

02

Structure of Atom

Quick Revision

Nature of electromagnetic radiation and experimental results regarding atomic spectra play an important role in development of Bohr's model.

1. According to Maxwell's electromagnetic wave theory, energy is emitted continuously from any source in the form of radiations travelling in wave form and associated with electric and magnetic fields oscillating perpendicular to each other and to the direction of radiation.

Characteristics of a wave are

- (i) **Wavelength** (λ) Distance between any two consecutive crests or troughs and are expressed in Å, nm, pm or m.
- (ii) **Frequency** (ν) Number of waves passing through a point in one second. Units are Hertz or s^{-1} .
- (iii) **Velocity** (c) Distance travelled by the wave in one second. Units are ms^{-1} .

$$c = \nu \times \lambda \Rightarrow \lambda = c / \nu$$

- (iv) **Wave number** ($\bar{\nu}$) Reciprocal of wavelength.

$$\bar{\nu} = \frac{1}{\lambda}$$

It's commonly used unit is cm^{-1} (not SI unit).

2. Particle Nature of Electromagnetic Radiation : Planck's Quantum Theory

- The ideal body, which emits and absorbs radiations of all frequencies is called a **black body** and the radiation emitted by such a body is called **black body radiation**.

- According to **Planck's quantum theory**, the radiant energy which is emitted or absorbed in the atom of small discrete packets of energy known as **quantum** and in case of light, the quantum of energy is called **photons**.

$$E = h\nu \text{ or } E = h \frac{c}{\lambda}$$

where, h = Planck's constant = 6.63×10^{-34} Js

E = Energy of photon or quantum

- If n is the number of quanta of a particular frequency and E_T be the total energy, then

$$E_T = n h \nu$$

3. 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.
- For each metal, there is a characteristic minimum frequency, known as **threshold frequency** (ν_0) below, which photoelectric effect is not observed.
- The number of electrons ejected is proportional to the intensity or brightness of light.
- Following the conservation of energy principle, the **kinetic energy of ejected electron** is given by the equation,

$$h\nu = h\nu_0 + \frac{1}{2} m_e v^2$$

Dual Nature of Electromagnetic Radiation

Light possesses both particle and wave like properties.

Whenever radiation interacts with matter, it displays particle-like properties in contrast to the wave-like properties.

4. Atomic Spectra

- The pictorial representation of arrangement of various types of EMR in their increasing order of wavelength (or decreasing order of frequency) is known as spectrum.
- The spectrum of radiation emitted by a substance that has absorbed energy in increasing order of wavelengths or decreasing frequencies is called as an **emission spectrum**.
- An **absorption spectrum** is like the photographic negative of an emission spectrum.
- The **line spectra of hydrogen** lies in three regions of electromagnetic spectrum, i.e. infrared, visible and UV-region.
- The set of lines in the visible region is known as **Balmer series**.
- The general formula for wave number of lines of different series of hydrogen spectrum is

$$\bar{\nu} = 109677 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{cm}^{-1}$$

where, $n_1 = 1, 2 \dots n_2 = n_1 + 1, n_1 + 2 \dots$

- The value 109677 cm^{-1} is called the Rydberg constant.
- The first five series of lines that correspond to $n_1 = 1, 2, 3, 4, 5$ are known Lyman, Balmer, Paschen, Brackett and Pfund series respectively.

5. Bohr's Model

The main postulates of this model are as follows :

- Energy of an electron is quantised.
The orbits or stationary states of electron are numbered, $n = 1, 2, 3$ or $K, L, M \dots$.
These integral numbers are known as **principal quantum number**.
- The energy of an electron is certain in the orbit, i.e. it does not change with time.
- The difference in energy ΔE is given by,

$$\Delta E = h\nu$$

$$\Rightarrow \nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

where, E_1 and E_2 are the energies of the lower and higher allowed energy states respectively.

- The angular momentum (mvr) of an electron, in a given stationary states is given as

$$mvr = \frac{nh}{2\pi}$$

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

Significance of Bohr's Model

This model is useful to explain the following facts :

- (i) **Calculation of Bohr radius** According to Bohr's model, radius of n^{th} orbit is given by the expression,

$$r_n = \frac{52.9 n^2}{Z} \text{ pm}$$

$$= \frac{0.0529 n^2}{Z} \text{ nm}$$

where, Z is the nuclear charge.

- (ii) **Calculation of energy of the electron**

The energy of the electron in the n^{th} orbit has been found to be

$$E_n = -R_H \left(\frac{1}{n^2} \right) \quad (n = 1, 2, 3, \dots)$$

where, $R_H = \text{Rydberg constant} = \frac{2\pi^2 m e^4}{h^2}$

$$= 2.18 \times 10^{-18} \text{ J (for } n = 1)$$

For n^{th} orbit,

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

$Z =$ atomic number of an atom

$$E_n = - \frac{13.595 \text{ eV}}{n^2} Z^2 \text{ per atom}$$

$$\approx - \frac{13.6}{n^2} Z^2 \text{ eV atom}$$

$$= - \frac{1311.8}{n^2} Z^2 \text{ kJ mol}^{-1}$$

$$\approx - \frac{1312}{n^2} Z^2 \text{ kJ mol}^{-1}$$

- (iii) **Calculation of frequency and wave number for a transition** The energy gap between the two orbits is given by equation,

$$\Delta E = E_f - E_i$$

$$\bar{\nu} = R_H \frac{v}{c} = 109677 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \text{cm}^{-1}$$

where, n_i and n_f stands for initial orbit and final orbit.

For absorption spectrum, $n_f > n_i$.

For emission spectrum, $n_i > n_f$.

Limitations of Bohr's Model

It fails to account for the finer details of the hydrogen atom spectrum observed by using spectroscopic technique. It could not explain the ability of atoms to form molecules by chemical bonds.

6. Towards Quantum Mechanical Model of an Atom

- In view of shortcoming of the Bohr's model, two important developments, i.e. dual behaviour of matter and Heisenberg uncertainty principle came into existence.
- **de-Broglie** explains the dual nature of electron (i.e. wave nature as well as particle nature)

$$\text{Hypothesis to be given, } \lambda = \frac{h}{mv} = \frac{h}{p}$$

where, λ = wavelength, v = velocity of particle, m = mass of particle, p = momentum

- **Heisenberg's uncertainty principle** This principle is a result of dual nature of matter and radiation.

According to this principle, it is impossible to determine at any given instant, both the momentum and the position of subatomic particles, like electron, simultaneously.

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

- Heisenberg uncertainty principle rules out the existence of definite paths or trajectories of electrons and other similar particles.
- The effect of Heisenberg uncertainty principle is significant only for motion of microscopic objects and is negligible for that of macroscopic objects. This is because in dealing with milligram sized or heavier objects, the associated uncertainties are hardly of real consequence.

- In case of microscopic object like an electron, $\Delta v \cdot \Delta x$ obtained is much larger and such uncertainties are of real consequence.
- The precise statement of the position and momentum of electrons have to be replaced by the statements of probability that the electron has at a given position and momentum.

7. Quantum Mechanical Model of Atom

- The branch of science that takes into account this dual behaviour of matter is (i.e. wave nature as well as particle nature) called **quantum mechanics**.
- **Schrodinger** derived an equation for an electron which describes the wave motion of an electron along any three axes.

For a system (such as an atom or molecule whose energy does not change with time), the Schrodinger equation is written as $\hat{H}\psi = E\psi$.

where, \hat{H} is a mathematical operator called **Hamiltonian**.

- The important features of quantum mechanical model of atom are :
 - (i) The energy of electron in atoms is quantised.
 - (ii) Both the exact position and exact velocity of an electron in an atom cannot be determined simultaneously.
 - (iii) An atomic orbital is the wave function ψ for an electron in an atom.
 - (iv) The probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function $|\psi|^2$ at that point, which is known as probability density and is always positive.

From the value of $|\psi|^2$ at different points within an atom, it is possible to predict the region around the nucleus, where electron will most probably be found.

8. Atomic Orbitals and Quantum Numbers

The set of four numbers which give a complete information about energy, shape, orientation and also spin of electron in an atom, are called quantum numbers.

There are four types of quantum numbers:

(i) **Principal quantum number (n)** It determines the size and to a large extent the energy of the orbital. It is always a positive integer with value of $n = 1, 2, 3, \dots$

- The principal quantum number also identifies the **shell**.
- All the orbitals of a given value of 'n' constitute a single shell of atom and are represented by the following letters.

$$n = 1, 2, 3, 4, \dots$$

$$\text{Shell} = K L M N \dots$$

- The 'sub-shells' are the orientations and shapes for your orbitals going in order by s, p, d, f .
 - Number of sub-shells in a shell = shell number.
 - The first sub shells has 1 orbital. Each successive sub shell adds 2 more orbital (1, 3, 5, 7, etc.)
 - Each orbital can hold only 2 electrons of opposite spin.
- (ii) **Azimuthal quantum number (l)** It determines the angular momentum of the electron and is also known as orbital angular momentum or subsidiary quantum number.

For a given value of n , the possible values of l are $l = 0, 1, 2, \dots, (n - 1)$.

e.g. If $n = 1$, value of l is only 0.

Value of l	0	1	2	3	4	5
Subshell notation	s	p	d	f	g	h
Number of orbitals	1	3	5	7	9	11

Angular momentum of the electron in an orbital = $\sqrt{l(l+1)} \frac{h}{2\pi} = \sqrt{l(l+1)} \hbar$

It also tells about the shape of orbitals of a subshell.

Energy of subshells : $s < p < d < f$.

(iii) **Magnetic quantum number (m_l)** It shows the behaviour of electron in a magnetic field. For a given value of l (subshell), $2l + 1$ possible values for m_l are given by

$$m_l = -l, -(l-1), -(l-2) \dots 0, \dots (l-2), (l-1), l$$

(iv) **Spin quantum number (s)** It tells about the spinning motion of the electron, i.e. clockwise or anti-clockwise.

For a given value of m ,

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

It helps to explain magnetic properties of the substances.

$$\text{Spin angular momentum} = \sqrt{s(s+1)} \frac{h}{2\pi}$$

- Number of subshells in n^{th} shell = n
- Number of orbitals in a subshell = $2l + 1$,
- Maximum number of electrons in a subshell = $2(2l + 1)$
- Number of orbitals in n^{th} shell = n^2
- Maximum number of electrons in n^{th} shell = $2n^2$.

9. Node and Nodal Plane

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

- (i) $(n - l - 1)$ = radial nodes
- (ii) l = angular or planar nodes
- (iii) $(n - 1)$ = total nodes

10. Shape of Atomic Orbitals

- **s-orbitals** Spherical with node.
- **p-orbitals** Dumb-bell in shape.
- **d-orbitals** Four d -orbitals have clover leaf shape with four lobes.

Three orbitals have lobes between the axis and are called d_{xy}, d_{yz}, d_{xz} .

Fourth has lobes along the axis and is called $d_{x^2-y^2}$.

Fifth has doughnut shape, where electron cloud is present at the centre and is called d_{z^2} .

11. Energies of Orbitals

The lower the value of $(n + l)$ for an orbital, the lower is its energy. If two orbitals have the same value of $(n + l)$, the orbital with lower value of n will have the lower energy.

12. Rules for Filling of Electrons in Orbitals

Filling of electrons into the orbitals of different atoms takes place according to the following discussed rules.

- (i) **Aufbau principle** In the ground state of the atoms, the orbitals are filled in order of their increasing energies.
 $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s,$
 $4f, 5d, 6p, 7s.$
- (ii) **Pauli's exclusion principle** No two electrons in an atom can have the same set of four quantum numbers.
 It can also be stated as, "only two electrons may exist in the same orbital and these electrons must have opposite spin". The maximum number of electrons in the shell with principal quantum number n is equal to $2n^2$.
- (iii) **Hund's rule** of maximum multiplicity states that "pairing of electrons in the orbitals belonging to the same subshell (p, d or f) does not take place until each orbital belonging to that subshell has got one electron each, i.e. it is singly occupied."
13. **Stability of Half-filled and Completely Filled Orbital**
- The ground state electric configuration of atom corresponds to lowest energy state and gives higher stability.
 - The electronic configuration of most of the atoms follows the basic rules. However, certain elements such as Cr or Cu do not follow the rules.
 - The extra stability of half-filled and fully-filled electronic configuration can be explained in terms of symmetry and exchange energy with the help of Hund's rule.
14. **Electronic Configuration of Elements**
- The arrangement of electrons in various shells, sub-shells and orbitals in an atom is termed as electronic configuration.
 - It is written in term of nl^x , where, n indicates the order of shell, l indicates the subshell and x indicates the number of electrons present in the sub-shell.

Objective Questions

Multiple Choose Questions

1. The value of Planck's constant is 6.63×10^{-34} Js. The speed of light is 3×10^{17} nm s⁻¹.
 Which value is closest to the wavelength (in nm) of a quantum of light with frequency of 6×10^{15} s⁻¹?
- (a) 10 (b) 25
 (c) 50 (d) 75
2. Calculate the energy in joule corresponding to light of wavelength 45 nm (Planck's constant, $h = 6.63 \times 10^{-34}$ Js; speed of light, $c = 3 \times 10^8$ nm s⁻¹).
- (a) 6.67×10^{15} (b) 6.67×10^{11}
 (c) 4.42×10^{15} (d) 4.42×10^{-18}
3. The ratio of the shortest wavelength of two spectral series of hydrogen spectrum is found to be about 9.

The spectral series are

- (a) Lyman and Paschen
 (b) Brackett and Pfund
 (c) Paschen and Pfund
 (d) Balmer and Brackett
4. Which of the following series of transitions in the spectrum of hydrogen atom fall in visible region?
- (a) Balmer series
 (b) Paschen series
 (c) Brackett series
 (d) Lyman series
5. Which transition in the hydrogen atomic spectrum will have the same wavelength as the Balmer transition (i.e. $n = 4$ to $n = 2$) of He⁺ spectrum?
- (a) $n = 4$ to $n = 3$ (b) $n = 3$ to $n = 2$
 (c) $n = 4$ to $n = 2$ (d) $n = 2$ to $n = 1$

6. What is the wave number of 4th line in Balmer series of hydrogen spectrum? ($R = 1,09,677 \text{ cm}^{-1}$)
- (a) $24,630 \text{ cm}^{-1}$ (b) $24,360 \text{ cm}^{-1}$
 (c) $24,730 \text{ cm}^{-1}$ (d) $24,372 \text{ cm}^{-1}$
7. The wavelength (in Å) of an emission line obtained for Li^{2+} during an electronic transition from $n_2 = 2$ to $n_1 = 1$ is ($R = \text{Rydberg constant}$)
- (a) $\frac{3R}{4}$ (b) $\frac{27R}{4}$
 (c) $\frac{4}{3R}$ (d) $\frac{4}{27R}$
8. Bohr's model can explain
- (a) the solar spectrum
 (b) the spectrum of hydrogen molecule
 (c) spectrum of any atom or ion containing one electron only
 (d) the spectrum of hydrogen atom only
9. The expression for Bohr's frequency rule is
- (a) $\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$
 (b) $\nu = \Delta E \cdot h = E_2 - E_1 \cdot h$
 (c) $\frac{\nu}{h} = \Delta E + h = (E_2 - E_1) + h$
 (d) $\nu = \frac{\Delta E}{h} = \frac{E_1 - E_2}{2}$
10. An electron can move only in those orbits for which its angular momentum is integral multiple of
- (a) $\frac{h}{4\pi}$ (b) $\frac{h}{2\pi}$ (c) $\frac{h}{\sqrt{2\pi}}$ (d) $h \cdot 2\pi$
11. For which of the following species, Bohr's theory is not applicable?
- (a) Be^{3+} (b) Li^{2+}
 (c) He^{2+} (d) H
12. Bohr radius for the hydrogen atom ($n = 1$) is approximately 0.530 \AA . The radius for the first excited state ($n = 2$) is (in Å)
- (a) 0.13 (b) 1.06 (c) 4.77 (d) 2.12
13. The wavelength of the radiation emitted, when in a hydrogen atom electron falls from infinity to stationary state 1, would be
- (Rydberg constant = $1.097 \times 10^7 \text{ m}^{-1}$)
- (a) 91 nm (b) 192 nm
 (c) 406 nm (d) $9.1 \times 10^{-6} \text{ nm}$
14. What is the energy (in eV) required to excite the electron from $n = 1$ to $n = 2$ state in hydrogen atom ? ($n = \text{principal quantum number}$)
- (a) 13.6 (b) 3.4
 (c) 17.0 (d) 10.2
15. The energy of second Bohr orbit of the hydrogen atom is -328 kJ mol^{-1} ; hence the energy of fourth Bohr orbit would be
- (a) -41 kJ mol^{-1}
 (b) $-1312 \text{ kJ mol}^{-1}$
 (c) -164 kJ mol^{-1}
 (d) -82 kJ mol^{-1}
16. Limitations of Bohr's model is/are
- (a) it fails to account for the finer details of the hydrogen atom spectrum observed by using sophisticated spectroscopic techniques
 (b) it is unable to explain the spectrum of atoms other than hydrogen
 (c) it is unable to explain the ability of atoms to form molecules by chemical bonds
 (d) All of the above
17. Relation between wavelength (λ) and momentum (P) of a material particle is
- (a) $\lambda = hP$ (b) $\lambda = h/P$
 (c) $\lambda = h + P$ (d) $\lambda = h - P$
18. If travelling at same speeds, which of the following matter waves have the shortest wavelength? (NCERT Exemplar)
- (a) Electron
 (b) Alpha particle (He^{2+})
 (c) Neutron
 (d) Proton

19. The momentum of a particle having a de-Broglie wavelength of 10^{-17} m is

(Given, $h = 6.625 \times 10^{-34}$ m)

- (a) 3.3125×10^{-7} kg m s⁻¹
- (b) 26.5×10^{-7} kg m s⁻¹
- (c) 6.625×10^{-17} kg m s⁻¹
- (d) 13.25×10^{-17} kg m s⁻¹

20. If E_e , E_α and E_p represent the kinetic energies of an electron, α -particle and a proton respectively, each moving with same de-Broglie wavelength then

- (a) $E_e = E_\alpha = E_p$
- (b) $E_e > E_\alpha > E_p$
- (c) $E_\alpha > E_p > E_e$
- (d) $E_e > E_p > E_\alpha$

21. As per de-Broglie's formula a macroscopic particle of mass 100 g and moving a velocity of 100 cm s⁻¹ will have a wavelength of

- (a) 6.6×10^{-29} cm
- (b) 6.6×10^{-30} cm
- (c) 6.6×10^{-31} cm
- (d) 6.6×10^{-32} cm

22. A body of mass x kg is moving with a velocity of 100 m s⁻¹. Its de-Broglie wavelength is 6.62×10^{-35} m. Hence, x is ($h = 6.62 \times 10^{-34}$ Js)

- (a) 0.25 kg
- (b) 0.15 kg
- (c) 0.2 kg
- (d) 0.1 kg

23. The wavelengths of electron waves in two orbits is 3 : 5. The ratio of kinetic energy of electrons will be

- (a) 25 : 9
- (b) 5 : 3
- (c) 9 : 25
- (d) 3 : 5

24. Which of the following statements is not correct regarding Bohr's model of hydrogen atom?

- (a) Energy of the electrons in the orbit is quantised
- (b) The electron in the orbit nearest to the nucleus has the lowest energy
- (c) Electrons revolve in different orbits around the nucleus

(d) The position and velocity of the electrons in the orbit cannot be determined simultaneously

25. Which of the following does not represent the mathematical expression for the Heisenberg uncertainty principle?

- (a) $\Delta x \cdot \Delta p \geq h/(4\pi)$
- (b) $\Delta x \cdot \Delta v \geq h/(4\pi m)$
- (c) $\Delta E \cdot \Delta t \geq h/(4\pi)$
- (d) $\Delta E \cdot \Delta x \geq h/(4\pi)$

26. In 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 m² s⁻¹, mass of electron, $e_m = 6.6 \times 10^{-31}$ kg)

- (a) 1.52×10^{-4} m
- (b) 5.10×10^{-3} m
- (c) 1.92×10^{-3} m
- (d) 3.84×10^{-3} m

27. Uncertainty in the position of an electron (mass = 9.1×10^{-31} kg) moving with a velocity 300 ms⁻¹, accurate upon 0.001% will be

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

- (a) 19.2×10^{-2} m
- (b) 5.76×10^{-2} m
- (c) 1.93×10^{-2} m
- (d) 3.84×10^{-2} m

28. The uncertainties in the velocities of two particles A and B are 0.05 and 0.02 ms⁻¹ respectively. The mass of B is five times to that of mass A. What is

the ratio of uncertainties $\left(\frac{\Delta x_A}{\Delta x_B} \right)$ in

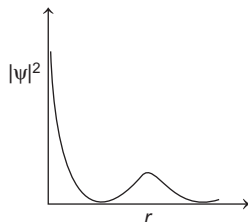
their positions?

- (a) 2
- (b) 0.25
- (c) 4
- (d) 1

29. In the Schrodinger equation, \hat{H} is

- (a) a mathematical operator called Hamiltonian operator
- (b) introduced by Schrodinger from the expression for the total energy of the system
- (c) Both (a) and (b)
- (d) None of the above

- 30 The graph between $|\psi|^2$ and r (radial distance) is shown below. This represents



- (a) 1s-orbital (b) 2p-orbital
(c) 3s-orbital (d) 2s-orbital
31. Principal, azimuthal and magnetic quantum numbers are respectively related to
(a) size, orientation and shape
(b) size, shape and orientation
(c) shape, size and orientation
(d) None of the above
32. The angular momentum of electrons in d orbital is equal to
(a) $\sqrt{6} \hbar$ (b) $\sqrt{2} \hbar$
(c) $2\sqrt{3} \hbar$ (d) $0 \hbar$
33. The value of azimuthal quantum number (l) is 2 then the value of principal quantum number (n) is
(a) 2 (b) 3
(c) 4 (d) 5
34. If azimuthal quantum number, $l = 0$ shape of orbital would be
(a) spherical
(b) dumbbell
(c) complex
(d) double dumbbell
35. For $n = 2$, the correct set of azimuthal and magnetic quantum numbers are
(a) $l = 2; m = -2, -1, 0, +1, +2$
(b) $l = 1; m = -2, -1, 0, +1, +2$
(c) $l = 0; m = -1, 0, +1$
(d) $l = 1; m = -1, 0, +1$

36. Orbital angular momentum depends on

(a) l (b) n and l
(c) n and m (d) m and s

37. Two electrons occupying the same orbital are distinguished by

(a) magnetic quantum number
(b) azimuthal quantum number
(c) spin quantum number
(d) principal quantum number

38. Match the quantum numbers given in Column I with the information provided by these given in Column II.

Column I (Quantum number)	Column II (Information provided)
A. Principal quantum number	1. Orientation of the orbital
B. Azimuthal quantum number	2. Energy and size of orbital
C. Magnetic quantum number	3. Spin of electron
D. Spin quantum number	4. Shape of the orbital

Codes

A B C D
(a) 2 4 1 3
(c) 2 4 3 1

(NCERT Exemplar)

A B C D
(b) 3 2 4 1
(d) 1 2 3 4

39. The number of orbitals associated with quantum numbers $n = 5, m_s = +\frac{1}{2}$ is

(a) 25 (b) 50 (c) 15 (d) 11

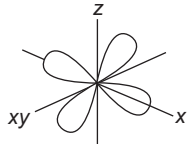
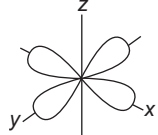
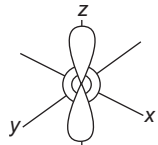
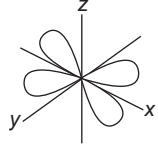
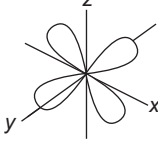
40. The number of radial nodes for $3p$ -orbital is.....

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

41. Total number of orbitals associated with third shell will be

(a) 2 (b) 4
(c) 9 (d) 3

42. Match the Column I with Column II and choose the correct options from the codes given below :

	Column I (Boundary surface diagram)	Column II (<i>d</i> -orbital)
A.		1. d_{z^2}
B.		2. d_{xy}
C.		3. d_{xz}
D.		4. $d_{x^2 - y^2}$
E.		5. d_{yz}

Codes

	A	B	C	D	E		A	B	C	D	E
(a)	4	5	2	1	3	(b)	3	4	5	2	1
(c)	5	3	1	4	2	(d)	5	4	1	2	3

43. The correct order of increasing energy of atomic orbitals is

- (a) $5p < 4f < 6s < 5d$
 (b) $5p < 6s < 4f < 5d$
 (c) $4f < 5p < 5d < 6s$
 (d) $5p < 5d < 4f < 6s$

44. Aufbau principle does not give the correct arrangement of filling up of the atomic orbitals in

- (a) Cu and Zn (b) Co and Zn
 (c) Mn and Cr (d) Cu and Cr

45. The representation of the ground state electronic configuration of He by box – diagram as $\boxed{\uparrow\uparrow}$ is wrong because it violates

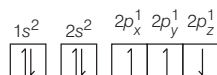
- (a) Heisenberg's uncertainty principle
 (b) Bohr's quantisation theory of angular momenta
 (c) Pauli exclusion principle
 (d) Hund's rule

46. Nitrogen has the electronic configuration $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$ and not $1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^0$ which is determined by

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

47. Which one is a wrong statement?

- (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

48. The correct distribution of four electrons in *p*-orbital would be

- (a) $\boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow}$ (b) $\boxed{\uparrow\downarrow} \boxed{\uparrow} \boxed{\uparrow}$
 (c) $\boxed{\uparrow} \boxed{\uparrow\downarrow} \boxed{\uparrow}$ (d) $\boxed{\uparrow} \boxed{\uparrow} \boxed{\uparrow\downarrow}$

49. Match the following rules given in Column I with their correct statements given in Column II.

Column I (Rules)	Column II (Statements)
A. Hund's rule	1. No two electrons in an atom can have the same set of four quantum numbers.
B. Aufbau principle	2. Half-filled and completely filled orbitals have extra stability.
C. Pauli exclusion principle	3. Pairing of electrons in the orbitals belonging to the same subshell does not take place until each orbital is singly occupied.
D. Heisenberg's uncertainty principle	4. It is impossible to determine the exact position and exact momentum of a subatomic particle simultaneously.
	5. In the ground state of atoms, orbitals are filled in the order of their increasing energies.

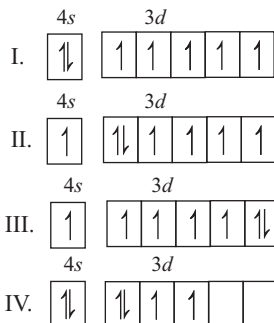
Codes

- A B C D
 (a) 3 5 1 4
 (b) 1 2 3 4
 (c) 2 1 3 4
 (d) 1 2 4 3

50. Which one of the following is the wrong statement?

- (a) de-Broglie's wavelength is given by $\lambda = \frac{h}{mv}$, where, m = mass of the particle
 v = group velocity of the particle
 (b) The uncertainty principle is $\Delta E \times \Delta t \geq h/4\pi$
 (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

51. Out of the following electronic arrangements for outer electronic configuration.



The most stable arrangement is

- (a) I (b) II (c) III (d) IV

52. 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) $5, 1, 0, +\frac{1}{2}$

53. The number of d -electrons in Fe^{2+} ($Z = 26$) is not equal to the number of electrons in which one of the following?

- (a) s -electrons in Mg ($Z = 12$)
 (b) p -electrons in Cl ($Z = 17$)
 (c) d -electrons in Fe ($Z = 26$)
 (d) p -electrons in Ne ($Z = 10$)

54. Which of the following ion shows maximum unpaired electrons ?

- (a) Fe^{3+} (b) CO^{3+} (c) Ni^{2+} (d) Cu^{2+}

55. Match species given in Column I with the electronic configuration given in Column II.

Column I	Column II
A. Cr	1. $[\text{Ar}]3d^8 4s^0$
B. Fe^{2+}	2. $[\text{Ar}]3d^{10} 4s^1$
C. Ni^{2+}	3. $[\text{Ar}]3d^6 4s^0$
D. Cu	4. $[\text{Ar}]3d^5 4s^1$
	5. $[\text{Ar}]3d^6 4s^2$

(NCERT Exemplar)

Codes

A	B	C	D	A	B	C	D
(a) 4	3	1	2	(b) 1	2	4	3
(c) 2	1	3	4	(d) 1	2	4	3

56. Match the following species given in Column I with their corresponding ground state electronic configuration given in Column II.

Column I (Atom / Ion)	Column II (Electronic configuration)
A. Cu	1. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$
B. Cu^{2+}	2. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$
C. Zn^{2+}	3. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
D. Cr^{3+}	4. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$
	5. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

Codes

A	B	C	D	A	B	C	D
(a) 2	1	3	4	(b) 3	4	1	5
(c) 1	2	4	3	(d) 5	2	3	4

Assertion-Reasoning MCQs

Directions In the following questions (Q.No. 57-71) a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices.

- (a) Both Assertion and Reason are correct statements and Reason is the correct explanation of the Assertion.
 (b) Both Assertion and Reason are correct statements, but Reason is not the correct explanation of the Assertion.
 (c) Assertion is correct, but Reason is incorrect statement.
 (d) Assertion is incorrect but Reason is correct statement.

57. **Assertion** de-Broglie equation has significance for any microscopic particles.

Reason de-Broglie wavelength is inversely proportional to the mass of the object.

58. **Assertion** The radius of the first orbit of hydrogen atom is 0.529 \AA .

Reason Radius for each circular orbit is $(r_n) = 0.529 \text{ \AA} (n^2 / Z)$, where $n = 1, 2, 3$ and $Z =$ atomic number.

59. **Assertion** Energies of the orbitals in hydrogen or hydrogen like species depend only on the quantum number ' n '.

Reason Energies of the orbitals in multi-electron atoms depend on quantum numbers ' n ' and ' l '.

60. **Assertion** It is impossible to determine the exact position and exact momentum of an electron simultaneously.

Reason The path of an electron in an atom is clearly defined.

61. **Assertion** Energy of the orbital increases with increase of principal quantum number.

Reason Energy is required in shifting away the negatively charged electron from the positively charged nucleus.

62. **Assertion** Spin quantum number can have the value $+1/2$ or $-1/2$.

Reason Here, (+) or (-) sign signifies the wave function.

63. **Assertion** Magnetic quantum number can have the value $m_l = -l, \dots, 0, \dots, l$.

Reason Magnetic quantum number specifies the shape of orbitals.

64. **Assertion** For a given principal quantum number, s, p, d, f, \dots , subshells, all have different energies.

Reason Mutual repulsion exists among the electrons in a multi-electron atoms.

65. **Assertion** Half-filled and fully-filled degenerate set of orbitals acquire extra stability.

Reason The reason for the above fact is the symmetry of such orbitals.

66. Assertion s -orbital electron will be more tightly bound to the nucleus than p -orbital electron.

Reason Z_{eff} experienced by the electron decreases with increase of azimuthal quantum number (l).

67. Assertion Shapes of the orbitals are represented by boundary surface diagrams of constant probability density.

Reason Boundary surface diagram helps in interpreting and visualising an atomic orbitals.

68. Assertion $5s$ -orbital has greater energy than $4s$.

Reason Energy of the orbital depends on the azimuthal quantum number.

69. Assertion Atomic orbital in an atom is designated by n , l , m_l and m_s .

Reason These play no role in designating electron present in an orbital.

70. Assertion In case of isoelectronic ions the ionic size increases with the increase in atomic number.

Reason The greater the attraction of nucleus, greater is the ionic radius.

71. Assertion Total number of electrons in a subshell is designated by $(2l + 1)$, where, l = azimuthal quantum number.

Reason l can have value $1, 2, \dots, n - 1$, where, n is principal quantum number.

Case Based MCQs

72. Read the passage given below and answer the following questions :

A total of four quantum numbers are used to describe completely the movement and trajectories of each electron within an

atom. Each electron in an atom has a unique set of quantum numbers; according to the Pauli Exclusion principle, no two electrons can share the same combination of four quantum numbers. Quantum numbers are important because they can be used to determine the electron configuration of an atom and the probable location of the atom's electrons.

In atoms, there are a total of four quantum numbers; the principal quantum number (n), the orbital angular momentum quantum number (l), the magnetic quantum number (m_l), and the electron spin quantum number (m_s). The principal quantum number, (n), describes the energy of an electron and the most probable distance of the electron from the nucleus.

In other words, it refers to the size of the orbital and the energy level an electron is placed.

The number of subshells, or l , describes the shape of the orbital. It can also be used to determine the number of angular nodes. The magnetic quantum number, (m_l) describes the energy levels in a subshell, and (m_s) refers to the spin on the electron, which can either be up or down. The value of the principal quantum number n is the level of the principal electronic shell (principal level). All orbitals that have the same n value are in the same principal level.

The size of the atom and its atomic radius increases. Because the atomic radius increases, the electrons are farther from the nucleus. Thus, it is easier for the atom to expel an electron because the nucleus does not have as strong a pull on it, and the ionisation energy decreases. We can designate a principal quantum number, n , and a certain subshell by combining the value of n and the name of the subshell (which can be found using (l).

The s -orbital, because the value of m_l can only be 0, can only exist in one plane. The

p-orbital, however, has three possible orientations because the value of m_l and so it has three possible orientations of the orbitals, shown by p_x , p_y and p_z . The pattern continues, with the *d*-orbital containing 5 possible orbital orientations, and *f* has 7.

In these questions (i-iv) a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices :

- (a) Assertion and Reason both are correct statements and Reason is correct explanation for Assertion.
- (b) Assertion and Reason both are correct statements but Reason is not correct explanation for Assertion.
- (c) Assertion is correct statement but Reason is incorrect statement.
- (d) Assertion is incorrect statement but Reason is correct statement.

(i) **Assertion** Only principal quantum number determines the energy of an electron in an orbital in sodium atoms.

Reason For one electron system, the expression of energy is same as that obtained in Bohr's theory.

(ii) **Assertion** *s*-orbital electron will be more tightly bound to the nucleus than *p*-orbital electron.

Reason Z_{eff} experienced by the electron decreases with increase of azimuthal quantum number (l).

(iii) **Assertion** Orbit and orbital are not synonymous.

Reason Orbital represents the circular path along which the electron moves but orbit represents the three dimensional space around the nucleus where probability of finding the electron is maximum.

(iv) **Assertion** Energy of electron is largely determined by its principal quantum number.

Reason Principal quantum number is a measure of the most probable distance of finding the electron around the nucleus.

Or

Assertion The clockwise or anti-clockwise motion/movement of e^- can be determined with the help of spin quantum number.

Reason Spin quantum number depends on the value of principal quantum number.

73. Read the passage given below and answer the following questions :

In other words, kinetic energy of the ejected electron is proportional to the frequency of the electromagnetic radiation.

Since, the energy of striking photon is $h\nu$ and the minimum energy required to eject the electron is $h\nu_0$ (also called **work function**, W_0) then the difference in energy ($h\nu - h\nu_0$) is transferred as the kinetic energy of the photoelectron.

Following the law of conservation of energy principle, the kinetic energy of the ejected electron is given by the equation,

$$h\nu = h\nu_0 + \frac{1}{2} m_e v^2$$

where, m_e is the mass of the electron moving with velocity (v).

The following questions (i-iv) are multiple choice questions. Choose the most appropriate answer :

- (i) The work function of a metal is 4.2 eV. If radiation of 2000Å fall on the metal then the kinetic energy of the fastest photoelectron is
 - (a) 1.6×10^{-19} J
 - (b) 16×10^{-10} J
 - (c) 3.2×10^{-19} J
 - (d) 6.4×10^{-10} J

- (ii) The number of electron ejected in the photoelectric experiment is proportional to the
- intensity of light
 - brightness of light
 - Both (a) and (b)
 - None of the above
- (iii) Kinetic energy of the ejected electron is
- equal to the frequency of the electromagnetic radiation
 - proportional to the frequency of the electromagnetic radiation
 - more than the frequency of the electromagnetic radiation
 - inversely proportional to the frequency of the electromagnetic radiation
- (iv) Magnitude of kinetic energy in an orbit is equal to
- half of the potential energy
 - twice of the potential energy
 - one fourth of the potential energy
 - None of the above

Or

Which of the following statements is correct?

- The energy of a quantum of radiation is proportional to its frequency (ν) is expressed by equation, $E = h\nu$
- With the help of quantum theory, Plank explained the distribution of intensity in the radiation from black body as a function of frequency or wavelength at different temperatures
- In photoelectric effect, there is no time lag between the striking of light beam and the ejection of electrons from metal surface
- All of the above

74. Read the passage given below and answer the following questions :

The characteristics of an orbital are expressed in terms of three numbers, called principal (n), azimuthal (l) and magnetic quantum numbers (m_l).

These numbers are obtained from the solutions of the Schrodinger wave

equation. Further, to represent the spin (rotation) of the electron about its own axis, a fourth quantum number, called spin quantum number has been introduced. n defines the shell, determines the size of the orbital and also to a large extent the energy of orbitals. There are n subshells in the n th shell. ' l ' identifies the subshell and determines the shape of the orbital. m_l designates the orientation of orbital. For a given value of l , m_l has $(2l + 1)$ values, the same as the number of orbitals per subshell. m_s refers to orientation of the spin of the electron.

In these questions (i)-(iv) a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices :

- Assertion and Reason both are correct statements and Reason is correct explanation for Assertion.
 - Assertion and Reason both are correct statements but Reason is not correct explanation for Assertion.
 - Assertion is correct statement but Reason is incorrect statement.
 - Assertion is incorrect statement but Reason is correct statement.
- (i) **Assertion** Energies of the orbitals in hydrogen or hydrogen like species depend only on the quantum number ' n '.
- Reason** Energies of the orbitals in multielectron atoms depend on quantum numbers ' n ' and ' l '.
- (ii) **Assertion** Energy of the orbital increases with increase of principal quantum number.
- Reason** Energy is required in shifting away the negatively charged electron from the positively charged nucleus.
- (iii) **Assertion** For a given principal quantum number, $s, p, d, f \dots$, subshells, all have different energies.
- Reason** Mutual repulsion exists among the electrons in a multielectron atoms.

(iv) **Assertion** $2p$ -orbitals do not have any spherical node.

Reason The number of nodes in p -orbitals is given by $(n - 2)$ where, n is the principal quantum number.

Or

Assertion Half-filled and fully filled degenerate set of orbitals acquire extra stability.

Reason The reason for the above fact is the symmetry of such orbitals.

75. Read the passage given below and answer the following questions :

The Heisenberg's uncertainty principle is a result of dual nature of matter and radiation. It was put forward by W. Heisenberg a German Physicist in 1927.

According to this principle, it is impossible to know simultaneously both the conjugate properties accurately. Both the position and the momentum of the particle at any instant can't be determined with absolute exactness or certainty. The uncertainty in measurement of position, Δx and the uncertainty of determination of momentum, ΔP are related by Heisenberg's relationship.

This principle rules out the existence of definite paths or trajectories of electrons and other similar particles. However, the effect of this principle is significant only in case of microscopic objects and is negligible in case of macroscopic object. Since, the uncertainty principle is such a basic result in quantum mechanics, typical experiments in quantum mechanics routinely observe aspects of it. Certain experiments, however, may deliberately test a particular form of the uncertainty principle as part of their main research program. These include, for example, tests of number-phase uncertainty relations in superconducting or quantum optics systems.

Applications dependent on the uncertainty principle for their operation include extremely low-noise technology such as that required in gravitational wave interferometers.

The following questions (i-iv) are multiple choice questions. Choose the most appropriate answer :

(i) If uncertainty in the position of electron is zero, the uncertainty in its momentum would be

- (a) $< \frac{h}{4\pi}$ (b) $\geq \frac{h}{4\pi}$
(c) zero (d) infinite

(ii) The uncertainty in position of an electron ($m = 9.1 \times 10^{-28}$ g) moving with a velocity 3×10^4 cm/s accurate upto 0.001% will be

- (a) 3.84 cm
(b) 1.92 cm
(c) 7.68 cm
(d) 5.76 cm

(iii) If the light of wavelength, λ is used to observe an electron then uncertainty in position of the electron would be

- (a) less than λ
(b) more than λ
(c) equal to λ
(d) equal to or greater than λ

(iv) If uncertainties in the measurement of position and momentum of an electron are equal, the uncertainty in the measurement of velocity is

- (a) 8.0×10^{12} ms⁻¹ (b) 4.2×10^{10} ms⁻¹
(c) 8.5×10^{10} ms⁻¹ (d) 6.2×10^{10} ms⁻¹

Or

The uncertainty in momentum of an electron is 1×10^{-5} kg m / s. The uncertainty in its position will be ($h = 6.62 \times 10^{-34}$ kg m² / s)

- (a) 2.36×10^{-28} m
(b) 5.25×10^{-28} m
(c) 2.27×10^{-30} m
(d) 5.27×10^{-30} m

76. Read the passage given below and answer the following questions :

Orbitals are regions or spaces where the probability of finding electrons is maximum. Qualitatively, these orbitals can be distinguished by their size, shape, and orientation.

An orbital of small size means there is more chance of finding the electron near the nucleus. Shape and orientation means the direction in which the probability of finding the electron is maximum. Atomic orbitals can be distinguished by quantum numbers.

Each orbital is designated by three quantum numbers n , l and m_l (magnetic quantum number) which define energy, shape, and orientation but these are not sufficient to explain spectra of multi-electron atoms. Spin quantum number (m_s) determines the spin of electrons. Spin angular momentum of the electron has two orientations relative to the chosen axis which are distinguished by spin quantum numbers m_s which can take values $+\frac{1}{2}$ and $-\frac{1}{2}$.

The following questions (i-iv) are multiple choice questions. Choose the most appropriate answer :

- (i) How many orbitals are associated with $n = 3$?
 (a) 3 (b) 6
 (c) 9 (d) 12

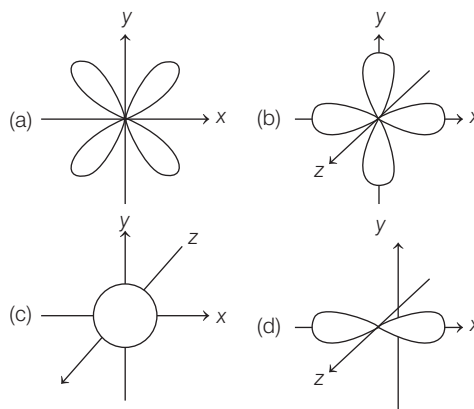
(ii) What will be the representation of $n = 2, l = 1$?

- (a) $2s$ (b) $2p$
 (c) $2sp$ (d) $3s$

(iii) How many electrons are possible in an orbital of $2s$?

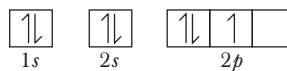
- (a) 1 (b) 2
 (c) $\frac{1}{2}$ (d) 4

(iv) What is the shape of 'p' orbital?



Or

What will be the value of m_s of the following?



- (a) $3\frac{1}{2}$ (b) $2\frac{1}{2}$
 (c) $\frac{1}{2}$ (d) $\frac{7}{2}$

ANSWERS

Multiple Choice Questions

1. (c) 2. (d) 3. (a) 4. (a) 5. (d) 6. (d) 7. (d) 8. (c) 9. (a) 10. (b)
 11. (c) 12. (d) 13. (a) 14. (d) 15. (d) 16. (d) 17. (b) 18. (b) 19. (c) 20. (d)
 21. (c) 22. (d) 23. (a) 24. (d) 25. (d) 26. (c) 27. (c) 28. (a) 29. (c) 30. (d)
 31. (b) 32. (a) 33. (b) 34. (a) 35. (d) 36. (a) 37. (c) 38. (a) 39. (a) 40. (d)
 41. (c) 42. (d) 43. (b) 44. (d) 45. (c) 46. (c) 47. (a) 48. (b) 49. (a) 50. (d)
 51. (a) 52. (c) 53. (b) 54. (a) 55. (a) 56. (b)

Assertion-Reasoning MCQs

57. (a) 58. (a) 59. (b) 60. (c) 61. (b) 62. (c) 63. (c) 64. (a) 65. (a) 66. (b)
 67. (a) 68. (b) 69. (d) 70. (d) 71. (d)

Case Based MCQs

72. (i)-(d), (ii)-(a), (iii)-(c), (iv)-(a, c) 73. (i)-(c), (ii)-(c), (iii)-(b), (iv)-(a, d)
 74. (i)-(b), (ii)-(b), (iii)-(a), (iv)-(a, c) 75. (i)-(d), (ii)-(b), (iii)-(a), (iv)-(a, d)
 76. (i)-(c), (ii)-(b), (iii)-(b), (iv)-(d, c)

EXPLANATIONS

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

Speed of light, $(c) = 3 \times 10^{17}$ nm s⁻¹

Frequency of quantam (ν) = 6×10^{15} s⁻¹

Wavelength (λ) = ?

$$\begin{aligned} \text{We know that, } \nu &= \frac{c}{\lambda}, \lambda = \frac{c}{\nu} \\ &= \frac{3 \times 10^{17}}{6 \times 10^{15}} = 0.5 \times 10^2 \text{ nm} = 50 \text{ nm} \end{aligned}$$

2. Given, $\lambda = 45 \text{ nm} = 45 \times 10^{-9} \text{ m}$ [$\because 1 \text{ nm} = 10^{-9} \text{ m}$]

The wavelength of light is related to its energy by the equation,

$$E = h\nu \quad [\because \text{where, } \nu = c / \lambda]$$

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

$$\begin{aligned} \text{Hence, } E &= \frac{6.63 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1}}{45 \times 10^{-9} \text{ m}} \\ &= 4.42 \times 10^{-18} \text{ J} \end{aligned}$$

Hence, the energy corresponds to the light of wavelength 45 nm is 4.42×10^{-18} J.

3. According to Rydberg's equation,

$$\frac{1}{\lambda} = \frac{R_H}{hc} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{or} \quad \frac{1}{\lambda} \propto \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

For shortest wavelength, i.e. highest energy spectral line, n_2 will be (∞).

For the given spectral series, ratio of the shortest wavelength of two spectral series can be calculated as follows :

$$(a) \frac{\lambda_L}{\lambda_P} = \frac{\frac{1}{3^2} - \frac{1}{\infty^2}}{\frac{1}{1^2} - \frac{1}{\infty^2}} = \frac{\frac{1}{9} - 0}{1 - 0} = \frac{1}{9}$$

$$(b) \frac{\lambda_{Bk}}{\lambda_{Pf}} = \frac{\frac{1}{5^2} - \frac{1}{\infty^2}}{\frac{1}{4^2} - \frac{1}{\infty^2}} = \frac{1}{25} \times \frac{16}{1} = \frac{16}{25}$$

$$(c) \frac{\lambda_P}{\lambda_{Pf}} = \frac{\frac{1}{5^2} - \frac{1}{\infty^2}}{\frac{1}{3^2} - \frac{1}{\infty^2}} = \frac{1}{25} \times \frac{9}{1} = \frac{9}{25}$$

$$(d) \frac{\lambda_B}{\lambda_{Bk}} = \frac{\frac{1}{4^2} - \frac{1}{\infty^2}}{\frac{1}{2^2} - \frac{1}{\infty^2}} = \frac{1}{16} \times \frac{4}{1} = \frac{1}{4}$$

Note Lyman = L ($n_1 = 1$), Balmer = B ($n_1 = 2$)

Paschen = P ($n_1 = 3$), Brackett = Bk ($n_1 = 4$)

Pfund = Pf ($n_1 = 5$)

4. Balmer series of transitions in the spectrum of hydrogen atom fall in visible region. Lyman series fall in ultraviolet while Paschen, Brackett and Pfund fall in infrared region.

$$5. \therefore \frac{1}{\lambda} = Z^2 \cdot R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

\therefore For He^+ ion, $Z = 2$

$$\frac{1}{\lambda} = 2^2 \cdot R \left[\frac{1}{2^2} - \frac{1}{4^2} \right]$$

$$\frac{1}{\lambda} = 4 \times R \times \frac{3}{16} = \frac{3}{4} R$$

The same value for H-atom is possible when electron jumps from $n = 2$ to $n = 1$,

$$\text{i.e. } \frac{1}{\lambda} = 1 \times R \left[\frac{1}{1} - \frac{1}{4} \right] \Rightarrow \frac{3}{4} R$$

$$6. \quad \bar{\nu} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

For Balmer series, $n_1 = 2$ and for 4th line in Balmer series, $n_2 = 6$

$$\therefore R_H = 1,09,677 \text{ cm}^{-1}$$

$$\bar{\nu} = 109677 \left[\frac{1}{2^2} - \frac{1}{6^2} \right]$$

$$= 109677 \left[\frac{1}{4} - \frac{1}{36} \right]$$

$$\bar{\nu} = 24,372 \text{ cm}^{-1}$$

$$7. \quad \frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Where, $R_H = R$, $Z = 3$
(\therefore for Li^{2+} , atomic number = 3)

$$n_2 = 2, n_1 = 1$$

$$\frac{1}{\lambda} = R(3)^2 \left(\frac{1}{(1)^2} - \frac{1}{(2)^2} \right)$$

$$= \frac{R \times 9 \times 3}{4}$$

$$\lambda = \frac{4}{27R}$$

8. As the Bohr's model is applicable only to hydrogen atom and hydrogen like species, i.e. to one electron system, thus Bohr's model can easily explain the spectrum of any atom or ion containing one electron only.
9. The frequency of radiation is absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE , is given by

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

where, E_1 and E_2 are the energies of the lower and higher allowed energy states respectively.

This expression is commonly known as Bohr's frequency rule.

10. An electron can move only in those orbits for which its angular momentum is integral multiple of $h/2\pi$.

This means angular momentum is quantised.

11. Bohr's atomic model is applicable only for hydrogen atom and H-like species, i.e. to the one electron system.

Since, He^{2+} does not contain one electron while all other species have one electron each, thus Bohr's model is not applicable to He^{2+} .

12. $r \propto n^2 / Z$

where, n = number of orbit

Z = atomic number

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

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

So,

$$\frac{r_1}{r_2} = \frac{n_1^2}{n_2^2}$$

$$\frac{0.530}{r_2} = \frac{1^2}{2^2}$$

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

$$13. \quad \frac{1}{\lambda} = \bar{\nu}_H = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

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

$$\lambda = \frac{1}{1.097} \times 10^7 = 9.11 \times 10^{-8} \text{ m}$$

$$= 91.1 \text{ nm} \approx 91 \text{ nm}$$

$$14. \quad \Delta E = 13.6 Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$= 13.6 \times (1)^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right)$$

$$= 13.6 \left(1 - \frac{1}{4} \right) = 13.6 \times \frac{3}{4} = 10.2 \text{ eV}$$

15. The energy of second bohr orbit of H-atom (E_2) is -328 kJ mol^{-1} because

$$E_2 = \frac{-1312}{2^2} \text{ kJ mol}^{-1}$$

$$E_n = -\frac{1312}{n^2} \text{ kJ mol}^{-1}$$

$$E_n = -\frac{1312}{4^2} \text{ kJ mol}^{-1} = -82 \text{ kJ mol}^{-1}$$

16. Limitations of Bohr's model are :

- (i) It fails to account for the finer details of the hydrogen atom spectrum observed by using sophisticated spectroscopic techniques.
- (ii) It is unable to explain the spectrum of atoms other than hydrogen.
- (iii) It is unable to explain the ability of atoms to form molecules by chemical bonds.

17. Relation between wavelength (λ) and momentum (p) of a material particle is

$$\lambda = \frac{h}{p}$$

This is popularly called as de-Broglie's equation.

18. From de-Broglie equation, $\lambda \propto \frac{1}{m}$

Greater the mass of matter waves, lesser is wavelength and *vice-versa*. In these matter waves, alpha particle (He^{2+}) has higher mass, therefore, shortest wavelength.

19. According to de-Broglie relation,

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

where, λ = wavelength
 h = Planck's constant
 p = momentum

Here, $h = 6.625 \times 10^{-34} \text{ J s}$

$$\lambda = 10^{-17} \text{ m}$$

$$\begin{aligned} \therefore p &= \frac{h}{\lambda} = \frac{6.625 \times 10^{-34}}{10^{-17}} \\ &= 6.625 \times 10^{-34} \times 10^{17} \\ &= 6.625 \times 10^{-17} \text{ kg m s}^{-1} \end{aligned}$$

20. de-Broglie wavelength

$$\lambda = \frac{h}{mv} \Rightarrow v = \frac{h}{m\lambda} \quad \dots(i)$$

$$\text{KE} = \frac{1}{2}mv^2 \quad \dots(ii)$$

On putting the value of v in Eq. (ii), we get

$$\begin{aligned} \text{KE} &= \frac{1}{2}m \left(\frac{h}{m \cdot \lambda} \right)^2 \\ \Rightarrow \text{KE} &= \frac{1}{2} \left(\frac{h^2}{m \cdot \lambda^2} \right) \end{aligned}$$

Hence, $\text{KE} \propto 1/m$ (if λ is same) and order of mass is as

$$m_e < m_p < m_\alpha$$

Thus, the order of KE is

$$E_e > E_p > E_\alpha$$

21. According to de-Broglie wavelength, $\lambda = \frac{h}{mv}$

Given, $m = 100 \text{ g}$, $v = 100 \text{ cm s}^{-1}$

and $h = 6.6 \times 10^{-34} \text{ J-s}$

$$= 6.6 \times 10^{-27} \text{ erg-s}$$

On substituting values, we get

$$\begin{aligned} \lambda &= \frac{6.6 \times 10^{-27}}{100 \times 100} \\ &= 6.6 \times 10^{-31} \text{ cm} \end{aligned}$$

22. According to de-Broglie equation,

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

Given, $\lambda = 6.62 \times 10^{-35} \text{ m}$

$$v = 100 \text{ m s}^{-1}$$

$$h = 6.62 \times 10^{-34} \text{ Js}$$

and $m = x \text{ kg}$

$$\therefore 6.62 \times 10^{-35} = \frac{6.62 \times 10^{-34}}{x \times 100}$$

$$x = 0.1 \text{ kg}$$

23. de-Broglie equation is,

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

$$\text{KE} = \frac{1}{2}mv^2$$

$$\text{or } v = \sqrt{\frac{2\text{KE}}{m}}$$

$$\lambda = \frac{h}{\sqrt{2m \text{KE}}}$$

$$\frac{(\text{KE})_1}{(\text{KE})_2} = \frac{\lambda_2^2}{\lambda_1^2} = \left(\frac{5}{3} \right)^2 = \frac{25}{9} \text{ or } 25 : 9$$

Hence, the ratio of kinetic energy of electrons will be 25 : 9.

24. The position and velocity of the electrons in the orbit cannot be determined simultaneously. This statement is not correct for Bohr's model of hydrogen atom. It is infact given by Heisenberg in his uncertainty principle.

25. From Heisenberg uncertainty principle

$$\Delta x \cdot \Delta P \geq \frac{h}{4\pi} \quad \dots(i)$$

$$\Delta x \cdot m\Delta v \geq \frac{h}{4\pi} \quad [\because \Delta p = m\Delta v]$$

$$\Delta x \cdot \Delta v \geq \frac{h}{4\pi m} \quad \dots(ii)$$

This principle is also applicable for pairs like energy time ($\Delta E \cdot \Delta t$) and angular momentum-angle ($\Delta \omega \cdot \Delta \theta$) along with position-momentum ($\Delta x \cdot \Delta P$).

$$\text{Thus, } \Delta E \cdot \Delta t \geq \frac{h}{4\pi} \quad \dots(iii)$$

26. By Heisenberg's uncertainty principle,

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

$$\Delta v = 0.005\% \text{ of } 600 \text{ m/s} = \frac{600 \times 0.005}{100} = 0.03$$

$$\Delta x \times 9.1 \times 10^{-31} \times 0.03 = \frac{6.6 \times 10^{-34}}{4 \times 3.14}$$

$$\text{Hence, } \Delta x = \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 0.03 \times 9.1 \times 10^{-31}} = 1.92 \times 10^{-3} \text{ m}$$

27. $\Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$

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

28. According to Heisenberg uncertainty principle,

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

where, Δx = uncertainty in position

m = mass of particle

Δv = uncertainty in velocity

According to question,

$$\Delta x_A \times m \times 0.05 = \frac{h}{4\pi} \quad \dots(i)$$

$$\Delta x_B \times 5m \times 0.02 = \frac{h}{4\pi} \quad \dots(ii)$$

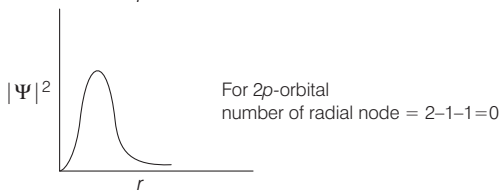
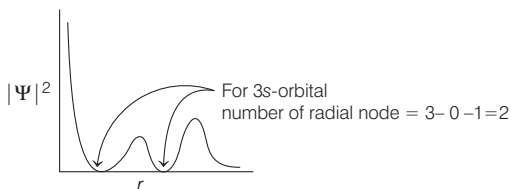
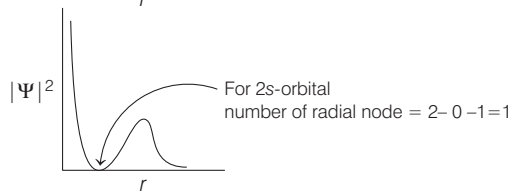
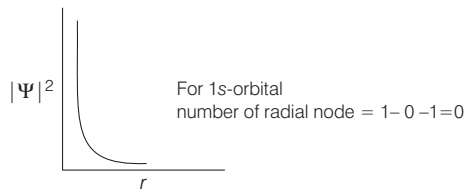
On dividing Eq. (i) by Eq. (ii), we get

$$\frac{\Delta x_A \times m \times 0.05}{\Delta x_B \times 5m \times 0.02} = 1$$

$$\Rightarrow \frac{\Delta x_A}{\Delta x_B} = \frac{5m \times 0.02}{m \times 0.05} = 2 \quad \text{or} \quad \frac{\Delta x_A}{\Delta x_B} = 2$$

29. In Schrodinger equation, \hat{H} is a mathematical operator called Hamiltonian. It was introduced by Schrödinger from the expression for the total energy of the system.

30. The graphs between $|\psi|^2$ and r are radial density plots having $(n-l-1)$ number of radial nodes. For 1s, 2s, 3s and 2p-orbitals these are respectively.



Thus, the given graph between $|\psi|^2$ and r represents 2s-orbital.

31. Principal, azimuthal and magnetic quantum numbers are respectively related to size, shape and orientation of the shell, subshell and orbitals.

32. Angular momentum of electrons in d -orbital is

$$= \sqrt{l(l+1)} \frac{h}{2\pi}$$

for d -orbital, $l = 2$

$$= \sqrt{2(2+1)} \hbar \quad \left(\because \hbar = \frac{h}{2\pi} \right)$$

Angular momentum = $\sqrt{6} \hbar$

- 33.** The value of azimuthal quantum number is given by $l = n - 1, n = l + 1$
 Here, $l = 2$, thus, $n = 2 + 1 = 3$
 Hence, the value of principal quantum number (n) is 3.
- 34.** For s -subshell, $l = 0$. Its shape is spherical.
- 35.** For $n = 2$, l can be 0 and 1.
 For $l = 0, m = 0$ and $l = 1, m = -1, 0, +1$.
- 36.** Orbital angular momentum, $mvr = \frac{h}{2\pi} \sqrt{l(l+1)}$.
 Hence, it depends only on ' l '. l can have values ranging from 0 to $(n - 1)$.
- 37.** Two electrons occupying the same orbital have equal spin but the directions of their spin are opposite. Hence, spin quantum number, s (represented $+1/2$ and $-1/2$) distinguishes them.
- 38.** The correct match is :
 $A \rightarrow (2); B \rightarrow (4); C \rightarrow (1); D \rightarrow (3)$
- (A) Principal quantum number is the most important quantum number as it determines the size and to large extent the energy of the orbital.
- (B) Azimuthal quantum number determines the angular momentum of the electron and defines the three-dimensional shape of the orbital.
- (C) Magnetic quantum number gives information about the spatial orientation of orbitals with respect to a standard set of coordinate axes.
- (D) Spin quantum number arises from the spectral evidence that an electron in its motion around the nucleus in an orbit also rotates or spin about its own axis.
- 39** According to quantum mechanical atom model, for each value of n (principal quantum number), there are ' n ' different values of l (azimuthal quantum number), i.e. $l = 0, 1, 2, \dots, (n - 1)$. And, for each value of l , there are $2l + 1$ different values of m_l (magnetic quantum number), i.e. $m_l = 0, \pm 1, \pm 2 \dots \pm l$.
 \therefore Total number of possible combinations of n, l and m_l , for a given value of n is n^2 , and each such combination is associated with an orbital. Each orbital can occupy a maximum of two

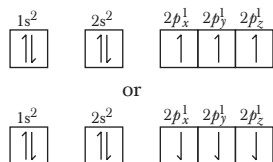
electrons, having a different value of spin quantum number (m_s), which are $+\frac{1}{2}$ or $-\frac{1}{2}$.

\therefore Number of orbitals associated with $n = 5$ is $n^2 = 25$. Each of those orbitals can be associated with $m_s = +\frac{1}{2}$ as well as $m_s = -\frac{1}{2}$.

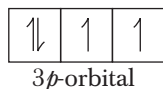
\therefore Answer = 25

- 40.** For a hydrogen atom wave function, there are $n - l - 1$ radial nodes and $(n - 1)$ total nodes.
 Number of radial nodes for $3p$ orbital = $n - l - 1$
 $= 3 - 1 - 1 = 1$
- 41.** Total number of orbitals associated with n^{th} shell = n^2
 \therefore Total number of orbitals associated with third shell = $(3)^2 = 9$
- 42.** The correct match is :
 $A \rightarrow (5); B \rightarrow (4); C \rightarrow (1); D \rightarrow (2); E \rightarrow (3)$
- 43.** According to Aufbau principle, the order in which the energies of the orbitals increases is as follows:
 $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d,$
 $5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, 8s$
 Hence, the correct order of increasing energy of orbital is $5p < 6s < 4f < 5d$.
- 44.** Aufbau principle does not give the correct arrangement of filling up of atomic orbitals in copper and chromium because half-filled and completely filled electronic configuration of Cr and Cu have lower energy and therefore, more stable.
 $\text{Cr}(Z = 24) = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$
 $\text{Cu}(Z = 29) = 1s^2, 1s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$
- 45.** According to Pauli exclusion principle, in any orbital, maximum two electrons can exist, having opposite spin.
- 46.** According to Hund's rule, electron pairing in p, d and f orbitals cannot occur until each orbital of a given subshell is singly occupied.
 Hence, $1s^2, 2s^2 2p_x^2 2p_y^1 2p_z^0$ electronic configuration is not possible for nitrogen.
- 47.** 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 sub-shell are singly occupied.

Moreover, the single orbitals must have the electrons with parallel spin. i.e.



48. According to Hund's rule, in p -orbital the distribution of electrons are as follows :



49. The correct match is

A → (3); B → (5); C → (1); D → (4)

(A) Hund's rule states that pairing of electrons in the orbitals belonging to the same subshell (p , d or f) does not take place until each orbital belonging to that subshell has got one electron each, i.e. it is singly occupied.

(B) Aufbau principle states that in the ground state of the atoms, the orbitals are filled in order of their increasing energies.

(C) According to Pauli exclusion principle, no two electrons in an atom can have the same set of four quantum numbers.

(D) Heisenberg's uncertainty principle states that it is impossible to determine the exact position and exact momentum of a subatomic particle simultaneously.

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

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

where, h = Planck's constant.

Thus, statement (a) is correct.

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

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

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

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

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

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

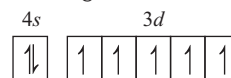
$$[\because \Delta E = F \cdot \Delta x, E = \text{energy}]$$

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.

51. Most stable arrangement is



Because,

(i) According to Aufbau principle, electrons enter in the subshell of an atom in the increasing order of energy.

(ii) According to Hund's rule of maximum multiplicity, pairing of electrons in the orbitals of a subshell does not take place until all orbitals of a subshell are singly occupied.

52. ${}_{37}\text{Rb} = {}_{36}[\text{Kr}]5s^1$. Its valence electronic configuration is $5s^1$.

So, quantum numbers for $5s^1$ electron are $n = 5$

$$l = 0 \quad (\text{for, } s\text{-orbital})$$

$$m = 0 \quad (\text{As, } m = -l \text{ to } +l)$$

$$s = +1/2$$

53. Electronic configuration of Fe^{2+} is $[\text{Ar}]3d^64s^0$.

\therefore Number of d -electrons = 6

$$\text{Mg} - 1s^2 2s^2 2p^6 3s^2 \quad (s\text{-electrons are } 6)$$

It matches with the d -electrons in Fe^{2+}

$$\text{Cl} - 1s^2 2s^2 2p^6 3s^2 3p^5 \quad (p\text{-electrons are } 11)$$

It does not match with the d -electrons in Fe^{2+}

$$\text{Fe} - [\text{Ar}] 3d^6 4s^2 \quad (d\text{-electrons are } 6)$$

It matches with the d -electrons in Fe^{2+}

$$\text{Ne} - 1s^2 2s^2 2p^6 \quad (p\text{-electrons are } 6)$$

It matches with the d -electrons in Fe^{2+} .

Hence, Cl has 11 electrons in p -subshell which does not match with number of d -electrons in Fe^{2+} .

54. (a) $\text{Fe}^{3+} = [\text{Ar}] 3d^5$

↑	↑	↑	↑	↑
---	---	---	---	---
- (b) $\text{Co}^{3+} = [\text{Ar}] 3d^6$

↑↓	↑	↑	↑	↑
----	---	---	---	---
- (c) $\text{Ni}^{2+} = [\text{Ar}] 3d^8$

↑↓	↑↓	↑	↑	↑
----	----	---	---	---
- (d) $\text{Cu}^{2+} = [\text{Ar}] 3d^9$

↑↓	↑↓	↑↓	↑	↑
----	----	----	---	---

Hence, the maximum unpaired electrons is present in Fe^{3+} ion, which is 5.

55. The correct match is :
 A → (4); B → (3); C → (1); D → (2)
 (A) $\text{Cr} (Z = 24) = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
 $= [\text{Ar}] 3d^5 4s^1$
 (B) $\text{Fe}^{2+} (Z = 26) = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^0$
 $= [\text{Ar}] 3d^6 4s^0$
 (C) $\text{Ni}^{2+} (Z = 28) = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^0$
 $= [\text{Ar}] 3d^8 4s^0$
 (D) $\text{Cu} (Z = 29) = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
 $= [\text{Ar}] 3d^{10} 4s^1$
56. The correct match is :
 A → (3); B → (4); C → (1); D → (5)
 (A) $\text{Cu} (Z = 29) : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
 (B) $\text{Cu}^{2+} (Z = 29) : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$
 (C) $\text{Zn}^{2+} (Z = 30) : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$
 (D) $\text{Cr}^{3+} (Z = 24) : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

57. According to de-Broglie equation,
 $\lambda (\text{wavelength}) = h/mv$.
 Because of inverse relation of wavelength and mass, the wavelength associated with ordinary objects (microscopic object) are so short (because of their large mass), that their wave properties cannot be detected.
 Both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

58. Radius, $r = \frac{n^2 h^2}{4\pi e^2 m Z} = \frac{n^2}{Z} \times 0.529 \text{ \AA}$
 With increase of n , r_n also increases, indicating a greater separation between the orbit and the nucleus.
 Both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

59. Energies of the orbitals in hydrogen or hydrogen like species depend only on the quantum number 'n'. Energies of the orbitals in multielectron atoms depend on quantum numbers 'n' and 'l', i.e. more than 1 quantum number.

Both Assertion and Reason are correct, but Reason is not the correct explanation of the Assertion.

60. Assertion is correct and Reason is incorrect.
 According to Heisenberg's uncertainty principle, the exact position and exact momentum of an electron cannot be determined simultaneously. Thus, the path of electron in an atom is not clearly defined.

61. Both Assertion and Reason are correct but Reason is not the correct explanation of Assertion.
 With the help of principal quantum number (n) the average distance of the electron can be determined.

Distance of the electron from the nucleus, energy and size of orbital increase as the value of principle quantum number 'n' increases.

Shell = *K L M N*
 $n = 1 \ 2 \ 3 \ 4 \ \dots\dots\dots$

62. Assertion is correct, but Reason is incorrect statement.
 Spin angular momentum of the electron, a vector quantity, can have two orientations (represented by + and - sign) relative to a chosen axis. These two orientations are distinguished by the spin quantum number m_s , equals to +1/2 or -1/2. These are called the two spin states of the electron and are normally represented by the two arrows ↑ (spin up) and (spin down) ↓ respectively.

63. Magnetic quantum number m_l can have values $m_l = -l, -(l-1), \dots 0, \dots (l-1), l$ (total $2l + 1$ values). It gives the information about the number of orbitals and its orientation.

Thus, Assertion is correct, but Reason is incorrect.

64. For a given principal quantum number, *s, p, d, f*, ... subshells, all have different energies because mutual repulsion exists among the electrons in a multi-electron atoms.

Thus, both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

65. Half-filled and fully-filled degenerate set of orbitals acquire extra stability because of the symmetry.

Thus, both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

66. *s*-orbital electron will be more tightly bound to the nucleus than *p*-orbital electron because *s*-orbital electrons are less shielded as compared to *p*-orbital electrons.

Z_{eff} experienced by the electron decreases with increase of azimuthal quantum number (*l*).

Thus, both Assertion and Reason are correct but Reason is not the correct explanation of Assertion.

67. Both Assertion and Reason are correct statements and Reason is the correct explanation of the Assertion.

For a given orbital only that boundary surface diagram of constant probability density $|\psi|^2$ is taken to be a good representation of the shape of the orbital which encloses a region or volume in which the probability of finding the electron is very high, i.e. 90 %.

68. According to ($n + l$) rule, energy level also depends on azimuthal quantum number.

Only in unielectronic species which are very few (H and related atoms), '*l*' is immaterial for deciding energy level.

Both Assertion and Reason are correct statements, but Reason is not the correct explanation of the Assertion.

69. Atomic orbital is designated by *n*, *l* and m_l while state of an electron in an atom is specified by four quantum numbers *n*, *l*, m_l and m_s .

Thus, Assertion is incorrect but Reason is correct statement.

70. In case isoelectronic ions, i.e. ions having the same number of electrons and different nuclear charge, the size decreases with increase in atomic number.

Ion	At. no.	No. of electrons	Ionic radii
Na ⁺	11	10	0.95 Å
Mg ²⁺	12	10	0.65 Å
Al ³⁺	13	10	0.50 Å

Thus, Assertion is incorrect but Reason is correct statement.

71. ($2l + 1$) gives the value for number of orbitals in that subshell not the electrons.

'*l*' can have only values of 0, 1, 2, 3 for '*s*', '*p*', '*d*' and '*f*' not only other value.

Thus, Assertion is incorrect but Reason is correct statement.

72. (i) Assertion is incorrect but Reason is correct. For multielectron atom, such as sodium, energy of electron is determined by both *n* as well as *l*.

(ii) Assertion and Reason both are correct statement and Reason is correct explanation of Assertion.

(iii) Assertion is correct but Reason is incorrect. Its correct is :

Orbit represents the circular path along which the electron moves but orbital represents the three dimensional space around the nucleus within which the probability of finding the electron is maximum.

(iv) Assertion and Reason both are correct and Reason is the correct explanation of Assertion.

Or

Assertion is correct but Reason is incorrect.

The value of spin quantum number can be either $+\frac{1}{2}$ or $-\frac{1}{2}$ and it is independent of value of principal quantum number.

73. (i) Given, $E_0 = 4.2 \text{ eV} = 4.2 \times 1.60 \times 10^{-19} \text{ J}$
 $= 6.72 \times 10^{-19} \text{ J}$

We know that, $(c) = 3 \times 10^8 \text{ m/s}$ [$1 \text{ \AA} = 10^{-10} \text{ m}$]

$$\therefore E = h\nu = \frac{hc}{\lambda}$$

$$\therefore E = \frac{6.63 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1}}{2000 \times 10^{-10} \text{ m}}$$

$$= 9.94 \times 10^{-19} \text{ J}$$

$$\therefore \text{Kinetic energy of electron emitted}$$

$$= (9.94 - 6.72) \times 10^{-19} \text{ J}$$

$$= 3.22 \times 10^{-19} \text{ J}$$

(ii) Number of electron ejected depends upon intensity and brightness of light.

(iii) Kinetic energy of ejected electron is proportional to frequency of electromagnetic radiation.

$$(iv) \text{ Kinetic energy in an orbit} = \frac{Ze^2}{8\pi\epsilon_0 r} \dots(i)$$

$$\text{Potential energy in an orbit} = -\frac{Ze^2}{4\pi\epsilon_0 r} \dots(ii)$$

On comparing Eqs. (i) and (ii), we get

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

Hence, the magnitude of kinetic energy in an orbit is equal to half of the potential energy.

Or

Option (d) is the correct answer as all these three options are incorrect.

- 74.** (i) Energies of the orbitals in hydrogen or hydrogen like species depend only on the quantum number ' n '. Energies of the orbitals in multielectron atoms depend on quantum numbers ' n ' and ' l ', i.e. more than 1 quantum number.

Thus, both Assertion and Reason are correct but Reason is not the correct explanation of Assertion.

- (ii) Thus, both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

- (iii) For a given principal quantum number, s, p, d, f, \dots subshells, all have different energies because mutual repulsion exists among the electrons in a multi-electron atoms.

Thus, both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

- (iv) Both Assertion and Reason statements are correct and Reason is the correct explanation of Assertion.

Or

Half-filled and fully-filled degenerate set of orbitals acquire extra stability because of the symmetry.

Thus, both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

75. (i) $\Delta x \cdot \Delta P \geq \frac{h}{2\pi}$

when, $\Delta x = 0$ ΔP becomes infinite.

- (ii) Uncertainty in velocity
 $= 3 \times 10^4 \times \frac{0.001}{100} = 0.3 \text{ cm/s}$

$$\Delta x \cdot \Delta v = \frac{h}{4\pi m} = \frac{6.6 \times 10^{-27}}{4 \times 3.14 \times 9.1 \times 10^{-28}}$$

$$\Delta x = \frac{6.6 \times 10^{-27}}{4 \times 3.14 \times 9.1 \times 10^{-28} \times 0.3} = 1.92 \text{ cm}$$

- (iii) The uncertainty in the position of electron would be less than λ .

- (iv) Given, $\Delta x = \Delta P$ or $\Delta x = m \cdot \Delta v$

From Heisenberg's uncertainty principle,

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

$$(\Delta v)^2 = \frac{h}{4\pi m^2}$$

$$\Delta v = \frac{1}{2m} \sqrt{\frac{h}{\pi}}$$

$$= \frac{1}{2 \times 9.1 \times 10^{-31}} \sqrt{\frac{6.63 \times 10^{-34}}{3.14}} = 7.98 \times 10^{12} \text{ ms}^{-1} \approx 8 \times 10^{12} \text{ ms}^{-1}$$

Or

$$\Delta x \cdot \Delta P = \frac{h}{4\pi}$$

$$\Delta x = \frac{6.63 \times 10^{-34}}{4 \times 3.14 \times 10^{-5}} = \frac{5.27 \times 10^{-35}}{1 \times 10^{-5}} = 5.27 \times 10^{-30} \text{ m}$$

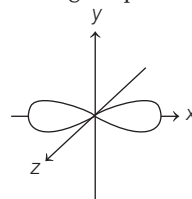
- 76.** (i) Number of orbitals $= n^2 = (3)^2 = 9$ orbitals.

9 orbitals are $3s, 3p_x, 3p_y, 3p_z, 3d_{x^2-y^2}, 3d_{z^2}, 3d_{xy}, 3d_{yz}$ and $3d_{xz}$.

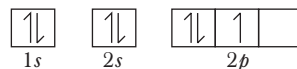
- (ii) $n = 2, l = 1 \Rightarrow 2p$

- (iii) Orbital can have a maximum of two electrons which must be of opposite spin.

- (iv) The following shape is of p_x -orbital.



Or



Number of unpaired electron = 1

\therefore Total spin of unpaired electrons = $\frac{1}{2}$

because spin of paired electrons is zero.