7 eV.

(i) Find the principal quantum number of initially excited level B.

(ii) Find the ionization energy for the gas atoms.

(iii) Find the maximum and the minimum energies of the emitted photons.

Sol: The electrons being present in *l* shell and another shell n_1. These are excited to higher level n_2 by absorbing 2.7 eV and on de-excitation emits six l and thus excited state n_2 comes to be 4 [$6 = \Sigma E_n = \Sigma(n_2 - 1)$ ∴ $n_2 = 4$]

Now, $E_1 = -\frac{R_H ch}{1^2}$;

$$E_n = -\frac{R_H ch}{n_1^2};$$

$$E_4 = -\frac{R_H ch}{4^2}$$

Since, de-excitation leads to different *l* having photon. Energy < 2.7 eV and thus absorption of 2.7 eV energy causing excitation to fourth shell then reemitting photon of > 2.7 eV is possible only when $n_1 = 2$ (the de-excitation from fourth shell occurs in first, second and third shells).

$E_4 - E_2 = 2.7$ eV; $E_4 - E_3 < 2.7$ eV

$E_4 - E_1 > 2.7$ eV

$\therefore E_n = E_2 = \frac{R_H \times c \times h}{2^2} = \frac{E_1}{2^2}$ since $n_1 = 2$

Also, $E_4 - E_2 - 2.7$ eV; $\therefore \left[\frac{-E_1}{4^2} + \frac{-E_1}{2^2}\right] = 2.7 \text{ eV}$

$\therefore E_1 = -14.4$ eV; IE = 14.4 eV

$$E_{max.} = E_4 - E_1 = -\frac{E_1}{4^2} + E_1; -\frac{14.4}{16} + 14.4 = 13.5 \text{ eV};$$

$$E_{min.} = E_4 - E_3 = \left[-\frac{E_1}{4^2} + \frac{E_1}{3^2}\right] = 0.7 \text{ eV}$$

Note: It is $_1H^2$ atom

Example 5: Two hydrogen atoms collide head on and end up with zero kinetic energy. Each atom then emits a photon of wavelength 131.6 nm. Which transition leads to this wavelength? How fast were the hydrogen atoms travelling before collision?

[$R_H = 1.097 \times 10^7$ m^{-1} and $m_H = 1.67 \times 10^{-27}$ kg]

Sol: With the given data calculate the transition levels using the Rydberg equation and solve for velocity by equating kinetic energy and the energy of a photon.

Wavelength emitted in UV region and thus

$n_1 = 1$; For H-atom $\therefore \frac{1}{\lambda} = R_H\left[\frac{1}{1^2} - \frac{1}{n^2}\right]$

$$\frac{1}{121.6 \times 10^{-9}} = 1.097 \times 10^7\left[\frac{1}{1^2} - \frac{1}{n^2}\right] \therefore n = 2$$

Also the energy released is due to collision and all the kinetic energy is released in the form of photon. Thus,

$$\frac{1}{2}mv^2 = \frac{hc}{\lambda}$$

Or $\frac{1}{2} \times 1.67 \times 10^{-27} \times v^2 = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{121.6 \times 10^{-3}}$

$\therefore v = 4.43 \times 10^4$ m sec^{-1}

Example 6: Let a light of wavelength λ and intensity T strike a metal surface to emit x electrons per second. Average energy of each electron is 'y' unit, What will happen to x and y when (a) λ is halved (b) intensity I is double?

Sol: (a) Rate of emission of electron is independent of wavelength. Hence, 'x' will be unaffected. Kinetic energy of photoelectron = absorbed energy − Threshold energy $y = \frac{hc}{\lambda} - w_0$

When I is halved, average energy will increases but it will not become double.

(b) Rate of emission of electron per second 'x' will become double when intensity I is double. Average energy of ejected electron, i.e. 'y' will be unaffected by increases in the intensity of light.

Example 7: The IP_1 of H is 13.6 eV. It is exposed to electromagnetic waves of 1028 Å and gives out induced radiation. Find the wavelength of these induced radiations:

Sol: From energy of H-atom, solve for the level. Thus, calculate the consecutive wavelength.

E_1 of H atom = −13.6 eV

Energy given to H atom

$-\frac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{1028 \times 10^{-10}} = 1.933 \times 10^{-18}$ J = 12.07 eV

$\therefore$ Energy of H atom after excitation

= −13.6 + 12.07 = −1.53 eV

$\therefore E_n = \frac{E_1}{n^2}; \therefore n^2 = \frac{-13.6}{-1.53} = 9; \therefore n = 3$

Thus, electron in H atom is excited to third shell.

$\therefore$ I induced $\lambda_1 = \frac{hc}{E_3 - E_1}$

$\therefore E_1 = -13.6$ eV; $E_3 = -1.53$ eV

$\therefore \lambda_1 = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{(-1.53 + 13.6 \times 1.602) \times 10^{19}} = 1028 \times 10^{10}$ m

$\therefore \lambda = 1028Å;$

$$\therefore \text{II induced } \lambda_2 = \frac{hc}{(E_2 - E_1)}$$

$$E_1 = -13.6 \text{ eV}; E_2 = -\frac{13.6}{4}\text{eV}$$

$$\therefore \lambda_2 = \frac{6.625 \times 10^{-14} \times 3.0 \times 10^8}{\left(-\frac{13.6}{4} + 13.6\right) \times 1.602 \times 10^{-19}}$$

$= 1216 \times 10^{-16}$ m = 1216 Å

$$\therefore \text{III induced } \lambda_3 = \frac{hc}{(E_2 - E_1)}$$

$$\therefore \lambda_2 = -\frac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{\left(-\frac{13.6}{9} + \frac{13.6}{4}\right) \times 1.602 \times 10^{-19}}$$

$= 6568 \times 10^{-10}$m = 6568 Å

Example 8: How many elements would be in the third period of the periodic table if the spin quantum number m_2 could have the value $-\frac{1}{2}$, 0 and $+\frac{1}{2}$?

Sol: Apply the data to the formulas of the quantum numbers.

n= 1, l = 0, m=0 $\quad m_s = -1/2, 0, +1/2$

l=1; m = −1, 0, +1

$m_s = -\frac{1}{2}, 0, +\frac{1}{2}$

$m_s = -\frac{1}{2}, 0, +\frac{1}{2}$

$m_s = -\frac{1}{2}, 0, +\frac{1}{2}$

l=2 ; m =−2, −1, 0, 0, +1, +2 $\left\{ m_f = -\frac{1}{2}, 0, +\frac{1}{2} \right.$ for each value of magnetic quantum no. $\}$

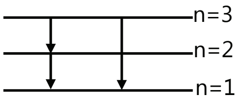
Number of elements = 3s(3e)

3p(9e)

3d(15e)

∴ 27 elements will be there in third period of periodic table.

Example 9: Consider the following two electronic transition possibilities in a hydrogen atom as pictured below:



(a) The electron drops from third Bohr orbit to second Bohr orbit followed with the next transition from second to first Bohr orbit.

(b) The electron drops from third Bohr orbit to first Bohr orbit directly. Show that the sum of energies for the transitions n = 3 to n = 2 and n = 2 to n = 1 is equal to the energy of transition for n =3 to n = 1.

Sol: Applying $\Delta E = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

For n = 3 to n = 2

$$\Delta E_{3\to2} = R_H\left[\frac{1}{2^2} - \frac{1}{3^2}\right] = R_H \times \frac{5}{36} \qquad \text{... (i)}$$

For n = 2 to n = 1

$$\Delta E_{2\to1} = R_H\left[\frac{1}{1^2} - \frac{1}{2^2}\right] = R_H \times \frac{3}{4} \qquad \text{... (ii)}$$

For n = 3 to n = 1;

$$\Delta E_{3\to1} = R_H\left[\frac{1}{1^2} - \frac{1}{3^2}\right] = R_H \times \frac{8}{9} \qquad \text{... (iii)}$$

Adding equation (i) and (ii)

$$\left(\frac{5}{36} + \frac{3}{4}\right) = R_H\left(\frac{5+27}{36}\right) = R_H \times \frac{8}{9}$$

Thus, $\Delta E_{3\to1}\ \Delta E_{3\to2} + \Delta E_{2\to1}$

Example 10: Consider the hydrogen atom to be a proton embedded in a cavity of radius a_0 (Bohr radius) whose charge is neutralized by the addition of an electron to the cavity in vacuum infinitely slowly. Estimate the average total energy of an electron in its ground state in a hydrogen atom as the work done in the above neutralization process. Also, if the magnitude of average KE is half the magnitude of average potential energy, find the average potential energy.

Sol: Coulombic force of attraction = Centrifugal force

$$\frac{1}{4\pi \in_0}\frac{Ze \times e}{a_0^2} = \frac{m\upsilon^2}{a_0}$$

Where, υ = velocity of electron

a_0 = distance between electron and nucleus

$$\frac{1}{4\pi \in_0}\frac{Ze^2}{a_0} = m\upsilon^2$$

$$KE = \frac{1}{2}m\upsilon^2 = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{2a_0}$$

$$PE = -2 \times KE = -2 \times \frac{1}{4\pi\varepsilon_0} \times \frac{Ze^2}{2a_0} = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{a_0}$$

JEE Main/Boards

Exercise 1

Q.1 In an oil drop experiment, the following charges (in arbitrary units) were found on a series of oil droplets: 4.5×10^{-18}, 3.0×10^{-18}, 6.0×10^{-18}, 7.5×10^{-18}, 9.0×10^{-18}. What is the charge on electron (in the same unit)?

Q.2 Arrange electron (e), proton (p), neutron (n) and α-particle (a) in the increasing order of their specific charges.

Q.3 With what velocity should an α-particle travel towards the nucleus of a copper atom so as to arrive at a distance 10^{-13} m from the nucleus of the copper atom? Atomic number of copper is 29. Mass of alpha particle is 4 amu.

Q.4 The wavelength of the Kα line for an element of atomic number 57 is λ. What is wavelength of the Kα line for the element of atomic number 29.

Q.5 The wavelength of an electromagnetic radiation is 600 nm. What is its frequency?

Q.6 Calculate the energy per quanta of an electron magnetic radiation of wavelength 6626Å.

Q.7 Calculate the Rydberg constant R_H if He^+ ions are known to have the wave length difference between first (of the longest wavelength) lines of Balmer and Lyman series equal to 133.7 nm.

Q.8 Suppose 10^{-17} J of light energy is needed by the interior of the human eye to see an object. How many photons of green light (λ = 550 nm) are needed to generate this minimum amount of energy?

Q.9 The bond energy of H−H bond is 104 kcal/mol. What is the largest wavelength of electromagnetic radiation needed to dissociate H_2 molecules? Assume that one photon may dissociate only one molecule.

Q.10 The work function of potassium is 2.25 eV. Would photoelectron emit when red light of 660 nm falls on potassium surface? If yes, what would be the maximum kinetic energy of electron liberated?

Q.11 The threshold frequency of a metal is 1.8×10^{14} Hz. Calculate the maximum kinetic energy of photoelectron liberated when the metal is irradiated by an electromagnetic radiation of wavelength 4000Å.

Q.12 A particle of mass 'm' moves along a circular orbit in a centro-symmetrical potential field $U(r) = Kr^2/2$. Using the Bohr quantization condition, find the permissible orbital radii of that particle.

Q.13 Light of wave length 2000Å falls on an aluminium surface (work function of aluminium 4.2 eV). Calculate (a) The kinetic energy of the fastest and slowest emitted photo electrons (b) Stopping potential. (c) Cut-off wavelength for Aluminium.

Q.14 Calculate the speed of electron revolving in the 3rd orbit of hydrogen atom.

Q.15 An electron is revolving at a distance of 4.761 Å from the hydrogen nucleus. Determine its speed.

Q.16 Calculate the ratio of time period of electron in the 2nd orbit of H-atom to that in the 3rd orbit of He^+ ion.

Q.17 Calculate the angular frequency of an electron occupying the second Bohr orbit of He^+ ion.

Q.18 Calculate the first four energy levels for electron in hydrogen atom.

Q.19 The dissociation energy of H_2 is 103.2 k cal mole^{-1}. Suppose H_2 molecules are irradiated with wavelength, λ = 2537Å. Assume that one photon is absorbed by and dissociated one molecule of H_2. How much of the photon energy is converted into kinetic energy of the dissociated atoms.

Q.20 Calculate the kinetic, potential and total energy of electron in the 3rd orbit of He^+ ion.

Q.21 Calculate the excitation energy of Li^{2+} ion in the ground state.

Q.22 Calculate the binding energy of electron in the ground state of He^+ ion.

Q.23 Electromagnetic radiation of wavelength 24 nm is just sufficient to ionize sodium atom. Calculate the ionization energy of sodium atom.

Q.24 A beam of electron accelerated with 4.64 V is passed through a tube containing mercury vapours. As a result of absorption, electronic changes occurred with mercury atoms and light was emitted if the full energy of single electron was converted into light, what was the wave number of emitted light?

Q.25 A proton and an electron, both at rest initially, combine to form a hydrogen atom in the ground state. A single photon is emitted in this process. What is its wavelength?

Q.26 Calculate the frequency of the radiation absorbed in the transition n = 2 to n = 4 in hydrogen atom.

Q.27 When electromagnetic radiations of wavelength λ nm fall on hydrogen atoms, electron excite from the ground state to a particular upper energy state. Subsequently, the atoms emit the radiations of six different wavelengths. Calculate the value of λ.

Q.28 The wavelength of H line in the Balmer series of hydrogen spectrum is 660 nm. What is the wavelength of H-line of this series

Q.29 Calculate the momentum of a photon of wavelength 10 Å.

Q.30 Electrons which have absorbed 10.20 eV and 12.09 eV in hydrogen atom can cause radiations to be emitted when they come back to ground state. Calculate in each come back to ground state. Calculate in each case the principal quantum no. of the orbit to which electron goes and the wavelength of the radiations emitted if it drops back to ground state.

Exercise 2

Single Correct Choice Type

Q.1 Which of the following does not characterize x-rays?

(A) The radiation can ionize gases

(B) It causes ZnS to show fluorescence

(C) Deflected by electric and magnetic fields

(D) Have wavelength shorter than ultraviolet rays.

Q.2 Which of the following is false regarding Bohr's model

(A) It introduces the idea of stationary states

(B) It explains the line spectrum of hydrogen

(C) It gives the probability of the electron near the nucleus

(D) It predicts that the angular momentum of electron in H-atom = nh/2π.

Q.3 The energy of an orbit in a hydrogen atom is given by the relation $E = \frac{\text{Constant}}{n^2}(\text{kJ mol}^{-1})$. Which of the following properties represents the constant in the above relation

(A) Electron affinity (B) Ionization energy

(C) Electro negativity (D) Bond energy

Q.4 The ratio of the energy of a photon of 2000Å wavelength radiation to that of 4000Å radiation is

(A) 1/4 (B) 4 (C) ½ (D) 2

Q.5 The energy of electron is maximum at

(A) Nucleus

(B) Ground state

(C) First excited state

(D) Infinite distance from the nucleus

Q.6 Which quantum number is not related with Schrödinger equation?

(A) Principal (B) Azimuthal

(C) Magnetic (D) Spin

Q.7 The shortest wavelength of He atom in Balmer series is X, then longest wavelength in the Paschen series of Li^{+2} is

(A) $\frac{36x}{5}$ (B) $\frac{16x}{7}$ (C) $\frac{36x}{5}$ (D) $\frac{5x}{9}$

Q.8 An electron in a hydrogen atom in its ground state absorbs energy equal to the ionization energy of Li^{+2}. The wavelength of the emitted electron is:

(A) 3.32×10^{-10} m (B) 1.17 Å

(C) 2.32×10^{-9} nm (D) 3.33 pm

Q.9 Given ΔH for the process $Li(g) \rightarrow Li^{+3}(g) + 3e^-$ is 19800 kJ/mole and IE_1 for Li is 520 then IE_2 and IE_3 of Li+ are respectively (approx. value)

(A) 11775, 7505 (B) 19280, 520

(C) 11775, 19280 (D) Data insufficient

Q.10 The ratio of difference in wavelengths of 1st and 2nd lines of Lyman series in H-like atom to difference in wavelength for 2nd and 3rd lines of same series is:

(A) 2.5: 1 (B) 3.5: 1 (C) 4.5: 1 (D) 5.5: 1

Q.11 The ratio of the radii of the first three Bohr orbit is

(A) 1: 0.5: 033 (B) 1: 2: 3

(C) 1: 4: 9 (D) 1: 8: 27

Q.12 Which combination of quantum number n, *l*, m, s for the electron in an atom does not provide a permissible solution of the wave equation?

(A) 3, 2, −2, +1/2 (B) 3, 3, 1, − ½

(C) 3, 2, 1, +1/2 (D) 3, 1, 1, −1/2

Q.13 The ratio of the energy of a photon of 2,000 Å wavelength radiation to that of 4,000 Å radiation is

(A) 1/4 (B) 4 (C) 1/2 (D) 2

Q.14 The orbital angular momentum of an electron in 2s orbital is

(A) $+\frac{1}{2}\left(\frac{h}{2\pi}\right)$ (B) Zero (C) $h/2\pi$ (D) $\sqrt{2}\times\frac{h}{2\pi}$

Q.15 If n and *l* are respectively the principal and azimuthal quantum number, then the expression for calculating the total number of electrons in any energy level is

(A) $\sum_{i=0}^{\ell-n-\ell} 2(2\ell+1)$ (B) $\sum_{i=0}^{\ell-n-\ell} 2(2\ell+1)$

(C) $\sum_{i=0}^{\ell-n+\ell} 2(2\ell+1)$ (D) $\sum_{i=0}^{\ell-n-\ell} 2(2\ell\times1)$

Q.16 The wavelength of a tennis ball of mass 6.0×10^{-2} kg moving at a speed of about 140 miles per hour is ($h = 6.63 \times 10^{-27}$ erg s)

(A) 1.8×10^{-30} cm (B) 1.8×10^{-32} cm

(C) 1.8×10^{-34} cm (D) None of these

Q.17 If radius of second stationary orbit (in Bohr's atom) is R. Then radius of third orbit will be

(A) R/3 (B) 9R (C) R/9 (D) 2.25 R

Q.18 The ratio of wave length of photon corresponding to the α-line of Lyman series in H-atom and β-line of Balmer series in He^+ is

(A) 1: 1 (B) 1: 2 (C) 1: 4 (D) 3: 16

Q.19 The value of $(n_2 + n_1)$ and for He^+ ion in atomic spectrum are 4 and 8 respectively. The wavelength of emitted photon when electron jump from n_2 to n_1 is

(A) $\frac{32}{9}R_H$ (B) $\frac{9}{32}R_H$ (C) $\frac{9}{32R_H}$ (D) $\frac{32}{9R_H}$

Q.20 Number of possible spectral lines which may be emitted in bracket series in H atom if electron present in 9th excited level returns to group level, are

(A) 21 (B) 6 (C) 14 (D) 7

Q.21 The first use of quantum theory to explain the structure of atom was made by:

(A) Heisenberg (B) Bohr

(C) Planck (D) Einstein

Q.22 The wavelength associated with a golf weighing 200 g and moving at a speed of 5 m/h of the order

(A) 10^{-10} m (B) 10^{-20} m

(C) 10^{-30} m (D) 10^{-40} m

Q.23 The longest wavelength of He^+ in Paschen series is "m", then shortest wavelength of Be^{+3} in Paschen series is (in terms of m):

(A) $\frac{5}{36}m$ (B) $\frac{64}{7}m$ (C) $\frac{53}{8}m$ (D) $\frac{7}{64}m$

Q.24 Consider the following nuclear reactions involving X and Y.

$$X \rightarrow Y + {}_2^4He\,;\ Y \rightarrow {}_8O^{18} + {}_1H^1$$

If both neutrons as well as protons in both the sides are conserved in nuclear reaction then moles of neutrons in 4.6 gm of X

(A) 2.4 NA (B) 2.4

(C) 4.6 (D) 0.2 NA

Q.25 Electromagnetic radiations having λ = 310Å are subjected to a metal sheet having work function = 12.8 eV. What will be the velocity of photoelectrons with maximum Kinetic energy

(A) 0, no emission will occur (B) 2.15×10^6 m/s

(C) $2.18\sqrt{2} \times 10^6 \text{m/s}$ (D) 8.72 × 106 m/s

Q.26 Assuming Heisenberg Uncertainty Principle to be true what could be the minimum uncertainty in de-Broglie wavelength of a moving electron accelerated by Potential Difference of 6V whose uncertainty in position is 7/22 n.m.

(A) 6.25Å (B) 6Å

(C) 0.625 Å (D) 0.3125 Å

Q.27 Correct statement(s) regarding 3P, orbital is/are

(A) Angular part of wave function is independent of angles θ and ϕ)

(B) No. of maxima when a curve is plotted between $4\pi r^2 R^2(r)$ vs. r are '2'

(C) 'rz' plane acts as nodal plane

(D) Magnetic quantum number must be '−1'.

Q.28 Choose the incorrect statement(s):

(A) Increasing order of wavelength is Micro waves > Radio waves > IR waves > visible waves > UV waves

(B) The order of Bohr radius is (r_n: where n is orbit number for a given atom) $r_1 < r_2 < r_3 < r_4$

(C) The order of total energy is (E_n: where n is orbit number for a given atom)

(D) The order of velocity of electron in H, He^+, Li^+, Be^{3+} species in second Bohr orbit is

$Be^{1+} > Li^{+2} > He^+ > H$

Q.29 Which is/are correct statement.

(A) The difference in angular momentum associated with the electron present in consecutive orbits of H-atom is $(n-1)\dfrac{h}{2\pi}$

(B) Energy difference between energy levels will be changed if, PE. At infinity assigned value of other than zero.

(C) Frequency of spectral line in a H-atom is in the order of $(2 \rightarrow 1) < (3 \rightarrow 1) < (4 \rightarrow 1)$

Previous Years' Questions

Q.1 Who discovered neutron ***(1982)***

(A) James Chadwick (B) William Crooks

(C) J.J. Thomson (D) Rutherford

Q.2 The radius of an atom is of the order of ***(1985)***

(A) 10^{-10} cm (B) 10^{-13} cm

(C) 10^{-15} cm (D) 10^{-8} cm

Q.3 Which one of the following constitutes a group of the isoelectronic species ***(2008)***

(A) NO^+, C_2^{2-}, CN^-, N_2 (B) CN^-, N_2, O_2^{2-}, C_2^{2-}

(C) N_2, O_2^-, NO^+, CO (D) C_2^{2-}, O^-_2, CO, NO

Q.4 Which one of the following groupings represents a collection of isoelectronic species ***(2003)***

(A) Na^+, Ca^{2+}, Mg^{2+} (B) $N3^-$, F^-, Na^+

(C) Be, A^{3+}, Cl^- (D) Ca^{2+}, Cs^+, Br

Q.5 The radius of which of the following orbit is same as that of the first Bohr's orbit of hydrogen atom ***(2004)***

(A) He^+ (n = 2) (B) Li^{2+} (n = 2)

(C) Li^{2+} (n = 3) (D) Be^{3+} (n = 2)

Q.6 The wavelength of the radiation emitted, when a hydrogen atom electron falls from infinity to stationary state 1, would be (Rydberg constant = 1.097×10^7 m^{-1}) ***(2004)***

(A) 406 nm (B) 192 nm

(C) 91 nm (D) 9.1×10^{-8} nm

Q.7 The ionization enthalpy of hydrogen atom is 1.313×10^6 J mol^{-1}. The energy required to excite the electron in the atom from n = 1 to n = 2 is ***(2008)***

(A) 6.56×10^5 J mol^{-1} (B) 7.56×10^5 J mol^{-1}

(C) 9.84×10^{-5} J mol^{-1} (D) 8.51×10^5 J mol^{-1}

Q.8 A gas absorbs a photon of 355 nm and emits at two wavelengths. If one of the emissions is at 680 nm, the other is at ***(2011)***

(A) 1035 nm (B) 325 nm

(C) 743 nm (D) 518 nm

Q.9 Calculate the wavelength (in nanometer) associated with a proton moving at $1.0 \times 10^3\ ms^{-1}$ (Mass of proton $= 1.67 \times 10^{-27}$ kg and $h = 6.63 \times 10^{-34}$ Js): ***(2009)***

(A) 0.032 nm (B) 0.40 nm

(C) 2.5 nm (D) 14.0 nm

Q.10 In an atom, an electron is moving with a speed of 600 m/s with an accuracy of 0.005%. Certainty with which the position of the electron can be located is ($h = 6.6 \times 10^{-34}\ kg\ m^2\ s^{-1}$, mass of electron $m = 9.1 \times 10^{-31}$ kg) ***(2009)***

(A) 1.52×10^{-4} m (B) 5.10×10^{-3} m

(C) 1.92×10^{-3} m (D) 3.84

Q.11 Which of the following sets of quantum number represents the highest energy of an atom? ***(2007)***

(A) n = 3, l = 1, m = 1, s = ±1/2

(B) n = 3, l = 2, m=1, s = −1/2

(C) n = 4, l = 0, m = 0, s = ±1/2

(D) n = 3, l = 0, m = 0, s = ±1/2

Q.12 In a multi-electron atom, which of the following orbital's described by the three quantum numbers will have the same energy in the absence of magnetic and electric fields

(1) n = 1, l = 0, m = 0 (2) n = 2, l = 0, m = 0
(3) n = 2, l = 1, m= 1 (4) n = 3, l = 2, m = 0
(5) n = 3, l = 2, m = 1 ***(2005)***

(A) (1) and (2) (B) (2) and (3)

(C) (3) and (4) (D) (4) and (5)

Q.13 The electronic configuration of an element is $1s^2\ 2s^2\ 3p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$. This represent its ***(2000)***

(A) Excited sate (B) Ground state

(C) Cationic form (D) Anionic form

Q.14 Which of the following sets of quantum number is correct for an electron in 4f orbital? ***(2004)***

(A) n = 4, l = 3, m = +1, s = +1/2

(B) n = 4, l = 4, m = −4, s = −1/2

(C) n = 4, l = 3, m = +4, s = +1/2

(D) n = 3, l = 2, m = −2, s = +1/2

Q.15 The electrons identified by quantum numbers n and λ ***(2012)***

(1) n = 4, λ = 1 (2) n = 4, λ = 0

(3) n = 3, λ = 2 (4) n = 3, λ = 1

Can be placed in order of increasing energy as

(A) (3) < (4) < (2) < (1) (B) (4) < (2) < (3) < (1)

(C) (2) < (4) < (1) < (3) (D) (1) < (3) < (2) < (4)

Q.16 In an atom, an electron is moving with a speed of 600m/s with an accuracy of 0.005%. Certainity with which the position of the electron can be located is

$$\begin{pmatrix} h = 6.6 \times 10^{-34}\ kg\ m^2\ s^{-1}\ \text{mass of electron, } e_m \\ = 9.1 \times 10^{-31}\ kg \end{pmatrix}$$ ***(2009)***

(A) 1.52×10^{-4} m (B) 5.10×10^{-3} m

(C) 1.92×10^{-3} m (D) 3.84×10^{-3} m

Q.17 Calculate the wavelength (in nanometer) associated with a proton moving at $1.0 \times 10^3\ ms^{-1}$ (Mass of proton $= 1.67 \times 10^{-27}$ kg and $h = 6.63 \times 10^{-34}$ Js): ***(2009)***

Q.18 The energy required to break one mole of Cl–Cl bonds in Cl_2 is 242 kJ mol^{-1}. The longest wavelength of light capable of breaking a single Cl − Cl bond is $\left(c = 3 \times 10^8\ ms^{-1} \text{ and } N_A = 6.02 \times 10^{23}\ mol^{-1}\right)$ ***(2010)***

(A) 594 nm (B) 640 nm

(C) 700 nm (D) 494 nm

Q.19 Ionisation energy of He^+ is 1.96×10^{-18} J $atom^{-1}$. The energy of the first stationary state (n = 1) of Li^{2+} is ***(2010)***

(A) 4.41×10^{-16} J $atom^{-1}$

(B) -4.41×10^{-17} J $atom^{-1}$

(C) -2.2×10^{-15} J $atom^{-1}$

(D) 8.82×10^{-17} J $atom^{-1}$

Q.20 Which of the following is the energy of a possible excited state of hydrogen? ***(2015)***

(A) +13.6 eV (B) –6.8 eV

(C) –3.4 eV (D) +6.8 eV

JEE Advanced/Boards

Exercise 1

Q.1 What is the relationship between the eV and the wavelength in meter of the energetically equivalent photon?

Q.2 What electronic transition in the He^+ would emit the radiation of the same wavelength as that of the first Lyman transition of hydrogen (i.e., for an electron jumping from n = 2 to n = 1)? Neglect the reduced – mass effect. Also calculate second ionization potential of He and first Bohr orbit for He^+. ($e = 1.65 \times 10^{-19}$ coulomb, $m = 9.1 \times 10^{-31}$ kg, $h = 6.626 \times 10^{-34}$ J, sec $c = 2.997 \times 10^8$ meter/sec and $e_0 = 8.854 \times 10^{-12}$ columb^2/newton metre^2)

Q.3 What acceleration potential is needed to produce an electron beam with an effective wavelength of 0.090 Å?

Q.4 In view of the uncertainty principle explain that the motion of an electron cannot be described in terms of orbit as proposed by Bohr.

Q.5 With what velocity should an α-particle travel towards the nucleus of a Cu-atom so as to arrive at distance 10^{-13} meter from the nucleus of the Cu-atom? (Cu = 29, $e = 1.6 \times 10^{-19}$C $a_0 = 8.85 \times 10^{-12}$ J^{-1} C^{-1} C^2m^{-1} $m_0 = 9.1 \times 10^{-31}$ kg)

Q.6 Calculate the velocity of an electron in the third orbit of the hydrogen atom. Also calculate the number of revolutions per second made by this electron around the nucleus.

Q.7 According to Bohr theory, the electronic energy of hydrogen atom in the n^{th} Bohr atom is given by $E = \dfrac{-21.76 \times 10^{-19}}{n^2}$ J. Calculate the longest wavelength of light that will be needed to remove an electron from the third Bohr orbit of the He^+ ion.

($h = 6.626 \times 10^{-34}$ J sec, $c = 3 \times 10^8$ m sec^{-1})

Q.8 Why the concept of orbit has been replaced by probability picture?

Q.9 What is meant by atomic orbital? Explain the concept of orbital in terms of probability density?

Q.10 Explain hydrogen spectrum.

Q.11 The λ of H_α line of Balmer series of 6500 Å. What is the l of H_β line of Balmer series.

Q.12 Calculate the frequency of the spectral line emitted when the electron in n = 3 in H atom de excites to ground state $R_H = 109737$ cm^{-1}.

Q.13 Estimate the difference in energy between 1st and 2nd Bohr orbit for a H atom. At what minimum atomic no., a transition from n = 2 to n = 1 energy level would result in the emission of X-ray with $\lambda = 3.0 \times 10^8$ m. Which hydrogen atom like species does this atomic no. corresponds to?

Q.14 What does the shape of an atomic orbital represent?

Q.15 How many nodes and spherical nodes are there in p_x orbital?

Q.16 Why is the electronic configuration $1s^2\ 2s^2\ 2p^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^4$ not correct for chromium? What is the its correct configuration (Atomic number of Cr is 24). Give proper explanation.

Q.17 The photo electric emission requires a threshold frequency v_0 for a certain metal λ_1 = 2200Å and λ_2 = 1900Å produce electrons with maximum kinetic energy KE_1 and KE_2. If $KE_2 = 2KE_1$ calculate v_0 and corresponding value.

Q.18 A near ultraviolet photon of 300 nm is absorbed by a gas and then re-emitted as two photons? One photon is red with wavelength 760 nm. What would be the wavelength of the second photon?

Q.19 Show that the wavelength of a 150 rubber ball moving with a velocity 50 m sec^{-1} is short enough to be observed.

Q.20 When a certain metal was irradiated with light frequency 1.6×10^{16} Hz, the photo electrons emitted had twice the kinetic energy as did photoelectrons emitted when the same metal was irradiated with light of frequency 1.0×10^{16} Hz. Calculate v_0 (threshold frequency) for metal.

Q.21 Magnetic moment of X^{st} ion of 3d series is B.M. What is atomic number of X^{34}?

Q.22 Iodine molecule dissociates into atoms after absorbing light of 4500 Å if one quantum of radiation is absorbed by each molecule. Calculate the kinetic energy of iodine?

Q.23 Energy required to stop the ejection of electron from Cu plate is 0.24 eV. Calculate the work function when radiations of $\lambda = 253.7$ nm strikes the plate.

Q.24 Calculate the energy emitted when electrons of 1.0 g atom of hydrogen undergo transition giving the spectral lines lowest energy in the visible region of its atomic spectra

$R_H = 1.1 \times 10^3\ m^{-1}$, $C = 3 \times 10^8$ m sec^{-1} and $h = 6.62 \times 10^{-34}$ Js.

Q.25 The characteristics X-rays wavelength for the lines of the K_α series in elements X and Y are 9.87 Å and 2.29 Å respectively. If Moseley's equation $\sqrt{v} = 4.9 \times 10^7 (Z - 0.75)$ is followed, what are atomic numbers of X and Y

Q.26 In the Balmer series of atomic spectra of hydrogen there is a line corresponding to wavelength 4744 Å. Calculate the number of higher orbits from which the electron drops to generate other line $[R \times C = 3.289 \times 10^{13}]$

Q.27 Assuming a spherical second and third Bohr orbits of the hydrogen atom is -5.42×10^{-12} ergs and -2.41×10^{-11} ergs respectively. Calculate the wavelength of the emitted radiation when the electron drops from third to second orbit.

Q.28 Assuming a spherical shape for the F nucleus, calculate the radius and the nuclear density of F nucleus of mass number 19.

Q.29 What conclusion may be drawn from the following results of? If a 10×10^{-1} kg body is traveling along the x-axis at 1 meter/sec within 0.01 meter/sec. Calculate the theoretical uncertainty in its position.

Q.30 What conclusion may be drawn from the following of? If an electron is traveling at 100 meter/sec. within 1 meter/sec. Calculate the theoretical uncertainty in its position.

[$h = 6.63 \times 10^{-34}$ J s, mass of electron $= 9.109 \times 10^{-31}$ kg]

Exercise 2

Single Correct Choice Type

Q.1 Bohr's concept of an orbit in an atom contradicts

(A) de Broglie's equation

(B) Pauli's principle

(C) Uncertainty principle

(D) Hund's rule

Q.2 It is a data sufficiency problem in which it is to be decided on the basis of given statements whether given question can be answered or not. No matter whether the answer is yes or no.

Question: Is the orbital of hydrogen atom $3p_x$?

Statement-I: The radial function of the orbital is

$$R(r) = \frac{1}{9\sqrt{6}a_0^{3/2}}(4-\sigma)\sigma e^{-\sigma/2}, \sigma = \frac{r}{2}$$

Statement-II: The orbital has 1 radial node and 0 angular mode.

(A) Statement-I alone is sufficient.

(B) Statement-II alone is sufficient

(C) Both together is sufficient.

(D) Neither is sufficient

Comprehension Type

Paragraph 1: The only electron in the hydrogen atom resides under ordinary conditions on the first orbit. When energy is supplied, the electron moves to higher energy orbit depending on the amount of energy absorbed. When this electron returns to any of lower orbits, it emits energy. Lyman series is formed when the electron returns to the lowest orbit while Balmer series is formed when the electron returns to second orbit. Similarly, Paschen, Brackett and Pfund series are formed when electron returns to the third, fourth and fifth orbits from higher energy orbits respectively.

Maximum number of lines produced when an electron jumps from nth level to ground level is equal to $\frac{n(n-1)}{2}$. For example, in the case of n = 4, number of lines produced is 6.

(4 → 3, 4 → 2, 4 → 1, 3 → 2, 3 → 1, 2 → 1). When an electron returns from n_2 to n_1 state, the number of lines in the spectrum will be equal to $\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$

If the electron comes back from energy level having energy E_2 to energy level having energy E_1, then the difference may be expressed in terms of energy of photon as:

$$E_2 - E_1 = \Delta E, \lambda = \frac{hc}{\Delta E}$$

Since h and c are constants, DE corresponds to definite energy, thus each transition from one energy level to another will produce a light of definite wavelength. This is actually observed as line in the spectrum of hydrogen atom. Wave number of line is given by the formula $\overline{v} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ Where R is a Rydberg's constant ($R = 1.1 \times 10^7\ m^{-1}$)

Q.3 The energy photon emitted corresponding to transition n = 3 to n = 1 is [$h = 6\ 0 \times 10^{-34}$ J –sec]

(A) 1.76×10^{-18} J (B) 1.98×10^{-18} J

(C) 1.76×10^{-17} J (D) None of these

Q.4 In a collection of H-atom, electrons make transition from 5th excited state to 2nd excited state then maximum number of different types of photons observed are

(A) 3 (B) 4 (C) 6 (D) 15

Q.5 The difference in the wavelength of the 1st line of Lyman series and 2nd line of Balmer series in a hydrogen atom is

(A) $\frac{9}{2R}$ (B) $\frac{4}{R}$

(C) $\frac{88}{15R}$ (D) None of these

Q.6 The wave number of electromagnetic radiation emitted during the transition of electron in between two levels of Li^{2+} ion whose principal quantum number sum is 4 and difference is 2 is

(A) 3.5 R (B) 4R

(C) 8R (D) $\frac{8}{9}R$

Paragraph 2: In the Rutherford's experiment, α-particles were bombarded towards the copper atoms so as to arrive at a distance of 10^{-13} meter from the nucleus of copper and then getting either deflected or traversing back. The α-particles did not move further closer.

Q.7 The velocity of the α-particles must be

(A) 8.32×10^8 cm/sec (B) 6.32×10^8 cm/sec

(C) 6.32×10^8 m/sec (D) 6.32×10^8 km/sec

Q.8 Which of the following metals can be used instead of gold in α-scattering experiment

(A) Pt (B) Na (C) K (D) Cs

Q.9 From the Rutherford's α-particle scattering, it can be concluded that

(A) $N \propto \sin^4 \frac{\theta}{2}$ (B) $N \propto \frac{1}{\sin^4 \theta}$

(C) $N \propto \frac{1}{\sin^4 \theta / 2}$ (D) $N = \sin\frac{\theta}{2}$

Q.10 Rutherford observed that

(A) 50% of the α-particles got deflected

(B) 99% of the α-particles got deflected

(C) 99% of the α-particles went straight without suffering any deflection.

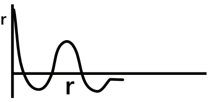
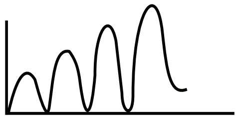
(D) Nucleus is negatively charged.

Match the Columns

Q.11 Match the entries in column I with entries in column II

Column I	**Column II**
(A) Electron moving in 2nd orbit in He^+ ion electron is	(p) Radius of orbit in which moving is 0.529Å
(B) Electron moving in 3rd orbit in H-atom	(q) Total energy of electron is (–)13.6 × 9eV
(C) Electron moving in 1st orbit in Li^{+2} ion	(r) Velocity of electron is $\frac{2.188 \times 10^8}{3}$ m/sec
(D) Electron moving in 2nd orbit is Be^{+3} ion	(s) De-broglie wavelength of Electron is $\sqrt{\frac{150}{13.6}}$Å

Q.12 Column I and column II contain data on Schrodinger Wave–Mechanical model, where symbols have their usual meanings. Match the columns.

Column I	**Column II**
(A) Ψ_r 	(p) 4s
(B) $\Psi_r^2 4\pi r^2$ 	(q) $5p_x$
(C) $\psi(\theta, \phi)$ = K (independent of θ and ϕ)	(r) 3s
(D) at least one angular node is present	(s) 6d

True/False Type

Q.13 Statement-I: Emitted radiations will fall in the visible range when an electron jumps from higher level to n = 2 in Li^{+2} ion.

Statement-II: Balmer series radiations belong to visible range in all H-like atoms.

(A) Statement-I true; Statement-II is true; Statement-II is the correct explanation of Statement-I.

(B) Statement-I true; Statement-II is true; Statement-II is not the correct explanation of Statement-I.

(C) Statement-I is true; Statement-II is false.

(D) Statement-I is false; Statement-II is true.

Previous Years' Questions

Q.1 The increasing order (lowest first) for the values of e/m (charges/mass) for electron (e), proton (p) ***(1984)***

(A) e, p, n α (B) n, p, e, α

(C) n, p, α, e (D) n, α, p, e

Q.2 Which of the following does not characterize X-rays ***(2000)***

(A) The radiation can ionize gases

(B) It causes ZnS to fluoresce

(C) Deflected by electric and magnetic fields

(D) Have wavelengths shorter than ultraviolet rays

Q.3 The number of nodal planes in a px orbital is ***(2001)***

(A) One (B) Two (C) Three (D) Zero

Q.4 If the nitrogen atom had electronic configuration $1s^1$ it would have energy lower than that of the normal ground state configuration $1s^2\ 2s^2\ 2p^3$, because the electrons would be closer to the nucleus, yet $1s^7$ is not observed because it violates ***(2002)***

(A) Heisenberg uncertainty principle

(B) Hund's rule

(C) Pauli exclusion principle

(D) Bohr postulate of stationary orbits

Q.5 Which hydrogen like species will have same radius as that of Bohr orbit of hydrogen atom? ***(2003)***

(A) n = 2, Li^{2+} (B) n = 2, Be^{3+}

(C) n = 2, He^+ (D) n = 3, Li^{2+}

Q.6 The number of radial nodes in 3s and 2p respectively are ***(2005)***

(A) 2 and 0 (B) 0 and 2

(C) 1 and 2 (D) 2 and 1

Q.7 When alpha particles are sent through a thin metal foil, most of them go straight through the foil because ***(1984)***

(A) Alpha particles are much heavier than electrons

(B) Alpha particles are positively charged

(C) Most part of the atom is empty space

(D) Alpha particles move with high velocity

Q.8 The ground state electronic configuration of nitrogen atom can be represented by ***(2004)***

(A) $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ (B) $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\downarrow}\boxed{\uparrow}$

(C) $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\downarrow}\boxed{\downarrow}$ (D) $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\downarrow}\boxed{\downarrow}\boxed{\downarrow}$

Read the following questions and answer as per the direction given below:

(A) Statement-I true; Statement-II is true; Statement-II is the correct explanation of Statement-I.

(B) Statement-I true; Statement-II is true; Statement-II is not the correct explanation of Statement-I.

(C) Statement-I is true; Statement-II is false.

(D) Statement-I is false; Statement-II is true.

Q.9 Statement-I: The first ionization energy of Be is greater than that of B.

Statement-II: 2p orbital is lower in energy than 2s. ***(2000)***

Paragraph 1: The hydrogen-like species Li^{2+} is in a spherically symmetric state S_1 with one radial node. Upon absorbing light the ion undergoes transition to a state S_2 has one radial node and its energy is equal to the ground state energy of the hydrogen atom. ***(2010)***

Q.10.1 The state S_1 is

(A) 1s (B) 2s (C) 2p (D) 3s

Q.10.2 Energy of the state S_1 in units of the hydrogen atom ground state energy is

(A) 0.75 (B) 1.50 (C) 2.25 (D) 4.50

Q.10.3 The orbital angular momentum quantum number of the state S_2 is

(A) 0 (B) 1 (C) 2 (D) 3

Q.11 According to Bohr's theory En = total energy

K_n = Kinetic energy K_n = Kinetic energy

V_n = Potential energy R_n = Radius of nth orbit

Match the following: ***(2006)***

Column I	**Column II**
(A) V_n/K_n =	(p) V_n/K_n =
(B) If radius of nth orbit $\propto E^x_n$, x=	(q) −1
(C) Angular momentum is lowest orbital	(r) −2
(D) $\frac{1}{r^n} \propto Z^y, y = ?$	(s) 1

Q.12 Match the entries in Column I with the correctly related quantum number (s) in column II. ***(2008)***

Column I	**Column II**
(A) Orbital angular momentum of the electron in a hydrogen-like atomic orbital	(p) Principal quantum number
(B) A hydrogen-like one-electron wave function obeying Pauli's principle	(q) Azimuthal quantum number
(C) Shape, size and orientation of hydrogen-like atomic orbital	(r) Magnetic quantum number
(D) Probability density of electron at the nucleus in Hydrogen-like atom	(s) Electron spin quantum number

Q.13 The maximum number of electrons that can have principal quantum number, n = 3 and spin quantum number, $m_s = -\frac{1}{2}$ is ***(2011)***

Q.14 The work function (Φ) of some metals is listed below. The number of metals which will show photoelectric effect when light of 300 nm wavelength falls on the metal is ***(2011)***

Metal	Li	Na	K	Mg	Cu	Ag	Fe	Pt	W
Ö(eV)	2.4	2.3	2.2	3.7	4.8	4.3	4.7	6.3	4.75

Q.15 (a) The Schrodinger wave equation for hydrogen atom is: $\psi_{2s} = \frac{1}{4(2\pi)^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$

Where, a_0 is Bohr's radius. Let the radial node in 2s be at r_0. Then find r in terms of a_0.

(b) A baseball having mass 100 g moves with velocity 100 m/s. Find out the value of wavelength of baseball. ***(2004)***

Q.16 (a) Calculate velocity of electron in first Bohr orbit of hydrogen atom (Given, $r = a_0$)

(b) Find de-Broglie wavelength of the electron in first Bohr orbit

(c) Find the orbital angular momentum of 2p-orbital in terms of h/2π units. ***(2005)***

Q.17 The atomic masses of He and Ne are 4 and 20 a.m.u., respectively. The value of the de Broglie wavelength of He gas at –73°C is "M" times that of the de Broglie wavelength of Ne at 727°C. M is ***(2013)***

Q.18 Not considering the electronic spin, the degeneracy of the second excited state(n = 3) of H atom is 9, while the degeneracy of the second excited state of H^- is ***(2015)***

Q.19 The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom is [is Bohr radius] ***(2015)***

(A) $\frac{h^2}{4\pi^2 ma_0^2}$ (B) $\frac{h^2}{16\pi^2 ma_0^2}$

(C) $\frac{h^2}{32\pi^2 ma_0^2}$ (D) $\frac{h^2}{64\pi^2 ma_0^2}$

PlancEssential Questions

JEE Main/Boards

Exercise 1

Q.1 Q.4 Q.9
Q.13 Q.16 Q.27

Exercise 2

Q.5 Q.7 Q.18
Q.19 Q.28

Previous Years' Questions

Q.7 Q.15

JEE Advanced/Boards

Exercise 1

Q.1 Q.7 Q.17
Q.19

Exercise 2

Q.4 Q.6 Q.9
Q.12

Previous Years' Questions

Q.8 Q.10.3 Q. 11

Answer Key

JEE Main/Boards

Exercise 1

Q.1 [1.5×10^{-18} unit.]

Q.2 [$n < \alpha < p < e$]

Q.3 [6.35×10^{6} m/s]

Q.4 [$\lambda_1 = 4\lambda$]

Q.5 [5×10^{14} s^{-1}]

Q.5 [3×10^{-19}]

Q.7 1.095×10^{5} cm^{-1}

Q.8 [≈28]

Q.9 [2741 Å]

Q.10 [No photoelectron will emit]

Q.11 [3.78×10^{-19} J]

Q.12 [$r = \left(\dfrac{n^2h^2}{4\pi^2 mk}\right)^{1/4}$]

Q.13 (A) 2.0 eV; (B) 2V; (C) 2970Å

Q.14 7.293×10^{5} m/s

Q.15 7.293×10^{5} m/s

Q.16 32/27

Q.17 2.09×10^{16} s^{-1}

Q.18 $E_a = E_1/n^2$

Q.19 6×10^{-20} J

Q.20 −6.044eV; + 6.044 eV; −12.088 eV.

Q.21 91.8 eV

Q.22 54.4eV

Q.23 494.73 kJ/mol

Q.24 3.75×10^4 cm^{-1}

Q.25 912.37 Å

Q.26 1.01×10^{15} Hz

Q.27 97.86 nm

Q.28 488.89 nm

Q.29 6.626×10^{-25} kg ms^{-1}

Q.30 n = 2 and 3; $\lambda = 1216$ Å; $\lambda = 1020$Å

Exercise 2

Single Correct Chioce Type

Q.1 C **Q.2** C **Q.3** B **Q.4** D **Q.5** D **Q.6** D **Q.7** B

Q.8 B **Q.9** A **Q.10** B **Q.11** C **Q.12** B **Q.13** D **Q.14** B

Q.15 A **Q.16** D **Q.17** D **Q.18** A **Q.19** C **Q.20** A **Q.21** B

Q.22 C **Q.23** D **Q.24** B **Q.25** C **Q.26** B **Q.27** B **Q.28** A

Q.29 C

Previous Years' Questions

Q.1 A **Q.2** D **Q.3** A **Q.4** B **Q.5** D **Q.6** C **Q.7** C

Q.8 C **Q.9** B **Q.10** C **Q.11** B **Q.12** D **Q.13** B **Q.14** A

Q.15 B **Q.16** C **Q.17** B **Q.18** A **Q.19** B **Q.20** C

JEE Advanced/Boards

Exercise 1

Q.1 1eV = 1.24×10^{-6} meter

Q.2 $n_1 = 2$, $n_2 = 4$, I.P. = 8.67×10^{-18} J,
r = 2.64×10^{-11} volts

Q.3 1.86×10^3 volts

Q.5 6.34×10^6 m/sec

Q.6 2.4×10^{14} sec^{-1}

Q.7 2.055×10^{-7} m/s

Q.11 4814.8 Å

Q.12 2.92×10^{15}

Q.13 Z = 2 He^+

Q.17 $\nu_0 = 1.148 \times 10^{15}$ sec^{-1}; $\lambda_0 = 2614.6$ Å

Q.18 495 nm

Q.19 8.84×10^{-35} m

Q.20 $\nu_0 = 4 \times 10^{15}$ Hz

Q.21 26

Q.22 2.2×10^{-20} J

Q.23 4.65 eV

Q.24 182.5 kJ

Q.25 $Z_x = 12$, $Z_y = 24$

Q.26 5

Q.27 $\lambda = 6.6 \times 10^3$ Å

Q.28 Volume = 2×10^{-37} cm^3 Density of molecules = 1.44×10^{14} gm/cm^3

Q.29 $\Delta n = 3 \times 10^{-30}$ m

Q.30 $\Delta n = 3 \times 10^{-5}$ m

This shows uncertainty in positions for larger particles is less whereas the uncertainty in position for smaller particles is larger. Hence for macro particles uncertainty in positions is not significant

Exercise 2

Single Correct Chioce Type

Q.1 C **Q.2** B

Comprehension Type

Paragraph 1: **Q.3** A B **Q.4** C **Q.5** B **Q.6** C

Paragraph 2: **Q.7** B **Q.8** A **Q.9** C **Q.10** C

Match the Columns

Q.11 A → s; B → r; C → q; D → p

Q.12 A → p; B → p, q, s; C → p, r; D → q, s

Assertion Reasoning Type

Q.13 D

Previous Years' Questions

Q.1 D **Q.2** C **Q.3** A **Q.4** C **Q.5** B **Q.6** A **Q.7** A, C

Q.8 A, D **Q.9** C **Q.10.1** B **Q.10.2** C **Q.10.3** B

Q.11 A → r; B → q; C → p; D → s

Q.12 A → q; B → p, q, r, s; C → p, q, r; D → p, q, r

Q.13 9 **Q.14** 4

Q.15 (A) Ro = 2ro, (B) 6.625×10^{-25} Å

Q.16 (A) 2.18×10^{6} ms^{-1} (B) 3.3 Å (C) $\sqrt{2}\left(\frac{h}{2\pi}\right)$

Q.17 5 **Q.18** 3 **Q.19** C

Solutions

JEE Main/Boards

Exercise 1

Sol 1: In an oil drop experiment, the obtained charges will be integral multiples of charge of electron.

Let charge of electron be u

u = GCD (4.5×10^{-18}, 3×10^{-18}, 6×10^{-18},

7.5×10^{-18}, 9×10^{-18}) and we know that

GCD (4.5, 3.6, 7.5, 9) = 1.5

∴ Charge of electron = u = 1.5×10^{-18} C

Sol 2: Let charge of electron be 'e_0' and mass of proton and neutron = m_0

$$SC_e = \frac{|e_0|}{\frac{m_0}{1837}} = 1837\frac{|e_0|}{m_0}$$

$$SC_p = \frac{|e_0|}{m_0}$$

$$SC_n = \frac{0}{m_0} = 0$$

$$SC_\infty = \frac{|2e_0|}{4m_0} = \frac{1}{2}\frac{|e_0|}{m_0}$$

[since α particle = He^{2+}]

$\therefore SC_n < SC_\alpha < SC_p < SC_e$

i.e. $[n < \alpha < p < e]$.

Sol 3: By conservation of energy

$\Delta PE = \Delta KE$

$$\Rightarrow \frac{1}{4\pi \epsilon_0} \times \frac{q_1 q_2}{r} = \frac{1}{2} mv^2$$

q_1 = charge of copper nucleus

q_2 = charge of α-particle

$$\Rightarrow \frac{9 \times 10^9 \times 29 \times 1.6 \times 10^{-19} \times 2 \times 1.6 \times 10^{-19}}{10^{-13}}$$

$$= \frac{1}{2} \times 4 \times 1.67 \times 10^{-27} \times v^2$$

$$v^2 = \frac{133.6}{3.3} \times 10^{12} \Rightarrow v = 6.34 \times 10^6 \text{ m/s}$$

Sol 4: By Moseley's law

$E = (10.2 \text{ eV})(2 - 1)^2$

$$\lambda \propto \frac{1}{E} \Rightarrow \lambda \propto \frac{1}{(Z-1)^2}$$

$$\frac{\lambda_{29}}{\lambda_{57}} = \frac{(57-1)^2}{(29-1)^2} = \frac{56^2}{28^2} = 4$$

$$\Rightarrow \lambda_{29} = 4\lambda_{57} \Rightarrow \lambda' = 4\lambda.$$

Sol 5: Frequency, $\nu = \frac{c}{\lambda} = \frac{3 \times 10^8}{600 \times 10^{-9}}$

$= 5 \times 10^{14}$ /sec

Sol 6: $E = \frac{hc}{\lambda} = \frac{6.66 \times 10^{-34} \times 3 \times 10^8}{6626 \times 10^{-10}} = 3 \times 10^{-19}$ J

Sol 7: First line of Lyman is He^{2+}

$$\frac{1}{\lambda} = R_H \times Z^2 \left[\frac{1}{1^2} - \frac{1}{2^2}\right] = R_H \times 4\left(\frac{3}{4}\right)$$

$$\frac{1}{\lambda} = 3R_H \qquad \lambda = \frac{1}{3R_H}$$

$$\therefore \Delta\lambda = \frac{1}{R_H}\left(\frac{9}{5} - \frac{1}{3}\right) = \frac{22}{15R_H} = 133.7 \times 10^{-17} \text{ cm}$$

$\therefore R_H = 1.085 \times 10^5 \text{ cm}^{-1}$

First line of Balmer is He^{2+}

$$\frac{1}{\lambda} = R_H \times Z^2 \left[\frac{1}{2^2} - \frac{1}{3^2}\right] = R_H \times Z^2 \left(\frac{5}{36}\right)$$

$$\frac{1}{\lambda} = \frac{5R_H}{9}$$

$$\lambda = \frac{9}{5R_H}$$

$\therefore R_H = 1.095 \times 10^5 \text{ cm}^{-1}$

Sol 8: Energy of each photon = $E_0 = \frac{hC}{\lambda}$

$$= \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{550 \times 10^{-9}} = 3.6 \times 10^{-19} \text{ J}$$

Number of photon required $= \frac{E}{E_0} = \frac{10^{-17}}{3.6 \times 10^{-19}}$

≈ 27.7

So we need 28 photons.

Sol 9: Energy required of H_2 molecule is

$$E_0 = \frac{104 \times 10^3 \times 4.2 \text{ J}}{6 \times 10^{2.3}} = 72.8 \times 10^{-20}$$

$= 7.28 \times 10^{-19}$ J

$$E_0 = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{E_0} = \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{7.28 \times 10^{-19}}$$

$= 2.74 \times 10^{-7}$ m = 2740 Å

Sol 10: Energy of photon = $\frac{hc}{\lambda}$

$$= \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{660 \times 10^{-9}} = 3 \times 10^{-19} \text{ J}$$

Work function = $2.25 \times 1.6 \times 10^{-19}$ J

$\approx 3.6 \times 10^{-19}$ J

As work function is greater than energy of photon, no photoelectron will be emitted.

Sol 11: Energy of photon = $\frac{hc}{\lambda}$

$$= \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{4 \times 10^3 \times 10^{-10}} = 4.95 \times 10^{-19} \text{ J}$$

Work function = $h\nu_0$

$= 6.6 \times 10^{-34} \times 1.8 \times 10^{14} = 1.18 \times 10^{-19}$ J

and $KE_{max} = E_{photon}$ − work function

$= 3.78 \times 10^{-19}$ J

Sol 12: According to Bohr,

$mvr = \frac{nh}{2\pi}$ and for equilibrium of electron.

$$\frac{mv^2}{r} = F$$

$$F = \frac{\partial U}{\partial r} = \frac{d\left(\frac{1}{2}kr^2\right)}{dr} = kr$$

$$\frac{mv^2}{r} = kr \qquad ...(i)$$

and from first equation

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

$$\Rightarrow m^2v^2r^2 = \frac{n^2h^2}{4\pi^2} \qquad ...(ii)$$

If we equate v_2 in both the equations

$$\Rightarrow \frac{kr^2}{m} = \frac{n^2h^2}{4\pi^2m^2r^2} \Rightarrow r^4 = \frac{n^2h^2}{4\pi^2mk}$$

$$\Rightarrow r = \left(\frac{n^2h^2}{k4\pi^2m}\right)^{1/4}$$

Sol 13: Energy of photon $= \frac{hc}{\lambda}$

$$= \frac{6.6\times10^{-34}\times3\times10^8}{2\times10^3\times10^{-10}}$$

$\approx 9.9 \times 10^{-19}$ J

$$\approx \frac{9.9\times10^{-19}}{1.6\times10^{-19}} \text{ eV} = 6.2 \text{ eV}$$

(a) For fastest moving electron

$KE = \frac{hc}{\lambda} - E_0 = 6.2 \text{ eV} - 4.2 \text{ eV} = 2.0 \text{ eV}$

for slowest moving electron

KE = 0

(b) Stopping potential $= \frac{KE_{max}}{e} = \frac{2eV}{e} = 2V$

(c) Cut-off wavelength $= \lambda_0 = \frac{hc}{E_0}$

$$= \frac{6.6\times10^{-34}\times3\times10^8}{4.2\times1.6\times10^{-19}}$$

$\approx 2.97 \times 10^{-7}$ m = 2970 Å

Sol 14: Speed of an electron in H-atom in nth orbit is

$v_n = \frac{2\pi ke^2}{h}\times\frac{Z}{n} = 2.18 \times 10^6 \times \frac{1}{n}$ and n = 3

$\therefore v = 7.29 \times 10^5$ m/s

Sol 15: Radius of nth orbit in H is

$r_n = 0.529 \times n^2$ Å

$\Rightarrow 0.529\, n^2 = 4.761 \Rightarrow n^2 = 9 \Rightarrow n = 3$

$v^3 = \frac{2.18\times10^6}{3} = 7.29 \times 10^5$ m/s

Sol 16: Time period of electron $= \frac{2\pi r}{v}$

$$\therefore t \propto \frac{n^2/Z}{Z/n} \Rightarrow t \propto \frac{n^3}{Z^2}$$

$$\therefore \frac{T_1}{T_2} = \frac{\frac{2^3}{1^2}}{\frac{3^3}{2^2}} = \frac{2^5}{3^3} = \frac{32}{27}$$

Sol 17: Angular frequency of an electron in an orbit is

$$f = \frac{2\pi}{T} = \frac{V}{2\pi r}\times2\pi = \frac{2.18\times10^6\times\frac{2}{2}}{2\times3.14\times0.529\times\frac{2^2}{2}\times10^{-10}} \times$$

2×3.14

2.08×10^{16} /sec

Sol 18: Energy of nth orbit in H atom is

$$E = \frac{-2\pi^2k^2me^4}{n^2h^2} = \frac{-13.6}{n^2} \text{ eV}$$

$E_1 = -13.6$ eV$E_2 = -3.4$ eV

$E_3 = -1.51$ eV$E_4 = -0.85$ eV

Sol 19: Energy of photon $= \frac{hC}{\lambda}$

$$= \frac{6.6\times10^{-34}\times3\times10^8}{2.537\times10^{-7}} = 7.8 \times 10^{-19} \text{ J}$$

Energy needed to dissociate 1 molecule of H_2

$$= \frac{103.2\times10^3\times4.2}{6\times10^{23}} = 7.22 \times 10^{-19} \text{ J}$$

$\therefore KE = (7.8 - 7.2) \times 10^{-19} \text{ J} = 6 \times 10^{-20}$ J

Sol 20: TE of 3rd orbit of He+ ion

$= 13.6 \times \frac{Z^2}{n^2}$ eV and Z = 2, n = 3

$\therefore$ TE = $-13.6 \times \frac{4}{9} = -6.044$ eV

PE = 2TE = -12.088 eV

KE = $-$TE = 6.044 eV

Sol 21: Excitation energy = Energy of 2nd orbit − Energy of 1st orbit

$E_{ex} = \frac{-13.6\times Z^2}{2^2} - \left(\frac{-13.6\times Z^2}{1^2}\right)$ and Z = 3

$\Rightarrow E_{ex} = 13.6 \times 9 \left(\frac{3}{4}\right) = 91.8$ eV

Sol 22: BE of electron in ground of He^{2+} ion

= − total energy of electron in that orbit.

$\therefore$ BE = −TE

$= -\left(-13.6\times\frac{Z^2}{n^2}\right) = 13.6 \times 4 = 54.4$ eV

Sol 23: IE of Na = Energy of photon × N

$= \frac{hC}{\lambda} = \frac{6.6\times10^{-34}\times3\times10^{8}}{242\times10^{-9}}\times N$

$= 8.18 \times 10^{-19} \times 6 \times 10^{23}$

$= 4.9 \times 10^{3}$ J/mol = 4.9 kJ/mole

Sol 24: E_0 = Energy of electron = 4.64 eV

$= 4.64 \times 1.6 \times 10^{-19}$ J

Energy of photon = $hc\bar{\nu}$

$\Rightarrow \bar{\nu} = \frac{E}{hc} \Rightarrow \bar{\nu} = \frac{4.64\times1.6\times10^{-19}}{6.6\times10^{-34}\times3\times10^{8}}$

$= 3.74 \times 10^{4}$ /cm

Sol 25: Change in energy = $TE_H = -13.6$ eV

$\Rightarrow 13.6 \text{ eV} = \frac{hc}{\lambda}$

$\Rightarrow \lambda = \frac{hc}{13.6\,\text{eV}}$

$= \frac{6.6\times10^{-34}\times3\times10^{8}}{13.6\times1.6\times10^{-19}} = 9.12 \times 10^{-8}$ m

≈ 912 Å

Sol 26: Energy absorbed in the transition

$= E_4 - E_2$

$= \frac{-13.6}{4^2} - \left(\frac{13.6}{2^2}\right) = 13.6\left[\frac{1}{4} - \frac{1}{16}\right]$

$= \frac{5\times13.6}{16} = 4.2$ eV

Energy of photon = $h\nu$

$\Rightarrow \nu = \frac{E}{h}$

$= \frac{4.2\times1.6\times10^{-19}}{6.6\times10^{-34}} = 1.01 \times 10^{15}$ Hz

Sol 27: Assume that the electron excites to orbit no. 'n'.

No. of subsequent emissions

$= \frac{(\Delta H)(\Delta n+1)}{2} = \frac{(n-1)(n-1+1)}{2}$

Given no. of subsequent emission = 6

$\Rightarrow \frac{n(n-1)}{2} = 6 \Rightarrow n = 4$

$\Rightarrow \frac{hc}{\lambda} = 13.6\left[\frac{1}{1^2} - \frac{1}{4^2}\right]$

$\Rightarrow \lambda = \frac{13.6\times\frac{15}{16}\times1.6\times10^{-19}}{6.6\times10^{-34}\times3\times10^{8}}$

$= 9.78 \times 10^{-8}$ m = 97.8 nm.

Sol 28: $\lambda_{H_\alpha} = \frac{hc}{E} = \frac{hc}{13.6\left[\frac{1}{2^2} - \frac{1}{3^2}\right]}$

$\lambda_{H_\beta} = \frac{hc}{13.6\left[\frac{1}{2^2} - \frac{1}{4^2}\right]}$

$\Rightarrow \frac{\lambda_{H_\beta}}{\lambda_{H_\alpha}} = \frac{\left[\frac{1}{4} - \frac{1}{9}\right]}{\left[\frac{1}{4} - \frac{1}{16}\right]}$

$$\Rightarrow \lambda_{H_\beta} = 660 \times \frac{\frac{5}{36}}{\frac{3}{16}} = 488.8\ \overset{\circ}{A}$$

Sol 29: Momentum of a photon = P = $\frac{h}{\lambda}$

$$= \frac{6.6 \times 10^{-34}}{10 \times 10^{-10}} = 6.6 \times 10^{-25}\ \text{kg m/s}$$

Sol 30: Energy of 2nd orbit of H = $\frac{-13.6}{2^2} = -3.4$ eV

given transitions have energies greater than

3.4 eV.

So $n_1 = 1$.

$$10.2 = 13.6\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\Rightarrow \frac{3}{4} = \frac{1}{1^2} - \frac{1}{n_2^2}$$

$$\Rightarrow \frac{1}{n_2^2} = \frac{1}{4} \Rightarrow n_2 = 2$$

$$\lambda = \frac{hC}{E} \text{ or } \frac{912\,\text{Å}}{\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]}$$

$$= \frac{912\,\text{Å}}{\frac{1}{1^2} - \frac{1}{2^2}} = 912 \times \frac{4}{3} = 1216\ \text{Å}$$

For 12.09 eV

$$12.09 = 13.6\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\frac{1}{1^2} - \frac{1}{n_2^2} = \frac{8}{9}$$

$$\Rightarrow n_2 = 3$$

$$\therefore \lambda = \frac{912\ \text{Å}}{\left[\frac{1}{1^2} - \frac{1}{3^2}\right]} = \frac{912 \times 9}{8} = 1020\ \text{Å}$$

Exercise 2

Single Correct Choice Type

Sol 1: (C) (A) As x-rays are high energetic photons, it can ionise gases.

(B) ZnS shows fluorescence in x-rays.

(C) As x-rays are photons, they are neither deflected by electric nor magnetic fields

(D) $E_{\text{rays}} > E_{\text{uv-rays}}$, so $\lambda_{\text{x-rays}} < \lambda_{\text{uv-rays}}$

Sol 2: (C) Bohr's model doesn't say anything about probability of finding an electron near nucleus. It gives discrete orbitals as locus for finding electrons.

Sol 3: (B) If we put x = 1 in E = $\frac{\text{constant}}{n^2}$ kJ/mole.

Constant is the negative of energy an electron first orbit.

So, it also the ionisation energy of H-atom.

Sol 4: (D) E = $\frac{hc}{\lambda}$

$$\text{So } \frac{E_1}{E_2} = \frac{hc/\lambda_1}{hc/\lambda_2} = \frac{\lambda_2}{\lambda_1} = \frac{4000}{2000} = 2$$

Sol 5: (D) Let's assume that the electron is at a distance 'r' from nucleus.

$$E_{\text{electron}} = \frac{-k.Z_e.e}{r}$$

as the energy is negative, the energy is maximum when $r \to \infty$, $E \to 0$.

Sol 6: (D) Schrodinger's equation depends on radius, shape and orbital orientation. So, it depends on n, ℓ, m.

But it doesn't depend on spin of the electron.

∴ So Schrondinger's equation is not related spin quantum number.

Sol 7: (B) $\frac{1}{x} = R_H \times Z^2\left[\frac{1}{2^2} - \frac{1}{n^2}\right]$

Z = 2

and shortest wavelength comes when $n \to \infty$

$$\Rightarrow \frac{1}{x} = R_H \times 4\left[\frac{1}{4}\right] = R_H$$

$\therefore$ Let x' be longest wavelength is Paschen of Li^{2+}.

Longest wavelength: $3 \rightarrow 4$

$$\frac{1}{x'} = R_H \times Z^2 \left[\frac{1}{3^2} - \frac{1}{4^2}\right]$$

$$\Rightarrow \frac{1}{x'} = R_H \times 9 \left[\frac{1}{9} - \frac{1}{16}\right] = \frac{7R_H}{16}$$

$$\frac{1}{x'} = \frac{7}{x16} \Rightarrow x' = \frac{16x}{7}$$

Sol 8: (B) $\frac{1}{\lambda} = R_H \times Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

$$\Rightarrow \lambda = \frac{912\,\text{Å}}{9\left[\frac{1}{1^2} - \frac{1}{\infty^2}\right]}$$

$\therefore$ E = 13.6 × 9 eV

Ionisation energy of H = 13.6 eV

KE of e^- = 13.6 × 8 eV

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2mkE}}$$

$$= \frac{6.6 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 13.6 \times 8 \times 1.6 \times 10^{-19}}}$$

$$= \frac{6.6 \times 10^{-34}}{6 \times 10^{-24}}; \approx 1.17\ \text{Å}$$

Sol 9: (A) IE_3 of Li is $Li^{2+} \xrightarrow[\Delta E]{} Li^{+3}$

$\Delta E = 13.6 \times Z^2$ eV per atom per mole.

$$IE_3 = \frac{13.6 \times 9 \times 1.6 \times 10^{-19} \times 6 \times 10^{23}}{1 \times 10^3}\ \text{kJ/mole}$$

= 11775 kJ/mole

IE_2 = 19800 − 11775 − 520 = 7505 kJ/mole

Sol 10: (B) $\Delta_1 = \dfrac{912}{\left[\frac{1}{1^2} - \frac{1}{2^2}\right]} - \dfrac{912}{\left[\frac{1}{1^2} - \frac{1}{3^2}\right]}$

1st line $1 \rightarrow 2$
2nd line $1 \rightarrow 3$
3rd line $1 \rightarrow 4$

$$= 912\left(\frac{4}{3} - \frac{9}{8}\right) = 912\left(\frac{5}{24}\right)$$

$$\Delta_2 = \frac{912}{\left[\frac{1}{1^2} - \frac{1}{3^2}\right]} - \frac{912}{\left[\frac{1}{1^2} - \frac{1}{4^2}\right]}$$

$$= 912\left[\frac{9}{8} - \frac{16}{15}\right] = 912\left(\frac{7}{120}\right)$$

$$\Delta_1 : \Delta_2 = \frac{5}{24} \times \frac{120}{7} = \frac{25}{7}$$

≈ 3.5

Sol 11: (C) $r_n = 0.529 \times n^2$ Å $\Rightarrow r_n \propto n^2$

$\therefore r_1 : r_2 : r_3 = 1 : 2^2 : 3^2$

Sol 12: (B) For a permissible solution of n, ℓ, m, s

$n - 1 \geq \ell, m \leq |\ \ell\ |, s = \pm \frac{1}{2}$

$\therefore$ 3, 3, 1, $-\frac{1}{2}$ is not permissible.

Sol 13: (D) $E \propto \frac{1}{\lambda}$

$$\Rightarrow \frac{E_1}{E_2} = \frac{\lambda_2}{\lambda_1} = 2$$

Sol 14: (B) Orbital angular momentum of an orbital is

$$L = \frac{h}{2\pi}\sqrt{\ell(\ell + 1)}$$

For 2s, $\ell = 0$

$\therefore L = 0$

Sol 15: (A) For each value of 'ℓ'

We have $2\ell + 1$ orbitals

$\therefore$ No. of electrons = $\sum_{\ell=0}^{n-1} 2(2\ell + 1)$

Sol 16: (D) $\lambda = \dfrac{h}{mv} = \dfrac{6.63 \times 10^{-27}}{6 \times 10^{-2} \times 1.4 \times 1.6 \times 10^2 \times \frac{5}{18}}$

$= 1.8 \times 10^{-27}$ m $= 1.8 \times 10^{-25}$ cm

Sol 17: (D) Given

$$R = 0.529 \times \frac{n^2}{Z}\ Å$$

$$\Rightarrow R = \frac{0.529}{Z} \times 4$$

$$R' = \frac{0.529 \times 3^2}{Z} = \frac{R}{4} \times 9 = \frac{9R}{4} = 2.25R$$

Sol 18: (A) $\lambda_1 = R_H \times 1^2 \left[\frac{1}{1^2} - \frac{1}{2^2}\right]$

$$\lambda_2 = R_H \times 2^2 \left[\frac{1}{2^2} - \frac{1}{4^2}\right] = RH \left[\frac{1}{1^2} - \frac{1}{2^2}\right]$$

$\Rightarrow \lambda_1 : \lambda_2 = 1 : 1$

Sol 19: (C) $n_1 + n_2 = 4$

$n_2^2 - n_1^2 = 8$

$\Rightarrow (n_2 + n_1)(n_2 - n_1) = 8$

$\Rightarrow n_2 - n_1 = 2$

$\Rightarrow n_1 = 1$

$n_2 = 3$

$$\frac{1}{\lambda} = \frac{1}{R_H \times Z^2} \times \frac{1}{\left[\frac{1}{1} - \frac{1}{3^2}\right]} = \frac{9}{32R_H}$$

Sol 20: (A) Brackett series $n_1 = 4$

n_2 can be from 9 to 5

∴ No. of lines in Brackett series are 9 − 4 = 5

Sol 21: (B) Bohr used quantum theory for quantising the angular momentum of electron in atom.

Sol 22: (C) $\lambda = \frac{h}{mv}$

$$= \frac{6.6 \times 10^{-34}}{2 \times 10^{-1} \times 5 \times \frac{5}{18} \times 1.6} = 10^{-33}\left(\frac{6.6 \times 18}{3.2 \times 25}\right)$$

It's in the order of 10^{-30} s.

Sol 23: (D) Paschen series → $n_1 = 3$

Longest wavelength → 3 → 4, Shortest 3 → ∞

$$\Rightarrow \frac{1}{m'} = R_H \times 4^2 \left[\frac{1}{3^2} - \frac{1}{\infty^2}\right]$$

$$\Rightarrow \frac{1}{m} = R_H \times Z^2 \left[\frac{1}{3^2} - \frac{1}{4^2}\right]$$

$$\Rightarrow \frac{m'}{m} = \frac{2^2}{4^2}\,\frac{7/144}{1/9} = \frac{7}{64}$$

$$\Rightarrow m' = \frac{7m}{64}$$

Sol 24: (B) $Y \rightarrow {}_9F^{19}$[since protons = 2s + 1, mass = 18 + 1]

$\Rightarrow X = {}_{11}Na^{23} \rightarrow$ 11 protons, 12 neutrons

23 g ⇒ 12 N neutrons

$$4.6\text{ g} \rightarrow \frac{12 \times 4.6}{23} = 2.4 \text{ moles of neutron}$$

Sol 25: (C) Energy of photon

$$E = \frac{hC}{\lambda} = \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{3.1 \times 10^{-8}} = 6.3 \times 10^{-18}\text{ J}$$

Work function= $12.8 \times 1.6 \times 10^{-19} = 2.04 \times 10^{-18}$ J

$KE_{max} = 4.26 \times 10^{-18}$ J

$$V = \sqrt{2KE_{max}/m_e} = 2.18\sqrt{2} \times 10^6 \text{ m/s}$$

Sol 26: (B) By de-Broglie hypothesis

$$\lambda = \frac{h}{p} \Rightarrow |\Delta\lambda| = \frac{h}{p^2}.|\Delta p|....(i) \left[\because \frac{d\lambda}{dp} = \frac{-h}{p^2}\right]$$

and by Uncertainity principle

$$\Delta x.\Delta p = \frac{\hbar}{2} \Rightarrow \Delta p \Rightarrow \frac{h}{4\pi\Delta x} \text{ and give } \Delta x = \frac{7}{22} \text{ nm}$$

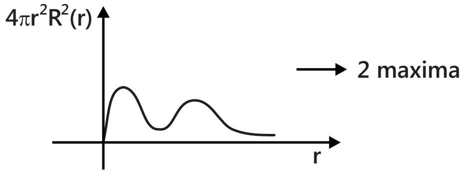
Put this in (i)

We get minimum Δλ as

$$|\Delta\lambda| = \frac{h}{p^2}.\frac{1}{4\pi\Delta x} = \frac{h^2}{4\pi p^2 \Delta x}$$

Sol 27: (B) For $3p_y$

ψ is not independent of θ, ϕ



2 → nodal plane

m can be 1 or 0 or −1.

Sol 28: (A) $\lambda_{radio} > \lambda_{micro}$

$r_n \propto n^2 \Rightarrow r_1 < r_2 < r_3 < r_4$

$E \propto -\dfrac{1}{n}$

$\therefore E_1 < E_2 < E_3 < E_4$ and $V \propto \dfrac{Z}{n}$

$\therefore Be^{+3} > Li^{+2} > He^{2+} > H$

Sol 29: (C) $L = \dfrac{nh}{2\pi}$

$L_n - L_{n-1} = \dfrac{h}{2\pi}$

ΔE doesn't depend on potential at ∞.

$KE \propto \dfrac{1}{r^2}$

∴ KE decreases on moving away from nucleus.

Previous Years' Questions

Sol 1: (A) James Chadwick discovered neutron ($_0n^1$).

Sol 2: (D) The radius of an atom is of the order of 10^{-8} cm

Sol 3: (A) NO^+ C_2^{2-} CN^- N_2

$14e^-$ $14e^-$ $14e^-$ $14e^-$

Sol 4: (B) N^{3-}, F^- and Na^+ (These three ions have e^- = 10, hence they are isoelectronic)

Sol 5: (D) $r_H = 0.529\ \dfrac{n^2}{z}$ Å

For hydrogen ; n = 1 and z = 1 therefore

r_H = 0.529 Å

For Be^{3+} : Z = 4 and n = 2 Therefore

$$r_{Be^{3+}} = \frac{0.529 \times 2^2}{4} = 0.529\text{Å}$$

Sol 6: (C) $\dfrac{1}{\lambda} = R\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$

$$\frac{1}{\lambda} = 1.097 \times 10^7 m^{-1}\left[\frac{1}{1^2} - \frac{1}{\infty^2}\right]$$

$\therefore l = 91 \times 10^{-9}$

We known 10^{-9} = 1 nm So, λ = 91 nm

Sol 7: (C) $\Delta E = 1.312 \times 10^6\left[\dfrac{1}{1^2} - \dfrac{1}{2^2}\right]$

$= 1.312 \times 10^6 \times \dfrac{3}{2} = 0.984 \times 10^6$ d

$= 9.84 \times 10^5$ J/mol.

Sol 8: (C) $E = E_1 + E_2$

$$\frac{hc}{\lambda} = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2} \Rightarrow \frac{1}{\lambda} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$$

$$\frac{1}{355} = \frac{1}{680} + \frac{1}{\lambda_2} \Rightarrow \lambda_2 = 742.76\text{nm}$$

Sol 9: (B) As

$$\lambda = \frac{h}{m\upsilon} = \frac{6.63 \times 10^{-34}}{1.67 \times 10^{-27} \times 1 \times 10^3} = 3.97 \times 10^{-10} m$$

$= 0.397 \times 10^{-9}$ m = 0.40 nm.

Sol 10: (C) $\Delta x + \Delta p = \dfrac{h}{4x}$

$\Delta x \times [m\Delta\upsilon] = \dfrac{h}{4x}$; $\Delta u = \dfrac{600 \times 0.005}{100} = 0.03$

So, $\Delta x\,[9.1 \times 10^{-31} \times 0.03] = \dfrac{6.6 \times 10^{-34}}{4 \times 3.14}$

$$\Delta x = \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 0.03 \times 10^{-31}} = 1.92 \times 10^{-3} m$$

Sol 11: (B) is the correct option because it has the maximum value of n + *l*

Sol 12: (D) (4) and (5) belong to 3d-orbital which are same energy.

Sol 13: (B) The electronic configuration is Cr (chromium element in the ground state) = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

Sol 14: (A) For 4f orbital electron n = 4

l = 3 (Because 0, 1, 2, 3)

s, p, d, f

m = + 3, +2, +1, 0, −1, −2, −3; s = +1/2

Sol 15: (B) 4p(2) 4s(3) 3d(4) 3p

According to (n + ℓ) rule, increasing order of energy

(4) < (2) < (3) < (1)

Sol 16: (C) $\Delta x.m\ \Delta v = \dfrac{h}{4\pi}$

$$\Delta x = \frac{h}{4\pi\ m\ \Delta\ v}$$

$$\Delta v = 600 \times \frac{0.005}{100} = 0.03$$

$$\Rightarrow \Delta x = \frac{6.625 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 0.03} = 1.92 \times 10^{-3}\ m$$

Sol 17: (B) $\lambda = \dfrac{h}{mv} = \dfrac{6.63 \times 10^{-34}}{1.67 \times 10^{-27} \times 10^{3}} \equiv 0.40$ nm

Sol 18: (A) Energy required for 1 Cl_2 molecule

$= \dfrac{242 \times 10^{3}}{N_A}$ Joules.

This energy is contained in photon of wavelength 'λ'.

$$\frac{hc}{\lambda} = E \Rightarrow \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{\lambda}$$

$$= \frac{242 \times 10^{3}}{6.022 \times 10^{23}}$$

$\lambda = 4947\ \overset{0}{A} \approx 494$ nm

Sol 19: (B) $IE_{He^+} = 13.6\ Z_{He^+}^2 \left[\dfrac{1}{1^2} - \dfrac{1}{\infty^2}\right] = 13.6\ Z_{He^+}^2$, where $\left(Z_{He^+} = 2\right)$

Hence, $13.6 \times Z_{He^+}^2 = 19.6 \times 10^{-18}\ J\ atom^{-1}$.

$$\left(E_1\right)_{Li^{+2}} = -13.6\ Z_{Li^{+2}}^2 \times \frac{1}{1^2}$$

$$= -13.6\ Z_{He^+}^2 \times \left[\frac{Z_{Li^{+2}}^2}{Z_{He^+}^2}\right]$$

$$= -19.6 \times 10^{-18} \times \frac{9}{4} = -4.41 \times 10^{-17}\ J/atom$$

Sol 20: (C) $\left(E_n\right)_H = -13.6\dfrac{1^2}{n^2}eV$

$n = 2 \Rightarrow E_2 = -3.4$ eV

JEE Advanced/Boards

Exercise 1

Sol 1: 1 eV = 1.6×10^{-19} J

Let λ be the wavelength of a photon of 1 eV energy.

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

$$\Rightarrow \lambda = \frac{hc}{E} = \frac{6.6 \times 10^{-34} \times 3 \times 10^{8}}{1.6 \times 10^{-19}}$$

= 12.3×10^{-7} m

= 1.23×10^{-6} m

Sol 2: 1st line in Lyman series of H

$$\frac{1}{\lambda} = R_H \times 1^2 \left[\frac{1}{1^2} - \frac{1}{2^2}\right]$$

In He^{2+}

$$\frac{1}{\lambda} = R_H \times Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\Rightarrow \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \times 2^2 = \frac{1}{1^2} - \frac{1}{2^2}$$

$$\Rightarrow \frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{1}{2^2} - \frac{1}{4^2}$$

$\Rightarrow n_1 = 2, n = 4$

IE_2 of He = $13.6 \times Z^2$ eV/atom

= $13.6 \times 4 \times 1.6 \times 10^{-19}$

= 8.67×10^{-18} J/atom

1st of $He^{2+} \rightarrow r = 0.529 \times \dfrac{n^2}{Z}$ Å

n = 1, Z = 2

∴ r = 0.264 Å

Sol 3: $\lambda = \frac{h}{mv}$ and $eV = \frac{1}{2}mv^2$

$\Rightarrow \lambda = \frac{h}{\sqrt{2meV}} \Rightarrow r = \frac{h^2}{2me\lambda^2}$

$= \frac{(6.6\times10^{-34})^2}{2\times9.1\times10^{-31}\times1.6\times10^{-18}\times(9\times10^{-12})^2}$

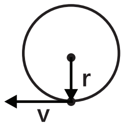
$= 10^5 \times 0.0186$

$= 1.86 \times 10^3$ Volts.

Sol 4: According to Heisenberg's Uncertainity principle, the position and momentum of a moving particle cannot be found exactly.

But according to Bohr, electrons move in a stationary circular orbit with a fixed velocity which contradicts Heisenberg principle.

According to Bohr,



if $\overline{r}$ is fixed, we can find $\overline{v}$ exactly.

Sol 5: Let it move with a velocity v.

From conservation of energy

$\Delta KE + \Delta PE = 0$

$\Rightarrow \frac{1}{2}mv^2 = \frac{1}{4\pi\epsilon_0}.\frac{q_1q_2}{r}$

$\Rightarrow \frac{1}{2} \times 4 \times 1.67 \times 10^{-27} \times v^2$

$= \frac{9\times10^{11}\times29\times2\times(1.6\times10^{-18})^2}{10^{-13}}$

$\Rightarrow v = \sqrt{4012} \times 10^5$ m/s $= 6.34 \times 10^6$ m/s

Sol 6: Velocity of electron in nth orbit of H atom is = $\frac{2.18\times10^6}{n}$ m/s

if n = 3

$v = 0.72 \times 10^6$ m/s

no. of revolutions per sec = $\frac{v}{2\pi r}$

$= \frac{0.72\times10^6 \text{ m/s}}{2\times3.14\times0.529\times3^2\times10^{-10}}$ M

$= 2.40 \times 10^{14}$ /sec

Sol 7: $E \propto \frac{Z^2}{n^2}$

Minimum energy of photon needed to remove electron in 3rd orbit of He+ is

$-21.76 \times 10^{-19} \times \frac{2^2}{3^2}$ J

$\therefore \frac{hc}{\lambda} = +21.76 \times 10^{-19} \times \frac{4}{9}$ J

$\Rightarrow \lambda = \frac{6.6\times10^{-34}\times3\times10^8}{21.76\times4\times10^{-19}} \times 9 = 2.04 \times 10^{-7}$ m

Sol 8: Bohr's theory has some failures

→ It can't explain the splitting of spectral lines in magnetic fields.

→ When the positions of electrons are recorded practically, the obtained results show that electrons don't move in a fixed and quantised orbit but they move in 3-dimensional orbitals which spread but nucleus to infinity.

But probability is high at Bohr's orbits compared to other regions

Sol 9: An atomic orbital is a mathematical function that describes the wave-like behaviours' of either one electron or a pair of electrons in an atom.

It gives us the probability of finding an electron at a certain point around the nucleus.

Each orbital in an atom is characterised by a unique set of values called quantum numbers they are

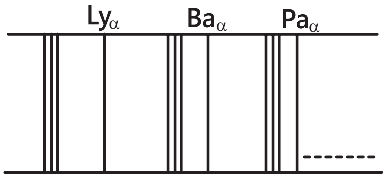
n → principle quantum number

l → Azimuthal quantum number

m → Magnetic quantum number

Sol 10: The emission spectrum of atomic hydrogen is divided into a number of spectral series with wavelength given by Rydberg's formula.

These observed spectral lines are due to electron moving between energy levels in the atom



Sol 11: $\frac{1}{\lambda} = R_HZ^2\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$

$$\frac{1}{6500\,\text{Å}} = R_H(1)\left(\frac{1}{2^2}-\frac{1}{3^2}\right)$$

In Balmer, H_α - $2 \to 3$

H_β - $2 \to 4$

$$\frac{1}{\lambda'} = R_H(1)\left(\frac{1}{2^2}-\frac{1}{4^2}\right)$$

$$\Rightarrow \frac{\lambda'}{6500} = \frac{\frac{1}{4}-\frac{1}{9}}{\frac{1}{4}-\frac{1}{16}} = \frac{\frac{5}{36}}{\frac{3}{16}} = \frac{20}{27}$$

λ' = 4814 Å

Sol 12: $\frac{1}{\lambda} = R_H \times Z^2\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$

Frequency $= \frac{C}{\lambda} = CR_HZ^2\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$

$$= 3 \times 10^8 \times 1.09 \times 10^7\left(1-\frac{1}{9}\right) = 2.9 \times 10^{15}\text{ Hz}$$

Sol 13: $\Delta E = E_2 - E_1$

$$= \frac{-13.6}{2^2}-\left(\frac{-13.6}{1^2}\right) = -3.4 + 13.6 = 10.2\text{ eV}$$

Energy of X-ray $\to \frac{hC}{\lambda} = \frac{6.6\times10^{-34}\times3\times10^{8}}{3\times10^{-8}}$

$= 6.6 \times 10^{-18}$ J

$\Delta E = Z^2 \times 10.2\text{ eV} = Z^2 \times 10.2 \times 1.6 \times 10^{-19}$ J

and $\Delta E = \frac{hc}{\lambda} \Rightarrow Z^2 \times 10.2 \times 1.6 \times 10^{-19} = 6.6 \times 10^{-18}$

$\Rightarrow Z^2 = 4 \Rightarrow Z = 2$ i.e. He

Sol 14: The shape of an atomic orbital is the locus where there is a significant probability of finding an electron of that orbital. For example, if we take an s-orbital → there is a good probability of finding electrons around a spherical surface of certain radius and p-orbital has a shape of a dumbbell.

Sol 15: For any orbital

Spherical radial nodes = $n - \ell - 1$

Angular nodes/nodal planes = ℓ

Total nodes = $n - 1$

Sol 16: Atomic number of chromium. Actual chromium configuration is$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$ but expected is $[Ar]\ 4s^2\ 3d^4$. The deviation can be explained by 2 reasons

1 → No. of exchange pairs. More the number of exchange pairs, more is the stabilisation energy.

2 → Spherical symmetry in both 4s and 3d orbitals.

So, it will be more stable which is not the case in $4s^2\ 3d^4$.

Sol 17: As we know

Energy of photon = Work function $\to KE_{max}$

$$\Rightarrow \frac{hc}{\lambda_1} = h\nu_0 + KE_1 \qquad \text{...(i)}$$

$$\frac{hc}{\lambda_2} = h\nu_0 + KE_2 \qquad \text{...(ii)}$$

Multiply (i) by (ii) and subtract from (ii)

$$\frac{2hc}{\lambda_1}-\frac{hc}{\lambda_2} = 2h\nu_0 - h\nu_0$$

$$\Rightarrow 3 \times 10^8\left(\frac{2}{2.2\times10^{-7}}-\frac{1}{1.9\times10^{-7}}\right) = \nu_0$$

$$\Rightarrow \nu_0 = 3 \times 10^{15}\left(\frac{1}{1.1}-\frac{1}{1.9}\right) = 1.14 \times 10^5\text{ Hz}$$

$$\lambda_0 = \frac{c}{\nu_0} = \frac{3\times10^{8}}{1.14\times10^{15}} = 2.61 \times 10^{-7}\text{ m}$$

Sol 18: By conservation of energy $E_0 = E_1 + E_2$

$\frac{hc}{\lambda_0} = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2}$ where λ_0 = 300 nm

λ_1 = 760 nm

$$\Rightarrow \frac{1}{\lambda_0} = \frac{1}{\lambda_1}+\frac{1}{\lambda_2} \Rightarrow \frac{1}{\lambda_2} = \frac{1}{\lambda_0}-\frac{1}{\lambda_1}$$

$$\Rightarrow \lambda_2 = \frac{\lambda_0\lambda_1}{\lambda_1-\lambda_0} = \frac{300(760)}{760-300} = 495.6\text{ nm}$$

Sol 19: By De-Broglie hypothesis

$$\lambda = \frac{h}{mv} = \frac{6.6\times10^{-34}}{0.15\times50} = 8.8 \times 10^{-35}\text{ m}$$

It is extremely low even compared to size of atoms. So, it's not observable.

Sol 20: According to conservation of energy $\frac{hc}{\lambda} = \omega_0 + KE_{max}$

when $\nu_1 = 1.6 \times 10^{16}$ Hz

$h\nu_1 = \omega_0 + KE_1$ .....(i)

when $\nu_2 = 10^{16}$ Hz and $KE_1 = 2KE_2$

$h\nu_2 = \omega_0 + KE_2$ .....(ii)

Multiply (ii) by 2 subtract (i) from it.

$2h\nu_2 - h\nu_1 = 2\omega_0 + 2KE_2 - (\omega_0 + KE_1) = \omega_0$

and $\omega_0 = h\nu_0$

$\Rightarrow 2h\nu_2 - h\nu_1 = h\nu_0$

$\Rightarrow \nu_0 = 2\nu_2 - 2\nu_1$

$= 2 \times 10^{16} - 1.6 \times 10^{16}$

$= 0.4 \times 10^{16}$

$= 4 \times 10^{15}$ Hz

Sol 21: The magnetic moment of an ion is

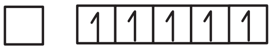
$M = \sqrt{n(n+2)}$ B.M. where n is the number of unpaired electron in the ion.

$\sqrt{n(n+2)} = \sqrt{35}$

$\Rightarrow n(n + 2) = 35 = 5 \times 7$

$\Rightarrow n = 5$

So, X^{3+} has 5 unpaired electron in 3d series.



$\therefore$ Atomic number = 18 + 5 + 3= 26

Sol 22: Bond energy of $I_2 \rightarrow$ 240 kJ/mole for 1 molecule

$$= \frac{240\times10^{3}}{6\times10^{23}} = 4 \times 10^{-19}\text{ J}$$

Energy of a photon = $\frac{hc}{\lambda}$

$$= \frac{6.66\times10^{-34}\times3\times10^{8}}{4.5\times10^{-7}} = 4.44 \times 10^{-19}\text{ J}$$

$\therefore$ KE of 2 Iodine atoms

$= 4.44 \times 10^{-19}\text{ J} - 4 \times 10^{-19}\text{ J}$

$= 0.44 \times 10^{-19}$ J

$\therefore$ KE of a single atom $= \frac{4.4\times10^{-20}}{2} = 2.2 \times 10^{-20}$ J

Sol 23: Energy of the incident photon, $E = \frac{hc}{\lambda}$

$$= \frac{6.6\times10^{-34}\times3\times10^{8}}{2.53\times10^{-7}} = 7.82 \times 10^{-19}\text{ J}$$

$$= \frac{7.82\times10^{-19}}{1.6\times10^{-19}}\text{ eV} = 4.89\text{ eV}$$

$\therefore$ Work function $= \frac{hc}{\lambda} - KE_{max}$

$= 4.89 - 0.24 = 4.65$ eV

Sol 24: 1 g atm $\rightarrow$ 1 N atoms

Lowest energy of visible region $\rightarrow$ Lowest energy line of Balmer series i.e. $3 \rightarrow 2$

$$E = E_3 - E_2 = \frac{-13.6}{n_1^2} - \left(\frac{-13.6}{n_2^2}\right)$$

$$\Rightarrow 13.6\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = 13.6\left(\frac{5}{36}\right) = 1.88\text{ eV}$$

Total energy $= 6 \times 10^{23} \times 1.88$ eV

$= 6 \times 10^{23} \times 1.88 \times 1.6 \times 10^{-19}$ eV

$= 18.2 \times 10^{4}$ J

= 182 kJ per 1.0 gram atom

Sol 25: For X

$\lambda = 9.87$ Å. Moseley's law = $\sqrt{\nu} = k(Z - \alpha)$

$$\nu = \frac{c}{\lambda} = \frac{3\times10^{8}}{9.87\times10^{-10}}$$

$= 3.03 \times 10^{17}$

$\sqrt{\nu} = \sqrt{30.3\times10^{16}}$

$= 5.51 \times 10^{8}$

$\Rightarrow 5.51 \times 10^{8} = 4.9 \times 10^{7} (2 - 0.75)$

$\Rightarrow Z - 0.75 = 11.245$

$\Rightarrow Z \approx 12.$

For Y

$\lambda = 2.29$ Å

$$\nu = \frac{c}{\lambda} = \frac{3\times10^{8}}{2.29\times10^{-10}}$$

$= 1.31 \times 10^{18}$

$\sqrt{\nu} = 1.14 \times 10^{9}$

$\Rightarrow 1.14 \times 10^{9} = 4.9 \times 10^{7} (2 - 0.75)$

$\Rightarrow 2 - 0.75 = 23.35$

$\Rightarrow Z \approx 24$

Sol 26: $\frac{1}{\lambda} = R\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$ and given that, its Balmer series so $n_1 = 2$

$$\Rightarrow \frac{1}{\lambda} = R\left[\frac{1}{2^2}-\frac{1}{n_2^2}\right]$$

$$\Rightarrow \frac{1}{\lambda}\times\frac{1}{R} = \frac{1}{2^2}-\frac{1}{n_2^2}$$

$$\Rightarrow \frac{912\,\text{Å}}{4344\,\text{Å}} = \frac{1}{2^2}-\frac{1}{n_2^2}$$

$$\Rightarrow 0.209 = \frac{1}{4}-\frac{1}{n_2^2}$$

$$\Rightarrow \frac{1}{n_2^2} = 0.0400$$

$\Rightarrow n_2^{\,2} = 25$

$\Rightarrow n_2 = 5$

Sol 27: Change in energy of electron = Energy of photon

$E = E_3 - E_2$

$= -2.41 \times 10^{-12} - (-5.42 \times 10^{-12})$

$= 3.01 \times 10^{-12}$ erg

$= 3.01 \times 10^{-19}$ J

$$\lambda = \frac{hc}{E} = \frac{6.6\times10^{-34}\times3\times10^{8}}{3.01\times10^{-19}}$$

$\approx 6.6 \times 10^{-7}$ m

$= 6.6 \times 10^{3}$ Å

Sol 28:

$r = r_0 . A^{1/3} = 1.4\times10^{-13}. A^{1/3}\text{cm}$

$= 1.4\times10^{-13}\times19^{1/3} = 5.07\times10^{-13}\,\text{cm}$

$$\text{Vol of F. Nucleus} = \frac{4}{3}\pi r^{3} = 7.17\times10^{-37}\,\text{cm}^{3}$$

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{19}{6.02\times10^{23}\times7.17\times10^{-37}}$$

$$= 0.44\times10^{14}\,\text{gm cm}^{-3}$$

Sol 29: From Heisenberg's Uncertainty principle

$$\Delta x\,.\Delta p \geq \frac{\hbar}{2}$$

$$\Rightarrow x.m\,\Delta V \geq \frac{h}{4\pi} \quad \Delta V = 2 \times 0.01 \text{ m/s}$$

$$\therefore \Delta x = \frac{6.6\times10^{-34}}{4\times3.14\times10^{-3}\times10^{-2}\times2} = \frac{6.6\times10^{-29}}{12.56\times2}$$

$\approx 3 \times 10^{-30}$ m

Though, there is some uncertainty in the position, it is extremely negligible, i.e. we cannot observe such deviations.

Sol 30: By Heisenberg's uncertainty principle and $\Delta V = 2$ m/s

$$\Delta x.\Delta p \geq \frac{\hbar}{2}$$

$$\Rightarrow \Delta x \times 9.109 \times 10^{-31} \times 2 = \frac{6.6\times10^{-34}}{4\times3.14}$$

$\Rightarrow \Delta x = 0.028 \times 10^{-3}$

$\approx 2.8 \times 10^{-5}$ m

Here, the uncertainty in position is quite high compared to size of an atom.

$\therefore$ From the above 2 problems, we can see that uncertainty in position for macroparticles is negligible, but there, is high uncertainty in case of micro particles.

Exercise 2

Single Correct Choice Type

Sol 1: (C) Bohr's model says that electron move in a stationary state with fixed velocities. So, it contradicts uncertainty principle.

Sol 2: (B) Statement-II seems to be irrelevant.

Comprehension Type

Paragraph 1:

Sol 3: (A, B) $E = 13.6\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$ eV

$$= 13.6\left[\frac{1}{1^2}-\frac{1}{3^2}\right] \times 1.6 \times 10^{-19}\text{ J}$$

$$\approx 13.6 \times \frac{8}{9} \times 1.6 \times 10^{-19}\text{ J}$$

$$= 1.93 \times 10^{-18}\text{ J}$$

Sol 4: (C) No. of lines = $\frac{(\Delta n)(\Delta n+1)}{2}$ where $\Delta n = n_1 - n_2$.

In this case

$n_1 = 6, n_2 = 3$

$\therefore$ lines = $\frac{3(4)}{2} = 6$.

Sol 5: (B) 1st line in Lyman

$$\frac{1}{\lambda} = R \times 1^2 \times \left[\frac{1}{1^2}-\frac{1}{2^2}\right] \Rightarrow \lambda = \frac{4}{3R}$$

2nd line in Balmer

$$\frac{1}{\lambda} = R \times 1^2 \left[\frac{1}{2^2}-\frac{1}{4^2}\right] \Rightarrow \lambda = \frac{16}{3R}$$

$$\lambda = \frac{12}{3R} = \frac{4}{R}$$

Sol 6: (C) Wave number = $\frac{1}{\lambda}$

$n_1 + n_2 = 4$

$n_2 - n_1 = 2$

$\Rightarrow n_1 = 1$

$n_2 = 3$

$$\frac{1}{\lambda} = R \times Z^2 \left[\frac{1}{1^2}-\frac{1}{3^2}\right] \text{ and } Z = 3$$

$$= R(9)\left(\frac{8}{9}\right) = 8R$$

Paragraph 2:

Sol 7: (B) $\Delta KE = \Delta PE$

$$\Rightarrow \frac{1}{2}mv^2 = \frac{1}{4\pi \in_0}\frac{q_1q_2}{r}$$

$$\Rightarrow \frac{1}{2} \times 4 \times 1.6 \times 10^{-27} \times v^2$$

$$= \frac{9\times10^{11}\times29\times2\times(1.6\times10^{-19})^2}{10^{-13}}$$

$$\Rightarrow v = \sqrt{4012} \times 10^5 \text{ m/s}$$

$$= 6.33 \times 10^6 \text{ m/s}$$

$$= 6.33 \times 10^8 \text{ cm/sec}$$

Sol 8: (A) Na, K, Cs can't be used as they are 1A group elements, they have only 1e⁻ in outer shell. So, they have less density and IE. So, Pt is suitable.

Sol 9: (C) This question is out of scope.

Though the value of N after several calculations comes out as

$$N(\theta) = \frac{nt}{4r^2}\left(\frac{2Z}{2k}\right)^2\left(\frac{e^2}{4\pi \in_0}\right)^2 \frac{1}{\sin^4\theta/2}$$

$\therefore N \propto \frac{1}{\sin^4\theta/2}$ (need not be included in the syllabus)

Sol 10: (C) In Rutherford's α-ray scattering experiment, most of the α-particles doesn't undergo any deflection. Few particles deviate through some angle and negligible no. of α-particles deflect for more than 90°.

Match the Columns

Sol 11: A → s; B → r; C → q; D → p

(A) 2nd orbit in $He^+ \rightarrow r = 0.529 \times \frac{2^2}{2}$ Å

$$\rightarrow E = -13.6 \times \frac{2^2}{2^2}\text{ eV}$$

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2mE}}$$

$$= \frac{6.6\times10^{-34}}{\sqrt{2\times9.1\times10^{-31}\times13.6\times1.6\times10^{-19}}} = \sqrt{\frac{150}{13.6}}\text{ Å}$$

(B) 3rd orbit in H-atom, $V \propto \frac{Z}{n}$

$$V = 2.18 \times \frac{Z}{n} = \frac{2.18}{3}\text{ m/s}$$

(C) 1st orbit Li^{2+} ion $\rightarrow E = -13.6 \times \frac{Z^2}{n^2} = (-13.6)\ 9$ eV

(D) 2nd orbit, Be^{3+} ion $\rightarrow r = 0.529 \times \frac{n^2}{Z}$

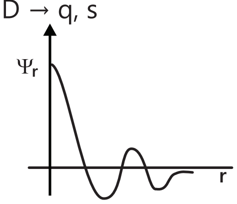
$$= 0.529 \times \frac{2^2}{Z} = 0.529\text{ eV}$$

Sol 12: A → p; B → p, q, s; C → p, r; D → q, s

(A) 4s, 5p, 6d, ……. show similar ψ

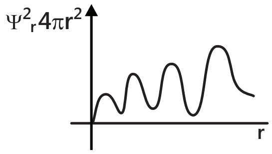
4s [since 3 maxima/minima locally]

$5p_x$, $6d_{xy}$ are not symmetric for all values of θ and ϕ.



4s, 5p, 6d, ……

(B)



(C) $\psi(\theta, \phi) = k$ (i.e. independent of θ, ϕ)

only for circularly symmetric orbitals.

4s, 3s

(D) At one angular nodes for any orbital, no. of angular nodes = ℓ.

$5p_x$, $6d_{xy}$

Assertion Reasoning Type

Sol 13: (D) In Li^{2+}, if $n_1 = 2$, and $n_2 > 2$, then the line may not be in visible region, as energy of that line is 9 times the corresponding line H atom (which is in visible region). So, Statement-I is false.

Previous Years' Questions

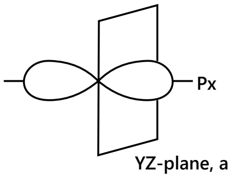
Sol 1: (D) Neutron has no charge, hence, e/m is zero for neutron. Next, α-particle (He^{2+}) has very high mass compared to proton and electron, therefore very small e/m ratio. Proton and electron have same charge (magnitude) but former is heavier, hence has smaller value of e/m.

e/m : n < α < p < e

Sol 2: (C) X-rays is electrically neutral, not deflected in electric or magnetic fields.

yz-plane, a nodal plane

Sol 3: (A) Nodal plane is an imaginary plane on which probability of finding an electron is minimum. Every p-orbital has one nodal plane:



YZ-plane, a nodal plane

Sol 4: (C) $1s^7$ violate Pauli exclusion principle, according to which an orbital cannot have more than two electrons.

Sol 5: (B) Expression for Bohr's orbit is $r_n = \frac{a_0 n^2}{Z} = a_0$

When n = 2, Z = 4.

Sol 6: (A) The number of radial nodes is given by expression $(n - l - 1)$

For 3s, number of nodes = 3 − 0 − 1 = 2

For 2p, number of nodes = 2 − 1 − 1 = 0

Sol 7: (A, C) Alpha particles passes mostly undeflected when sent through thin metal foil mainly because

(A) It is much heavier than electrons.

(C) Most part of atom is empty space.

Sol 8: (A, D) Then these electrons in the 2p orbital must have same spin, no matter up spin or down spin.

Sol 9 (C) Statement-I is correct, Be ($1s^2$, $2s^2$) has stable electronic configuration, removing an electron requires more energy than the same for B ($2p^1$). Reason is incorrect (Aufbau principle)

Sol 10.1: (B) S_1 is spherically symmetrical state, i.e., it corresponds to an s-orbital. Also, it has one radial node.

Number of radial nodes = $n - l - 1$

$\Rightarrow n - 0 - 1 = 1$

(i) n = 2, i.e., S_1 = 2s orbital

Sol 10.2: (C) (ii) Ground state energy of electron in H-atom (E_H)

$$E_H = k\frac{Z^2}{n^2} = k(Z = 1, n = 1)$$

For S_1 state of Li^{2+}.

$$E = \frac{k(3)^2}{2^2} = \frac{9}{4}k = 2.25k$$

Sol 10.3: (B) (iii) In S_2 state, $E(Li^{2+}) = k$ (given)

$$\Rightarrow k = \frac{9k}{n^2}$$

$\Rightarrow n = 3$

Since, S_2 has one radial node.

$3 - l - 1 = 1$

$\Rightarrow l = 1$

Sol 11: A → r; B → q; C → p; D → s

(A) $V_n = \frac{1}{4\pi\in_0}\left(\frac{Ze^2}{r}\right)$

$$K_n = \frac{1}{8\pi\in_0}\left(\frac{Ze^2}{r}\right) \Rightarrow \frac{V_n}{K_n} = -2(R)$$

(B) $E_n = -\frac{Ze^2}{8\pi\in_0 r} \propto r^{-1}$

$\Rightarrow x = -1(Q)$

(C) Angular momentum = $\sqrt{l(l+1)}\frac{h}{2\pi}$ = 0 in 1s orbital.

(D) $r_n = \frac{a_0 n^2}{Z} \Rightarrow \frac{1}{r_n} \propto Z(S)$

Sol 12: A → q; B → p, q, r, s; C → p, q, r; D → p, q, r

(A) Orbital angular momentum

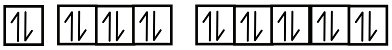
(L) = $\sqrt{l(l+1)}\frac{n}{2\pi}$ i.e,L depends on azimuthal quantum number only.

(B) To describe a one electron wave function, the quantum numbers n, *l* and m are needed. Further to abide by Pauli exclusion principle, spin quantum number (s) is also needed.

(C) For shape, size and orientation, only n, *l* and m are needed.

(D) Probability density (ψ^2) can be determined if n, *l* and m are known.

Sol 13: When n = 3, *l* = 0, 1, 2, i.e., there are 3s, 2p and 3d orbital. If all these orbitals are completely occupied as



Total 18 electrons, 9 electrons with s = + $\frac{1}{2}$ and 9 with s = $-\frac{1}{2}$

Alternatively: In any nth orbit, there can be a maximum of $2n^2$ electrons. Hence, when n = 3, number of maximum

Electrons − 18. Out of these 18 electrons, 9 can have spin −1 /2 and remaining nine with spin = + 1/2

Sol 14: Energy of photon

$$\frac{hc}{\lambda}J = \frac{hc}{e\lambda}eV = \frac{6.625\times10^{-34}\times3\times10^{8}}{300\times10^{-9}\times1.602\times10^{-19}} = 4.14eV$$

For photoelectric effect to occur, energy of incident photons must be greater than work function of metal. Hence, only Li, Na, K and Mg have work functions less than 4.14V.

Sol 15: At radial node, ψ_2 must vanish i.e.

$$\psi_{2r}^2 = 0 = \left[\frac{1}{4\sqrt{2\pi}}\right]^2\left(2-\frac{r_0}{a_0}\right)^2 e^{-\frac{r_n}{a_0}}$$

$$\Rightarrow 2-\frac{r_0}{a_0} = 0$$

$\Rightarrow r_0 = 2a_0$

(b) $\frac{h}{mv} = \frac{6.625\times10^{-34}}{100\times10^{-3}\times100} = 6.625\times10^{-35}m$

= 6.625×10^{-25} Å (negligibly small)

Sol 16: $mvr = \frac{nh}{2\pi}$

$$v = \frac{nh}{2\pi mr} = \frac{6.625\times10^{-34}}{2\times3.14\times9.1\times10^{-31}\times0.529\times10^{-10}}$$

= 2.18×10^6 ms^{-1}.

(b) $\lambda = \frac{h}{mv} = \frac{6.625\times10^{-34}}{9.1\times10^{-31}\times2.18\times10^{6}}$

= 0.33×10^{-9} m = 3.3 Å

(c) Orbital angular momentum (L) = $\sqrt{l(l+1)}\frac{h}{2\pi}$

$= \sqrt{2}\left(\frac{h}{2\pi}\right)$ [∵ for p-orbital, *l* = 1]

Sol 17: Since, $\lambda = \frac{h}{mV} = \frac{h}{\sqrt{2M\,K.E.}}$ (since KE. ∝ T)

$$\Rightarrow \lambda \propto \frac{1}{\sqrt{MT}}$$

For two gases,

$$\frac{\lambda_{He}}{\lambda_{Ne}} = \sqrt{\frac{M_{Ne}\ T_{Ne}}{M_{He}\ T_{He}}} = \sqrt{\frac{20}{4}\times\frac{1000}{200}}$$

$= \sqrt{25} = 5$

Sol 18: Single electron species don't follow the $(n+l)$ rule but multi electron species do.

Ground state of H^- = $1s^2$

First excited state of H^- = $1s^1$, $2s^1$

Second excited state of H^- = $1s^1$, $2s^0$, $2p^1$

Sol 19: (C) As per Bohr's postulate,

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

$$\text{So, } v = \frac{nh}{2\pi mr}$$

$$KE = \frac{1}{2} mv^2$$

$$\text{So, } KE = \frac{1}{2} m\left(\frac{nh}{2\pi mr}\right)^2$$

$$\text{Since, } r = \frac{a_0 \times n^2}{z}$$

So, for 2nd Bohr orbit

$$r = \frac{a_0 \times 2^2}{1} = 4a_0$$

$$KE = \frac{1}{2}m\left(\frac{2^2h^2}{4\pi^2m^2 \times (4a_0)^2}\right)$$

$$KE = \frac{h^2}{32\pi^2 ma_0^2}$$