

## DAY TWO

# Atomic Structure

### Learning & Revision for the Day

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| <ul style="list-style-type: none"><li>• Atomic Models</li><li>• Bohr's Model</li></ul> | <ul style="list-style-type: none"><li>• Dual Nature of Matter (de-Broglie Relationship)</li><li>• Heisenberg's Uncertainty Principle</li></ul> | <ul style="list-style-type: none"><li>• Quantum Mechanics</li><li>• Electronic Configuration of Atom</li><li>• Quantum Numbers</li></ul> |
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An atom is the smallest particle that takes part in a chemical reaction. It contains three fundamental subatomic particles namely electrons, protons and neutrons.

### Discovery of Fundamental Subatomic Particle

- **Cathode rays** were discovered by Sir J J Thomson. These rays were a stream of fast moving negatively charged particles, called **electrons**.
- **Anode rays** were discovered by Goldstein. These rays consist of positively charged particles, called **protons**.
- **Neutrons** are neutral particles and discovered by Chadwick. Neutrons are the heaviest particles of the atom.

**NOTE** Other subatomic particles are positron, neutrino, antineutrino, antiproton and meson.

### Atomic Number (Z) and Mass Number (A)

- The number of protons present in the nucleus of an atom is equal to its atomic number.  
 $Z = \text{number of protons in atom's nucleus or number of electron around atom's nucleus}$
- Mass number ( $A$ ) = number of protons + number of neutrons  
In case of neutral atom, number of protons and number of electrons are equal.
- **Representation of an Atom** An atom is generally represented by the following symbol



where,  $Z$  represents the atomic number and  $A$  represents mass number.

### Different Atomic Species

- Isotopes** Species with same atomic number but different mass numbers are called isotopes.  
e.g.  ${}_1\text{H}^1, {}_1\text{H}^2$
- Isobars** Species with same mass number but different atomic numbers are called isobars.  
e.g.  ${}_{18}\text{Ar}^{40}, {}_{19}\text{K}^{40}$

(iii) **Isotones** Species having same number of neutrons are called isotones.

e.g.  ${}_1\text{H}^3, {}_2\text{He}^4$

(iv) **Isoelectronic** Species having same number of electrons are called isoelectronic species.

e.g.  $\text{N}_2\text{O}, \text{CO}_2$

## Atomic Models

The atomic models which well describe the atomic structure are given below:

### Thomson's Model of Atom

Thomson assumed that an atom is a sphere of positive charges uniformly distributed, with the electrons scattered as points throughout the sphere. This was also known as plum pudding model.

### Rutherford's Model of Atom

Rutherford proposed the nuclear model of atom. According to this model,

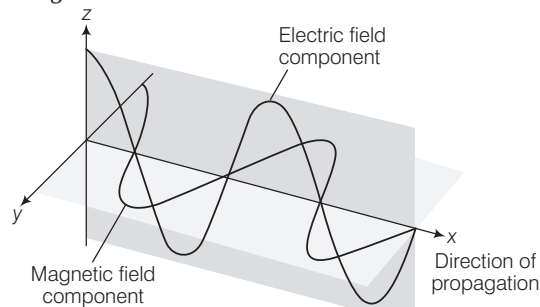
- The positive charge and most of the mass of the atom was densely concentrated in extremely small region, called the nucleus by Rutherford.
- The nucleus is surrounded by electrons that move around the nucleus with very high speed in circular path, called orbits.
- Electrons and the nucleus are held together by electro static forces of attraction.

## Development Leading to the Bohr's Model of Atom

Nature of electromagnetic radiations and spectrum play an important role in the development of Bohr's model.

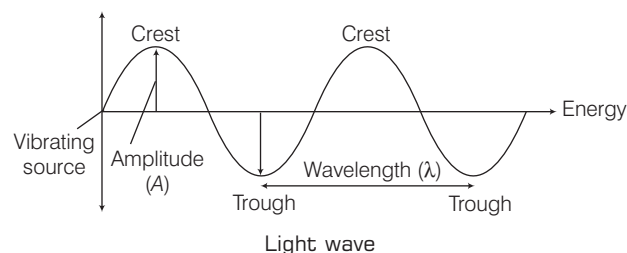
- James Maxwell explains the interaction between the charged bodies and the behaviour of electrical and magnetic fields on macroscopic level.
- He suggested that when electrically charged particle moves under acceleration, alternating electrical and magnetic fields are produced and transmitted.

These fields are transmitted in the form of waves called **electromagnetic waves**.



Electric field and magnetic field components of wave

- A wave is a periodic disturbance in space or in a medium that involves elastic displacement of material particles or a periodic change in some physical quantities such as temperature, pressure, electric potential, electromagnetic field. Thus, wave motion represents propagation of a periodic disturbance carrying energy.



## Planck's Quantum Theory

### (Particle Nature of Electromagnetic Radiation)

The radiant energy which is emitted or absorbed discontinuously in the form of small discrete packets known as **quantum** and in case of light, the quantum of energy is called **photon**.

$$E = h\nu \quad (c = \nu\lambda)$$

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

where,  $h$  = Planck's constant =  $6.63 \times 10^{-34}$  J-s

$E$  = energy of photon or quantum

## Photoelectric Effect

The phenomenon of ejection of electrons from a metal surface when a light of certain frequency strikes on its surface is called **photoelectric effect**.

- The minimum energy required to eject electrons from a surface is called **work function** ( $W_0$ )

$$\text{Work function } (W_0) = h\nu_0 = \frac{hc}{\lambda_0}$$

Here,  $\nu_0$  is called **threshold frequency**, the minimum frequency of incident radiation to eject electrons from the metal surface.

$\lambda_0$  is **threshold wavelength**, the maximum wavelength in incident radiation below which, electrons can be emitted from metal surface is called threshold wavelength.

- If a photon of energy  $E$  is incident of a metallic surface, then it is absorbed by the surface and electrons are emitted. The energy ( $E$ ) is consumed in two ways; in during work function and providing kinetic energy to emitted electrons.

$$\therefore E = W_0 + \text{KE}$$

$$h\nu = h\nu_0 + \text{KE}$$

$$\therefore \text{KE} = h(\nu - \nu_0)$$

If velocity of ejected electrons is  $v$ , then  $\frac{1}{2}mv^2 = h(\nu - \nu_0)$

## Bohr's Model

Bohr gave the model of stationary energy orbits within an atom. The important formulae related to Bohr's model are:

- Angular momentum,  $(mvr) = \frac{nh}{2\pi}$ ,  $n = 1, 2, 3, \dots$
- Bohr's radius,  $(r_n) = r_0 \frac{n^2}{Z}$ ,  $r_n = 0.529 \times \frac{n^2}{Z} \text{ \AA}$   
The above relation suggests that with an increase of energy levels ( $n$ ), the radius of atom also increases,  
thus,  $\frac{r_1}{r_2} = \frac{n_1^2}{n_2^2}$
- Energy of electron in  $n$ th Bohr's orbits,  
 $(E_n) = -\frac{13.6Z^2}{n^2} \text{ eV/atom}$
- Potential energy,  $(E_p) = \frac{-Ze^2}{4\pi\epsilon_0 r}$
- Speed of electron in  $n$ th Bohr's orbit,  $v_n = \frac{2.18 \times 10^6 Z}{n} \text{ ms}^{-1}$
- Number of revolutions made by an electron in  $n$ th Bohr's orbit  $= \frac{v_n}{2\pi r}$  round/s
- Centrifugal force of orbiting electrons = coulombic attraction by nucleus, i.e.  $\frac{mv^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2}$

## Atomic Spectra of Hydrogen

Bohr also explained the atomic spectra of hydrogen on the basis of his atomic model. The set of lines in the visible region is known as **Balmer series**, that in ultraviolet region as **Lyman series** and there are three sets of lines in infrared region namely **Paschen**, **Brackett** and **Pfund series**.

Wave number ( $\bar{\nu}$ ) is defined as reciprocal of the wavelength,

$$\text{i.e. } \bar{\nu} = \frac{1}{\lambda} \quad \bar{\nu} = RZ^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ and so on.}$$

where,  $\lambda$  = wavelength  $R$  = Rydberg constant =  $109677 \text{ cm}^{-1}$

(i) For Lyman series  $n_1 = 1, n_2 = 2, 3, 4$

(ii) For Balmer series  $n_1 = 2, n_2 = 3, 4, 5, \dots$

(iii) For Paschen series  $n_1 = 3, n_2 = 4, 5, 6, \dots$

Wave number ( $\bar{\nu}$ ) and frequency ( $\nu$ ) of radiations emitted when electron drops from  $n_2$  to  $n_1$  are obtained by following expressions.

$$\bar{\nu} = 109678 \text{ (cm}^{-1}) \times Z^2 \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ (For hydrogen, } Z = 1 \text{)}$$

$$\nu = 3.289 \times 10^{15} \text{ (s}^{-1}) \times Z^2 \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

### NOTE

- (i) The number of spectral lines in the spectrum when the electron comes from  $n$ th level to the ground level will be  $\frac{n(n-1)}{2}$ .

- (ii) The intensities of spectral lines decreases with increase the value of  $n$ . e.g. the intensity of first Lyman series ( $2 \rightarrow 1$ ) is greater than second line ( $3 \rightarrow 1$ ) and so on.

## Emission and Absorption Spectra

- Emission spectrum** The spectrum of radiation emitted by a substance that has absorbed energy (either by passing electric discharge through a gas at low pressure or by heating the substance to high temperature) is called an **emission spectrum**. Atoms, molecules or ions that have absorbed radiation are said to be in **excited state**.
- Absorption spectrum** It is like the photographic negative of an emission spectrum. To obtain an absorption spectra a continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths.

## Limitations of Bohr's Model

Bohr left the following facts unexplained

- Fine structure of atom.
- Spectrum of multielectron system.
- Zeeman effect and Stark effect (i.e. splitting of spectral lines under the influence of magnetic and electric field respectively).
- Three dimensional existence of atom.
- Dual nature of electron.

## Dual Nature of Matter (de-Broglie Relationship)

Light is said to have dual character, i.e. it behaves like matter (particle) and wave both. Some properties like interference, diffraction can be explained on the basis of wave nature of light, while the phenomena like photoelectric effect, black body radiation, etc. can be explained on the basis of particle nature of light.

In 1924, Louis de-Broglie explained that like light, matter also show dual behaviour, there is a wave associated with moving particle, known as **matter waves or de-Broglie waves**.

de-Broglie explains the dual nature of electron (i.e. wave nature as well as particle nature)

$$\lambda = \frac{h}{mv} = \frac{h}{P}$$

where,  $\lambda$  = wavelength,  $v$  = velocity of particle  
 $m$  = mass of particle,  $P$  = momentum

The number of de-Broglie wavelengths in a given Bohr's orbit is always equal to the orbit number, which is given by the following relationship

$$mvr = \frac{nh}{2\pi} \Rightarrow 2\pi r = \frac{nh}{mv} = n\lambda$$

## Bohr's Theory vs de-Broglie Equation

As de-Broglie realised, the simplest way to introduce quantum ideas into an atomic model was to describe wave properties to the electron. A standing wave must have integral wavelengths with no possibility of fractional wavelengths with this superposition.

## Heisenberg's Uncertainty Principle

It states that it is impossible to determine at any given instant, both the momentum and the position of subatomic particles like electron, simultaneously  $\Delta x \cdot \Delta P \geq \frac{h}{4\pi}$ .

where,  $\Delta x$  = uncertainty in position,

$\Delta P$  = uncertainty in momentum

## Quantum Mechanics (Concept of Orbital)

On the basis of dual nature of matter and Heisenberg's uncertainty principle, Erwin Schrodinger developed a new branch of science, called quantum mechanics.

## Schrodinger Wave Equation

- Schrodinger derived an equation for an electron which describes the wave motion of an electron wave along any of three axis, i.e. x, y and z. This equation is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - U) \psi = 0$$

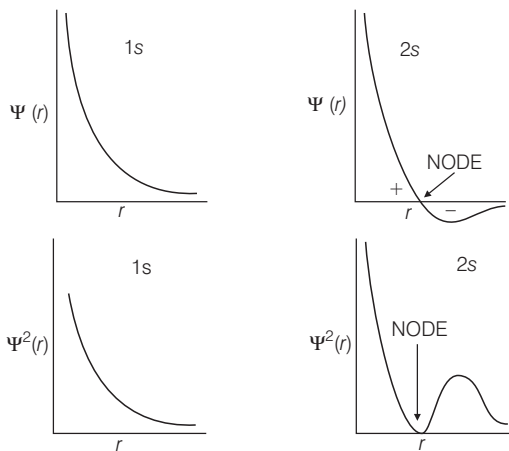
where,  $\psi$  = wave function,  $m$  = mass of electron

$E$  = permissible total energy of electron

$U$  = potential energy of electron =  $-\frac{Ze^2}{r}$ ,

$h$  = Planck's constant

- For H-atom, the equation is solved on the basis of  $\hat{H}\psi = E\psi$  where,  $\hat{H}$  is the total energy operation, called Hamiltonian, if the sum of kinetic energy operation ( $\hat{T}$ ) and potential energy operator ( $\hat{V}$ ), is the total energy,  $E$  of the system,  $\hat{H} = \hat{T} + \hat{V}$ ,  $(\hat{T} + \hat{V}) \psi = E\psi$
- The atomic orbitals or orbital wave functions can be represented by the product of two wave functions,
  - radial wave function and
  - angular wave function
- The orbital wave function  $\psi$  has no significance but  $\psi^2$  has a significance, it measures the electron probability density at a point in an atom. Variation of  $\psi$  and  $\psi^2$  with distance from nucleus for 1s and 2s orbitals



Radial probability curves

- A node is a region of space, where probability of finding an electron is zero.

(i)  $(n - l - 1)$  = radial nodes      (ii)  $l$  = angular nodes

(iii)  $(n - 1)$  = total nodes

## Concept of Shell and Subshell

According to wave mechanical model, the structure of atom can be summarised as

- The electron in an atom are arranged in **shells** or different energy levels which are indicated by numbers, 1, 2, 3, ... or letters K, L, M, ...
- Within each shell, there are **subshells** or sub levels which are designated as s, p, d and f.
- Electrons of different energy levels are present in discrete volumes of different shapes, sizes and orientations in the sub-levels around the nucleus.
- Each of such discrete volume is called an orbital** which has the maximum probability of finding a particular electron of a particular energy level.
- Each orbital may hold up to two electrons of exactly equal energy provided they have opposite spins.

## Shapes of s, p and d-orbitals

On the basis of probability calculations, the different shapes have been assigned to the orbitals, which are given as below:

- Spherical shape for s-orbitals.
- Dumb-bell shape for p-orbitals.
- Double dumb bell shape for  $d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}$  orbitals whereas doughnut shape for  $d_{z^2}$ -orbital

## Electronic Configuration of Atom

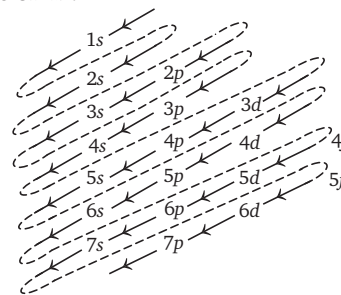
The arrangement of electrons in various shells, subshells and orbitals in an atom is termed as electronic configuration. It is written as  $n l^x$ , where  $n$  = order of shell,  $l$  = subshell and  $x$  = number of electrons present.

e.g. Cr =  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$  ( $Z = 24$ )

## Rules for Filling Electrons in Orbitals

There are some rules for filling the electrons in orbitals are given below:

- Aufbau Principle** "Electrons are filled to the various orbitals, in the order of increasing energy starting with the orbital of lowest energy". As a working rule, a new electron enters in an empty orbital for which the value of  $(n + l)$  is minimum, if the value of  $(n + l)$  is same for two or more orbitals, the new electron enters in an orbital having lower value of 'n'.



The energy of atomic orbitals for H-atom varies as:  
 $1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f$

- (ii) **Hund's Rule of Maximum Multiplicity** "Electrons never pair up until each orbital of a given subshell contains one electron or is singly occupied.

e.g.  $2p^3$ 

↑	↑	↑
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## Quantum Numbers

Quantum numbers are just like address of electrons. There are four types of quantum numbers which are given below:

### 1. Principle Quantum Number ( $n$ )

It gives an idea about the position and energy of an electron. Principal quantum number represents shell number.

$n = 1, 2, 3 \dots$  or (Only positive integers)

### 2. Azimuthal Quantum Number ( $l$ ) or Angular Quantum Number

It represents the subshells ( $s, p, d, f$ ) and angular momentum of the electron. It tells about the shape of subshells. It is also called the angular momentum quantum number.

$$l = 0 \text{ to } (n - 1)$$

$$l = 0 \text{ for } s; l = 1 \text{ for } p$$

$$l = 2 \text{ for } d; l = 3 \text{ for } f$$

### 3. Magnetic Quantum Number ( $m_l$ )

It represents orbitals and orientation of electrons.

$$m = -l \text{ to } +l$$

Total value of  $m = (2l + 1)$

$$n^2 = \text{number of orbital in subshell}$$

$s$ -subshell contains only one orbital.  $p$ -subshell has three orbitals  $p_x, p_y, p_z$  axis. In  $d$ -subshell, there are five orbitals corresponding to  $-2, -1, 0, +1, +2$   $[(2l + 1) = 5]$ . These five orbitals are represented as  $d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}, d_{z^2}$ . In  $f$ -subshell, there are seven orbitals. Maximum number of electrons in a subshell is equal to  $2(2l + 1)$ .

### 4. Spin Quantum Number ( $m_s$ )

The two orientations of an electron in an orbital are distinguished by spin quantum number  $m_s$ .

$$m_s = +1/2 \text{ or } \uparrow \quad (\text{spin up clockwise})$$

$$m_s = -1/2 \text{ or } \downarrow \quad (\text{spin down anticlockwise})$$

maximum number of electrons in a main energy level

$$= 2n^2 \text{ and total spin} = \pm \left( \frac{1}{2} \times n \right)$$

### Pauli's Exclusion Principle

"No two electrons in an atom can have the same set of all the four quantum numbers" or one can say that no two electrons can have the same quantised states.

The maximum number of electrons in the different subshells are

$$s\text{-subshell} = 2, \quad p\text{-subshell} = 6,$$

$$d\text{-subshell} = 10, \quad f\text{-subshell} = 14$$

## Stability of Half-Filled and Completely Filled Orbitals

- When a set of equivalent orbitals (degenerate orbitals) is either fully filled or half-filled, i.e. each containing one or a pair of electrons, the atom gain more stability.
- This effect is more dominant in  $d$  and  $f$ -subshells. Therefore, the outershell configuration for Cr is  $3d^5, 4s^1$  and for Cu is  $3d^{10}, 4s^1$ .

### Examples

(i) Cr (atomic number 24)  $- 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$

(ii) Cu (atomic number 29)  
 $- 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$

(iii) Nb (atomic number 41)  
 $- 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^4, 5s^1$

(iv) Mo (atomic number 42)  
 $- 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^5, 5s^1$

(v) Ru (atomic number 44)  
 $- 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^7, 5s^1$

(vi) La (atomic number 57)  $- 5d^1, 6s^2$

(vii) Lu (atomic number 71)  $- 4f^{14}, 5d^1, 6s^2$

(viii) Ac (atomic number 89)  $- 6d^1, 7s^2$

## DAY PRACTICE SESSION 1

# FOUNDATION QUESTIONS EXERCISE

- 1** Which of the following statements about the electron is incorrect?  
 (a) It is negatively charged particle  
 (b) The mass of electron is equal to the mass of neutron  
 (c) It is a basic constituent of all atoms  
 (d) It is a constituent of cathode rays
- 2** Deuterium nucleus contains  
 (a)  $1p + 1n$  (b)  $2p + 0n$  (c)  $1p + 1e^-$  (d)  $2p + 2n$
- 3** Which of the following is a pair of isoelectronic species?  
 (a)  $\text{Cl}_2$ ,  $\text{O}_3$ ,  $\text{ICl}_2^-$  (b)  $\text{ICl}_2^-$ ,  $\text{ClO}_2^-$   
 (c)  $\text{IF}_2^+$ ,  $\text{I}_3^-$  (d)  $\text{ClO}_2^-$ ,  $\text{ClF}_2^+$
- 4**  $\text{Be}^{2+}$  is isoelectronic with which of the following ions?  
 (a)  $\text{H}^+$  (b)  $\text{Li}^+$  (c)  $\text{Na}^+$  (d)  $\text{Mg}^{2+}$  → NEET 2017
- 5** Which of the following feature of an atom is not a direct result of Rutherford's experiment?  
 (a) Extraordinary hollow nature of atom  
 (b) Existence of circular electronic orbits  
 (c) Small size of the nucleus  
 (d) Exceptionally high density of the nucleus
- 6** Calculate the wavelength of light required to break the bond between two chlorine atoms in a chlorine molecule. The  $\text{Cl} - \text{Cl}$  bond energy is  $243 \text{ kJ mol}^{-1}$   
 ( $h = 6.6 \times 10^{-34} \text{ Js}$ ;  $c = 3 \times 10^8 \text{ ms}^{-1}$ , Avogadro's number =  $6.02 \times 10^{23} \text{ mol}^{-1}$ )  
 (a)  $4.91 \times 10^{-7} \text{ m}$  (b)  $4.11 \times 10^{-6} \text{ m}$   
 (c)  $8.81 \times 10^{-31} \text{ m}$  (d)  $6.26 \times 10^{-21} \text{ m}$
- 7** The energies  $E_1$  and  $E_2$  of two radiations are 25 eV and 50 eV respectively. The relation between their wavelengths, i.e.  $\lambda_1$  and  $\lambda_2$  will be. → CBSE-AIPMT 2011  
 (a)  $\lambda_1 = 2\lambda_2$  (b)  $\lambda_1 = 4\lambda_2$  (c)  $\lambda_1 = \frac{1}{2}\lambda_2$  (d)  $\lambda_1 = \lambda_2$
- 8** The value of Planck's constant is  $6.63 \times 10^{-34} \text{ J-s}$ . The speed of light is  $3 \times 10^{17} \text{ nms}^{-1}$ . Which is closest to the wavelength in nanometer of a quantum of light with frequency of  $6 \times 10^{15} \text{ s}^{-1}$ ?  
 (a) 10 (b) 25 (c) 50 (d) 75
- 9** If the photon of the wavelength 150 pm strikes an atom and one of its inner bond electrons is ejected out with a velocity of  $1.5 \times 10^7 \text{ ms}^{-1}$ , what is the energy with which it is bond to the nucleus?  
 (a)  $1.2 \times 10^2 \text{ eV}$  (b)  $2.15 \times 10^3 \text{ eV}$   
 (c)  $7.6 \times 10^3 \text{ eV}$  (d)  $8.12 \times 10^3 \text{ eV}$
- 10** The kinetic energy of an electron emitted from a surface of a metal by light of wavelength  $5.5 \times 10^{-8} \text{ cm}$  (Threshold frequency for the metal is  $3.62 \times 10^{12} \text{ s}^{-1}$ ), is  
 (a)  $6.6 \times 10^{-27} \text{ erg}$  ( $5.5 \times 10^{17} \text{ s}^{-1} - 3.62 \times 10^{12} \text{ s}^{-1}$ )  
 (b)  $6.6 \times 10^{-27} \text{ erg}$  ( $-5.5 \times 10^{17} \text{ s}^{-1} - 3.62 \times 10^{12} \text{ s}^{-1}$ )  
 (c)  $6.6 \times 10^{-27} \text{ erg}$  ( $-5.5 \times 10^{17} \text{ s}^{-1} + 3.62 \times 10^{12} \text{ s}^{-1}$ )  
 (d)  $6.6 \times 10^{-27} \text{ erg}$  ( $5.5 \times 10^{17} \text{ s}^{-1} + 3.62 \times 10^{12} \text{ s}^{-1}$ )
- 11** Bohr radius for the hydrogen atom ( $n = 1$ ) is approximately  $0.530 \text{ \AA}$ . The radius for the first excited state ( $n = 2$ ) is (in  $\text{\AA}$ )  
 (a) 0.13 (b) 1.06 (c) 4.77 (d) 2.12
- 12** The wavelength corresponding to maximum energy for hydrogen is 91.2 nm. The corresponding wavelength for  $\text{He}^+$  ion is  
 (a) 2.28 nm (b) 22.8 nm (c) 182.4 nm (d) 364.8 nm
- 13** The wavelength of the radiation emitted when  $n$  a hydrogen atom electron falls from infinity to first stationary state would be ( $R_H = 1.097 \times 10^7 \text{ m}^{-1}$ )  
 (a) 91 nm (b) 191 nm (c) 209 nm (d) 314 nm
- 14** The de-Broglie wavelength associated with a ball of mass 1 kg having kinetic energy 0.5 J is  
 (a)  $6.626 \times 10^{-34} \text{ m}$  (b)  $13.20 \times 10^{-34} \text{ m}$   
 (c)  $10.38 \times 10^{-21} \text{ m}$  (d)  $6.626 \times 10^{-34} \text{ m}$
- 15** Match the Column I a with Column II and choose the correct codes.
- | Column I                   | Column II                 |
|----------------------------|---------------------------|
| A. $mvr = \frac{nh}{2\pi}$ | 1. de-Broglie equation    |
| B. $\lambda = \frac{h}{p}$ | 2. Electrons total energy |
| C. $\frac{-e^2}{2r}$       | 3. Paschen series         |
| D. Infrared                | 4. Bohr's equation        |
- Codes**
- | A     | B | C | D |
|-------|---|---|---|
| (a) 4 | 1 | 2 | 3 |
| (b) 4 | 1 | 3 | 2 |
| (c) 1 | 3 | 4 | 2 |
| (d) 2 | 1 | 3 | 4 |
- 16** Uncertainty in the position of an electron (mass =  $9.1 \times 10^{-31} \text{ kg}$ ) moving with a velocity  $300 \text{ ms}^{-1}$ , accurate upon 0.001% will be ( $h = 6.63 \times 10^{-34} \text{ Js}$ )  
 (a)  $19.3 \times 10^{-2} \text{ m}$  (b)  $5.76 \times 10^{-2} \text{ m}$   
 (c)  $1.93 \times 10^{-2} \text{ m}$  (d)  $3.84 \times 10^{-2} \text{ m}$
- 17** The measurement of the electron position is associated with an uncertainty in momentum, which is equal to  $1 \times 10^{-18} \text{ g-cm/s}$ . The uncertainty in electron velocity is (mass of an electron is  $9 \times 10^{-28} \text{ g}$ )



- (a)  $1 \times 10^9 \text{ cm s}^{-1}$  (b)  $1 \times 10^6 \text{ cm s}^{-1}$   
(c)  $1 \times 10^5 \text{ cm/s}^{-1}$  (d)  $1 \times 10^{11} \text{ cm s}^{-1}$

**18** The first orbital of H is represented by

$$\psi = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{3/2} e^{-r/a_0}, \text{ where } a_0 = \text{Bohr's orbit}$$

The probability of finding the electron at a distance  $r$  from the nucleus is

- (a)  $\psi = \psi^2 dr$  (b)  $\int \psi^2 4\pi r^2 dv$   
(c)  $\psi^2 \cdot 4\pi r^2 dr$  (d)  $\int \psi \cdot dv$

**19** The electronic configuration of gadolinium (at. no. = 64) is

- (a)  $[\text{Xe}] 4f^8, 5d^9, 6s^2$  (b)  $[\text{Xe}] 4f^7, 5d^1, 6s^2$   
(c)  $[\text{Xe}] 4f^6, 5d^2, 6s^2$  (d)  $[\text{Xe}] 4f^3, 5d^5, 6s^2$

**20** Choose the correct option for the filling of electrons in the orbitals of an atom

- (a)  $5s, 4p, 3d, 4d, 5s$  (b)  $3d, 4p, 4s, 4d, 5s$   
(c)  $3d, 4s, 4p, 4d, 5s$  (d)  $4s, 3d, 4p, 5s, 4d$

**21** In Cu (at. no. = 29),

- (a) 14 electrons have spin in one direction and 15 electrons other direction  
(b) 13 electrons have spin in one direction and 16 electrons in other direction  
(c) one electron can have spin only in the clockwise direction  
(d) None of the above is correct

**22** In a given atom, no two electrons can have the same values of all the four quantum numbers. This is called

- (a) Hund's rule (b) Pauli exclusion principle  
(c) Aufbau principle (d) Uncertainty principle

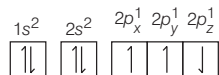
**23** Let  $10^{-16} \text{ J}$  of light energy is required by the interior of human eye to see an object. The number of photons of green light ( $\lambda = 550 \text{ nm}$ ) needed to see the object are approximately equal to

- (a) 278 (b) 290  
(c) 258 (d) 295

**24** Which one is a wrong statement?

→ NEET 2018

- (a) The electronic configuration of N-atom is



- (b) An orbital is designated by three quantum numbers while an electron in an atom is designated by four quantum numbers  
(c) Total orbital angular momentum of electron in 's' orbital is equal to zero  
(d) The value of  $m$  for  $d_{z^2}$  is zero

**25** What is the maximum numbers of electrons that can be associated with the following set of quantum numbers?

$$n = 3, l = 1, m = -1$$

→ NEET 2013

- (a) 6 (b) 4 (c) 2 (d) 10

**26** Maximum number of electrons in a subshell with  $l = 3$  and  $n = 4$  is

→ CBSE-AIPMT 2012

- (a) 14 (b) 16  
(c) 10 (d) 12

**27** The correct set of four quantum numbers for the valence electron of rubidium atom ( $Z = 37$ ) is

- (a)  $5, 1, 1 + \frac{1}{2}$  (b)  $6, 0, 0, +\frac{1}{2}$   
(c)  $5, 0, 0, +\frac{1}{2}$  (d)  $5, 1, 0, +\frac{1}{2}$

**28** Which of the following is non-permissible?

- (a)  $n = 4, l = 3, m = 0$  (b)  $n = 4, l = 2, m = 1$   
(c)  $n = 4, l = 4, m = 1$  (d)  $n = 4, l = 0, m = 0$

**29** The total number of atomic orbitals in fourth energy level of an atom is

→ CBSE-AIPMT 2011

- (a) 16 (b) 32  
(c) 4 (d) 8

**30** Two electrons occupying the same orbital are distinguished by

→ NEET 2016, Phase II

- (a) magnetic quantum number  
(b) azimuthal quantum number  
(c) spin quantum number  
(d) principle quantum number

**31** If an electron has spin quantum number of  $+\frac{1}{2}$  and a magnetic quantum number of  $-1$ , it cannot be represented in a

- (a) s-orbital (b) p-orbital  
(c) d-orbital (d) f-orbital

**32** If  $n$  and  $l$  are respectively the principle and azimuthal quantum numbers, then the expression for calculating the total number of electrons in any energy level is

- (a)  $\sum_{l=1}^{l=n} 2(2l+1)$  (b)  $\sum_{l=1}^{l=n-1} 2(2l+1)$   
(c)  $\sum_{l=0}^{l=n+1} 2(2l+1)$  (d)  $\sum_{l=0}^{l=n-1} 2(2l+1)$

**33** Which of the following statement is correct?

- (a) The electronic configuration of Cr is  $[\text{Ar}] 3d^5 4s^1$  (Atomic number of Cr = 24)  
(b) The magnetic quantum number can never have negative value  
(c) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type (Atomic number of Ag = 47)  
(d) For valency electron of potassium value of  $n$  is 2

**34** Which of the following statement is correct?

- (a) The position and velocity of electrons in the orbit can be determined simultaneously  
(b) The half filled and completely filled orbitals are more stable  
(c) The number of protons and neutrons are always equal  
(d) The energy of 1s and 2s-orbitals are equal for hydrogen atom

## DAY PRACTICE SESSION 2

# PROGRESSIVE QUESTIONS EXERCISE

- 1** A particle *A* moving with a certain velocity has the de-Broglie wavelength of 1 Å. For particle *B* with mass 25% of *A* and velocity 75% of *A*, calculate the de-Broglie wavelength.

(a) 3 Å      (b) 5.33 Å      (c) 6.88 Å      (d) 0.48 Å

- 2** Choose the correct statement among the following.

(a)  $\psi^2$  represents the of the electron finding in an atomic orbital  
 (b) The number of peaks in radial distribution is  $(n - l)$   
 (c) A node is a point in space around nucleus where the wave function  $\psi$  has zero value  
 (d) All of the above

- 3** The set of quantum number for 19th electrons of chromium ( $Z = 24$ ) is

(a) 4, 0, 0, +  $\frac{1}{2}$       (b) 4, 1, -1, +  $\frac{1}{2}$   
 (c) 3, 2, 2, +  $\frac{1}{2}$       (d) 3, 2, -2, +  $\frac{1}{2}$

- 4** The ratio of the difference in energy between the first and second Bohr orbit to that between the second and the third Bohr orbit is

(a)  $\frac{1}{2}$       (b)  $\frac{1}{3}$       (c)  $\frac{4}{9}$       (d)  $\frac{27}{5}$

- 5** The frequency of radiation emitted when electron falls from  $n = 4$  to  $n = 1$  in a hydrogen atom will be (Given ionisation energy of H =  $2.18 \times 10^{-18}$  J atom $^{-1}$  and  $h = 6.625 \times 10^{-34}$  Js)

(a)  $1.54 \times 10^{15}$  s $^{-1}$       (b)  $1.03 \times 10^{15}$  s $^{-1}$   
 (c)  $3.08 \times 10^{15}$  s $^{-1}$       (d)  $2.00 \times 10^{15}$  s $^{-1}$

- 6** The wavelength of a spectral line emitted by hydrogen atom in the Lyman series is  $\frac{16}{15R}$  cm. What is the value of  $n_2$ ? (where,  $R$  = Rydberg constant)

(a) 2      (b) 3      (c) 4      (d) 1

- 7** The hydrogen like ion *M* have ionisation energy greater than that of another hydrogen like ion *N*. Let  $r$ ,  $u$ ,  $E$  and  $L$  be the radius of orbit, speed of electron, energy of the atom and orbital angular momentum of the electron respectively. Which of the following is correct for ground state

(a)  $r_M > r_N$       (b)  $L_M > L_N$       (c)  $u_M > u_N$       (d)  $E_M > E_N$

- 8** Four different sets of quantum numbers for 4 electrons are given below:

$$e_1 = 4, 0, 0, -\frac{1}{2}; \quad e_2 = 3, 1, 1, -\frac{1}{2};$$

$$e_3 = 3, 2, 2, +\frac{1}{2}; \quad e_4 = 3, 0, 0, +\frac{1}{2}.$$

The order of energy of  $e_1$ ,  $e_2$ ,  $e_3$  and  $e_4$  is

(a)  $e_1 > e_2 > e_3 > e_4$   
 (b)  $e_4 > e_3 > e_2 > e_1$   
 (c)  $e_3 > e_1 > e_2 > e_4$   
 (d)  $e_2 > e_3 > e_4 > e_1$

- 9** A mercury lamp of 600W emits monochromatic radiation of wavelength 313.3 nm. The number of photons emitted from the lamp per second are [ $h = 6.626 \times 10^{-34}$  J-s, velocity of light =  $3 \times 10^8$  ms $^{-1}$ ]

(a)  $1 \times 10^{21}$       (b)  $1 \times 10^{20}$       (c)  $1 \times 10^{23}$       (d)  $1 \times 10^{22}$

- 10** In an atom, an electron is moving with a speed of 500 m/s with an accuracy of 0.006%. 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,  $m_e = 9.1 \times 10^{-31}$  kg)

(a)  $3.89 \times 10^{-3}$  m      (b)  $6.10 \times 10^{-3}$  m  
 (c)  $1.62 \times 10^{-4}$  m      (d)  $1.92 \times 10^{-3}$  m

- 11** Which one is the wrong statement?

→ NEET 2017

(a) de-Broglie's wavelength is given by  $\lambda = \frac{h}{mv}$ , where  $m$  is mass of the particle,  $v$  = group velocity of the particle  
 (b) The uncertainty principle,  $\Delta E \times \Delta t \geq h / 4\pi$   
 (c) Half-filled and fully filled orbitals have greater stability due to greater exchange energy, greater symmetry and more balanced arrangement  
 (d) The energy of 2s-orbital is less than the energy of 2p-orbital in case of hydrogen like atoms

- 12** The maximum probability of finding electron in the  $d_{xy}$  orbital is

(a) along the x-axis      (b) along the y-axis  
 (c) at an angle of 90° from the x-axis and y-axis  
 (d) at an angle of 45° from the x-axis and y-axis

- 13** Choose the correct option among the following in which the two species are both isoelectronic and isotopic?

(Atomic numbers : Ca = 20, Ar = 18, Mg = 12, K = 19, Fe = 26)

(a)  $^{40}\text{Ca}^{2+}$  and  $^{40}\text{Ar}$       (b)  $^{24}\text{Mg}^{2+}$  and  $^{25}\text{Mg}$   
 (c)  $^{39}\text{K}^+$  and  $^{40}\text{K}^+$       (d)  $^{56}\text{Fe}^{3+}$  and  $^{57}\text{Fe}^{2+}$

- 14** If azimuthal quantum number could have value of also (in addition to normal value), then EC of Ti ( $Z = 22$ ) would have been

(a)  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^2$   
 (b)  $1s^2, 1p^6, 2s^2, 2p^6, 3s^2, 3d^4$   
 (c)  $1s^2, 1p^6, 2s^2, 2p^6, 3s^1, 3d^5$   
 (d)  $1s^2, 1p^6, 2s^2, 2p^6, 2d^6$



# ANSWERS

## SESSION 1

1 (b)	2 (a)	3 (d)	4 (b)	5 (b)	6 (a)	7 (a)	8 (c)	9 (c)	10 (a)
11 (d)	12 (b)	13 (a)	14 (a)	15 (a)	16 (c)	17 (a)	18 (c)	19 (b)	20 (d)
21 (a)	22 (b)	23 (a)	24 (a)	25 (c)	26 (a)	27 (c)	28 (c)	29 (a)	30 (a)
31 (c)	32 (d)	33 (a)	34 (b)						

## SESSION 2

1 (b)	2 (d)	3 (a)	4 (d)	5 (c)	6 (c)	7 (c)	8 (c)	9 (a)	10 (d)
11 (d)	12 (d)	13 (c)	14 (a)						

# Hints and Explanations

## SESSION 1

1  $m_e = 9.109 \times 10^{-31} \text{ kg}$   
 $m_n = 1.675 \times 10^{-27} \text{ kg}$

2 Deuterium, an isotope of hydrogen, is  ${}_1\text{H}^2$ . Thus, it contains 1 proton and 1 (2 – 1) neutron in its nucleus.

3 Number of electrons in  $\text{ClO}_2^-$   
 $= 17 + 16 + 1 = 34$  electrons  
 Number of electrons in  $\text{ClF}_2^+$   
 $= 17 + 18 - 1 = 34$  electrons

Hence,  $\text{ClO}_2^-$  and  $\text{ClF}_2^+$  are isoelectronic species.

4 Since, electronic configuration of  
 $\text{Be} = 1s^2, 2s^2$        $\text{Be}^{2+} = 1s^2$   
 $\text{Li} = 1s^2, 2s^1$        $\text{Li}^+ = 1s^2$

$\therefore$  Both have same no. of  $e^-$  thus are iso-electronic. It means both  $\text{Be}^{2+}$  and  $\text{Li}^+$  have 2 electrons.

5 Rutherford's model of an atom gives the information about the hollow nature of atom, small size of nucleus and exceptionally high density of the nucleus.

6 Energy required to break one Cl — Cl bond =  $\frac{\text{Bond energy per mole}}{\text{Avogadro's number}}$   
 $= \frac{243 \times 10^3}{6.023 \times 10^{23}} \text{ J}$

Let, the wavelength of the photon required to break one Cl — Cl bond be  $\lambda$ .

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

$$= \frac{6.6 \times 10^{-34} \times 3 \times 10^8 \times 6.023 \times 10^{23}}{243 \times 10^3}$$

$$= 4.91 \times 10^{-7} \text{ m}$$

7  $E_1 = 24 \text{ eV}$ ,  $E_2 = 50 \text{ eV}$

$$E_1 = \frac{hc}{\lambda_1} \text{ and } E_2 = \frac{hc}{\lambda_2}$$

$$\text{or } \frac{E_1}{E_2} = \frac{\lambda_2}{\lambda_1} \text{ or } \frac{25}{50} = \frac{\lambda_2}{\lambda_1} \text{ or } \lambda_1 = 2\lambda_2$$

8 Given, Planck's constant,

$$h = 6.63 \times 10^{-34} \text{ Js}$$

$$\text{Speed of light, } c = 3 \times 10^{17} \text{ nm s}^{-1}$$

Frequency of quantum light

$$\nu = 6 \times 10^{15} \text{ s}^{-1}$$

Wavelength,  $\lambda = ?$

$$\text{We know that, } \nu = \frac{c}{\lambda}$$

$$\text{or } \lambda = \frac{c}{\nu} = \frac{3 \times 10^{17}}{6 \times 10^{15}}$$

$$= 0.5 \times 10^2 \text{ nm} = 50 \text{ nm}$$

9 Energy of photon,

$$E = \frac{hc}{\lambda} = \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{1.5 \times 10^{-10}}$$

$$= 1.32 \times 10^{-15} \text{ J}$$

Energy of ejected electron,

$$E = \frac{1}{2} m v^2 = \frac{1}{2} \times 9.1 \times 10^{-31} \times (1.5 \times 10^7)^2$$

$$= 1.024 \times 10^{-16}$$

Total energy of photon

= binding energy of electron + energy of ejected electron  $1.32 \times 10^{-15}$

$$= \text{binding energy} + 1.024 \times 10^{-16}$$

$\therefore$  Binding energy

$$= (1.32 \times 10^{-15}) - (1.024 \times 10^{-16})$$

$$= 1.2176 \times 10^{-15} \text{ J} = \frac{1.2176 \times 10^{-15}}{1.6 \times 10^{-19}} \text{ eV}$$

$$= 7.6 \times 10^3 \text{ eV}$$

10  $\nu = \frac{c}{\lambda} = \frac{3 \times 10^{10} \text{ cm s}^{-1}}{5.5 \times 10^{-8} \text{ cm}} = 5.5 \times 10^{17} \text{ s}^{-1}$

$$\text{Further, } \frac{1}{2} m u^2 = h(\nu - \nu_0)$$

$$= 6.6 \times 10^{-27} (5.5 \times 10^{17} \text{ s}^{-1} - 3.62 \times 10^{12} \text{ s}^{-1})$$

11  $I \propto n^2 / Z$  where,  $n$  = number of orbit

$Z$  = atomic number

$$\therefore r_1 \propto n_1^2$$

$$r_2 \propto n_2^2 \text{ (} Z = 1 \text{ for H-atom)}$$

$$\text{So, } \frac{r_1}{r_2} = \frac{n_1^2}{n_2^2} \Rightarrow \frac{0.530}{r_2} = \frac{1^2}{2^2}$$

$$\therefore r_2 = 0.530 \times 4 = 2.120 \text{ \AA}$$

12 From Rydberg's equation,

$$\bar{\nu} = \frac{1}{\lambda} = R Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \Rightarrow \frac{1}{\lambda} \propto Z^2$$

$$\therefore \frac{\lambda(\text{He}^+)}{\lambda(\text{H})} = \frac{Z^2(\text{H})}{Z^2(\text{He}^+)} \frac{\lambda(\text{He}^+)}{912} = \frac{1}{4}$$

$$\text{or } \lambda(\text{He}^+) = \frac{91.2}{4} = 22.8 \text{ nm}$$

13  $\frac{1}{\lambda} = R \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$ ,

$$\frac{1}{\lambda} = 1.097 \times 10^7 \text{ m}^{-1} \left[ \frac{1}{1^2} - \frac{1}{\infty^2} \right]$$

$$\lambda = 91 \times 10^{-9} = 91 \text{ nm}$$

14  $\lambda = \frac{h}{\sqrt{2mKE}} = \frac{6.626 \times 10^{-34}}{\sqrt{2 \times 1 \times 0.5}}$   
 $= 6.626 \times 10^{-34} \text{ m}$

15 (A) According to Bohr, among the infinite number of possible circular orbitals, an electron can revolve only in those orbitals whose angular momentum ( $mvr$ ) is an integral multiple of the factor  $\frac{h}{2\pi}$ , i.e.  $mvr = \frac{nh}{2\pi}$

This equation is known as Bohr's equation.

(B)  $\lambda = \frac{h}{p}$  is known as de-Broglie equation.

(C) Total energy of an electron,

$$E = \text{KE} + \text{PE} = \frac{e^2}{2r} + \left( \frac{-e^2}{r} \right) = -\frac{e^2}{2r}$$

(D) In infrared region, Paschen series of lines is obtained.

$$16 \quad \Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$$

$$\Delta x = \frac{6.63 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 300} \\ \times 0.001 \times 10^{-2} \\ = 0.01933 = 1.93 \times 10^{-2} \text{ m}$$

$$17 \quad \text{Given, } \Delta p = 1 \times 10^{-18} \text{ g cm s}^{-1} \\ (\text{uncertainty in momentum})$$

$$\text{Mass} = 9 \times 10^{-28} \text{ g}$$

$$\Delta p = m \Delta v$$

$$1 \times 10^{-18} = 9 \times 10^{-28} \times \Delta v$$

(uncertainty in velocity)

$$\Delta v = 1 \times 10^9 \text{ cm s}^{-1}$$

18 The probability of the electron being in an infinitesimal region  $dV$  at a distance  $r$  is given as Probability  $= \psi^2 dV$

$\therefore$  1st orbital is spherically symmetrical

$$\therefore V = \frac{4}{3} \pi r^3 \text{ or } dV = 4\pi r^2 dr$$

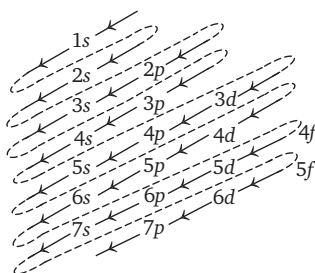
$$\therefore \text{Probability} = \psi^2 \cdot 4\pi r^2 dr$$

$$19 \quad \text{Gd}_{64} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}$$

$$4s^2 4p^6 4d^{10} 4f^7, 5s^2 5p^6 5d^1, 6s^2$$

$$\text{or } [\text{Xe}] 4f^7, 5d^1, 6s^2$$

20 The sequence of energy level can be remembered by the systematic diagram as shown below.



Hence, the correct order is

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

$$21 \quad {}_{29}\text{Cu} = [\text{Ar}]^{18} 3d^{10} 4s^1$$

All electrons are paired except  $4s^1$ . Hence,  $14e^-$  have spin in one direction and  $15e^-$  in the other direction.

22 According to Pauli's exclusion principle "no two electrons in an atom can have the same values of all the four quantum numbers."

In  $1s^2$ ,

for I electron  $n = 1, l = 0, m = 0, s = +\frac{1}{2}$

for II electron  $n = 1, l = 0, m = 0, s = -\frac{1}{2}$

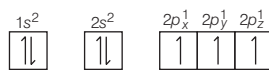
It means if the values of  $n, l$ , and  $m$  are same, then the value of spin quantum number must be different, i.e.  $+1/2$  and  $-1/2$ .

$$23 \quad E = nh\nu \quad E = \frac{nhc}{\lambda}$$

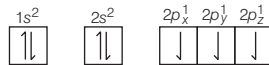
$$n = \frac{E\lambda}{hc} = \frac{10^{-16} \times 550 \times 10^{-9}}{6.6 \times 10^{-34} \times 3 \times 10^8}$$

$$= 277.77 \approx 278$$

24 According to Hund's rule "the pairing of electrons in the orbitals of a particular subshell does not take place until all the orbitals of a subshell are singly occupied. Moreover, the singly orbitals must have the electrons with parallel spin. i.e.



or



$\therefore$  Option (a) is the incorrect option.

25 The orbital of the electron having  $n = 3, l = 1$  and  $m = 1$  is  $3p_z$  (as  $nl_m$ ) and an orbital can have a maximum of two electrons with opposite spins,

$\therefore 3p_z$  orbital contains only two electrons or only 2 electrons are associated with  $n = 3, l = 1, m = -1$

26  $n$  represents the main energy level and  $l$  represents the subshell.

If  $n = 4$  and  $l = 3$ , the subshell is  $4f$ .

In  $f$  subshell, there are 7 orbitals and each orbital can accommodate a maximum of two electrons, so, maximum number of electrons in  $4f$ -subshell  $= 7 \times 2 = 14$

$$27 \quad {}_{37}\text{Rb} = {}_{36}[\text{Kr}] 5s^1$$

Its valence electron is  $5s^1$

So,  $n = 5, l = 0$  (for  $s$ -orbital)

$$m = 0 \text{ (As } m = -l \text{ to } 0 \text{ to } +l) \quad s = +\frac{1}{2}$$

28 According to the rules for quantum number the possible values of  $n, l, m$  and  $s$  are

$n = 1$  to  $\infty$ , any whole number,

$l = 0$  to  $(n-1)$  for every value of  $n$ .

$m = -l$  to  $0$  to  $+l$ , for every value of  $l$ ,

$$\text{and } s = \frac{1}{2} \text{ or } -\frac{1}{2}$$

$$(a) \quad n = 4, l = 3, m = 0$$

All the values are according to rules.

$$(b) \quad n = 4, l = 2, m = 1$$

All the values are according to rules.

$$(c) \quad n = 4, l = 4, m = 1$$

$\therefore$  The value of  $l$  can have maximum  $(n-1)$  value, i.e. 3 in this case.

$\therefore$  This set of quantum numbers is non-permissible.

$$(d) \quad n = 4, l = 0, m = 0$$

All the values are according to rules.

$\therefore$  Choice (a), (b) and (d) are permissible.

29  $m = -1$  is not possible for  $s$ -orbital (e.g.  $l = 0$ )

$$30 \quad \text{Number of atomic orbitals in an orbit} \\ = n^2 = 4^2 = 16$$

31 Two electrons occupying the same orbital has equal spin but the directions of their spin are opposite. Hence, spin quantum number  $s$  (represented  $+1/2$  and  $-1/2$ ) distinguishes them.

32 Total values of electrons in a subshell  $= 2(2l+1)$ , where  $l$  varies from 0 to  $(n-1)$

$$\sum_{l=0}^{l=n-1} 2(2l+1) = \left[ \sum_{l=0}^{l=n-1} l + n \right]$$

$$= 2 \left[ 2 \left\{ \frac{n(n-1)}{2} \right\} + n \right] = 2n[n-1+1] = 2n^2$$

Thus, total number of electrons in a

$$\text{shell} = \sum_{l=0}^{l=n-1} 2(2l+1) = 2n^2$$

33 1.  $\text{Cr} = [\text{Ar}] = 3d^5 4s^1$  an exception of Aufbau principle.

2. For a given value of  $l$ ,  $m$  can have any value from  $-l$  to  $+l$ . So it can have negative value.

3. Ag is in copper group with  $d^{10}s^1$  configuration, i.e. 46 electrons are spin paired.

$$4. \quad \text{EC of K (19)} \\ = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$$

The valence electron is present in  $4s^1$ .

Hence, the value of principal quantum number ( $n$ ) is 4.

34 (i) According to Heisenberg's uncertainty principle, it is possible to measure simultaneously the position and momentum of a particle.

(ii) The number of protons and neutrons are not always equal, but number of protons are equal to the number of electrons.

(iv) The energy of  $1s$  and  $2s$ -orbitals are not equal according to Aufbau's principle as principle quantum numbers are 2 for  $2s$  and 1 for  $1s$ . Thus, energy of  $2s$  orbital is for more greater than  $1s$  orbital.

## SESSION 2

$$1 \quad \lambda_A = \frac{h}{m_A v_A} \text{ and } \lambda_B = \frac{h}{m_B v_B}$$

$$\frac{\lambda_A}{\lambda_B} = \frac{m_B v_B}{m_A v_A}$$

Here,  $m_B = 25\%$  of  $m_A = 0.25 m_A$

$v_B = 75\%$  of  $v_A = 0.75 v_A$

$$\therefore \frac{1}{\lambda_B} = \frac{0.25 m_A \times 0.75 v_A}{m_A \times v_A}$$

or  $\lambda_B = 5.33 \text{ \AA}$

2 All statements are correct.

3 ( $Z = 24$ ) =  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$   
For 19th electron (i.e.  $4s^1$ )

$$n = 4, l = 0, m = 0, s = +\frac{1}{2}$$

$$4 \quad E_1 - E_2 = 1312 \times Z^2 \left( \frac{1}{1^2} - \frac{1}{2^2} \right)$$

$$= 1312 \times Z^2 \left( \frac{3}{4} \right)$$

$$E_2 - E_3 = 1312 \times Z^2 \left( \frac{1}{2^2} - \frac{1}{3^2} \right)$$

$$= 1312 \times Z^2 \left( \frac{5}{36} \right)$$

From Eq. (i) and (ii), we get

$$\frac{E_1 - E_2}{E_2 - E_3} = \frac{3 \times 36}{4 \times 5} = \frac{27}{5}$$

5 Ionisation energy of H

$$= 2.18 \times 10^{-18} \text{ J atom}^{-1}$$

$$\therefore E_1 = (\text{energy of } 1s\text{-orbit of H-atom})$$

$$= 2.18 \times 10^{-18} \text{ J atom}^{-1}$$

$$\Rightarrow E_n = \frac{-2.18 \times 10^{-18}}{n^2} \text{ J atom}^{-1}$$

( $\because Z = 1$  for H-atom)

Now,  $\Delta E = E_4 - E_1$

$$= \frac{-2.18 \times 10^{-18}}{4^2} - \frac{-2.18 \times 10^{-18}}{1^2}$$

$$= -2.18 \times 10^{-18} \times \left[ \frac{1}{4^2} - \frac{1}{1^2} \right]$$

$$= -2.18 \times 10^{-18} \times \left( -\frac{15}{16} \right)$$

$$= +2.0437 \times 10^{-18} \text{ J atom}^{-1}$$

$$v = \frac{\Delta E}{h} = \frac{2.0437 \times 10^{-18} \text{ J atom}^{-1}}{6.625 \times 10^{-34} \text{ Js}}$$

$$= 3.084 \times 10^{15} \text{ s}^{-1} \text{ atom}^{-1}$$

6 For Lyman series,

$$\frac{1}{\lambda} = R \left[ \frac{1}{1^2} - \frac{1}{n_2^2} \right] \Rightarrow \frac{15R}{16} = R \left[ \frac{1}{1^2} - \frac{1}{n_2^2} \right]$$

$$\frac{15R}{16R} = \left[ \frac{n_2^2 - 1}{n_2^2} \right]$$

$$\Rightarrow \frac{15}{16} = \frac{n_2^2 - 1}{n_2^2}$$

$$15n_2^2 = 16n_2^2 - 16$$

$$\Rightarrow n_2^2 = 16, n_2 = 4$$

7 We know,

$$E = -13.6 \cdot \frac{Z^2}{n^2} \text{ eV}$$

$$\text{So, ionisation energy} = \frac{13.6Z^2}{n^2} \text{ eV}$$

given,  $IE_M > IE_N$ , so,  $E_M < E_N$

that means  $Z_M > Z_N$

$$\text{Now, } r \propto \frac{n^2}{Z}$$

$$r_N > r_M$$

$$\text{Also, } \mu \propto \frac{Z}{n}$$

$$\therefore u_M > u_N$$

Thus, (c) is the correct option.

8 Energy order,  $n = 3 < n = 4$

$$l = 0 < l = 1 < l = 2$$

Therefore, the order is

$$e_3 > e_1 > e_2 > e_4.$$

9  $600 \text{ W} = 600 \text{ J s}^{-1}$  ( $1 \text{ W} = 1 \text{ J s}^{-1}$ )

i.e. Energy emitted per sec =  $600 \text{ J}$

$$\text{Energy of one photon, } E = h\nu = h \frac{c}{\lambda}$$

$$= \frac{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1}}{313.3 \times 10^{-9} \text{ m}}$$

$$= 6.344 \times 10^{-19} \text{ J}$$

$\therefore$  Photons emitted per sec

$$= \frac{600}{6.344 \times 10^{-19}}$$

$$= 1 \times 10^{21}$$

$$10 \quad \Delta v = \frac{0.006}{100} \times 500 \text{ ms}^{-1}$$

$$= 3 \times 10^{-2} \text{ ms}^{-1}$$

$$\Delta x \times m \Delta v = \frac{h}{4\pi}$$

$$\therefore \Delta x = \frac{h}{4\pi m \Delta v}$$

$$= \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.14 \times 9.1 \times 10^{31} \text{ kg} \times 3 \times 10^2 \text{ ms}^{-1}}$$

$$= 1.92 \times 10^{-3} \text{ m}$$

11 (a) According to de-Broglie's equation,

$$\text{Wavelength } (\lambda) = \frac{h}{mv}$$

Where,  $h$  = Planck's constant.

(b) According to Heisenberg uncertainty principle, the uncertainties of position ( $\Delta x$ ) and momentum ( $p = m\Delta v$ ) are related as

$$\Delta x \Delta p \geq \frac{h}{4\pi} \text{ or, } \Delta x \cdot m \Delta v \geq \frac{h}{4\pi}$$

$$\Delta x \cdot m \Delta a \cdot \Delta t \geq \frac{h}{4\pi}$$

$$\left[ \frac{\Delta v}{\Delta t} = \Delta a, a = \text{acceleration} \right]$$

$$\text{or } \Delta x \cdot F \Delta t \geq \frac{h}{4\pi} \quad [\because F = m \cdot \Delta a]$$

$$\text{or, } \Delta E \cdot \Delta t \geq \frac{h}{4\pi}$$

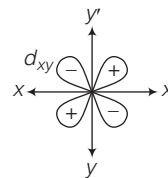
[ $\because \Delta E = F \cdot \Delta x$ ,  $E$  = energy]

Thus, statement (b) is correct.

(c) The half and fully filled orbitals have greater stability due to greater exchange energy, greater symmetry and more balanced arrangement. Thus, statement (c) is correct.

(d) For a single electronic species like H, energy depends on value of  $n$  and does not depend on  $l$ . Hence, energy of  $2s$ -orbital and  $2p$ -orbital is equal in case of hydrogen like species. Therefore, statement (d) is incorrect.

12 The lobes of  $d_{xy}$  orbital are oriented in between the axes at an angle  $45^\circ$  the probability of finding electron in a  $d_{xy}$  orbital is maximum at an angle of  $45^\circ$  from  $x$  and  $y$  axis.



13 Among the given species,  $39_{K^+}$  and  $40_{K^+}$  have same number of electrons, thus are isoelectronic. Also, they have different number of neutrons, means they differ in their atomic masses hence option (c) is the correct Answer.

14 Ti ( $Z = 22$ ) belongs to 1st series of d-block elements. It has two electrons in  $3d$ -subshell hence its correct electronic configuration is  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^2$ .